

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

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DOI:

[10.1016/j.atmosenv.2013.10.003](https://doi.org/10.1016/j.atmosenv.2013.10.003)

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Document Version

Early version, also known as pre-print

Citation for published version (Harvard):

Rauert, C, Lazarov, B, Harrad, S, Covaci, A & Stranger, M 2014, 'A review of chamber experiments for determining specific emission rates and investigating migration pathways of flame retardants', *Atmospheric Environment*, vol. 82, pp. 44-55. <https://doi.org/10.1016/j.atmosenv.2013.10.003>

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Manuscript Number:

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

Article Type: Review Article

Keywords: Emission Chamber; Specific Emission rate; Flame Retardants; Mass transfer to dust

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Abstract: The widespread use of flame retardants (FRs) in indoor products has led 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.



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The Editor,
Atmospheric Environment

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

1 **HIGHLIGHTS**

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

10

1 **TITLE**

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

4

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22 **Abstract**

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

44

45 **Keywords**

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

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64 **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- <i>n</i> -butylphthalate	TBBPA	Tetrabromobisphenol-A
EF	Emission Factor	TBEP (TBOEP)	tri (2-butoxyethyl) 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(<i>n</i> -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

65

66 **1. Introduction**

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

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

88 Hexabromocyclododecane (HBCD) is another additive BFR. It is used widely to flame
89 retard polystyrene foams for thermal insulation of buildings, back coating of fabrics for
90 furniture, and HIPS used in enclosures for electronic equipment, such as TVs (Harrad et al.,
91 2010a; Weil and Levchik, 2007). Currently HBCDs are also under consideration for listing
92 under the Stockholm Convention (UNEP, 2012). Tetrabromobisphenol-A (TBBPA) on the
93 other hand has been used as both a reactive FR, in epoxy and polycarbonate resins for printed
94 circuit boards and electronic equipment, and as an additive FR in HIPS or ABS resins
95 (Abdallah et al., 2008). When used as a reactive FR, it can still be emitted to the surrounding
96 environment, if an excess of non-polymerized TBBPA is present in the final treated product
97 (Abdallah et al., 2008). The global demand for TBBPA increased on average by 19% per year
98 between 1992 and 1998, with demand continuing to grow by 8-9% per year between 1998 and
99 2004 (ECHA, 2006).

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

108 The reported known or estimated worldwide production volumes of the above
109 mentioned FRs are summarised in Table 2. Limited information is publicly available
110 regarding production volumes, especially for NBFRs and PFRs, and is provided here with
111 caution given the associated uncertainty. If a newer chemical is not yet listed with the
112 European Chemicals Agency (ECHA) then it is assumed the chemical is produced below
113 1000 tonnes per year i.e. it is deemed a "low production volume chemical". The limited
114 information on production volumes/market demand introduces significant uncertainty to
115 attempts to identify which FRs (if any) are used in any given product, as well as efforts to
116 estimate emissions from such products and the microenvironments within which they are
117 located.

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

126 Despite the known presence of FRs in indoor environments and their potential adverse
127 effects, little is known about their emission and/or migration pathways into air and dust, a gap
128 exacerbated by a lack of consistent data on their physicochemical properties. In particular,
129 estimations of vapour pressure (V_P) and octanol to air partitioning coefficients (K_{OA}) are
130 unreliable, rendering calculation of realistic emission factors (EFs) and specific emission rates
131 (SERs) highly uncertain, as shown by Prevedouros et al. (2004) who calculated EFs of PBDEs -
132 47, -99 and -153 from previously reported V_P and K_{OA} data. The European Commission of
133 Health Consumers (EU, 2011) uses V_P as the standard method to calculate emissions of FRs

