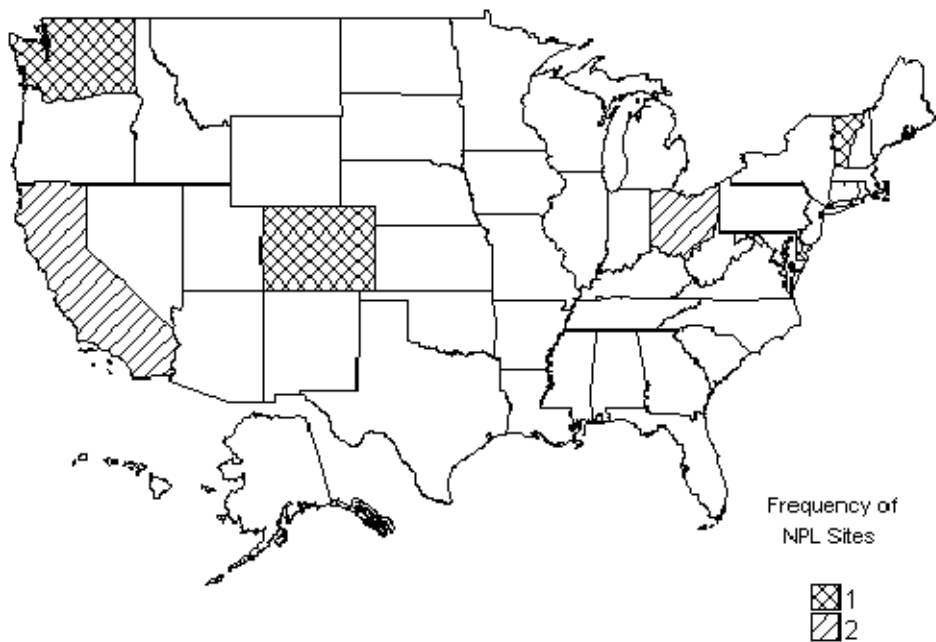# 6. POTENTIAL FOR HUMAN EXPOSURE

6.1   OVERVIEW

Phosphate ester flame retardants have been identified in at least 8 of the 1,699 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007). However, the number of sites evaluated for phosphate ester flame retardants is not known. The frequency of these sites can be seen in Figure 6-1.

Phosphate ester flame retardants are released to the environment through their use in industrial and consumer products. Since their introduction in the 1940s and popularization in the 1970s, these anthropogenic compounds have been frequently detected in water, soil, and air (Muir 1984). Trialkyl, triaryl and trihaloalkyl/aryl, and mixed 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 (Ashford 1994; Andresen and Bester 2006; IPCS 1990; Lide 2008; Lewis 2007; Owens et al. 2007; Watts and Linden 2009; Weil 2001; Wolf and Kaul 2005).

Water is the most common medium in which phosphate ester flame retardants are detected in the environment. Phosphate ester flame retardant presence is widespread in surface water and groundwater of the United States and other foreign countries, primarily due to landfill leaching of PVC plastics and polyurethane foams, effluent from industrial sources, and spills of hydraulic fluids. Many hydraulic fluids are composed of mixtures of phosphate esters and are consequently released into the environment as a mixture as indicated, for example, in the Toxicological Profile for Hydraulic Fluids (ATSDR 1997). Ultimately, these primary contaminated waters are transported to secondary sources, such as drinking water, by treated sewage, agricultural runoff, and deposition from snow and rain (Andresen et al. 2004; Fries and Puttmann 2001; Gomez-Belinchon et al. 1988; Ishikawa et al. 1985; Lee and Rasmussen 2006; Meyer and Bester 2004; Muir 1984; Peterman et al. 1980; Reemtsma et al. 2006; Watts and Liden 2008, 2009). Hydrolysis, although slow due to poor solubility and pH dependence, is the most important abiotic fate process for phosphate esters (Boethling and Cooper 1985). Biodegradation via hydrolysis from microbial esterases in river water, lake water, sewage, and sludge takes place in <10 days (Howard and Deo 1979; Mayer et al. 1981; Muir et al. 1980; Saeger et al. 1979).

6. POTENTIAL FOR HUMAN EXPOSURE

Figure 6-1. Frequency of NPL Sites with Phosphate Ester Flame Retardants

Frequency of
NPL Sites

⊠ 1
⧄ 2

Derived from HazDat 2007

In soil and sediment, phosphate ester flame retardants are considered persistent as they have a tendency to adsorb strongly, thus limiting the availability of these substances to microorganisms (Boethling and Cooper 1985; Muir 1984). Phosphate esters generally have a low water solubility and relatively high octanol/water partition coefficient (K_{ow}), which results in high soil adsorption coefficients (K_{oc}). Muir (1984) reported K_{oc} values ranging from 151 to 14,350 for several of the selected phosphate esters with the highest for TCP. Reports from soil analyses at military bases and airports have confirmed the presence of some phosphate esters, particularly TnBP, as it represents a major component in hydraulic fluid Skydrol 500B, Skydrol LD, and Hyjet IV (Monsanto Co. 1980). In addition, sediments of rivers and lakes have been shown to contain these compounds (Ishikawa et al. 1985; Muir et al. 1989). Volatilization and biodegradation are potential fate processes for phosphate esters adsorbed to soils (Anderson 1993; Muir 1984, 1989).

Diffusion into air from plastics, textiles, adhesives, and electronics accounts for numerous reports of phosphate esters in indoor air (Carlsson et al. 2000; Garcia et al. 2007; Hutter et al. 2006; Ingerowski et al. 2001, 2003; Otake et al. 2004, 2001; Owens et al. 2007; Sjodin et al. 2001). Outdoor air sampled near places where hydraulic fluids are used, such as at airports and outside of newly constructed homes and buildings, have indicated the presence of these phosphate esters (Haraguchi et al. 1985; Monsanto Co. 1980; Saito et al. 2007).

Ingestion of food or water is the primary exposure pathway that humans have to the phosphate ester flame retardants discussed in this profile. Exposure to phosphate esters via direct or indirect dermal adsorption from treated matricies is also possible, but unlikely due to the chemical and physical properties that make flame retardants useful. Young children are at an increased exposure risk due to the potential for oral exposure via dissolution of phosphate esters from repeated sucking on treated materials (NRC 2000). Inhalation is also a potential route of exposure primarily in indoor air from PVC plasticizers, floor polishes, electronics, and textiles.

Average daily intakes (ADIs) have been estimated for the U.S. population for TnBP, TPP, TBEP, TCPP, and TCEP (Gunderson 1988, 1995a, 1995b). The estimated ADI values are generally in the ng/kg body weight/day range. Additional sources of exposure for the general population include inhalation of air and ingestion of drinking water containing these phosphate esters. Occupational exposure may be greater than exposure to the general population for employees in industries where significant quantities of phosphate esters are manufactured or used.

