

CPSC Staff Statement on Toxicology Excellence for Risk Assessment (TERA) Report  
“Environmental Concentrations and Consumer Exposure Data for Selected Flame Retardants  
(TDCPP, TCPP, TEP, TPP)”<sup>1</sup>

June 2015

The report titled, “Environmental Concentrations and Consumer Exposure Data for Selected Flame Retardants (TDCPP, TCPP, TEP, TPP),” presents environmental and consumer exposure data on tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tris(chloropropyl) phosphate (TCPP), triethyl phosphate (TEP), and triphenyl phosphate (TPP) conducted by TERA under Contract CPSC-D-12-0001, Task Order 0008.

This report first provides an introduction. It is then discussed by flame retardant (FR) chemical. Each FR chemical section contains the same type of information. First, TERA provides information on the FR’s chemical and physical properties and its use. Next, TERA provides human exposure data, both domestic and international, from the following media: indoor and ambient air, water, food, dust, and consumer products. Absorption, distribution, metabolism, excretion, and biomonitoring studies are summarized next. Each chemical-specific section concludes with existing exposure assessment and exposure estimate summaries and a discussion.

The introduction discusses background on FR chemicals and how the information and data was obtained for the review. For all chemicals, concentrations were assessed in indoor air and dust, drinking water, food, and consumer products, including children’s products, upholstered furniture, mattresses, apparel, household products, building materials, and electronics. Biomonitoring data and result of available exposure studies and estimates were also compiled. Observations noted throughout the process of writing this document were summarized and include : 1) there is a basic lack of monitoring data in environmental media for these FRs, 2) much of the data are available outside of the U.S., 3) emission or migration rates of these FRs from products is limited, 4) dermal exposure uncertainty exists due to lack of testing, 5) use of particular FRs changes due to problems identified and substitutions employed, and 6) dust and vapor may contribute to total indoor air concentrations.

Based on this report, TDCPP is a widely used flame retardant in the U.S. and has been measured in water, dust, consumer products (upholstered furniture, baby products with polyurethane foam, and electronics), and air. Contact with dust appears to be the main source of exposure for consumers to TDCPP. Biomonitoring studies have demonstrated significant correlations between urinary BDCPP in humans and TDCPP dust concentrations. Normal hand-to-mouth activity was found to be the primary route of exposure; however, incidental hand-to-mouth activity occurs over a person’s entire life. This activity occurs most often and most significantly in children, and therefore, children may have greater exposures than adults. Estimated exposure intakes were also noted and summarized for TDCPP.

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<sup>1</sup> This statement was prepared by the CPSC staff, and the attached report was produced by TERA for CPSC staff. The statement and report have not been reviewed or approved by, and do not necessarily represent the views of, the Commission.

This report states that the use of TCPP has been driven by its use as a substitute for pentabromodiphenyl ether (pentaBDE), which has been banned or phased out around the world over the past 10 – 20 years. TCPP has been measured in water, dust, consumer products, and indoor and ambient air. TCPP has also been detected in urine and breast milk. The available literature indicates that TCPP concentrations are highest in the air and dust of indoor environments. Breathing contaminated indoor air and contact with dust appears to be the main possible sources of TCPP exposure to consumers. The data show that homes with TCPP treated carpet, carpet backing, or wall coverings could present the highest potential for TCPP exposure to consumers because the large surface-area-to-volume ratio of these products could ultimately produce the highest indoor air and dust concentrations. As with TDCPP, normal hand-to-mouth activity was found to be the primary route of exposure; however, incidental hand-to-mouth activity occurs over a person's entire life. This activity occurs most often and most significantly in children, and therefore, children may have greater exposures than adults. Estimated exposure intakes were also noted and summarized for TCPP.

Based on the limited available data and physical properties of TEP, the primary mode of exposure for U.S. consumers to TEP is from treated polymers used in indoor products, such as carpet, carpet backing, furniture, or wall covering. TEP is expected to ultimately appear in air or possibly in the ambient moisture present in house dust, due to its relatively high affinity for water and air versus organic matter. Biomonitoring data have detected TEP in breast milk. The use and properties profile for this chemical suggest that the potential for human exposure (inhalation, dermal, hand-to-mouth oral) could be relatively high in indoor environments that have large surface areas of TEP-treated polymer products. However, the use patterns of these products are not known and significant human exposure may not exist.

TPP has been detected in various media including outdoor and indoor air, surface water, groundwater, house dust, food, and consumer products. The primary sources of exposure to TPP for consumers appear to be dust and inhalation of vapors and particulates in the indoor air. Drinking treated surface water contaminated with TPP could also represent a significant source of exposure if the TPP is not removed during treatment. Biomonitoring data have detected TPP in urine, breast milk, an adipose tissue, which demonstrates some uptake of TPP. Limited exposure data exist in the U.S., and data from other countries may introduce uncertainty into exposure estimates because TPP levels in other countries may not be representative of U.S. levels.



TERA

**Environmental Concentrations  
and Consumer Exposure  
Data for Selected Flame Retardants  
(TDCPP, TCPP, TEP, TPP)**

**Task Order 8  
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## Abbreviations and Acronyms

AC	Activity coefficient
ADD	Average Daily Dose
ADME	Absorption, Distribution, Metabolism, and Excretion
ATSDR	Agency for Toxic Substances and Disease Registry
AUC	Area under the plasma concentration-time curve
BDCPP	Bis (1, 3-dichloro-2-propyl) phosphate
BPA-BDPP	Bisphenol A bis (diphenylphosphate)
CalEPA	California Environmental Protection Agency
CCRIS	Chemical Carcinogenesis Research Information System
CEH	Center for Environmental Health
COFPL	Castor oil phosphate flame-retarded polyol
CPSC	Consumer Product Safety Commission
DPP	Diphenyl phosphate
EC	European Commission
ECHA	European Chemicals Agency
EDTA	Ethylenediaminetetraacetic acid
EG	Expandable graphite
EINECS	European Inventory of Existing Commercial Substances
EtO <sub>3</sub> PO	Ethyl phosphate
HSDB	Hazardous Substances Data Bank
ICRP	International Commission on Radiological Protection
ICSC	International Civil Service Commission
IPCS	International Programme on Chemical Safety
MFO	Mixed function oxidase
NADPH	Nicotinamide Adenine Dinucleotide Phosphate-oxidase
NRC	National Research Council
NSC	National Safety Council
NTP	National Toxicology Program
OECD	Organisation for Economic Co-operation and Development
PBDPP	Resorcinol bis-(diphenylphosphate)
PEC	Predicted Environmental Concentration
PentaBDE	Pentabromodiphenyl ether
PU	Polyurethane
PUF	Polyurethane foam
PVC	Polyvinylchloride
RfD	Oral reference dose
SIDS	Screening Information Data Sets
SKF-525A	2-Diethylaminoethyl-2,2-diphenylvalerate-HCl

SOCMA	Synthetic Organic Chemical Manufacturers Association
SPE	Solid phase extraction
SPME	Solid-phase microextraction
SVOCs	Semi-Volatile Organic Compounds
TBB	2-ethylhexyl-2,3,4,5-tetrabromobenzoate
TBPH	Bis(2-ethylhexyl)2,3,4,5-tetrabromophthalate
TCPP	Tris(chloropropyl) phosphate
TDCPP	Tris(1,3-dichloro-2-propyl) Phosphate
TEP	Triethyl Phosphate
TERA	Toxicology Excellence for Risk Assessment
TMCPPs	Tris monochloropropyl phosphates
TPhP	Triphenyl Phosphate
TPP	Triphenyl Phosphate
TWA	Time weighted average
U.S. EPA	U.S. Environmental Protection Agency
U.S. FDA	U.S. Food and Drug Administration
USGS	U.S. Geological Survey
VP	Vapor pressure
WWTF	Waste water treatment facility

## 1 Introduction

This document compiles available human exposure information on the following four flame retardants:

- Tris(1,3-dichloro-2-propyl) phosphate (TDCPP); CASN 13674-87-8
- Tris(chloropropyl) phosphate, mixture of isomers (TCPP); CASN 13674-84-5, 76649-15-5, 76025-08-6, 6145-73-9, 26248-87-3
- Triethyl phosphate (TEP); CASN 78-40-0
- Triphenyl phosphate (TPP or TPhP); CASN 115-86-6

Flame retardant chemicals are added to materials to increase a product's resistance to ignition or to decrease the spread of flames. They are used in many different types of consumer products, including upholstery and mattresses, toys, children's products, electrical devices, appliances, building materials, and apparel. Various flame retardants or their metabolites have been detected in human fluids or tissues, indicating human exposure and absorption of at least some of these chemicals.

Toxicology Excellence for Risk Assessment (TERA) reviewed available literature and data relating to human exposure of the selected flame retardants. Data were obtained from assessments of the flame retardants prepared by United States (U.S.) government agencies and other authoritative bodies. We also searched the scientific literature for available data on human exposures and environmental measurements of flame retardants. In particular, data on concentrations in indoor air and dust, concentrations in potential drinking water as well as consumer products, including children's products, upholstered furniture, mattresses, apparel, household products, building materials, and electronics were sought. The information is compiled by "media" with data on measured concentrations identified in ambient air, indoor air, household dust, drinking water (and surface and groundwater), and food presented in tables. Available measurements of concentrations in consumer products, such as electronics, furniture, mattresses, toys, and building materials, are also presented. Results of available biomonitoring studies and exposure estimates, if any, are also included. Appendix A includes a description of the literature search strategy, key words, and databases searched.

It should be noted that this report compiles data from a variety of sources. We have not evaluated the quality of the studies and their results; rather we included all the relevant data we found. The estimates described in the exposure assessment sections are presented "as is" without a detailed analysis and critique of the methodology, assumptions, or underlying data quality. Further review on the quality and representativeness of these studies would be needed before using these data to estimate human exposures.

In reviewing the results and compilation of the available literature, it is apparent that there is a dearth of quality exposure information for these flame retardants to quantify human exposure. We observed several common elements from our review.

***There is a basic lack of monitoring data in environmental media for these chemicals.***

The U.S. Geological Survey (USGS) has conducted sampling for some of the flame retardants in drinking water and U.S. waters, but there is no systematic or routine monitoring in place by the federal government. Most of the studies we identified focused on measurements in heavily industrialized rivers where, presumably, contamination was suspected due to manufacturing. Several studies noted the ability of treatment to remove particular flame retardants from drinking water influent or manufacturing effluent. For some flame retardants, treatment reduced concentrations and in other cases it did not.

***Much of the available information is from studies outside of the U.S.***

We found limited U.S. data for these flame retardants. Data from other countries may introduce uncertainty into exposure estimates because particular flame retardant levels in other countries may not be representative of products, flame retardants, and building parameters found in the U.S. Within the U.S., California has traditionally had more stringent flame retardant regulations, and levels of flame retardants in dust in California may be higher than in other parts of the country.

***Limited data on emission or migration rates from products and materials containing the flame retardant chemicals.***

Unlike concentrations in environmental media (e.g., air, water, dust), flame retardant concentrations measured in consumer products and building materials cannot be used directly as a proxy for concentration levels to which consumers are exposed. Any product that contains a flame retardant has the potential to contribute to household dust levels. To develop realistic consumer exposure concentrations, the flame retardant levels in these products would need to be paired with experimental or monitoring results that reflect the availability of the specific compound to leave these products and be available to enter the body. These data are not generally available. Alternatively, emission or migration rates could be used to model or estimate exposures for:

- Near-field exposure for persons proximate to the product
- Far-field exposure in the room and building
- Long term rate of flame retardant input to the space

For example, the work of Carlsson et al. (2000) detecting and measuring TPP in air sampled in the breathing zone of a computer user could be used to estimate exposure. Another example is

the work of Saito et al. (2007) measuring the actual rate of migration of TPP from the outer case of an electronic device to a solid extraction disk.

Without the data to make the link between concentrations and exposure levels, the data on flame retardant content in a product provides only a qualitative indication of the ultimate availability of that flame retardant to be released into the indoor environment, either into the air or dust. The rate of release will depend upon the individual products, their physical and chemical properties, and how they are used.

***Flame retardants used in many products come in contact with people's skin, but there is uncertainty associated with percutaneous exposure due to a lack of testing.***

An area of uncertainty is exposure potential from dermal contact with or without ingestion from mouthing of objects containing a flame retardant. The general mechanism for diffusion out of treated plastics and into dust is relatively well understood based on first principle models (e.g., : <http://www.epa.gov/nrmrl/appcd/mmd/i-sovc.html>). Similarly, the potential for hand-to-mouth transfer of dust is understood and established. This is not the case for dermal or mouthing transfer of flame retardants from contact with treated objects. The potential dermal or mouth exposure to a flame retardant as it is diffusing and being "expressed" from the treated plastic is not well understood or documented. The flame retardant molecules will have some rate of dermal penetration if they are in contact with the skin. This exposure route may be particularly important for children's items, such as changing table pads, infant sleep positioners, portable crib mattresses, and nursing pillows, as well as clothing. Transfer and ingestion via child-mouthing of these items, toys, and treated furniture in general is another area of uncertainty.

***Changes in usage of particular flame retardants as manufacturers and government agencies identify potential problems and substitute alternative flame retardants.***

As government agencies, manufacturers, and consumers are more aware of flame retardant usage and potential exposures, usage patterns change, with new chemicals substituting for old or different concentrations and chemicals used in new products. Past measurements may not be representative of current conditions, with changing product content or usage patterns. Also, the time frame of these exposure events suggests that the exposure potential could continue to grow for months or years after the initial use and placement of treated objects indoors.