134 from products. As V_P and K_{OA} are highly correlated (Moeckel et al., 2010), similar emission
135 estimates are expected using these estimated values. This is often not the case (Prevedouros et
136 al., 2004), and Moeckel et al. (2010) suggest that using reported V_P values represents a ‘worst-
137 case’ scenario due to the unreliability of available data and the influence of the matrix from
138 which emission is being predicted. Dust to air partition coefficients, also directly related to
139 K_{OA} and hence reliant on the accuracy of available data, can predict equilibrium
140 concentrations in air and dust thus permitting calculation of the mass transfer of semi-volatile
141 organic compounds (SVOCs) to particulates or dust (Schripp et al., 2010). Limited information
142 is available on migration pathways of FRs into particulates/dust with proposed hypotheses
143 including: deposition after volatilisation of the more volatile FRs, abrasion of fine particles
144 from treated products through wear-and-tear thus allowing transfer of less volatile FRs, and
145 transfer via direct contact between the treated product and dust (Figure 1). Deposition of the
146 less volatile congeners, particularly PBDE-209, may also occur to a limited extent, resulting
147 in the relatively low ng/g level concentrations reported in some studies (Kefeni and Okonkwo,
148 2012). Multiple migration pathways may also occur concurrently with lower level background
149 contamination from atmospheric deposition overlaid with inputs from abraded particles/fibres.

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

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

163 The aims of this review are thus to: 1) summarise the available evidence for the
164 influence of putative sources on indoor contaminations with FRs; 2) collate studies using
165 emission chambers to elucidate SERs and mass transfer to dust of FRs; 3) summarise the
166 different chamber configurations/methodological approaches used; 4) identify

167 limitations/difficulties encountered with chamber experiments, and 5) identify knowledge
168 gaps and future research directions.

169

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

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

180 Although this relationship is sometimes blurred by source misclassification (Allen et
181 al., 2007; Gevao et al., 2006; Wu et al., 2007), generally, higher indoor concentrations of BFRs
182 are associated with the presence of greater numbers of electronic equipment or PUF-
183 containing furniture (offices rather than houses) (D'Hollander et al., 2010; Gevao et al., 2006;
184 Mandalakis et al., 2008; Watkins et al., 2011). Mandalakis et al. (2008) reported air from a Greek
185 office accommodating network servers and telecommunications infrastructure to display
186 elevated Σ PBDE concentrations of 11,000 pg/m^3 (nearly two orders of magnitude greater than
187 the next highest sample) strongly suggesting electrical equipment to be a significant source of
188 PBDE contamination. Thuresson et al. (2012) analysed dust from offices, houses and
189 apartments, day care centres, and cars in Sweden, also reporting significantly higher
190 concentrations of PBDEs and HBCDs in dust from offices (average Σ PBDEs = 1200 and
191 Σ HBCDs = 300 ng/g) compared to houses (average Σ PBDEs = 510 and Σ HBCDs = 100 ng/g).
192 However, Σ PentaBDEs were even higher in day care centres, with an average concentration
193 of 240 ng/g, suggested to be due to the number of foam mattresses present. Fulong and Espino
194 (2013) investigated dust from 8 different university microenvironments in the Philippines with
195 the highest BDE-209 concentrations occurring in a small computer centre containing four old
196 and new computers (4,000 ng/g). The lowest levels were present in an office lounge
197 containing only one TV set (1,000 ng/g). Similarly, Kefeni and Okonkwo (2012) reported the
198 highest dust concentrations of BDE-209 (600 ng/g) in a South African office containing the
199 highest number of old computers, sofas, foam chairs and electronics of those offices studied.

200 Concentrations of Σ PBDEs in dust from Hong Kong workplaces exceeded those in
201 homes by 2 to 60 times as reported by Kang et al. (2011). In this study electronics factories
202 displayed the highest concentrations (2,000 to 40,000 ng/g), likely due to the electrical
203 equipment (particularly computers) assembled in the factories. Chen et al. (2008) investigated
204 atmospheric Σ PBDE concentrations in Chinese houses, offices and other workplaces and
205 concentrations were generally higher in workplaces than houses, but not significantly. The
206 office with the highest concentration of Σ PBDEs (8,000 pg/m³) contained 28 computers and
207 31 PUF-containing chairs, whereas the office with the lowest reported concentration
208 (200 pg/m³) contained only 15 computers. The computers in the second office were not in use
209 and the ambient temperature was lower (8°C), possibly resulting in lower emissions of the
210 more volatile congeners.