The selected phosphate esters indicated in Table 4-1 have been frequently detected in the environment due to their commercial production, use, and disposal. However, other compounds that were not selected are also reported in the environmental monitoring literature. Mixtures of several phosphate esters present in a single monitoring sample are commonplace. According to the surveyed literature, the most prevalent phosphate esters in all environmental and dietary samples appear to be TnBP and TPP. Consequently, a significant portion of the noted studies pertain to these compounds. TCP and TPP are commonly used together in hydraulic fluids and lubricants and are detected together in environmental media (IPCS 1990). TBEP is also quite prevalent due to its presence in floor polishes, while the chlorinated phosphate esters, TCEP, TCPP, and TDCP, all appear much less frequently in the literature. TiBP appears the most infrequently in published monitoring studies of the environment or food.

6.2   RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ 10 or more full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes ≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 2005).

6.2.1   Air

There is no information on releases of phosphate ester flame retardants to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997).

Phosphate ester flame retardants are generally liquids in their pure form at 25 °C and have moderate Henry's Law constants (10^{-4}–10^{-8} atm-m^3/mol) and vapor pressures (10^{-2}–10^{-7} mm Hg); therefore, if

aerosolized, they should exist in the vapor phase or vapor phase and particulate phase (Muir 1984). Halogenated phosphate esters have a reduced vapor pressure and solubility, which generally aid in retention of these compounds as additives. Releases to the air likely occur from industrial sources, such as the manufacture, production, and transportation of pure phosphate esters, as well as diffusion from products containing phosphate esters.

Semi-volatile flame retardant hydraulic fluids could account for aerosolized phosphate esters lost from seal leakage, plastics, or vinyl car seats (EPA 1979). Skydrol 500B, a hydraulic fluid, contains 65–75% TnBP. In 1979, TnBP was detected in airport air over Vancouver, British Colombia at concentrations of 0.01–0.3 mg/m^3 (Monsanto Co. 1980).

6.2.2   Water

There is no information on releases of phosphate ester flame retardants to the water from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997).

Phosphate ester flame retardants are released to environmental surface water and groundwater primarily from leaching of hydraulic fluid spills and discarded or landfilled PVC, polyurethane foam, electronic wall coverings, and other flame retardant materials (Muir 1984).

6.2.3   Soil

There is no information on releases of phosphate ester flame retardants to the soil from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997).

Phosphate ester flame retardants are released to soil from the use of waste water for irrigation, the disposal of flame retardant plastics in landfills, the leakage of hydraulic fluids, or the deposition of aerosolized phosphate esters (Muir 1984).

6.3   ENVIRONMENTAL FATE

6.3.1   Transport and Partitioning

Phosphate esters are synthetic compounds that are present in the air, water, and soil due to their use primarily as flame retardants, hydraulic fluids, and plasticizers. The ability of phosphate esters to enter

the atmosphere as vapors depends greatly upon the vapor pressure of the individual compound.
Therefore, phosphate esters can be present in the vapor phase or particulate phase (EPA 1979; Muir
1984).

Phosphate esters generally have low water solubilities and relatively high K_{ow} values, which result in high
K_{oc} values. Muir (1984) reported the K_{oc} values for TPP, TCP, TnBP, TBEP, TCEP, and TDCP as 7,850,
14,350, 3,592, 2,311, 151, and 2,591, respectively, using data from Kenaga and Goring (1980). TCEP, as
apparent from the K_{oc} values, is particularly mobile in soil and has the greatest potential to leach into
groundwater. Relative to pesticides, the high K_{oc} of the other phosphate esters indicate relatively low
leaching potential. The fate and distribution of several phosphate esters were studied in laboratory
experiments using river water, pond water, and sediment mesocosms (Muir et al. 1989). Following
addition of each compound to the water column, rapid partitioning into the sediment was observed in each
case. Volatilization of phosphate esters from dry soils is unlikely given the vapor pressures and
adsorption coefficients; however, volatilization from moist soil is possible given the range of Henry's
Law constants (10^{-4}–10^{-8} atm-m^3/mol) and vapor pressures (10^{-2}–10^{-7} mm Hg) (Muir 1984).

TnBP, TPP, TCEP, and TDCP have been reported to have a moderate potential to bioaccumulate in
aquatic organisms based on their K_{ow} values (Sasaki et al. 1981). Bioconcentration of phosphate esters
requires assessment by using not only the K_{ow} or water solubility, but also the capacity of absorption and
metabolic behavior (Sasaki et al. 1981, 1982). Bioaccumulation ratios in fish (rainbow trout) are reported
to range from 133 to 2,807 (Muir et al. 1981). Phosphate esters have been detected in fish, sediment, and
water at or near the site of hydraulic fluid use (Mayer et al. 1981).

Uptake or degradation of TCEP in water was nearly nonexistent, resulting in very low bioaccumulation
for this compound as analyzed for bioconcentration in killifish and goldfish using both a static water
system and a continuous flow test system. Muir et al. (1983a) calculated the bioconcentration factors
(BCFs) for TPP as 573 and 561 for rainbow trout and fathead minnows, respectively, using ^{14}C-labeled
TPP. The results from the same study determined that meta- and para-TCP had BCFs of 1,420 and 784 in
rainbow trout and 928 and 596 in fathead minnows, respectively (Muir et al. 1983a). It was found that, in
general, the hydrolysis rate of the phosphate ester had a greater effect on bioconcentration than the
hydrophobicity of the compound (Muir et al. 1983a).

6.3.2   Transformation and Degradation

6.3.2.1   Air

These compounds are capable of degrading through reaction with hydroxyl radicals, which is the main route of atmospheric degradation for most organic substances. Predicted hydroxyl radical rate constants range from 10^{-12} to 10^{-11} cm^3/molecule-second and corresponding atmospheric half-lives are on the order of 1–12 hours for the selected phosphate esters assuming a constant atmospheric hydroxyl radical concentration of 1.5×10^6 hydroxyl radicals per cm^3 (Meylan and Howard 1993). Particulate-phase phosphate esters are subject to wet and dry deposition, while semi-volatile phosphate esters have the potential to hydrolyze to diesters, monoesters, and phosphoric acid (Ishikawa et al. 1992). Phosphate esters maintain oxidative stability at isothermal or room temperature conditions; however, thermal decomposition of these substances predominates at high temperature in the presence of air (Shankwalkar and Placek 1992).

6.3.2.2   Water

Hydrolysis is the most important abiotic fate process for phosphate esters proceeding stepwise to release alkyl and aryl alcohols (Boethling and Cooper 1985). The rate of hydrolysis is highly dependent on pH, temperature, presence of catalytic reagents, and stability of the conjugate acid or base, as well as the dielectric constant of the solvent (Katagi 2002). Phosphate esters are highly pH-dependent and generally are resistant to hydrolysis in neutral or acidic water (pH 5.0–7.0), but readily degrade in more alkaline conditions (pH 9.0–9.5) (Howard and Deo 1979; Mayer et al. 1981; Muir 1984). Half-lives of TPP at pH 8.2, 9.0, and 9.5 were 7.5, 3.0, and 1.3 days, respectively, indicating much faster hydrolysis as alkalinity increases. TPP hydrolysis was measured in distilled, lake, and river water. The results showed that the pseudo first-order rate constants for distilled water, Lake Ontario water, and Seneca River water were 0.93, 0.64, and 0.34 days^{-1}, corresponding to half-lives of 0.75, 1.0, and 2.0 days, respectively (Howard and Deo 1979).