***Both dust and vapors may contribute to total concentrations in indoor air.***

Depending upon the flame retardant's properties, a particular flame retardant may or may not be anticipated to become airborne as a vapor out of organic substrates indoors. However, particulates, such as dust, are quite mobile and can become airborne. The flame retardant could be distributed within the indoor environment in dust on surfaces with a lesser amount of the

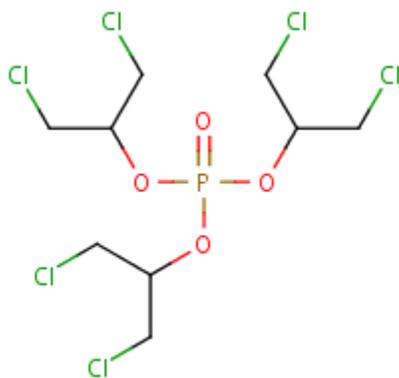
flame retardant containing dust being airborne. An exception to this rule of low airborne levels would be relatively “dusty” rooms where the dust has been allowed to accumulate and/or activities occurs that tend to continually entrain the dust into the air. In these indoor environments, relatively high levels of airborne flame retardant (dissolved in dust) may be found. This, as well as computer equipment and furniture, may explain some rare reports of relatively high levels of flame retardant in the indoor air of an office or hospital ward (see for example, Marklund et al., 2005a).

## 2 Tris(1,3-dichloro-2-propyl) Phosphate (TDCPP) (CAS 13674-87-8)

### 2.1 TDCPP Chemical and Physical Properties

Tris(1,3-dichloro-2-propyl) Phosphate (TDCPP) is a widely used flame retardant and is a clear, viscous liquid with a faint odor (HSDB, 2013). The water solubility value of 7.0 mg/L at 24 °C indicates that TDCPP has low solubility in water but it is soluble in most solvents and will adsorb to solids and sediments in water based on an estimated soil-water coefficient ( $K_{oc}$ ) value of 1100 (HSDB, 2013). Measured vapor pressure values for TDCPP range from  $1 \times 10^{-2}$  to  $1.4 \times 10^{-3}$  at 30 °C and 25 °C, respectively. These values indicate that TDCPP will exist in both the vapor and particulate phases in the atmosphere (HSDB, 2013). Significant volatilization from water surfaces is not expected based on an estimated Henry's Law constant of  $2.61 \times 10^{-9}$  atm·m<sup>3</sup>/mol at 25 °C (HSDB, 2013).

**Figure 2-1. Molecular Structure of TDCPP** (ChemIDPlus, 2014)



**Table 2-1. CAS Registry Number and Synonyms for TDCPP** (ChemIDPlus, 2014; CalEPA, 2011)

<b>CAS registry/RN</b>	13674-87-8
<b>Synonyms</b>	Fyrol FR-2, Antiblaze 195; TDCPP; TDCP; chlorinated Tris; 2-Propanol, 1,3 dichloro-, phosphate (3:1); Tris[2-chloro-1-(chloromethyl)ethyl]phosphate; Tris(1,3dichloroisopropyl)phosphate

**Table 2-2. Physical and Chemical Properties of TDCPP** (ChemIDPlus, 2014; HSDB, 2013)

Molecular Formula	C <sub>9</sub> H <sub>15</sub> Cl <sub>6</sub> O <sub>4</sub> P
Molecular Weight	430.90
Melting Point	27 °C
Boiling Point	236-237 °C (at 5 mm Hg)

Density	1.48 kg/L (at 25 °C)
Solubility (in water)	7.0 mg/L (at 24 °C)
Log K <sub>ow</sub>	3.65
Vapor Pressure (range of values)	1 x10 <sup>-2</sup> torr (at 30 °C) (IPCS, 1998) 1.4 x10 <sup>-3</sup> torr (at 25 °C) (Cobb and Bhooshan, 2006) 2.7 x10 <sup>-5</sup> torr (at 25 °C) treated foam (Cobb and Bhooshan, 2005)
Henry's Law Constant	2.61 x10 <sup>-9</sup> atm- m <sup>3</sup> /mol (at 25 °C)

Semi-Volatile Organic Compounds (SVOCs), such as TDCPP, are typically characterized by a relatively high molecular weights, low vapor pressure/volatility, low or moderate solubility in water and a high octanol-water partition coefficient (K<sub>ow</sub>). To a significant degree, these properties determine the fate of TDCPP in the environment, which impacts the potential for human exposure. The high K<sub>ow</sub> means it will be lipophilic and partition into any sediment layers in an environmental water column. In the indoor environment, it will not be highly present in the air as a vapor but will readily partition into and be present in available organic rich substrates like house dust.

Because of its properties and fate in the indoor environment, the vapor pressure (VP) of pure TDCPP can be misleading in estimating its potential to become airborne as a vapor. Taking the highest measured vapor pressure at an elevated but possible ambient temperature of 30°C (86°F) results in the following estimation of a maximum or saturated airborne concentration:

$$(0.01\text{torr}/760\text{torr}) (1,000,000) (430.9/24.4) = 232 \text{ mg/m}^3$$

All monomers (including monomeric flame retardants) embedded within polymer matrices will move out of that matrix into surrounding media following classic laws of diffusion. Given a time frame of many months or a few years, a significant portion of the monomer will diffuse out of the polymer.

In reality, TDCPP would never be expected to exist as a pure material indoors. Initially, it is embedded in the polymer matrix of a material and, after it diffuses out of the matrix, it comes to the surface. TDCPP is then associated with house dust (common house dust is made up in large part of human skin cells that have been shed, which are essentially organic in nature). As such, house dust is essentially an organic substrate. In this case, the 0.01 torr VP at 30°C (86°F) of pure TDCPP is highly attenuated via what is known as Raoult's Law:

$$(\text{VP of Pure TDCPP})(\text{Mole Fraction of TDCPP in substrate}) = \text{VP over the substrate}$$

This is for "ideal mixtures" of TDCPP in various substrates (e.g., polyurethane [PU] foam or typical house dust). For real world mixtures, a thermodynamic activity coefficient (AC) is added.

(VP of Pure TDCPP)(Mole Fraction of TDCPP in substrate)(AC) = VP over the substrate

Indeed, one study reports a 25°C vapor pressure over foam of  $2.7 \times 10^{-5}$  torr versus  $1.4 \times 10^{-3}$  torr (at 25°C) for the pure TDCPP (Cobb and Bhooshan, 2005). This represents an attenuation of over 98%.

Some work has been done to measure or estimate TDCPP releases from some products. ECHA, in its risk assessment (ECHA, 2009), included an appendix (Appendix B) that presented some test results on TDCPP studies of PU foam, and estimated release rates. Saito et al. (2007) measured emission rates of TDCPP from a computer monitor (see Section 3.3.5).

## 2.2 TDCPP Uses

TDCPP is a high production volume chemical used as an additive flame retardant (CalEPA, 2011). Specifically, it is used in flexible PU foams in flame retardant furniture and other products, such as textiles, plastics, resins, and rubbers (CalEPA, 2011). It is also used secondarily as a plasticizer in a number of these same product types (CalEPA, 2011; HSDB, 2013) and as an additive in hydraulic fluids, solvents, extraction agents, antifoam agents, adhesives, and coatings for electronic devices (ATSDR, 2009).

TDCPP was voluntarily removed from use in children's sleepwear in the late 1970s, but TDCPP still has widespread use in other children's products (CalEPA, 2011; Stapleton et al., 2011). Annual demand for TDCPP was estimated at 10-50 million pounds in 2006 (ATSDR, 2009).

With the phase-out of pentabromodiphenyl ether (pentaBDE) as a fire retardant nation-wide and its ban in California, the use of TDCPP has grown significantly, especially in flexible PU foam (CalEPA, 2011). TDCPP is now one of the most commonly used flame retardants found in upholstered furniture (Stapleton et al., 2009) and baby products with PU foam (Stapleton et al., 2011).

## 2.3 TDCPP Human Exposure

TDCPP is found throughout the environment in various media including indoor and ambient air, water, and food. It is also found in consumer products, child-specific products, furniture, and electronics. TDCPP in PU foam or any polymer matrix is not chemically bound to the polymer. Thus, it will continually diffuse out of plastics, electronics, or PU foam-containing products and into indoor environments especially in dust (Marklund et al., 2003). Due to its ubiquitous presence in, and relative ease of release from, foam products, TDCPP has been detected in dust in homes, offices, automobiles, and daycare centers worldwide. Concentrations of TDCPP in various media and a summary of exposure assessments and estimates found in the literature are presented below.

The available literature on concentrations of TDCPP in relevant environmental media and consumer products is heavily focused on concentrations in dust, reflecting what is reasonably considered to be perhaps the most important exposure pathway of concern for children and others. Children's overall exposure to flame retardants will be influenced by their hand-to-mouth behavior and subsequent ingestion of TDCPP containing material, particularly dust. Frequent hand washing is associated with lower flame retardant levels on the hands (Stapleton et al., 2014). Children can also receive exposure to this flame retardant via dermal contact with polymer surfaces containing TDCPP, especially bedding and changing areas.

### ***2.3.1 TDCPP in Indoor and Ambient Air***

Likely sources of phosphate ester flame retardants in indoor air include: polyvinylchloride (PVC) plasticizers, floor polishes, electronics (plastic cabinets), polyurethane foams, upholstery, furniture, and textiles (ATSDR, 2012, Reemtsma et al., 2008, Canada Gazette, 2011; Marklund et al., 2005). Both particulates and vapors contribute to exposure (Garcia et al., 2007 as cited by ATSDR, 2012).

Relatively little TDCPP is anticipated to become airborne as a vapor out of organic substrates indoors. However, particulates, such as dust, are quite mobile and can become airborne. Thus, TDCPP could be distributed within the indoor environment in dust on surfaces with a lesser amount of the TDCPP containing dust being airborne. An exception to this rule of low airborne levels would be relatively "dusty" rooms where the dust has been allowed to accumulate and/or activities occurs that tend to continually entrain the dust into the air. In these indoor environments, relatively high levels of airborne TDCPP (dissolved in dust) may be found. This, as well as computer equipment and furniture, may explain some rare reports of relatively high levels of TDCPP in the indoor air of an office or hospital ward (Marklund et al., 2005a).

TDCPP air concentrations (particulates and vapors) have been measured in offices, other workplaces, child care centers, electronic dismantling centers, cars, and houses, as well as various public places (Saito et al., 2007; Marklund et al., 2005a; Bradman et al., 2012; Hartmann et al., 2004). The TDCPP concentrations measured in indoor air range from 0.04-150 ng/m<sup>3</sup> (Table 2-3) (Saito et al., 2007; Yang et al., 2014, Hartmann et al., 2004; Bradman et al., 2012; Reemtsma et al., 2008; Marklund et al., 2005a; Kanazawa et al., 2010; Staaf and Ostman, 2005a,b). Reemtsma et al. (2008) reviewed the available literature and reported TDCPP air concentrations from several studies (Hartmann et al., 2004; Marklund et al., 2005a; Saito et al., 2007; Staaf and Ostman, 2005a). They calculated a mean of 21,000 ng/m<sup>3</sup> from the reported study values.

Stauffer Chemical Co. (1983, cited in ATSDR, 2009) conducted a retrospective cohort study to examine the exposure of 289 workers employed in the manufacture of TDCPP with time-

weighted average (TWA) exposure levels of 400-500 ng/m<sup>3</sup>. The authors did not find a correlation between TDCPP exposure and any medical conditions (ATSDR, 2009).

**Table 2-3. TDCPP Concentrations in Indoor Air**

Country	Location	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
United States	California, Child care centers	Indoor air	Mean: 0.59 ng/m <sup>3</sup> Max: 0.1-1.99 ng/m <sup>3</sup>	Bradman et al., 2012	PU foam cartridges, room conditions recorded during sampling
	TDCPP manufacturing plant	Indoor air	Estimated 400-500 ng/m <sup>3</sup> TWA	Stauffer, 1983 as cited in ATSDR, 2009	Occupational retrospective cohort study
Sweden	Stockholm, Car	Indoor air	5 ng/m <sup>3</sup>	Staaf and Ostman, 2005a,b	Stationary sampler with SPE cartridge containing an aminopropyl silica phase (25 mg, 1 ml)
	Stockholm, electronic dismantling facility	Indoor air	7 ng/m <sup>3</sup>		
	Homes	Indoor air	<0.5 ng/m <sup>3</sup>	Marklund et al., 2005a	Stationary sampler with SPE Cartridge
	Day care center	Indoor air	59 ng/m <sup>3</sup>		
	Hospital ward	Indoor air	150 ng/m <sup>3</sup>		
	Radio shop, textile shop	Indoor air	<0.2 ng/m <sup>3</sup> <0.4 ng/m <sup>3</sup>		
	Prison	Indoor air	6 ng/m <sup>3</sup>		
	University lobby	Indoor air	1.7 ng/m <sup>3</sup>		
Office	Indoor air	35 ng/m <sup>3</sup>			

Country	Location	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
Sweden	Furniture store	Indoor air	0.8 ng/m <sup>3</sup>		
	Plastics factories	Indoor air	<0.5 ng/m <sup>3</sup>		
	Laboratory	Indoor air	<0.3 ng/m <sup>3</sup>		
	Public places, hotel, library, dance hall, bowling alley	Indoor air	Range: <0.2-<0.7 ng/m <sup>3</sup>		
Switzerland	Zurich, Cars, furniture stores, offices, electronics stores, theater	Indoor air	<0.11 ng/m <sup>3</sup>	Hartmann et al., 2004	TDCPP not detected in any sample, MDL was 0.11 ng/m <sup>3</sup>
China	Hangzhou, Offices	Indoor air	Mean: 2.25 ng/m <sup>3</sup> Median: 0.63 ng/m <sup>3</sup> Range: 0.04-14.30 ng/m <sup>3</sup>	Yang et al., 2014	Particulate matter filter
Japan	Tokyo, House	Indoor air	Range: ND-0.60 ng/m <sup>3</sup>	Saito et al., 2007	Sampled using quartz fiber Filter (47 mm), first stage and a solid phase extraction disk (empore <sup>tm</sup> Disk C18, 47mm), second stage. MDL = 0.72 ng/m <sup>3</sup>
	Tokyo, New house	Indoor air	1.3 ng/m <sup>3</sup>		
	Tokyo, Office	Indoor air	Range: ND-8.7 ng/m <sup>3</sup>		
	Sapporo, House	Indoor air	Median: <MDL ng/m <sup>3</sup> Range: <MDL-61.4 ng/m <sup>3</sup>	Kanazawa et al., 2010	MDL = 11.5 ng/m <sup>3</sup> ; Sampled using a solid phase extraction disk (empore <sup>tm</sup> Disk C18, 47mm)

Country	Location	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
Austria	Elementary schools	Indoor air	Mean: 90,000 ng/m <sup>3</sup> (90 µg/m <sup>3</sup> ) Max: 4,200,000 ng/m <sup>3</sup> (4,200 µg/m <sup>3</sup> )	Hutter et al., 2013	Sampled 2 classrooms in spring and fall; used glass filter attached to Digital High Volume sampler for PM <sub>10</sub>

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

max – maximum; TWA – time weighted average; DL- detection limit; ND – non detect; MDL – method detection limit; SPE – Solid Phase Extraction

Less data were located regarding TDCPP in ambient air, and measured concentrations were much lower than those seen in indoor environments. TDCPP was measured outside child care centers at concentrations up to 4.4 ng/m<sup>3</sup> in the U.S. (Bradman et al., 2012) and outside areas where hydraulic fluids are used (airports, newly constructed homes and buildings) at concentrations up to 4.7 ng/m<sup>3</sup> in Japan (Haraguchi et al., 1985 as cited in ATSDR, 2009). See Table 2-4 below.

