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Environmental fate & effects of new generation flame retardants

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Summary

There is a pressing need for substituting several halogenated flame retardants, given the human and environmental health concerns of many of these compounds. Halogen Free Flame Retardants (HFFRs) have been suggested as alternatives and are already being marketed, although their potential impact on the environment cannot be properly assessed because of a lack of information regarding their environmental and ecotoxicological properties. The aim of this study was to determine the aquatic fate and effects of a selection of HFFRs that are currently being applied in polymers as alternatives of hazardous brominated flame retardants. To this end, the following objectives have been set:

- ❖ 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 toxicity of HFFRs to *Daphnia magna*.

The selection of HFFRs was made together with several end users and producers based on compatibility, performance and suitability in polymer applications. Fourteen HFFRs were selected, being: aluminum trihydroxide (ATH), antimony trioxide (ATO), magnesium hydroxide (MHO), zinc borate (ZB), zinc hydroxystannate (ZHS) and zinc stannate (ZS) (inorganic flame retardants and synergists); aluminum diethylphosphinate (ALPI), bisphenol-A bis(diphenylphosphate) (BPA-BDPP or BDP), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (or dihydrooxa-phosphaphenanthrene) (DOPO), resorcinol bis(diphenylphosphate) (PBDPP or RDP) and triphenylphosphate (TPHP or TPP) (organophosphorus compounds and

salts); melamine polyphosphate (MPP) (nitrogen based organic flame retardant); ammonium polyphosphate (APP), and pentaerythritol (intumescent systems). The current state of knowledge about 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 the HFFRs selected (**Chapter 2**). Toxicity data included ecotoxicity, in vivo and in vitro toxicity endpoints. 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 were given preference to 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, and, similarly, 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 were at least partly caused by a lack of adequate quantitative analytical methodologies. The review showed that enhanced transparency of methodologies used in experimental studies is needed. TPP has been studied quite extensively and it is clearly persistent, bioaccumulative and toxic. So far, RDP and BDP have been reported to exert low to high ecotoxicity and to be persistent. The compounds ATH and ZB exerted high toxicity to some species and ALPI appeared to be persistent, and has low to moderate reported ecotoxicity. DOPO and MPP may be persistent, but this characteristic was based merely on no more than two studies, clearly indicating a lack of information. Many degradation studies have been performed on pentaerythritol, and show its low persistence, with a few exceptions. However, there was too little information on the bioaccumulation potential of pentaerythritol. In most reports APP was shown to have low PBT properties; however, moderate ecotoxicity was reported in two studies. $\text{Mg}(\text{OH})_2$, ZHS and ZS do not show high

bioaccumulation potential or toxicity, but large data gaps exist for these compounds also. Obviously, further research was required to obtain insight in the fate and effects of HFFRs in the aquatic environment.

To accurately determine the concentrations of HFFRs in water, a reliable analytical methodology was needed. The inorganic HFFRs investigated in this thesis could be measured straightforwardly with ICP-AES analysis (chapters 4 and 5). With the exception of TPP, very few publications on the analysis of aromatic OPFR in particular existed and none were available for DOPO. Therefore, an analytical procedure based on SPE and LC-MS/MS was developed (**Chapter 3**) for the determination of aromatic organophosphorus HFFRs in water and sewage treatment plant (STP) effluents. Applying these newly developed analytical tools, the aqueous solubilities of BDP, DOPO and RDP were experimentally determined at 3.9, 2200 and 0.047 mg L⁻¹, respectively. The applicability of the method for monitoring BDP and RDP in effluents was demonstrated and in the effluent of one out of three Dutch STPs sampled a concentration of 10 ng L⁻¹ of BDP was detected. Hence, the method developed in the present study presents a major step towards environmental monitoring of these currently emerging organophosphorus HFFRs.

Using the new analytical methods, information on the environmental fate of the aromatic HFFRs TPP, RDP and BDP was determined (**Chapter 4**), 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 FRs and their potential degradation products. TPP was biodegraded and mineralised most rapidly and achieved the OECD requirement for ready biodegradability (60% of theoretical maximum mineralisation within 28 days). Primary biodegradation was also rapid for RDP, but 60% mineralisation was not achieved during the test, suggesting that transformation products of RDP may accumulate. Primary degradation of BDP was very slow and very low CO₂ production was observed for this compound.

