

# VU Research Portal

## Occurrence and Fate of Alternative Flame Retardants in the Environment

Brandsma, S.H.

2014

### **document version**

Publisher's PDF, also known as Version of record

[Link to publication in VU Research Portal](#)

### **citation for published version (APA)**

Brandsma, S. H. (2014). *Occurrence and Fate of Alternative Flame Retardants in the Environment*.

### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

### **Take down policy**

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

### **E-mail address:**

[vuresearchportal.ub@vu.nl](mailto:vuresearchportal.ub@vu.nl)

## Chapter 1. General introduction

## 1. Flame retardants

The exact number of chemicals on the global market is not known (UNEP Global Chemical Outlook (GCO), 2012) but we know that our current society is built on chemicals that are used in many products and applications. The European REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) program is the legislative framework on chemicals of the European Union (EU). The aim is to reduce the risk of chemicals for humans and environment. More than 100,000 chemicals have been registered. Polymers and plastics contain about 80% of industry's output worldwide and contain a variety of chemicals used as plasticizers, polymer property modifiers, fillers, stabilizers, surfactants, flame retardants (FRs), etc. Some of these chemicals, such as FRs, are used in a high percentage in the products. FRs are added to plastics and other polymer materials according to flammability standards for fire safety (Alaee et al., 2003). In the past three major groups of brominated flame retardants (BFRs) were used: polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), and hexabromocyclododecane (HBCD). These BFRs were added in high levels (2-25% per weight of product) to plastic and polymer materials to meet fire safety standards. A large variety of polymer-FR formulations have been developed that meet the fire safety- and other technical requirements. BFRs are relatively popular because they hardly impair the plastic characteristics, are very effective as FR in relatively low amounts compared to other FRs and are relatively cheap.

Unfortunately, some BFRs have unintended negative effects on the environment and human health. Some of them show a strong bioaccumulation in aquatic and terrestrial food chains, some are very persistent and some show serious toxicological effects such as endocrine disruption. During the last decade an increasing number of reports have presented evidence of these negative effects caused by BFRs. A number of BFRs (PBDEs, HBCD, and TBBPA in particular) can be found in substantial concentrations in the human food chain, human tissues and breast milk (Schantz et al., 2003, Hites, 2004; Fångström et al., 2005; Schecter et al., 2005; She et al., 2007, Toms et al., 2011, Domingo, 2012, Covaci et al., 2012, Law et al., 2014). The report on exponentially increasing PBDE concentrations in Swedish human milk was particularly alarming (Norén and Meyronité, 2000), but was later followed by reports on even higher BFR concentrations in human milk from the USA (Schecter et al., 2008). Zegers et al. (2003) showed strongly increasing PBDE and especially decaBDE concentrations with time in sediment cores from the Dutch Wadden Sea, the Oslofjord and a German lake. Morris et al. (2004) reported the occurrence of TBBPA and relatively high levels of HBCD in various west-European environmental compartments such as eel from Belgium, sewage sludge from the UK, Ireland and The Netherlands and in various fish species from the North Sea. De Boer et al. (1998) and Boon et al. (2002) demonstrated that PBDEs were accumulating in marine food chains and even into lung-breathing animals such as seals, sperm whales and porpoises. Meanwhile in addition to these well-known BFRs, newer classes of BFRs have been detected in the environment such as decabromodiphenylethane (DBDPE) and 1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE) that were used as alternatives for Deca-BDE and Octa-BDE, respectively (Kierkegaard et al., 2004; Hoh et al.,

2005). Also, Firemaster 550 containing a mixture of bis (2-ethylhexyl) 2,3,4,5- tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB) is used as alternative for Penta-BDE in polyurethane foam (PUF) (Stapleton et al., 2009). More recent studies showed that novel FRs are also detected in the environment (De Wit et al., 2011; Covaci et al., 2011; Lopez et al., 2011; Ballesteros-Goméz et al., 2014). In addition to BFRs also other alternative FR groups such as organophosphorus-based FRs (PFRs) have been reported in the environment (Sunkvist et al., 2010; Kim et al., 2011; Van der Veen and De Boer, 2012). Apart from reports on FR concentrations in the outdoor environment, FRs have been found in the indoor environment as well. The presence of BFRs, PFRs and novel FRs have been reported in house dust (Stapleton et al., 2004, 2009; Harrad et al., 2008; Van der Veen and De Boer, 2012; Ali et al., 2013) The presence of these FRs in electronics, cushions, carpets and furniture may result into a release of some FRs in our homes. Consequently, uptake of some FRs through dust may be an important route for human FR exposure and differs from uptake routes of polychlorobiphenyls (PCBs) for which food intake is the primary exposure route. Previous toxicological research demonstrated that some BFRs could exert a range of adverse health effects, including endocrine disruption and neurotoxicity. Recent studies identified the brain and nervous system as some of the most vulnerable targets for the toxic actions of PBDEs (Kodavanti et al., 2005; Mundy et al., 2004; Viberg et al., 2006; Dingemans et al., 2007, 2008).

Due to the bans and restrictions on PBDEs the use of alternative FRs is necessary to meet the fire safety standards. Banning and restricting specific BFRs implies a serious risk of the introduction of alternatives which the risks for the environment and human health are unknown and could possibly be even higher than those of the BFRs. A current review showed that many data gaps exist there is an substantial lack of knowledge on the toxicity, persistency and bioaccumulation of many of the alternatives (Waaijers et al., 2013). Furthermore, it is important that substitution options do not adversely affect the function and reliability of the end products.

#### *1.1.1. General mode of action*

FRs are applied to polymer materials to lower the ignition potency, reduce the spread of a fire, suppress smoke formation and prevent the polymer from dripping. The working mechanisms of FRs are strongly depending on the FR and the product it is used in. In general there are five FR mechanisms that act in the condensed or the gas phase (Troitzsch et al., 1998; Rakotomalala et al., 2010).

