Chemosphere 88 (2012) 1119–1153

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Review

Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis

Ike van der Veen *, Jacob de Boer

VU University, Institute for Environmental Studies (IVM), De Boelelaan 1087, 1081 HV, Amsterdam, The Netherlands

ARTICLE INFO

Article history:
Received 23 December 2011
Received in revised form 22 March 2012
Accepted 26 March 2012
Available online 25 April 2012

Keywords:
PFR
Phosphorus flame retardant
Properties
Occurrence
Toxicity
Analysis

ABSTRACT

Since the ban on some brominated flame retardants (BFRs), phosphorus flame retardants (PFRs), which were responsible for 20% of the flame retardant (FR) consumption in 2006 in Europe, are often proposed as alternatives for BFRs. PFRs can be divided in three main groups, inorganic, organic and halogen containing PFRs. Most of the PFRs have a mechanism of action in the solid phase of burning materials (char formation), but some may also be active in the gas phase. Some PFRs are reactive FRs, which means they are chemically bound to a polymer, whereas others are additive and mixed into the polymer. The focus of this report is limited to the PFRs mentioned in the literature as potential substitutes for BFRs. The physico-chemical properties, applications and production volumes of PFRs are given. Non-halogenated PFRs are often used as plasticisers as well. Limited information is available on the occurrence of PFRs in the environment. For triphenyl phosphate (TPhP), tricresylphosphate (TCP), tris(2-chloroethyl)phosphate (TCEP), tris(chloropropyl)phosphate (TCPP), tris(1,3-dichloro-2-propyl)phosphate (TDCPP), and tetrekis(2-chlorethyl)dichloroisopentyldiphosphate (V6) a number of studies have been performed on their occurrence in air, water and sediment, but limited data were found on their occurrence in biota. Concentrations found for these PFRs in air were up to 47 $\mu g\ m^{-3}$, in sediment levels up to 24 $mg\ kg^{-1}$ were found, and in surface water concentrations up to 379 $ng\ L^{-1}$. In all these matrices TCPP was dominant. Concentrations found in dust were up to 67 $mg\ kg^{-1}$, with TDCPP being the dominant PFR. PFR concentrations reported were often higher than polybrominated diphenylether (PBDE) concentrations, and the human exposure due to PFR concentrations in indoor air appears to be higher than exposure due to PBDE concentrations in indoor air.

Only the Cl-containing PFRs are carcinogenic. Other negative human health effects were found for Cl-containing PFRs as well as for TCP, which suggest that those PFRs would not be suitable alternatives for BFRs. TPhP, diphenylcresylphosphate (DCP) and TCP would not be suitable alternatives either, because they are considered to be toxic to (aquatic) organisms. Diethylphosphinic acid is, just like TCEP, considered to be very persistent. From an environmental perspective, resorcinol-bis(diphenylphosphate) (RDP), bisphenol-A diphenyl phosphate (BADP) and melamine polyphosphate, may be suitable good substitutes for BFRs.

Information on PFR analysis in air, water and sediment is limited to TCEP, TCPP, TPhP, TCP and some other organophosphate esters. For air sampling passive samplers have been used as well as solid phase extraction (SPE) membranes, SPE cartridges, and solid phase micro-extraction (SPME).

For extraction of PFRs from water SPE is recommended, because this method gives good recoveries (67–105%) and acceptable relative standard deviations (RSDs) (<20%), and offers the option of on-line coupling with a detection system. For the extraction of PFRs from sediment microwave-assisted extraction (MAE) is recommended. The recoveries (78–105%) and RSDs (3–8%) are good and the method is faster and requires less solvent compared to other methods.

For the final instrumental analysis of PFRs, gas chromatography–flame photometric detection (GC–FPD), GC-nitrogen–phosphorus detection (NPD), GC–atomic emission detection (AED), GC–mass

* Corresponding author.
E-mail addresses: ike.van.der.veen@ivm.vu.nl (I. van der Veen), jacob.de.boer@ivm.vu.nl (J. de Boer).

0045-6535/$ - see front matter
http://dx.doi.org/10.1016/j.chemosphere.2012.03.067

spectrometry (MS) as well as liquid chromatography (LC)–MS/MS and GC–Inductively-coupled plasma–MS (ICP–MS) are used. GC–ICP–MS is a promising method, because it provides much less complex chromatograms while offering the same recoveries and limits of detection (LOD) (instrumental LOD is 5–10 ng mL^{-1}) compared to GC–NPD and GC–MS, which are frequently used methods for PFR analysis. GC–MS offers a higher selectivity than GC–NPD and the possibility of using isotopically labeled compounds for quantification.

Contents

1. Introduction

Flame retardants (FRs), which are chemicals added to materials both to prevent combustion and to delay the spread of fire after ignition, are used in polymers since the 1960s (Kemmlein et al., 2003; EFRA, 2007). To meet fire safety standards, set up in regulations like the California Technical Bulletin (TB) 117 for furniture (BHFTI, 2000), and the Underwriters' Laboratories 94, (UL94), the Standard for safety of flammability of plastic materials for parts in devices and appliances (US-EPA, 2007) FR are used more and more. FRs may have different compositions. They may contain halogens (bromine and chlorine), phosphorus, nitrogen, metals, minerals based on aluminum and magnesium, or they may be based on borax, antimony trioxide, molybdenum, or the FR may be a nanocomposite (EFRA, 2007).

According to the European Flame Retardants Association (EFRA) (CEFIC, 2007), the total consumption of FRs in Europe in 2006 was 465 000 tonnes, of which 10% were brominated flame retardants (BFRs) (Fig. 1). Many halogenated chemicals, such as some BFRs and polychlorinated biphenyls (PCBs), have proven to be persistent, bioaccumulative, and/or toxic in the environment, and to animals and humans. For over four decades, halogenated FRs have been in the focus of concern for public health, resulting in the production of PCBs being forbidden in 1973 (Aresta et al., 2003). Nowadays the production and use of BFRs are restricted more and more by the European Union (EU) and they have been voluntary phased out in the USA (BSEF, 2011). The production of pentaBDE mixtures has been forbidden in the EU in 2003 (EU, 2003), and the use of the frequently used decabromodiphenyl ether (decaBDE) in electrical and electrical equipment has been forbidden in Europe (Betts, 2008). In 2009 the United Nations Environment Programme (UNEP) has decided in a meeting of the parties of the Stockholm Convention on persistent organic pollutants (POPs) that octaBDE and pentaBDE are officially labeled as POPs (decision SC-4/14, SC-4/18 (UNEP, 2009)). These developments have urged the use of alternatives for these BFRs.

Phosphorus flame retardants (PFRs), which have already been used for over 150 years (Andrae, 2007), are considered as suitable alternatives for BFRs. Because of the need for vapor-phase activity, a number of volatile PFRs, tributyl phosphate (TBP), triphenyl phosphate (TPhP), and triphenylphosphine oxide (TPPO), have been identified as possible substitutes for bromine-containing formulations used in textile back-coatings (Horrocks et al., 2007).

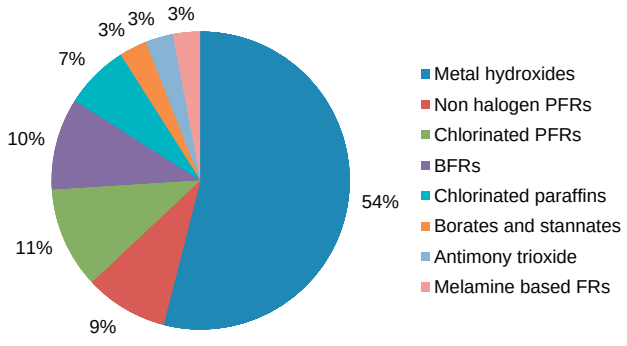


Fig. 1. Industry estimate of total consumption of flame retardants in Europe 2006. Total = 465 000 metric tonnes (CEFIC, 2007).

PFRs, in 2006 responsible for 20% of the FR consumption in Europe (Fig. 1) cannot only be applied in a wider range of fiber types in textile (Andrae, 2007), but are also compatible with other processing chemicals, and are easy to use (Andrae, 2007). Some of the PFRs facilitate the recyclability of printed circuit boards, as it is more feasible, and cost effective to recover copper from halogen free circuit boards (McPherson et al., 2004). Not only several BFRs are being replaced by PFRs, but also the halogen containing PFRs may need to be substituted by non-halogenated PFRs. McPherson et al. (2004) mention, as an example, the substitution of tris(2-chloroethyl)phosphate (TCEP), and tris(chloropropyl)phosphate (TCPP) with boiling points of 351 °C and 342 °C by resorcinol-bis(diphenylphosphate) (RDP) with boiling point 587 °C because it is less volatile, and therefore less likely to be released into the environment.

The human and environmental impacts differ from one phosphorus compound to another. Red phosphorus (RP), and ammonium polyphosphate (APP) are the least problematic FRs to use, but some health effects of PFRs cannot be ignored (McPherson et al., 2004).

If PFRs would be used as an alternative for PBDEs, it is important to avoid compounds, which are more persistent, bioaccumulative and toxic to humans and to the environment than BFRs. Pakalin et al. (2007) reported 27 potential substitutes for decaBDE, of which 16 are halogenated and 11 are non-halogenated. From these 27 chemicals, 6 were organo PFRs, e.g. RDP, bisphenol-A diphenyl phosphate (BADP), TPhP, diphenylcresylphosphate (DCP), melamine polyphosphate, and diethylphosphinic acid. The first three of these were also suggested by McPherson et al. (2004) as BFR alternatives for acrylonitrile–butadiene-styrene (ABS)/polycarbonate (pc) plastics. The German Federal Environmental Agency carried out a research project on substitution of hazardous FRs. The examined FRs included the earlier mentioned RDP, but also the halogenated PFR TCPP (Leisewitz et al., 2000). TCPP, tris(1,3-dichloro-2-propyl)phosphate (TDCPP) and tetrekis(2-chlorethyl)dichloroisopentyldiphosphate (V6) are mentioned by the Scientific Committee on Health and Environmental Risks (SCHER, 2007a) to be potential substitutes of BFRs.

The focus of this report is limited to the PFRs as substitutes for PBDEs, with addition of tricresylphosphate (TCP) and the halogen containing TCEP. The physiological properties, the occurrence, environmental fate, toxicological data and analytical methods for these PFRs are described.

2. Characteristics

PFRs can be divided in three main groups. The first group contains the inorganic PFRs, including frequently used RP and

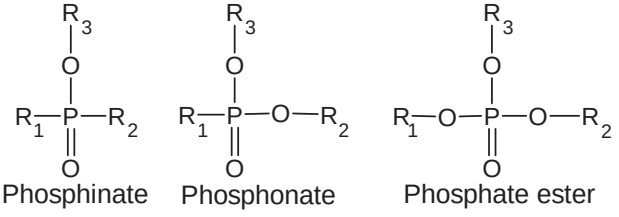


Fig. 2. General structure of organophosphorus flame retardants (EFRA, 2007).

Table 1
Names and structures of the studied PFRs.

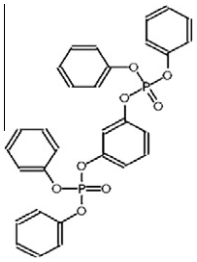
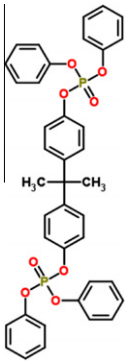
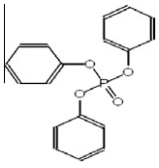
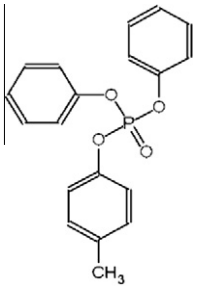
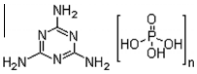
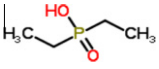
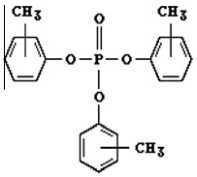
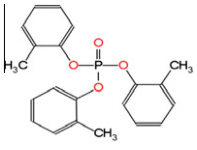
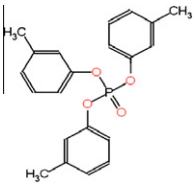
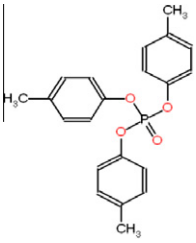
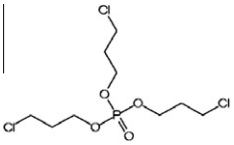
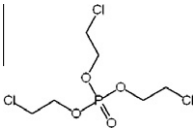
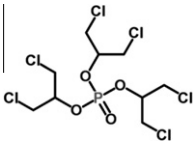
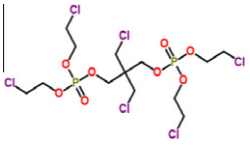
Structure	Cas number	Name	Abbreviation used in literature
	57583-54-7 125997-21-9	– Resorcinol-bis(diphenyl)phosphate – Tetraphenyl resorcinol diphosphate – Resorcinol diphenyl-phosphate – Tetraphenyl resorcinolbisphosphate – Tetraphenyl resorcinol bis(diphenylphosphate) – (3-diphenoxyphosphoryloxyphenyl) diphenyl phosphate – Phosphoric acid, 1,3-phenylene tetraphenyl ester – m-Phenylenebis(diphenyl phosphate)	RDP
	5945-33-5 181028-79-5	– Bisphenol-A diphenyl phosphate – Phosphoric acid, (1-methylethylidene) di-4,1-phenylene tetraphenyl ester	BADP BAPP BPADP BDP
	115-86-6 56803-37-3 68937-40-6	– Triphenyl phosphate – Triphenoxyphosphine oxide – Phosphoric acid, triphenyl ester – Triphenyl phosphoric acid ester – Triaryl phosphates butylated – Tertbutylphenyl diphenyl phosphate	TPhP TPP
	26444-49-5	– Diphenylcresylphosphate – Cresyl diphenyl phosphate – Phosphoric acid methylphenyl diphenyl ester – Diphenyl cresol phosphate – Diphenyl tolyl ester phosphoric acid – Diphenyl tolyl phosphate – Cresyl phenyl phosphate – Cresol diphenyl phosphate – Methyl phenyl diphenyl phosphate – Monocresyl diphenylphosphate – Phosphoric acid cresyl diphenyl ester – Tolyl diphenyl phosphate	DCP CDP DPK
	218768-84-4	– Melamine phosphate – Melaminepolyphosphate	
	225789-38-8	– Diethylphosphinic acid	
	1330-78-5	– Tricresylphosphate: Mixture of: – tri-o-cresylphosphate – tri-m-cresylphosphate – tri-p-cresylphosphate – Tritolyl phosphate – Trimethylphenyl phosphate – Phosphoric acid, tritolyl ester	TCP, TCrP
	78-30-8	– Tri-o-cresylphosphate – Phosphoric acid tris(2-methylphenyl) ester – Tri-o-tolyl phosphate – Tri-2-tolyl phosphate – Tri-2-methyl-phenyl phosphate – Phosphoric acid, tri-o-tolyl ester	o-TCP, TOCP, TOTP, ToCrP

Table 1 (*continued*)

Structure	Cas number	Name	Abbreviation used in literature
	563-04-2	– Tri-m-cresylphosphate – Phosphoric acid tris(3-methylphenyl) ester – Tri-m-tolyl phosphate – Trimetacresyl phosphate – Phosphoric acid, tri-m-tolyl ester – Tri-3-tolyl phosphate – Tri-3-methyl-phenyl phosphate	m-TCP, TMTP
	78-32-0	– Tri-p-cresylphosphate – Phosphoric acid tris(4-methylphenyl) ester – Tri-p-tolyl phosphate – Tri-4-tolyl phosphate – Tri-4-methyl-phenyl phosphate – Triparacresyl phosphate – Phosphoric acid, tri-p-tolyl ester	p-TCP, TPCP, TPTP
	1067-98-7	– Tris(chloropropyl)phosphate	TCPP TCIPP
	115-96-8	– Tris(2-chloroethyl)phosphate – Tris(beta-chloroethyl) phosphate – 2-chloroethanol phosphate – Phosphoric acid, tris(2-chloroethyl)ester – Tris(2-chloroethyl) orthophosphate – Tris(chloroethyl)phosphate	TCEP TClEP
	13674-87-8	– Tris(1,3-dichloro-2-propyl)phosphate – Tris-(2-chloro-, 1-chloromethyl-ethyl)-phosphate – 1,3-dichloro-2-propanol phosphate – Phosphoric acid tris(1,3-dichloro-2-propyl ester) – Tris(1,3-dichloroisopropyl)phosphate – Tris(1-chloromethyl-2-chloroethyl)phosphate – Tri(beta,beta'-dichloroisopropyl)phosphate	TDCP TDCPP
	38051-10-4	– Tetrekis(2-chlorethyl)dichloroisopentyldiphosphate – Phosphoric acid, 2,2-bis(chloromethyl)-1,3-propanediyl tetrakis(2-chloroethyl) ester – 2,2-Bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate) – 2,2-Bis(chloromethyl)-1,3-propanediyl tetrakis(2-chloroethyl) bis(phosphate) – 2,2-Bis(chloromethyl)propane-1,3-diyl tetrakis(2-chloroethyl) bis(phosphate)	V6

Stuer-Lauridsen et al. (2006), Chemspider (2011) and Sigma-Aldrich (2011).

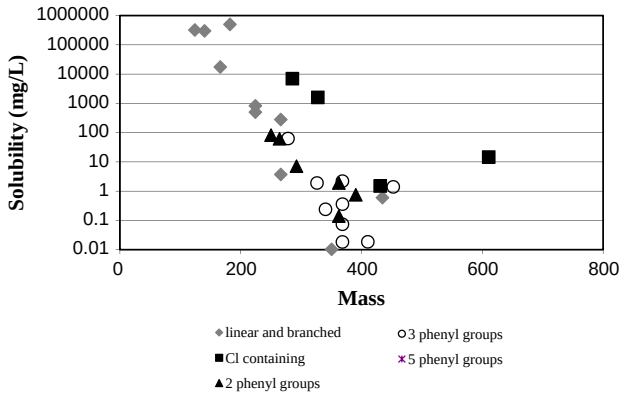


Fig. 3. Solubility (mg L^{-1}) versus molecular mass.

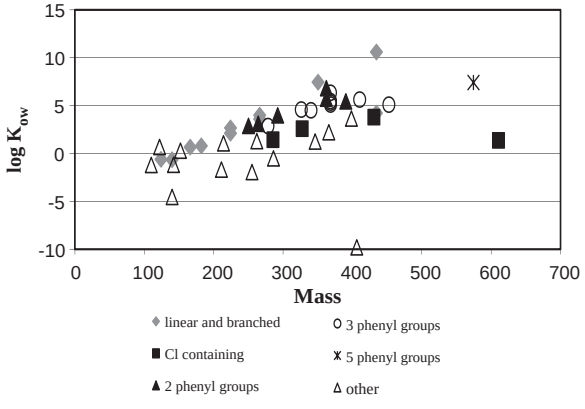


Fig. 4. log K_{ow} versus molecular mass.

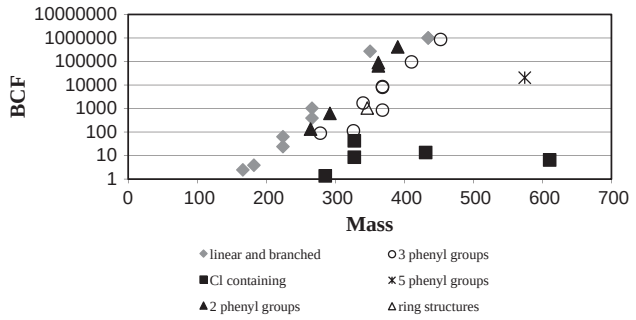


Fig. 5. Bioconcentration factor versus molecular mass.

Table 2
Properties of chlorine containing PFRs.

Name	BCF	M	Cl (atoms)	Cl (% m m^{-1})
Tris(2-chloroethyl)phosphate	1.37	287	3	38
1-(Bis(2-chloroethoxy)phosphinyl)ethyl 2-chloroethyl (1-(((2-chloroethoxy)(2-chloroethyl)phosphinyl)oxy)ethyl)phosphonate	6.49	613	5	29
Tris(chloroiso-propyl)phosphate	8.51	329	3	33
Tris(1,3-dichloro-2-propyl)phosphate	13.5	434	6	50
Tris(chloropropyl) phosphate	42.4	329	3	33
Tetrekis(2-chlorethyl)dichloroisopentyldiphosphate	17.07	580	6	37

APP. The second group consists of the organic PFRs. Three different general structures of these PFRs can be recognized: the organophosphate esters (OPEs), the phosphonates, and the phosphinates (Fig. 2) (EFRA, 2007). The third group is the widely used group of halogenated PFRs. These combine the properties of both the halogen and the phosphorus components. The presence of the halogen also increases the lifetime of the FR in the end-product by decreasing its mobility in the polymer (Fisk et al., 2003). Examples of halogenated PFRs are TCPP and TCEP (Table 1). Within these three groups two basic types of PFRs can be recognized. The first type being reactive FRs, which are reactive components chemically built into a polymer molecule (WHO, 1997). Due to the chemical binding, losses during the lifetime of the product are limited (Fisk et al., 2003).

The second type encompasses the additive FRs, which are mixed into the polymer (WHO, 1997). The additive FRs may decrease in concentration during the lifetime of the treated product and, therefore, the flame retardancy properties can decrease in time (Fisk et al., 2003). The major groups of additive PFRs are polyols, phosphonium derivatives, phosphonates and phosphate esters, which include trialkyl derivatives such as triethyl or trioctyl phosphate, triaryl derivatives such as TPhP, and aryl–alkyl derivatives such as 2-ethylhexyldiphenyl phosphate (WHO, 1997). In Table 1, an overview of the PFRs studied is given, with their structures and names.

2.1. Physicochemical properties

There is a great variation in physiological properties of PFRs. For example di-ammonium phosphate (DAP) (Sigma-Aldrich, 2011), and dimethyl methyl phosphonate (DMMP) (Akzo, 2003) are highly soluble in water, while trixylenyl phosphate (TXP) and isodecyldiphenyl phosphate (IDPP) are immiscible with water. In Appendix A, an overview of the solubility's of the studied PFRs is given. Fig. 3 shows the solubility of PFRs versus the molecular mass. The solubility decreases by increasing molecular mass. In case their hydrolysis half life are equal the PFRs with lower masses are therefore more likely to be found in the aquatic environment than those with higher molecular masses, which is confirmed by the log K_{ow} values of the PFRs as can be seen in Fig. 4. Most of the PFRs have a positive log K_{ow} value, which means they are more lipophilic than hydrophilic. The log K_{ow} values vary considerably between the different PFR groups. The WHO (2000) gives a calculated log K_{ow} value of −9.8 for tetrakis(hydroxymethyl) phosphonium sulfate (THPS). In contrast with that, a log K_{ow} value of 10.6 was found for trioctyl phosphate (Chemspider, 2011). These two compounds mark both ends of the log K_{ow} range for all PFRs found in the literature for this study. The log K_{ow} values of the PFRs studied are listed in Appendix A.

The wide range of log K_{ow} values for PFRs from −9.8 till 10.6 is in contrast with the log K_{ow} values of the BFRs of which the values range from 4.3 to 9.9 (Asamoah, 2005). BFRs are, therefore, much more lipophilic than PFRs.

Henry's law constants at 25 °C of the studied PFRs vary between 2.8×10^{-4} atm-m^3 mole^{-1}, for tri-iso-butyl phosphate (TiBP) (Chemspider, 2011), until 1.7×10^{-23} atm-m^3 mole^{-1}, for THPS (Syrres, 2011). The wide range of Henry's law constant values of PFRs indicates that the distribution of PFRs over air and environmental waters like the oceans is highly variable. The Henry's law constants of the PFRs studied are also listed in Appendix A.

There is also a great variety in vapor pressures and bioconcentration factors (BCF). The vapor pressure at 25 °C ranges from 1.9 mm Hg for dimethyl phosphonate (DMHP) to 9.5×10^{-21} mm Hg for THPS and the BCF ranges from 1.37 for TCEP to 10^6 for trioctyl phosphate and tris(2-ethylhexyl)phosphate (TEHP). The vapor pressure and BCF's of the PFRs studied are listed in Appendix A including other physicochemical properties like boiling point, melting point and flash point. Fig. 5 shows the relation between the BCFs of several PFRs and their molecular mass. The BCF generally increases with increasing molecular mass, except for chlorine containing compounds. The non-halogen PFRs with higher molecular masses are therefore more likely to be found in nature than those with lower molecular masses. For the chlorine containing PFRs no relation can be found between the BCF, the molecular mass or the amount of chlorine in the molecule (Table 2).

2.2. Flame retarding mechanisms

In case of fire the solid materials are decomposed by heat into flammable gases, which will be on fire. There are several FR mechanisms to prevent fire, of which the most effective ones are reactions in the gas phase and reactions in the solid phase (EFRA, 2007). In the gas phase halogenated FRs remove H^+ and OH^- radicals from the flammable gasses, by reaction with the Br and Cl atoms. The removal of the H^+ and OH^- radicals results in a slowdown of the burning process, and reduces the spreading of the fire. The effectiveness of the halogenated FRs is depending on the number of halogen atoms present in the molecule (CEFIC, 2007).

It is impossible to describe one single working mechanism for PFRs (Schmitt, 2007). Halogenated FRs act in the gas phase, whereas non-halogenated PFRs mainly act in the solid phase of burning materials. When phosphorus is heated it will react, and form a polymeric form of phosphoric acid. This acid causes a char layer, which shields the material from oxygen, in that way preventing the formation of flammable gasses. Another mechanism of action of PFRs is offering a partial gas phase contribution to the flame extinguishing effect, which is comparable to bromine- or chlorine containing FRs (CEFIC, 2007; EFRA, 2007; Schmitt, 2007; Chen et al., 2008). When halogens and phosphorus are both present in polymer systems, they act independently and therefore additively (WHO, 1997).