Comparatively, dialkyl and diaryl phosphate esters have been found to be far less susceptible to hydrolysis than the corresponding triesters, likely due to the primary species being an anion. Dichloroalkyl phosphate esters such as TDCP are more labile than monochloroalkyl phosphate esters such as TCEP and TCPP (Hartley 1959; Muir 1984). Therefore, once the first ester substituent is hydrolyzed, removal of the second and third ester becomes much more difficult.

Aqueous base-catalyzed hydrolysis occurs via an S_N2-like nucleophilic attack on the phosphorus atom by OH⁻ on one of the tetrahedral faces, forming a transient tetracoordinate trigonal bipyramidal intermediate, followed by departure of the leaving group to form a phosphate diester. This mechanism and structure are evidenced by ^{18}O labeling and crystallographic data, respectively (Davis and Richardson 1980; Katagi 2002; Vernon 1959). Given this mechanism, electron-withdrawing substituents, such as halogens, increase the electrophilicity of the phosphorus, whereas electron-donating substituents are stabilizing (Davis and Richardson 1980). Through coordination, certain metal ions such as Ir, Rh, Co, Cu, Zn, and Mn have shown to facilitate phosphate ester hydrolysis. Low environmental concentrations of dissolved transition metals in the aquatic environment do, however, make this an unlikely mechanism. Heterogeneous reactions with suspended or sedimentary mineral phases have been shown to hydrolyze some phosphate esters (Baldwin et al. 1995).

Nonhalogenated phosphate esters are degraded by microorganisms in activated sludge; however, the halogenated phosphate esters are resistant to biodegradation. Standard biodegradation tests indicated that TnBP, TCP, and TPP are readily biodegradable, but TCPP is not. TPP achieved 83–94% of its theoretical biochemical oxygen demand (BOD) and TnBP achieved 89–91% of its theoretical BOD in 28 days using an activated sludge as inoculum and the modified MITI (OECD 301C) test (IPCS 2004, 2006). TCP achieved primary biodegradation in excess of 97% using a 4-week-long, semi-continuous activated sludge test and 100% in a river die-away study. In a CO_2 evolution study with TCP, 78.6% of theoretical CO_2 was evolved in 7 days and 82.1% was evolved in 28 days (Saeger 1979). In a 48-hour waste water treatment simulation, 40–60% of TCP was degraded (Ishikawa et al. 1985). TCPP achieved 0% of its theoretical BOD in 28 days using the same test (IPCS 2000a) and showed no decrease in concentration in landfill leachate after 80 days under aerobic conditions (Kawagoshi et al. 2002). Biodegradation is generally initiated by hydrolysis of the ester bond by microbial esterases (Yamada 1987). The hydrolysis product of TnBP, butanol, can be used as a carbon source (Thomas and Macaskie 1996, 1998). Consequently, several naturally isolated *Pseudomonas* cultures were found to substantially degrade TnBP by metabolizing and growing on minimal TnBP media as the feedstock (Thomas et al. 1997). Ninety-six percent of both TnBP and TPP was degraded upon addition of activated sludge (Saeger et al. 1979). Takahashi et al. (2008) isolated a mixed bacterial culture capable of degrading previously nonbiodegradable chlorinated phosphate esters TCEP and TCPP. A mixed culture primarily composed of *Acidovorax* spp., *Aquabacterium* spp., and *Sphingomonas* spp. degraded TCEP, while a mixed culture of *Acidovorax* spp. and *Sphingomonas* spp. was found to degrade TCPP.

Efforts to enhance the degradation of halogenated phosphate esters such as TCPP at water treatment facilities have been investigated (Watts and Linden 2008, 2009). The addition of ozone and hydrogen peroxide to produce photochemically generated hydroxyl radicals in aqueous solution was shown to be an effective method of increasing the oxidation of TCEP and TCPP in bench scale experiments. High initial levels of hydrogen peroxide are used in conjunction with a powerful ultraviolet light source to initiate the formation of hydroxyl radicals (Watts and Linden 2009).

Removal of phosphate esters from waste water can require additional processing. Halogenated phosphate esters, including TCEP, are particularly biorecalcitrant and are emerging as significant contaminants from waste water pollution into freshwater resources (Watts and Linden 2008). Ishikawa and Baba (1988) recognized the pH dependence of hydrolysis while attempting to hydrolyze phosphate esters with aqueous chlorine. Chlorination had little effect on TCEP and TCPP at all pHs and only achieved 50% degradation at pH 7 for TnBP and TPP.

6.3.2.3 Sediment and Soil

Muir et al. (1989) studied the fate and degradation of four phosphate esters, including TPP, in sediment/water systems and observed rapid degradation of these substances. The average half-lives of TPP in pond sediments were 2.8 days at 25 °C, 2.8 days at 10 °C, and 11.9 days at 2 °C; in river sediments, the average half-life was 7.0 days. Comparatively, in the same study, meta-TCP had average half-lives in pond sediments of 3.2 days at 25 °C, 4.1 days at 10 °C, and 16.3 days at 2 °C; in river sediments, the average half-life was 10.1 days. Under anaerobic soil conditions, TPP had a half-life of 32 days (Anderson 1993), while sterile soil produced nearly quantitative recovery of TPP after 101 days. TCEP soil attenuation was <33% from waste waters passed through soil columns for 1 month (Watts and Linden 2008).

6.4   LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to phosphate ester flame retardants depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of phosphate ester flame retardants in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on phosphate ester flame retardants levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is

bioavailable. The analytical methods available for monitoring phosphate ester flame retardants in a variety of environmental media are detailed in Chapter 7.

6.4.1   Air

Several phosphate esters were detected in the ambient air of Kitakyushu, Japan and measured by gas chromatography-mass spectrometry (GC-MS) at concentrations ($\mu g/m^3$) of 0.0023 (TnBP), 0.0053 (TCPP), 0.0047 (TDCP), and 0.0022 (TPP) in 1983 (Haraguchi et al. 1985). Several phosphate esters were detected in outdoor air from eight sites in Tokyo, Japan including TnBP (0–1.7 ng/m^3), TCPP (0–3.1 ng/m^3), and TBEP (0–1.1 ng/m^3) (Saito et al. 2007). TCP was not detected in this study. Atmospheric samples collected near heavily industrialized areas in Japan contained TCP at concentrations ranging from 11.5 to 70.3 ng/m^3 (IPCS 1990). TCP was qualitatively identified in fly ash and stack emissions from refuse combustion (Junk and Ford 1980). TCP was detected in air samples near production sites in West Virginia at levels of 0.01–2 ng/m^3 (Boethling and Cooper 1985).

