Environmental fate & effects of new generation flame retardants
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Chapter 1

General Introduction
In the middle ages, open fire places and the use of candles and ovens easily caused fires in the overcrowded wooden cities, the most well-known example being the Great Fire of London in 1666 (Porter, 1998). Already in 1421 a great fire destroyed large parts of the city of Amsterdam, by that time also mostly consisting of wooden buildings. When in 1452 disaster struck again and countless houses were burned to the ground (Figure 1), the city board required that from then on all houses should be made of stone instead of the cheaper wood (Bakker, 2008). In fact, this could be considered as one of the first official regulations demanding the use of flame retardant materials to prevent fire casualties.

Figure 1: Illustration of the big fire of Amsterdam in 1452, etching made by S. Fokke around 1750-1770. Copyright Stadsarchief Amsterdam, the Netherlands

In the second half of the 20th century, the exponentially growing number of applications of plastics provided a new flame retardancy challenge (Thompson et al., 2009), as plastics are readily combustible because of their high carbon and hydrogen content. Today it is estimated that about 7.5 million fires occur globally per year, with around 75,000 fire deaths and around 650,000 fire related injuries (Centre of Fire Statistics of CTIF et al., 2006). These vast losses of
life and property resulted in public pressure to provide safer materials and lead to governmental regulatory action. Nowadays, several regulations are included in legislation in order to increase fire safety in homes, but also in public places and transport (Inspectie Leefomgeving en Transport, Ministerie van Infrastructuur en Milieu (2014); Nederlands Instituut Fysieke Veiligheid (NIFV), 2013). To achieve safety requirements, chemical additives known as flame retardants (FRs) can be incorporated into many products used in daily life, such as furniture, electrical switches, laptops, mobile phones and cars (American Chemistry Council). The plastics industry is the largest consumer of FRs, followed by the textile industry (IHS Chemical, 2011). FRs make up about 27% of the polymer performance additives market (Murphy, 2001) and worldwide more than 2 million tonnes of FR were used in 2013 (Ceresana Consulting, 2014).

1.1 Flame retardancy

Flame retardants can prevent fire in several ways, all acting on at least one of the three prerequisites of a fire: combustible material (e.g. wood, polymers, or flammable gasses released from such), heat to ignite the fire and an oxidizing agent (mostly oxygen) to reduce the fuel, which sustains the fire (Yoon et al., 2013; Gilman, 1999; LeVan, 1984; Rakotomalala et al., 2010). Generally, there are four conventional types of FRs; halogenated-, inorganic-, organophosphorus- and organonitrogen-FRs. Halogenated FRs can release halogens that primarily act in the vapor phase by radical capturing. This interrupts the exothermic process of fire and suppresses combustion (Dasari et al., 2013). Mainly chlorinated and/or brominated organic compounds are used as these halogens have an enthalpy of dissociation with carbon similar to the heat generated from combustion (D'Silva et al., 2004). Brominated FRs (BFRs) are often preferred because they are more effective than chlorinated FRs (CFRs) and require lower quantities for similar fire resistance (D'Silva et al., 2004; BSEF & EBFRIP 2014).

Inorganic FRs, frequently metal hydrates such as aluminum trihydroxide (ATH) or magnesium hydroxide (MHO), can act as heat sinks by endothermically releasing water vapor (dehydration), which then also dilutes combustible pyrolysates (Chen and Wang, 2010). Additionally, inorganic compounds can decompose upon heat exposure, forming a protective
glassy layer or char which shields the material from oxygen and heat (charring) (Dasari et al., 2013).

Relatively small, volatile organophosphorus- and organonitrogen FRs, such as triphenyl phosphate, can be active in the vapor phase, just as halogenated FRs (Yoon et al., 2013). Less volatile compounds can also act in the condensed phase by charring (Lu and Hamerton, 2002). The organo-P and organo-N FRs are also frequently used as synergist in intumescent systems. Such agents swell when exposed to heat to form porous foam that acts as a barrier to heat, oxygen and combustible gasses (Dasari et al., 2013).

### 1.2 Environmental concerns about conventional flame retardants

BFRs are the largest group of FRs applied in plastics, accounting for 39% of the total economic value (Murphy, 2001). They are preferred because of their low impact on the polymer’s characteristics, effectiveness in relatively low concentrations compared to other FRs (Alaee et al., 2003), and relatively low costs of production (Birnbaum and Staskal, 2004). FRs can either be chemically bound to the material (reactive component) or physically mixed (additive component) with the material they are applied to (ENFIRO 2008). When the FRs are applied as an additive component, they are not part of the molecules of the material itself and can therefore be more easily released into the environment (Birnbaum and Staskal, 2004).