The environmental effects were studied by testing the aquatic toxicity of the HFFRs to the commonly used test organism *Daphnia magna*. To this end, a large selection of new generation flame retardants was screened for their short term toxicity, performing the standardized OECD 202 acute daphnid immobility tests (**Chapter 5**). Our results revealed that four HFFRs (MPP, MHO, ZHS and ZS) were showing no effect at their Sw (saturated water concentration) and three had a low toxicity ($EC_{50} > 10 \text{ mg L}^{-1}$; APP, ALPI and DOPO), suggesting that these compounds are not hazardous. ATO had a moderate toxicity ($EC_{50} = 3.01 \text{ mg L}^{-1}$, 95% CL: 2.76-3.25) and TPP and the brominated reference compound tetra bromobisphenol A were highly toxic to *D. magna* ($EC_{50} = 0.55 \text{ mg L}^{-1}$, 95% CL: 0.53-0.55 and $EC_{50} = 0.60 \text{ mg L}^{-1}$, 95% CL: 0.24-0.97 respectively). ATH and BDP caused limited mortality at water saturated concentrations (26 and 25% respectively) and have a low solubility ($< 10 \text{ mg L}^{-1}$). Increased toxicity of these compounds may be observed when for instance decreasing pH could increase solubility.

Toxicity mostly increases with increasing exposure time, since specific effects on sublethal chronic end points need time to become expressed. Daphnids were exposed to ALPI and DOPO - two compounds shown to exert low acute toxicity - in 21 days reproduction tests (**Chapter 6**), following OECD guideline 211, in order to determine the sublethal chronic parameters reproductive output and population growth rate. The toxicity of ALPI increased from a 48 h LC_{50} of 18 mg L^{-1} to a 21 day LC_{50} value of 3.2 mg L^{-1} , resulting in an acute-to-chronic ratio of 5.6. The lower chronic LC_{50} value may imply a change in classification of ALPI from low to moderate toxicity. ALPI also affected sublethal chronic parameters, with an EC_{50} of 2.8 mg L^{-1} for cumulative reproductive output and of 3.4 mg L^{-1} for population growth rate, revealing a nonspecific mode of action, as the lethal and sublethal effect concentrations were in the same order of magnitude. DOPO showed sublethal effects with an EC_{50} value of 48 mg L^{-1} for cumulative reproductive output and an EC_{50} value of 73 mg L^{-1} for population growth rate. The toxicity of DOPO to *D. magna* can thus be classified as

low and likely occurred above environmentally relevant concentrations, but we identified specific effects on reproduction.

This thesis work fills some of the existing knowledge gaps on the environmental fate and effects of new generation flame retardants in the aquatic environment. In **Chapter 7** the current state of knowledge was discussed, as well as the impact of these findings on standard guideline testing and hazard evaluation. The fact that structurally similar HFFRs, i.e. OPFRs, have different biodegradation potentials showed that commonly used methods as read across and QSARs cannot be used safely to predict the environmental fate of untested HFFRs. Experimental verification is at this stage the only reliable way to determine the persistence of untested analogue OPFRs. Under the REACH legislation, the minimally required ecotoxicity tests can be waived for poorly soluble compounds. However, as observed here for the HFFRs studied, this is not always justified. During this project, it became clear that some data on HFFRs were concealed, incomplete or non guideline-based, leading to unnecessary repetition of standard experiments and making it difficult to include the data in regulatory risk assessment. Several chapters of this thesis showed the dilemma between the need for extrapolation with its associated uncertainties and the need for more reliable, though expensive and time consuming, experimental verification. With the growing evidence of unwanted adverse side effects of several HFFRs, we have to carefully balance the direct risk reduction of fire spread against the potential global impact of contaminants on the long term. It is concluded that with the newly obtained insight in the hazards of HFFRs, support is provided for the application of environmentally compatible flame retardants.