**Table 2-4. TDCPP Concentrations in Ambient Air**

Country	Location	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
United States	California, Child care centers	Outdoor air	Mean: 0.72 ng/m <sup>3</sup> Maximum: 4.4 ng/m <sup>3</sup>	Bradman et al., 2012	PUF cartridges, collected in outdoor play area
Japan	Kitakyushu District	Outdoor ambient air, near hydraulic fluid use	4.7 ng/m <sup>3</sup> (0.0047 µg/m <sup>3</sup> )	Haraguchi et al., 1985	High-volume sampler fitted with a glass fiber filter and XAD-7 resins (20g)

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses. PUF = polyurethane foam

### 2.3.2 TDCPP in Water

No measurements of TDCPP concentrations in U.S. drinking water were located. TDCPP concentrations measured in finished drinking water in Canada ranged from 0.1-23 ng/L (Williams and Lebel, 1981; Williams et al., 1982; Lebel et al., 1981 as cited in HSDB, 2013).

Measurements of TDCPP in ground and surface waters used for drinking water sources in the U.S. (25 states and Puerto Rico) were all below the reporting limit of 500 ng/L (Focazio et al., 2008; Barnes et al., 2008). TDCPP measurements ranged from non-detectable to 600 ng/L in streams in the U.S. (Lee and Rasmussen, 2006; Stackelberg et al., 2004; Kolpin et al., 2002; Kolpin et al., 2004). Concentrations of TDCPP before and after drinking water treatment were not available for comparison. Concentrations of TDCPP have also been measured in surface waters in Canada, Germany, Japan, the Netherlands, and Italy, in snow in Sweden, and snow and rain in Germany. See Table 2-5 below.

**Table 2-5. TDCPP Concentrations in Water**

Country	Location	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
United States	25 States and Puerto Rico	Ground and surface water; 74 raw, untreated drinking water sources	All measured below 500 ng/L Reporting limit: 500 ng/L (0.5 µg/L)	Focazio et al., 2008; Barnes et al., 2008	USGS – sites known or suspected to have some human and/or animal wastewater sources upstream or up gradient
	Kansas, Johnson County 2002-2003	Streams	500 ng/L (0.5 µg/L)	Lee and Rasmussen, 2006	< 500 m downstream from the facility
		Downstream from WWTF	Mean: 400 ng/L (0.4 µg/L) Max: 600 ng/L (0.6 µg/L)		
	Geo Survey 30 states	Streams	Median: 100 ng/L (0.1 µg/L) Max: 160 ng/L (0.16 µg/L)	Kolpin et al., 2002	
	Iowa	Streams	Range: ND-400 ng/L (ND-0.4 µg/L)	Kolpin et al., 2004	
	Urbanized area	Stream	Range: 60-250 ng/L (0.06-0.25 µg/L)	Stackelberg et al., 2004	
Canada	12 municipalities	Finished drinking water	Range: 0.1-15.7 ng/L	Williams et al., 1982	Water from the Great Lakes

Country	Location	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
Canada	6 Ontario municipalities	Finished drinking water	Range: 0.2-1.8 ng/L	Lebel et al., 1981 as cited in HSDB, 2013	Ontario water treatment plants
	29 municipalities	Finished drinking water	Range: 0.3-23 ng/L	Williams and Lebel, 1981	Water treatment plants, sources include rivers, lakes and ground water
Germany	Hessen - Schwarzbach, Modau, Winkelbach, Weschnitz	Fresh water	Mean: 117 ng/L Median: 80 ng/L Max: 1284 ng/L	Quednow and Puttman, 2008	
	Elbe estuary plume	River estuary plume	~3 ng/L	Andresen et al., 2007	
	Kleiner Feldberg	Rain	Median: 24 ng/L Max: 31 ng/L	Regnery and Puttmann, 2009	
		Snow	Median: 40 ng/L Max: 113 ng/L		
	Wasserkuppe	Rain	Median: 2 ng/L Max: 2 ng/L		
		Snow	Median: 5 ng/L Max: 23 ng/L		
	Bekond	Rain	Median: 9 ng/L Max: 53 ng/L	Regnery and Puttmann, 2009	
		Snow	Median: 17 ng/L Max: 83 ng/L		
	Schmuecke	Rain	Median: 17 ng/L Max: 25 ng/L		
		Snow	Median: 12 ng/L Max: 52 ng/L		
Frankfurt	Rain	Median: 7 ng/L Max: 32 ng/L			

Country	Location	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
Japan	Yodo River	River	Polluted area Range: 100-900 ng/L (0.1-0.9 µg/L) Less polluted area Range: 0-700 ng/L (0-0.7 µg/L)	Fukushima et al., 1992	Trend of concentration from 1976-1990
Netherlands	Rhine Delta	River	Range: 0-55 ng/L (0-0.055 µg/L)	Hendricks et al., 1994	
	Ruhr, Mohne, Lenne Rivers, and tributaries	River	~50 ng/L	Andresen et al., 2004	
	Rhine	River	Range: 13-36 ng/L		
	Lippe	River	17 ng/L		
	Meuse River and tributaries	River	Range: 150-450 ng/L (0.15-0.45 µg/L)	Jeuken and Barreveld, 2004	
Sweden	Finland Municipal airport	Snow	12 ng/L Road 1	Marklund et al., 2005b	Collected 2 m from major intersection
		Snow	230 ng/L Road 2		Collected 100 m from major intersection
		Snow	8 ng/L Road 3		Collected 250 m from major intersection
		Snow	5 ng/L Airport 1		Collected at the side of runway
		Snow	4 ng/L Airport 2		Collected at the side of runway
		Snow	15 ng/L Airport 3		Collected in parking lot

Country	Location	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
Italy	Albano - Volcanic Lake	Surface water	Monthly means Range: 5-60 ng/L	Bacaloni et al., 2008	
			Range: 20-1335 ng/L Large range in March		
	Vico - Volcanic Lake	Surface water	Monthly means Range: 2-35 ng/L		
	Martignano - Volcanic Lake	Surface water	Monthly means Range: 2-23 ng/		

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

WWTF – waste water treatment facility; max – maximum; ND – non detect; m – meter

### 2.3.3 TDCPP in Food

TDCPP was not detected in any of the foods sampled in market basket samples collected from grocery stores in 30 different sectors of the U.S. (Daft, 1982).

### 2.3.4 TDCPP in Dust

Given TDCPP's properties and the quantity of data found on dust, it would appear that the dominant mechanism for human exposure is diffusion of TDCPP out of materials to the surface where it partitions into dust, which can then be ingested. TDCPP has been measured in dust in a variety of settings. Several studies (Stapleton et al., 2009, 2014; Meeker and Stapleton, 2010, Meeker et al., 2013; Carignan et al., 2013) found TDCPP in a majority of the dust samples (vacuum cleaner bag collection) they analyzed in Boston homes with concentrations ranging from less than 7 ng/g to a high of 56,090 ng/g. Dodson et al. (2012) reported TDCPP concentrations in California houses ranging from 730-24,000 ng/g (2006) and 920-44,000 ng/g (2009). TDCPP concentrations in Canadian homes ranged from 120-77,000 ng/g in fresh dust and 120-77,000 ng/g in household dust from a vacuum cleaner (Fan et al., 2014). House dust concentrations of TDCPP have also been reported in homes in Belgium, Japan, Germany, Sweden, Egypt, and Spain; only in Japan were house dust levels greater than that seen in the U.S. and Canada. The highest level reported in homes in Japan was 864,040 ng/g in floor dust (Araki et al., 2014).

Concentrations ranging from 730 ng/g to 70,931 ng/g have been measured in California child care centers (Bradman et al., 2012; Dodson et al., 2012). Carignan et al. (2013) measured levels of TDCPP in office space in the U.S. (60-72,00 ng/g). Flame retardant concentrations have been measured in a U.S. commercial airplane (Allen et al., 2013). TDCPP concentrations ranged from 580-19,000 ng/g in floor dust and 1,200-22,000 ng/g in air vent dust in this airplane (Allen et al., 2013).

TDCPP has been detected and measured in dust of vehicles in several countries. TDCPP is used in PU foam in car seats (Brommer et al., 2012; Stapleton et al., 2009). Carignan et al. (2013) measured levels of TDCPP in vehicles (<30-326,000 ng/g). Abdallah and Covaci (2014) measured TDCPP levels ranging from less than the limit of quantification to 283 ng/g in cars in Egypt. Brommer et al. (2012) found a maximum of 620,000 ng/g in the dust of German cars.

Concentrations of TDCPP have been measured in a variety of additional indoor environments, including offices and other work places, shops, hospitals, hotels and other public places in several different countries. Concentrations in these locations ranged widely, with the maximum concentration reported of 56,200 ng/g (Van den Eede et al., 2011).

Reemtsma et al. (2008) reviewed the literature at that time and reported TDCPP dust concentrations measured in several studies (Garcia et al., 2007; Marklund et al., 2003; Ingerowski et al., 2001) and calculated a mean of 5,300 ng/g from the reported study values.

Compared to other media, given incidental ingestion dust rates of between the range of 50 to 100 mg per day, dust appears to be a dominant environmental conduit for potential human exposure to TDCPP. See Table 2-6 below.

**Table 2-6. TDCPP Concentrations in Dust**

Country	Location	Media/Area	TDCPP Concentrations <sup>1</sup>	Reference	Notes
United States	Boston, MA	House	Geo Mean: 1,890 ng/g Range: <90-56,090 ng/g	Stapleton et al., 2009	Household vacuum cleaner bag collection
		House	Geo Mean: 1,880 ng/g Range: <107-56,090 ng/g	Meeker and Stapleton, 2010	Household vacuum cleaner bag collection
		House, main living area	Geo Mean: 4,210 ng/g (4.21 µg/g) Range: 560-30,600 ng/g (0.56-30.6 µg/g)	Carignan et al., 2013	Vacuum collection through cellulose extraction thimble
		House, bedroom	Geo Mean: 1,400 ng/g (1.40 µg/g) Range: 270-18,200 ng/g (0.27-18.2 µg/g)		

Country	Location	Media/ Area	TDCPP Concentrations <sup>1</sup>	Reference	Notes	
United States		Office	Geo Mean: 6,060 ng/g (6.06 µg/g) Range: 60-72,00 ng/g (0.06-72.0 µg/g)			
		Vehicle	Geo Mean: 12,500 ng/g (12.5 µg/g) Range: <30-326,000 ng/g (<0.03-326 µg/g)			
		House	Geo Mean: 74.2 ng/g Range: <7.0-530 ng/g	Stapleton et al., 2014		Hand wipe samples
		House	Geo Mean: 2,730 ng/g Range: 621-13,110 ng/g			Household vacuum cleaner bag collection
	California, San Francisco Bay area	House	Median: 2,800 ng/g Range: 730-24,000 ng/g	Dodson et al., 2012	2006 collection, vacuum cleaner with cellulose extraction thimble	
		House	Median: 2,100 ng/g Range: 920-44,000 ng/g		2011 collection, vacuum cleaner with cellulose extraction thimble	
	California,	Child care centers	Mean: 6,189 ng/g Median: 2,265 ng/g Range: 765-70,931 ng/g	Bradman et al., 2012	Measured with real time air monitoring	
	Airplane	Floor	Mean: 2,100 ng/g Range: 580-19,000 ng/g	Allen et al., 2013	Vacuum cleaner collection	
		Air vent	Mean: 5,600 ng/g Range: 1,200-22,000 ng/g			
Canada	134 Urban homes	House	Median: 2,700 ng/g (2.7 µg/g) Range: 120-7,7000 ng/g (0.12-77 µg/g)	Fan et al., 2014	Fresh/active dust collected using a Pullman Holt vacuum sampler by a trained technician	
			Median: 2,000 ng/g (2.0 µg/g) Range: 110-101,000 ng/g (0.11-101 µg/g)		Household vacuum cleaner collection	