1) Radical quenching in the gas phase; BFRs like PBDEs work mainly through this mode by interfering with the highly reactive  $O\bullet$  and  $OH\bullet$  radicals that feed the fire. During combustion the FR will break down in free halogen radicals which further react to halides. These halides quench the normal reactions that would take place in a fire by reacting with the highly reactive  $O\bullet$  and  $OH\bullet$  radicals to form less active molecules (like water) and halogen radicals. This mechanism is also called

radical scavenging: replacing the oxygen by a halogen in the reaction with the product, in that way limiting combustion.

2) Thermal barrier; FRs can also work by forming a char barrier at the surface of the condensed phase to reduce the heat transfer from the fire to the combusting product. PFRs act through this mode, forming a glassy layer of phosphoric acid and generating an intumescent char. However, some PFRs also act through radical quenching.

3) Thermal quenching; Metal hydroxides can undergo endothermic degradation whereby the metal hydroxides decompose to metal oxides and water. During this process the water evaporates and cools the polymer and dilutes the flammable gases. Metal hydroxides can act in both the condensed and the gas phase of a fire.

4) Inert gas dilution; During combustion metal hydroxides and some nitrogen based FRs such as melamine polyphosphate (MPP) release an inert gas that will dilute the oxygen supply to the fire.

5) Physical dilution; Inserted fillers can act as heat sink by increasing the heat capacity of the material or reduce the fuel contents. Examples of inert fillers are nanocomposites, glass fibers and minerals such as talc.

Some FRs may function by more than one mechanism such as MPP whereby the nitrogen groups act as inert gas dilution and the phosphoric acid acts as thermal barrier. Metal hydroxides undergo thermal quenching and inert gas dilution (Pinfa 2009; Rakotomalala et al. 2010).

FRs can be added to polymer material in three ways: i) as an additive, ii) reactive or iii) polymeric based (Guerra et al., 2001). Additive FRs are incorporated into the polymer material by physically mixing. There is no chemical reaction involved in this process. Additive FRs such as PBDEs and HBCD are not bound into the polymer material and can therefore also more easily leach out. Reactive FRs, such as TBBPA, 9,10-Dihydro-9-oxa-10-phosphaphenanthrene oxide (DOPO) and m-phenylene methyl phosphonate (Fyrol PMP) are covalently bound to the polymer material in which they are used. A disadvantage of the reactive FRs can be that they have a strong effect on the properties of the polymer compared to additive FRs. An advantage is that the reactive FRs do not easily leach from the product. Polymeric FRs such as brominated polystyrene (BPS) have in general a very high molecular weight and are incorporated in the backbone of the polymer and are less bioavailable.

### *1.1.2. Loading levels*

The amount of FRs required in the polymer to meet fire safety regulations is depending on the type of FRs and the polymer. BFRs work more effectively than metal hydroxides. Therefore, metal hydroxides require a higher FR loading. In Table 1 the FR loading levels are given for some common FR groups (Weil and Levchik, 2009; US EPA, 2014a). The wide range of the FR loading is influenced by the different polymer materials. Some polymers need a substantially higher FR loading than others to meet the same flame retardancy.

Table 1.1. Typically FR loading levels in % per product weight (Table copied from US EPA, 2014).

FR group	Loading (%)
BFRs	2 to 25%
Aluminium Hydroxide	13 to 60%
Magnesium Hydroxide	53 to 60%
Chlorophosphates	9 to 10%
Organophosphorus	5 to 30%

Adding a synergist in combination with an FR to polymer materials decreases the FR loading. A synergist is not an FR but it increases the efficiency of the FR. Therefore, lower amounts of the FR can be added to the product. An example of a synergist which is used in combination with halogenated FRs such as BDE209 is antimony trioxide (ATO). Also zinc stannate (ZS) and nanoclay can be used as synergist in combination with inorganic phosphorus and nitrogen based FRs. Combining FRs is another way of increasing the efficiency of the FR and decreasing the FR loading. For instance, a combination of resorcinol bis-(diphenylphosphate) (PBDPP) with bisphenol A bis (diphenylphosphate)(BPA-BDPP) or/and tris(phenyl) phosphate (TPHP) is more effective than using only one of these compounds (Levchik and Weil, 2006).

### 1.1.3. Restrictions in use

FRs are incorporated into polymer material to meet fire safety standards. PBDEs have been used for decades as FRs because of their good flame repelling properties, low costs, stability and ease of incorporation in polymer products. The three main commercial PBDE mixtures used were Penta-, Octa- and Deca-BDE. The commercial Penta-BDE mixture has been used since the 1960s, mainly in polyurethane foam (PUR) in furniture, car seats and carpet paddings. The commercial Octa-BDE mixture was used in acrylonitrile butadiene styrene (ABS), polybutylene terephthalate polyamides and high impact polystyrene (HIPS). DecaBDE was mainly used in HIPS for television and computer housings and upholstery fabrics. These commercial PBDE mixtures were all used as additive FRs. During use they can easily leach out (Alaee et al., 2003).

The commercial Penta-BDE and Octa-BDE mixtures are therefore listed as persistent organic pollutants (POP) under the Stockholm convention and were banned in the EU in 2003 and voluntarily phased out in the US in 2004 (BSEF, 2014). More recently, the commercial Deca-BDE mixture was banned from use in electrical and electronic equipment in the EU. Furthermore, the Bromine Science and Environmental Forum (BSEF) has decided, in cooperation with the US Environmental Protection Agency (EPA), to voluntarily phase out the production of DecaBDE by 2013 (BSEF, 2014). The ban and phase out has led to an increase in use and production of alternative FR groups.