There are several ways through which FRs can end up in the environment. Common pathways are the release with effluents from FR producing factories (Watanabe and Sakai, 2003), with stack gas from waste incineration facilities (Soderstrom and Marklund, 2002), with leachates from landfills (Morris et al., 2004) and discharge from recycling and dismantling sites (Nyholm et al., 2013). For the aquatic environment, waste water appears to be a major source of FRs contamination. It is observed for both halogenated- and non-halogenated FR that they are only partially, or sometimes not at all, eliminated from the influent and are therefore released into natural waters with the effluent (Andresen et al., 2004; Meyer and Bester, 2004; Rayne and Ikonomou, 2005; Stackelberg et al., 2004). The aquatic environment should be protected from possible contaminations, not only from an ethical point of view, but also because human
health depends on unpolluted healthy aquatic ecosystems for clean drinking water (Ritter et al., 2002; WHO & UNEP 2014).

Once released into the environment, the question remains what potential harm the FRs could do. The last decades many of the most widely applied halogenated FRs (HFRs) proved to be highly debatable compounds. Polybrominated biphenyls (PBBs), which showed severe negative effects on the environment, have already been banned (1970’s to 2000, depending on the congener and the country) (OSPAR, 2001 (2004 updated); World Health Organisation (WHO), 1994). Polybrominated diphenyl ethers (PBDEs) also turned out to be toxic and environmentally persistent (D'Silva et al., 2004; Birnbaum and Staskal, 2004; Pijnenburg et al., 1995; de Wit, 2002) and as a result most congeners are currently banned, or being phased out (United Nations Environment Programme (UNEP) and Stockholm Convention - Press release, 8 May 2009; European Parliament (EP), 2002). The PBDEs formed about 25-50% of the total production volume of BFRs (depending on the region) and together with hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) they were the majority of BFRs produced (Birnbaum and Staskal, 2004). HBCD (a mixture of three main chiral diastereomers) may induce cancer via a non-mutagenic mechanism (Helleday et al., 1999) and it is classified as a persistent, bioaccumulative and toxic (PBT) compound by the European Chemicals Agency (ECHA) (2008b). As HBCD is listed as being PBT, its usage in the EU will be restricted from the 21st of August 2015 (BSEF 2014). For TBBPA, the remaining frequently used BFR, environmental risks for soil, sediment and aquatic organisms have now also been identified (WHO 1995; European Union, 2008b), however there are currently no legislative restrictions on its application (European Union, 2008a). Nevertheless, TBBPA is on the Danish list of undesirable substances (Danish EPA 2009). Several CFRs as well, show negative effects on the environment and human health. Dechlorane Plus is a frequently used CFR, with production volumes of 10-1,000 tonnes per year in the EU and in the U.S. it is produced or imported in quantities of more than 450 tonnes per year (Sverko et al., 2011). Recently, it has been identified as possibly bioaccumulative and persistent and it is a candidate compound for the United Nations Stockholm list of Persistent Organic Pollutants (POPs) (Sverko et al., 2011; Feo et al., 2012). Trischloro-ethyl phosphate (TCEP) was already banned in the eighties because of its carcinogenity, however, it is still not completely removed from the market (van...
Trischloro-propyl phosphate (TCPP) and trisdichloro-propyl phosphate (TDCP) are other high production volume FRs, which are both potentially carcinogenic (van der Veen and de Boer, 2012; Shaw et al., 2010). It is thus concluded that ignorance of the environmental fate and (eco)toxicological effects of BFRs and CFRs has caused much damage and eventually lead to a ban of several HFRs.

1.3 Halogen free flame retardants

Given the human and environmental health concerns, there is a pressing need for substituting many of the HFRs with alternative flame retardants. Several alternative halogenated as well as non-halogenated compounds have been suggested as suitable substitutes (European Chemicals Agency (ECHA), 2009; European Chemicals Bureau et al., 2007; McPherson et al., 2004). However, some of the suggested alternative HFRs show also negative toxic and environmental effects (Shaw et al., 2010; European Chemicals Bureau et al., 2007). In addition, HFRs can release large amounts of corrosive gasses (hydrogen halides), that corrode metal components and cause damage to sensitive electronics, which can make applications dangerous (Dasari et al., 2013). Thus due to both the environmental and technical concerns HFRs appeared to be less suitable, leading to a demand for halogen free flame retardants (HFFRs). Consequently, HFRs are rapidly losing market shares to HFFRs, which are now growing about 4% annually (Ceresana Consulting, 2014). HFFRs include inorganic-, as well as organophosphorus- and organonitrogen- FRs. Due to product innovation, the consumption of organophosphorus FRs (OPFRs) in particular is increasing at much higher rates than was anticipated. An average annual growth (AAG) rate of 5% is predicted for the coming decade for products based on organophosphates (ChemEurope, 2011). This is reflected by the increase in research and patents on many of these compounds (Levchik and Weil, 2006). Several furniture manufacturers already voluntarily replaced BFRs with alternative HFFRs (Betts, 2007) and in 2007, only 26% of the total European FR consumption still consisted of halogenated compounds, whereas 74% were alternative HFFRs (Phosphorus, Inorganic and Nitrogen Flame Retardants Association (Pinfa), 2009). HFFRs are thus already being produced commercially on a large scale and production volumes reach more than thousands of tonnes.
per year (Pinfa 2009). The fast increase in production and application of HFFRs raises the question whether these alternative FRs are indeed less harmful substances than the BFRs they substitute. Aluminum trihydroxide, applied in electrical and electronic equipment and construction, is by far the most used HFFR covering 70% of the total market demand in 2012 (PR Web, 2013), and is produced in 1,000,000 to 10,000,000 tonnes per year (ECHA accessed 2014, March). However, depending on the speciation, aluminum is associated with serious adverse health effects (Alzheimer disease), as well as negative environmental effects (high toxicity in acidified soils and waters) (Berthon, 2002; Kucera et al., 2008; Horicka et al., 2006). The presence of such potentially harmful products on the market as supposedly safer alternatives, questions what kind of legislation actually protects man and the environment from hazardous compounds. As of 2007, chemicals that are launched on the market fall under the European regulation on registration, evaluation, authorization and restriction of chemicals (REACH) (European Union, 2006). REACH requires the registration and safety testing of chemicals that are produced and used in the EU (in ≥ 1 tonne year\(^{-1}\) quantities), in order to minimize their impact on human health and the environment. There are guidance documents on how to deal with toxicity changes due to metal speciation, but it is not mandatory to test for these possible changes (ECHA 2008a). At production volumes starting from 1 tonne year\(^{-1}\), minimal requirements include a standard toxicity test on one aquatic invertebrate, as well as one aquatic plant. If a chemical is produced in quantities of less than 10 tonnes per year but more than 1 tonne year\(^{-1}\), as is the case for many individual HFFRs (see chapter 2), the chemical safety report or assessment is quite limited and thorough studies including long term ecotoxicity testing and primary biodegradation studies are not mandatory. Hence, such data for HFFRs are virtually lacking.