The content of phosphorus in PFRs varies from 8.2% for bis(4-carboxyphenyl) phenylphosphine oxide (BCPPO) (Chemspider, 2011) to almost 100% for RP (Schmitt, 2007). A minimum amount of PFR is needed to form a char layer. Once the layer is formed there is no need for more FR.

2.3. Potential substitutes for PBDEs?

PFRs can either be inorganic or organic. Most commonly used inorganic PFRs are RP and APP. These two flame retardants are active in the solid phase of burning materials, based on char forming (see Section 2.2). The organic PFRs are discussed in the following paragraphs (Leisewitz et al., 2000; Schmitt, 2007).

2.3.1. Phosphorus flame retardants

2.3.1.1. Resorcinol-bis(diphenylphosphate). RDP is an aryl phosphate, which is applied as an additive FR. It is used as a substitute for halogenated FRs as well as for TPhP because it has a lower volatility, a higher thermal stability, and a higher P-content in comparison to TPhP (Leisewitz et al., 2000; Pawlowski and Schartel, 2007). This would not be of influence on the FR efficiency if RDP was only working in the solid phase of burning materials. The primary mechanism of RDP is the solid phase mechanism, but in addition, a (weaker) gas phase mechanism is also assumed. The active substance content lies between 10 and 11% of phosphorus weight, depending on the product (Leisewitz et al., 2000). RDP is used as a substitute for TCEP and TCPP as it is less volatile (McPherson et al., 2004), and therefore less likely to be released into the environment.

The structure of RDP is shown in Table 1. RDP is thermally stable (Leisewitz et al., 2000), has a boiling point of 587 °C (Chemspider, 2011), but, according to Leisewitz et al. (2000), it already decomposes above 300 °C. RDP is liquid at room temperature (Leisewitz et al., 2000), and in case of fire, carbon oxides and phosphorus oxides are formed. The phosphorus oxides transform into acids when they are in direct contact with humid mucous membranes (Leisewitz et al., 2000). RDP is very poorly soluble in water (1.11×10^{-4} mg L^{-1} (Syrres, 2011)), has a very high log K_{ow} of 7.41 (Pakalin et al., 2007), and a vapor pressure of 2.1×10^{-8} mm Hg by 25 °C (Syrres, 2011). The log K_{oa} is not known, however according to the vapor pressure transfer to indoor air cannot be excluded (Leisewitz et al., 2000).

2.3.1.2. Bisphenol-A diphenyl phosphate. BADP is an aryl phosphate of which the structure is shown in Table 1. BADP is active in the condensed phase as well as in the gas phase (Pawlowski and Schartel, 2007), which is in contrast with the mechanism of most of the PFRs, which are active in the solid phase through char formation (see Section 2.2).

BADP has a log K_{ow} of 4.5 (Pakalin et al., 2007), and according to Pakalin et al. (2007) the calculated BCF of BADP is 3.16. Because of the high volatility of TPhP (Pawlowski and Schartel, 2007), BADP is nowadays often used as its substitute, because it is less likely to be released into the environment.

2.3.1.3. Triphenyl phosphate. TPhP (see Table 1), an aryl phosphate, is an additive FR (Björklund et al., 2004), which is only active in the gas phase (Pawlowski and Schartel, 2007). It is one of the most effective FRs for many polymers. During thermal degradation TPhP forms phosphoric acid. This acid reacts and forms pyro phosphoric acid, which acts as heat transfer barrier in the condensed phase (Lee et al., 2002). TPhP is solid at room temperature, has a melting point of 49 °C (Fisk et al., 2003), a boiling point of 370 °C (WHO, 1991), a solubility of 1.9 mg L^{-1} (Fisk et al., 2003), a vapor pressure of 1.2×10^{-6} mm Hg (Chemspider, 2011), and a log K_{ow} of 4.59 (Fisk et al., 2003). Because of their high volatility, RDP and BADP are nowadays often used as a substitute (Pawlowski and Schartel, 2007), because they are less likely to be released into the environment.

2.3.1.4. Diphenylcresylphosphate. DCP is an additive FR (see Table 1) (Björklund et al., 2004), which is liquid at room temperature, has a melting point of -38 °C (Fisk et al., 2003) and a boiling point of 235 °C (Stuer-Lauridsen et al., 2006). DCP has a solubility of 0.24 mg L^{-1} (Fisk et al., 2003), a vapor pressure 4.7×10^{-6} mm Hg (Syrres, 2011), and a log K_{ow} of 4.51 (Fisk et al., 2003). The BCF of DCP is 1711 (Chemspider, 2011).

2.3.1.5. Melamine polyphosphate. Melamine polyphosphate (see Table 1) is a phosphorus and nitrogen containing FR, which is chemically built into a polymer molecule. At room temperature melamine polyphosphate is a white, fine crystalline powder with no odor, and a boiling- and melting point higher than 400 °C (ASCC, 2006). Melamine polyphosphate has a water solubility, which is lower than 0.1 g L^{-1} at 22 °C (PINFA, 2011), a vapor pressure of 1.82×10^{-12} mm Hg at 25 °C (Chemspider, 2011), and a log K_{ow} of −2.3 (PINFA, 2011).

2.3.1.6. Diethylphosphinic acid. Diethylphosphinic acid (see Table 1) is a FR, which is often formed and released during the gas phase, by decomposition of FR materials (Anonymous, 2008). Diethylphosphinic acid has a boiling point of 320 °C (Chemspider, 2011), and a vapor pressure of 6.8×10^{-5} mm Hg at 25 °C (Chemspider, 2011).

2.3.1.7. Tricresylphosphate. TCP is a non-flammable, clear, faintly yellow, viscous odorless liquid (WHO, 1990; Bolgar et al., 2008), which is a mixture of mainly three isomers: tri-ortho-cresylphosphate (o-TCP) (cas no. 78-30-8), tri-meta-cresylphosphate (m-TCP) (cas no. 563-04-2), and tri-para-cresylphosphate (p-TCP) (cas no. 78–32-0). TCP has a low water solubility of 0.36 mg L^{-1}, and a log K_{ow} of 5.11. In an alkaline medium it can easily be hydrolyzed to dicresylphosphate and cresol, but it is stable in neutral and acidic media (WHO, 1990). The structures of TCP and its three main isomers are shown in Table 1. Besides the three main isomers, other isomers might also be present in the TCP mixture like the ortho-ortho-meta (oom), ortho-ortho-para (oop), omm, omp, opp, mmp, and mpp isomers (De Nola et al., 2008).

2.3.2. Halogen containing phosphorus flame retardants

2.3.2.1. Tris(chloropropyl)phosphate. TCPP (see Table 1) is a clear, colorless liquid (WHO, 1998), which is a halogen containing PFR, used as an additive FR (EFRA, 2007). The trade product consists of a mixture of four halogenated phosphoric acid esters of which the main components are tris(chloroiso-propyl)phosphate (75%) and bis(1-chloro-2-propyl)-2-chloropropyl-phosphate (15–30%) (Leisewitz et al., 2000). TCPP represents approximately 80% of the chlorinated PFRs in Europe and is by volume the most important PFR (Leisewitz et al., 2000).

TCCP has a solid phase fire performance mechanism as well as a gas phase, in which the phosphorus is active in the solid phase and the chlorine in the gas phase. TCPP has a boiling point of 342 °C, but above 150 °C TCPP already decomposes. Phosphorus acid and chloropropanol are formed in the presence of acids and bases. In case of fire, carbon monoxide, carbon dioxide, phosphorous compounds (phosphorous oxides such as phosphorpentoxide) and hydrochloric acid are formed. TCPP is well soluble in water (1.6 g L^{-1}) (WHO, 1998), has a log K_{ow} of 2.59 (WHO, 1998), and a vapor pressure of 100 Pa (=0.75 mm Hg) at 20 °C (Leisewitz et al., 2000). Moderate transmissions of TCPP from open sources into indoor air can thus not be excluded.

2.3.2.2. Tris(2-chloroethyl)phosphate. TCEP (see Table 1) is an additive FR (Björklund et al., 2004), of which, in case of fire, the phosphorus is active in the solid phase. However the compound also has a gas phase mechanism of action through the chlorine (see Section 2.2). TCEP has a boiling point of 351 °C (WHO, 1998), and is a stable compound on short-term exposure at 150 °C, but it rapidly decomposes above 220 °C to form carbon monoxide, hydrogen chloride, 2-chloroethane and dichloroethane. Hydrolytic stability of TCEP decreases with increasing temperature and pressure or ex-

Table 3
Properties of phosphorus compounds used in hydraulic fluids or in PVC.

	Application	Solubility (mg L^{-1})	Boiling point (°C)	Melting point (°C)	Density (g mL^{-1} at 25 °C)	Flash point (°C)
DCP	PVC[a], HF	0.24	235	−38	1.2	212
DMMP	HF[b]	3.22×10^5	181	−48	1.079	69
2-Ethylhexyl diphenyl phosphate	PVC, HF	1.9	421	−30	1. 103	222
IDPP	PVC	0.75	448	−50	1.08	238
Isopropylphenyl diphenyl phosphate	HF	2.2	424	89	1.196	224
Octyl diphenyl phosphate	PVC	0.14	426	87	1.105	225
TBP	HF	280	289	−80	0.986	146
TCP	PVC, HF	0.36	439	77	1.201	232
TCEP	PVC	7000	351	−55	1.39	202
TEHP	PVC	0.6	220	87	0.93	207
TEP	PVC	5.00×10^5	216	−56	1.066	116
TPhP	PVC, HF	1.9	370	49	1.265	220
Trioctyl phosphate	PVC	9.47×10^{-6}	415	89	0.928	218
Tris(isopropyl-phenyl) phosphate	PVC	1.4	490	−19	1.108	263
TXP	PVC, HF	1.86×10^{-2}	491	90	1.154	264

UNEP (1998), WHO (1998), Lassen and Lokke (1999), UNEP (2002), Fisk et al. (2003), Stuer-Lauridsen et al. (2006), ATSDR (2009), US-EPA (2009), Chemspider (2011) and Syrres (2011).
[a] Polyvinylchloride.
[b] Hydraulic fluids.

treme pH (WHO, 1998). TCEP is well soluble in water (solubility 7.0 g L^{-1}) (ATSDR, 2009) with a log K_{ow} value of 1.44 (ATSDR, 2009), and a vapor pressure of 1.1×10^{-4} mm Hg at 25 °C (Chemspider, 2011). Sigma-Aldrich (2011) gives a code N to TCEP, which means that TCEP is dangerous for the environment. The compound is considered not very bioaccumulative (BCF of 1.37, Chemspider, 2011).

2.3.2.3. Tris(1,3-dichloro-2-propyl)phosphate. TDCPP (see Table 1) is a viscous colorless liquid, which is a halogen containing PFR, used as an additive FR in resins, latexes and foams (WHO, 1998; Green et al., 2008). Most of those foams are used in the automotive industrie and some are used in furniture. TDCPP is used in the same kind of products as TCPP, but because of the higher price of TDCPP it is only used in applications where a more effective FR is required (EU, 2008a). Stapleton et al. (2009) analyzed 26 foam samples from the US sampled between 2003 and 2009. The most often detected flame retardant, detected in 15 samples, was TDCPP with a concentration of 1–5% (w/w). Also in baby products containing polyurethane foam, which must meet the California TB 117 (see Section 1), TDCPP is the most common flame retardant detected (36% of the tested products) (Stapleton et al., 2011).

TDCPP has a boiling point of 457 °C (Chemspider, 2011), a solubility in water of 1.5 mg L^{-1}(Chemspider, 2011), a log K_{ow} value of 3.8 (WHO, 1998), and a vapor pressure of 7.4×10^{-8} mm Hg at 25 °C (Syrres, 2011). Sigma-Aldrich (2011) gives a code N to TDCPP, which means that TCEP is dangerous for the environment. TDCPP is not readily degraded in sewage sludge. Studies have demonstrated limited degradation of TDCPP in natural waters and it is rapidly metabolized by fish. Bioconcentration factors are low (3–107), and the half-life of elimination in killifish is 1.65 h. (WHO, 1998).

2.3.2.4. Tetrekis(2-chlorethyl)dichloroisopentyldiphosphate. V6. (see Table 1) is an additive FR, which is in Europe only produced by one producer (SCHER, 2007b). V6 was only available with a purity of >90% and containing TCEP (4.5–7.5% (w/w)) (EU, 2008b). Nowadays V6 is available without the impurity of TCEP (EU, 2008b). V6, TCPP and TDCPP have a chemical similarity and a similar use pattern (EU, 2008a). V6 is only used together with TCPP and TDCPP in applications where a more effective FR is required to meet specific criteria (EU, 2008b). V6 is mainly used in polyurethane foam in the automotive and furniture industries (Herzke et al., 2007; SCHER, 2007b), but it has also been detected in baby products containing polyurethane foam in 15% of the tested products (Stapleton et al., 2011). V6 has a boiling point of 620 °C (Chemspider, 2011), a solubility in water of 2.1 mg L^{-1}(Chemnet, 2012), a log K_{ow} value of 1.9 (Chemspider, 2011), and a vapor pressure of 1.2×10^{-14} mm Hg at 25 °C (Chemspider, 2011).

3. Production and use

3.1. Applications

Organophosphates are used for two reasons: the halogenated ones as FRs, while the non-halogenated ones are mostly used as plasticizers (Andresen et al., 2004). The non-derivatised alkyl phosphates such as TBP, TiBP, TPhP and tris-(butoxyethyl)-phosphate (TBEP) are predominantly used as plasticizers, lubricants and to regulated pore sizes, though in some cases, they are also used as FRs (Andresen et al., 2004). Some PFRs, such as TPP are also used in combination with halogenated and non-halogenated flame retardants in different commercial mixtures commonly added to polyurethane foam. TPP has been applied together with PentaBDE in foam. PFRs are used in many products. Some examples are TBEP used in floor polish, DCP in ABS pc-blends, and TBEP and TBP in lacquers (WHO, 1997, 2000; Andresen et al., 2004). In Appendix B, an overview of the PFRs studied with their applications is given.

Many PFRs are used in a wide range of commercial products. For some products several PFRs are used, while for other applications only one or a few phosphorus compounds are known. Several phosphorus containing compounds are used in hydraulic fluids. DMMP, DCP, TPhP, TCP, isopropylphenyl diphenyl phosphate, 2-ethylhexyldiphenyl phosphate, TXP and TBP are all known to be used for this application (WHO, 1990, 1997, 1998; Akzo, 2003; Andresen et al., 2004). Another example of the use of PFRs is in PVC, in which triethyl phosphate (TEP), DCP, TPhP, TCEP, TCP, TEHP, trioctyl phosphate, tris(isopropyl-phenyl)phosphate, IDPP, octyl diphenyl phosphate, 2-ethylhexyldiphenyl phosphate and TXP can be used as plasticizers (WHO, 1990, 1997, 1998; Lassen and Lokke, 1999; WHO, 2000; Björklund et al., 2004). The physicochemical properties of these compounds vary except in the densities, which are all in the same range (Table 3). A number of other applications to which PFRs are added include the use in textiles, rubber, polyurethane foam, antistatic agent, cellulose, cotton, cutting oils, electronic equipment such as video display units cables, casting resins, glues, engineering thermoplastics, epoxy resins, and phenolics resins.

Table 4
Production/usage volumes of the studied PFRs.

PFR	Production/usage volume (tones)	Location	Year
RDP	>1500 year^{-1}	Europe	1995
	0	Finland	2006–2008
	<227	United States	2006
	6	Sweden	2008
BADP	0	Sweden	2004–2007
	454–4500	United States	2006
TPhP	4500–22 700	United States	1998
	20 000–30 000	Europe (excl. Eastern Europe)	2000
	4500–22 700	United States	2002
	55	Norway	2004
	6.7	Norway	2005
	1592	Sweden	2005
	4500–22 700	United States	2006
	18.4	Norway	2008
	2.3–16.7 year^{-1}	Denmark	2004–2008
	9.8–57.1 year^{-1}	Finland	2004–2008
	46.0–88.0 year^{-1}	Sweden	2003–2008 (excl. 2005)
DCP	>1500 year^{-1}	Europe	1995
	<227	United States	2006
	0.2	Norway	2008
	2.1	Denmark	2008
	4.9	Finland	2008
	2.0	Sweden	2008
Melamine polyphosphate	Not applicable		
Diethylphospinic acid	Not applicable		
TCP	454–4500	United States	1998
	454–4500	United States	2002
	454–4500	United States	2006
	0.8	Norway	2008
	0.6	Denmark	2008
	3.6	Finland	2008
	5.0	Sweden	2008
TCPP	22 950 year^{-1}	Europe	1995
	2750 year^{-1}	UK	1995
	40 000	Worldwide	1997
	50	Norway	2001
	42.7	Norway	2008
	177	Denmark	2008
	16 429	Finland	2008
	132	Sweden	2008
TCEP	2040 year^{-1}	Europe	1995
	400 year^{-1}	UK	1995
	1286	Norway	2003
	798.5	Norway	2004
	1598	Finland	2004
	227–454	United States	2006
	261.3	Norway	2008
	0.1	Denmark	2008
	198	Finland	2008
	0	Sweden	2008
TDCPP	8000	Worldwide	1997
	4500–22 700	United States	1998
	<10 000	Europe	2000
	132.8	Denmark	2000
	134.1	Denmark	2001
	134.1	Denmark	2002
	4500–22 700	United States	2002
	4500–22 700	United States	2006
V6	454–4500	United States	1998
	<5000	Europe	2000
	<454	United States	2002

WHO (1997), UNEP (2002), US-EPA (2002), US-EPA (2006), EU (2008a, 2008b), Green et al. (2008) and SPIN (2011).

3.2. Production volumes

The total consumption of FRs in Europe in 2006 was 465 000 tonnes (CEFIC, 2007). PFRs were responsible for 20% thereof, of which 9% were non-halogen PFRs and 11% were chlorine containing PFRs (CEFIC, 2007). In Table 4 an overview of the studies PFRs is given with their production or usage volumes. Out of this table some observations can be made. Since 2003 the use of TCEP in Norway and Finland decreased significantly from 1598 tonnes in 2004 to 198.4 in 2008, which can be explained by the fact that TCEP is no longer produced in Europe (Green et al., 2008). On the other hand, the use of TCPP has continued to grow since the

mid-1960s, especially in rigid and flexible polyurethane foams, which might be explained by the fact that TCPP is often used as replacement of TCEP (WHO, 1998; Björklund et al., 2004). For TPhP Green et al. (2008) mentioned in their report the decrease of TPhP usage in Norway from 55 ton in 2004 to 6.7 ton in 2005. However, as can be seen in Table 4, the usage in Norway has increased again since then to 18.4 tonnes in 2008 (Spin, 2011). Remarkable is the use of TPhP in Sweden, which varied between 46.0 and 88.0 tonnes from 2003 till 2008, except for 2005 when the use was much higher with 1592.0 tonnes (SPIN, 2011).

4. Occurrence and behavior in the environment

Many of the PFRs are additives, and not chemically bonded to the final products, which may result in an easy release to the environment (Rodriguez et al., 2006). PFRs have already been detected in indoor air (Weschler, 1980, 1984; Carlsson et al., 2000; Otake et al., 2001; Sjödin et al., 2001; Hartmann et al., 2004), house dust (Marklund et al., 2003; Kawahara and Yanagisawa, 2003 cited in Ni et al. (2007); van den Eede et al., 2011), drinking water (Stackelberg et al., 2007), sediment and biota. Results from laboratory experiments of Regnery and Püttmann (2010) showed rapid degradation of TBEP, TBP and TiBP by sunlight. The chlorinated PFRs TCEP and TCPP, however, seemed to be resistant to degradation by sunlight. Whether photodegradation also has an effect on the concentrations of the PFR in a lake is not yet proven.

4.1. Non-halogen PFRs

PFRs have been detected in indoor air (Weschler, 1980, 1984; Otake et al., 2001; Sjödin et al., 2001). Carlsson et al. (1997) reported PFRs in a number of indoor environments such as offices, day care centers, hospitals and school buildings with concentrations ranging from less than 1 ng m^{-3} up to 250 ng m^{-3}. Otake et al. (2001) reported four OPEs in indoor air of six different houses in Tokyo, Japan, in the range <0.4–100 ng m^{-3}. The concentration is likely depending on the kind and amount of furniture, building material and electronic equipment that are located in the room, the temperature, and the degree of ventilation (Carlsson et al., 1997).

4.1.1. Resorcinol-bis(diphenylphosphate)

There are no data available on occurrence of RDP, or its degradation products, in the environment. Analysis of samples from the vicinity of manufacturing and processing plants is as necessary as analysis on house dust in houses, in which consumer goods such as electronic devices containing RDP are found. There is evidence that RDP containing fumes and aerosols are released during the application of RDP at production sites. According to McPherson et al. (2004) bioaccumulation is unlikely for RDP. However, the BCF of RDP is 20453 (Chemspider, 2011), which suggests that some bioaccumulation may occur. Leisewitz et al.(2000) state that accumulation in organisms is unlikely due to the observed metabolism, resulting in polar degradation products.

4.1.2. Bisphenol-A diphenyl phosphate

There are no data available on BADP levels in the environment.

4.1.3. Triphenyl phosphate

Triaryl phosphates (including TPhP) enter the aquatic environment mainly via hydraulic fluid leakages as well as by leaching and volatilization from plastics, and, to a minor extent, from manufacturing processes (Lassen and Lokke, 1999). TPhP rapidly adsorbs to sediments, and its biodegradation is rapid (WHO, 1997; Lassen and Lokke, 1999). The BCFs measured for several species of fish range from 6 to 18900 and the depuration half-life ranges from 1.2 to 49.6 h. TPhP is not considered persistent or bioaccumulative (Pakalin et al., 2007).

4.1.3.1. Air. TPhP has often been detected in urban air, although the levels are low (Lassen and Lokke, 1999). TPhP has been detected in indoor air (Björklund et al., 2004), as well as in indoor dust (Marklund et al., 2003). Air samples from three indoor environments (two lecture rooms and one office) containing computers, tables and chairs, were tested for the occurrence of a number of organophosphate compounds by Björklund et al. (2004). In all rooms TPhP was found (1.5–4 ng m^{-3}. In an earlier study by Carlsson et al. (2000) the covers of brand-new cathode ray tube (CRT) video display units (VDUs) were shown to emit high levels of TPhP. In another study, air samples were collected in a recently renovated kindergarten and a lecture room with a computer, 24 TFT flat screen VDUs, tables and chairs. The concentration of TPhP in the kindergarten was 0.3 ng m^{-3} and in the lecture room 1.6 ng m^{-3} (Tollbäck et al., 2006), which was in the same range as found in the study of Björklund et al. (2004) mentioned above. The air of various indoor environments at 12 locations in and around Zurich, Switzerland, was analyzed in a study from Hartmann et al. (2004). The tested sites included three offices, two furniture stores, three electronics stores, a theater and three cars. TPhP concentrations detected were 0.19–5.7 ng m^{-3}. TPhP concentrations were analyzed in two lecture halls, one with and one without computers, and an electronics dismantling facility by Staaf and Ostman (2005). Only two organophosphate triesters were detected in the lecture hall without computers, and only four organophosphate triesters were detected in the computer hall. TPhP was not detected in the lecture hall without computers. In the computer hall TPhP was found at a concentration of 1 ng m^{-3}. In the electronics dismantling facility nine OPEs were identified, with concentrations ranging from 2 to 130 ng m^{-3}. TPhP was found at a concentration of 17 ng m^{-3}. Other studies showed concentrations of TPhP of <0.05–47000 ng m^{-3} in indoor air in Norway in 2007 (Green et al., 2008), concentrations of TPhP of <1.2–10 ng m^{-3} in indoor air of Japan (Otake et al., 2001) and <0.1–23 ng m^{-3} in indoor air of Sweden (Marklund et al., 2005a). In Denmark the maximum allowable concentration of TPhP in workplace air is 3 mg m^{-3} (Lassen and Lokke, 1999). The Occupational Safety and Health Administration (OSHA) set a legal limit of 3 mg m^{-3} for TPhP in air averaged over an 8-h work day (ATSDR, 2009)). The maximum environmental levels reported above are with 47 μg m^{-3} in air far below the limits.

4.1.3.2. Surface water. TPhP is found to biodegrade extensively under both aerobic and anaerobic conditions in various test systems. Half lives in water/sediment simulation tests range from 3 to 12 d in river water/sediment and pond sediment, whereas half lives ranging from 50 to 60 d were observed in pond hydrosoil. Based on the available data, TPhP is not considered to meet the persistent or very persistent criteria (half-life >40 d and >60 d in freshwater, respectively and half-life >120 d and >180 d in freshwater sediment (Pakalin et al., 2007). TPhP has been analyzed in river samples (Andresen et al., 2004). The concentrations in the River Ruhr (Germany) were found to be up to 40 ng L^{-1}, which is far below the maximum environmental levels reported for river water (7900 ng L^{-1}) by the Danish Environmental Protection (EPA) (Lassen and Lokke, 1999). Three rivers (Danube, Schwechat and Liesing) as well as the corresponding sediments were selected for monitoring the occurrence of some OPEs in the aquatic environment in Austria. Sampling was performed in summer 2005. The average discharges of the rivers were 1900 m^3 s^{-1}, 7.9 m^3 s^{-1} and 0.38 m^3 s^{-1}. The River Danube was sampled in two different locations (upstream and downstream of Vienna) (Martínez-Carballo

et al., 2007). TPhP concentrations in the water samples from the River Danube at Nussdorf were 6 ng L^{-1} and at Haslau <4.4 ng L^{-1}. In the River Schwechat and the River Liesing concentrations of 7 and 10 ng L^{-1} were detected (Martínez-Carballo et al., 2007). Bacaloni et al. (2007) analyzed river water from the Tiber (Italy) in June and November 2006 and found levels of TPhP of 11 and 165 ng L^{-1}. Levels of TPhP determined in influent and effluent samples of Norway in 2007 were respectively 3100–14000 ng L^{-1} and 1700–3500 ng L^{-1} (Green et al., 2008). In Sweden respectively 76–290 ng L^{-1} and 41–130 ng L^{-1} was detected (Marklund et al., 2005b), and in Spain <0.015–0.47 ng L^{-1} and < 0.015–0.22 ng L^{-1} was detected (Rodriguez et al., 2006). Meyer and Bester (2004) determined the elimination efficiency in two sewage treatment plants (STPs) of the Ruhr/Rhine area. In the STP with a two-stage biological treatment 57 ± 24% of TPhP was eliminated. In the other STP, a single stage activated sludge plant, the elimination of TPhP was 75 ± 10%.