Country	Location	Media/ Area	TDCPP Concentrations <sup>1</sup>	Reference	Notes
Belgium	Flemish region	House	Mean: 570 ng/g (0.57 µg/g) Median: 360 ng/g (0.36 µg/g) Range: 80-6,640 ng/g (<0.08-6.64 µg/g)	Van den Eede et al., 2011	Vacuum dust samples
		Carpenter workshop, second-hand store, electronics stores, laboratory	Mean: 4,610 ng/g (4.61 µg/g) Median: 760 ng/g (0.76 µg/g) Range: 80-56,200 ng/g (<0.08-56.2 µg/g)		
Japan		House, floor	Median: 2,800 ng/g (2.8 µg/g) Max: 864,040 ng/g (864.04 µg/g)	Araki et al., 2014	Hand held vacuum cleaner
		House, multi-surface	Median: 10,810 ng/g (10.81 µg/g) Max: 593,140 ng/g (593.14 µg/g)		
	Sapporo	House, floor	Median: 4,000 ng/g (4 µg/g) Range: 1,200-105,000 (<1.2-105 µg/g)	Kanazawa et al., 2010	Vacuum cleaner bag collection
		House, multi-surface	Median: 22,300 ng/g (22.3 µg/g) Range: 5,800-127,000 (5.8-127 µg/g)		
Germany	Various	Car	Range: <80-620,000 ng/g	Brommer et al., 2012	
		House	Range: <80-110 ng/g		
		Office	Range: <80-290 ng/g		
Sweden	Various	Houses	Range: 390-1,100 ng/g (0.39-1.1 µg/g)	Marklund et al., 2003	Vacuum cleaner bag collection
		Day care center	1,800 ng/g (1.8 µg/g)		
		Hospital, wards, office	Range: 560-2,100 ng/g (0.56-2.1 µg/g)		

Country	Location	Media/ Area	TDCPP Concentrations <sup>1</sup>	Reference	Notes	
Sweden		Radio shop, textile shop	Range: 200-590 ng/g (0.2-0.59 µg/g)			
		Hotel	910 ng/g (0.91 µg/g)			
		Prison	53,000 ng/g (53 µg/g)			
		University lobby	5,700 ng/g (5.7 µg/g)			
		Office	67,000 ng/g			
		Computer screen	290,000 ng/m <sup>2</sup>			Wipe test samples, location of computer not reported
		Computer cover	170,000 ng/m <sup>2</sup>			Wipe test samples, location of computer not reported
		Public places, hotel, library, dance hall, aircraft	Range: 840-7,000 ng/g (0.84-7 µg/g)			Vacuum cleaner bag collection
			Mean: 2,300 ng.g (2.3 µg/g)	Bergh et al., 2012 as cited in Fan et al., 2014		
Egypt	Assiut, Egypt	Car	Median: 61 ng/g Range: <LOQ-283 ng/g	Abdallah and Covaci, 2014	LOQ = 3 x SD of blank values divided by 50 mg (value not reported); collected with a	
		House	Median: 72 ng/g Range: <LOQ-557 ng/g			
		Office	Median: 49 ng/g Range: <LOQ-490 ng/g			

Country	Location	Media/ Area	TDCPP Concentrations <sup>1</sup>	Reference	Notes
Egypt		Micro-environment (coffee shops, restaurants, supermarkets)	Median: 416 ng/g Range: <LOQ-1,616 ng/g		dust buster vacuum
Spain	Northwest of Spain	House	Avg: 350 ng/g (0.35 µg/g)	Garcia et al., 2007	Household vacuum cleaner bag collection

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

avg – average; max – maximum; geo mean – geometric mean; min – minimum; LOQ- limit of quantification

### 2.3.5 TDCPP in Consumer Products

Concentrations of TDCPP measured in consumer products cannot be used directly as a proxy for concentration levels to which consumers are exposed. To develop realistic consumer exposure concentrations, the flame retardant levels in these products would need to be paired with experimental or monitoring results that reflect the availability of the compound to leave these products and enter the body. For TDCPP there is scant information on migration rates that would be needed to estimate actual exposure concentrations.

TDCPP has been found in flexible PU foams (automotive interiors, flame resistant furniture, and upholstery), textiles, plastics, resins, and rubbers and is a plasticizer in these same products (CalEPA, 2011; HSDB, 2013). It has been found in a variety of baby products (Stapleton et al., 2011). Hospital and prison mattresses are generally treated with TDCPP (Marklund et al., 2003). TDCPP is also used as an additive in hydraulic fluids, solvents, extraction agents, antifoam agents, adhesives, and coatings for electronic devices (ATSDR, 2009). Some of these products may be used as, or incorporated into, consumer products. Only limited work has been done and reported characterizing the concentrations of TDCPP in consumer products. Primary exposure routes for TDCPP in consumer products would be oral ingestion (e.g., children’s mouthing of materials or products, or incidental ingestion of dust) and potentially dermal exposure. See Table 2-7 below.

#### 2.3.5.1 TDCPP in Children and Baby Products

TDCPP was found in samples of foam from baby product collected by individuals in the U.S. and sent to Stapleton and colleagues for testing (Stapleton et al., 2011). Products included car seats, changing table pads, infant sleep positioner, portable crib mattress, nursing pillows, baby carrier, high chair, nursery rocking chairs/glidiers, baby walkers, baby carrier, and a bath

mat/sling. TDCPP was the most common flame retardant detected in these samples (36% of the 101 samples) at levels approximately 3-4% by product weight. Stapleton and colleagues (2011) reported a range of 2,400,000-124,000,000 ng/g (2.4-124 mg/g) with a mean of 39,220,000 ng/g (39.22 mg/g) of TDCPP in these various baby products and suggested that infants may have a greater exposure than adults given the prevalence of TDCPP in baby products. The Center for Environmental Health (2013) found TDCPP in 9 of 24 children’s foam nap mats that were purchased in 2012 (concentrations not reported).

**2.3.5.2 TDCPP in Furniture**

Stapleton et al. (2012) collected and analyzed 102 PU foam samples from residential couches purchased from 1985-2010 (samples were collected and donated by individuals from numerous cities in the U.S.). Flame retardants were detected in 85% of samples with TDCPP in 36% of the samples purchased between 1985-2005 and 52% of the samples purchased after 2005. TDCPP concentrations averaged  $4.487 \times 10^7$  ng/g (Stapleton et al., 2012) (Table 2-7). In 2009, Stapleton and colleagues analyzed 26 PU foam samples from chairs, pillows, couches, mattress pads, and a futon (samples were collected and donated by individuals from numerous cities in the U.S.). TDCPP was found in 15 of the 26 samples and was the most common flame retardant identified. The TDCPP percent by weight of the products ranged from 1-5% (Stapleton et al., 2009). Nagase et al. (2003) measured TDCPP concentrations of 4,500 ng/g and 10,200 ng/g in cushions.

**2.3.5.3 TDCPP in Electronic Products**

Kajiwara et al. (2011) extensively analyzed consumer electronic components in Japan for flame retardants, and found a maximum of 35 ng/g of TDCPP in an AC adapter from a laptop computer. Most other analyses were below the detection limit of 2 ng/g (Kajiwara et al., 2011). A chamber study of TDCPP emission rates from a computer monitor reported a rate of 280 ng of TDCPP per square meter of surface area per hour (Saito et al., 2007).

**Table 2-7. TDCPP Concentrations in Consumer Products**

Country	Item	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
United States	Chairs, pillows, couches, mattress pads, and a futon	Foam	1-5% by weight of product	Stapleton et al., 2009	Donated PU foam samples from numerous cities in U.S. TDCPP was found in 15 of the 26 samples

Country	Item	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
United States	1 Car seat, 1 changing table pad, 1 sleep positioner, 1 portable mattress, 10 nursing pillows, 1 baby carrier, 1 infant bath mat/sling	Foam	Mean: 39,220,000 ng/g (3.922mg/g) Range: 2,400,000-124,000,000 ng/g (2.4-124 mg/g)	Stapleton et al., 2011	Donated PU foam samples from numerous cities in U.S. TDCPP was found in 36% of 101 baby product samples
	Couches	PU foam	Avg: 44,870,000 ng/g (44.87 mg/g)	Stapleton et al., 2012	Donated PU foam samples from numerous cities in U.S. TDCPP found in 42 of 102 samples
Japan	Laptop computer	Chassis	<2 ng/g	Kajiwara et al., 2011	Items purchased new in Japan in 2008
		Keyboard top	<2 ng/g		
		PC boards	9.0 ng/g		
		Cooling fan and speakers	14 ng/g		
		AC adapter	35 ng/g		
		LCD panel	<2 ng/g		
	LCD TVs; purchased new in Japan in 2008	Rear cover	<2 ng/g	Kajiwara et al., 2011	Two TVs sampled
		Front cover	<2 ng/g		
		Power board	<2 ng/g		
		PC board for power and fluorescent	<2 ng/g		
		Other PC boards	<2 ng/g		
		LCD panel	<2 ng/g		

Country	Item	Media	TDCPP Concentrations <sup>1</sup>	Reference	Notes
Japan	Other products; purchased new in Japan in 2008	Curtains	<2 ng/g	Kajiwara et al., 2011	Two samples
		Electrical outlets	<5 ng/g		Two samples
		Insulation boards	<2-6 ng/g		Two samples
		Wallpaper	<20 ng/g		Four samples
	Household products	Cushion	4,500 ng/g (4.5 µg/g)	Nagase et al., 2003	
		Cushion	10,200 ng/g (10.2 µg/g)		
	Computer monitors	Chamber air	Range: ND-280 ng/m <sup>2</sup> /hr (ND-0.28 µg/m <sup>2</sup> /hr)	Saito et al., 2007	Emission rate from computer monitor

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are in shown in parentheses.

ND – not detected; hr – hour; avg – average; PU – polyurethane foam

## 2.4 TDCPP ADME and Biomonitoring Studies

TDCPP is well absorbed by all routes of exposure. Nomeir et al. (1981) administered 0.876 mg/kg of carbon-14 labeled Fyrol FR-2 (TDCPP) to rats both orally and dermally. In the dermal studies, Nomeir et al. (1981) reported that TDCPP was readily absorbed from the skin; however, the rate of absorption (time to maximum plasma concentration [T<sub>max</sub>]) was not evaluated. Similarly, greater than 90% of an oral dose was absorbed from the gastrointestinal tract. Neither study evaluated relative bioavailability (ascertained as the area under the plasma concentration-time curve [AUC]) to the parent compound or its metabolites following oral or dermal exposure. In a separate study, Hughes et al. (2001) evaluated dermal absorption in skin removed (and mounted in flow-through diffusion cells) from adult female hairless mice following application of 20, 100, or 200 pmol TDCPP. The greatest percent of the dose was absorbed between 6 and 12 hours. The 24-hour cumulative percent of the dose in the receptor fluid was 57, 45, and 39% for the 20, 100, and 200 pmol solutions, respectively. Reportedly, 28–35% of the applied radioactivity remained in the skin in this study.

A considerable amount of data are available on the distribution of TDCPP-derived metabolites, which are summarized in Table 2-8 below. TDCPP and its brominated analog bis(1,3-dichloro-2-propyl) phosphate (BDCPP) have been reportedly identified in human adipose tissue (LeBel and Williams, 1983 as cited in HSDB, 2013; LeBel et al., 1989); breast milk (Sundkvist et al., 2010); and also seminal fluid (Hudec et al., 1981). Nomeir et al. (1981) conducted an extensive analysis

of the metabolism and distribution of TDCPP in rodents. They reported that relative to intravenous administration, tissue distribution of TDCPP-derived radioactivity was unaffected by the size of the dose, with the liver and kidneys acquiring the highest concentration of radioactivity. In the reported series of experiments, Nomeir et al. (1981) observed that tissue/blood ratios of radioactivity were also similar regardless of exposure route. The single exception was higher lung concentrations observed after intravenous administration, which was interpreted as suggesting that significant first-pass metabolism occurs in the lungs that was not observed with other routes (Nomeir et al., 1981). This could be attributable to a high rate of metabolism in other tissues (e.g., liver metabolism with oral or intraperitoneal administration), which would result in formation of metabolites in sites outside the lungs, or a longer  $T_{max}$  associated with dermal or gastrointestinal absorption, which reduces peak metabolite concentrations in lung tissue. At 4 hours following dermal exposure, the relative tissue levels of radioactivity, in decreasing order, were: liver > lung > skin > blood > kidneys > adipose > muscle (Nomeir et al., 1981). Together these data suggest that tissue distribution is similar for oral and dermal routes of administration and independent of dose. Available data do not permit characterization of the bioavailability of parent TDCPP following either oral or dermal exposures (Nomeir et al., 1981; Lynn et al., 1981).

TDCPP is metabolized by oxidative and conjugation mechanisms in the liver, particularly NADPH-dependent microsomal mixed function oxidases and, to a lesser extent, glutathione-dependent conjugation reactions. Parent TDCPP was found to have an extremely short half-life of < 5 minutes following intravenous administration (Lynn et al., 1981). Following a single intraperitoneal injection of  $^{14}C$ -TDCPP to male Sprague-Dawley rats Lynn et al. (1981) reported that a major component (approximately 69% of the radioactivity on a molar basis) was identified as the metabolite (BDCPP) along with the dimethyl derivative of 1,3-dichloro-2-propyl phosphate. Another component was 1,3-dichloro-2-propanol. Thus, within minutes following intravenous administration, the radioactivity quantified in tissues and excreta is predominantly metabolites, not parent compound (Lynn et al., 1981).