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

221 Van den Eede et al. (2011) compared levels of PFRs in Belgian homes and stores and
222 found a general trend of higher concentrations in stores. In a similar vein, Brommer et al.
223 (2012) analysed dust from German microenvironments for PFRs, PBDEs and DBDPE with
224 concentrations in offices and cars generally higher than in homes for all analysed FRs,
225 consistent with the above mentioned trend. Webster et al. (2010) compared levels of PFRs in
226 US homes, offices and cars with offices containing 2 times higher concentrations than homes
227 of bis (2-ethylhexyl) 2,3,4,5-tetrabromophthalate or TBPH (BEH-TEBP) (2,037 ng/g
228 compared to 932 ng/g in homes) and cars containing four fold higher concentrations than
229 homes of tris(1,3-dichloro-2-propyl) phosphate or TDCPP (TDCIPP). NBRs were also
230 measured with similar levels of 2-ethylhexyl 2,3,4,5-tetrabromobenzoate or TBB (EH-TBB)
231 found in the three microenvironment categories (260 ± 30 ng/g), suggesting different sources
232 of PFRs and NBRs. In the UK, Harrad et al. (2008a) investigated levels of DBDPE and
233 BTBPE in house, office and car dust with offices and cars generally containing higher

234 concentrations than houses. One house dust sample however had high concentrations of both
235 DBDPE and BTBPE at 3,400 and 1,900 ng/g respectively. Concentrations of NBRs in UK
236 day care and primary school dust have also been reported (Harrad et al., 2010b), with one
237 sample containing unusually high levels of BTBPE at > 45 µg/g. Putative sources of this
238 contamination were not able to be determined.

239 The general trend of higher concentrations in microenvironments with larger numbers
240 of putative sources shows the importance of assessing FR emissions from these sources. For
241 this reason, SERs from treated products constitute important information to ascertain the rate
242 at and extent to which a given FR is emitted from such products into the surrounding
243 microenvironment. As mentioned above, the wide range of FRs present in goods and
244 materials used indoors can easily lead to source misclassification. Often essential information
245 about the product such as which FR is present or its age is not available, making classification
246 difficult. Objects suspected to contain FRs have been classified together in studies (Allen et al.,
247 2007), when it is unknown if the product has been treated with a given FR (Gevao et al., 2006)
248 making statistically significant correlations difficult to ascertain.

249 No statistically significant correlations between putative sources and PBDE
250 concentrations in air were reported in a study of Kuwait homes (Gevao et al., 2006). The
251 absence of a correlation was attributed to insufficient information on which products had been
252 treated with PBDEs. A study by Hazrati and Harrad (2006) reported significantly higher PBDE
253 concentrations in air from a UK room containing numerous PUF-containing chairs and PCs,
254 than in rooms with fewer sources. However, consistent evidence of significant correlation
255 between putative PBDE sources and indoor contamination was not detected in this study.
256 Likewise, Kang et al. (2011) did not find significant correlations between PBDE concentrations
257 in Hong Kong house dust and house characteristics; including numbers of foam furniture and
258 electronic appliances present, age of the house, floor area, and carpet coverage. Tan et al.
259 (2007) did not detect significant correlations between PBDE concentrations in indoor dust and
260 microenvironment characteristics in Singapore, such as number of TVs/computers, flooring
261 material and floor area. In the German microenvironment study of Brommer et al. (2012), tris
262 (1-chloro-2-propyl) phosphate or TCPP (TCIPP) concentrations and numbers of foam
263 containing items in the sampled area were not significantly correlated. PBDEs were also
264 detected in this study, although generally at much lower levels, suggesting the possibility of
265 source misclassification, whereby some products contained PBDEs rather than PFRs.

266 Allen et al. (2007) reported no statistically significant correlations between USA indoor
267 air concentrations of PBDEs and the number of furniture or electronic items in the room or

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

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

286

287 **3. Source attribution via studies of within-room and within-building spatial and** 288 **temporal variation in contamination**

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

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

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

323

324 **4. Modelling Studies**

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

333 Multimedia fugacity models have been used to estimate emissions from entire
334 populated areas, such as a model of PBDE emissions from central Stockholm (Palm, 2001),

335 recently adapted to include a module representing a generic indoor environment (Palm
336 Cousins, 2012). The model utilizes data on the use, lifetime, and movement of treated products
337 in an 8-compartment steady state, multimedia chemical fate model. The estimated air
338 concentrations of PBDE congeners were similar to the concentrations reported in other
339 studies. However soil concentrations differed by up to a factor of 100. This difference is
340 likely due to uncertainties in the model and the lack of reported measured concentrations in
341 soil from the Stockholm area.