### 1.4 Aims and objectives

Several HFFRs are already being marketed, although their potential impact on the environment cannot yet be properly assessed. The aim of this study was therefore to determine the aquatic fate and effects of a selection of HFFRs that are currently replacing BFRs in polymers. To this purpose, the following objectives have been set:
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➢ To identify the current state of knowledge on PBT properties of a selection of HFFRs and to prioritize those for further research;

➢ To develop analytical methods to determine organophosphorus HFFRs in water;

➢ To quantify the aerobic biodegradation of organophosphorus HFFRs;

➢ To assess the acute and chronic aquatic ecotoxicity of HFFRs.

1.5 Outline of the thesis

The selection of HFFRs studied in this thesis was made together with several end users based on compatibility, performance and suitability as potential alternatives of HFRs (chapter 2). First the current state of knowledge on these HFFRs was assessed by reviewing the publicly available data (up to September 2011), making an inventory of the physical-chemical properties, production volumes, persistence, bioaccumulation and toxicity of our selection of HFFRs (Chapter 2). Ecotoxicity data as well as effects on mammals and data on in vitro toxicity endpoints were reported. The available data were classified based on the REACH system, meaning that the categories “high,” “moderate,” or “low” toxicity were assigned to the data. During this literature search, data published in peer-reviewed scientific papers was preferred over those in reports and other so-called grey literature. The transparency of the experimental setup used to obtain such data was considered of high importance, as well as study details that were provided on test conditions and results. Although primary sources were preferred, in some cases secondary reports were cited (trusted independent sources such as UNEP and US EPA).

Large data gaps were identified for the physical-chemical and the PBT properties of the reviewed HFFRs, which was at least partly caused by a lack of adequate quantitative analytical methodologies. Therefore, in Chapter 3 an analytical procedure based on SPE and LC-MS/MS is presented for the determination of aromatic organophosphorus HFFRs in water and sewage treatment plant (STP) effluent. Applying these newly developed analytical tools,
the aqueous solubilities of BDP, DOPO and RDP were experimentally determined and HFFRs were analysed in the effluent of a Dutch STP. 

To study the environmental fate of the aromatic HFFRs, in Chapter 4 their persistency was determined by quantifying the mineralisation and primary biodegradation rate in activated sludge. Mineralisation was monitored by measuring CO₂ production by means of GC analysis, whereas biodegradation was monitored by LC-MS/MS analysis of the FR and their potential degradation products.

Finally the aquatic ecotoxicity of the HFFRs was assessed. To this purpose, a large selection of new generation flame retardants was screened for their short term toxicity to the commonly used aquatic test organism *Daphnia magna*, performing the standardized OECD 202 acute daphnid immobility tests (Chapter 5). The data obtained from these toxicity tests were classified based on the REACH system, meaning that the categories “high”, “moderate” and “low” toxicity were assigned to the HFFRs.

Since toxicity tends to increase with increasing exposure time and specific effects on sublethal life history end points need time to become expressed, ALPI and DOPO were subjected to chronic toxicity testing (Chapter 6). Daphnids were exposed to these HFFRs in 21 day reproduction tests, following OECD guideline 211, examining the sublethal life-cycle parameters reproductive output and population growth rate. It was attempted to attribute the daphnid life cycle responses to the mode of action of the FR.

This thesis provided missing knowledge on the environmental fate and effects of new generation flame retardants in the aquatic environment. Chapter 7 discusses the current state of knowledge and specifically focuses on the impact of these findings on standard guideline testing and hazard evaluation.