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Occurrence and Fate of Alternative Flame Retardants in the Environment

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Summary

In *Chapter 2.1* a brief literature review of PFR analysis is provided as well as a report of an interlaboratory study that was organized. The aim of the interlaboratory study was to transfer knowledge on PFR analysis among laboratories, and to investigate how well the laboratories perform on the analysis of PFRs in indoor and outdoor samples. The results of this interlaboratory study showed that comparable problems were observed as e.g. found for BDE209 in the beginning of 2000s. Lack of internal standards and background contamination were the major problem observed for BDE209 (De Boer et al., 2002). The same problems were observed for some of the PFRs. The background contamination for the PFRs was probably due to the use of PFRs as FR and plasticizers in various products (Marklund et al. 2003; Van der Veen and De Boer 2012). Also the relatively high concentrations ($\mu\text{g/g}$ level) of PFRs observed in house dust worldwide (*Chapter 4.1 and 4.2*) indicates that contamination from dust may easily occur. Not all participating laboratories suffered from blank problems, which indicates that it is possible to control the blanks. Recommendations to control background contamination and improve the analytical performance are given in *Chapter 2.1*. The results from the spiked fish oil and house dust were in general good. However, poor results were observed for the sediment sample. The problems were probably rather related to the very low PFR levels in the sediment sample used, close to or even lower than the blank levels observed by some of the participants, than to the matrix itself. Still the use of non-destructive cleanup methods, PFRs degrade after treatment with a base or acids makes it challenging to remove matrices such as lipids. In *Chapter 4.3* we describe a method to analyze PFRs in biota and sediment. During method validation GC-EI-MS was compared with LC-ESI-MS/MS. Some ion-suppression was observed for three (TMPP, TEHP and EHDPP) of the ten PFRs studied with LC-ESI-MS/MS. Still LC-ESI-MS/MS was selected as the most robust tool for analyzing PFRs in biota samples over GC-MS due to matrix interferences on the GC column. At the time the analyses were performed, only two commercial internal standards were available. Due to the growing interest in PFRs in the environment, since 2013 more commercial internal standards have been made available. This will improve the reliability of the PFR data.

PBDPP and BPA-PBDPP are used in consumer products such as televisions as alternative for Deca-BDE. In products purchased before 2006 only PBDPP was found with detectable levels up to 7.8% per product weight (*Chapter 3.1*). However, in products purchased after 2012 both PBDPP and BPA-BDPP were detected in much lower concentrations (0.002-0.3%). These levels are not high enough in polymers to work effectively as an FR, which may indicate that PBDPP and BPA-BDPP were not the main FRs added and were probably used as part of a mixture together with other FRs. Another hypothesis might be that the low levels result from recycling of polymers containing PBDPP and BPA-PBDPP. Our study indicated that PBDPP and BPA-PBDPP are used in consumer products and may be an important source for the elevated levels observed in house dust (*Chapter 4.2*). This indicated that humans may get exposed to these FR by inhalation and ingestion. More research is needed on the toxicity and metabolism of these novel FR to better understand their risks.

Inorganic and metal based FRs may dissociate when they end up in the environment, which makes it rather difficult to study the fate of these FRs in the environment. To better understand the fate of these inorganic and metal based FR we studied the leaching behaviour of these FRs from different polymer-FR formulations (*Chapter 3.2*). Two leaching protocols were tested. The TCLP protocol uses worse-case leaching conditions to simulate a municipal waste landfill and the DIN 38414-S4 determines leaching by water. The leachability of the inorganic/metal based FRs were compared with that of the BFRs they substitute. Inorganic/metal based FRs easily leach from the polymer materials and differences were observed between the different polymer-FR formulations. Overall the leaching behaviour of the FRs seems to be highly effected by the polymer type.