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

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

363 Zhang et al. (2009) studied a UK office environment for which PBDE concentrations
364 were reported previously by Hazrati and Harrad (2006), supplemented by additional
365 measurements of PBDE concentrations in the PUF containing chairs and carpet in the office.
366 A multimedia fugacity model was developed and applied to the office using these data and
367 EFs for scenarios based on two different computers in the office calculated to be 5.4 and 35
368 $\text{ng } \Sigma\text{PBDE/h}$. An estimate of emissions from treated computers in use in North America was

369 calculated at ~8.5-55 kg per year. The values reported by Zhang et al. (2009) are in line with
370 EFs for computers derived from chamber studies by Kemmlein et al. (2003). Although some
371 modelling studies have reported EFs that are consistent with each other, many uncertainties
372 remain. To address these, improved knowledge of the physicochemical properties of FRs,
373 combined with direct determination of EFs and SERs from chamber studies is recommended.
374

375 **5. Chamber studies**

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

390

391 **5.1. Chamber studies on emissions of FRs**

392 There are only a few chamber studies focussing on emissions of FRs from indoor
393 materials published in peer-reviewed journals (Bakó-Biró et al., 2004; Kemmlein et al., 2003; Ni
394 et al., 2007; Salthammer et al., 2003). This is likely due to the difficulties of determining low
395 concentrations and the need for longer studies in order to reach steady state conditions in the
396 chamber. In fact, there are few cases where a limited number of days (e.g. less than 50 days)
397 is sufficient to measure time-release behaviour of SVOCs at room temperature (Clausen and
398 Kofoed-Sørensen, 2009) and longer experimental durations are often impractical. Kemmlein et
399 al. (2003) reported equilibrium conditions after 60 days in a 0.02 m² glass test chamber for
400 TCPPE emissions from insulating boards. Investigations at elevated temperature are useful as
401 the experimental time needed to reach steady state conditions are reduced and in some cases
402 loss to sink effects is reduced (Clausen et al., 2012). Increasing the temperature however may

403 decrease the relevance of chamber experiments to relating results back to ‘real world’
404 scenarios. Specific details of the reported chamber studies are listed in Table 3 and a summary
405 of the reported specific emission rates of FRs is given in Table 4.

406 Kemmlein et al. (2003) measured emissions of a broad range of FRs (PBDEs, HBCDs,
407 TBBPA and PFRs) from different types of building materials and consumer goods (e.g.
408 computers, TVs, printed circuit boards). All products, with the exception of a TV housing unit
409 and a PC housing, were obtained directly from the manufacture and tested immediately. The
410 experiments were conducted in three types of emission test chambers: two glass cells (0.001
411 m³ and 0.02 m³) and a standard volatile organic compound (VOC) emission stainless steel test
412 chamber (1 m³). Emission chamber conditions were controlled at 23 ± 0.1 °C (50 ± 3% RH)
413 for building materials and consumer goods, and at 60 ± 0.1 °C (8 ± 3% RH) to simulate
414 operational conditions of printed circuit boards. Active air sampling was conducted using a
415 glass tube equipped with pre-cleaned PUF plugs. Tris (2-chloro-isopropyl) phosphate or
416 TCPP (TCIPP) was one of the most commonly emitted PFRs in PUF applications and
417 depending on the sample, area specific emission rates (SERa) of TCPP (TCIPP) varied in the
418 range of 21 ng/m²h (upholstery stool) to 140 µg/m²h (assembly foam with rough surface).
419 Emissions of HBCD from polystyrene insulating boards were investigated with emissions not
420 detected in air after a test period of more than 100 days. This may be due to high experimental
421 LODs (between 0.09 and 1.8 ng/m³), an issue also reported by Bakó-Biró et al. (2004) for
422 SVOCs. Also, low sampling volumes (5-40 m³) may be of relevance as SERs or SVOCs have
423 shown to be strongly dependent on the air exchange rate in the chamber (Clausen et al., 2010).
424 However, after rinsing the chamber walls with solvent, 21 µg/m² (0.02 m³ chamber) and 0.33
425 µg/m² (0.001 m³ chamber) were recovered for ΣHBCDs. The reported SERa of ΣHBCD from
426 polystyrene insulating boards, calculated from these concentrations, varied between 0.1
427 ng/m²h and 29 ng/m²h.