TnBP is a component of two formulations of hydraulic fluid, Skydrol 500B and Skydrol LD. Consequently, TnBP was detected in the air at the CP air test facility at Vancouver International Airport at a concentration of 0.04–0.3 mg/m^3 (Monsanto Co. 1980), indicating that phosphate ester hydraulic fluids may be released during aircraft maintenance operations from equipment using phosphate ester hydraulic fluids.

The use of phosphate esters as an additive to flexible plastics, such as PVC and polyurethane foams, and their ability to leach from the polymer matrix often leads to their detection in indoor air at low levels. Phosphate esters have been found in indoor air from both homes and offices (Carlsson et al. 2000; Garcia et al. 2007; Hutter et al. 2006; Ingerowski et al. 2001, 2003; Otake et al. 2004, 2001; Owens et al. 2007; Sjodin et al. 2001). PVC plasticizers, floor polishes, and flame retardants for electronics and textiles are the primary contributors of phosphate esters to indoor air. PVC-containing plasticizer is a stiff resin but softens and expands upon heating and remains this way when cooled due to the molecular changes that take place (Otake et al. 2001, 2004). Phosphate esters are not chemically bound to host materials and consequently, can be emitted to the surrounding air as vapor or particulates depending on the vapor pressure of the compound (Carlsson et al. 2000; Garcia et al. 2007).

Recognition that phosphate esters, particularly TCEP and TCPP, were impacting indoor air took place in 1993 in Japan. TCEP was used in wall coverings and television sets in Japan until its carcinogenic

properties were suspected and it was replaced with TCPP (Saito et al. 2007). In Tokyo, Japan, several

phosphate esters were detected in indoor air environments. In 18 houses sampled, concentration ranges

(ng/m^3) were 0–30.6 (TnBP), 0–1,260 (TCPP), 0–136 (TCEP), 0–13.7 (TBEP), and 0–0.60 (TDCP). In

addition, 14 office buildings had concentration ranges (ng/m^3) of 0.46–21.7 (TnBP), 0–0.86 (TPP), 0–

57.6 (TCPP), 0–42.1 (TCEP), 0–118 (TBEP), and 0–8.7 (TDCP) (Saito et al. 2007). In a newly

constructed home in Tokyo, Japan, indoor air concentrations (ng/m^3) were 36.6 (TnBP), 5.5 (TCPP),

1.2 (TCEP), 71.0 (TBEP), and 1.3 (TDCP). TBEP was determined to originate from the floor polishing

agent, while TnBP originated from the polyolefin wall and ceiling coverings (Saito et al. 2007).

Migration rates of TDCP and TCP were measured as 0.28 and 5.9 μg/m^2-hour, respectively, from

computer monitors, and migration rates of TCPP and TCEP were measured as 1.7 and 13.0 μg/m^2-hour,

respectively, from TV sets using an interior surface to solid extraction disk (Saito et al. 2007). This

indicates that migration from electronic devices to air is occurring at ambient temperatures.

6.4.2   Water

Phosphate esters are commonly detected in surface water, groundwater, sewage, waste water, and

drinking water due to their presence in many commercial products and the ability to leach or diffuse from

their anthropogenic source (Watts and Linden 2009). These contaminants are widely distributed in the

aquatic environment (Ishikawa et al. 1985; Muir 1984). In the United States, the presence of phosphate

esters has been reported in waters from the Delaware River, the Great Lakes region, and several Midwest

rivers; phosphate esters have also been detected in water at foreign locations such as Japan, the

Netherlands, Germany, and Canada (Muir 1984). Conventional treatment of drinking water in the United

States showed that removal of TnBP, TBEP, TCEP, and TDCP was incomplete (Andresen and Bester

2006). In particular, TCEP is resistant to conventional potable water and waste water treatments (Meyer

and Bester, 2004; Reemtsma et al. 2006; Watts and Liden 2008, 2009). Several studies have measured

phosphate esters in surface waters from Wisconsin (Peterman et al. 1980), Kansas (Lee and Rasmussen

2006), and Germany (Andresen et al. 2004; Fries and Puttmann 2001). Phosphate esters have also been

detected in coastal waters from Spain (Gomez-Belinchon et al. 1988) and Japan (Ishikawa et al. 1985).

Pedersen et al. (2005) detected TCEP, TCPP, TBEP, and TDCP flame retardants in agricultural runoff

from fields irrigated with treated effluent in Ventura County, California.

Waters from waste water treatment facilities (WWTF) discharged into lakes, rivers, streams, and

tributaries of various watersheds are known to contain phosphate esters. A number of studies indicate

influent and effluent of WWTF testing positive for phosphate esters (Jackson and Sutton 2008; Marklund

2005b; Pedersen et al. 2005; Reemtsma et al. 2006; Thruston et al. 1991). Therefore, introduction of these anthropogenic compounds into the environment is augmented if an effective purification is not performed to remove or degrade phosphate esters at the WWTF.

Analysis of several streams in Johnson County, Kansas in 2002–2003 revealed the presence of phosphate ester flame retardants. On average, concentrations of 0.5 µg/L of TnBP, TPP, TBEP, TCEP, and TDCP were reported in these streams. In addition, several water samples collected and analyzed near a WWTF in the same area contained TBEP and TDCP. The mean concentrations of TBEP and TCDP in the effluent were 4.4 and 0.4 µg/L, respectively, and 2.0 and 0.4 µg/L <500 m downstream from the treatment plant. Maximum concentrations of 15 and 0.6 µg/L for TBEP and TDCP, respectively, were measured in the immediate effluent, and maximum levels of 6.2 and 0.6 µg/L, respectively, were measured <500 m downstream (Lee and Rasmussen 2006). A comprehensive study conducted by the U.S. Geological Survey from 1999 to 2000 analyzed surface water samples from 139 streams obtained in 30 states across the continental United States (Kolpin et al. 2002). TCEP, TDCP, and TPP were detected in 57.6, 12.9, and 14.1% of the surface water samples tested over this 2-year period, respectively. The maximum concentrations of TCEP, TDCP, and TPP were reported as 0.54, 0.16, and 0.22 µg/L, respectively, with median levels of 0.1, 0.1, and 0.04 µg/L, respectively (Kolpin et al. 2002).

Municipal waste water effluent collected from a treatment plant leading to the Oder River, Germany, contained mean levels of 622, 352, and 2,955 ng/L of TnBP, TCEP, and TBEP, respectively, in specimens obtained during a 2002–2003 sampling period (Fries and Puttmann 2003). Mean levels of TnBP, TCEP, and TBEP measured in the influent to the plant were 15,404, 986, and 12,835 ng/L, respectively. The concentration of TnBP, TCEP, and TBEP in river water at various sampling points in the river downstream from the plant ranged from 69 to 1,044 ng/L (TnBP), from not detected to 1,036 ng/L (TCEP), and from 121 to 952 ng/L (TBEP). Groundwater samples obtained from areas adjacent to the river contained TnBP, TCEP, and TBEP at ranges from not detected to 1,120, from not detected to 312, and from 154 to 410 ng/L, respectively.

