5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

Phosphate esters are a class of anthropogenic organic compounds found in the environment as a result of release from commercial and industrial products (Watts and Linden 2009). Phosphate esters, TnBP, TiBP, TBEP, and TCEP are produced by chemical synthesis via condensation of phosphorus oxychloride and an alkyl or aryl alcohol (Davis and Richardson 1980; HSDB 2009; Kelly 2006; Muir 1984) at low temperatures and pressures to avoid formation of alkyl chlorides (Muir 1984). TPP and TCP are made by heating either phosphorus pentachloride or phosphorus oxychloride with phenol and cresol, respectively. (HSDB 2011). Cresol is often derived from petroleum refining or coal tar and is consequently available in various grades containing a mixture of ortho-, meta-, and para- isomers. The resulting TCP produced commercially is generally a complex mixture (HSDB 2011). TDCP is produced via the epoxide opening of epichlorohydrin in the presence of phosphorus oxychloride (Weil 2001), and TCPP is similarly produced with propylene oxide and sometimes TCEP with ethylene oxide (Muir 1984).

Worldwide production of flame retardants in 1992 was estimated at 600,000 metric tons with 102,000 metric tons representing phosphate ester-derived flame retardants. In 2001, estimates increased to 1,217,000 and 186,000 metric tons, respectively (Hartmann et al. 2004). Use of flame retardants in the United States totaled an estimated 622,000 metric tons in 2007 (Fink et al. 2008). This represents an increase of 58 thousand metric tons, or 10% over the 2004 level. The value of these products rose from $844 million in 2004 to $1,126 million in 2007, a 33% increase, (Fink et al. 2008) and U.S. flame retardant demand is expected to grow at a 2–3% average annual rate through 2012 (Fink et al. 2008) due to an increase in restrictions for competing polybrominated diphenyl ethers (PDBE) (Hartmann et al. 2004; Quintana and Reemtsma 2006).

TnBP production in 1975 was > 908 kg (1 metric ton) (HSDB 2009) and is currently estimated by the 2006 Inventory Update Reporting (IUR) to be in the range of 1–10 million pounds (EPA 2010).

TiBP production is not listed with the EPA or other agencies as it appears that this chemical is produced predominantly outside of the United States.

TBEP production is estimated by the 2006 IUR in the range of 1–10 million pounds (EPA 2010).

TPP production in 1975 was > 908 kg (1 metric ton) (HSDB 2009) and is currently estimated by the 2006 IUR to be in the range of 10–50 million pounds (EPA 2010).

TCP production is estimated by the 2006 IUR in the range of 1–10 million pounds (EPA 2010).

TCEP production in 1975 was estimated to be > 908 kg (1 metric ton) (HSDB 2009) and is currently estimated by the 2006 IUR to be in the range of 500,000–1 million pounds (EPA 2010).

TCPP annual worldwide demand exceeded 40,000 metric tons in 1997 (IPCS 1998) and currently is estimated by the 2006 IUR to be produced in the range of 10–50 million pounds (EPA 2010).

TDCP annual worldwide demand was 8,000 metric tons in 1997 (IPCS 1998) and is currently estimated by the 2006 IUR to be produced in the range of 10–50 million pounds (EPA 2010).

No information is available in the TRI database on facilities that manufacture or process phosphate ester flame retardants because this chemical is not required to be reported under Section 313 of the Emergency Planning and Community Right-to-Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986) (EPA 1998a).

5.2 IMPORT/EXPORT

Imports of TBEP and TCEP were reported to be negligible in 1972, while all other selected phosphate esters were not listed as being imported (HSDB 2009). No export data were available for the selected phosphate ester compounds discussed in this profile.

5.3 USE

Trialkyl, triaryl, and trihaloalkyl/aryl, and mixed phosphate esters have been used since the 1940s in industrial consumer products (Muir 1984). Phosphate esters represent an important class of commercial additives used as flame retardants, plasticizers, hydraulic fluids, solvents, extraction agents, antifoam agents, adhesives, and coatings for electronic devices (Andresen and Bester 2006; Ashford 1994; Lewis 2007; Lide 2008; Owens et al. 2007; Watts and Linden 2009; Weil 2001; Wolf and Kaul 2005). A summary of applications of the selected phosphate ester flame retardants is shown in Table 5-1.

Table 5-1. Applications of Phosphate Ester Flame Retardants

Compound Name	Flame retardant	Plasticizer	Hydraulic fluid	Floor finish, wax	Lacquer, paint, glue	Anti-foam agent	Industrial processes
Tributyl phosphate (TnBP)		X	X	X	X	X	X
Triisobutyl phosphate[a] (TiBP)		X			X	X	
Tris(2-butoxy-ethyl) phosphate (TBEP)	X	X		X	X	X	
Triphenyl phosphate (TPP)	X	X	X		X		
Trecresyl phosphate[b] (TCP)	X	X	X		X		
Tri-(2-chloro-isopropyl) phosphate (TCPP)	X	X					
Tris(1,3-di-chloro-2-propyl) phosphate (TDCP)	X	X			X		
Tris(2-chloro-ethyl) phosphate (TCEP)	X	X			X		X

[a] TiBP Datasheet, Anderson et al. 2004, 2006.
[b] IPCS 1990.