Elimination of radiolabeled TDCPP is primarily by renal elimination, and to a lesser extent by biliary/fecal elimination. Nomeir et al. (1981) showed a total of 47% and 21% of an intravenously-administered, radiolabeled dose is excreted in the urine and feces, respectively, within 10 days of administration. In addition, as much as 20% of an intravenous dose is exhaled as  $CO_2$  within 24 hours of administration. The total body burden of TDCPP reportedly decreases rapidly after exposure with greater than 80% of the total dose excreted in the first 24 hours. However, traces of TDCPP-derived radioactivity, essentially metabolites, were still detected in most tissues 10 days after exposure (Matthews and Anderson, 1979). Nomeir et al. (1981) showed that the major metabolite excreted in the urine was BDCPP, which accounted for 67.2% of the total radioactivity in the urine. Of the remaining  $^{14}C$ -TDCPP-derived radioactivity, ~32% was present as an unidentified polar metabolite, 0.29% was identified as 1,3-dichloro-2-propyl

phosphate and 0.45% was unchanged parent compound. Like Nomeir et al., Lynn et al. (1980, 1981) also identified BDCPP as the major metabolite component of the urine (62% of urine radioactivity), feces (51% of radioactivity), and bile over a 5-day period following administration, with only trace amounts of the parent compound detected. Elimination of TDCPP-derived radioactivity in the bile exceeded excretion in feces, indicating that a portion of the material in bile was subject to enterohepatic recirculation (Matthews and Anderson, 1979).

In separate studies, mice were administered a single intravenous injection of  $^{14}\text{C}$ -TDCPP, and six hours later, the covalent binding of radioactivity to DNA, RNA, and protein from liver, muscle, and kidney was monitored. The highest concentration of radioactivity was found in the liver (Morales and Matthews, 1980). Lynn et al. (1981) observed that the 1,3-dichloro-2-propanol metabolite displayed mutagenic activity without S9 activation in the *S. typhimurium* TA100 tester strain for mutagenesis. BDCP and 1,3-dichloro-2-propyl phosphate did not display mutagenic activity in the TA100 strain either in the presence or absence of S9 activation (Lynn et al., 1981).

In summary, TDCPP is rapidly and extensively absorbed through the gastrointestinal tract (Herr et al., 1991; Nomeir et al., 1981; NTP, 1994; SOCMA, 1992; Mathews and Anderson, 1979); when applied dermally it is also rapidly absorbed through the skin of rats (Nomeir et al., 1981; Hughes et al., 2001). Lynn et al. (1981) reports that metabolism was the main form of elimination of TDCPP.

TDCPP has been measured at a concentration from not detected to 110 ng/g in human adipose tissue, 5,000-50,000 ng/mL in seminal fluid, and 0.0621-37.3 ng/mL in urine (Carignan et al., 2013; Dodson et al., 2014; Hudec et al., 1981; LeBel et al., 1989; Hoffman et al., 2014; Meeker et al., 2013). TDCPP was found at a mean concentration of 4.3 ng/g and a maximum of 5.3 ng/g in human breast milk (Sundkvist et al., 2010). Meeker et al. (2013) analyzed 106 urine samples from 45 men for BDCPP and diphenyl phosphate (DPP), metabolites of TDCPP. BDCPP was detected in 91% and DPP in 96% of urine samples. Paired house dust and urine samples showed a significant correlation between urinary BDCPP and TDCPP dust concentrations (Meeker et al., 2013). Carignan et al. (2013) found 100% detection of BDCPP in 31 urine samples (mean of 0.41 ng/mL). Dust levels in each volunteer's house, car and office were also measured. The authors found that office dust was a statistically significant predictor of urinary BDCPP (Carignan et al., 2013). Dodson et al. (2014) found a mean concentration of 0.46 ng/mL, a median of 0.09 ng/mL, and a maximum of 3.9 ng/mL of the urinary metabolite, BDCPP. See Table 2-8 below for human biomonitoring data.

**Table 2-8. TDCPP Biomonitoring Data**

Country	Tissue/fluid	TDCPP Concentrations <sup>1</sup>	Reference	Notes
United States	Human seminal fluid	Range: 5,000-50,000 ng/mL (5-50 µg/mL)	Hudec et al., 1981	
	Human milk lipids	Median: 4.3 ng/g	Sundkvist et al., 2010	
		Max: 5.3 ng/g		
	Urine metabolites BDCPP and DPP	Geo Mean: 1.9 ng/mL DPP	Hoffman et al., 2014	Pregnant women volunteers from North Carolina
		Max: 37.3 ng/mL DPP		
		Geo mean: 1.3 ng/mL BDCPP		
		Max: 19.9 ng/mL BDCPP		
Urine metabolites BDCPP and DPP	Geo mean: 0.31 ng/mL DPP	Meeker et al., 2013	Male volunteers from a reproductive study, house dust levels also measured, see Table 2-6	
	Max: 9.84 ng/mL DPP			
	Geo mean: 0.13 ng/mL BDCPP			
	Max: 25.0 ng/mL BDCPP			
Urine metabolite BDCPP	Geo mean: 0.408 ng/mL (408 pg/mL) Range: 0.0621-1.76 ng/mL (62.1-1,760 pg/mL)	Carignan et al., 2013	Male and female volunteers; house, car and office dust levels also measured, see Table 2-6	
Urinary metabolite BDCPP	Mean: 0.46 ng/mL Median: 0.09 ng/mL Max: 3.9 ng/mL	Dodson et al., 2014	Samples collected from 16 non-smoking adults living in northern California.	
Canada, Ontario	Human adipose tissue	Range: ND-32 ng/g	LeBel et al., 1989	DL = 1 ng/g; Greater omentum tissue harvested from cadavers; samples from six municipalities

Country	Tissue/fluid	TDCPP Concentrations <sup>1</sup>	Reference	Notes
Canada, Ontario	Human adipose tissue	Range: 0.5-110 ng/g	LeBel and Williams, 1983 as cited in HSDB, 2013	

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses. ND – not detected; DL – detection limit; max – maximum; geo mean – geometric mean; DPP – diphenyl phosphate; BDCPP – bis (1,3-dichloropropyl) phosphate

## 2.5 TDCPP Exposure Assessments and Estimates

Several authoritative agencies have estimated exposures to TDCPP for adults and/or children (ECHA, 2008; Babich, 2006; NRC, 2000), and NRC compared its estimates to toxicity values to characterize risk. In addition, several publications were reviewed where the authors estimated exposure levels (e.g., Abdallah and Covaci, 2014; Yang et al., 2014; Stapleton et al., 2009; Van den Eede et al., 2011).

It should be noted that multiple approaches exist to calculate the average daily intake, each utilizing different values, institutional practices and accepted assumptions about many factors (e.g., safety factors, using high end or average values for intake estimates, assumptions about food intake, derivation of those values for subpopulations, such as children, toddlers). In an exposure assessment, choices for those values and the assumptions and approaches should be discussed and defended.

ECHA looked at occupational and indirect exposures and consumer exposure to TDCPP from flexible PU foam used in upholstery, cars and bedding (ECHA, 2008). They used data on TDCPP, supplemented with information on tris(2-chloro-1-methylethyl) phosphate (TCPP) and worst case assumptions, to estimate combined TDCPP exposure. The following combined exposure estimates are the sum of consumer and indirect exposures via oral, inhalation and dermal routes (ECHA, 2008, Table 4.42):

Local exposure<sup>2</sup>             $6.99 \times 10^{-4}$  mg/kg/day  
Regional exposure<sup>3</sup>       $1.52 \times 10^{-5}$  mg/kg/day

ECHA (2008) estimated an average daily human intake of TDCPP from indoor air based upon emission chamber tests conducted with PU foam containing TCPP and typical human

<sup>2</sup> Local reflects the largest local site.

<sup>3</sup> Regional refers to semi-industrialized European Union geographic area with a surface area of 40,000 km<sup>2</sup> and a population of 20 million people.

consumption and inhalation rates. A worst-case approach gave a reasonable worst-case inhalation exposure value (indoor concentration) of  $3.8 \mu\text{g}/\text{m}^3$  -24 hours TWA. Using default values of a 70 kg person inhaling  $20 \text{ m}^3$  of air per 24-hour day and assuming 100% absorption, the inhalation body burden was calculated as  $1 \mu\text{g}/\text{kg}$  (ECHA, 2008). For a typical exposure, ECHA used a concentration of  $2.8 \mu\text{g}/\text{m}^3$  and adjusted the exposure for 18 hours out of 24 hours to estimate a body burden of  $0.6 \mu\text{g}/\text{kg}$ . ECHA noted that these estimates are likely to be overestimates of exposure to TDCPP because they are based on TCPP data. These inhalation estimates are for exposure from PU foam-containing items, such as upholstered furniture, and do not include exposure from other sources. ECHA also calculated reasonable worst-case body burden for dermal exposure to adults of  $0.0011 \text{ mg}/\text{kg}$  ( $1.1 \mu\text{g}/\text{kg}$ ) for potential dermal exposure from TDCPP from flexible PU foam. For oral exposure, ECHA used values for tris(2-chloroethyl) phosphate (TCEP).

The U.S. CPSC staff prepared a preliminary risk assessment on flame retardants in upholstered furniture foam and calculated an Average Daily Dose (ADD) of TDCPP of  $9.5 \times 10^{-3} \text{ mg}/\text{kg}\cdot\text{d}$  for adults and  $2.6 \times 10^{-2} \text{ mg}/\text{kg}\cdot\text{d}$  for children (Babich, 2006). The extensive assessment utilized available exposure measurements and modeling for concentrations and migration rates from the furniture foam and textiles. It summed indirect and direct estimates for inhalation, oral and dermal routes of exposure, but vapor inhalation dominated the daily intake (>97%) (Babich, 2006).

The National Research Council (NRC, 2000) conducted an upper bound worst-case screening assessment of the risk and exposure of several flame retardants including TDCPP. NRC developed risk values for oral and inhalation routes of exposure and calculated hazard indices to provide an indication of potential risk. They estimated a daily dermal dose rate of  $2.6 \times 10^{-3} \text{ mg}/\text{kg}/\text{day}$  for adults. When divided by the NRC-developed oral reference dose (RfD) of  $0.005 \text{ mg}/\text{kg}/\text{day}$ , the result is a hazard index of 0.52 (NRC, 2000), indicating that TDCPP is not expected to present a hazard for dermal exposure in worst-case scenarios (NRC, 2000). The inhalation time-average concentration of  $0.48 \mu\text{g}/\text{m}^3$  for adult exposure to particles was divided by the NRC developed inhalation reference concentration of  $0.018 \text{ mg}/\text{m}^3$  resulting in a hazard index of 0.027; again indicating that TDCPP would not present a hazard by the inhalation route of exposure for particles (data were insufficient to determine vapor hazard) (NRC, 2000). An oral daily dose of  $0.04 \text{ mg}/\text{kg}/\text{day}$  for a child was estimated. When divided by the NRC-derived RfD this results in a hazard index of 8, indicating that TDCPP could present a hazard by oral exposure in worst-case scenarios (NRC, 2000).

Abdallah and Covaci (2014) measured concentrations of TDCPP in homes, cars, coffee shops, restaurants, and supermarkets in Egypt and used these concentrations to estimate exposure to adults and toddlers. For adults, the authors assumed  $20 \text{ mg}/\text{day}$  or  $50 \text{ mg}/\text{day}$  (mean and high ingestion rates, respectively) and an average adult body weight of 70 kg. For toddlers, they

assumed a dust ingestion rate of 50 mg/day (mean) and 200 mg/day (high) and an average toddler body weight of 20 kg. They also assumed 100% absorption of the intake in the absence of experimental data. Plausible dust ingestion exposure scenarios used average and median concentrations measured in the study. The estimates for TDCCP from incidental ingestion of indoor dust ranged from 1.6 ng/day (mean exposure scenario) to 7.5 ng/day (high exposure scenario) for adults and 4.0 ng/day to 30 ng/day for toddlers (mean and high exposure scenarios, respectively) (Abdallah and Covaci, 2014).

Yang et al. (2014) measured suspended particulate matter collected from offices for a number of organophosphate flame retardants, including TDCPP. The measured concentrations of TDCPP in airborne dust were used to estimate inhalation exposure for adults using U.S. EPA and International Commission on Radiological Protection (ICRP) models for deposition efficiency and flux of inhaled particles in the respiratory tract. The authors assumed a dust inhalation rate of 16 m<sup>3</sup>/day, a body weight of 70 kg, and an 8-hour exposure (Yang et al., 2014). The authors reported a median exposure of 0.05 ng/kg/day and a 95<sup>th</sup> percentile exposure of 1.09 ng/kg/day for adults using the U.S. EPA model and a median exposure of 0.01 ng/kg/day and a 95<sup>th</sup> percentile exposure of 0.2 ng/kg/day for adults using the ICRP model (Yang et al., 2014).

Van den Eede et al. (2011) analyzed dust samples from Flemish homes and shops for multiple organophosphate flame retardants, including TDCPP. For adults, the authors assumed 20 mg/day or 50 mg/day (average and high ingestion rates, respectively) and an average body weight of 70 kg. For toddlers they assumed a dust ingestion rate of 50 mg/day (average) and 200 mg/day (high) and an average toddler body weight of 12.3 kg. The daily ingestion exposure for toddlers was 9.8 ng/kg/day for average ingestion and 255 ng/kg/day for high ingestion; adult exposure was 0.7 ng/kg/day for average ingestion and 11 ng/kg/day for high ingestion for general organophosphate flame retardants (not TDCPP specifically).