## 2. Alternative flame retardants

Alternative FRs can be divided in six groups, halogenated, organophosphorus, inorganic/metal based, nitrogen based, nanocomposites and bio-based FRs.

Halogenated FRs include all FRs containing halogens. The brominated FRs DBDPE and BTBPE used as alternatives for Deca-BDE and Octa-BDE, respectively, also belong to this category (Kierkegaard et al., 2004; Hoh et al., 2005). Other examples are BEH-TEBP and EH-TBB, which are bromine containing FRs used in the commercial FR mixture Firemaster 550 used as alternative for Penta-BDE (Stapleton et al., 2009). However, there are many more halogenated FRs such as for example the chlorinated paraffins and many others that can be used as alternatives for the PBDEs. There are already more than 80 brominated compounds registered as FRs (Alaee et al., 2003; Covaci et al., 2011). Some of these have already been detected in the indoor and outdoor environment, indicating at least a certain persistency (Covaci et al., 2011). Halogenated flame retardants are used in a variety of materials, including textiles, electronics, building materials, plastics and foams.

PFRs with and without halogen atoms in their structure are on the market for decades. Some were already reported in the late 1970s in sediment samples from the US (Sheldon and Hites 1978). The use and production of this alternative group of FRs increased after the ban and restriction of the commercial PBDE mixtures (BCC research, 2013, Van den Eede et al., 2011). The most common ones are the chlorinated organophosphorus compounds tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP) and tris(1,3-dichloroisopropyl) phosphate (TDCIPP), which are used in polyurethane foam (PUF), textiles, plastics, wood preservation coating and unsaturated polyester resins. High PFR concentrations have been detected in house dust with levels that exceed those of the PBDEs, HBCD and TBBPA (Stapleton et al., 2009; Van den Eede et al., 2011; Ali et al., 2013). In general, PFRs seem to be less persistent than the BFRs and limited data is available on their toxicity. However, PFRs with halogen atoms in their structure may be more persistent than those without halogens (Van der Veen and De Boer, 2012). The properties, production, environmental occurrence, toxicity and analysis of PFRs have been recently reviewed by Van der Veen and De Boer, (2012). PFRs are used in some upholstered furniture, foam mattresses, textiles, television casings, rubber and plastics.

Different inorganic metal based compounds such as aluminum trihydroxide (ATH) and magnesium dihydroxides (MDH) are used as FRs. Metal hydroxides are easy to obtain, cheap and not toxic. Relatively high loadings (30-60%) are required to obtain sufficient flame retardancy. This may have a strong influence on the material properties. Metal based FRs are therefore also used as synergist in combination with other FRs such as the metal phosphinates. Two other inorganic metal based compounds which are primary used as alternative non-toxic synergist for antimony trioxide ( $Sb_2O_3$ ) are zinc hydroxy stannate (ZHS) and zinc stannate (ZS). ZHS and ZS are also used in halogen-free formulations and are particularly effective as partial replacement for ATH and MDH (Cusack, 2005).

Another metal based FR that is increasingly used as halogen-free FR (HFFR) as viable alternative for BFRs is aluminum diethylphosphinate (ALPi). Due to its high phosphorus content, good thermal stability and lower affinity to moisture, ALPi is used in a number of different applications. The FR efficiency increases when ALPi is used in combination with MPP as synergist. Inorganic metal based FRs are used in some plastics, paints, adhesives, rubber, textile back coatings, wires and cables.

One of the most commonly used nitrogen based FRs are melamine, melamine cyanurate (MC) and melamine polyphosphate (MPP). Melamine is mainly used in PUR foams. MC and MPP are used in nylons, and melamine in combination with ammonium polyphosphate (APP) in polypropylene intumescent formulations (Pinfa, 2014). Nitrogen based compounds are used as FR and as synergist in combination with other FRs such as ALPi.

Nanocomposites like organo-clays are passive FRs which indicate that they don't undergo any chemical reaction to reduce the fire but work by physical dilution. In general, nanocomposites will not stop the fire but delay it, therefore they need to be used in combination with other FRs to pass fire tests. Nanocomposites can be used in polyamides, polycarbonate, epoxy's, polyurethane and PVC. An advantage of nanocomposites is that they can improve the properties of the polymer. There is limited information about the toxicity of nanocomposites.

The last group of alternative FRs are based on bio-based materials. Alongi et al. (2013) and Carosio et al. (2014) found that deoxyribonucleic acid (DNA) from herring sperm and caseins from milk increase the flame retardancy of textiles. Carosio et al. (2014) showed that polyester and polyester-cotton treated with casein decrease the burning rate by 70 to 40%, respectively. Alongi et al. (2013) observed that DNA treated cotton fabrics do not burn at all during the horizontal flammability tests using an methane flame for 3 sec. Other studies describing the working of bio-based FRs are Hoffendahl et al. (2013), Reti et al. (2009) and Howell et al. (2011). These bio-based FRs may be used in the future as viable "green" alternatives, but more research is needed in bio-based FRs.

### **3. Alternative assessment studies of flame retardants**

As described in paragraph 1.2, there are numerous alternative FRs on the market. The ban on some of the commercial BFR mixtures has ensured that manufactures are constantly looking for viable alternatives. Many alternative FRs still have similar types of structures, which may imply similar risks for the environment and human health as the BFRs, and may subsequently result in new bans and restrictions of these alternative FRs. Therefore, adequate risk assessment is essential when developing alternative FRs. Viable substitution options for the banned BFRs should be safe for the environment and have a proper FR efficiency at the same time, without adversely affecting the functioning and reliability of the end product. Alternative assessment studies could contribute to achieve this goal.