Source: Marklund et al. 2003

Flame retardants generally function in the vapor phase, where the enthalpy-generating combustion occurs, and serve to slow or hinder the ignition or growth of a fire (Gann and Gilman 2003). There are five specific mechanisms by which flame retardancy may occur: physical dilution, chemical interaction, inert gas dilution, thermal quenching, or protective coatings (Mack 2004). Phosphate ester flame retardation mechanisms vary based on structure and properties, but generally function by suppressing flammability of pyrolysis products (vapor-phase mechanism) or by chemical interaction through changing the nature of the decomposition products (Weil 2001). In general, the effectiveness of a particular phosphorus compound depends strongly on the nature of the matrix polymer but, for chemically similar compounds, the flame-retardant effectiveness often increases with increasing phosphorus content (Granzow 1978). Halogens play an important part in contributing to flame retardancy, although this contribution is offset by the lower phosphorus content. The halogens reduce vapor pressure and water solubility, thus aiding retention of these additives (Weil 2001).

Due to an increased demand for fire safety in commercial products, flame retardant use substantially increased during the 1960s and 1970s (Muir 1984). In particular, products made from synthetic polymers are treated with phosphate esters (Weil 2001). The chlorinated haloalkyl phosphates, TCPP, TDCP, and TCEP, are most commonly used as flame retardants in both rigid and flexible polyurethane foam, and some textiles (Anderson et al. 2004).

The nonderivatized alkyl and aryl phosphates, TnBP, TiBP, TBEP, TCP and TPP, all function predominantly as industrial plasticizers in polymers, rubbers, plastics, and vinyl resins, as well as flame retardants (Anderson et al. 2004, 2006). Phosphate esters are added to flexible plastics such as polyvinyl chloride (PVC) and polyurethane foams in low part per hundred concentrations (Muir 1984). Addition of phosphate esters often effects the flammability of rigid plastics such as PVC by dilution of the highly flammable chlorinated plasticizers (Green 1992). Phosphate esters can, however, change polymer decomposition chemistry when combusted (Gann and Gilman 2003). Advantages of phosphate esters over traditional plasticizers include low corrosivity of the combustion gases, lack of effect on polymer transparency, and suppression of afterglow. Disadvantages include volatility, sensitivity to hydrolysis, and negative effects on the heat distortion temperatures of plastics (Wolf and Kaul 2005). When used as flame retardants in polymers, phosphate esters typically represent 1–30% of the composition of the polymer with an average of 5–15% (Hartmann et al. 2004).

TnBP, TPP and TCP are used as hydraulic fluids with flame retardant properties predominantly present as mixtures of various alkyl- and aryl-substituted phosphate esters (Anderson et al. 2004; Batt et al. 1992;

IPCS 1990). They are recognized as replacements to polychlorinated biphenyls (PCBs) (Gomez-Belinchon et al. 1988; Muir 1984). Phosphate esters generally have better fire resistance than mineral oils and are less hazardous than PCBs. The lubricating properties are generally good; however, the high temperature stability is fair. Decomposition products, such as phosphoric acid, can be corrosive, deteriorate paints and finishes, and cause swelling of many seal materials in hydraulic systems (Denniston 1995).

TnBP is used as a solvent for cellulose esters, lacquers, natural gums, herbicide solutions, and carbonless copying systems and as an extractant in the nuclear fuel reprocessing and other metals (Anderson et al. 2004; Thomas and Macaskie 1996). Some trialkyl phosphates, $O{=}P(OR)_3$, are outstanding solvents for nitrates, especially $(UO_2)(NO_3)_2$, and are therefore important in uranium processing (Fee 2005). TnBP forms weak complexes with the neutral metal nitrates, affecting the solubilizing of the actinides in the organic phase (Godfrey et al. 1996). TnBP is the most frequently used solvent in liquid-liquid extraction for fuel reprocessing via a process known as the PUREX process (Plutonium Uranium Refining by EXtraction) (Dodi and Verda 2001; Godfrey et al. 1996; Stevens et al. 2007). This method enables recycling of extracted uranium and plutonium from an aqueous nitric acid phase (Dodi and Verda 2001) and is considered the most convenient method to retreat spent fuel (Lamouroux et al. 2000). Due to the acidic nature of the process, some decomposition of TnBP to dibutyl phosphate (DBP) and monobutyl phosphate (MBP) occurs via dealkylation of one or two butoxy groups, respectively (Dodi and Verda 2001).

TiBP is used as a pore size regulator for concrete, while TnBP shows excellent antifoam properties in concrete (Anderson et al. 2004; Andresen and Bester 2006). TBEP is also found in some floor polishes. TCEP was phased out due to toxicity issues (EPA 2010). Electronic equipment can contain various phosphate esters (Carlsson et al. 2000; Marklund et al. 2003).

5.4 DISPOSAL

No data are available on the disposal of specific phosphate ester flame retardants; however, hydraulic fluids containing phosphate esters do have recommended disposal methods. Used phosphate ester hydraulic fluids are not listed as hazardous wastes and can be recycled or burned for energy recovery. In general, the newer phosphate ester hydraulic fluids do not contain known chemicals or other materials that are listed in 40 CFR 261 (Resource Conservation and Recovery Act [RCRA]). Recycling of some flame retardant-containing products, including some plastics, has been found possible (Lorenz and Bahadir 1993; Mayer et al. 1993).

With the exception of TnBP, the selected phosphate ester flame retardants are regulated under the Toxic Substances Control Act (TSCA) of 1976, requiring the reporting of record-keeping, testing, and restrictions to the EPA. The High Production Volume Challenge (HPV) program, administered by the EPA, challenges companies to report health and environmental effects data publicly for chemicals produced or imported in the United States in quantities of 1 million pounds or more per year. All of the selected chemicals except TiBP appear on this list.