Stapleton et al. (2009) measured concentrations of TDCPP, TCPP, and TPP in house dust extracts from 50 Boston MA homes. They estimated cumulative exposure to these organophosphate flame retardants as well as data on four others (TBB, PBDEs, TBPH, and HCBDD) and using the geometric mean concentration for each flame retardant and lower bound dust ingestion rates from U.S. EPA (100 mg dust/day for a child; 20 mg dust/day for an adult). For children, the average estimated cumulative exposure was about 1600 ng/day; for the adult it was about 325 ng/day, with a majority of the exposure from TPP, TDCPP and PBDEs (Stapleton et al., 2009).

## **2.6 TDCPP Discussion**

TDCPP is a widely used flame retardant in the U.S. and has been measured in water, dust, consumer products, and air. Concentrations of TDCPP are highest in dust of indoor environments, and contact with dust appears to be the main source of exposure for consumers to

TDCPP. The highest dust concentrations of TDCPP were measured on the tested surfaces that were presumably proximate to the TDCPP treated polymers. Normal hand-to-mouth activity is the primary route of exposure. Incidental hand-to-mouth activity occurs over a person's entire life, but it occurs most often and most significantly in children. Therefore, children may have greater exposures than adults. The U.S. EPA estimates daily dust/dirt ingestion rates for children in the range of 50 to 100 mg per day, with adults at a lower but still substantial amount of 30 mg per day (central tendency) in the general population for dust ingested daily (U.S. EPA, 2011). Biomonitoring studies have demonstrated significant correlations between urinary BDCPP in humans and TDCPP dust concentrations (Meeker et al., 2013; Carignan et al., 2013).

Carignan et al. (2013) detected a metabolite of TDCPP in 100% of 31 urine samples (mean of 0.41 ng/mL) of people living in Boston, Massachusetts. Dust levels in each volunteer's house, car and office were also measured. The authors found that office dust was a statistically significant predictor of urinary BDCPP (Carignan et al., 2013). Dust concentrations measured in cars were much greater (maximum 326,000 ng/g) than concentrations in houses or offices (maximum values of 30,600 ng/g and 72,000 ng/g, respectively) (Carignan et al., 2013). According to a recent blog, a study done by the Harvard Health Watch shows an average of 101 minutes per day are spent driving by the average American (Bjarki, 2015).

TDCPP is now one of the most commonly used flame retardants found in upholstered furniture (Stapleton et al., 2009) and baby products with PU foam (Stapleton et al., 2011). TDCPP is in flexible PU foams also used in automotive interiors, textiles, plastics, resins, and rubbers and is a plasticizer in these same products (CalEPA, 2011; HSDB, 2013). These may be sources for TDCPP measurement in home dust as well as PU foam used in car interiors. In addition, electronic equipment has been shown to emit TDCPP (Saito et al., 2007).

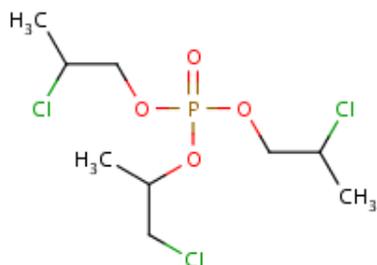
ECHA estimated an average daily intake of  $1.52 \times 10^{-5}$  mg/kg/day to  $6.99 \times 10^{-4}$  mg/kg/day for combined exposures to consumers and indirect exposures via oral, inhalation, and dermal routes (ECHA, 2008). For oral exposure, ECHA used values for TCPP. They estimated a reasonable worst-case inhalation body burden of 1  $\mu\text{g}/\text{kg}$  bw/day for adults (ECHA, 2008) based on TCPP data, and calculated reasonable worst-case body burden to adults of 1.1  $\mu\text{g}/\text{kg}/\text{day}$  for potential dermal exposure from TDCPP from flexible PU foam. NRC (2000) estimated an oral daily dose of 0.04 mg/kg/day TDCPP for a child; an average daily dermal dose rate of  $2.6 \times 10^{-3}$  mg/kg/day for adults; and inhalation time weighted average (TWA) concentration of 0.48  $\mu\text{g}/\text{m}^3$  for adult exposure to particles. Several authors of studies reporting measurements of TDCPP in dust also used their measured concentrations to estimate daily exposures.

### 3 Tris(chloropropyl) phosphate, mixture of isomers (TCPP) (CAS 13674-84-5, 76649-15-5, 76025-08-6, 6145-73-9, 26248-87-3)

#### 3.1 TCPP Chemical and Physical Properties

Tris(1-chloro-2-propyl) phosphate (TCPP), and its isomers are used as flame retardants, mainly in polyurethane foams. It is a colorless liquid with a mild odor (HSDB, 2013). The flame retardant product marketed as TCPP (or other synonyms) is a mixture of the isomers (ECHA, 2009). The solubility of TCPP in water ranges from 1.2-1.6 g/L, and it is soluble in most organic solvents (HSDB, 2013; IPCS, 1998); it will adsorb to solids and sediments in water based on an estimated soil-water coefficient ( $K_{oc}$ ) value of 290 (HSDB, 2013). The log octanol/water partition coefficient of TCPP is 2.59 (IPCS, 1998). U.S. EPA (2011) reports an estimated vapor pressure of  $9.23 \times 10^{-3}$  mm Hg at 25 °C and an estimated Henry's Law constant of  $5.96 \times 10^{-8}$  atm·m<sup>3</sup>/mol (at 25 °C).

**Figure 3-1. Molecular Structure of TCPP** [tris(1-chloro-2-propyl) form, CAS number 13674-84-5 ] (ChemIDPlus, 2014)



**Table 3-1. CAS Registry Number and Synonyms for TCPP and Isomers** (ChemIDPlus, 2014)

Chemical Name	CAS Registry/RN	Synonyms
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Chemical Name	CAS Registry/RN	Synonyms
Tri-(2-chloroisopropyl) phosphate	13674-84-5	Tris(1-chloro-2-propyl) phosphate; Tris(1-chloro-2-propyl)phosphate; Tris(2-chloroisopropyl)phosphate; 2-Propanol, 1-chloro-, 2,2',2''-phosphate; 2-Propanol, 1-chloro-, phosphate (3:1); Phosphoric acid, tris(2-chloro-1-methylethyl) ester; Tris(1-chloro-2-propyl)phosphate; Amgard TMCP; BRN 1842347; CCRIS 6111; EC 237-158-7; EINECS 237-158-7; Hostaflam OP 820
2-chloro-1-methylethyl bis(2-chloropropyl) ester Phosphoric acid	76649-15-5	Bis(2-chloropropyl) 2-chloro-1-methylethyl phosphate; Bis(2-chloropropyl) 2-chloroisopropyl phosphate; Phosphoric acid, 2-chloro-1-methylethyl bis(2-chloropropyl) ester
bis(2-chloro-1-methylethyl) 2-chloropropyl Phosphoric acid	76025-08-6	Bis(2-chloro-1-methylethyl) 2-chloropropyl phosphate; Phosphoric acid, bis(2-chloro-1-methylethyl) 2-chloropropyl ester
2-Chloro-1-propanol phosphate (3:1)	6145-73-9	Fyrol PCF; Tris(2-chloropropyl) phosphate; Tris(beta-chloropropyl) phosphate; 1-Propanol, 2-chloro-, 1,1',1''-phosphate; Antiblaze 80; AP 33; EINECS 228-150-4; NSC 524664
1-Propanol, chloro-, phosphate (3:1)	26248-87-3	Tri(chloropropyl) phosphate; Tris(chloropropyl)phosphate; Tris(monochloropropyl) phosphate; 1-Propanol, 2-chloro-, phosphate (3:1), mixed with 1-chloro-2-propanol phosphate (3:1); 1-Propanol, chloro-, phosphate (3:1) (8CI,9CI); FG 8115; FG 8115S

**Table 3-2. Physical and Chemical Properties of TCPPa** (ChemIDPlus, 2014; HSDB, 2013)

Molecular Formula	C <sub>9</sub> H <sub>18</sub> Cl <sub>3</sub> O <sub>4</sub> P
Molecular Weight	327.57
Melting Point	-40 °C
Boiling Point	>270 °C (ChemIDPlus, 2014) 235-248 °C (HSDB, 2013)
Density	1.29 (at 25 °C)
Solubility (in water)	1.2 g/L (HSDB, 2013) 1.6 g/L (IPCS, 1998)

Log K <sub>ow</sub>	2.59 (ChemIDPlus, 2014) 3.65 (HSDB, 2013)
Vapor Pressure	2.02 x 10 <sup>-5</sup> torr (at 25 °C) (ChemIDPlus, 2014) 9.23 x 10 <sup>-3</sup> torr (at 25 °C) (U.S. EPA, 2011)
Henry's Law Constant	5.96 x 10 <sup>-8</sup> torr (at 25 °C)

<sup>a</sup>The chemical/physical properties reported are for Tri-(2-chloroisopropyl) phosphate (13674-84-5) only. Chemical/physical properties were not available for the other isomers.

Semi-Volatile Organic Compounds (SVOCs), such as TCPP are typically characterized by relatively high molecular weights, low vapor pressure/volatility, low or moderate solubility in water and a high octanol-water partition coefficient. To a significant degree, these properties determine the fate of TCPP in the environment, which impacts the potential for human exposure. The high octanol-water partition coefficient means it will be lipophilic or “fat loving”; that is, it will partition into any sediment layers in an environmental water column. In the indoor environment, it will not be highly present in the air as a vapor but will readily partition into and be present in available organic rich substrates like house dust.

Because of its properties and fate in the indoor environment, the vapor pressure (VP) of pure TCPP can be misleading in estimating its potential to become airborne as a vapor. Taking the highest measured vapor pressure at typical room temperature of 25°C (73°F) results in the following estimation of a maximum or saturated airborne concentration:

$$(0.01\text{torr}/760\text{torr}) (1,000,000) (327,6/24.4) = 177 \text{ mg/m}^3$$

All monomers (including monomeric flame retardants) embedded within polymer matrices will move out of that matrix into surrounding media following classic laws of diffusion. Given a time frame of many months or a few years, a significant portion of the monomer will diffuse out of the polymer. In reality, TCPP would never be expected to exist as a pure material indoors. Initially, it is in the polymer matrix and, after it diffuses out of the matrix, it comes to the surface. TCPP is then associated with house dust, which is primarily composed of human skin cells that have been shed. As such, house dust is essentially an organic substrate. In this case, an estimated 0.01 mmHg VP at 25°C (73°F) of pure TCPP is highly attenuated via what is known as Raoult's Law:

$$(\text{VP of Pure TCPP})(\text{Mole Fraction of TCPP in substrate}) = \text{VP over the substrate}$$

This is for “ideal mixtures” of TCPP in various substrates (e.g., polyurethane foam or typical house dust). For real world mixtures, a thermodynamic activity coefficient (AC) is added.

$$(\text{VP of Pure TCPP})(\text{Mole Fraction of TCPP in substrate})(\text{AC}) = \text{VP over the substrate}$$

Some work has been done to measure or estimate TCPP releases from products. ECHA, in its risk assessment (ECHA, 2009), included an appendix (Appendix B) that presented some test results on TCPP studies of PU foam, and estimated TCPP release rates. Saito et al. (2007) measured air concentrations of TCPP in a newly built house in Tokyo but did not detect any migration from surfaces of building materials. Migration rates of TCCP from products have been measured from upholstery at rates of up to  $77 \mu\text{g m}^{-2}$  (Kemmlin et al., 2003, as cited by Marklund et al., 2005a) and from TV sets at a rate of  $1.7 \mu\text{g/m}^2\text{-hour}$  (Saito et al., 2007).

### 3.2 TCPP Uses

TCPP is most commonly used as an additive flame retardant, primarily in production of PU (e.g., upholstered furniture, rigid foams for building insulation and refrigerator casings) and in some textiles (Anderson et al., 2004; ATSDR, 2009; Environment Agency, 2003; ECHA, 2009). ECHA reports that most TCPP is used in rigid PU foam in construction, with less used in flexible foams of upholstery and bedding (ECHA, 2009). ECHA also notes that because of its volatility and potential for fogging, TCPP is not often used in flexible PU applications in automobiles. TCPP use is increasing due to new technological developments allowing for its use in these products (ECHA, 2009).

Chlorinated alkyl phosphate esters (particularly TCPP) were identified as possible substitutes for pentabromodiphenyl ether (pentaBDE) to be implemented in risk reduction strategies (EC, 2001)

### 3.3 TCPP Human Exposure

TCPP is found throughout the environment in various human exposure-related media including indoor and ambient air, indoor dust, water, and to a lesser extent food. It is also found in consumer products, building products, child-specific products, furniture, and electronics. TCPP in polyurethane foam or any polymer matrix is not chemically bound to the polymer. It has been detected in dust in homes, offices, automobiles, and daycare centers worldwide. Concentrations of TCPP in various media, as well as a summary of exposure assessments and estimates found in the literature search, are presented below.

The available literature on concentrations of TCPP in relevant environmental media and consumer products is heavily focused on concentrations in air and dust, reflecting what is reasonably considered to be perhaps the most important exposure pathways of concern for children and others. In addition to their potential exposure to off-gassed vapors of TCPP treated items indoors, children's overall exposure to this flame retardant will be influenced by their hand-to-mouth and direct mouth-to-surface behavior and subsequent ingestion of TCPP containing material, particularly dust. Frequent hand washing is associated with lower flame retardant levels on the hands (Stapleton et al., 2014).