4.1.3.3. Drinking water. Stackelberg et al. (2007) performed a study on a drinking water treatment (DWT) plant in a drainage basin of a heavily populated, highly urbanized area, in which more than 50 STPs discharge effluents to the two streams that provide source water for the DWT plant. The DWT plant treats and provides an average of 235 million L d^{-1} to about 850000 people. In the finished water samples no TPhP was detected (LOD 0.5 μL).

4.1.3.4. Sediment. TPhP was not detected in the sediment samples from the River Danube at Nussdorf (Austria) (see Section 4.1.3.2), although it was found in the water sample. At Haslau the TPhP concentration in the sediment sample was <0.79 μg kg^{-1} dw. In the River Schwechat (Austria) and the River Liesing (Austria), concentrations of 160 and 4.3 μg kg^{-1} dw were found in the sediment samples (Martínez-Carballo et al., 2007). The Danish EPA (Lassen and Lokke, 1999) performed an assessment on alternative FRs for BFRs. They reported maximum environmental levels in sediment of 4000 ng g^{-1}. No sample location was given. Green et al. (2008) performed a study on PFR levels in environmental samples from Norway. They analyzed sediments of one landfill site and one car demolishing site of Norway in 2007. TPhP concentrations detected were <38–5000 μg kg^{-1}. Another study was performed in 2010 by Leonards et al. (2011) who found TPhP levels of <0.10–6.8 μg kg^{-1} in sediment samples of Norway.

4.1.3.5. Dust. Stapleton et al. (2009) analyzed 50 dust samples collected from home vacuum cleaners from the Boston, MA area between 2002 and 2007 for TCPP, TDCPP and TPhP. The detection frequency of TPhP was >96% and the concentration range found was <150 ng g^{-1}–1.8 mg g^{-1}. Van den Eede et al. (2011) investigated the presence of PFRs in three SRMs certified for other organic contaminants in indoor dust. TPhP levels found were 0.70–0.99 μg g^{-1}. In other dust samples Van den Eede et al. (2011) detected TPhP levels of 0.04–34.2 μg g^{-1}.

4.1.3.6. Biota. Only a few studies on PFRs in biota are known. Lassen and Lokke, 1999 reported maximum levels of TPhP in fish of 600 μg kg^{-1}. No sample location was given. Green et al. (2008) analyzed mussel and cod liver from Norway, and no TPhP was detected. Evenset et al. (2009) reported 5.7–13 μg kg^{-1} in fish liver, 0.3–3.2 μg.kg in fish muscle, and 0.6–3.3 seabird liver from Norway. Leonards et al. (2011) reported TPhP in beach crab, cod liver, trout and in bird blood and bird eggs from Norway, with the highest concentration of 44 μg kg^{-1} found in trout. TPhP levels of blue mussel and of burbot liver were below the LOD of 0.05–0.23 μg kg^{-1} and 1.4–5.4 μg kg^{-1}. Sundkvist et al. (2010) analyzed biota, herring, perch, mussels, eelpout and salmon, from Swedish lakes and coastal areas. In all samples TPhP was detected, with levels ranging from 4.2 to 810 ng g^{-1} and the highest level found in carp from freshwater close to a source. Campone et al. (2010) set up a detection method for PFRs in fish tissue and analyzed 24 fish samples without finding any PFRs, with a LOD of 0.8 μg kg^{-1} for TPhP.

4.1.4. Diphenylcresylphosphate

Sigma-Aldrich (2011) gives a code N to DCP, which means DCP is dangerous for the environment. There are no data available in the literature on DCP occurrences in the environment.

4.1.5. Melamine polyphosphate

Melamine polyphosphate has a low bioaccumulation (McPherson et al., 2004). Although very little of the notified polymer is likely to be released to the water compartment, the relatively high average molecular weight (>10000 g mol^{-1}) and charged nature of the polymer indicates low potential for bioaccumulation (ASCC, 2006). There are no data available in the literature on melamine polyphosphate occurrences in the environment.

4.1.6. Diethylphosphinic acid

Diethylphosphinic acid is considered to be very persistent, but is not considered to meet the criteria for bioaccumulation (Stuer-Lauridsen et al., 2006). There are no data available in the literature on diethylphosphinic acid occurrences in the environment.

4.1.7. Tricresylphosphate

TCP is mainly released into the environment from end-point use, while a little is released during production of TCP (Lassen and Lokke, 1999). With a BCF of 8.56×10^3, bioaccumulation could be expected. In the aquatic environment biodegradation is rapid, being almost complete in river water within 5 d. In sewage sludge the half life of TCP is 7.5 h, and in 24 h up to 99% of TCP has degraded. Abiotic degradation is slower with a half life of 96 d (WHO, 1990). The isomers of TCP have different degradation rates, with o-TCP degrading faster than m-TCP and p-TCP.

4.1.7.1. Air. A number of studies have been performed on the analysis of TCP in air. In a study of Tollbäck et al. (2006) air samples were collected in a kindergarten and a lecture room in Sweden (see Section 4.1.3). The concentration of TCP detected in the lecture room was 0.4 ng m^{-3}, but TCP was not detected in the kindergarten. In another study, air of various indoor environments at 12 locations in and around Zurich, Switzerland, was analyzed for the presence of TCP (Hartmann et al., 2004) (see Section 4.1.3). At most of the sample locations (9) TCP was found below the LOD of 0.41 ng m^{-3}. TCP was detected in the theater (2.1 ng m^{-3}) and in one off the offices (0.37 ng m^{-3}). In one of the electronic stores TCP was found below the LOD at night, and 0.21 ng m^{-3} at day time. In Denmark the maximum allowable concentration of TCP in workplace air is 0.1 mg m^{-3} (Lassen and Lokke, 1999). The concentrations observed are far below this limit.

4.1.7.2. Surface water. In 2005, three rivers (Danube, Schwechat and Liesing) as well as the corresponding sediments were sampled in Austria (see Section 4.1.3). TCP was not detected (<7.9 ng L^{-1}) in water samples from those rivers (Martínez-Carballo et al., 2007). Bacaloni et al. (2007) analyzed river water from the Tiber (Italy) in June and November 2006. No TCP was detected (<0.1 ng L^{-1}).

4.1.7.3. Sediment. Due to its low water solubility and high adsorption to particulates TCP rapidly adsorbs to sediment and soil (WHO, 1990). TCP concentrations in sediment from the River Danube were <1.5 μg kg^{-1} dw. In sediment from the River Schwechat (Austria) and the River Liesing (Austria) concentrations of 39 and 6.3 μg kg^{-1} dw were found (Martínez-Carballo et al., 2007). TCP

levels in Norwegian sediments ranged from <0.05–288 ng g^{-1} (Leonards et al., 2010).

4.1.7.4. Dust. Van den Eede et al. (2011) investigated the presence of PFRs in three SRMs certified for other organic contaminants in indoor dust. TCP levels found were 0.77–1.12 μg g^{-1}. In other dust samples Van den Eede et al. (2011) found TCP levels of <0.04–12.5 μg g^{-1}.

4.1.7.5. Biota. Only a few studies are known on PFRs in biota. Evenset et al. (2009) analyzed but did not find TCP In biota from Norway. LODs were 0.2 μg kg^{-1} for whole fish, 0.08–0.2 μg kg^{-1} for fish muscle, 2 μg kg^{-1} for fish liver, and 0.6 for seabird liver. Leonards et al. (2011) analyzed and did not detect TCP in beach crab, blue mussel, burbot liver, cod liver, trout, bird blood, bird eggs and sediment samples of Norway, with LODs ranging from 0.04 μg kg^{-1} for blue mussel to 5.1 μg kg^{-1} for cod liver. Sundkvist et al. (2010) analyzed biota, herring, perch, mussels, eelpout and salmon, from Swedish lakes and coastal areas. In all samples, except in the herring (<0.3–<0.4 μg kg^{-1}) and in perch from Öresjön (<2.1 μg kg^{-1}), TCP was detected, with levels ranging from 3.0 to 137 μg kg^{-1} with the highest level found in perch from freshwater close to a source. Campone et al. (2010) analyzed 24 fish samples and did not detect PFRs, with an LOD of 3.1 μg kg^{-1} for TCP.

4.2. Halogen containing PFRs

4.2.1. Tris(chloropropyl)phosphate

According to Leisewitz et al. (2000) TCPP is difficult to degrade, so it has to be assumed that it might accumulate in food chains (Leisewitz et al., 2000). Kawagoshi et al. (2002) tested the degradation of organophosphorus esters in leachate from a sea-based solid waste disposal site, and found that TCPP showed low degradability. No decrease was observed under anaerobic condition. TCPP has been found in aquatic systems. Concentrations in surface water range between 0.05 and 10 μg L^{-1} (Leisewitz et al., 2000). River sediments showed concentrations of up to 165 μg kg^{-1} dw. There are no data with respect to the occurrence of TCPP in sewage sludge and soil. Concentrations of 1–14 mg kg^{-1} TCPP in dust have been reported (Leisewitz et al., 2000).

4.2.1.1. Air. TCPP has been detected in indoor air (Carlsson et al., 1997), as well as in indoor dust (Marklund et al., 2003). The source of this contamination was electronic equipment such as computers (Carlsson et al., 2000). A number of studies have been performed to determine TCPP in air. In Sweden, air samples from three indoor environments (see Section 4.1.3) were analyzed for a number of organophosphate compounds (Björklund et al., 2004). In all three rooms the dominating compound was found to be TCPP at concentrations of 91–850 ng m^{-3}. Air of 12 indoor locations in and around Zürich, Switzerland, was analyzed for the presence of TCPP (Hartmann et al., 2004) (see Section 4.1.3). TCPP was found up to 260 ng m^{-3} in a 9-year old car, while only low levels (23 ng m^{-3}) were found in a new car. TCPP concentration in a 1-year old car was < 0.12 ng m^{-3}. Furniture stores, a theater and an office had moderate levels of TCPP ranging from 46 to 130 ng m^{-3}. TCPP was not detected in any of the electronics stores or the other office sampled. TCPP in air from a kindergarten and a lecture room in Sweden (see Section 4.1.3) were 77 and 1006 ng m^{-3}, respectively. The most abundant OPE in both rooms was TCPP. All other organophosphate triesters ranged 0.1–9 ng m^{-3} in the kindergarten and 0.3–15 ng m^{-3} in the computer room (Tollbäck et al., 2006). TCPP was the major compound in air from two lecture halls and of an electronics dismantling facility in Sweden, with a concentration of 762 ng m^{-3} in the lecture hall without computers and a concentration of 1080 ng m^{-3} in the computer hall. In the electronics dismantling TCPP was found at a concentration of 22 ng m^{-3} (Staaf and Ostman, 2005) (see Section 4.1.3). Other studies showed concentrations of TCPP in indoor air in Sweden of 10–570 ng m^{-3} (Marklund et al., 2005a) and in Norway of <0.2–49 ng m^{-3} (Green et al., 2008). In Tokyo residences the maximum concentration of TCPP in indoor air was >10 μg m^{-3} (Saito et al., 2001 cited in Ni et al., 2007).

4.2.1.2. Water. TCPP concentrations of 80–100 ng L^{-1} were found in River Rhine (Germany) water and of 100 ng L^{-1} in the River Lippe (Germany) (Andresen et al., 2004). TCPP concentrations in the River Ruhr (Germany) varied between 20 and 200 ng L^{-1} (Andresen et al., 2004). Regnery and Püttmann (2010) also analyzed surface water from Germany. They found TCPP concentrations ranging from <4–379 ng L^{-1}, with the highest concentrations found in lake Nidda at Oxbow. TCPP is supposed to be introduced into surface water through STPs (Fries and Püttmann, 2001; Andresen et al., 2004). TCPP has been analyzed in several rivers and STP effluents. All STPs, which were sampled by Andresen et al. (2004), contribute considerably to the load of TCPP in the respective rivers as typical concentrations of 50–400 ng L^{-1} in the effluents were reported. There was no relationship between the TCPP concentrations in effluents and the amount of inhabitants served by the STPs (Andresen et al., 2004). In 2005, three rivers (Danube, Schwechat and Liesing) as well as the corresponding sediments were sampled in Austria (see Section 4.1.3). TCPP concentrations in the water samples from the River Danube at Nussdorf were 43 ng L^{-1} and at Haslau 33 ng L^{-1}. In the River Schwechat and the River Liesing concentrations of 170 and 110 ng L^{-1} were found) (Martínez-Carballo et al., 2007). Bacaloni et al. (2007) analyzed river water from the River Tiber (Italy) and found levels of TCPP of 117 and 54 ng L^{-1}. TCPP concentrations in STP influents from an urban sewage plant of Spain, which receives mainly wastewater from a 125 000 inhabitants city, ranged 0.32–0.72 ng L^{-1} and in the STP effluents from the same STP 0.31–0.91 ng L^{-1} (Rodriguez et al., 2006), which is far below the range of 50–400 ng L^{-1} reported by Andresen et al. (2004) mentioned above in effluent samples from Germany. TCPP concentrations in STP influents and effluents from a STP near Dortmund (Germany), which processes 200 000 m^3 waste water per day, were 240–1000 and 230–610 ng L^{-1}, respectively (Bester, 2005). This effluent concentration is comparable to concentrations reported by Andresen et al. (2004). TCPP concentrations in the influent showed a high variability. The elimination rate of TCPP in STPs also exhibits a high variability but is generally low (0–41% d^{-1}) ((Bester, 2005). Meyer and Bester (2004) showed with their study (See Section 4.1.3.2) that no elimination of TCPP took place in the two STPs studied. Other studies showed concentrations of TCPP of 1860–2590 ng L^{-1} in influent and 1700–2100 ng L^{-1} in effluent of Norway (Green et al., 2008), concentrations of TCPP of 1.1–18 μg L^{-1} in influent and 1.5–24 μg L^{-1} in effluent of Sweden (Marklund et al., 2005b), concentrations of TCPP of 980 ng L^{-1} in influent and 320 ng L^{-1} in effluent of Japan (Ishikawa et al., 1985 cited in Green et al., 2008) and concentrations of TCPP of 270–1400 ng L^{-1} in effluent of Austria (Martínez-Carballo et al., 2007).

4.2.1.3. Sediment. In sediments from Liverpool Bay and the Rivers Mersey and Tees (UK), eight different PFRs have been determined with TCPP being the dominant PFR with concentrations up to 180 μg kg^{-1} dw (VU-IVM, 2007). TCPP concentrations in sediment samples from the River Danube at Nussdorf (Austria) were <0.6 μg kg^{-1} dw, although TCPP was detected in the water samples, and at Haslau 20 μg kg^{-1} dw was found. In sediment samples from the River Schwechat (Austria) and the River Liesing (Austria) concentrations of 1300 and 95 μg kg^{-1} dw were found (Martínez-Carballo et al., 2007). Green et al. (2008) reported TCPP in sediment

from Norway of 63–24000 μg kg^{-1}. Leonards et al. (2011) found TCPP levels of <0.15–54 μg kg^{-1}.

4.2.1.4. Dust. Stapleton et al. (2009) analyzed 50 dust samples from the Boston, MA area (see Section 4.1.3). The detection frequency of TCPP was 24%, but this low frequency can be due to a co-elution problem at the detection with GC-mass spectrometry (MS). The concentrations found were <140–5490 ng g^{-1}. Van den Eede et al. (2011) detected TCPP levels of 0.19–73.7 μg g^{-1} in Belgian dust samples.

4.2.1.5. Biota. Green et al. (2008) found TCPP below the limit of detection (LOD) for mussel and cod liver with detection limits up to 30 μg kg^{-1}. Evenset et al. (2009) reported 1.4–2.9 μg kg^{-1} TCPP in fish muscle and 5.5–8.9 μg kg^{-1} of TCPP in fish liver from Norway. Leonards et al. (2011) reported TCPP in beach crab, blue mussel, burbot liver, trout, bird blood and bird eggs, with the highest concentration of 17 μg kg^{-1} in burbot liver. TCPP levels in cod liver were below the LOD of 26 μg kg^{-1}). Sundkvist et al. (2010) analyzed biota, herring, perch, mussels, eelpout and salmon, from Swedish lakes and coastal areas. In all samples TCPP was detected, with levels ranging from 23–1300 ng g^{-1} with the highest level found in mussels from marine water. Campone et al. (2010) reported TCPP below the LOD of 1 μg kg^{-1}.

4.2.2. Tris(2-chloroethyl)phosphate

4.2.2.1. Air. TCEP was detected in indoor air (Björklund et al., 2004), as well as in indoor dust (Marklund et al., 2003). Air samples from three indoor environments (see Section 4.1.3) were also tested (Björklund et al., 2004). TCEP was present in all rooms. Concentrations found ranged 1.4–15 ng m^{-3}. The TCEP concentrations are substantially lower than those of TCPP from the same study, which probably can be explained by the continuing increase of the use of TCPP and the replacement of TCEP by TCPP as an FR for toxicity reasons (WHO, 1998; Björklund et al., 2004). The concentration of TCEP in a kindergarten was 3 ng m^{-3} and in a lecture room 9 ng m^{-3} (see Section 4.1.3) (Tollbäck et al., 2006), comparable to levels found by Björklund et al. (2004). TCEP was not detected in a lecture hall without computers (see Section 4.1.3). In a computer hall TCEP was found at a concentration of 3 ng m^{-3} (Staaf and Ostman, 2005). In an electronics dismantling facility TCEP was found at a concentration of 10 ng m^{-3} (Staaf and Ostman, 2005). Other studies reported TCEP concentrations of <0.2–23 ng m^{-3} in air from Norway (Green et al., 2008) and 0.4–730 ng m^{-3} in air from various indoor environments (Marklund et al., 2005a).

4.2.2.2. Surface water. TCEP has been analyzed in several rivers and STP influents and effluents. Three rivers (Danube, Schwechat and Liesing) as well as the corresponding sediments were sampled in 2005 in Austria (see Section 4.1.3). TCEP concentrations in the water samples from the River Danube at Nussdorf were 23 ng L^{-1} and at Haslau 13 ng L^{-1}. In the River Schwechat and the River Liesing TCEP concentrations of 130 and 37 ng L^{-1} were found (Martínez-Carballo et al., 2007). Bacaloni et al. (2007) analyzed river water from the Tiber (Italy) and found TCEP levels of <1.5 and 7 ng L^{-1}. Regnery and Püttmann (2010) analyzed surface water from Germany. They found concentrations ranging from <3 to 184 ng L^{-1}, with the highest concentrations found in lake Nidda at Oxbow. Andresen et al. (2004), who reported TCEP concentrations in STP effluents of Germany from 5 to 130 ng L^{-1}, stated that, like TCPP, TCEP also passes STPs. This is confirmed by the study of Rodriguez et al. (2006), who found TCEP in influents of Spain between <0.025 and 0.30 ng L^{-1} and in effluents levels between <0.025 and 0.70 ng L^{-1}. The study of Marklund et al. (2005b) confirmed that TCEP passes through STPs. They found TCEP levels in influents from Sweden between 90 and 1000 ng L^{-1} and in effluents of 350–890 ng L^{-1}. Also Meyer and Bester (2004) confirmed with their study (see Section 4.1.3.2) that TCEP passes STPs with no elimination at all. In Norway TCEP concentrations in influents were 2000–2500 ng L^{-1} and in effluents 1600–2200 ng L^{-1} (Green et al., 2008), which is much higher than the levels mentioned before for Germany, Spain and Sweden.

4.2.2.3. Drinking water. Stackelberg et al. (2004) reported TCEP levels of <0.099 μg L^{-1} in drinking water, and Stackelberg et al. (2007) performed a study on a DWT plant described in Section 4.1.3. In the finished water samples the TCEP concentrations were 4–99 ng L^{-1}. TCEP was also analyzed in drinking water from Dongbok Lake and Paldang Lake, in South Korea (Kim et al., 2007), which are the reservoirs of all drinking water for the neighboring cities. The concentration of TCEP found in the DWT facility from Dongbok Lake was 14 ng L^{-1}, and in that from the Paldang Lake 25 ng L^{-1}.

4.2.2.4. Sediment. Green et al. (2008) reported TCEP near a car demolishing site of 2300–5500 μg kg^{-1}, much higher than those found in the sediment samples of a landfill site, which ranged from 27 to 380 μg kg^{-1}. Leonards et al. (2011) performed a study on sediment samples from Norway. Samples were taken at Kåfjorden, Trondheim, Oslo and Mjøsa. TCEP concentrations found ranged from <0.16 to 8.5 μg kg^{-1}. TCEP concentration in a sediment sample from the River Danube at Nussdorf (Austria) was <7.7 μg kg^{-1} dw while at Haslau TCEP was not detected. In the River Schwechat (Austria) the TCEP concentrations in sediment was 160 μg kg^{-1} dw and in the River Liesing (Austria) TCEP was not detected (Martínez-Carballo et al., 2007). With a solubility of 7.0×10^3 (Fisk et al., 2003) TCEP is well soluble in water and although it was not found in all sediment samples, TCEP was detected in all corresponding river water samples (see Section 4.2.2.2).

4.2.2.5. Dust. Van den Eede et al. (2011) detected TCEP levels of 0.39, 0.62 and 0.70 μg g^{-1} in three SRMs certified for other organic contaminants in indoor dust. In other dust samples TCEP levels found by Van den Eede et al. (2011) were <0.08–5.46 μg g^{-1}.

4.2.2.6. Biota. Green et al. (2008) reported TCEP levels in cod liver from Norway of <5 μg kg^{-1} and <10–23 μg kg^{-1} for mussel. Evenset et al. (2009) found TCEP levels of 0.5–5.0 μg kg^{-1} in fish muscle tissue and 13–26 μg kg^{-1} in fish liver. Leonards et al. (2011) detected TCEP in beach crab (Trondheim), blue mussel (Oslofjord), fish samples, in blood of white-tailed eagle (from various locations) and in shag egg from Sklinna. Levels varied from <0.06 μg kg^{-1} for blue mussel to 8.6 μg kg^{-1} for burbot liver. Sundkvist et al. (2010) analyzed biota, herring, perch, mussels, eelpout and salmon, from Swedish lakes and coastal areas. TCEP concentrations found were <2.0–160 ng g^{-1}, with the highest level found in perch from fresh water close to a source. Campone et al. (2010) reported TCEP < 0.4 μg kg^{-1} in 24 fish samples.

4.2.3. Tris(1,3-dichloro-2-propyl)phosphate

A risk assessment report of TDCPP is available from the EU (2008a). In this report is concluded that TDCPP does meet the criteria of being persistent or very persistent in the environment, but it does not meet the criteria of being bioaccumulative or toxic in the environment. Kawagoshi et al. (2002) tested the degradation of organophosphorus esters in leachate from a sea-based solid waste disposal site (see Section 4.2.1), and found a low degradability for TDCPP. No decrease was observed under anaerobic condition.

4.2.3.1. Air. TDCPP was detected in air samples. Air of various indoor environments at 12 locations in and around Zurich, Switzerland, was analyzed for the presence of TDCPP (Hartmann et al.,

Table 5
Levels of PFRs in the environment.