Phosphate esters are widely used as incombustible plasticizers in Japan and, as a consequence, have been detected in the environment. Samples collected and analyzed in 1989–1990 from the Yodo River, Osaka City Rivers, Osaka Bay, and Yamato River in Japan indicated the presence of phosphate ester flame retardants. The most prevalent phosphate ester detected was TCPP at 13.1 µg/L in the Yamato River; however, TCEP, TnBP, TDCP, and TPP were also detected at lower concentrations (Fukushima et al. 1992).

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Three volcanic lakes located in Central Italy were examined for the presence of phosphate esters (Bacaloni et al. 2008). Due to their location, the lakes lack emissaries and tributaries and sewage treatment plant inputs. Therefore, contamination can occur only via local anthropogenic activities or long-range transport and deposition from rainfall or runoff processes. The results of this study indicated the presence of TCEP, TCPP, TDCP, TPP, TiBP, TnBP, and TBEP in all three of these lakes at the parts per trillion (ng/L) level, with a noticeable seasonal variation for several of the compounds. For each of the three lakes, maximum concentrations of the phosphate esters tended to occur during the late summer to autumn months, which coincide with heavy tourist activity and increased vehicular traffic at all three locations. The mean monthly range of concentrations at all three lakes were as follows: TCEP, not detected to 64 ng/L; TCPP, 2–62 ng/L; TDCP, 2–60 ng/L; TPP 2–21 ng/L; TiBP, 1–380 ng/L; TnBP, 3–784 ng/L; and TBEP, 8–127 ng/L.

Aerosolized phosphate esters are subject to wet deposition. TPP and TnBP were identified, but not quantified, in rainwater samples obtained from Los Angeles, California (Kawamura and Kaplan 1983), and snowfall samples from various areas of Northern Sweden (Marklund 2005a). TnBP was detected in the snowfall at an airport in Sweden at levels as high as 23,000 ng/kg, likely as a consequence of its use in aircraft hydraulic fluids. TnBP, TCEP, and TBEP were detected in rainwater samples collected in Bahnbrucke, Germany at levels of 911, 121, and 394 ng/L, respectively (Fries and Puttmann 2003).

TnBP is frequently used as a solvent in liquid-liquid extraction for uranium and plutonium fuel reprocessing. Consequently, it has been detected in storage ponds and waste streams at nuclear fuel reprocessing sites. TnBP and uranium concentrations in a typical fuel rod storage pond were 300 and 142 μM, respectively (Thomas and Macaskie 1996).

TCEP, TDCP, and TPP were analyzed in groundwater samples from 47 sites in 18 different states as part of a national reconnaissance program of water quality in the United States (Barnes et al. 2008). TCEP was detected in 29.8% of the samples tested at a maximum concentration of 0.737 μg/L. TDCP and TPP were detected in 2.1 and 4.3% of the groundwater samples tested, respectively; however, all detections were below the reporting level. Focazio et al. (2008) studied the frequency of detection of phosphate esters and 96 other compounds in 25 ground- and 49 surface-water sources used for public drinking water systems from 25 different states and Puerto Rico. TCEP, TDCP, TnBP, and TPP were detected in 20.3, 12.2, 8.1, and 1.35% of the samples tested, respectively. The maximum concentration of TnBP was 0.74 μg/L; however, all of the other compounds were detected below the reporting limit of 0.5 μg/L.

TPP was identified, but not quantified, in water samples collected from groundwater and treated water obtained from 31 wells in the Piedmont and Highlands regions of Northern New Jersey (Stiles et al. 2008). In a 1979 survey of treated potable drinking water from 29 municipalities across Canada, the presence of TnBP, TCEP, TDCP, TPP, TCP, and TBEP was frequently observed. TBEP was the most commonly detected phosphate ester with levels as high as 560 ng/L (Williams et al. 1981). TCP was detected at levels of 0.4–1.8 ng/L in 5 of 12 samples of municipal drinking water collected at treatment plants in the Great Lakes region of Canada (Williams et al. 1982). Phosphate esters were detected in untreated surface water from the Ruhr River in Germany; reported concentrations of TCPP, TCEP, and TDCP were 50–150, 10–130, and 10–40 ng/L, respectively (Andresen and Bester 2006). Following treatment of the water, the concentrations were all reduced to 0.3–3 ng/L (Andresen and Bester 2006).

6.4.3   Sediment and Soil

Available literature suggests that halogenated phosphate esters are somewhat persistent organic compounds when adsorbed to soils and sediments (Boethling and Cooper 1985; Muir 1984). However, Muir et al. (1989) found that nonhalogenated phosphate esters, particularly TPP, are degraded in <3 days. In general, partitioning of phosphate esters provides potential for contact with sediments in lakes, rivers, and sea floors.

A national survey conducted in 1977–1978 in Japan resulted in the detection of TnBP at concentrations of 8–130 ng/g in rivers sediments, 3–24 ng/g in estuary sediments, and 2–240 ng/g in sea sediments (Ishikawa et al. 1985). TCP was detected in 2 of 75 sea sediment samples at concentrations of 1.06 and 2.16 µg/g (Ishikawa et al. 1985). Phosphate ester levels of 0.1–1 µg/g have been detected in river sediments of industrial areas contaminated with triaryl-based hydraulic fluids (Ishikawa et al. 1985; Muir et al. 1989). Commercial and military use of phosphate ester hydraulic fluid is estimated to result in up to 80% of the consumption of these to be lost to unrecovered leakage. Consequently, air force bases have reported detection of several phosphate esters, including TPP, in soils (David and Seiber 1999b; Monsanto Co. 1980). TCP was reported in sediments collected from the Detroit river (0.23–1.3 mg/kg) and Sparrows Point in the Baltimore Harbor (0.4–0.6 mg/kg) (Boethling and Copper 1985). Due to the high sedimentation coefficient of TCP, several studies in Japan have detected TCP in sediments with levels ranging from 4 to 2,160 ng/g (IPCS 1990). In Glil-Yam, Israel, Muszkat et al. (1993) reported the presence of TnBP at 25 ppb in effluent used for crop irrigation. A national survey in 1977–1978 resulted in the detection of TCEP in sea sediments at a concentration of 90 ng/g (Ishikawa et al. 1985).