Different chemical alternative assessment (CAA) studies have been described (O'Brien, 2000; Rossi et al., 2006; Lavoie et al., 2010; Howard, 2014). Howard (2014) observed that these studies all tried to accomplish similar goals.

- Avoid substitution of a chemical by an alternative of which the risks for the environment and human health could also be high or even higher (regrettable substitution)
- Explore multiple options instead of one single substitution option.
- Focus on the hazard evaluation rather than including a time consuming exposure assessment
- Propose a selection of chemicals with the lowest available hazard profile, instead of keeping the risk below a threshold.

The Design of the Environment (DfE) program of the US EPA already used CAA for the following commercial FR groups: Deca-BDE, HBCD and FRs used in PUR foams (US EPA, 2014a, b, and c). CAA is used to identify viable alternatives by evaluating their health and environmental hazards, which can be used by decision makers and manufactures to find a viable substitution for BFRs. Also in Japan a CAA was performed on HBCD. (Masunaga et al., 2013). Substitution of high production chemicals can have a direct impact on the human risk and the environmental exposure (Howard, 2014). Therefore, it is very important that the assessment reports contain viable information that can be used by decision makers to identify the proper FRs. The missing information makes it rather difficult to include these compound in a CAA. The ban on Penta-BDE has for example led to an increase in use of Firemaster 550. This compound was unknown at the time the CAA was performed on Penta-BDE (Howard, 2014). However, this compound is now used as alternative FR for Penta-BDE and seems to be persistent, bioaccumulative and toxic as well (US EPA 2014c; Covaci et al., 2011). The disadvantages of CAA compared to a more extensive risk assessment is that it may suffer from insufficient data. Therefore, it is very important that chemical manufacturers are more open with regard to their chemical evaluation data, which are nowadays mostly confidential. Until now this data is only available for authorities (e.g. ECHA and EPA in the US). The main advantage of CAA compared to a risk assessment is that instead of providing a negative list about specific FRs, it provides a list of viable alternative FRs, which are less harmful for humans and environment.

#### **4. ENFIRO**

The main part of the studies included in this PhD thesis were conducted within the ENFIRO (Life Cycle Assessment of Environment-Compatible Flame Retardants: Prototypical Case Study) project (ENFIRO, 2013). The selection of the alternative FRs that were studied in this PhD thesis were mainly based on the selection that was made within the ENFIRO project.

#### 4.1. Introduction

Scientists worldwide are concerned about environmental and human safety because of the presence of FRs in food chains and humans. Therefore, and in addition to a critical review of the use of FRs in products, there is an urgent need for FRs that meet all fire safety standards and have an environmentally safe behavior at the same time. Suitable alternatives for BFRs, like various HFFRs, exist and those have been used already for some time in parallel to the BFRs. However, comprehensive environmental and toxicity studies hardly exist for most of these chemicals. Consequently, it would be possible that these alternatives for BFRs may show similar or even stronger detrimental effects than the BFRs themselves. This could easily lead to another loop of environmental analyses, toxicological tests, scientific and political debates, legislation, subsequently followed by bans of use and production. Such cycles have occurred before with polychlorinated biphenyls (PCBs), tetrachlorobenzyltoluenes (Ugilecs), and with Penta-BDEs and HBCD. The European research project ENFIRO had the ambition to stop these ongoing cycles. Through a pro-active approach, alternatives for specific BFRs were suggested that meet fire safety regulations, can be produced without problems by the industry, do not bioaccumulate and show no significant toxic effects on humans, plants or wildlife. By making such alternative FRs available through a collaborative study of universities and industries many years otherwise spent on monitoring, analysis, etc. are saved as well as many lives of test animals. The developed method of source control may also be applied for similar substitution cases and the approach and the results of ENFIRO will be useful for similar substitution studies, e.g. within REACH.

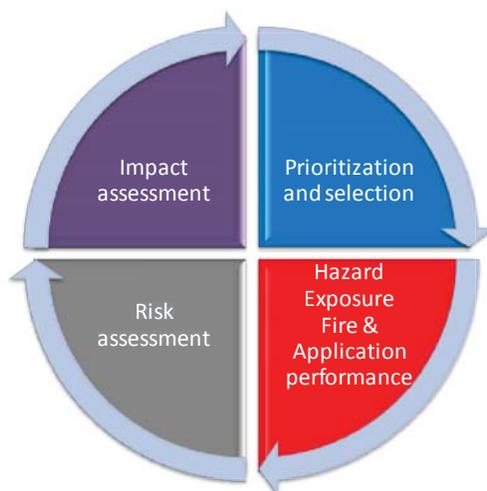


Figure 1.1: ENFIRO chemical alternative cycle.

#### 4.2. Approach

The ENFIRO strategy was divided in four main studies: i) prioritization and selection of alternatives, ii) hazard exposure and fire application performance, iii) risk assessment and iv) impact assessment (Fig. 1.1).

Based on literature, industrial information and prioritizing schemes developed within the project, alternative FRs were selected that could serve as viable alternatives to specific BFRs. During the prioritization and selection step three criteria were used to select alternatives, i) the alternative FRs were halogen free, ii) commercially available, and iii) could replace the BFRs in marketable polymers. The commercially viable alternative FRs selected in combination with polymers are listed in Table 1.2. After selecting these 15 HFFRs, information was collected on the hazard, exposure, fire performance, persistency, bioaccumulation and toxicity (PBT), physical-chemical properties and economic aspects such as cost of the FR and technical implementation. To fill these gaps in information, *in-vitro* and *in-vivo* health and environmental hazard characterization screening studies were performed. The selected FR-polymer applications were assessed on fire performance, application studied, weathering and leaching of the FRs from the polymers to water and air. To provide initial information on human and environmental exposure modelling test, persistency tests (OECD 301 and 309) leaching tests and environmental and human monitoring was carried out. Assessment of all these data resulted in a fine-tuned selection of viable FR-polymer combinations. All information from the hazard and exposure assessment tests were used for a risk assessment. The outcome of that assessment, together with socio-economic information was used in a life cycle assessment. The project followed a pragmatic approach, avoiding recommendations of environment-compatible substitution options that would not be viable for implementation by industry.