Matrix	PFR	Lowest level reported	Location	References	Highest level reported	Location	References
Indoor air	TPhP	<0.05 ng m^{-3}	Norway	Green et al. (2008)	47 μg m^{-3}	Norway	Green et al. (2008)
	TCP	<0.41 ng m^{-3}	Sweden	Hartmann et al. (2004)	2.1 ng m^{-3}	Theater, Sweden	Hartmann et al. (2004)
	TCPP	<0.12 ng m^{-3}	1-Year old car, Sweden	Hartmann et al. (2004)	1080 ng m^{-3}	Computer hall	Staaf and Ostman (2005)
	TCEP	ND ng m^{-3}	Lecture hall	Staaf and Ostman (2005)	730 mg m^{-3}	Office	Marklund et al. (2005a)
	TDCPP	<0.11 ng m^{-3}	Sweden	Hartmann et al. (2004)	150 ng m^{-3}	Hospital ward	Marklund et al. (2005a)
	V6	<0.2 ng m^{-3}	Norway	Green et al. (2008)	5.2 ng m^{-3}	Norway	Green et al. (2008)
Surface water	TPhP	<4.4 ng L^{-1}	Danube, Austria	Martínez-Carballo et al. (2007)	165 ng L^{-1}	Tiber, Italy	Bacaloni et al. (2007)
	TCP	<0.1 ng L^{-1}	Tiber, Italy	Bacaloni et al. (2007)	<7.9 ng L^{-1}	Austria	Martínez-Carballo et al. (2007)
	TCPP	<4 ng L^{-1}	Meerfelder Maar, Holzmaar, Lake Windsborn, Germany	Regnery and Püttmann (2010)	379 ng L^{-1}	Lake Nidda at Oxbow, Germany	Regnery and Püttmann (2010)
	TCEP	<1.5 ng L^{-1}	Tiber, Italy	Bacaloni et al. (2007)	184 ng L^{-1}	Lake Nidda at Oxbow, Germany	Regnery and Püttmann (2010)
	TDCPP	<0.7 ng L^{-1}	Tiber, Italy	Bacaloni et al. (2007)	50 ng L^{-1}	River Ruhr, Germany	Andresen et al. (2004)
Drinking water	TPhP	ND ng L^{-1}	Unknown	Stackelberg et al. (2007)	<500 ng L^{-1}	Unknown	Stackelberg et al. (2004)
	TCP	No data found in the literature					
	TCPP	No data found in the literature					
	TCEP	4 ng L^{-1}	Unknown	Stackelberg et al. (2007)	99 ng L^{-1}	Unknown	Stackelberg et al. (2004)
	TDCPP	<0.25 μg L^{-1}	Unknown	Stackelberg et al. (2004)			
Influent	TPhP	<0.015 ng L^{-1}	Spain	Rodriguez et al. (2006	14 μg L^{-1}	Norway	Green et al. (2008
	TCP	No data found in the literature					
	TCPP	0.32 ng L^{-1}	Spain	Rodriguez et al. (2006)	18 μg L^{-1}	Sweden	Marklund et al. (2005b)
	TCEP	<0.025 ng L^{-1}	Spain	Rodriguez et al. (2006)	2500 ng L^{-1}	Norway	Green et al. (2008)
	TDCPP	210 ng L^{-1}	Sweden	Marklund et al. (2005b)	820 ng L^{-1}	Norway	Green et al. (2008)
	V6	<500 ng L^{-1}	Norway	Green et al. (2008)			
Effluent	TPhP	<0.015 ng L^{-1}	Spain	Rodriguez et al. (2006)	3.5 μg L^{-1}	Norway	Green et al. (2008)
	TCP	<13 ng L^{-1}	Austria	Martínez-Carballo et al. (2007)	55 ng L^{-1}	Austria	Martínez-Carballo et al. (2007)
	TCPP	0.31 ng L^{-1}	Spain	Rodriguez et al. (2006)	24 μg L^{-1}	Sweden	Marklund et al. (2005b)
	TCEP	<0.025 ng L^{-1}	Spain	Rodriguez et al. (2006)	2200 ng L^{-1}	Norway	Green et al. (2008)
	TDCPP	20 ng L^{-1}	Germany	Andresen et al. (2004)	740 ng L^{-1}	Norway	Green et al. (2008)
	V6	<500 ng L^{-1}	Norway	Green et al. (2008)			
Sediment	TPhP	<0.10 μg kg^{-1}	Norway	Leonards et al. (2011)	160 μg kg^{-1}	Liesing, Austria	Martínez-Carballo et al. (2007)
	TCP	<0.05 μg kg^{-1}	Norway	Leonards et al. (2011)	288 μg kg^{-1}	Norway	Leonards et al. (2011)
	TCPP	<0.15 μg kg^{-1}	Norway	Leonards et al. (2011)	24000 μg kg^{-1}	Norway	Green et al. (2008)
	TCEP	ND μg kg^{-1}	Danube, Austria	Martínez-Carballo et al. (2007)	5500 μg kg^{-1}	Car demolishing site, Norway	Green et al. (2008)
	TDCPP	<0.09 μg kg^{-1}	Norway	Leonards et al. (2011)	8800 μg kg^{-1}	Car demolishing site, Norway	Green et al. (2008)
	V6	<27 μg kg^{-1}	Lamdfill site, Norway	Green et al. (2008)	2800 μg kg^{-1}	Car demolishing site, Norway	Green et al. (2008)
Biota	TPhP	<0.05 μg kg^{-1}	Blue mussel, Norway	Leonards et al. (2011)	810 μg kg^{-1}	Carp, Sweden	Sundkvist et al. (2010)
	TCP	<0.04 μg kg^{-1}	Blue mussel, Norway	Leonards et al. (2011)	137 μg kg^{-1}	Perch (close to a source), Sweden	Sundkvist et al. (2010)
	TCPP	<0.2 μg kg^{-1}	Blue mussel, Norway	Leonards et al. (2011)	17 μg kg^{-1}	Burbot liver, Norway	Leonards et al. (2011)
	TCEP	<0.06 μg kg^{-1}	Blue mussel, Norway	Leonards et al.	160 μg kg^{-1}	Perch, Sweden	Sundkvist et al.

Table 5 (*continued*)

Matrix	PFR	Lowest level reported	Location	References	Highest level reported	Location	References
				(2011)			(2010)
	TDCPP	<0.025 μg kg^{-1}	Beach crab, Norway	Leonards et al. (2011)	140 μg kg^{-1}	Perch, Sweden	Sundkvist et al. (2010)
	V6	<0.01 μg kg^{-1}	Blood, Norway	Leonards et al. (2011)	<20 μg kg^{-1}	Cod liver/mussel Norway	Green et al. (2008)
Dust	TPhP	<150 ng g^{-1}	Boston, MA area	Stapleton et al. (2009)	1.8 mg g^{-1}	Boston, MA area	Stapleton et al. (2009)
	TCP	<0.04 μg g^{-1}		Van den Eede et al. (2011)	12.5 μg g^{-1}		Van den Eede et al. (2011)
	TCPP	<140 ng g^{-1}	Boston, MA area	Stapleton et al. (2009)	14 mg kg^{-1}	Unknown	Leisewitz et al. (2000)
	TCEP	No data found in the literature					
	TCEP	<0.08 μg g^{-1}		Van den Eede et al. (2011)	5.46 μg g^{-1}		Van den Eede et al. (2011)
	TDCPP	<80 ng g^{-1}		Van den Eede et al. (2011)	67 mg kg^{-1}		Marklund et al. (2003)

2004) (see Section 4.1.3). At all sample locations TDCPP was found below the LOD of 0.11 ng m^{-3}. TDCPP was not detected in a lecture hall without computers (see Section 4.1.3), but in a computer hall concentration detected were 2 ng m^{-3} (Staaf and Ostman, 2005). In an electronics dismantling facility TDCPP was found at a concentration of 7 ng m^{-3} (Staaf and Ostman, 2005). Other studies reported TDCPP concentrations of < 0.04–18 ng m^{-3} in air from Norway (Green et al., 2008) and < 0.2–150 ng m^{-3} in air from various indoor environments (Marklund et al., 2005a).

4.2.3.2. Surface water. TDCPP has been analyzed in several rivers and STP influents and effluents. Three rivers (Danube, Schwechat and Liesing) as well as the corresponding sediments were sampled in 2005 in Austria (see Section 4.1.3). TDCPP concentrations in the water samples from the River Danube at Nussdorf were 7 ng L^{-1} and at Haslau < 3.0 ng L^{-1}. In the River Schwechat and the River Liesing TDCPP concentrations of 15 and 19 ng L^{-1} were found (Martínez-Carballo et al., 2007). Bacaloni et al. (2007) analyzed river water from the Tiber (Italy) in June and November 2006. No TDCPP was detected (<0.7 ng L^{-1}). Andresen et al. (2004) reported TDCPP concentrations of 50 ng L^{-1} in water samples from the River Ruhr (Germany) and 20–120 ng L^{-1} in STP effluents of Germany. Meyer and Bester (2004) show with their study (See Section 4.1.3.2) that no elimination of TDCPP took place in the two STPs studied. The study of Marklund et al. (2005b) confirmed that TDCPP passes through STPs. They found TDCPP levels in influents from Sweden between 210 and 450 ng L^{-1} and in effluents of 130–340 ng L^{-1}. In Norway TDCPP concentrations in influents were 630–820 ng L^{-1} and in effluents 86–740 (Green et al., 2008), and in Spain TDCPP. In a study, performed by Stackelberg et al. (2004) TDCPP levels in drinking water reported were <0.25 μg L^{-1}.

4.2.3.3. Sediment. Green et al. (2008) reported TDCPP levels of <250–8800 μg kg^{-1} in sediments from a location near a car demolishing site. Those levels were in the same range as levels of TDCPP found in the sediment samples of a landfill site, which ranged from 1500–4100 μg kg^{-1}. Leonards et al. (2011) performed a study on sediment samples from Norway. Samples were taken at Kåfjorden, Trondheim, Oslo and Mjøsa. TDCPP concentrations found ranged from <0.09–1.0 μg kg^{-1}. TDCPP was not detected (<0.64 μg kg^{-1}) in sediment samples from the Rivers Danube (Austria), Schwechat (Austria), and Liesing (Austria) (Martínez-Carballo et al., 2007).

4.2.3.4. Dust. TDCPP was detected in indoor dust in higher concentrations than TCEP and TCPP. Concentrations found by Marklund et al. (2003) ranged 0.20–67 mg kg^{-1}. Samples taken from a prison and from an office contained about 100 times higher levels of TDCPP than those taken from a hospital office or from a textile shop. Meeker and Stapleton (2010) analyzed 50 house dust samples. TDCPP concentrations found were <107 ng g^{-1}–56 μg g^{-1}. Van den Eede et al. (2011) investigated the presence of PFRs in three SRMs certified for other organic contaminants in indoor dust. TDCPP was the second most abundant compound in all SRMs with levels of 1.75, 1.78 and 2.02 μg g^{-1}. In other dust samples Van den Eede et al. (2011) found levels of TDCPP of <0.08–56.2 μg g^{-1}.

4.2.3.5. Biota. Green et al. (2008) reported TDCPP levels in cod liver from Norway of <5 μg kg^{-1} and <10–30 μg kg^{-1} for mussel. Evenset et al. (2009) found TDCPP levels of <0.3–6.7 μg kg^{-1} in fish muscle tissue and <0.3–6.7 μg kg^{-1} in fish liver, while TDCPP in seabird liver were <1.5 μg kg^{-1}. Leonards et al. (2011) detected TDCPP in bird egg (<0.72–1.9 μg kg^{-1}) and in bird blood (<0.11–0.16 μg kg^{-1}), TDCPP levels in other biota samples analyzed by Leonards et al. (2011) were all <LOD, with LODs varying from <0.025 μg kg^{-1} for beach crab to <7.8 μg kg^{-1} for cod liver. Sundkvist et al. (2010) analyzed biota, herring, perch, mussels, eelpout and salmon, from Swedish lakes and coastal areas. TDCPP concentrations found were <1.1–140 μg kg^{-1}, with the highest level found in perch from fresh water close to a source. Campone et al. (2010) analyzed 24 fish samples from Sweden. No TDCPP was detected (LOD < 9 μg kg^{-1}).

4.2.4. Tetrekis(2-chlorethyl)dichloroisopentyldiphosphate

According to the SCHER V6 is not a PBT substance (SCHER, 2007b), but in a risk assessment report of V6 of the EU (2008b) it was concluded that V6 does meet the criteria of being persistent or very persistent in the environment. Only a limited number of studies have been found in the literature on V6 levels in the environment. V6 concentrations detected in air from Norway were <0.2–5.2 ng m^{-3} and concentrations in influents and effluents were <500 ng L^{-1} (Green et al., 2008). No data on V6 concentrations in surface and drinking water were found in the literature studied. Green et al. (2008) reported V6 concentrations of <59–2800 μg kg^{-1} in sediment from a location near a car demolishing site, which was much higher than those found in the sediment samples of a landfill site, which ranged from <27–<50 μg kg^{-1}. No V6 was detected in cod liver and mussel from Norway in 2008 (<20 μg kg^{-1}) (Green et al., 2008). In none of the biota samples from Norway analyzed in a study of Leonards et al. (2011)

Table 6
Toxicological information of a number of PFRs.

	Reproductive toxicity	Developmental and birth defect effects	Chromosome abnormalities	Inhalation toxicity	Acute toxicity	Aquatic toxicity $L(E)C_{50}$	Chronic toxicity LD_{50}
RDP	NOAEL = 20 000 mg kg^{-1} d^{-1} 2-gen. study (Pakalin et al., 2007; US-EPA, 2007)	No adverse effects found (Pakalin et al., 2007)	Not found (Washington State, 2006; US-EPA, 2007)	0.1 mg L^{-1} (Leisewitz et al., 2000)			>5000 mg kg^{-1} (rat) (US-EPA, 2007)
BADP		NOAEL = 1000 mg kg^{-1} d^{-1} (US-EPA, 2007)	Not found (US-EPA, 2007)		LD_{50} > 2000 mg kg^{-1} rat (Australian Government, 2000; Washington State, 2006)		NOEC > 0.02 mg L^{-1} (daphnia)/>1000 mg kg^{-1} (rat) (US-EPA, 2007)
TPhP		NOAEL = 690 mg kg^{-1} d^{-1} (US-EPA, 2007)			Acute toxic to fish, shrimps and daphnia's (Lassen and Lokke, 1999)	Acutely toxic to water organisms (Leisewitz et al., 2000)/very toxic to aquatic ecosystems (McPherson et al., 2004)	NOEC = 0.1 mg L^{-1} (daphnia)/3500–10 800 mg kg^{-1} (rat) (US-EPA, 2007)
DCP	Reproductive toxin (Washington State, 2006)	Developmental toxicity (Washington State, 2006)	Not found (US-EPA, 2007)	Relatively high (Washington State, 2006)	LD_{50} > 1000 mg kg^{-1} (US-EPA, 2007)	Moderate aquatic toxicity (Washington State, 2006)	
Melamine poly-phosphate					LD_{50} > 2000 mg kg^{-1} (ASCC, 2006; PINFA, 2011)		
Diethyl-phosphinic acid			Not found (US-EPA, 2007)		LD_{50} > 2000 mg kg^{-1} (US-EPA, 2007)	Toxic effects at levels much higher than water solubility (Stuer-Lauridsen et al., 2006)	NOAEL = 1000 mg kg^{-1} d^{-1} (rat) (US-EPA, 2007)
TCP	Possible reproductive toxin (McPherson et al., 2004)						
TCPP				LD_{50} > 4.6 mg L^{-1} –>17.8 mg L^{-1} (Leisewitz et al., 2000)	LD_{50} = 500–4200 mg kg^{-1} (Leisewitz et al., 2000)		NOEL = 36 mg kg^{-1} bw (Leisewitz et al., 2000)
TCEP	Reproductive toxin (Chapin et al., 1997; WHO, 1998)				LD_{50} = 0.5–1.41 g/kg in rats (WHO, 1998)	Toxic to aquatic organisms (Leisewitz et al., 2000; Sigma–Aldrich, 2011)	
TDCPP		No developmental effects (ATSDR, 2009)		Harmful (Sigma-Aldrich, 2011)	LD_{50} > 2000 mg kg^{-1} rat (dermal) 2000 mg kg^{-1} rat (oral) (WHO, 1998)		NOEL = 15.3 mg kg^{-1} bw per day LOEL = 62 mg kg^{-1} per day (WHO, 1998)
V6	Increase in thyroid weight in males and females (EU, 2008b)	NOAEL = 29 mg kg^{-1} bw d^{-1}	Increase in the frequency of cells with chromosome aberrations		LC_{50} = 10–100 mg L^{-1} (EU, 2008b)		NOEC = >3.7 mg L^{-1} (interverbrates) 10 mg L^{-1} (algae) (EU, 2008b)

Table 6 (*continued*)

	Reproductive toxicity	Developmental and birth defect effects	Chromosome abnormalities	Inhalation toxicity	Acute toxicity	Aquatic toxicity $L(E)C_{50}$	Chronic toxicity LD_{50}
RDP	Not mutagenic (Washington State, 2006; US-EPA, 2007)		0.76 mg L^{-1} (US-EPA, 2007)	12.4 mg L^{-1} (US-EPA, 2007)	Minimal effect on human health (McPherson et al., 2004)		
BADP	not mutagenic (Washington State, 2006; US-EPA, 2007)		Exceeds solubility (US-EPA, 2007)	Exceeds solubility		Minimal irritation (US-EPA, 2007)/no irritation (Australian Government, 2000)	Minimal irritation (US-EPA, 2007)/no irritation (Australian Government, 2000)
TPhP	Not mutagenic (Lassen and Lokke, 1999)	0.26–2.0 mg L^{-1} (US-EPA, 2007)	1.0–1.2 mg L^{-1} (US-EPA, 2007)	0.36–290 mg L^{-1} (US-EPA, 2007)	Low impact on human health (McPherson et al., 2004)	Moderate irritation (US-EPA, 2007)	No irritation (Lassen and Lokke, 1999; US-EPA, 2007)
DCP	Not mutagenic (Washington State, 2006; US-EPA, 2007)	1.0 mg L^{-1} (US-EPA, 2007)	3.7 mg L^{-1} (US-EPA, 2007)	1.3 mg L^{-1} (US-EPA, 2007)			Slight to moderate irritation (US-EPA, 2007)
Melamine poly-phosphate	Not mutagenic (McPherson et al., 2004)				Low health effects (McPherson et al., 2004)	Slight irritation (ASCC, 2006)/no irritation (PINFA, 2011)	No irritation (ASCC, 2006; PINFA, 2011)
Diethyl-phosphinic acid	Not mutagenic (US-EPA, 2007; PINFA, 2011)	Exceeded the water solubility (US-EPA, 2007)	Exceeds the water solubility (US-EPA, 2007)	Exceeds water solubility (US-EPA, 2007)		Slight irritation (US-EPA, 2007)	No irritation (US-EPA, 2007)
TCP	Negative in Salmonella Mutagenicity test (WHO, 1990)			Differ per type: 0.061–0.75 mg L^{-1} (Fisk et al., 2003); <1 mg L^{-1} (rainbow trout); 8700 mg L^{-1} (tidewater silverside) (Lassen and Lokke, 1999).	Major hazard to human health (Lassen and Lokke, 1999).		Harmful (Sigma–Aldrich, 2011)
TCPP	Potentially carcinogenic (Ni et al., 2007)			51 mg L^{-1} (WHO, 1998)		Irritating (Leisewitz et al., 2000)	Irritation (Leisewitz et al., 2000)
TCEP	Carcinogenic for animals (WHO, 1998)			6.3–250 mg L^{-1} (Fisk et al., 2003)	Negative effects on human health (Björklund et al., 2004)		
TDCPP	Carcinogenic (Andresen et al., 2004) Not genotoxic (WHO, 1998)	>2.8 mg L^{-1}(EU, 2008a)	3.8 mg L^{-1}, 4.6 mg L^{-1} (Eu, 2008a)	1.1 mg L^{-1} (Fisk et al., 2003)			Irritation (Sigma-Aldrich, 2011)
V6	Not mutagenic (EU, 2008b)						No irritation (EU, 2008b)

V6 was detected either, with LODs varying from <0.01 μg kg^{-1} for blood to <0.4 μg kg^{-1} for cod liver.

4.3. Summary of PFR levels in the environment

In Table 5, an overview is given of the environmental levels of TPhP, TCP, TCPP, TCEP, TDCPP, and V6. TCPP is the most dominant PFR present in all of these studies, which is explained by its high production volume (see Section 3.2) and its relatively persistent character. Environmental concentrations of the studied PFRs in indoor air are comparable to reported concentrations (2.5–157.9 pg m^{-3}) for PBDEs in indoor air samples from 20 urban residences in the Greater Boston area (MA, USA) (Allen et al., 2007). PBDE concentrations found in computer rooms in China in 2004 (0.7–4925 pg m^{-3} (Chena et al., 2008), are much lower than concentrations found for the studied PFRs. This is also true for PBDE 209 in computer rooms in China (80.1–13 732 pg m^{-3}, Chena et al., 2008), which is much lower than those reported for TCPP.

Reported concentrations of ∑PBDE in sediment from Schwechat (Austria), were 10.4 μg kg^{-1} dw (Moche et al., 2005 cited in Law et al., 2008). This is much lower than the PFR concentrations in sediment from in the same river. A comparison of PFR concentrations to PBDE concentrations in water was not made, because PBDEs are more lipophilic and concentrations in water will be lower than those of the less lipophilic PFRs. A comparison of PFR concentrations in biota to PBDE concentrations in biota is not made either because of the limited data available for PFRs in biota. In general PFR concentrations reported were higher than those of PBDEs, and the human exposure to PFRs by indoor air is considerably higher than due to PBDEs in indoor air.

5. Toxicological information

Fifty percent of the fire casualties are due to smoke and gases (EFRA, 2007). In all fires toxic products are formed from incomplete combustion of organic materials like plastics, wood, textiles, and paper. Carbon monoxide (CO) is responsible for the death of 80% of those persons who die due to fire gases (Leisewitz et al., 2000). Besides CO, many other toxic components can be formed in fires, such as hydrogen cyanide, hydrogen chloride, but also more complex products like polycyclic aromatic hydrocarbons (PAHs) and halogenated dioxins and furans. The latter are formed in much lower quantities and are not relevant as regards acute toxic effects, but they can have chronic health effects (Leisewitz et al., 2000). When FRs are used, the spread of fire is reduced, which can result in smaller amounts of toxic gases being released. A number of studies have been carried out on the toxic effects of PFRs, their effects on human health and their impact on the environment. The US-EPA performed an evaluation on the toxicity of alternatives to DecaBDE (US-EPA, 2007) and concluded that although insufficient toxicity data were available on toxicity of the alternatives, some alternatives, like BADP and RDP, do appear to be safer than DecaBDE. According to McPherson et al. (2004) human and environmental impacts of the PFRs cannot be ignored. In this chapter, the toxicity of a number of organic and halogen containing PFRs is described. In Table 6, an overview of the collected toxicological information is given.

5.1. Non-halogen PFRs

Most organophosphates show strong hemolytic effects (decomposition of red blood cells). Although these effects are mainly found in rats, adverse biological effects related to humans, such as hemolytic and reproductive effects, have also been reported (Latendresse et al., 1994; Chapin et al., 1997).

5.1.1. Resorcinol-bis(diphenylphosphate)

RDP is potentially not problematic as a substitute for decaBDE (US-EPA, 2007), but only few health and environmental toxicity data are available for RDP. RDP has a minimal effect on human health (McPherson et al., 2004). NOEL (rat organs) was 0.1 mg L^{-1} (inhalative) (Leisewitz et al., 2000). Neither mutagenicity and chromosome abnormalities, nor other genotoxic effects in a mouse micronucleus assay were found (Washington State, 2006). To determine the reproductive toxicity a 2-generation rat study for RDP (Pakalin et al., 2007) was performed with concentration in feed of 1000, 10 000, and 20 000 mg kg^{-1}. A NOEL of F1 and F2 offspring of >20 000 mg kg^{-1} were found. The study reported no adverse effects on reproductive performance or fertility parameters (Pakalin et al., 2007). For the determination of teratogenicity, rabbits were exposed for a period of 6–28 d by gavage. The NOEL was determined to be higher than 1000 mg kg^{-1} bw. A moderate accumulation in lungs and bones was reported for a combination of RDP together with TPhP, in animal experiments. Lung weight gain, liver amplification and eye irritation were found in rats after oral and inhalative tests (Leisewitz et al., 2000), but Leisewitz et al. (2000) also reported contradictory statements concerning effects on the eye and irritations on the mucous membranes. RDP is not mutagenic and no chromosomal abnormalities were observed (US-EPA, 2007). For the reproductive and developmental effects a NOEL of 20 000 mg kg^{-1} d^{-1} was found in a 2-generation rat study. This was the highest dose tested. An LD_{50} > 5000 mg kg^{-1} was reported for rat (US-EPA, 2007), an LC_{50} of 12.4 mg L^{-1} for fish, and an EC_{50} of 0.76 mg L^{-1} for daphnia immobilization. Since no data could be found in the literature on environmental levels of RDP, it is impossible to calculate a PEC/PNEC ratio, but concluding from the available toxic information, it seems not problematic to use RDP as a substitute for BFRs.

5.1.2. Bisphenol-A diphenyl phosphate

BADP is a potential substitute of decaBDE (US-EPA, 2007). It has a low acute toxicity (>2000 mg kg^{-1} rat), is neither mutagenic in bacteria, nor mutagenic in the Ames test, nor mutagenic in a reverse mutation assay (Washington State, 2006). BADP did not increase incidence of chromosomal aberrations in Chinese hamster lung cells (Australian Government, 2000), it appeared to be non-clastogenic in an in vitro Chinese hamster ovary (CHO) cell assay with and without metabolic activation, and non-clastogenic in mice bone marrow cells (at 2000 mg kg^{-1} at 0 and 24 h by oral gavage) (Washington State, 2006). For the determination of the teratogenicity, rats were exposed for a period of 6–19 d by gavage. The NOEL was determined to be 1000 mg kg^{-1} bw, which was the highest dose tested. In another study, rats were exposed for a period of 8–19 d by gavage. The NOEL was again determined to be 1000 mg kg^{-1} bw (Pakalin et al., 2007). BADP is not mutagenic and shows no chromosomal abnormalities (US-EPA, 2007). A NOEL of 1000 mg kg^{-1} d^{-1} was found for developmental effects, which was the highest dose tested. LD_{50}values were higher than 1000 mg kg^{-1} in rats. The NOECs for fish and daphnia exceeded the solubility. For the chronic toxicity a NOEC of >0.02 mg L^{-1} was found for daphnia reproduction. BADP shows minimal skin and eye irritation (US-EPA, 2007). Since no data could be found in the literature on environmental levels of BADP, it is impossible to calculate a PEC/PNEC ratio, but concluding from the available toxic information, it is not problematic to use BADP as a substitute for BFRs.