6.4.4   Other Environmental Media

In 1982, the Food and Drug Administration (FDA) found detectable levels of phosphate esters present in food samples during a portion of the annual Pesticide Screening program. The presence of these phosphate esters in foodstuffs presumably arose from the diffusion of these substances through the wrapping material used to package the food (Daft 1982). Since 1982, phosphate ester flame retardants are regularly tested for in various foods by the FDA's Total Diet Study. The results obtained are summarized in Table 6-1. No data were available for TiBP, TCP, or TDCP from this study (FDA 2006). The most frequently identified phosphate ester flame retardant was TPP, which also had the highest reported content. TPP was found in caramels and margarine at approximately 0.04 ppm. In baby foods, turkey and vegetables contained the highest level of TPP at approximately 0.02 ppm. TnBP was the second most frequently detected phosphate ester, but most levels measured were below 0.004 ppm, with baby cereal (prepared with water) and applesauce being the highest (FDA 2006).

In a study based in the United Kingdom, similar to the U.S. based FDA Total Diet Study, the most prevalent of the selected phosphate esters were TnBP and TPP, occurring in meats, cereals, nuts, and some vegetables (Gilbert et al. 1986).

House dust has been found to contain phosphate esters such as TCEP and TCPP (Garcia et al. 2007; Hutter et al. 2006; Ingerowski et al. 2001; Marklund 2003). TBEP was measured at levels of 4,300– 7,800 mg/kg in house dust prior to removal of the cleaning polish on the floor. Once a wet cleaning was performed, the level of TBEP dropped to 410 mg/kg after 3 months and to 90 mg/kg after 6 months (Hutter et al. 2006). Dust samples obtained from different private residences (houses) located in the northwest of Spain were found to contain levels of TBEP as high as 18.5 μg/g. Other phosphate esters were also detected in the dust samples at average concentrations (μg/g) of 0.21 (TiBP), 0.25 (TnBP), 1.7 (TCEP), 3.9 (TCPP), 0.35 (TDCP), 2.6 (TPP), and 9.9 (TBEP) (Garcia et al. 2007).

Phosphate esters were detected in soft polyurethane foam samples at levels of 0.4–0.7 μg/g for TnBP, 0.8–3.1 μg/g for TCEP, 0.9–3.1 μg/g for TCPP, 4.5–10.2 μg/g for TDCP, 4.7–23.3 μg/g for TPP, and 1.6 μg/g for TBEP (Nagase et al. 2003). TCP was detected on the inside surface of automobile windows, presumably due to its use as a plasticizer in interior automobile plastics (Boethling and Cooper 1985).

Table 6-1. Phosphate Ester Flame Retardant Levels in Food

Food item	Level (ppm)
Tributyl phosphate (TnBP)	
Rice, white, enriched, cooked	0.00011
Oatmeal, plain, cooked	0.00014
Cream of wheat (farina), enriched, cooked	0.00200
Corn flakes cereal	0.00314
Fruit-flavored cereal, presweetened	0.00018
Shredded wheat cereal	0.00123
Raisin bran cereal	0.00018
Crisped rice cereal	0.00086
Oat ring cereal	0.00034
Apple (red), raw (with peel)	0.00043
Applesauce, bottled	0.00430
Orange juice, frozen concentrate, reconstituted	0.00045
Grapefruit juice, frozen concentrate, reconstituted	0.00091
Prune juice, bottled	0.00089
Dill cucumber pickles	0.00023
Sugar, white, granulated	0.00045
Peach, canned in light/medium syrup	0.00045
Tomato juice, bottled	0.00018
Baby food, cereal, mixed, dry, prepared with water	0.00432
Tris(2-butoxyethyl) phosphate (TBEP)	
Oatmeal, plain, cooked	0.00368
Bread, whole wheat	0.00114
Candy, caramels	0.00075
BF, juice, apple	0.00018
Peach, canned in light/medium syrup	0.00039
Popsicle, fruit-flavored	0.00225
Tri-(2-chloroisopropyl) phosphate (TCPP)	
Apple (red), raw (with peel)	0.00082
Pear, raw (with peel)	0.00009
Prunes, dried, uncooked	0.00015
Apple juice, bottled	0.00005
Tomato catsup	0.00030
Tomato juice, bottled	0.00032
Baby food, arrowroot cookies	0.00018

Table 6-1. Phosphate Ester Flame Retardant Levels in Food

Food item	Level (ppm)
Triphenyl phosphate (TPP)	
Peas, green, frozen, boiled	0.00023
Rolls, white, soft, enriched	0.00075
Bread, whole wheat	0.00036
Tortilla, flour	0.00050
Bread, rye	0.00039
Strawberries, raw/frozen	0.00028
Lemonade, frozen concentrate, reconstituted	0.00041
Sauerkraut, canned	0.00025
Broccoli, fresh/frozen, boiled	0.00023
Asparagus, fresh/frozen, boiled	0.00023
Tomato, raw	0.00341
Mashed potatoes with margarine and milk, prepared from instant	0.0025
Scalloped potatoes, homemade	0.00023
Soup, vegetable beef, canned, condensed prepared with water	0.00068
White sauce homemade	0.00285
Margarine, regular (salted)	0.04068
Butter, regular (salted)	0.00175
Cream substitute, non-dairy, liquid/frozen	0.00102
Candy, caramels	0.04503
Fruit drink, from powder	0.00023
Wine, dry table, red/ white	0.00068
Bread, cracked wheat	0.00057
Crackers, graham	0.00045
Sweet cucumber pickles	0.00025
Beef and vegetable stew, canned	0.00975
Baby food, juice, apple-banana	0.00295
Baby food, zwieback toast	0.00400
Baby food, vegetables and turkey	0.02175

Table 6-1. Phosphate Ester Flame Retardant Levels in Food

Food item	Level (ppm)
Tris(2-chloroethyl) phosphate (TCEP)	
Peas, green, frozen, boiled	0.00182
Oatmeal, plain, cooked	0.00002
Cream of wheat (farina), enriched, cooked	0.00259
Rolls, white, soft, enriched	0.00008
Broccoli, fresh/frozen, boiled	0.00014
Green beans, fresh/frozen, boiled	0.00159
Baby food, turkey and rice	0.00048
Baby food, peas	0.00002
Bread, cracked wheat	0.00002
Eggplant, fresh, peeled, boiled	0.00175
Candy, hard, any flavor	0.00002
Sweet cucumber pickles	0.00005
Baby food, teething biscuits	0.00006
Soup, Oriental noodles (ramen noodles), prepared with water	0.00725
Baby food, pears and pineapple	0.00002

Source: FDA Total Diet Study Market Baskets 1991–2003 (FDA 2006)

6.5   GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Exposure to phosphate esters can occur through ingestion of food and water containing phosphate esters or inhalation of vapors or particulates released from flame retardant materials. Dermal exposure can occur through direct contact with flame-retarded textiles occurs; however, these substances are not highly absorbed through dermal routes. As fabrics and foams treated with phosphate ester flame retardants wear, they can shed small fibers and produce particles that could be ingested or inhaled if ≤10 μm (NRC 2000). The most significant route of exposure to the general population is via ingestion of food or water contaminated with phosphate ester flame retardants (Fiserova-Bergerova and Pierce 1990; Hartmann et al. 2004; Hughes et al. 2001; IPCS 1997).