PFRs were studied in house and car dust. Nine PFRs were detected in high levels ($\mu\text{g/g}$ range) in all house dust samples (*Chapter 4.1*). The house dust was dominated by TBOEP which is used as plasticizer and in floor polish (Marklund et al., 2003; Kajiwara et al., 2011). No significant differences between dust collected on and around electronics were observed for the PFRs, with the exception of TMPP and TPHP. Electronics may, therefore, have a limited contribution to the PFR levels in house dust, and the high levels are due to other sources in houses. PFRs were also detected in dust collected from cars and were dominated by TDCIPP with is used as an FR in polyurethane foam of the car seat. The PFR patterns observed in house and car dust were clearly different. However, by excluding the most dominant PFRs, TBOEP and TCDIPP, a more comparable pattern was observed. This may indicate that car dust can be a mixture of dust from the car and dust from other source like houses and offices which are carried into the car.

Two relatively new PFRs, PBDPP and BPA-BDPP, were detected in house dust from three different countries in Europe (*Chapter 4.2*). PBDPP and BPA-BDPP were detected at relative high levels ($\mu\text{g/g}$ range) in the house dust collected from electronics. Levels of BPA-BDPP were higher than the levels of PBDPP. Lower levels were observed in dust collected around the electronics, which indicates that electronics are a source of PBDPP and BPA-PBDP. The same pattern was observed in house dust from Sweden and Greece. A strong positive correlation was observed between TPHP and PBDPP or BPA-BDPP, which is probably related to the use of TPHP as byproduct in the PBDP and BPA-BDPP technical mixtures. The finding of PBDPP and BPA-BDPP in house dust from various indoor environments implies that Europeans are continuously exposed to these compounds via dust inhalation and ingestions. Estimates of exposure were calculated for toddlers and adults.

PFRs haven been detected in pelagic and the benthic food webs from the river Western Scheldt (The Netherlands) (*Chapter 4.3*). The detection frequency of the PFRs (6-56%) was lower than that of the BFRs (50-97%). However, the concentrations of some of the PFRs were higher that the BFRs. All PBDEs undergo trophic magnification, with the exception of BDE209. Indications for trophic magnification was only observed in the benthic food web for three PFRs (TBOEP, TCIPP and TCEP) of the 10 studied PFRs. Most PFRs undergo trophic dilution in both food webs. PFRs can easily be metabolized (WHO, 1990, 1991, 1997, 1998, 2000). Therefore, the finding of PFRs in biota samples from the Western Scheldt imply that emissions and exposure to these PFRS may be relatively high and continuous. The

increased demand for PFRs following the ban and phase out of the PBDEs may lead to a further increase of environmental levels and a higher exposure of organisms to PFRs.

References.

De Boer, J., Cofino, W.P. First world-wide interlaboratory study on polybrominated diphenylethers (PBDEs). *Chemosphere*. **2002**, 46, 625-633.

Kajiwara, N., Noma, Y., Takigami H., Brominated and organophosphate flame retardants in selected consumer products on the Japanese market in 2008. *J. Hazard Matter*. **2011**, 192, 1250-1259.

Marklund, A., Andersson, B., Haglund, P., 2003. Screening of organophosphorus compounds and their distribution in various indoor environments. *Chemosphere*. **2003**. 53, 1137–1146.

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

WHO, **1990**. EHC 110. Tricresyl phosphate. Geneva, Switzerland.

WHO, **1991**. EHC 112: Tri-n-butyl phosphate. Geneva, Switzerland.

WHO, **1997**. EHC 192: Flame retardants: A general introduction. Geneva, Switzerland

WHO, **1998**. EHC 209: Flame retardants: Tris(chloropropyl)phosphate and Tris(2-chloroethyl)phosphate. Geneva, Switzerland.

WHO, **2000**. EHC 209: Flame retardants: Tris(2-butoxyethyl) phosphate, Tris(2-ethyl-exyl) phosphate and Tetrakis(hydroxymethyl) phosphonium salts. Geneva, Switzerland.