5.1.3. Triphenyl phosphate

TPhP is potentially problematic as replacement of decaBDE (US-EPA, 2007). A number of studies have been performed on the toxicity of TPhP, with different conclusions. Andresen et al. (2004) reported TPhP is possibly neurotoxic, and Ni et al. (2007) mention an association of TPhP with delayed neurotoxicity. Pakalin et al. (2007) on the contrary mention a low neurotoxicity. The Danish EPA (Lassen and Lokke, 1999) found no evidence of TPhP causing neurotoxicity in animal experiments and ATSDR (2009) reported that no symptoms or physical or laboratory findings were detected over the years on a small group of operators in a TPhP production plant, compared to unexposed groups. TPhP is suspected of being a sensitizer for allergies according to Hartmann et al. (2004), who concluded this from the Environmental Health Criteria (EHC) 111 (1991). A single case of allergy could also have been due to TCP (Carlsen et al., 1986 cited in WHO, 1991). Hence, it is not possible to conclude that TPhP is a sensitizer for allergies. TPhP has been shown to cause contact dermatitis (Camarasa and Serra-Baldrich, 1992 cited in Björklund et al., 2004), and it can inhibit human blood monocyte carboxylesterase, which affects the immunologic defense system (Saboori et al., 1991). The World Health Organization (WHO) (1991) concludes as water concentrations of TPhP in the environment are low, toxic effects on aquatic organisms are unlikely, and since TPhP is removed rapidly from the tissues of fish after exposure and BCFs are moderate, bioaccumulation is not considered to be a hazard. Leisewitz et al. (2000) stated that TPhP is acutely toxic to water organisms (Leisewitz et al., 2000), and Lassen and Lokke (1999) state that TPhP is the most acute toxic triaryl phosphate to fish, shrimps and daphnia. The growth of algae is completely inhibited at TPhP concentrations of 1 mg L^{-1} or more, but is stimulated at lower concentrations. The acute toxicity index of TPhP for fish (96 h LC_{50}) ranges from 0.36 mg L^{-1} in rainbow trout to 290 mg L^{-1} in bluegills (Lassen and Lokke, 1999). TPhP has a low impact on human health, but is very toxic to aquatic ecosystems (McPherson et al., 2004). Animal data indicate the low toxicity of TPhP, and TPhP produces no irritant effects on animal skin (Lassen and Lokke, 1999). TPhP is not mutagenic (Lassen and Lokke, 1999; US-EPA, 2007). Meeker and Stapleton (2010) reported that TPhP in house dust may be associated with altered hormone levels and decreased sperm concentration. For the developmental and birth defect effects in rats a NOEL of 690 mg kg^{-1} d^{-1}, was found which was the highest dose tested (US-EPA, 2007). For the acute toxicity in rats LD_{50} values of 3500–10800 mg kg^{-1} were found and for algal inhibition an EC_{50} of 0.26–2.0 mg L^{-1} was reported. The LC_{50} of daphnia was 1.0–1.2 mg L^{-1}, and the LC_{50} for fish was 0.36–290 mg L^{-1}. For the chronic toxicity an estimated NOEC for daphnia of 0.1 mg L^{-1} was found and a NOEC of 0.0014 mg L^{-1} was found for survival and growth of fish. According to the US-EPA (2007) this level is of high concern. TPhP shows no skin irritation and moderate eye irritation (US-EPA, 2007). Since the highest concentration found for TPhP in surface water was 40 ng L^{-1} (see Section 4.1.3) and the estimated NOEC for daphnia was 0.1 mg L^{-1}, the PEC/PNEC ratio for water compartments is 0.0004, which means no adverse effects are expected.

5.1.4. Diphenylcresylphosphate

According the US-EPA (2007) DCP is potentially problematic for replacement of decaBDE. DCP has a low acute oral toxicity in multiple species. The inhalation toxicity tested with sheep (LC_{50} > 0.37 mg m^{-3} h^{-1}), is relatively high. DCP has a reproductive and developmental toxicity and has a moderate aquatic toxicity (Washington State, 2006). According to Sigma-Aldrich (2011) DCP is toxic to aquatic organisms and it may cause chronic adverse effects. In contrast with this, the US-EPA (2007) reported that no fish data are available. DCP is not mutagenic and shows no chromosomal abnormalities (Washington State, 2006; US-EPA, 2007). For the reproductive and developmental effects in rats, a NOEL for sperm effects was found to be 60 mg kg^{-1} d^{-1}. For the acute toxicity in rats, mice, rabbits, and guinea pigs LD_{50}values higher than 1000 mg kg^{-1} were reported and for the algal inhibition an EC_{50} of 1.0 mg L^{-1} was reported. The EC_{50} of daphnia immobilization was 3.7 mg L^{-1}, and the LC_{50} for fish was 1.3 mg L^{-1}. A NOEC of 0.55 mg L^{-1} was found for algal inhibition and a NOEC of 0.12 mg L^{-1} was found for daphnia. DCP shows slight to moderate skin irritation (US-EPA, 2007). Since no data could be found in the literature on environmental levels of DCP, it is impossible to calculate a PEC/PNEC ratio, but concluding from the available toxic information, it is not problematic to use DCP as a substitute for BFRs.

5.1.5. Melamine polyphosphate

The acute toxicity (LD_{50}) of melamine polyphosphate was higher than 2000 mg kg^{-1} bw for rats (ASCC, 2006; PINFA, 2011). Melamine polyphosphate causes no skin irritation (ASCC, 2006; PINFA, 2011). Melamine polyphosphate causes no eye irritation either (PINFA, 2011), but the ASCC (2006) reported that melamine polyphosphate was slightly irritating to the eye. All irritation effects were completely recovered within 48 h. Melamine polyphosphate has low health effects and there is no evidence of irritation, cancer induction or mutagenicity (McPherson et al., 2004). The only ecotoxicity available for the melamine polyphosphate is algal toxicity (LC_{50} > 3 mg L^{-1}, NOEC = 3 mg L^{-1}). In all test concentrations undissolved material was observed, so the polymer is not toxic to algae up to the limit of its solubility (ASCC, 2006). Since no data could be found in the literature on environmental levels of melamine polyphosphate, it is impossible to calculate a PEC/PNEC ratio, but concluding from the available toxic information, it seems not problematic to use melamine polyphosphate as a substitute for BFRs.

5.1.6. Diethylphosphinic acid

According to the US-EPA (2007), there is insufficient data available to decide whether diethylphosphinic acid is a proper substitute for decaBDE. The Danish EPA stated diethylphosphinic acid does not appear to have a stronger negative impact on the environment, and human health than decaBDE (Stuer-Lauridsen et al., 2006). No mutagenic activity was observed for Salmonella typhimurium and in a cytogenetic in vitro assay with and without metabolic activation. Diethylphosphinic acid does not seem to pose a mutagenic risk (Stuer-Lauridsen et al., 2006). The results of aquatic toxicity tests, performed by Stuer-Lauridsen et al. (2006), with diethylphosphinic acid, indicate that toxic effects occur at levels much higher than the estimated water solubility with LC_{50} values higher than 100 mg L^{-1}, corresponding to measured concentrations between 11–33.7 mg L^{-1}. Unfortunately, Stuer-Lauridsen et al. (2006) do not mention the tested species. However, based on these data, diethylphosphinic acid is not considered to be toxic (Stuer-Lauridsen et al., 2006). Diethylphosphinic acid is not mutagenic and shows no chromosomal abnormalities (US-EPA, 2007). For the systemic toxicity a NOEL of 1000 mg kg^{-1} d^{-1} was found for rats, which was the highest dose tested. For the acute toxicity in rats an LD_{50} higher than 2000 mg kg^{-1} d^{-1} was reported and for daphnia and for fish the LC_{50} exceeds the water solubility. The NOEC for algal inhibition exceeded the water solubility and a NOEC of 1–10 mg L^{-1} was found for daphnia. No fish NOEC is reported. Diethylphosphinic acid showed no skin irritation, and only a slight eye irritation (US-EPA, 2007). Since no data could be found in the literature on environmental levels of diethylphosphinic acid, it is impossible to calculate a PEC/PNEC ratio, but concluding from the available

toxic information, it seems not problematic to use diethylphosphinic acid as a substitute for BFRs.

5.1.7. Tricresylphosphate

The toxicity of TCP, used as an anti-wear additive in aircraft turbine engine oil, has been of great concern. This is largely based on the o-TCP isomer content (De Nola et al., 2008). The toxicity of TCP differs per isomer. The o-isomer (o,o,o) was initially considered to be the most toxic isomer, with a MAC value of 0.1 mg m^{-3} (=0.0065 ppm) for 8 h, and it has been removed as much as possible from commercial products (Lassen and Lokke, 1999; Ten Berge et al., 2005). However, the three mono-o-cresyl isomers of TCP (omm, omp, opp) and the two di-o-cresyl phosphate isomers (oom, oop) are now regarded as being 10 times and 5 times, respectively, more toxic than o-TCP. The other isomers, which contain only meta and para are not considered to be neurotoxic (De Nola et al., 2008). TCP is considered to pose a major hazard to human health (Lassen and Lokke, 1999). It is harmful if swallowed and harmful in contact with skin (Sigma-Aldrich, 2011). It is a possible reproductive toxin (McPherson et al., 2004) and it is toxic to the central nervous system (Bolgar et al., 2008). However, TCP produced from synthetic cresol, which contains less than 0.1% of o-cresol, is not neurotoxic (Lassen and Lokke, 1999). The 50% growth inhibitory concentration of TCP to freshwater algae ranges from 1.5 to 5.0 mg L^{-1}. The rainbow trout is adversely affected by TCP concentrations <1 mg L^{-1}, with sign of chronic poisoning, but the tidewater silverside (*Menidia peninsulae*) has a LC_{50} value of 8700 mg L^{-1} (Lassen and Lokke, 1999). For daphnia a 48-h LC_{50} was found to be 5.6 mg L^{-1} and a 2-week NOEL for daphnia (mortality, growth, reproduction) was 0.1 mg L^{-1}. The 96-h LC_{50} values for three fish species varied between 4.0 and 8700 mg TCP L^{-1} (WHO, 1990). However, other studies showed 96-h LC_{50} values from 0.061 to 0.75 mg L^{-1}, of which the latest test concentrations exceed the water solubility (Fisk et al., 2003). Hence, TCP is considered to be hazardous for the environment and toxic to aquatic organisms. (Sigma-Aldrich, 2011). For food contact applications TCP is not approved by the FDA (Bolgar et al., 2008).

5.2. Halogen containing PFRs

5.2.1. Tris(chloropropyl)phosphate

TCPP is considered to be potentially carcinogenic (Ni et al., 2007). The acute oral, the inhalative and the dermal toxicity have been tested in rats (Leisewitz et al., 2000). The LD_{50} values ranged 500–4200 mg kg^{-1} bw, higher than 4.6 mg L^{-1} to higher than 17.8 mg L^{-1} and 1230–5000 mg kg^{-1} bw, respectively. TCPP is not acutely toxic, and for the chronic toxicity a NOEL of 36 mg kg^{-1} bw was found (Leisewitz et al., 2000). TCPP accumulates in the liver and kidneys, whereas it is metabolized in hydroxides of phosphorous acid, which was shown in animal experiments (Leisewitz et al., 2000). TCPP decreases cell number and alters neurodifferentiation (Dishaw et al., 2011).

TCPP is irritating to skin and eyes of rats (Leisewitz et al., 2000). TCPP has a documented 96-h LC_{50} value of 51 mg L^{-1} for fathead minnow (*Pimephales promelas*) and a NOEC of 9.8 mg L^{-1} (WHO, 1998; Fisk et al., 2003). These concentrations are clearly above the concentrations measured in water (Leisewitz et al., 2000).

No hazard data are available for outdoor air (Leisewitz et al., 2000). Since the highest concentration found for TCPP in surface water was 200 ng L^{-1} (see Section 4.2.1) and a NOEC of 9.8 mg L^{-1} was reported, the PEC/PNEC ratio for water compartments is 0.00002, which means no adverse effects are expected. Although the conclusion from the PEC/PNEC ratio is that the compound can be used, it is not recommended to use TCPP as a substitute for BFRs, because TCPP accumulates in the liver and kidneys and it is potentially carcinogenic.

5.2.2. Tris(2-chloroethyl)phosphate

TCEP is toxic to aquatic organisms and it may cause chronic adverse effects (Sigma-Aldrich, 2011). TCEP is carcinogenic for animals (WHO, 1998), is a neurotoxin in rats and mice (Tilson et al., 1990; Umezu et al., 1998) and has beem shown to induce adverse reproductive effects in rats (Chapin et al., 1997). Adverse biological effects related to humans have also been reported, such as hemolytic and reproductive effects, like reduced fertility, a longer estrous cycle length, reduced sperm motility and reduced sperm density (Chapin et al., 1997). LC_{50} values reported for fish (96-h) by Fisk et al. (2003) varied from 6.3 to 250 mg L^{-1}. Toxic effects of TCEP in animals and people are not well-known, but Lehner et al. (2010) linked acute deaths of dogs after ingestion of car seat cushions, which contained large amounts of TCEP, but potential interaction among different compounds is possible. Summarizing the toxic effects reported, it seems obvious that since the 1980s worldwide use and production of TCEP is being phased out for toxicity reasons (WHO, 1998), which means that TCEP may not be produced and used any longer. However, according to Quednow and Püttmann (2009), TCEP is not regulated by legislation, but has been replaced in some products under consumer pressure. In August 2009 Environment Canada and Health Canada proposed a risk management objective for TCEP, with the objective to reduce exposures to TCEP by eliminating it from furniture and electronic products (e.g., televisions and computers); adhesives; non-apparel textiles; upholstery; the back-coating of carpets; rubber and plastics; and paints and varnishes in the home. The risk management being considered is to prohibit the use of TCEP in these products and materials. The final extent of this prohibition will be determined upon further consultation and discussion with stakeholders (Government of Canada, 2009). Large quantities of TCEP have already been used in buildings, and these may remain active sources for several years (Andresen et al., 2004). According to the SCHER, the PEC/PNEC ratios are below 1 for all compartments, but mostly above 0.1 for both the aquatic and the terrestrial compartments (SCHER, 2006). This means no adverse effects are expected. Although the conclusion from the PEC/PNEC ratio is that the compound can be used, it is not recommended to use TCEP as a substitute for BFRs. When the concentrations in the environment will increase, the PEC/PNEC ratio will also increase and may become higher than 1, implying that it is not safe to use TCEP. Beside the PEC/PNEC ratio, a lot of other toxic effects were reported, which also indicates that TCEP is not a proper substitute for BFRs.

5.2.3. Tris(1,3-dichloro-2-propyl)phosphate

TDCPP is harmful when inhaled (Sigma-Aldrich, 2011). It can enter the body, where it easily can enter the blood stream (ATSDR, 2009). Tumors were observed in the liver, kidneys and testes of rats which were fed with TDCPP for 2 years (ATSDR, 2009). According to ATSDR (2009) there is no significant relation found between exposure to TDCPP and cancer, but Andresen et al. (2004) and the WHO (1998) report TDCPP is carcinogenic. Mutagenicity data show that TDCPP is not genotoxic (WHO, 1998). No developmental effects were observed by rats exposed to TDCPP during pregnancy (ATSDR, 2009). Dishaw et al. (2011) performed a study on the neurotoxicity of TDCPP and found that TDCPP showed concentration-dependent neurotoxicity, inhibited DNA synthesis, and decreased cell number and altered neurodifferentiation. No adverse effect on cell viability or grow was detected, but elevated oxidative stress was shown. TDCPP showed to be more neurotoxic than TCEP and TCPP, which only promoted the cholinergic phenotype. TDCPP data on LD_{50} for rats by the oral and dermal route were 2300 and >2000 mg kg^{-1} bw respectively (WHO, 1998). The toxicity to fish

was determined to 1.1 mg L^{-1} (96 h LC_{50}) (Fisk et al., 2003). Acute toxicity data determined for daphnia were 3.8 mg L^{-1} and 4.6 mg L^{-1} (48 h EC_{50}; EU, 2008a). Results of algal inhibition test gave 72 and 96 h EC_{50} values of >2.8 mg L^{-1} (EU, 2008a). A NOEL of 15.3 mg kg^{-1} bw d^{-1} was determined for mice and the lowest-observed level (LOEL) for increased liver weight was 62 mg kg^{-1} bw d^{-1} (WHO, 1998). TDCPP is irritating to the skin (Sigma-Aldrich, 2011).

5.2.4. Tetrekis(2-chlorethyl)dichloroisopentyldiphosphate

V6. is more toxic to fish and invertebrates than TCEP, and it may cause long term effects in the aquatic environment. For V6 a NOEL was determined as 15 mg kg^{-1} d^{-1} (Herzke et al., 2007). NOEC values for daphnia and algae are >1 mg L^{-1} (Green et al., 2008). Acute toxicity LC_{50} values for fish, daphnia and algae are 10–100 mg L^{-1} (EU, 2008b). NOEC for chronic toxicity for interverbrates and algae are >3.7 and 10 mg L^{-1} (EU, 2008b). There is no indication that V6 is neurotoxic. V6 is not mutagenic, and no significant skin irritation was observed (EU, 2008b). Reproductive toxicity studies show an increase in thyroid weight in males and females, and an increase in the frequency of cells with chromosome aberrations was observed. No effects were detected on the male or female reproductive systems. The NOAEL for developmental toxicity is 29 mg kg^{-1} bw d^{-1}. No data are available on inhalation and dermal repeated dose toxicity (EU, 2008b).

6. PFRs versus BFRs

PFRs haven been used as FR because of their different or complementary use and function compared BFRs (see Section 2.2). However, nowadays PFRs are also used as substitutes for BFRs because the use of the latter are restricted more and more. Phosphorus compounds have some advantages compared to BFRs. During a fire toxic by-products are created from BFRs. Due to the char, which is formed when using PFRs, emission of gases is reduced and in that way the release of toxic gases from phosphorus-based compounds is far lower than of BFRs (McPherson et al., 2004). In addition, when using PFRs, the combustion gases are not contaminated with additional corrosive gases (HCl, HBr) from the FR (Lenoir et al., 1994 cited in Hörold, 1999; Hörold, 1999). According to the available environmental and toxicity data (see Sections 4 and 5), no problems are expected when replacing BFRs by RDP, BADP, or melamine polyphosphate. Only the Cl-containing PFRs are proven to be carcinogenic, and severe negative human health effects were found for Cl-containing PFRs as well as for TCP (see Section 5), which makes those PFRs unsuitable as alternatives for BFRs. TPhP, DCP and TCEP would also not be suitable alternatives for BFRs, because they are considered to be toxic to (aquatic) organisms and/or (potential) carcinogenic (Section 5). Diethylphosphinic acid is, just like TCEP, considered to be very persistent, which does not make diethylphosphinic acid a proper substitute for BFRs either. In conclusion, based on the currently available environmental and toxicity data, RDP, BADP and melamine polyphosphate may be considered as suitable substitutes for BFRs, but TPhP, DCP, diethylphosphinic acid, TCP, TCPP and TCEP are not recommended as alternatives for BFRs.

7. Environmental analytical methods

7.1. Sampling and extraction

7.1.1. Air

Several techniques are used for air sampling for PFR analysis. Ni et al. (2007) developed a passive flux sampler, and Hartmann et al. (2004) collected air samples on polyurethane foam plugs (PUFs) at a sampling rate of 4 L min^{-1} taken for approximately 8 h. Tripropyl phosphate was added as an internal standard prior to extraction with methylene chloride and ultrasonication (US). The extracts were transferred into hexane followed by rotary-evaporation to 100 μL, and transferred into injection vials. Tollbäck et al. (2006) collected air samples using C8 Empore solid phase extraction (SPE) membranes. The analytes trapped in the membrane are completely desorbed with methanol, using an extraction cell connected online to an HPLC gradient pump. Sampling with Empore SPE has some advantages. This technique enables the collection of analytes in both the vapor phase and in particulate matter, and, in addition, the membranes can be coupled directly to an LC system for extraction and analyses, which simplifies sample preparation and reduces analysis time (Tollbäck et al., 2006). Staaf and Ostman (2005) used SPE cartridges for air sampling. SPE cartridges are suitable for online coupling with HPLC, with the same benefit of simplifying sample preparation and reduction of analysis time. A general advantage of using SPE cartridges for air sampling is the possibility of fractionation of the sample during extraction/elution of the cartridge with different portions of solvent. A disadvantage of SPE cartridges is the higher backpressure when pumping air through a cartridge, compared to standard air sampling adsorbents. Thus, the method is limited to the use of small SPE cartridges, i.e. containing 10–25 mg of stationary phase/adsorbent (Staaf and Ostman, 2005). Four different SPE stationary phases, aminopropylsilica (25 mg, 1 mL), 2,3-dihydroxypropoxypropylsilica (25 mg), cyanopropylsilica (25 mg) and ENV + (10 mg), were tested by Staaf and Ostman (2005). Elution of the SPE cartridge was performed with *n*-hexane, methyl-tertiary-butyl ether (MTBE) and/or acetone to find the optimal SPE stationary phase and a suitable elution solvent. The aminopropyl silica phase showed the most suitable properties of all stationary phases tested. Extraction and elution of the OPEs from the cartridge was done with MTBE. Recoveries of all OPEs tested were 95–116% with an RSD of 1–9% based on five replicates. LODs for the SPE sampling method with GC–NPD detection were 0.1–0.3 ng m^{-3}. Sampling with glass fiber filters was also tested by Staaf and Ostman (2005). The OPEs were extracted from the filters by US with acetone. Tripentyl phosphate was used as a volumetric internal standard and was added just prior to analysis. When comparing concentrations measured after SPE cartridge sampling with those obtained from a glass fiber filter sampling, the results agree rather well, except for three of the analyzed OPEs (Staaf and Ostman, 2005). TEP showed an almost 5-fold higher concentration in the measurements using the SPE adsorbent. A probable explanation is that due to the low molecular weight (182) and a relatively high vapor pressure (0.393 mm Hg) it might evaporate from the filter during sampling. Tributoxy phosphate also showed a higher concentration after SPE. This is explained by the more laborious handling during the extraction of the filters. This compound tends to adsorb to glass surfaces and is therefore difficult to determine with good precision and accuracy (Staaf and Ostman, 2005). TCPP showed about half the concentration when analyzed after SPE compared to the filter. In this case the glass fiber filter method showed a precision with an RSD of 68%, which is the reason no definite conclusions can be drawn for this compound (Staaf and Ostman, 2005). The recovery of TCPP was 105% in a recovery test. With air samples the use of more MTBE and acetone was tested, but this did not result in a higher concentration of TCPP. A possible explanation for finding only half of the concentration of TCPP could be the efficiency of the sampling itself. Therefore, SPE should rather be used than a glass fiber filter for sampling air for PFR analysis except for TCPP. While Staaf and Ostman (2005) used acetone for the extraction of PFRs from a glass fiber filter, Carlsson et al. (1997) used dichloromethane (DCM) to compare Soxhlet extraction to US. The

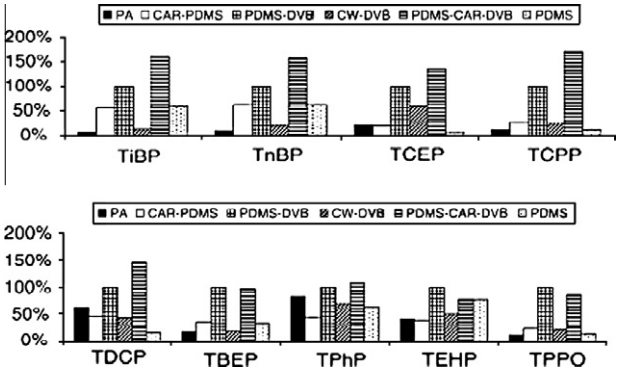


Fig. 6. Extraction efficiencies for different SPME fibers. Normalized responses to the PDMS–DVB fiber (Rodriguez et al., 2006).

recovery of TBEP with Soxhlet extraction was 37%, while US yielded a recovery of >95% (Carlsson et al., 1997). The low recovery after Soxhlet extraction was due to adsorption to the large glass surfaces of the equipment and to the rotary evaporator flask used (Carlsson et al., 1997). Another advantage of using US is the short time needed compared to Soxhlet extraction (Carlsson et al., 1997). Air sampling by Björklund et al. (2004) was performed using anodized aluminum sampler holders equipped with a 25 mm binder-free A/E borosilicate glass fiber filter and a back-up cellulose AP10 filter connected to battery-operated personal sampler pumps operating with a flow of 3 L min^{-1} for 8 h. As internal standard, diphenyl methyl phosphate was added to each filter prior to extraction. US extraction was performed with DCM. The extracts were evaporated under a nitrogen stream. Another air sampling technique for PFR analysis used by Isetun et al. (2004) was solid phase micro-extraction (SPME) – time-weighted average (TWA) sampling. SPME is a simple sampling technique with several major advantages, including time-efficiency and low solvent consumption. Analyte losses also tend to be relatively low (Isetun et al., 2004). In quantitative SPME, measurements are normally taken after the analyte has reached partitioning equilibrium between the fiber and the sample matrix. However, equilibrium settling of semi-volatile compounds in air with SPME often takes several h. Time-weighted average (TWA) sampling using SPME under non-equilibrium conditions is much faster and proved to be a good alternative for normal SPME (Isetun et al., 2004). The most important variables when using TWA are the fiber coating and the air velocity during sampling (Isetun et al., 2004).