Data regarding dietary intake of phosphate ester flame retardants in children and adults in the United States are available only for select compounds and years. In 1980 and 1981–1982, ADI values of TCEP for adults were 0.041 and 0.055 μg/kg, respectively. In 1981–1982, the ADI for TnBP was found to be 0.025 μg/kg. This value was determined by measuring of TnBP in meats and fruits, and TCEP in cereals (Gantrell 1986). The ADI was calculated by Gunderson (1988, 1995a, 1995b) from the reported FDA Total Diet Study and these data are summarized in Table 6-2. Mean daily intakes for male and female teenagers aged 14–16 were highest for TPP ranging from 1.6 to 18.2 ng/kg/day. For male and female adults aged 25–30, TPP also had the highest mean daily intakes, ranging from 0.8–18.4 ng/kg/day. Both male and female adults aged 60–65 showed the highest mean daily intake for TBEP, ranging from 0.2 to 16.8 ng/kg/day. TPP was also quite prevalent for this age group. No data were reported for TiBP, TCP, or TDCP (Gunderson 1988, 1995a, 1995b).

In the United Kingdom, a diet study modeled after the U.S. Total Diet Study determined a total daily intake of 0.075–0.105 mg/day for trialkyl/aryl phosphates. The most prevalent of the selected phosphate esters were TnBP and TPP, found in meats, cereals, nuts, and some vegetables (Gilbert et al. 1986).

In Canada, TDCP was detected in human adipose tissue by LeBel and Williams (1983, 1986) in concentrations that ranged from not detectable (<0.001 μg/kg) to 257 μg/kg. In later studies, samples from four out of six cities showed no detectable TDCP; however, two concentrations ranged up to 32 μg/kg. (LeBel and Williams, 1983, 1986; LeBel et al. 1989). Using negative chemical ionization mass spectrometry (LC-MS-NCI) with a limit of detection of 0.01 μg, Hudec et al. (1981) found concentrations of TDCP in the seminal fluid of 34 out of 123 student donors ranging from 5 to 50 μg/L.

Table 6-2. Dietary Phosphate Ester Flame Retardant Intake

Age group	Mean (ng/kg body weight/day)		
	1982–1984[a]	1984–1986[b]	1986–1991[c]
Tributyl phosphate (TnBP)			
6–11 months	38.9	42.5	3.0
2 years	27.7	33.1	2.5
14–16 years, females	3.5	4.5	0.5
14–16 years, males	5.0	6.6	0.7
25–30 years, females	3.3	4.0	0.3
25–30 years, males	2.7	3.1	0.3
60–65 years, males	5.4	6.2	0.4
60–65 years, females	6.2	7.1	0.4
Triphenyl phosphate (TPP)			
6–11 months	0.3	1.8	15.7
2 years	4.4	16.0	34.8
14–16 years, females	1.6	5.8	16.3
14–16 years, males	1.2	5.0	18.2
25–30 years, females	0.8	3.3	12.8
25–30 years, males	1.6	5.5	18.4
60–65 years, males	0.5	2.4	11.4
60–65 years, females	0.5	2.4	15.8
Tris(2-butoxyethyl) phosphate (TBEP)			
6–11 months	2.9	0.2	5.2
2 years	14.4	1.5	3.7
14–16 years, females	8.4	0.7	1.2
14–16 years, males	7.7	1.1	1.1
25–30 years, females	12.9	0.4	2.0
25–30 years, males	10.7	0.8	0.9
60–65 years, males	16.8	0.2	3.4
60–65 years, females	13.7	0.2	2.8
Tri-(2-chloroisopropyl) phosphate (TCPP)			
6–11 months	No data	No data	0.1
2 years	No data	No data	0.2
14–16 years, females	No data	No data	0.1
14–16 years, males	No data	No data	0.1
25–30 years, females	No data	No data	0.1
25–30 years, males	No data	No data	0.1
60–65 years, males	No data	No data	0.1
60–65 years, females	No data	No data	

Table 6-2. Dietary Phosphate Ester Flame Retardant Intake

	Mean (ng/kg body weight/day)		
Age group	1982–1984[a]	1984–1986[b]	1986–1991[c]
Tris(2-chloroethyl) phosphate (TCEP)			
6–11 months	No data	4.9	No data
2 years	No data	6.5	No data
14–16 years, females	No data	2.1	No data
14–16 years, males	No data	1.1	No data
25–30 years, females	No data	1.8	No data
25–30 years, males	No data	1.3	No data
60–65 years, males	No data	3.1	No data
60–65 years, females	No data	2.6	No data

[a]Gunderson 1988 (ADI 1982–1984).
[b]Gunderson 1995a (ADI 1984–1986); expressed as μg/kg body weight/day in source.
[c]Gunderson 1995b (ADI 1986–1991); expressed as μg/kg body weight/day in source.

Morgan and Hughes (1981) tested workers manufacturing triaryl phosphate esters, including TPP, for cholinesterase activity to determine its efficacy as a biomarker for absorption. The results showed that it is not adequately sensitive to be used as a biomarker for phosphate ester absorption.

Three primary uses that account for the greatest potential worker exposure include aircraft manufacturing, hydraulic system component manufacturing, and commercial airline operations (Batt et al. 1992). In addition, workers in industries that manufacture plastics, floor polishes, wall coverings, and electronics may have a greater-than-average potential for exposure. Since TnBP and TCP are widely used in hydraulic and turbine oils, a study by Solbu and Daae et al. (2011) investigated exposures to pilots by measuring air and surface samples in various aircrafts following a recent flight. TCP was detected in 39% of the wipe samples but only 4% of the air samples, while TnBP was detected in all of the samples.

A survey conducted by NIOSH from 1981 to 1983 collected data on potential occupational exposures to chemical agents. These data provided estimates that indicated that the numbers of workers potentially exposed to TPP, TCP, TnBP, TBEP, TCEP, and TCPP were 91,754, 239,503, 109,402, 257,421, 5,073, and 120 respectively (NIOSH 1990).

6.6   EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in Section 3.7, Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Exposure of children to phosphate ester flame retardants is likely to occur primarily through diet, indoor air, or by contact with flame retardant-treated plastics or fabrics. Young children are likely to have an increased oral exposure risk. Children may repeatedly suck on furnishing fabrics, plastics, or polished

surfaces, presenting potential dissolution of leachable flame retardants. Effective phosphate ester flame retardants are dependent upon retention in the applied matrix, and are therefore likely chosen based upon their ability to resist extraction from the matrix (NRC 2000). Children and infants may be exposed to phosphate ester flame retardants through ingestion of dust in homes where plastics, foams, floor polishes, or wall covering products containing phosphate esters are used (Hutter et al. 2006).