428 Salthammer et al. (2003) also investigated various polyurethane products (e.g. insulating
429 foams, flooring materials) for emissions of triethyl phosphate (TEP). A self constructed glass
430 chamber of 1m³ volume was used with controlled experimental conditions of 23°C (45% RH).
431 However Tenax TA sorptive material, commonly used for analysis of VOCs, was used for
432 analyte capture rather than PUF plugs as in the Kemmlein et al. (2003) study. The calculated
433 SERa for TEP after 24 h, was > 100 µg/m²h for products which were less than 5 weeks old
434 and obtained directly from the manufacturer. In all experiments the measured SERa decreased
435 over time and after 168 h only traces were measured, showing the importance of product age
436 when testing volatile compounds.

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

452 Bakó-Biró et al. (2004) measured the emissions from a personal computer system in a
453 1 m³ glass test chamber. Samples from the exhaust airflow of the chamber were collected on
454 Tenax TA for VOCs and also XAD-II for SVOCs. Although the presence of BFRs was
455 expected in the tested PC systems, no emissions were detected in the air samples. It was
456 presumed this result was due to the poor sensitivity of the analytical method (LOD 20 µg/m³).
457 The test temperature increased from 24 °C at the start of the experiment to 32 °C during the
458 experiment due to heat released from the working computer system. Carlsson et al. (2000) also
459 reported increased temperatures of up to 50 °C on the top outlet cover of video display units
460 (VDUs) during operational conditions. In this experiment, emissions from brand new VDUs
461 were monitored in two furnished offices (57.8 m³ and 25.9 m³). The VDUs were kept in
462 continuous operation mode for 8 days in the 57.8 m³ office (short-term emission study) and
463 183 days in the 25.9 m³ office (long-term emission study) with emissions collected on PUFs.
464 Prior to the test background concentrations of selected PFRs such as tri(*n*-butyl) phosphate
465 (TNBP), tris(2-chloroethyl) phosphate (TCEP), tri(chloropropyl) phosphate (TCIPP), tri(2-
466 butoxyethyl) phosphate (TBOEP) and triphenyl phosphate (TPHP), were measured in both
467 office modules without the presence of VDUs. After one day of sampling in the presence of
468 the VDUs, triphenyl phosphate (TPHP) was measured at concentrations of up to 82 ng/m³
469 (57.8 m³ office) and 94 ng/m³ (25.9 m³ office). After 8 days, the concentrations of triphenyl
470 phosphate (TPHP) decreased to 40% of the concentrations detected on day 1 in both offices.

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

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

490

491 **5.2. Chamber studies on mass transfer to dust of SVOCs**

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

500 Schripp et al. (2010) investigated the mass transfer of the SVOCs di(2-
501 ethylhexyl)phthalate (DEHP) and di-*n*-butylphthalate (DnBP) to different samples of house
502 dust, soil and sand from emission sources. Deposition of volatilised phthalates was
503 investigated in 0.5 m³ stainless steel chambers using different air velocities. Glass plates,
504 coated with pure phthalate or with plasticized wall paint containing 1% w/w of phthalate,

505 were placed inside the chamber along with 3 g of house dust, soil or sand. Significant
506 increases of DHEP were not seen in any of the solid matrices, potentially due to incomplete
507 equilibrium inside the chamber. Significant increases in concentrations detected in all the
508 different dust or soil matrices were reported for DnBP with higher concentrations (>10 times
509 higher) seen in dust and soil than in sand. This is likely due to the different organic carbon
510 contents of the solid matrices influencing the level of deposition, and a weak correlation was
511 reported between phthalate uptake and the organic carbon content of a matrix. Greater
512 concentrations in dust/soil were also associated with higher air velocities inside the chamber,
513 due to different emission behaviours in each scenario. A higher air velocity increases
514 vaporisation of analytes and increases subsequent mass transfer to dust.