7.1.2. Water

Andresen et al. (2004) analyzed 7 PFRs including, TCEP, TCPP, TDCPP, and TPhP, in surface waters. For extraction of the water samples liquid–liquid extraction (LLE) with toluene was used. D_{27}-TBP was added as internal standard. The final volume of the extract was 1 mL. For TCEP the LLE extractions gave very poor recoveries (31% with RSD 33%), but when SPE, with extraction solvents MTBE and toluene, was used recoveries increased to 67% for TCEP with an RSD of 15%. The recoveries for the LLE extraction off all other determined compounds were 89–107% with 12–27% RSD. Using LLE for extracting PFRs from aqueous samples has many disadvantages, such as the requirement of large volumes of organic solvents, foam formation, length of extraction time, chemical background originating from glassware and difficulties in automation (Fries and Püttmann, 2001). An advantage of SPME on the other hand is the absence of matrix effects, although TEHP cannot be determined with this method. This is not only a disadvantage of SPME, but also of SPE with OASIS HLB. Another potential shortcoming of SPME, particularly when using direct sampling, is the dependence of the extraction yield from the sample type. In such a case, quantification should be performed using the time consuming standard addition method (Rodriguez et al., 2006). Kim et al. (2007) analyzed surface, drinking and waste water. All target compounds were extracted using hydrophilic–lipophilic balance SPE cartridges (Waters HLB), with a sample intake of 1000 mL. Methanol was used for elution of the compounds, followed by methanol/MTBE (10/90). The recoveries found for all the compounds ranged from 68% to 112% with RSDs <20%. Rodrıguez et al. (2006) tested the feasibility of SPME for the determination of several PFRs, including TCEP, TCPP, and TPhP in water with GC–NPD. Six different types of SPME fibers were tested: poly(dimethylsiloxane) (PDMS, 100 μm film thickness); polyacrylate (PA, 85 μm film thickness); carboxen–PDMS (CAR–PDMS, 75 μm film thickness); poly(dimethylsiloxane)-divinylbenzene (PDMS–DVB, 65 μm film thickness); carbowax–DVB (CW–DVB, 75 μm film thickness); PDMS–CAR–DVB (30/50 μm film thickness). Fig. 6 shows the extraction efficiency of the different fibers. Responses for each compound were normalized to those achieved with the PDMS–DVB one. Maximum efficiencies were achieved using PDMS–DVB and PDMS–CAR–DVB fibers. PDMS–DVB showed no carry-over effect, where with PDMS–CAR–DVB important memory effects (ca. 40% of the peak area in the first desorption) were noticed for TPhP. These results show that the PDMS–DVB fiber was the best fiber for extracting PFRs from water. Results of this SPME method were compared to an SPE method with OASIS HLB cartridges (60 mg), which were eluted with ethyl acetate. Recoveries for the SPE method were 83–105% for all tested compounds, except for TEHP (not detected – 51.8%). Sorption of TEHP on glass material used for preparing the spiked samples, and association to dissolved organic matter in the case of sewage water, may be responsible for the losses of this compound. LOQs of the method, except for TEHP, ranged from 0.005 to 0.010 ng mL^{-1} and the RSDs were 1.9–16.7% (Rodriguez et al., 2006). Bacaloni et al. (2007) tested three SPE sorbents for PFR analyses (including TCEP, TCPP, TDCPP, TCP, and TPhP) of water, LC-18, Oasis HLB and Bakerbond (Hydrophilic-DVB). Bakerbond showed the highest recovery (82–108%, 35% for TMP) for the analytes, and in addition, this cartridge provided a faster extraction procedure.

7.1.3. Sediment

A number of PFR analyses in sediment have been reported. Ishikawa et al. (1985) analyzed sediment, which was collected with an Ekman-Berge dredge instrument. Seven PFRs were analyzed, including TCEP, TCPP, TCP and TPhP. All samples were collected in 3 L glass bottles that had been cleaned with acetone. Extraction of PFRs was performed with acetone and for clean up a Florisil column (10 × 1 cm) was used. For the extraction of PFRs from sediments from rivers in Spain and the USA, microwave-assisted extraction (MAE) was used by García-López et al. (2009). Ethyl acetate, DCM and acetone, were tested as extraction solvents, resulting in extraction with acetone followed by extraction with ACN providing the best results for the extraction of PFRs with MAE. Silica cartridges of 50 mg were used for cleanup of the extracts. An advantage of MAE is the limited time needed and the small amounts of solvents needed compared to other extraction methods like Soxhlet extraction, reflux heating, ultrasound-assisted solvent extraction or combination of sonication and shaking with acetone first and methanol second. Martínez-Carballo et al. (2007) analyzed PFRs in sediments from Austria. They performed extraction of PFRs from the sediment with ultrasound-assisted solvent extraction with ethyl acetate/acetonitrile (ACN) (30:70, v/v) after drying of the sediment samples at 30 °C and sieving below

0.63 μm. Sediment samples of Norway were extracted by Green et al. (2008) with US and shaking with methanol and MTBE, followed by centrifugation. The extraction was repeated twice and the pooled extract was extracted with water to remove the methanol. Clean up was performed on a PSA-column. Leonards et al. (2011) analyzed freeze dried sediment samples from Norway and performed extraction with accelerated solvent extraction (ASE350) with DCM:acetone (1:1, v/v), after addition of internal standards (TMP-d9, TBP-d27, TPhP-d15, and tripentyl phosphate). The matrix was removed by gel permeation chromatography (GPC). Clean up of the extracts was performed with a silica gel fractionation, with the first fraction containing the matrix (15% diethyl ether (DEE) in hexane), the second fraction containing most of the cyclic PFR, (15% DEE in hexane), and the third fraction containing the aliphatic PFR (acetone). Faction 3 was further cleaned with a hydrid SPE column (Supelco).

7.1.4. Biota

Biota samples were analyzed by Green et al. (2008), who added tri-n-pentylphosphate (TAP) as a recovery standard to the homogenized samples. Extraction was performed twice with acetone:MTBE on a shaking machine. The acetone was removed by shaking with water. After drying, the extract was cleaned through partition extraction with hexane and ACN. Evenset et al. (2009) homogenized biota samples with a mortar and pestle after freeze drying. Extraction was performed twice with MTBE on a shaking machine after addition of TAP as recovery standard. Clean up was carried out by either GPC or through partition extraction with hexane and ACN. Leonards et al. (2011) homogenized biota samples with a blender and with a mortar after freeze drying. Extraction was performed with ASE with DCM:acetone (1:1, v/v), after addition of internal standards (TMP-d9, TBP-d27, TPhP-d15, and tripentyl phosphate). Clean up of the extracts was performed with silica gel and a SPE column similar to the clean up of the extracts of the sediment samples (see Section 7.1.3). Sundkvist et al. (2010) added TBP-d27 as internal standard to frieze dried biota. Extraction was performed by ASE, with ethyl acetate–cyclohexane (5:2, v/v) and cyclohexane–DEE (9:1, v/v) followed by a cleaning with GPC with cyclohexane–ethyl acetate (3:1, v/v). Campone et al. (2010) tested elution solvents and solvent amounts in matrix solid-phase dispersion with florisil and alumina. The best results were obtained by rinsing with 5 mL *n*-hexane/DCM (1:1, v/v) and elution with 10 mL *n*-hexane/acetone (6:4 v/v).

7.2. Analysis

7.2.1. Air

Ni et al. (2007) separated and determined PFRs by gas chromatography-flame photometric detection (GC–FPD). The GC was equipped with an HP-1 column (30 m × 0.25 mm i.d., 0.32 μm film thickness). The injection volume was 3.0 μL and a pulsed-splitless injection mode was used. LODs and LOQs were 15–30 and 50–100 ng/disk respectively. The recovery of all analyzed PFRs, except for TMP (78.4%), were in the range 85–105%. The relative standard deviation (RSD) for five repeated determinations was 4.6%. Hartmann et al. (2004) analyzed PFRs on a GC–MS in the single ion monitoring (SIM) mode, with the GC being equipped with a 30 m DB-5 column. 2.0 μL was splitless injected, resulting in method recoveries from 62% for TPhP to 100% for TEHP, but a method recovery was not reported for TCPP or TDCPP. Recovery of the internal standards ranged from 52% to 144%. The LOD was determined as three times the noise level. The LOQ was taken to be 10 times the LOD (0.19–2.5 ng m^{-3}), which is a remarkable approach, because more often the LOQ is taken as three times LOD or 10 times the noise. A nitrogen-phosphorus detector (NPD) was used by Björklund et al. (2004) for the determination of 11 PFRs, including TCEP, TCPP, and TPhP, in indoor air. The GC was equipped with a DB-5 column (30 m × 0.25 mm × 0.10 μm) and a split/splitless injector. Björklund et al. (2004) also performed the analysis of PFRs with a GC-ion trap MS with collision-induced dissociation (CID) in electron impact (EI) mode and in positive-ion chemical ionization (PICI) mode, with the same column and injector. The PFRs were analyzed in SIM and selected-reaction monitoring (SRM) mode respectively. PICI was selected as the preferred ionization method rather than EI since lower energies are involved and, hence, less fragmentation is observed. GC–MS/MS–PICI showed tailing peaks in the chromatograms due to the high polarity of the low-mass compounds. A more polar stationary phase than DB-5 would result in better chromatography, but the DB-5 column was selected because of its potential to separate the relevant PFRs. The method LOD of GC/PICI-CID-SRM was in the range 0.1–1.4 ng m^{-3}, which is about 50-fold lower than with GC/EI-SIM for the alkylated and chloroalkylated compounds. Tri-n-propyl phosphate, TCEP and TPhP were not detectable in EI-SIM when monitoring m/z 99. The instrumental LOD with NPD was below 5 pg, which is lower than PICI-CID-SRM for some of the PFRs (2–34 pg). Tollbäck et al. (2006) performed PFR analyses with liquid chromatography (LC) - MS with a C8 column (Phenomenex C8, 150 mm × 4.6 mm, 5 μm), and with a C18 column (Apollo C18, 250 mm × 4.6 mm, 5 μm). The mobile phase consisted of methanol:H_2O with 1 mM trifluoroacetic acid (TFA). The flow rate used was 1.0 mL min^{-1}, but the eluate from the analytical column was split such that the flow rate of the solution entering the MS was 0.15 mL min^{-1}. A triple quadrupole MS with an electrospray ionization (ESI) interface operating in positive mode was the selected detection method. The internal standard used was deuterated TPhP. The C8 column provided better results than C18 columns. With the C18 columns the most polar peaks were not effective refocused. When adding water, analytes were strongly retained at the C8 column, which results in sharp and symmetric peaks. TFA was used to adjust the pH so that metals cations were more efficiently suppressed, which resulted in lower LODs. The LODs calculated for a sample volume of 1440 L ranged between 0.4 and 19 pg m^{-3}. Recoveries were higher than 95% and the RSDs were <8%. Staaf and Ostman (2005) performed a PFR analysis on a GC–NPD with a factor four GC-column (highly inert capillary column, with the lowest bleed specifications) (30 m × 0.25 mm × 0.1 μm, Varian Inc, Lake Forest, CA) with split/splitless injection. A number of samples were analyzed by GC–MS to verify the identity of the OPEs. The internal standard trihexyl phosphate was added to the SPE cartridge after sampling. Recoveries of all OPEs tested were 95–116% with an RSD of 1–9% based on five replicates. LODs for the SPE sampling method with GC–NPD detection were 0.1–0.3 ng m^{-3}. An overview of the methods and quality parameters of the mentioned studies together with five other studies (Carlsson et al., 1997; Otake et al., 2001; Sjödin et al., 2001; Isetun et al., 2004; Green et al., 2008) for the analysis of PFRs in air samples is given in Appendix C. All off these studies include the determination of TCEP, TCPP and TPhP and some the determination of TCP, TDCPP, and V6, but, unfortunately, for the analysis of RDP, BADP, melamine polyphosphate and diethylphosphinic acid in air no data could be found in the literature.

7.2.2. Water

Andresen et al. (2004) analyzed water samples for 7 PFRs with GC–MS equipped with a PTV injector. 1 μL was injected with PTV splitless on a DB-5 MS column (30 m × 0.25 mm × 0.25 μm). Kim et al. (2007) performed analysis by LC–MS/MS equipped with an Synergy Max-RP C12 column (250 mm × 4.6 mm × 4 μm) on which 10 μL extract was injected. 0.1% formic acid (v/v) in H_2O

(A) and 100% methanol (B) were used as eluent with a flow rate of 700 μL min^{-1}. The recoveries found for all the compounds ranged from 68% to 112% with RSD <20%. The LOD of TCEP was with 10 ng L^{-1} higher than those of the other studied compounds due to occasional blank contamination (Kim et al., 2007). Rodriguez et al. (2006) used GC–NPD for determining levels of PFRs in water (see Section 7.1.2). Two capillary columns, DB-5 (30 m × 0.25 mm × 0.25 μm) and SPB-1701 (30 m × 0.25 mm × 0.25 μm), were compared. With the DB-5 column all the compounds were separated except TBEP and TPhP. The selectivity of the DB-5 column towards these two compounds was temperature dependent. The separation between TBEP and TPhP could be improved with the SPB-1701 column. At this column, however, the retention time of TCEP matches exactly with that of an isomer of TCPP. LOQ values were 5–10 ng mL^{-1} and the repeatability of the injection for standards at different concentration levels was around 2–3%. An overview of the methods and quality parameters of the mentioned studies, together with five other studies (Fries and Püttmann, 2001; Bester, 2005; Martínez-Carballo et al., 2007; Quednow and Püttmann, 2009; Regnery and Püttmann, 2010) for the analysis of PFRs in water, is given in Appendix D. All these studies include the determination of TCEP, TCPP and TPhP, and some the determination of TCP, but for the analysis of RDP, BADP, melamine polyphosphate and diethylphosphinic acid in water no data could be found in the literature.

7.2.3. Sediment

Ishikawa et al. (1985) used GC–FPD for the analysis of PFRs in sediment, resulting in recoveries of 78–95% and LODs of 2–10 ng g^{-1}. Sediment samples of Norway were analyzed by Green et al. (2008) with GC–MS for all compounds except V6, which was analyzed with GC–NPD. Also Leonards et al. (2011) analyzed sediment samples from Norway by GC–MS in the EI mode. Martínez-Carballo et al. (2007) on the other hand performed PFR analyses with LC-MS/MS. The analytical column used by Martínez-Carballo et al. (2007) was a Luna C8 column (150 mm × 2 mm × 5 μm). Eluents were H_2O and methanol each modified with 0.1% (v/v) formic acid and 10 mM ammonium acetate, and the injection volume was 10 μL. A triple quad MS in the positive ion mode was used. Quantification of all compounds was made by multiple reaction monitoring (MRM). LOQs were 0.48 to 11 μg kg^{-1}, and recoveries ranged from 74 to 104%. García-López et al. (2009) analyzed sediment samples on a GC–Inductively coupled plasma–MS (GC–ICP–MS) equipped with an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). Conventional and pulsed splitless were compared as injection modes. With the pulsed splitless method the injection into the column is faster, which reduces the chance of analyte decomposition and/or adsorption on the internal surface of the liner. In addition, it provides a narrow injection band in the head of the GC column. A 2–3-fold improvement in the peak height of target compounds was achieved compared to conventional splitless. For the ICP–MS nitrogen was used as additional gas in the central argon plasma channel to enhance phosphorus ionization. The addition of small amounts of alternate gases (N_2, O_2, He) is usually employed to improve the LODs of elements with high ionization potentials such as phosphorus (García-López et al., 2009). Recoveries for the MAE–ICP–MS method were between 78% and 105% and the LOQs varied from 2 to 4 ng g^{-1}. An overview of these methods and related quality parameters is given in Appendix E. These studies include the determination of TCEP, TCPP, TDCPP, V6, TPhP, and TCP, but not RDP, BADP, melamine polyphosphate and diethylphosphinic acid.

7.2.4. Biota

Different techniques can be used to perform PFR analyses in extracts of biota. Green et al. (2008) and Evenset et al. (2009) both used a GC–MS to analyze biota samples, while Leonards et al. (2011) used LC–MS/MS. For V6 analyses Green et al. (2008) used GC–NPD. Sundkvist et al. (2010) analyzed PFRs in biota samples from Sweden by GC–HRMS, and Campone et al. (2010) determined PFRs by GC–NPD. An overview of these methods and related quality parameters is given in Appendix F. These studies include the determination of TCEP, TCPP, TPhP, TDCPP, V6, and TCP, but not RDP, BADP, melamine polyphosphate and diethylphosphinic acid.

7.2.5. Motor oil

De Nola et al. (2008) analyzed TCP and its isomers in aircraft turbine engine oils. GC-time of flight (TOF)-MS was used for characterization of the 10 isomers of TCP in a standard mixture. To separate the isomers from the oil HPLC fractionation was performed prior to GC–pulsed FPD (PFPD) analyses. The latter is a highly sensitive method, which could well be used for analysis of trace quantities of isomers of TCP, after the initial peak assignment had been made by MS. The instrumental LOD and LOQ of the PFPD analyses were 13 and 43 pg, respectively.

7.3. Advantages and disadvantages of PFR analysis techniques

For detection of PFRs in extracts several techniques are available: GC–FPD, GC–MS, GC–NPD, LC–MS/MS, GC–atomic emission detection (AED), GC–PFPD and GC–ICP–MS. According to Björklund et al. (2004), advantages of using GC–NPD are low LODs, and high sensitivity for phosphorus containing compounds. García-López et al. (2009) mention as disadvantage of NPD detection an unsatisfactory selectivity for PFRs. Another disadvantage is that NPD does not offer the possibility for positive identification. MS, on the other hand, is a more powerful identification tool (Björklund et al., 2004). It has a higher selectivity and the possibility of using isotopically labeled compounds for quantification. There is a good correlation between NPD and MS results, although the repeatability was generally better with GC/PICI-CID-SRM. The instrumental LOD with NPD was <5 pg and with MS 2–34 pg. TPhP could not be quantified using NPD with a DB-5 column, since a coëluting compound interfered with the detection (Björklund et al., 2004). The use of another column, for example a HP-1 column (tested by Otake et al. (2001)) or a factor four column (tested by Staaf and Ostman (2005)) for the determination of TPhP is recommended.

A disadvantage of GC–MS–EI is the extensive fragmentation of alkylated phosphates that disables a proper identification. GC–MS–PICI is helpful in the identification of the alkylated phosphates (Carlsson et al., 1997; Björklund et al., 2004). However, GC–MS–PICI has a limited sensitivity (García-López et al., 2009). With GC–MS in SIM mode, interfering peaks occurred often in samples, although these were not present in standards (Hartmann et al., 2004). This resulted in the need to use the 2nd, 3rd or 4th most abundant peaks for identification and quantification of most analytes, which again resulted in higher LODs. The method LOD with GC/PICI-CID-SRM is about 50-fold lower than with GC/EI–SIM for the alkylated and chloroalkylated compounds (Björklund et al., 2004). A disadvantage of using GC–AED is the need for separate injections for oxygen, phosphorus, and carbon/chlorine determination. When using LC–MS detection for PFR analysis the formation of stable complexes with metal cations such as Na^+ (e.g. $[M + Na]^+$ and $[2\,M + Na]^+$) that may be present in the samples, is disadvantageous. The relative abundance of these complexes is influenced by the concentration of metal cations and the pH. By adjusting the pH the complexes formed with metals cations are more efficiently suppressed, which results in lower LODs (0.4–19 pg m^{-3}) (Tollbäck et al., 2006). Compared to GC–NPD, GC–MS and LC–MS/MS, ICP–MS provides much less complex chromatograms, while offering similar recoveries and LODs (García-López et al., 2009).

7.4. Precautions

PFRs may be present in laboratory air, and laboratory equipment can be contaminated if no precautions are taken. Soaking all glassware in a solution of ethanol containing 5% (w/w) NaOH or 5% (w/v) non-ionic surfactant solvent and rinsing afterwards with H_2O, ethanol and acetone can avoid blank problems (Staaf and Ostman, 2005; Bacaloni et al., 2007). To avoid blanks from the sampling devices, glass fiber filters can be ultrasonicated in methanol, acetone, and DCM, cellulose support discs can be ultrasonicated in DCM (Staaf and Ostman, 2005), PUFs can be washed with H_2O, acetone, and DCM, and finally Soxhlet-extracted for 12 h in DCM (Carlsson et al., 1997; Staaf and Ostman, 2005). The widespread use of TCP in plastics and hydraulic fluids can cause contamination of analytical reagents. Therefore, care must be taken to avoid contamination of analytical reagents in order to obtain accurate data in trace analysis of TCP (WHO, 1990). TBEP blanks can be found with SPME extraction when using hermetically sealed vessels, with a Teflon-layered silicone septum and an aluminum cap. Experiments of Rodriguez et al. (2006) showed that the septum was responsible for the TBEP. To avoid this blank problem, aluminum foil could be used instead of a septum to cover sample vessels (Rodriguez et al., 2006). TBEP adsorption to glass surfaces was observed by Carlsson et al. (1997). Tributoxy phosphate adsorption to glass was observed by Staaf and Ostman (2005). Therefore, the use of glassware should be avoided when extracting or cleaning samples for PFR analysis. Instead of glassware plastic materials may be used, but these need to be tested. Teflon hould be avoided. An alternative would be to develop and validate a simple method for extracting the PFRs from the glassware prior to GC or LC analysis.

7.5. Conclusions

For extraction of PFRs from water samples LLE, SPE and SPME are used. SPME and SPE with Oasis HLB cartridges are not suitable for the whole range of PFRs, because TEHP is not extracted. SPE with other cartridges may give better results, but those have not been tested yet for TEHP. LLE has many disadvantages (large solvent volumes, foam formation, long extraction times, chemical background from glassware and difficulties in automation). However, it does give acceptable recoveries (63–107%) and RSDs (4–27%). Because of the mentioned disadvantageous of LLE, it is recommended to use SPE, because this method also gives good recoveries (67–105%) and RSDs (<20%), but it does not have the disadvantages of LLE, and it offers the possibility for online coupling with a detection system, which makes the sample clean up and extraction less laborious. The SPE method should be tested with other cartridges than OASIS HLB for extraction of TEHP. For the extraction of PFRs from sediment it is recommended to use MAE. The recoveries (78–105%) and RSDs (3–8%) are good and the method has some advantages compared to other methods, like limited time and small amounts of solvent needed. For the final instrumental analysis of PFRs, several techniques, such as GC–FPD, GC–NPD, GC–AED, GC–MS, LC–MS/MS and GC–ICP–MS are being used. GC–ICP–MS looks like the most promising method, because it provides much less complex chromatograms while offering the same recoveries and LODs (instrumental LOD is 5–10 ng mL^{-1}) as with other detection techniques, like GC–NPD and GC–MS. Advantages of using MS instead of NPD are the higher selectivity and the option of using isotopically labeled compounds for quantification.