#### *4.3. Environmental and human exposure to alternative flame retardants*

The main part of this PhD thesis is focusing on the exposure and fate part of the ENFIRO project (ENFIRO 2013). The objective was to provide a quantitative assessment of the environmental exposure that could be anticipated from use of alternative FRs in different polymer materials. FRs are used in high concentrations in polymers materials such as, PUR foam in couches, carpet padding, isolation material, curtains, electronic equipment etc. During use the FR may leach out into the indoor environment, ending up in house dust. Through the waste water treatment plant (WWTP) or end of life, FRs may end up in the outdoor environment. One of the task was field monitoring of the alternative FRs in several European countries to assess the environmental contamination. To assess the indoor exposure, sampling was carried out in micro-environments where products containing FRs were used (e.g. homes, cars). Key matrices for environmental and human exposure (e.g. landfill leachates, sewage sludge, food, dust, sediment, fish etc.). A model in the ENFIRO project was used to guide the sampling, and alternative FRs were analyzed using established analytical methods. The measured concentrations were compared with the concentrations predicted by the model. This allowed the evaluation of the environmental behavior and exposure assessment provided by the model.

Seven of the fifteen selected HFFRs that were studied in ENFIRO were inorganic/metal based FRs. Inorganic/metal based FRs are stable in the plastic (polymer) products. However, once in the environment, they dissociate in ions. Monitoring HFFRs in the environment is therefore difficult. To

provide information on the occurrence and fate of HFFRs in the environment leaching experiments were performed.

*Table 1.2. List of selected commercially viable alternative FRs in combination with polymers that were studied in ENFIRO.*

Polymer material	Main BFR	Application	Proposed HFFR
Epoxy resins	TBBPA	Printed circuit boards, electronic components encapsulations, technical laminates	9,10-Dihydro-9-oxa-10-phosphaphenanthrene oxide (DOPO), aluminium hydroxide (ATH), Fyrol PMP
Epoxy encapsulates	Deca-BDE	Electrical Encapsulating & Casting	Melamine polyphosphate (MPP), Boehmite, aluminium diethylphosphinate (AlPi), ATH, zinc hydroxy stannate (ZHS), zinc stannate (ZS), zinc borate (ZB)
HIPS/PPE	Deca-BDE/Sb <sub>2</sub> O <sub>3</sub>	Housings for business machines, dashboards, toys, equipment's for refrigerator, telephones, and other consumer electronics	Resorcinol bis (biphenyl phosphate) (PBDPP), bis phenol A bis (biphenyl phosphate) (BPA-BDPP), tris(phenyl) phosphate (TPHP)
PC/ABS	Deca-BDE/Sb <sub>2</sub> O <sub>3</sub>	Housings for business machines, dashboards, toys, equipment's for refrigerator, telephones, and other consumer electronics	PBDPP, BPA-BDPP, TPHP
Polyamide 6 Polyamide 6,6	Brominated polystyrene (BPS)/ Sb <sub>2</sub> O <sub>3</sub>	Electrical & electronic equipment, connectors, switches etc., encapsulated electronic components	AlPi, MPP, ZB, ZS, melamine cyanurate (MC)
Polybutylene terephthalate (PBT)	Brominated polystyrenes/ Sb <sub>2</sub> O <sub>3</sub>	Electrical & electronic equipment, connectors, switches etc., encapsulated electronic components	AlPi, nanoclay (organo-clays based on montmorillonite, nano-MMT)
Ethylene vinyl acetate (EVA)	Deca-BDE/Sb <sub>2</sub> O <sub>3</sub>	Wire & cable	ATH, magnesium hydroxide (Mg(OH) <sub>2</sub> ) ATH coated with zinc hydroxy stannate (ZHS), Boehmite
Textile coatings	Deca-BDE/Sb <sub>2</sub> O <sub>3</sub>	Protective clothing, carpets, curtains, upholstered fabrics, tents, interior in public transportation	Ammonium polyphosphate (APP), pentaerythritol (PER), MPP, ZB
Intumescent coating: High impact polystyrene (HIPS)	Deca-BDE/Sb <sub>2</sub> O <sub>3</sub>	Housings of electronic products	Novel application attempting to reach V(0) for pure HIPS with intumescent coating based on ammonium polyphosphate (APP), PER, MPP

## 5. Scope of the Thesis

The scope of this thesis is to study the occurrence and fate of alternative FRs in the indoor and outdoor environment. This scope can be sub-divided in three parts:

- 1) Development and improvement of the analysis of alternative FRs
- 2) Investigation of the occurrence of alternative FRs in consumer products and understanding their leaching behavior
- 3) Determining the occurrence and fate of alternative FRs in the indoor and outdoor environment

In the first part of this thesis a brief literature review of PFR analysis is provided as well as a report of an interlaboratory study that was organized (*Chapter 2*). The aim of the interlaboratory study was to transfer knowledge on PFR analysis among laboratories and to investigate how well the laboratories perform. The analysis of a relative new group of compounds such as PFRs in various matrices is challenging, especially when the compounds of interest show a large variation in structures and have a wide range in  $K_{ow}$  values, as observed for the PFRs studied in this thesis.

In the third chapter of this thesis electronic equipment was studied as a possible source of two relatively new PFRs (PBDPP and BPA-BDPP) for the indoor environment (*Chapter 3.1*). Different consumer products were screened for these two PFRs using a novel analytical method that was recently developed.