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

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

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

536

537 **6. Research gaps and future perspectives**

538 **6.1. Sink Effects**

539 A commonly reported issue for chamber studies of SVOCs like FRs is loss to sink
540 effects, as compounds with higher boiling points have increased adsorption to chamber walls
541 (Uhde and Salthammer, 2006). Methods suggested to reduce this loss include lining the chamber
542 with a Teflon coating and electroplating stainless steel wall surfaces (Destailats et al., 2008), or
543 using hand polished surfaces such as in the Field and Laboratory Emission Cell (FLEC), for a
544 greater reduction of active sites (Clausen et al., 2004). Reducing contact time through increased
545 air exchange rates and decreasing chamber surface to volume ratios, using new approaches
546 such as passive flux samplers (Ni et al., 2007), may help reduce these effects, but as yet no
547 comparative studies have investigated this. Procedures for eliminating sink effects have not
548 been reported, however investigations of post-experiment recovery of lost analytes have been
549 reported. These methods include heating the chamber to elevated temperatures, collecting
550 subsequent air emissions; and rinsing the chamber walls with solvent, to determine
551 concentrations recovered from the chamber walls (Katsumata et al., 2008; Kemmlein et al., 2003).
552 Heating an emission chamber to 80°C has recovered detectable concentrations of BDE47,
553 BDE99 and BDE100 (Kemmlein et al., 2003). A cooled plate (fogging device) inside the
554 chamber has also been used as a means of assessing sink effects (Uhde et al., 2001). Kemmlein
555 et al. (2003) placed convex glass pieces inside the emission chamber throughout experiments.
556 The glass piece was rinsed with toluene, post experiment, with detectible concentrations of
557 TBBPA (64-116 ng/m³) recovered.

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

568 Even with an accurate measure of sink effects, limitations exist for chamber
569 experiments when extrapolating information to indoor models as the isolated chamber
570 conditions differ from those in the environment being simulated. Indoor environments
571 themselves provide other surfaces that act as FR sinks, such as thin films on glass windows
572 (Butt et al., 2004). Typically, sink effects within an indoor environment are unknown and as

573 test chambers do not easily mimic “real-world” fluctuating environmental conditions (Schripp
574 et al., 2010), there is difficulty in extrapolating results from emission chamber tests to indoor
575 microenvironments. The lack of a thorough investigation into sink effects, especially for FRs,
576 highlights this as an increasingly important area of research to: 1) determine the extent of this
577 absorption loss on FR analysis, and 2) correctly report EFs and SERs, as well as subsequent
578 levels of deposition to dust from treated products.

579

580 **6.2. Appropriate conditions for a standardized testing method**

581 One standardized method (ISO, 2011) exists for investigating area specific emission
582 rates of SVOCs (defined as any organic compound with a boiling point in the range of 240-
583 260°C to 380-400°C) in a Micro-chamberTM. Operation of the chamber at 200-220°C, post
584 experiment, is required to recover greater than 80% of SVOCs in a standard solution. As
585 SVOCs vary considerably in their physicochemical properties, it is unreasonable to assume
586 this level of recovery is achievable for all SVOCs, including FRs. As stated in the ISO 16000-
587 25:2011 standard, the extent of loss is dependent on the compound and additional tests are
588 encouraged to ‘increase understanding of these [sink] effects’. Not all commercially available
589 standard test chambers have the capability for higher temperatures, which is also likely to
590 affect some FRs through thermal degradation or thermal rearrangement. The HBCD
591 diastereomers in the technical formula rearrange from the γ -HBCD to the α -HBCD
592 diastereomer at temperatures above 100°C (Heeb et al., 2008), hence more appropriate standard
593 procedures are needed. Air flow rates can also differ between experiments as chambers have
594 been operated at lower flow (3 mL/min (Bakó-Biró et al., 2004)) than average indoor scenarios
595 (~20 mL/min (Bakó-Biró et al., 2004)) to improve LODs but in a standardized cases for testing
596 VOC emissions, higher air flows are required (100-200 mL/min) (ECMA, 2010).

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

607 the treated product between the two tests, stressing the importance of careful experimental
608 design for chamber experiments.

609 The standardized methods for VOC testing recommend conducting chamber
610 experiments at room temperature (23°C) (ECMA, 2010). Operating electronics however can
611 reach temperatures of 50°C (Carlsson et al., 2000) and chamber experiments with functioning
612 electronics inside have increased chamber temperatures to at least 32°C (Bakó-Biró et al.,
613 2004). As such, calculating emissions from products at room temperature may not be relevant
614 for determining total exposure, so this is also an important consideration when designing
615 chamber experiments. The operational state of electronics, whilst tested in the emission
616 chamber, is another variable. Whether the equipment is idle, in standby mode, partly
617 operational or in full operation for the duration of the test can influence the emissions
618 detected (Destailats et al., 2008). The ECMA (2010) standardized method for testing VOCs
619 from computers requires testing whilst tapping keystrokes on the computer, but this will not
620 simulate all systems in action. Underestimations of emissions produced by fully functioning
621 equipment and contamination by fine particle abrasion causing migration to dust may result,
622 leading to underestimations of levels of exposure. Age and operational state of the material
623 along with chamber temperature are important considerations for designing relevant chamber
624 experiments, yet little is known about variations in results caused by these parameters.
625 Research is required to provide relevant standardized methods, with appropriate experimental
626 parameters specified, to create uniformity in the reported literature.