Appendix A. Physicochemical properties of PFRs

Cas. number	Name	Abbreviation	Reactive/additive FR	Boiling point (°C)	Melting point (°C)	Flash point (°C)	Solubility in water ($mg\ L^{-1}$) at 25 °C	Vapor pressure (mm Hg) at 25 °C	Henry's Law constant ($atm\text{-}m^3\ mole^{-1}$) at 25 °C	log K_{ow}	Soil adsorption coefficient: log K_{oc}	Bio-accumulation/bioconcentration factor (BCF)
10124-31-9	Ammonium orthophosphate			158			Freely soluble in water	1.4		−2.15		
68333-79-9	Ammonium polyphosphate	APP, AP	Additive		275 284–286		1×10^4	1.4		−2.15		
	3,9-Bis-carboxyethyl-2,4,8,10-tetraoxa-3,9-diphosphaspiro [5,5]undecane-3,9-dioxide											
803-19-0	Bis(4-carboxyphenyl) phenylphosphine oxide	BCPPO		643	337	343	17.8	2.1×10^{-17}	2.1×10^{-19}	2.22	2.60	3.16
4351-70-6	1-(Bis(2-chloroethoxy) phosphinyl)ethyl 2-chloro ethyl (1-(((2-chloroethoxy) (2-chloroethyl)phosphinyl) oxy)ethyl)phosphonate			644		619	14.6	2.1×10^{-8}	1.4×10^{-17}	1.37	2.12	6.49
4090-51-1	Bis(5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorin amyl) oxide			343	−19.83	161	0.908	1.5×10^{-4}	4.2×10^{-7}	4.28	3.70	1047
5945-33-5	Bisphenol A diphenyl phosphate	BADP, BDP	Additive	680	41–90	377	0.4151	9.0×10^{-6}		4.5	4.53	3.16
	Carboxyethyl-phenylphosphinic acid	CEPPA		509	157–158	262	1.13×10^4	3.5×10^{-11}	4.9×10^{-15}	1.06	1.00	3.16
	4-Carboxyphenyl phenylphosphinic acid	CPPPA		556	249–250	290	729	3.5×10^{-13}	2.6×10^{-16}	1.29	1.00	3.16
7783-28-0	Di-ammonium phosphate	DAP		158	155		Freely soluble in water	1.4		−2.15		
78-38-6	Diethyl ethyl phosphonate	DEEP		198	−13	93	Miscible	0.52	2.9×10^{-6}	0.66	1.42	2.46
2781-11-5	Diethyl N,N – bis(2-hydroxyethyl) amino methyl phosphonate			399	83	195	1.00×10^6	5.1×10^{-8}	2.6×10^{-15}	−1.94	2.97	3.16
813-76-3	Diethylphosphinic acid 3,9-Dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5,5]-undecane-3,9-dioxide			320	−14 309–312	136	7.52×10^4	6.8×10^{-5}	3.5×10^{-8}	0.68	0.59	3.16
756-79-6	Dimethyl methyl phosphonate	DMMP		181	−48	69	3.22×10^5	1.2	1.3×10^{-6}	−0.61	0.59	3.16
868-85-9	Dimethyl phosphonate	DMHP, DMP		171	−52	70	1×10^6	1.9	3.3×10^{-6}	−1.2	0.42	2.62
20120-33-6	3-(Dimethylphosphono) propionic acid methyloamide			419	84	207	1×10^6	8.8×10^{-9}	4.0×10^{-16}	−1.68	2.16	3.16
18755-43-6	Dimethyl propyl phosphonate			185	−25	80	3.40×10^4	0.97	2.2×10^6	0.29	1.53	3.16
26444-49-5	Diphenylcresylphosphate	DCP, CDP, DPK	Additive	235	−38	212	0.24	4.7×10^{-6}	4.4×10^{-8}	4.51	3.93	1711

60763-39-5	Diphenyl isopropyl phosphate			348	84	178	7.13	1.0×10^{-4}	6.0×10^{-8}	3.98	3.54	621
115-89-9	Diphenyl methyl phosphate		Additive	322	88	163	61.6	5.3×10^{-4}	3.4×10^{-8}	3.10	3.06	133
838-85-7	Diphenylphosphate	DPK, DPP		378	86	182	82	2.2×10^{-6}	1.1×10^{-10}	2.88	2.08	5.44
1241-94-7	2-Ethylhexyldiphenyl phosphate		Additive	421	−30	222	1.90	6.5×10^{-7}	2.5×10^{-7}	5.73	4.21	6.49×10^{4}
61451-78-3	Hydroxymethylphenyl phosphinic acid			283	138–139	125		2×10^{-3}			0.63	
29761-21-5	Isodecyldiphenyl phosphate	IDPP		448	−50	238	0.75	8.3×10^{-8}	4.4×10^{-7}	5.44	5.56	4.17×10^{5}
28108-99-8	Isopropylphenyl diphenyl phosphate	IPPP	Additive	424	89	224	2.2	5.2×10^{-7}	7.7×10^{-8}	5.31	4.33	7.97×10^{3}
218768-84-4	Melamine polyphosphate		Reactive	558	>400	325	<100[a]	1.8×10^{-12}		−2.3	0.62	
115-88-8	Octyl diphenyl phosphate			426	87	225	0.14	4.7×10^{-7}	2.5×10^{-7}	6.82	5.09	8.96×10^{4}
	(6-Oxido-6H-dibenz[c,e][1,2]oxa phosphorin-6-yl)-methanol			451	158–159	226		6.5×10^{-9}				
63562-33-4	[(6-Oxido-6H-dibenz[c,e][1,2]oxa phosphorin-6-yl)-methyl]-butanedioic acid	DDP		578	189–191	304	109	3.3×10^{-14}	2.0×10^{-18}	1.25	2.06	3.16
1779-48-2	Phenylphosphinic acid	PPA		285	85	126	7.52×10^{4}	1×10^{-3}	9.9×10^{-10}	−1.18	0.034	3.16
4351-70-6	Phosphonic acid, (1-(((2-loroethoxy)(2-chloroethyl)phos-phyinyl)oxo)-ethyl|)-			644		619	14.6	9.3×10^{-16}	1.4×10^{-17}	1.37	2.12	6.49
41203-81-0	Phosphonic acid, methyl(5-methyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl) methyl,methylester, P-oxide			369	85	191	2.47×10^{4}	2.6×10^{-5}	3.2×10^{-10}	−0.51	1.10	3.16
	p-Methoxyphenylhydroxy methylphosphinic acid	HMPPA		482	161–163	246		4.1×10^{-10}				
53534-65-9	p-Methoxyphenyl-phosphinic acid			325	114–115	150	4.7×10^{4}	10.0×10^{-5}	7.8×10^{-11}	0.13	1.00	3.16
7723-14-0	Red phosphorus	RP	Additive	468	162	30	Insoluble	2.6×10^{-2}	1.7×10^{-4}	−0.27	1.16	3.16
57583-54-7	Resorcinol-bis(diphenyl)phosphate	RDP	Additive	587		322	1.11×10^{-4}	2.1×10^{-8}	2.9×10^{-13}	7.41	4.63	2.05×10^{4}
55566-30-8	Tetrakis(hydroxymethyl) phosphonium sulfate	THPS	Reactive	111	−35		1×10^{6}	9.5×10^{-21}	1.7×10^{-23}	−9.8		
	2,4,8,10-Tetraoxa-3,9-diphosphaspiro[5,5]-undecane-3,9-dioxide bis-melamine salt				320–324							
38051-10-4	Tetrekis(2-chlorethyl) dichloroisopentyl-diphosphate	V6	Additive	620	90	588	2.1	1.2×10^{-14}	6.5×10^{-6}	1.9	2.9	17.07
126-73-8	Tributyl phosphate	TBP, TnBP	Additive	289	−80	146	280	1.1×10^{-3}	1.5×10^{-7}	4.00	3.28	1.03×10^{3}

(*continued on next page*)

Physicochemical properties of PFRs (*continued*)

Cas. number	Name	Abbreviation	Reactive/additive FR	Boiling point (°C)	Melting point (°C)	Flash point (°C)	Solubility in water (mg L^{-1}) at 25 °C	Vapor pressure (mm Hg) at 25 °C	Henry's Law constant (atm-m^3 $mole^{-1}$) at 25 °C	log K_{ow}	Soil adsorption coefficient: log K_{oc}	Bio-accumulation/bioconcentration factor (BCF)
1330-78-5	Tricresyl phosphate	TCP	Additive	439	77	232	0.36	1.8×10^{-7}	9.2×10^{-7}	5.11	4.35	8.56×10^{3}
78-40-0	Triethyl phosphate	TEP	Additive	216	−56	116	5.00×10^{5}	0.29	3.5×10^{-6}	0.8	1.68	3.88
2528-39-4	Trihexyl phosphate			354	86	182	1.03×10^{-2}	7.0×10^{-5}	1.1×10^{-4}	7.45	5.43	2.72×10^{5}
126-71-6	Tri-iso-butyl phosphate	TiBP	Additive	264	16	126	3.72	1.3×10^{-2}	2.8×10^{-4}	3.6	3.05	391
513-02-0	Tri-iso-propyl phosphate		Additive	222	4	102	501	0.15	8.1×10^{-5}	2.12	2.25	24.01
563-04-2	Tri-m-cresylphosphate	m-TCP, TMTP		442	90	234	1.84×10^{-2}	1.4×10^{-7}	2.9×10^{-6}	6.34	4.35	8.56×10^{3}
512-56-1	Trimethyl phosphate	TMP	Additive	197	−10	84	3.00×10^{5}	5.6×10^{-3}	2.5×10^{-7}	−0.65	1.10	3.16
513-08-6	Tri-n-propyl phosphate	TPP	Additive	254	27	121	827	2.9×10^{-2}	8.2×10^{-6}	2.67	2.83	63.1
1330-78-5	Tri-o-cresylphosphate	o-TCP, TOCP, TOTP		410	11	232	1.84×10^{-2}	1.8×10^{-7}	9.2×10^{-7}	5.48	4.36	8.56×10^{3}
1806-54-8	Trioctyl phosphate		Additive	415	89	218	9.47×10^{-6}	1.1×10^{-6}	2.7×10^{-3}	10.6	6.47	1.00×10^{6}
78-32-0	Tri-p-cresylphosphate	p-TCP, TPCP, TPTP		439	77	232	7.4×10^{-2}	1.8×10^{-7}	9.2×10^{-7}	5.48	4.36	8.56×10^{3}
115-86-6	Triphenyl phosphate	TPhP	Additive	370	49	220	1.9	1.2×10^{-6}	3.3×10^{-6}	4.59	3.72	113
791-28-6	Triphenylphosphine oxide	TPPO	Additive	463	87	234	62.8	2.6×10^{-8}	5.3×10^{-10}	2.87	2.94	89.4
78-51-3	Tris(2-butoxyethyl)phosphate	TBEP, TBOP, TBXP	Additive	414	−70	159	1.20×10^{3}	2.1×10^{-7}	1.2×10^{-11}	3.65	4.38	1.08×10^{3}
115-96-8	Tris(2-chloroethyl)phosphate	TCEP, TClEP	Additive	351	−55	202	7.0×10^{3}	1.1×10^{-4}	3.3×10^{-6}	1.44	2.48	1.37
13674-84-5	Tris(chloroisopropyl)phosphate	TCPP	Additive	359	72	218	1.60×10^{3}	0.75	6.0×10^{-8}	2.59	2.21	8.51
1067-98-7	Tris(chloropropyl)-phosphate	TCPP	Additive	342	−40	312	1.6×10^{3}	1.9×10^{-6}	6.0×10^{-8}	2.59	2.71	42.4
13674-87-8	Tris(1,3-dichloro-2-propyl)phosphate	TDCP, TDCPP, TDIP	Additive	457	88	378	1.50	7.4×10^{-8}	2.6×10^{-9}	3.8	2.35	13.5
78-42-2	Tris(2-ethylhexyl)phosphate	TEHP	Additive	220	87	207	0.6	2.0×10^{-6}	9.6×10^{-5}	4.22	6.87	1.00×10^{6}
1067-12-5	Tris(hydroxymethyl) phosphine oxide			505	68	259	1×10^{6}	2.6×10^{-12}	1.5×10^{-12}	−4.54	0.88	3.16
68937-41-7	Tris(isopropyl-phenyl)phosphate			490	−19	263	1.4	2.9×10^{-9}	2.9×10^{-7}	5.1	5.80	8.63×10^{5}
25155-23-1	Trixylenyl phosphate	TXP		491	90	264	1.86×10^{-2}	5.2×10^{-8}	7.2×10^{-8}	5.63	5.3	9.59×10^{4}

WHO (1990, 1991), UNEP (1996), WHO (1997), UNEP (1998), WHO (1998), Lassen and Lokke (1999), Australian Government (2000), Leisewitz et al. (2000), UNEP (2000), WHO (2000), UNEP (2001, 2002), Fisk et al. (2003), Björklund et al. (2004), UNEP (2004), Rodriguez et al. (2006), Pakalin et al. (2007), Pawlowski and Schartel (2007), Wang et al. (2007), ATSDR (2009), US-EPA (2009, 2010), Chemspider (2011), EC JRC (2011), PINFA (2011) and Syrres (2011) and Chemnet (2012).

[a] at 22 °C.

Appendix B. Applications of PFRs

Name	Abbreviation	Application
Ammonium orthophosphate		Cellulose, textile (WHO, 1997)
Ammonium polyphosphate	APP	Casting resins, cellulose, electronic equipment such as video display units cables, casting resins, glues, epoxy and polyester resins, insulation materials, paints and coatings, plastic, polyolefins, polypropylene, thermoplastics, textile, sealants, polyurethane foam (rigid and flexible) (WHO, 1997; Lassen and Lokke, 1999; Leisewitz et al., 2000; McPherson et al., 2004)
1-[1-[1-[Bis(2-chloroethoxy) phosphoryl]ethoxy -(2-chloroethoxy) phosphoryl]ethoxy-(2-chloro-ethyl) phosphoryl]oxy-2-chloro-ethane		Polyurethane foam (WHO, 1997)
Bisphenol A diphenyl phosphate	BADP	Thermoplastic resins (Australian Government, 2000)
Di-ammonium phosphate	DAP	Textile (WHO, 1997)
Diphenylcresylphosphate	DCP	Hydraulic fluids, PVC, ABS pc-blends, engineering thermoplastics, food packaging, paints and coatings, rubber (WHO, 1997)
Diethyl ethyl phosphonate	DEEP	Paints and coatings, unsaturated polyesters, polyurethane foam (WHO, 1997; EFRA, 2011)
Diethyl N,N – bis(2-hydroxyethyl) amino methyl phosphonate		Textile, polyurethane foam (WHO, 1997; EFRA, 2011)
Dimethyl-3-(hydroxymethylamino)-3-oxopropyl phosphonate		Cellulose (WHO, 1997)
Dimethyl phosphonate	DMHP	Paints and coatings, textile (WHO, 1997)
Dimethyl methyl phosphonate	DMMP	Antistatic agent, antifoam agent, hydraulic fluids, paints and coatings, polyester resins, unsaturated polyesters, polyurethane foam, textile (WHO, 1997; Lassen and Lokke, 1999; Akzo, 2003; EFRA, 2011)
Dimethyl propyl phosphonate	DMPP	Polyurethane foam (EFRA, 2011)
2-Ethylhexyldiphenyl phosphate		Hydraulic fluids, PVC, food packaging (WHO, 1997)
Isodecyldiphenyl phosphate	IDPP	PVC (WHO, 1997)
Isopropylphenyl diphenyl phosphate		Hydraulic fluids, engineering thermoplastics (WHO, 1997)
Melamine polyphosphate		Plastic material for furniture, electrical housings and electrical components (ASCC, 2006)
Octyl diphenyl phosphate		PVC, coatings, paints and coatings, rubber (WHO, 1997)
Oligomeric phosphate-phosphonate		Coatings (Horrocks et al., 2007)
Phenylphosphinic acid	PPA	Polyamides
Phosphonic acid, (2-((hydroxymethyl) carbamyl) ethyl)-, dimethylester		Cellulose, cotton, protective clothing, rayon, textile (WHO, 1997; Lassen and Lokke, 1999; Leisewitz et al., 2000)
Phosphonic acid, methyl(5-methyl-2-methyl-1,3,2-dioxaphosphori-nan-5-yl) methyl, methylester, P-oxide		Polyester fabrics, polyester fibers, polyurethane foam (WHO, 1997; Fisk et al., 2003; Quednow and Püttmann, 2009)
Resorcinol-bis(diphenylphosphate)	RDP	Engineering thermoplastics, polyurethane foam (WHO, 1997; Lassen and Lokke, 1999; Pakalin et al., 2007)
Red phosphorus	RP	Electronic equipment such as video display units cables, casting resins, glues, engineering thermoplastics, epoxy resins, phenolics resins, plastic, polyamides, polyester resins, thermoplastics, textile, polyurethane foam (WHO, 1997; Lassen and Lokke, 1999; Leisewitz et al., 2000)
Tetrekis(2-chlorethyl)dichloroisopentyldiphosphate	V6	Polyurethane foam (Fisk et al., 2003)
Tris(2-butoxyethyl)phosphate	TBEP	Antifoam agent, floor polish, lacquers, plastic, rubber, solvent (WHO, 2000; Andresen et al., 2004)
Tributyl phosphate	TBP	Antifoam agent, hydraulic fluids, lacquers, extractant for metal complexes, plastic, solvent (Andresen et al., 2004; Sigma-Aldrich, 2011)
Tricresylphosphate	TCP	Hydraulic fluids, PVC, cellulose, cutting oils, plastic, polystyrene, thermoplastics, transmission fluids, solvent (WHO, 1997; Lassen and Lokke, 1999; Bolgar et al., 2008, 1990)
Tris(2-chloroethyl)phosphate	TCEP	PVC, cellulose, coatings, polyester resins, textile, polyurethane foam (WHO, 1998; Andresen et al., 2004)
Tris(chloroiso-propyl)phosphate	TCPP	Polyurethane foam (WHO, 1998; Andresen et al., 2004)
Tris(1,3-dichloro-2-propyl)phosphate	TDCPP	Plastic, textile, polyurethane foam (WHO, 1998; Andresen et al., 2004)
Tris(2-ethylhexyl)phosphate	TEHP	PVC, cellulose, paints and coatings, rubber, solvent, polyurethane foam (WHO, 2000, 1997)
Triethyl phosphate	TEP	PVC, polyester resins (to lower the overall viscosity of the formulations) high- viscosity polyol formulations, polyurethane foam (WHO, 1997; EFRA, 2011)
Tetrakis(hydroxymethyl) phosphonium sulfate	THPS	Biocide, cellulose, cotton (WHO, 2000)
Triphenyl phosphate	TPhP	Hydraulic fluids, PVC, electronic equipment such as video display units cables, casting resins, glues, engineering

(*continued on next page*)

		thermoplastics, phenylene-oxide-based resins, phenolics resins (WHO, 1997; Lassen and Lokke, 1999; Andresen et al., 2004; Björklund et al., 2004)
Tris(hydroxymethyl) phosphine oxide		Polystyrene (WHO, 1997)
Tris(isopropyl-phenyl) phosphate		PVC, engineering thermoplastics (WHO, 1997)
Trioctyl phosphate		PVC, paints and coatings, rubber, solvent, polyurethane foam (WHO, 1997)
Trixylenyl phosphate	TXP	Hydraulic fluids, PVC (WHO, 1997)

Appendix C. Air sampling, extraction and detection methods for PFRs

Sampling	Extraction	Final volume (μL)	Detection	Column	Injection volume (μL)	Injection mode	Method LOD	Instrumental LOD	LOQ	Recovery (%)	RSD (%)	References
Passive flux sampler			GC–FPD	HP-1 (30 m × 0.25 mm × 0.32 μm)	3	Pulsed-splitless	15-30 ng/disk		50-100 ng/disk		4.6	Ni et al. (2007)
PUF	US with methylene chloride	100	GC–MS	DB-5 (30 m)	2	Splitless			0.19-2.5 ng m^{-3}			
(calculated as 10 × LOD)	62-100		Hartmann et al. (2004)									
Anodized aluminum sampler holders	US with DCM		GC–NPD	DB-5 (30 m × 0.25 mm × 0.10 μm)		Split/splitless		<5 pg				Björklund et al. (2004)
with a 25mm binder-free A/E borosilicate glass fiber filter and a back-up cellulose			GC–MS/MS PICI (ion-trap)	DB-5 (30 m × 0.25 mm × 0.10 μm)		Split/splitless	0.1–1.4 ng m^{-3}	2–34 pg				Björklund et al. (2004)
AP10 filter			GC–MS EI (ion-trap)	DB-5 (30 m × 0.25 mm × 0.10 μm)		Split/splitless	5–70 ng m^{-3}					Björklund et al. (2004)
C8 Empore SPE membranes	Methanol, extraction cell connected online to HPLC pump		LC-MS/MS ESI	Phenomenex C8 (150 mm × 4.6 mm × 5 μm)			0.4–19 pg m^{-3}			>95	<8	Tollbäck et al. (2006)
Aminopropyl silica SPE cartridge	MTBE		GC–NPD	Factor four column (30 m × 0.25 mm × 0.1 μm)		splitless	0.1–0.3 ng m^{-3}			95-116	1- 9	Staaf and Ostman (2005)
Personal sampling equipment: glass fiber filter + two PUF plugs	US with DCM	100	GC–NPD	DB-5 (30 m × 0.25 mm × 0.10 μm)		Splitless				>95		Sjödin et al. (2001)
Glass tube containing charcoal granules	US with toluene		GC–FPD	HP-1 (30 m × 0.32 mm × 0.25 μm)	1	Pulsed-splitless		10 pg		84-100	0.7-6.4	Otake et al. (2001)
Personal sampling equipment: glass fiber filter + two	Soxhlet extraction with DCM		GC–NPD	DB-5 (30 m × 0.25 mm × 0.1 μm)		Split/splitless				>95 TBEP-37		Carlsson et al. (1997).

Air sampling, extraction and detection methods for PFRs (*continued*)

Sampling	Extraction	Final volume (μL)	Detection	Column	Injection volume (μL)	Injection mode	Method LOD	Instrumental LOD	LOQ	Recovery (%)	RSD (%)	References
PUF plugs												
Personal sampling equipment: glass fiber filter + two PUF plugs	US with DCM		GC–NPD	DB-5 (30 m × 0.25 mm × 0.1 μm)		Split/ splitless		<5 pg		>95 TBEP->95		Carlsson et al. (1997)
Personal sampling equipment: glass fiber filter + two PUF plugs	US with DCM		GC-AED.	DB-5 (40 m × 0.25 mm × 0.1 μm)								Carlsson et al. (1997)
Personal sampling equipment: glass fiber filter + two PUF plugs	US with DCM		GC–MS EI and PICI quadrupole)	DB-5 (30 m × 0.25 mm × 0.1 μm)		On-column		>GC–NPD (Otake et al., 2001)				Carlsson et al. (1997)
SPME (TWA)			GC–NPD	DB-5 (30 m × 0.25 mm × 0.25 μm)	Fiber	Splitless		<2 ng m^{-3}				Isetun et al. (2004)
NILU air sampler (MiniPUR): glass fiber filter + two PUF plugs	Soxhlet extraction with MTBE		GC–MS (all PFRs except V6)	Varian VF-5MS (30 m × 0.25 mm × 0.25 μm)	1	Splitless	<0.01-0.2 ng m^{-3}					Green et al. (2008)
NILU air sampler (MiniPUR): glass fiber filter + two PUF plugs	Soxhlet extraction with MTBE		GC–MS (only V6)	RXI-5MS (15 m × 0.25 mm × 0.25 μm)	1	Column mode						Green et al. (2008)

Appendix D. Water sampling, extraction and detection methods for PFRs

Extraction technique	Extraction solvent	Final volume (mL)	Detection	Column	Injection volume (μL)	Injection mode	Method LOD	Instrumental LOD	LOQ	Recovery (%)	RSD (%)	References
LLE	Toluene	1	GC–MS	DB-5 MS (30 m × 0.25 mm × 0.25 μm)	1	PTV splitless				89–107	12–27	Andresen et al. (2004)
SPE	– MTBE – Toluene	1	GC–MS	DB-5 MS (30 m × 0.25 mm × 0.25 μm)	1	PTV splitless				67 (TCEP)	15 (TCEP)	Andresen et al. (2004)
SPME (PDMS–DVB)			GC–NPD	DB-5 (30 m × 0.25 mm × 0.25 μm)	1	Splitless	0.010–0.025 ng mL^{-1}		5–10 ng mL^{-1}		3–13 15–18 (TEHP)	Rodriguez et al. (2006)
SPE (Oasis HLB)	Ethylacetate	1	GC–NPD	DB-5 (30 m × 0.25 mm × 0.25 μm)	1	Splitless	0.005–0.010 ng mL^{-1}		5–10 ng mL^{-1}	83–105 0–51.8 (TEHP)	1.9–16.7	Rodriguez et al. (2006)
LLE	DCM	1	LC–ESI–	Luna C8 (150 mm × 2 mm	10			0.52–	2.6–	63–94		Martínez-Carballo

(*continued on next page*)

Water sampling, extraction and detection methods for PFRs (*continued*)

Extraction technique	Extraction solvent	Final volume (mL)	Detection	Column	Injection volume (μL)	Injection mode	Method LOD	Instrumental LOD	LOQ	Recovery (%)	RSD (%)	References
			MS/MS	× 5 μm)				1.7 μg L^{-1}	13 ng L^{-1}			et al. (2007)
SPE (Bond Elut PPL)	ACN:methanol (1:1, v/v)		GC–MS	FS-Supreme1-5 (30 m × 0.25 μm)	1	Splitless	1 ng L^{-1}			83–89	9.9–14	Fries and Püttmann (2001)
LLE	Toluene	1	GC–MS (EI)	DB-5MS (30 m × 0.25 mm × 0.25 μm)	1	PTV splitless			100 ng L^{-1} (TCPP)	71 (TCPP)	4 (TCPP)	Bester (2005)
SPE (HLB)	– Methanol – Methanol/ MTBE (10/90)	1	LC–MS/ MS	Synergy Max-RP C12 (250 mm × 4.6 mm × 4 μm)	10			10 ng L^{-1}		68–112 (TCEP)	<20	Kim et al. (2007)
SPE (Bond Elut)	ACN:methanol (1:1)	0.1	GC–MS (EI)	BP-X5 (30 m × 0.25 mm × 0.25 μm)	1	Splitless	5 ng L^{-1}			110 (TCEP)		Quednow and Püttmann (2009)
SPE (Bakerbond: hydrophilic polymer)	Methanol	500	LC–ESI–MS/MS	Alltech: Alltima C18 (250 mm × 2.1 mm × 5 μm)	50				0.5–3.9 ng L^{-1}	>80 (TMP 35)	2.7–9.9	Bacaloni et al. (2007)
SPE (Bond Elut PPL)	ACN:methanol (1:1, v/v)		GC–MS						3–30 ng L^{-1}	72–99		Regnery and Püttmann (2010)

Appendix E. Sediment sampling, extraction and detection methods for PFRs

Extraction technique	Extraction solvent	Final volume (mL)	Detection	Column	Injection volume (μL)	Injection mode	Method LOD	Instrumental LOD	LOQ	Recovery (%)	RSD (%)	References
Shaking	Acetone		GC–FPD							78–95		Ishikawa et al. (1985)
Ultrasound-assisted solvent extraction	Ethyl acetate: ACN (30:70, v/v)		LC–MS/MS	Luna C8 (150 mm × 2 mm × 5 μm)	10				0.48–11 μg kg^{-1}	74–104		Martínez-Carballo et al. (2007)
MAE	– Acetone – ACN	0.2	GC–ICP–MS	HP-5 capillary column (30 m × 0.32 mm × 0.25 μm)	2	Splitless		5–10 ng mL^{-1}	2–4 ng g^{-1}	78–105	3–8	García-López et al. (2009)
ASE	DCM: acetone (1:1, v/v)	0.2	GC–MS EI-mode	SGE BPX-5 column (25 m × 0.22 mm × 0.25 μm)	1	Splitless			0.10–0.16 ng g^{-1}			Leonards et al. (2011)
US, shaking and centrifugation	– Methanol – MTBE		GC–MS (all PFRs except V6)	Varian VF-5MS (30 m × 0.25 mm × 0.25 μm)	1	Splitless			38-2000 μg kg^{-1}			Green et al. (2008)
US, shaking and centrifugation	– Methanol – MTBE		GC–MS (only V6)	RXI-5MS (15m × 0.25 mm × 0.25 μm)	1	Column mode						Green et al. (2008)

Appendix F. Biota sampling, extraction and detection methods for PFRs

Extraction technique	Extraction solvent	Final volume (mL)	Detection	Column	Injection volume (μL)	Injection mode	Method LOD	Instrumental LOD	LOQ	Recovery (%)	RSD (%)	References
Shaking	– Acetone – MTBE		GC–MS (all PFRs except V6)	Varian VF-5MS (30 m × 0.25 mm × 0.25 μm)	1	Splitless	5–40 μg kg^{-1}					Green et al. (2008)
Shaking	– Acetone – MTBE		GC–MS (only V6)	Varian VF-5MS (30 m × 0.25 mm × 0.25 μm)	1	Column mode						Green et al. (2008)
Shaking	MTBE		GC–MS	Varian VF-5MS (30 m × 0.25 mm × 0.25 μm)	1	Splitless						Evenset et al. (2009)
ASE	DCM:acetone (1:1, v/v)	0.2	LC–MS/MS	Luna C18 (150 mm × 3 mm × 3 μm)	1				0.04–2 ng g^{-1}			Leonards et al. (2011)
Matrix solid-phase dispersion with florisil and alumina: gravity flow elution	Hexane:acetone (6:4, v/v).		GC–NPD	Agilent: DB-5 (30 m × 0.32-mm × 0.25 μm)	1	Splitless	0.2–9 μg kg^{-1}		0.7–30 μg/kg	65–110	2–9	Campone et al. (2010)
ASE	Ethyl acetate–cyclohexane (5:2, v/v)	0.8	GC–HRMS.	J&W Scientific: DB-5 (30 m × 0.25 mm × 0.25 μm)	1	Splitless	0.05–11 ng g^{-1} (TDCPP 11 ng g^{-1}, TBEP 23 ng g^{-1})			64–110 (perch)		Sundkvist et al. (2010)

References

Akzo (dmmp consortium), 2003. Robust Summaries & Test Plan: Phosphonic Acid, Methyl-, Dimethyl Ester. Test Plan for Dimethylphosphonate Cas No. 756–79-6, 201–15083 (23 December 2003). <www.epa.gov/HPV/pubs/summaries/phsphnmd/c15083.pdf>.