Another part of *Chapter 3* is a study on the leaching behavior of alternative FRs (PBDPP, BPA-BDPP and inorganic and metal based FRs) from polymer materials as a potential route to the outdoor environment (*Chapter 3.2*). The polymer-FR formulations used for this study were formulations optimized from a fire safety perspective and present in realistic plastic products such as television casing or switches. Different properties of leaching (particle size, pH, polymer properties) were studied to better understand the leaching behavior.

In *Chapter 4* of this thesis we focused on the presence of PFRs in the indoor and outdoor environment. Different studies showed that PFRs are worldwide occurring in the indoor environment, especially in house dust, the PFR levels can exceed BFR levels (Stapleton et al., 2009; Van den Eede et al., 2011; Ali et al., 2013). Inhalation and ingestion of house dust is an important human exposure pathway of FRs (Jones-Otazo et al., 2005). Dust was collected in three European countries on and around electronic equipment to investigate if electronics are a source of PFR for house dust (*Chapter 4.1*). The same dust samples were analyzed to study the occurrence of the two novel PFRs (PBDPP and BPA-BDPP), which are used as viable alternatives for DecaBDE in TV/flat screen housings and other electronic consumer products (*Chapter 4.2*).

Regards the outdoor environment, PFRs have been detected in water, sediment and sewage sludge and recently the first results on PFRs in biota samples have been reported (Sundkvist et al., 2010; Kim et al., 2011; Chen et al., 2012). Data on the occurrence of PFRs in biota is still very limited. In *Chapter*

4.3 we, therefore, studied the occurrence and food web transfer of PFRs and BFRs in an estuarine pelagic and benthic food web in the Netherlands (Western Scheldt estuary). This final chapter is followed by a synthesis (discussion, conclusions, and outlook) in *Chapter 5*.

## References

- Alaee, M., Arias, P., Sjödin, A., and Bergman, Å. An overview of commercially used brominated flame retardants, their application, their use patterns in different countries/regions and possible modes of release. *Environ. Int.*, **2003**, 29, 683–689.
- Ali, N., Ali, L., Mehdi, T., Dirtu, A. C., Al-Shammari, F., Neels, H., Covaci, A. Levels and profiles of organochlorines and flame retardants in car and house dust from Kuwait and Pakistan : Implication for human exposure via dust ingestion. *Environ. Intern.*, **2013**, 55, 62-70.
- Alongi, J., Carletto, R. A., Di Blasio, A., Carosio, F., Bosco, F., Malucelli, G. DNA: a novel, green, natural flame retardant and suppressant for cotton. *J. Mater. Chem. A*, **2013**, 1, 4779-4785.
- Ballesteros-Goméz, A., deBoer, J., Leonards, P. E. G. A novel brominated triazine-based flame retardant (TTBP-TAZ) in plastic consumer products and indoor dust. *Environ. Sci. Technol.*, **2014**, 48, 4468-4474.
- BCC research, Flame Retardant Chemicals: Technologies and Global markets. **2013**. Report code: CHM014L. <http://www.bccresearch.com>.
- Boon, J. P., Lewis, W. E., Tjoen-a-Choy, M., Allchin, C. R., Law, R. J., de Boer, J., ten Hallers-Tjabbes, C., Zegers, B. N. Levels of polybrominated diphenylethers (PBDE) in animals representing different trophic levels of the North Sea. *Environ. Sci. Technol.*, **2002**, 36, 4025-4032.
- BSEF (Bromine Science and Environmental Forum) <http://www.bsef.com/regulation> assessed July 2014).
- Carosio, F., Di Blasio, A., Cuttica, F., Alongi, J., Malucelli, G. Flame retardancy of polyester and polyester-cotton blends treated with caseins. *Ind. Eng. Chem. Res.*, **2014**, 53, 3917-3923.
- Chen, D., Letcher, R. J., Chu, S. Determination of non-halogenated, chlorinated and brominated organophosphate flame retardants in herring gull eggs based on liquid chromatography-tandem quadrupole mass spectrometry. *J. Chromatogr. A*, **2012**, 1220, 169-174.
- Covaci, A., Geens, T., Roosens, L., Ali, N., Van den Eede, N., Ionas, A. C., Malarvannam, G., Dirtu, A. C. Human Exposure and Health Risks to Emerging Organic Contaminants. *Handb. Environ. Chem.*, **2012**, 20, 243–305.
- Covaci, A., Harrad, S., Abdallah, M. A. E., Ali, N., Law, R. J., Herzke, D., de Wit, C. A. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. *Environ. Int.*, **2011**, 37, 532–556.
- Cusack, P.A: "Proceedings of High Performance Fillers", Rapra Technology, **2005**, Cologne, Germany, Paper 6.
- De Boer, J., Wester, P.G., Klamer, H.J.C., Lewis, W.E., Boon, J.P. Do flame retardants threaten ocean life? *Nature*, **1998**, 394, 28–29.
- De Wit, C. A., Kierkegaard, A., Richlund, N., Sellström, U. Emerging Brominated Flame Retardants in the Environment. *Handb. Environ. Chem.*, **2011**, 16, 241-286.
- Dingemans, M. M. L., Ramakers, G. M. J., Gardoni, F., Van Kleef, R. G. D. M., Bergman, A., Di Luca M., Van den Berg, M., Westerink, R. H. S. , Vijverberg, H. P. M. Neonatal exposure to brominated flame retardant BDE-47

reduces long-term potentiation and postsynaptic protein levels in mouse hippocampus. *Environ. Health Perspect.*, **2008**, 115, 865-870.