627

628 **6.3. Particulate generation and mass transfer to dust**

629 Another consideration for SVOC measurements, requiring further research, is particle
630 generation from laser printers and subsequent ozone reactions inside the chamber (Lee et al.,
631 2001). Printer generated VOCs react with ozone to form secondary organic aerosols (Wang et
632 al., 2012) suggesting the possibility of similar reactions with SVOCs that influence
633 measurements of emissions of FRs. As emitted SVOCs can be present in both the gas and
634 particle phases of air due to their lower vapour pressure (Weschler and Nazaroff, 2008)
635 preferential adsorption to generated particles will also effect emission, or gas phase,
636 measurements. Enhanced emissions from the product due to the presence of particulates is
637 also a necessary area for research, as mass transfer to particulates (dust) can be an additional
638 emission pathway increasing total emissions of volatiles (Clausen et al., 2004). Particles also
639 have an important role in transport of SVOCs to indoor environments and contribute to
640 exposure via inhalation (Benning et al., 2013) hence these interactions are an important area for

641 future research. At the time of this review there were no reported studies investigating the
642 gas-particle interactions of emitted FRs. However phthalates, particularly DEHP, have been
643 reported in these studies providing insights into future directions for FR studies. The study by
644 Benning et al. (2013) conducted emission chamber investigations of DEHP, emitted from vinyl
645 flooring, and the interaction with ammonium sulphate particles. The mass transfer of DEHP
646 was increased with the presence of particles, with the partitioning to particles suggested to be
647 affected by inorganic compared to organic particles, the particle surface area, or the degree of
648 coverage of the particle surface area by the sorbed SVOC. As SVOCs sorb to particles, the
649 organic matter content of the particle increases, promoting further partitioning to the particle
650 (Weschler and Nazaroff, 2008).

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

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

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

691

692 **Acknowledgements**

693 The research for this review has received funding from the European Union Seventh
694 Framework Program (*FP7/2007-2013*) under grant agreement No 264600 (INFLAME
695 project)

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

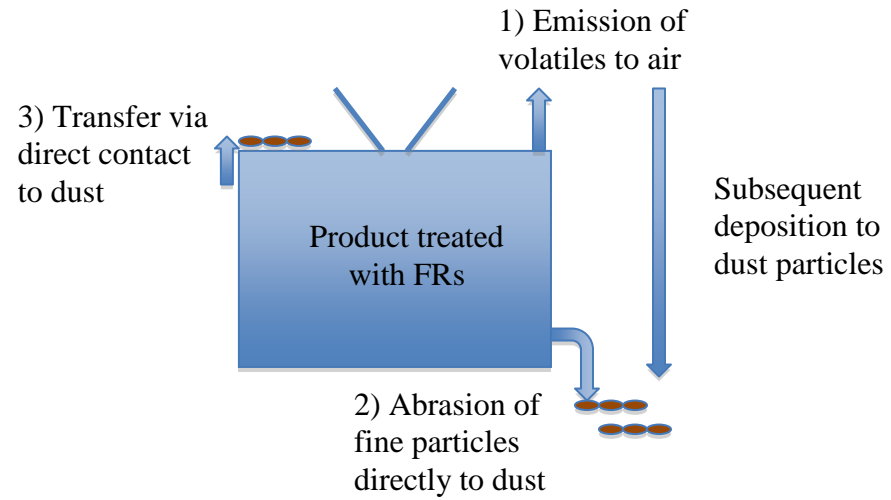


Table 1: Summary of uses of various PFRs and NBFRs

<i>Class of FR</i>	<i>Compound/functional group</i>	<i>Use</i>	<i>Reference</i>
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-butoxyethyl) 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	(Kemmllein 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			
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
<i>Building materials, SERa, µg/m².h</i>			
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	
<i>Electronics</i>			
TV set housing, SERa, ng/m ² .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	