In 1980, the ADIs of TnBP for infants and toddlers were 0.051 and 0.132 μg/kg, respectively. In 1979 and 1980, TCEP was found to have an ADI of 0.016 and 0.004 μg/kg, respectively, in infants and 0.009 μg/kg and none detected, respectively, in toddlers. These were determined by measuring TnBP in cereals and TCEP in fruits (Gantrell 1985). Mean daily intakes for 6–11-month-old children were highest for TnBP between 1982 and 1986, ranging from 38.9 to 42.5 ng/kg//day. This number dropped significantly to 0.3 ng/kg/day in the last study published in 1986–1991. The next greatest exposure of 6–11-month-old children via diet appears to be TPP, with an ADI of 15.7 ng/kg/day in 1986–1991. The exposure data indicated that 2-year-old children could have exposures >30 ng/kg/day of TnBP and TPP (Gunderson 1988, 1995a, 1995b).

6.7   POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Phosphate esters do not occur naturally in the environment; therefore, potential high exposures are limited to occupational or indoor environments. Occupational exposure to phosphate ester flame retardants may occur during the manufacture, use, transport, processing, or disposal/recycling of flame retardants. Due to the presence of phosphate esters in turbine and hydraulic fluids, particularly TCP and TnBP, pilots may have a high risk of exposure (Solbu and Daae 2011). Routes of exposure could include inhalation, dermal contact, or ingestion. Living or working in an environment where there is an excess of flame retardant-treated products such as wall coverings, plastics, or electronics could contribute to a higher-than-average exposure. Additionally, living in an area where phosphate ester-contaminated effluent is used for drinking water or crop irrigation could contribute to a higher-than-average exposure (Fiserova-Bergerova and Pierce 1990; IPCS 1997).

6.8   ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of phosphate ester flame retardants is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the

initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of phosphate ester flame retardants.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.8.1   Identification of Data Needs

Physical and Chemical Properties.   Table 4-2 summarizes many of the relevant physical and chemical properties of the selected phosphate ester flame retardants. The only data need is for measured Log K_{ow} and vapor pressures for TiBP.

Production, Import/Export, Use, Release, and Disposal.   According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information for 2006, became available in February of 2008. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Current data on the use of each selected phosphate ester flame retardants are available and displayed in Table 5-1. Production, import, and export data are scarce and difficult to find, but estimates are provided by the EPA High Production Volume (HPV) Challenge Program or the Hazardous Substance Data Bank (HSDB) for all selected phosphate ester flame retardants. No data were available for manufacturers for TCPP, TCP, and TiBP as indicated in Table 5-1 (EPA 2006; HSDB 2009). A data need exists for release and disposal of phosphate ester flame retardants.

Environmental Fate.   The environmental entry mechanism of phosphate esters, as well as transport and partitioning, is highly dependent on the specific compound. The environmental fate mechanisms of groups within the selected compounds (e.g., halogenated, alkyl, and aryl phosphate esters) are well understood (Muir 1984). Hydrolysis and adsorption are the primary forces that influence phosphate ester environmental fate and are well documented (Howard and Deo 1979; Kenaga and Goring 1980; Mayer et al. 1981; Muir 1984). No data needs are identified.

Bioavailability from Environmental Media.   A data need exists for bioavailability of phosphate
ester flame retardants from various media. Minimal data exist in the form of human monitoring, but
several studies suggest that absorption of phosphate esters can occur via ingestion of foods and water
contaminated with effluent or landfill leachate, inhalation of indoor and some outdoor air near airports
and military installations, or dermal contact with contaminated soils or water (Fiserova-Bergerova and
Pierce 1990; IPCS 1997; Monsanto Co. 1980; Saito et al. 2007).

Food Chain Bioaccumulation.   Sufficient bioaccumulation data are available for TnBP, TPP, TCP,
TCEP, and TDCP (Muir 1980, 1983a; Sasaki et al. 1981, 1982); however, a data need exists for
bioaccumulation of TiBP, TBEP, and TCPP.

Exposure Levels in Environmental Media.   **R**eliable monitoring data for the levels of phosphate
ester flame retardants in contaminated media at hazardous waste sites are needed so that the information
obtained on levels of phosphate ester flame retardants in the environment can be used in combination with
the known body burden of phosphate ester flame retardants to assess the potential risk of adverse health
effects in populations living in the vicinity of hazardous waste sites.

Extensive reports are available regarding quantifiable levels of phosphate ester flame retardants detected
in the environment. More specifically, extensive monitoring data exist on phosphate ester flame
retardants in water (Andresen et al. 2004; Fries and Puttmann 2001; Gomez-Belinchon et al. 1988;
Ishikawa et al. 1985; Lee and Rasmussen 2006; Meyer and Bester 2004; Muir 1984; Peterman et a 1980;
Reemtsma et al. 2006; Watts and Liden 2008, 2009) and indoor air (Carlsson et al. 2000; Garcia et al.
2007; Hutter et al. 2006; Ingerowski 2001, 2003; Otake et al. 2004, 2001; Owens et al. 2007; Sjodin et al.
2001). Studies detecting phosphate ester flame retardants in outdoor air are more sparse (Haraguchi et al.
1985; Monsanto Co. 1980; Saito et al. 2007). Additional data of phosphate ester flame retardants in soil
and in food, as well as more recent average daily intake data, would be useful for estimating human
exposure. In particular, there is a data need for environmental concentrations of TiBP.

Exposure Levels in Humans.   Given that these compounds are considered emerging pollutants in
some of the literature, there are relatively little data concerning levels of phosphate ester flame retardants
in humans. There are, however, studies that reported levels of TDCP in human adipose tissue (Lebel and
Williams 1983, 1986) and in the seminal fluid of student donors (Hudec et al. 1981). A data need exists
for additional information regarding levels of these substances in blood, and urine from individuals with

potentially high exposures such as children and infants. A data need exists for studies addressing biomarkers as a method for determining exposure to mixtures of phosphate esters.

This information is necessary for assessing the need to conduct health studies on these populations.

Exposures of Children. Children are exposed to phosphate ester flame retardants by the same routes as adults. In addition, oral exposure can occur from dissolution of phosphate ester treated materials since children are more likely to repeatedly suck on these materials (NRC 2000). A data need exists for levels of phosphate esters in blood and urine from children with known environmental exposure, as well as concentrations present in breast milk or infant formula to better estimate total exposure. Gantrell (1985) and Gunderson (1988, 1995a, 1995b) addressed only TnBP, TPP, TCEP, TCPP, and TBEP over a limited number of years (1982–1991). A data need exists for updated exposure in the form of ADI for children with the aforementioned compounds as well as new data regarding of TiBP and TDCP exposures.

Child health data needs relating to susceptibility are discussed in Section 3.12.2, Identification of Data Needs: Children's Susceptibility.

Exposure Registries.   No exposure registries for phosphate ester flame retardants were located. This substance is not currently one of the compounds for which a sub-registry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for sub-registries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

6.8.2   Ongoing Studies

No ongoing studies pertaining to the environmental fate of phosphate ester flame retardants were identified in a search of the Federal Research in Progress database (FEDRIP 2009).