### 3.3.1 TCPP in Indoor and Ambient Air

Likely sources of phosphate ester flame retardants in indoor air include: polyvinylchloride (PVC) plasticizers, floor polishes, electronics (plastic cabinets), PU foams, upholstery, furniture, and textiles (ATSDR, 2012, Reemtsma et al., 2008; Canada Gazette, 2011; Marklund et al., 2005). Both particulates and vapors contribute to exposure (Garcia et al., 2007 as cited by ATSDR, 2012). TCPP can be emitted from products found in homes and other buildings, including emissions from rigid and soft PU foams and recycled plastics used as flooring materials (Salthammer et al., 2003, as cited by Marklund, 2005a).

Relatively little TCPP is anticipated to become airborne as a vapor out of organic substrates indoors. However, particulates, such as dust, are quite mobile and can become airborne. Thus, TCPP could be distributed within the indoor environment in dust on surfaces with a lesser amount of the TCPP containing dust being airborne. An exception to this rule of low airborne levels would be relatively “dusty” rooms where the dust has been allowed to accumulate and/or activities occurs that tend to continually entrain the dust into the air. In these indoor environments, relatively high levels of airborne TCPP (dissolved in dust) may be found.

TCPP in particulates and vapors has been measured in indoor settings, including houses, offices and other workplaces, schools and child care centers, university buildings, stores, prisons, hospitals, and public places. Concentrations have also been measured in electronic dismantling centers, plastics factories, and cars. The concentrations of TCPP measured in indoor air ranged from not detected to 570 ng/m<sup>3</sup>. The highest levels were measured by Marklund et al. (2005a) in a prison (570 ng/m<sup>3</sup>) and a university lobby (440 ng/m<sup>3</sup>).

**Table 3-3. TCPP Concentrations in Indoor Air**

Country	Location	Media	TCPP Concentrations <sup>1</sup>	Reference	Notes
Germany	Daycare center	Indoor air	Mean: 4.1 ng/m <sup>3</sup> Median: 2.7 ng/m <sup>3</sup> Max: 45 ng/m <sup>3</sup>	Fromme et al., 2014	
Sweden	Library	Indoor air	47.3 ng/m <sup>3</sup>	Sanchez et al., 2003	Stationary sampler performed with a personal sampler holder made of anodized Aluminum
	New car	Indoor air	61.4 ng/m <sup>3</sup>		
	Private home	Indoor air	10.0 ng/m <sup>3</sup>		
	Laboratory	Indoor air	112 ng/m <sup>3</sup>		
	School building	Indoor air,	LOD-14 ng/m <sup>3</sup>	Carlsson et al.,	Stationary

Country	Location	Media	TCP Concentrations <sup>1</sup>	Reference	Notes
		three schools	1.5-41 ng/m <sup>3</sup>	1997	sampling with a personal sampler with a glass fiber filter, values are means of non-identified isomer levels. LOD = 0.5 ng/m <sup>3</sup>
			1.1-35 ng/m <sup>3</sup>		
	Day care	Indoor air	2.9-34 ng/m <sup>3</sup>		
	Office	Indoor air	1.4-34 ng/m <sup>3</sup>		
	Homes	Indoor air	38-210 ng/m <sup>3</sup>		
	Day care center	Indoor air	28 ng/m <sup>3</sup>		
Sweden	Hospital ward	Indoor air	69 ng/m <sup>3</sup>	Marklund et al., 2005a	Stationary sampler with SPE Cartridge
	Radio shop, textile shop	Indoor air	10 ng/m <sup>3</sup> , 32 ng/m <sup>3</sup>		
	Prison	Indoor air	570 ng/m <sup>3</sup>		
	University lobby	Indoor air	440 ng/m <sup>3</sup>		
	Office	Indoor air	160 ng/m <sup>3</sup>		
	Furniture store	Indoor air	73 ng/m <sup>3</sup>		
	Plastics factories	Indoor air	32 ng/m <sup>3</sup>		
	Laboratory	Indoor air	31 ng/m <sup>3</sup>		
	Public places, hotel, library, dance hall, bowling alley	Indoor air	Range: 40-79 ng/m <sup>3</sup>		
	Day care center (10)	Indoor air	Median: 8.4 ng/m <sup>3</sup> Range: 1.3-72 ng/m <sup>3</sup>	Bergh et al., 2011, as cited in Fromme et al., 2014	

Country	Location	Media	TCPP Concentrations <sup>1</sup>	Reference	Notes
	Day care center (1)	Indoor air	77 ng/m <sup>3</sup>	Tollback et al., 2006, as cited in Fromme et al., 2014	C8 Empore solid phase extraction (SPE) membranes
Japan	Tokyo, 1 newly built House	Indoor air , migration from surface	Air: 5.5 ng/m <sup>3</sup> , migration: ND	Saito et al., 2007	Sampled using quartz fiber Filter (47 mm), first stage and a solid phase extraction disk (empore <sup>tm</sup> Disk C18, 47mm), second stage. LOD 0.33 µg/m <sup>2</sup> /hour
	Tokyo, 18 Houses	Indoor air	Median: 1.9 ng/ m <sup>3</sup> Range: ND-1260 ng/m <sup>3</sup>	Saito et al., 2007	Quartz fiber Filter (47 mm), MDL = 0.94 ng/m <sup>3</sup>
	Tokyo, 14 Offices	Indoor air	Median: 6.0 ng/ m <sup>3</sup> Range: ND-57.6 ng/m <sup>3</sup>	Saito et al., 2007	Quartz fiber Filter (47 mm), MDL = 0.94 ng/m <sup>3</sup>
China	Hangzhou, Office	Indoor air	Mean: 24.20 ng/m <sup>3</sup> Median: 7.76 ng/m <sup>3</sup> Range: 0.83-81.04 ng/m <sup>3</sup>	Yang et al., 2014	Particulate matter
Not Specified	Not specified	Indoor air	Range: 6-60 ng/m <sup>3</sup>	Wensing et al., 2005, as cited in Weschler and Nazaroff, 2008	Sampling not specified

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

max – maximum, DL- detection limit, LOD- Limit of Detection, ND – non detect; SPE – Solid Phase Extraction

Less information was located regarding TCPP in ambient air, and measured concentrations were much lower than those seen in indoor environments. TCPP was measured in a coastal

environment in Germany at a concentration of 1.2 ng/m<sup>3</sup> (Moller et al., 2011) and in Tokyo, Japan concentrations ranged from not detectable to 3.1 ng/m<sup>3</sup>. Ambient air measurements near where hydraulic fluids are used (airports, newly constructed homes and buildings) were up to 5.3 ng/m<sup>3</sup> in Japan (Haraguchi et al., 1985 as cited in ATSDR, 2009). See Table 3-4 below for TCPP concentrations in ambient air.

**Table 3-4. TCPP Concentrations in Ambient Air**

Country	Location	Media	TCPP Concentrations <sup>1</sup>	Reference	Notes
Germany	North Sea	Ambient air	1.2 ng/m <sup>3</sup> (1,200 pg/m <sup>3</sup> )	Moller et al., 2011	High volume pump to obtain (300 m <sup>3</sup> sample) aboard ship at sea
Japan	Kitakyushu District	Outdoor ambient air, near hydraulic fluid use	5.3 ng/m <sup>3</sup> (0.0053 µg/m <sup>3</sup> )	Haraguchi et al., 1985 as cited in ATSDR, 2009	High-volume Sampler fitted with a glass fiber filter and XAD-7 resins (20g)
	Tokyo, 8 samples around houses and offices (verandas, eaves)	Ambient air	Median: ND Range: ND-3.1ng/m <sup>3</sup>	Saito et al., 2007	Quartz fiber Filter (47 mm), MDL=0.94 ng/m <sup>3</sup>

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

ND – non detect; MDL – maximum detection limit

### 3.3.2 TCPP in Water

TCPP concentrations in finished drinking water were not located. However, investigators have measured TCPP in surface and ground waters in a number of countries, including the U.S. (Andresen et al., 2004; Andresen and Bester 2006; Bacaloni et al., 2008; Bacaloni et al., 2007; Bollman et al., 2012; Fukushima et al., 1992; Garcia Lopez, 2010; Gorga 2015; Gross et al., 2004; Ishikawa et al., 1985; Knepper et al., 1999; Martinez-Carballo et al., 2007; Regnery et al., 2011; Rodil et al., 2012; Stepien et al., 2013; Yoon et al., 2010). These studies generally looked for TCPP in rivers in industrialized areas, and some measurements were taken directly below TCPP discharges; therefore, the concentrations reported likely represent the highest one would expect to find. Surface water levels range from 0 to 34 ng/L in the Santa Ana River in

California (Gross et al., 2004), with levels reaching 2,900 ng/L below a discharge point in the Los Angeles and San Gabriel Rivers (Sengupta, 2014). The highest concentration reported outside the U.S. was 13,100 ng/L in the Yamato River in Japan (Fukushima et al., 1992). See Table 3-5 below.

**Table 3-5. TCP P Concentrations in Water**

Country	Location	Media	TCP P Concentrations <sup>1</sup>		Reference	Notes
United States	California, Santa Ana River	Surface water	Range: 0-34 ng/L		Gross et al., 2004	4-8 L samples collected every 4 months from April-December 2002
	California: Los Angeles and San Gabriel Rivers	Surface water	Max: 2,150 ng/L (July)	Max: 2,900 ng/L (October)	Sengupta 2014	Samples collected below discharge points in July and October 2011.
Germany	Rhine River	Surface water	Range: 80-100 ng/L		Andresen et al., 2004	
	Lippe River		100 ng/L			
	River Elbe	Surface Water	Range: 40-250 ng/L		Bollman et al., 2012	
	German Bight	Surface water	Range: 3-28 ng/L			
	Rhine River	Surface water	Range: 75-160 ng/L			
	Rhine River	Surface water	Range: 30-150 ng/L (0.03-0.15 µg/L)		Knepper et al., 1999	
Hesse Streams	Surface water	502 ng/L	Median: 417 ng/L	Quednow and Puttman, 2008		

Country	Location	Media	TCPP Concentrations <sup>1</sup>		Reference	Notes
	Ruhr River	Surface water, reservoir	Mean: 54±7.6 ng/L	Max: 65 ng/L	Andresen and Bester 2006	
Germany	Hessian Ried	Groundwater (precipitation infiltration)	Median: <LOQ	Max: 6 ng/L	Regnery et al., 2011	LOQ = 4 ng/L
	Hessian Ried	Groundwater (riverbank filtration)	Median: 38 ng/L	Max: 1,795 ng/L		
	Oder River	Surface Water	Range: 217-2353 ng/L		Stepien et al., 2013	
Groundwater wells		Range: 14-406 ng/L				
Austria	Danube River	Surface water	Range: 33-43 ng/L		Martinez-Carballo et al., 2007	
	Schwechat River		170 ng/L			
	Liesig River		110 ng/L			
Japan	Yamato River	Surface water	Mean: 13,100 ng/L (13.1 µg/L)		Fukushima et al., 1992	Trend of concentration from 1976-1990
Spain	Iberia	Groundwater	Median: 47 ng/L		Rodil et al., 2012	77 samples collected during two monitoring campaigns conducted 2010-2011
		Llobregat River (Surface water)	1,100 ng/L (estimated from graph)		Gorga, 2015	
		Ebro River (Surface water)	Max: 6,500 ng/L (estimated from graph)			

Country	Location	Media	TCPP Concentrations <sup>1</sup>		Reference	Notes
Spain		Jucar River (Surface water)	300 ng/L (estimated from graph)			
		Guadalquivir River (Surface water)	600 ng/L (estimated from graph)			
Not Specified	River (4)	Surface water	3 rivers known discharge: 24-64 ng/L	1 river downstream of sewage plant: 430 ng/L	Garcia Lopez, 2010	Single samples from 4 rivers
South Korea	Seoul	Han River (Surface water)	Mean: 197 ng/L	Range: 100-310 ng/L	Yoon et al., 2010	
		Creek (Surface water)	Mean: 403 ng/L	Range: 210-590 ng/L		
Italy	Volcanic Lake	Albano Lake (Surface water)	Means: 6-62 ng/L (monthly)		Bacaloni et al., 2008	Detection limit not reported
		Vico Lake (Surface water)	Means: 2-27 ng/L (monthly)			
	Well. Near Vico Lake	Ground water	Range: ND-12 ng/L			
	River Tiber	Surface water	54 ng/L and 117 ng/L		Bacaloni et al., 2007	2 samples, June 2006, November 2006

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

WWTF – waste water treatment facility; max – maximum; ND – not detected; LOQ – level of quantification

### 3.3.3 TCPP in Food

The U.S. Food and Drug Administration (U.S. FDA) conducted a 10-year market-basket survey of 234 food items (1982 and 1991). TCPP was identified in a number of products. The highest residue found was in pears (9.3 ng/g) (U.S. FDA's Total Diet Study, as cited by ATSDR 2009 and by Kan-Do Office and Pesticides Team, 1995) (see Table 3-6). Based upon U.S. FDA's

Total Diet Study results from 1986-1991, Gunderson (1995a) calculated a mean daily intake of 0.001 ug TCPP/kg bw/day for all age groups from infant through age 65, with the exception of 2 year olds, whose mean daily intake was estimated at 0.002 ug/kg/day.

**Table 3-6. TCPP Concentrations in Food**

Country	Study Type	Food	TCPP Concentrations <sup>1</sup>	Reference	Notes
United States	Market-basket survey	Pear	9.3 ng/g (0.0093 µg/g)	U.S. FDA Total Diet Study , as cited by ATSDR 2009 and Kan-Do Office and Pesticides Team, 1995	234 food items were evaluated over a 10-year period between 1982 and 1991.
		Apple	0.82 ng/g (0.00082 µg/g)		
		Tomato juice	0.30 ng/g (0.00030 µg/g)		
		Baby food	0.18 ng/g (0.00018 µg/g)		
		Prunes	0.15 ng/g (0.00015 µg/g)		
		Apple juice	0.05 ng/g (0.00005 µg/g)		

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

### 3.3.4 TCPP in Dust

Given the properties of TCPP and the quantity of data found on dust, it would appear that dust ingestion is one of the primary sources of human exposure to TCPP, alongside inhalation from off gassing of TCPP in consumer products and other materials.