Allen, J.G., McClean, M.D., Stapleton, H.M., Nelson, J.W., Webster, T.F., 2007. Personal exposure to polybrominated diphenyl ethers (PBDEs) in residential indoor air. Environ. Sci. Technol. 41, 4574–4579.

Andrae, N.J., 2007. Durable and Environmentally Friendly Flame Retardants for Synthetics. M.Sc. Thesis, North Carolina State University, Raleigh, North Carolina.

Andresen, J.A., Grundmann, A., Bester, K., 2004. Organophosphorus flame retardants and plasticisers in surface waters. Sci. Total Environ. 332, 155–166.

Anonymous, 2008. Flame retardants: some recent developments. Plast, Addit. Compd. 10, 20–21.

Aresta, M., Caramuscio, P., De Stefano, L., Pastore, T., 2003. Solid state dehalogenation of PCBs in contaminated soil using NaBH4. Waste Manage. 23, 315–319.

Asamoah, R.K., 2005. Accumulation from Soil of Structurally Diverse Brominated Flame Retardants in Earthworms. 20 Point Master Thesis, Environmental Chemistry, Department of Chemistry, Umea University, Sweden.

ASCC (Australian Safety and Compensation Council), 2006. Melapur 200 and Polymer in Exolit OP 1312. National Industrial Chemicals Notification and Assessment Scheme. Full Public Report.

Agency for Toxic Substances and Disease Registry (ATSDR), 2009. United States Department of Health and Human Services 2009. Draft Toxicological Profile for Phosphate Ester Flame Retardants (September).

Australian Government, 2000. National Industrial Chemicals Notification and Assessment Scheme, Full Public Report on Fyrolflex BDP. Department of Health and Aging.

Bacaloni, A., Cavaliere, C., Foglia, P., Nazzari, M., Samperi, R., Lagana, A., 2007. Liquid chromatography/tandem mass spectrometry determination of organophosphorus flame retardants and plasticizers in drinking and surface waters. Rapid Commun. Mass Spectrom. 21, 1123–1130.

Bester, K., 2005. Comparison of TCPP concentrations in sludge and wastewater in a typical German sewage treatment plant—comparison of sewage sludge from 20 plants. J. Environ. Monit. 7, 509–513.

Betts, K., 2008. Does a key PBDE break down in the environment? Environ. Sci. Technol. 42, 6781.

Bureau of Home Furnishings and Thermal Insulation (BHFTI), 2000. State of California Department of Consumer Affairs. Bureau of Home Furnishings and Thermal Insulation, March 2000. Technical Bulletin 117. Requirements, Test Procedure and Apparatus for Testing the Flame Retardance of Resilient Filling Materials Used in Upholstered Furniture.

Björklund, J., Isetun, S., Nilsson, U., 2004. Selective determination of organophosphate flame retardants and plasticizers in indoor air by gas chromatography, positive-ion chemical ionization and collision-induces dissociation mass spectrometry. Rapid Commun. Mass Spectr. 18, 3079–3083.

Bolgar, M., Hubball, J., Groeger, J., Meronek, S., 2008. Handbook for the Chemical Analysis of Plastic and Polymer Additives. CRC Press Taylor & Francis Group, New York (2007025615).

Bromine Science and Environmental Forum (BSEF), <http://www.bsef.com/> (accessed 12.12.11).

Camarasa, J.G., Serra-Baldrich, E., 1992. Allergic contact dermatitis from triphenyl phosphate. Contact Derm. 26, 264–265.

Campone, L., Piccinelli, A.L., Östman, C., Rastrelli, L., 2010. Determination of organophosphorous flame retardants in fish tissues by matrix solid-phase dispersion and gas chromatography. Anal. Bioanal. Chem. 397, 799–806.

Carlsen, L., Andersen, K.E., Egsgaard, H., 1986. Triphenyl phosphate allergy from spectacle frames. Contact Derm. 15, 274–277.

Carlsson, H., Nilsson, U., Becker, G., Östman, C., 1997. Organophosphate ester flame retardants and plasticisers in the indoor environment: analytical methodology and occurrence. Environ. Sci. Technol. 31, 2931–2936.

Carlsson, H., Nilsson, U., Östman, C., 2000. Video display units: an emission source of the contact allergenic flame retardant triphenyl phosphate in the indoor environment. Environ. Sci. Technol. 34, 3885–3889.

CEFIC, 2007. European Flame Retardants Association (EFRA). What are FRs? Flame Retardant Market Statistics. <www.cefic-efra.eu> (accessed 30.03.07).

Chapin, R.E., Sloane, R.A., Haseman, J.K., 1997. The relationships among reproductive endpoints in Swiss mice, using the reproductive assessment by continuous breeding database. Fundam. Appl. Toxicol. 38, 129–142.

Chemnet, 2012. <http://www.chemnet.com/cas/> (accessed 11.03.12).

Chemspider, 2011. <http://www.chemspider.com/Search.aspx> (accessed 31.10.11).

Chen, X., Hu, Y., Song, L., 2008. Thermal behaviors of a novel UV cured flame retardant coatings containing phosphorus, nitrogen and silicon. Polym. Eng. Sci. 48, 116–123.

Chena, L., Mai, B., Xu, Z., Peng, X., Han, J., Ran, Y., Sheng, G., Fu, J., 2008. In- and outdoor sources of polybrominated diphenyl ethers and their human inhalation exposure in Guangzhou, China. Atmos. Environ. 42, 78–86.

De Nola, G., Kibby, J., Mazurek, W., 2008. Determination of ortho-cresyl phosphate isomers of tricresyl phosphate used in aircraft turbine engine oils by gas chromatography and mass spectrometry. J. Chromatogr. A 1200, 211–216.

Dishaw, L.V., Powers, C.M., Ryde, I.T., Roberts, S.C., Seidler, F.J., Slotkin, T.A., Stapleton, H.M., 2011. Is the PentaBDE replacement, tris (1,3-dichloropropyl) phosphate (TDCPP), a developmental neurotoxicant? Studies in PC12 cells. Toxicol. Appl. Pharmacol. 256, 281–289.

EFRA, 2007. Frequently Asked Questions. Brussels (January 2007).

EFRA, 2011. Other Phosphorus Flame Retardants. Flame Retardant Fact Sheet (20 September).

EU, 2003. Directive 2003/11/EC, Official Journal of the European Union L42/45-46.

European Union (EU), 2008a. Tris[2-Chloro-1-(Chloromethyl)ethyl] Phosphate (TDCP) CAS No.: 13674-87-8. EINECS No.: 237-159-2. Risk Assessment Report.

EU, 2008b. 2,2-Bis(Chloromethyl) Trimethylene Bis[bis(2-Chloroethyl) Phosphate] (V6) CAS No.: 38051-10-4. EINECS No.: 253-760-2. Risk Assessment Report.

European Commission (EC), 2011. JRC (Joint Research Centre), Institute for Prospective Technological Studies (IPTS), 2011. Discussion on "Hazardous Substances" Criterion Investigation of Request for Derogation. Draft Report (1–29 September 2011).

Evenset, A., Leknes, H., Christensen, G.N., Warner, N., Remberger, M., Gabrielsen, G.W., 2009. Screening of New Contaminants in Samples from Norwegian Arctic. NIVA Report 4351-1, SPFO-Report 1049/2009. TA-2510/2009. ISBN:978-82-449-0065-2.

Fisk, P.R., Girling, A.E., Wildey, R.J., 2003. Prioritisation of Flame Retardants for Environmental Risk Assessment. Produced for Environment Agency, United Kingdom.

Fries, E., Püttmann, W., 2001. Occurrence of organophosphate esters in surface water and ground water in Germany. J. Environ. Monit. 3, 621–626.

García-López, M., Rodríguez, I., Cela, R., Kroening, K.K., Caruso, J.A., 2009. Determination of organophosphate flame retardants and plasticizers in sediment samples using microwave-assisted extraction and gas chromatogra phy with inductively coupled plasma mass spectrometry. Talanta 79, 824–829.

Government of Canada, 2009. Environment Canada Health Canada Proposed Risk Management Approach for Ethanol, 2-Chloro-, Phosphate (3:1) or Tris (2-Chloroethyl) Phosphate (TCEP). Chemical Abstracts Service Registry Number (CAS RN): 115–96-8 (August 2009).

Green, N., Schlabach, M., Bakke, T., Brevik, E.M., Dye, C., Herzke, D., Huber, S., Plosz, B., Remberger, M., Schøyen, M., Uggerud, H.T., Vogelsang, C., 2008. Screening of Selected Metals and New Organic Contaminants 2007. NIVA Report 5569-2008, SPFO-Report 1014/2008. TA-2367/2008. ISBN:978-82-577-5304-7.

Hartmann, P.C., Burgi, D., Giger, W., 2004. Organophosphate flame retardants and plasticizers in indoor air. Chemosphere 57, 781–787.

Herzke, D., Schlabach, M., Mariussen, E., Uggerud, H., Heimstad, E., 2007. A Literature Survey on Selected Chemical Compounds. TA-2238/2007.

Hörold, S., 1999. Phosphorus flame retardants in thermoset resins. Polym. Degrad. Stab. 64, 427–431.

Horrocks, A.R., Davies, P.J., Kandola, B.K., Alderson, A., 2007. The potential for volatile phosphorus-containing flame retardants in textile back-coatings. J. Fire Sci. 25, 523–540.

Isetun, S., Nilsson, U., Colmsjo, A., Johansson, R., 2004. Air sampling of organophosphate trimesters using SPME under non-equilibrium conditions. Anal. Bioanal. Chem. 378, 1847–1853.

Ishikawa, S., Taketomi, M., Shinohara, R., 1985. Determination of trialkyl and triaryl phosphates in environmental samples. Water Res. 19, 119–125.

Kawagoshi, Y., Nakamura, S., Fukunaga, I., 2002. Degradation of organophosphoric esters in leachate from a sea-based solid waste disposal site. Chemosphere 48, 219–225.

Kawahara, J., Yanagisawa, Y., 2003. Organophosphorus compound in indoor environment. J. Soc. Indoor Environ. Jpn. 6, 180–181.

Kemmlein, S., Hahn, O., Jann, O., 2003. Emissions of organophosphate and brominated flame retardants from selected consumer products and building materials. Atmos. Environ. 37, 5485–5493.

Kim, S.D., Cho, J.W., Kim, I.S., Vanderford, B.J., Snyder, S.A., 2007. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. Water Res. 41, 1013–1021.

Lassen, C., Lokke, S., 1999. Danish Environmental Protection Agency (EPA), Brominated Flame Retardants: Substance Flow Analysis and Assessment of Alternatives. DK EPA Report No. 494 1999.

Latendresse, J.R., Brooks, C.L., Capen, C.C., 1994. Pathologic effects of butylated triphenyl phosphate-based hydraulic fluid and tricresyl phosphate on the adrenal gland, ovary, and testis in the Fischer-344 rat. Toxicol. Pathol. 22, 341–352.

Law, R.J., Herzke, D., Harrad, S., Morris, S., Bersuder, P., Allchin, C.R., 2008. Levels and trends of HBCD and BDEs in the European and Asian environments, with some information for other BFRs. Chemosphere 73, 223–241.

Lee, K., Kim, J., Bae, J., Yang, J., Hong, S., Kim, H.K., 2002. Studies on the thermal stabilization enhancement of ABS; synergistic effect by triphenyl phosphate and epoxy resin mixtures. Polymer 43, 2249–2253.

Lehner, A.F., Samsing, F., Rumbeiha, W.K., 2010. Organophosphate ester flame retardant-induced acute intoxications in dogs. J. Med. Toxicol. 6, 448–458.

Leisewitz, A., Kruse, H., Schramm, E., 2000. Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals. Results and Summary Overview. Environmental Research Plan of the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Research, Report 297 44 542 (December).

Lenoir, D., Becker, L., Thumm, W., Kettrup, A., Hauk, A., Sklorz, M., Bergmann, G., Hutzinger, O., 1994. Evaluation of ecotoxicological properties from incineration of new duroplastic materials without halogen as flame retardant. In: Conference on Flame Retardancy of Polymeric Materials, Stamford, Connecticut, USA.

Leonards, P., Steindal, E.H., van der Veen, I., Berg, V., Bustnes, J.O., van Leeuwen, S., 2011, Screening of Organophosphor Flame Retardants 2010. SPFO-Report 1091/2011. TA-2786/2011.

Marklund, A., Andersson, B., Haglund, P., 2003. Screening of organophosphorus compounds and their distribution in various indoor environments. Chemosphere 53, 1137–1146.
Marklund, A., Andersson, B., Haglund, P., 2005a. Organophosphorus flame retardants and- plasticizers in air from various indoor environments. J. Environ. Monit. 7, 814–819.
Marklund, A., Andersson, B., Haglund, P., 2005b. Organophosphorus flame retardants and plasticizers in Swedish sewage treatment plants. Environ. Sci. Technol. 39, 7423–7429.
Martínez-Carballo, E., González-Barreiro, C., Sitka, A., Scharf, S., Gans, O., 2007. Determination of selected organophosphate esters in the aquatic environment of Austria. Sci. Total Environ. 388, 290–299.
McPherson, A., Thorpe, B., Blake, A., 2004. Brominated Flame Retardants in Dust on Computers: The Case for Safer Chemicals and Better Computer Design. Clean Production Action Report. <http://www.computertakeback.com/problem/bfr_report_pages1-43.pdf>.
Meeker, J.D., Stapleton, H.M., 2010. House dust concentrations of organophosphate flame retardants in relation to hormone levels and semen quality parameters. Environ. Health Perspect. 118, 318–323.
Meyer, J., Bester, K., 2004. Organophosphate flame retardants and plasticisers in wastewater treatment plants. J. Environ. Monit. 6, 599–605.
Moche, W., Stephan, K., Thanner, G., 2005. Levels of PBDE in sediments along the course of the River Danube through Austria. Organohal. Compd. 67, 475–478.
Ni, Y., Kumagai, K., Yanagisawa, Y., 2007. Measuring emissions of organophosphate flame retardants using a passive flux sampler. Atmos. Environ. 41, 3235–3240.
Otake, T., Yoshinaga, J., Yanagisawa, Y., 2001. Analysis of organic esters of plasticizer in indoor air by GC-MS and GC-FPD. Environ. Sci. Technol. 35, 3099–3102.
Pakalin, S., Cole, T., Steinkellner, J., Nicolas, R., Tissier, C., Munn, S., Eisenreich, S., 2007. Review on Production Processes of Decabromodiphenyl Ether (decaBDE) Used in Polymeric Applications in Electrical and Electronic Equipment, and Assessment of the Availability of Potential Alternatives to decaBDE, European Report EUR 22693 EN, Brussel, Belgium.
Pawlowski, K.H., Schartel, B., 2007. Flame retardancy mechanisms of triphenyl phosphate, resorcinol bis(diphenyl phosphate) and bisphenol A bis(diphenyl phosphate) in polycarbonate/acrylonitrile–butadiene–styrene blends. Polym. Int. 56, 1404–1414.
Phosphorus, Inorganic & Nitrogen Flame retardant Association (PINFA), 2011. Human Health and Environmental Fact Sheet, MELAPUR 200 70 (20 September).
Quednow, K., Püttmann, W., 2009. Temporal concentration changes of DEET, TCEP, terbutryn, and nonylphenols in freshwater streams of Hesse, Germany: possible influence of mandatory regulations and voluntary environmental agreements. Environ. Sci. Pollut. Res. 16, 630–640.
Regnery, J., Püttmann, W., 2010. Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany. Water Res. 44, 4097–4104.
Rodriguez, I., Calvo, F., Quintana, J.B., Rubi, E., Rodil, R., Cela, R., 2006. Suitability of solid-phase microextraction for the determination of organophosphate flame retardants and plasticizers in water samples. J. Chromatogr. A 1108, 158–165.
Saboori, A.M., Lang, D.M., Newcombe, D.S., 1991. Structural requirements for the inhibition of human monocyte carboxylesterase by organophosphorus compounds. Chem.-Biol. Interact. 80, 327–338.
Saito, I., Onuki, A., Seto, H., 2001. Determination of organic phosphate triesters in indoor and outdoor air. Aerosol Res. Jpn. 16, 209–216.
Scientific Committee on Health and Environmental Risks (SCHER), 2006. Opinion on Risk Assessment Report on Tris (2-Chloroethyl) Phosphate (TCEP) Environmental Part Cas No.: 115-96-8 (4 July).
SCHER 2007a. Risk Assessment Report on Tris[2-Chloro-1-(Chlo romethyl)ethyl]phosphate (TDCP) Environmental Part Cas No.: 13674-87-8.
SCHER, 2007b. Risk Assessment Report on 2,2-Bis(chloromethyl)trimethylene Bis[bis(2-chloroethyl)phosphate] (V6) Environmental Part Cas No.: 38051-10-4.
Schmitt, E., 2007. Phosphorus-based flame retardants for thermoplastics. Plast., Addit. Compd. 9, 26–30.
Sigma-Aldrich, Sigmaaldrich, 2011. <http://www.sigmaaldrich.com> (accessed 31.10.11).
Sjödin, A., Carlsson, H., Thuresson, K., Sjölin, S., Bergman, A., Östman, C., 2001. Flame retardants in indoor air at an electronics recycling plant and at other work environments. Environ. Sci. Technol. 35, 448–454.
SPIN, 2011. SPIN Offline Edition v2.03. Database of the Use of Chemical Substances in the Nordic Countries.
Staaf, T., Ostman, C., 2005. Indoor air sampling of organophosphate trimesters using solid phase extraction (SPE) adsorbents. J. Environ. Monit. 7, 344–348.
Stackelberg, P.E., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Henderson, A.K., Reissman, D.B., 2004. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. Sci. Total Environ. 329, 99–113.
Stackelberg, P.E., Gibs, J., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Lippincott, R.L., 2007. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. Sci. Total Environ. 377, 255–272.
Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A., Webster, T.F., 2009. Detection of organophosphate flame retardants in furniture foam and US house dust. Environ. Sci. Technol. 43, 7490–7495.
Stapleton, H.M., Klosterhaus, S., Keller, A., Ferguson, P.L., van Bergen, S., Cooper, E., Webster, T.F., Blum, A., 2011. Identification of flame retardants in polyurethane foam collected from baby products. Environ. Sci. Technol. 45, 5323–5331.
Stuer-Lauridsen, F., Cohr, K.H., Thorup Andersen, T., 2006. Danish EPA, Health and Environmental Assessment of Alternatives to Deca-BDE in Electrical and Electronic Equipment. DK EPA Report (July).
Sundkvist, A.M., Olofsson, U., Haglund, P., 2010. Organophosphorus flame retardants and plasticizers in marine and fresh water biota and in human milk. J. Environ. Monit. 12, 943–951.
Syrres, 2011. <http://www.syrres.com/esc/physdemo.htm> (accessed 31.10.11).
Ten Berge, W.F., Heesen, T.J., Jongeneelen, F.J., 2005. IndusTox Consult. Selectie Publieke Grenswaarden. Ontwerp van Selectie-Variabelen en Opstellen van de Lijst Publieke Grenswaarden. Eindrapport. Rapport 2005018. Nijmegen (22 November).
Tilson, H.A., Veronesi, B., McLamb, R.L., Matthews, H.B., 1990. Acute exposure to tris(2-chloroethyl) phosphate produces hippocampal neuronal loss and impairs learning in rats. Toxicol. Appl. Pharmacol. 106, 254–269.
Tollbäck, J., Tamburro, D., Crescenzi, C., Carlsson, H., 2006. Air sampling with Empore solid phase extraction membranes and online single-channel desorption/liquid chromatography/mass spectrometry analysis: determination of volatile and semi-volatile organophosphate esters. J. Chromatogr. A 1129, 1–8.
Umezu, T., Yonemoto, J., Soma, Y., Suzuki, T., 1998. Tris(2-chloroethyl) phosphate increases ambulatory activity in mice. pharmacological analyses of its neurochemical mechanism. Toxicol. Appl. Pharmacol. 148, 109–116.
UNEP PUBLICATIONS, 1996. Trimethyl Phosphate Cas No.: 512-56-1. SIDS Initial Assessment Report. For SIAM 4, Organisation for Economic Co-operation and Development (OECD), Tokio, Japan, pp. 1–37 (20–22 May).
UNEP PUBLICATIONS, 1998. Triethyl Phosphate Cas No.: 78-40-0. SIDS Initial Assessment Report. For SIAM 5, Organisation for Economic Co-operation and Development (OECD), Geneva, Switzerland, pp. 1–18 (October).
UNEP PUBLICATIONS, 2000. Tris(1-chloro-2-propyl)phosphate Cas N°: 13674–84-5. SIDS Initial Assessment Report. For SIAM 4, Organisation for Economic Co-operation and Development (OECD), Arlington, USA, pp. 117–163.
UNEP PUBLICATIONS, 2001. Tributyl Phosphate Cas No.: 126-73-8. SIDS Initial Assessment Report. For 12th SIAM, Organisation for Economic Co-operation and Development (OECD), Paris, France, pp. 1–132 (June).
UNEP PUBLICATIONS, 2002. Triphenyl Phosphate Cas No.: 115-86-6. SIDS Initial Assessment Report. For SIAM 15, Organisation for Economic Co-operation and Development (OECD), Boston, Massachussetts, pp. 1–151 (22–25 October).
UNEP PUBLICATIONS, 2004. Dimethyl Phosphonate Cas No.: 868-85-9. SIDS Initial Assessment Report. For SIAM 18, Organisation for Economic Co-operation and Development (OECD), Paris, France, pp. 1–131 (20–23 April).
UNEP, 2009. Outcome of the Fourth Meeting of the Conference of the Parties Relevant to the Work of the Persistent Organic Pollutants Review Committee. Stockholm Convention on Persistent Organic Pollutants, UNEP/POPS/POPRC.5/INF/3 (29 July).
US-EPA (United States–EPA), 2002. 1998–2002 Inventory Update Reporting (IUR) Production Volume Ranges, Downloadable 1998–2002 IUR Public Database. <http://www.epa.gov/oppt/iur/tools/data/2002>.
US-EPA, 2006. IUR, Downloadable 2006 IUR Public Database. <http://www.epa.gov/oppt/iur/tools/data/2006archive>.
US-EPA, 2007. Report on Alternatives to the Flame Retardant DecaBDE: Evaluation of Toxicity, Availability, Affordability, and Fire Safety Issues. A Report to the Governor and the General Assembly, Illinois.
US-EPA, 2009. Screening-Level Hazard Characterization. Hazard Characterization Document (September).
US-EPA, 2010. Screening-Level Hazard Characterization Trixylenyl Phosphate CASRN 251555-23-1. Hazard Characterization Document (June).
van den Eede, N., Dirtu, A.C., Neels, H., Covaci, A., 2011. Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust. Environ. Int. 37, 454–461.
VU-IVM. Amsterdam, The Netherlands, 2007. Minutes of the Quasimeme Workshop on Brominated Flame Retardants (23–24 April). <www.quasimeme.org>.
Wang, L.S., Kang, H.B.W.S.B., Wang, R., 2007. Solubilities, thermostabilities and flame retardance behaviour of phosphorus-containing flame retardants and copolymers. Fluid Phase Equilib. 258, 99–107.
Washington State, 2006. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Department of Ecology Publication No. 05-07-048, Department of Health, Publication No. 334-079 (January).
Weschler, C.J., 1980. Characterization of selected organics in size-fractionated indoor aerosols. Environ. Sci. Technol. 14, 428–431.
Weschler, C.J., 1984. Indoor–outdoor relationships for nonpolar organic constituents of aerosol particles. Environ. Sci. Technol. 18, 648–652.
World Health Organization (WHO), 1990. EHC 110: Tricresyl Phosphate, Geneva, Switzerland.
WHO, 1991. EHC 111: Triphenyl 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 218: Flame Retardants: Tris(2-butoxyethyl) phosphate, Tris(2-Ethylhexyl) Phosphate and Tetrakis (Hydroxymethyl) Phosphonium Salts, Geneva, Switzerland.