Dingemans, M. M. L., de Groot, A., van Kleef, R. G. D. M., Bergman, Å., van den Berg, M., Vijverberg, H. P. M., Westerink, R. H. S. Hydroxylation increases the neurotoxic potential of BDE47 to affect exocytosis and Ca<sup>2+</sup> homeostasis in PC12 cells. *Environ. Health Perspect.*, **2008**, 116, 637-643.

Domingo, J. L. Polybrominated diphenyl ethers in food and human dietary exposure: a review of the recent scientific literature. *Fd. Chem Toxicol.*, **2012**, 50, 238–249.

ENFIRO Final Report 2013 - ENFIRO (Life Cycle Assessment of Environment-compatible Flame Retardants ( Prototypical case study)FP&-Environment, nr 226563, last updated 2013-06-12. [http://cordis.europa.eu/publication/rcn/15697\\_en.html](http://cordis.europa.eu/publication/rcn/15697_en.html) assessed July 2014.

Fängström, B., Strid, A., Grandjean, P., Weihe, P., Bergman, A. A retrospective study of PBDEs and PCBs in human milk from the Faroe Islands. *Environ. Health*. **2005**, 4, 1-9.

Guerra, P., Alaei, M., Eljarrat, E., Barceló, D. Introduction to brominated flame retardants: commercially products, applications, and physicochemical properties. Eljarrat, E., Barcelo, D., (Eds.), *Brominated Flame Retardants*, Springer, Berlin/Heidelberg (**2011**), pp. 1–17.

Harrad, S., Ibarra, C., Abdallah, M. A. E., Boon, R., Neels, H., Covaci, A. Concentrations of brominated flame retardants in dust from United Kingdom cars, houses and offices: causes of variability and implications for human exposure. *Environ Int.*, **2008**, 34, 1170–1175.

Hites, R. A. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ. Sci. Technol.*, **2004**, 38, 945-956.

Hoffendahl, C., Fontaine, G., Bourbigot, S. Flame retardancy of bio-based polyether-block-amide polymer (PEBAX). *Polymer Degradation and Stability*, **2013**, 98, 1247–1255.

Hoh, E., Zhu, L., Hites, R. A. Novel flame retardants, 1,2-bis-(2,4,6-tribromophenoxy)-ethane and 2,3,4,5,6-pentabromoethylbenzene, in United States' environmental samples. *Environ. Sci. Technol.*, **2005**, 39, 2472.

Howard, G. J. Chemical alternatives assessment: the case of the flame retardants. *Chemosphere*. **2014**, DOI: 10.1016/j.chemosphere.2014.02.034.

Howell, B. A., Carter, K. E., Dangalle, H. Flame retardants based on tartaric acid: a renewable by-product of the wine industry. *Renewable and Sustainable Polymers*. **2009**, Chapter 9, 133-152.

Jones-Otazo, H., Clarke, J. P., Diamond, M. L., Archbold, A. J., Ferguson, G., Harner, T., Richardson, G. M., Ryan, J. J., Wilford, B. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environ. Sci. Technol.*, **2005**, 39, 5121-5130.

Kierkegaard, A., Björklund, J., Fridén, U. Identification of the flame retardant decabromodiphenylethane in the environment. *Environ. Sci. Technol.*, **2004**, 38, 3247-3253.

Kim, J. W., Isobe, T., Chang, K. W., Amano, A., Maneja, R. H., Zamora, P. B., Siringan, F. P., Tanabe, S. Levels and distribution of organophosphorous flame retardants and plasticizers in fishes from Manila Bay, the Philippines. *Environ. Pollut.*, **2011**, 159, 3653-3659.

Kodavanti, P. R., Ward, T. R., Ludewig, G., Robertson, L. W., Birnbaum, L. S. Polybrominated diphenyl ether (PBDE) effects in rat neuronal cultures: 14C-PBDE accumulation, biological effects, and structure-activity relationships. *Toxicol. Sci.*, **2005**, 88, 181-192.

Lavoie, E. T., Heine, L. G., Holder, H., Rossi, M. S., Lee, R. E., Connor, E. A., Vrabel, M. A., Difiore, D. M., Davies, C. L. Chemical alternatives assessment: enabling substitution to safer chemicals. *Environ. Sci. Technol.*, **2010**, 44, 9244-9249.

Law, R. J., Covaci, A., Harrad, S., Herzke, D., Abdallah, M. A. E., Fernie, K., Toms, L. L., Tagigami, H. Levels and trends of PBDEs and HBCDs in the global environment: Status at the end of 2012. *Environ. Int.*, **2014**, 65, 147-158.

Lopez, P., Brandsma, S. H., Leonards, P. E. G., De Boer, J. Optimization and development of analytical methods for the determination of new brominated flame retardants and polybrominated diphenyl ethers in sediment and suspended particulate matter. *Anal Bioanal. Chem.*, **2011**, 400, 871-883.

Masunaga, S., Kotani, K., Kobayashi, T., Miyake, A., Hondo, H., Managaki, S. Comparative risk assessment between flame retardants, hexabromocyclododecane and its substitutes, Japan, Annual Meeting of the Society of Environment, **2013**, p. 55 (2013.9.3-4; GRANShip, Shizuoka).

Morris, S., Allchin, C. R., Zegers, B. N., Haftka, J. J., Boon, J. P., Belpaire, C., Leonards, P. E. G., van Leeuwen, S. P. J., de Boer, J. Distribution and fate of HBCD and TBBPA brominated flame retardants in North Sea Estuaries and aquatic food webs. *Environ. Sci. Technol.*, **2004**, 38, 5497-5504.

Mundy, W. R., Freudenrich, T. M., Crofton, K. M., DeVito, M. J. Accumulation of PBDE-47 in primary cultures of rat neocortical cells. *Toxicol. Sci.*, **2004**, 82, 164-169.

Norén, K., Meyronité, D. Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20-30 years. *Chemosphere*. **2000**, 40-1111-1123.

O'Brien, M. Making better environmental decisions: an alternative to risk assessment. The MIT Press, Cambridge, Mass, **2000**, ISBN 987-0262650533.

Pinfa (Phosphorus, Inorganic & Nitrogen Flame retardants Association) Innovation flame retardants in E&E Applications-non-halogenated phosphorus, inorganic and nitrogen flame retardants. June **2009**, 2<sup>nd</sup> edition.

Pinfa (Phosphorus, Inorganic & Nitrogen Flame retardants Association) <http://www.pinfa.eu/non-halogenated-pin-frs/nitrogen-based-flame-retardants.html> Assessed July **2014**.

Rakotomalala, M., Wagner, S., Döring, M. Recent development in halogen free flame retardants for epoxy resins for electrical and electronic applications. *Materials*. **2010**, 3, 4300-4327.

Reti, C., Casetta, M., Duquesne, S., Delobel, R., Soulestin, J. Intumescent biobase-poly lactide films to flame retard nonwovens. *J. Eng. Fib. Fab.*, **2009**, 4, 33-39.

Rossi, M., Tickner, J., Geiser, K. Alternatives assessment framework, Version 1.0. Lowell Center for Sustainable Production, University of Massachusetts Lowell. **2006**, <<http://www.chemicalspolicy.org/alternativesassessment.lowellcenter.php>>.

Schantz, S. L., Widholm, J. J., Rice, D. C. Effects of PCB exposure on neuropsychological function in children. *Environ. Health Perspect.*, **2003**, 111, 357-576.

Schechter, A., Päpke, O., Tung, K. C., Joseph, J., Harris, T. R., Dahlgren, J. Polybrominated diphenyl ether flame retardants in the U.S. population: current levels, temporal trends, and comparison with dioxins, dibenzofurans, and polychlorinated biphenyls. *J. Occup. Environ. Med.*, **2005**, 47, 199-211.

Schechter, A., Harris, R., Musumba, A., Päpke, O. Brominated Flame Retardant in US foods. *Molec. Nutr. Fd Res.*, **2008**, 266-272.

She, J., Holden, A., Sharp, M., Tanner, M., Williams-Derry, C., Hooper, K. Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in breast milk from the Pacific Northwest. *Chemosphere*, **2007**, 67, S307-317.

Sheldon, L. S.; Hites, R. A. Organic compounds in the Delaware River. *Environ. Sci. Technol.*, **1978**, 12, 1188-1194.

Stapleton, H., Dodder, N., Offenberg, J., Schantz, M. M., Wise, S. Polybrominated Diphenyl Ethers in house dust and clothes dryer lint. *Environ. Sci. Technol.*, **2004**, 925-931.

Stapleton, H. M., Klosterhaus, S., Eagle, S., Fuh, J., Meekers, J. D., Blum, A., Webster, T.F. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. *Environ. Sci. Technol.*, **2009**, 43, 7490–7495.

Sundkvist, A. M., Olofsson, U., Haglund, P. Organophosphorous flame retardants and plasticizers in marine and freshwater and human milk. *J. Environ. Monit.*, **2010**, 12, 943-951.

Toms, L. Hearn, L., Sjödin, A., Mueller, J. Human Exposure to Brominated Flame Retardants. E. Eljarrat, D. Barceló (Eds.), *Brominated Flame Retardants*, Springer Berlin/Heidelberg. **2011**, pp. 203–239.

Troitzsch, J. H. "Overview of flame retardants, fire and fire safety, markets and applications, mode of action and main families, role in fire gases and residues." *Chemistry Today.*, **1998**, 16, 1- 19.

US EPA (**2014a**) (United States Environmental Protection Agency) An alternative assessment for the flame retardant decabromodiphenyl ether (Deca-BDE). Final report. January 2014.

US EPA (**2014b**) (United States Environmental Protection Agency) Flame retardant alternatives for hexabromocyclododecane (HBCD). Final report. June 2014.

US EPA (**2014c**) (United States Environmental Protection Agency) Flame retardants used in flexible polyurethane foam: an alternative assessment update. Final report. June 2014.

Van den Eede, N., Dirtu, A.C., Neels, H., Covaci, A. Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust. *Environ. Int.*, **2011**, 37, 454–461.

Van der Veen, I., de Boer, J. Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis, *Chemosphere*, **2012**, 88, 1119-1153.

Viberg, H., Johansson, N., Fredriksson, A., Eriksson, J., Marsh, G., Eriksson, P. Neonatal exposure to higher brominated diphenyl ethers, hepta-, octa-, or nonabromodiphenyl ether, impairs spontaneous behavior and learning and memory functions of adult mice. *Toxicol. Sci.*, **2006**, 92, 211-218.

Waaaijers, S. L., Kong, D., Hendriks, H. S., de Wit, C. A., Cousins, I. T., Westerink, R. H., Leonards, P. E. G., Kraak, M. H., Admiraal, W., de Voogt, P., Parsons, J. R. Persistence, Bioaccumulation, and Toxicity of Halogen-Free Flame Retardants. *Rev. Environ. Contam. Toxicol.*, **2013**, 22, 1-71.

Weil, E. and Levchik, S. Flame Retardants for Plastics and Textiles: Practical Applications, Hanser Publishers, **2009**, Munich/Cincinnati, OH. ISBN 978-1-56990-454-1.

Zegers, B. N., Lewis, W. E., Booij, K., Smittenberg, R., Boer, W., de Boer, J., Boon, J. P. Levels of polybrominated diphenylether flame retardants in sediment cores from Western Europe. *Environ. Sci. Technol.*, **2003**, 37, 3803-3807.