TCPP has been measured in dust in various countries in houses, daycare centers, offices, cars hospitals, prisons, hotels, stores, laboratory, and a carpenter workshop. Only one study was found on measurements in the U.S. Stapleton et al. (2009) found levels ranging from less than 140 (MDL) to 5,490 ng/g in the dust of homes in Boston, MA. These levels are lower than those measured in many studies in other countries. In Canada, Fan et al. (2014) recorded TCPP levels in household dust ranging from 1,100 ng/g to 56,000 ng/g. In Belgium, levels in household dust ranged from 190 ng/g to 73,637 ng/g, while levels in shops and workspace ranged from 580 to 24,400 ng/g (Van den Eede et al., 2011). Multiple studies measuring TCPP in various environments in Germany observed TCPP concentrations in houses of 370-375,000 ng/g, in daycares of up to 47,000 ng/g, in offices of 180 ng/g to 9,400 ng/g, and in cars of 1,400 to 4,300 ng/g (Ingerowski et al., 2001; Fromme et al., 2014; Brommer et al., 2012). Ali et al. (2012) measured TCPP in residential dust in New Zealand at levels ranging from 250 ng/g to 350 ng/g. In Spain, Garcia et al. (2007) measured TCPP at levels of 1,700 ng/g to 42,000 ng/g in household dust. Marklund et al. (2003) measured levels of TCPP in dust of Swedish homes ranging from

470-930 ng/g and levels in shops and various public places ranged from 890 ng/g to 50,000 ng/g (maximum values found in a university lobby). Marklund et al. (2003) also measured dust concentrations with wipe samples on a computer screen and a monitor cover (220 – 370 ng/m<sup>2</sup>). See Table 3-7 below.

**Table 3-7. TCPP Concentrations in Dust**

Country	Location	Media/ Area	TCPP Concentrations <sup>1</sup>		Reference	Notes
United States	Boston, MA	House	Geo mean: 572 ng/g	Range: <MDL- 5,490 ng/g	Stapleton et al., 2009	Household vacuum cleaner bag collection. Detected in 24 of 50 homes. MDL=140 ng/g
Canada		House	Median: 1,400 ng/g (1.4 µg/g)	Max: 56,000 ng/g (56 µg/g)	Fan et al., 2014	FD method (fresh/active dust)
			Median: 1,100 ng/g (1.1 µg/g)	Max: 4,900 ng/g (49 µg/g)		HD method (household vacuum cleaner)
Belgium	Flemish region	House	Mean: 4,820 ng/g (4.82 µg/g) Median: 1,380 ng/g (1.38 µg/g)	Range: 190- 73,637 ng/g (0.19-73.637 µg/g)	Van den Eede et al., 2011	Vacuum dust samples
		Carpenter workshop, second-hand store, electronics stores, laboratory	Mean: 5,160 ng/g (5.16 µg/g) Median: 2,940 ng/g (2.94 µg/g)	Range: 580- 24,400 ng/g (<0.58-24.4 µg/g)		
Germany		Pooled homogenized sample from 20 buildings, mostly residences.	Arith mean: 1160-2350 ng/g (1.16-2.35 mg/kg) Geo mean: 380-680 ng/g (0.38-0.68 mg/kg) Max: 33,00-375,000 ng/g (33 to 375 mg/kg)		Ingerowski et al., 2001	Conventional vacuum with filter from clients with health problems, results from 3 laboratories

Country	Location	Media/ Area	TCPP Concentrations <sup>1</sup>	Reference	Notes
Germany		Daycare center	Mean: 4650 ng/g (4.65 mg/kg) Median: 2680 ng/g (2.68 mg/kg) Max: 47,000 ng/g (47.0 mg/kg)	Fromme et al., 2014	ALK dust filter mounted on a sampler connected to a vacuum cleaner, vacuumed for 5-10 minutes
	Various	Car	Range: 1,400-4,300 ng/g	Brommer et al., 2012	
		House	Range: 370-960 ng/g		
		Office	Range: 180-9,400 ng/g		
New Zealand		Residential	Range: 250-350 ng/g (0.25-0.35 µg/g)	Ali et al., 2012	Vacuum cleaner bag collection
Sweden	Various	Houses	Range: 470-930 ng/g (0.47-0.93 mg/kg)	Marklund et al., 2003	Vacuum cleaner bag collection and wipe test samples from computer screens and covers
		Day care center	2,500 ng/g (2.5 mg/kg)		
		Hospital, wards, office	Range: 2,300-5,300 ng/g (2.3-5.3 mg/kg)		
		Textile shop, Radio shop	Range: 1,400-2,300 ng/g (1.4-2.3 mg/kg)		
		Hotel	890 ng/g (8.9 mg/kg)		
		Prison	890 ng/g (8.9 mg/kg)		
		University lobby	50,000 ng/g (50 mg/kg)		
		Office	73,000 ng/g (73 mg/kg)		
		Computer screen	370 ng/m <sup>2</sup>		
		Computer cover	220 ng/m <sup>2</sup>		

Country	Location	Media/ Area	TCPP Concentrations <sup>1</sup>		Reference	Notes
Sweden		Public places, hotel, library, dance hall, aircraft	Range: 1,500-2,900 ng/g (1.5-2.9 mg/kg)			
	Day care centers (10)	Indoor dust	Median: 3,100 ng/g (3.1 mg/kg) Range: 800-12,000 ng/g (0.8-12 mg/kg)		Bergh et al., 2011, as cited in Fromme et al., 2014	
Spain	Northwest of Spain	House	Mean: 3,900 ng/g (3.9 µg/g)	Range: 1,700-4,200 ng/g (1.7-4.2 µg/g)	Garcia et al., 2007	Household vacuum cleaner bag collection
Not Specified	Not specified	Not specified	Range: 300-3,000 ng/g (0.3-3 µg/g)		Wensing et al., 2005, as cited in Weschler and Nazaroff, 2008	Sampling not specified

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

avg – average; max – maximum; MDL – method detection limit; geo mean – geometric mean; arith mean – arithmetic mean; min – minimum

### 3.3.5 TCPP in Consumer Products

Concentrations of TCPP measured in consumer products cannot be used directly as a proxy for concentration levels to which consumers are exposed. To develop realistic consumer exposure concentrations, the flame retardant levels in these products would need to be paired with experimental or monitoring results that reflect the availability of the compound to leave these products and enter the body. For TCPP, there is limited emission or migration rate data available, which would be needed to estimate actual exposure concentrations.

TCPP has been found in a variety of baby products (Stapleton et al., 2011), household products (Ingerowski et al., 2012; Nagase et al., 2003), and also in electronics (Saito et al., 2007; Kajiwara et al., 2011). Primary exposure routes for TCPP in consumer products would be inhalation exposure from the off gassing of large TCPP containing sources indoors (e.g., carpet, carpet backing, floor sealing material), oral ingestion (e.g., children’s mouthing of materials or

products, along with incidental ingestion of dust by all ages) and, to a lesser extent, dermal exposure.

Migration rates of TCPP from products have been measured from upholstery at rates of up to 77  $\mu\text{g}/\text{m}^2$ -hour (Kemmlin et al., 2003, as cited by Marklund, 2005a) and from TV sets at a rate of 1.7  $\mu\text{g}/\text{m}^2$ -hour (Saito et al., 2007). See Table 3-8 below.

### ***3.3.5.1 TCPP in Children and Baby Products***

TCPP was found in baby products samples from car seats, changing table pads, sleep positioners, mattresses, nursing pillows, baby carriers, and rocking chairs. Stapleton and colleagues (2011) reported levels of TCEP ranging from 1.11- 14.4 mg/g (mean 5.49 mg/g) in 16 of the 101 commonly used baby product samples tested. They found that concentrations of TCEP and TCPP were much lower in general than the other three flame retardants in their study (TDCPP, TPP, and TBPH) and thought that this may indicate that TCEP and TCPP are minor components of flame retardant mixtures. The Center for Environmental Health (2013) found TCPP in 3 of 24 children's foam nap mats that were sampled in 2012 (no quantification).

### ***3.3.5.2 TCPP in Household Products***

Much higher levels of TCPP were measured in numerous household products available in Germany, including carpet, mattresses, and products used in home building, with values ranging from 150,000 ng/g in wood preservation coating to 180,000,000 ng/g in polyurethane foam fillers (Ingerowski et al., 2012). Nagase et al. (2003) measured TCPP levels of 900 ng/g to 3,100 ng/g in Japanese furniture cushions. Some of these products (e.g., carpeting and floor sealers) have large surface areas from which to diffuse TCPP into dust; combined with the high concentrations, these materials create potential for large exposures.

### ***3.3.5.3 TCPP in Electronic Products***

Kajiwara et al. (2011) analyzed components of LCD TVs and laptop computers in Japan and found concentrations of up to 150 ng/g in the AC adapter of a laptop. A chamber study of TCPP emission rates from a computer monitor reports a rate of not detected to 1,700 ng of TCPP per square meter of surface area per hour (Saito et al., 2007).

**Table 3-8. TCPP Concentrations in Consumer Products**

Country	Item	Media	TCPP Concentrations <sup>1</sup>	Reference	Notes
United States	Baby products, donated used and purchased new	Car seats, changing table pads, sleep positioners, portable mattresses, nursing pillows, rocking chairs	Range: 1,110,000-14,400,000 ng/g (1.11-14.4 mg/g)	Stapleton et al., 2011	TCPP detected in 16 of 101 product samples tested
Not Specified	Not Specified	Upholstery	77 µg/m <sup>2</sup> -hour	Kemmlein et al., 2003, as cited by Marklund 2005a	Migration rate
Japan	Laptop computer	Chassis	100 ng/g	Kajiwara et al., 2011	Two TVs sampled
		Keyboard top	11 ng/g		
		PC boards	34 ng/g		
		Cooling fan and speakers	4.0 ng/g		
		AC adapter	150 ng/g		
		LCD panel	12 ng/g		
	LCD TV; purchased new in Japan in 2008	Rear cover	4.0 ng/g TV1 10 ng/g TV2	Kajiwara et al., 2011	
		Front cover	9.0 ng/g TV1 14 ng/g TV2		
		Power board	52 ng/g TV1		
		PC board for power and fluorescent	5.5 ng/g TV1 16 ng/g TV2		
		Other PC boards	23 ng/g TV1 26 ng/g TV2		
		LCD panel	4.0 ng/g TV1&2		
Other products; purchased new in Japan in 2008	Curtains	<3 ng/g	Kajiwara et al., 2011	Two samples	

Country	Item	Media	TCPP Concentrations <sup>1</sup>	Reference	Notes
Japan	Other products; purchased new in Japan in 2008	Electrical outlets	12 ng/g 85 ng/g	Kajiwara et al., 2011	Two samples
		Insulation boards	28 ng/g 37 ng/g		Two samples
		Wallpaper	Range: 60-100 ng/g		Four samples
	Household products	Cushion	Range: 900-3,100 ng/g (0.9-3.1 µg/g)	Nagase et al., 2003	
	TV Set	Chamber air	Range: ND-1,700 ng/m <sup>2</sup> -hr (ND- 1.7 µg/m <sup>2</sup> -hr)	Saito et al., 2007	Migration rate from TV set; MDL = 330 ng/m <sup>2</sup> -hr (0.33 µg/m <sup>2</sup> -hr)
Germany		Wood preservation coatings	150,000 ng/g (150 mg/kg)	Ingerowski et al., 2001	Sample materials obtained from individual test locations that showed high dust concentrations. 0.1-1 g per sample. Authors only reported the highest concentration found in given specimen by one of three laboratories.
		Mattresses (polyurethane)	1,500,000 ng/g (1,500 mg/kg)		
		Wall paper (glass fiber)	1,100,000 ng/g (1,100 mg/kg)		
		Carpet backing (polyurethane)	13,100,000 ng/g (13,100 mg/kg)		
		Foam fillers (polyurethane)	180,000,000 ng/g (180,000 mg/kg)		
		Floor sealing material	220,000 ng/g (220 mg/kg)		

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are in shown in parentheses.

ND – not detected; MDL – method detection limit

### 3.4 TCPP ADME and Biomonitoring Studies

A study in rats indicates that TCPP is absorbed following oral dosing (Minegishi et al., 1988). Studies of elimination for selected phosphate ester flame retardants indicate that urine is the main route of elimination for most of them and that there are differences among species and between male and female animals of the same species. A comparative study of <sup>14</sup>C-labeled TDCPP, TCPP, and TCEP reported that, in rats, approximately 60% of the administered TCPP was excreted in the urine (Minegishi et al., 1988). Elimination from blood occurs in two phases with the first phase taking 12-14 hours and the second phase taking 42-59 hours. TCPP reached the

maximum tissue concentration at 5.7 hours after dosing. Tissue/blood ratios were low in the brain, heart, muscle, and testes; ratios were moderate in adipose tissue, the spleen, and lung; ratios were high in the kidneys and liver indicating enterohepatic circulation (Minegishi et al., 1988). The highest level of radioactivity was found in the liver seven days following dosing, and the longest elimination half life was 103 hours for adipose tissue (Minegishi et al., 1988).

A metabolite of TCPP was found in 21% of urine samples collected from 312 children exposed to multiple flame retardants, with median levels of less than 20 ng/L (0.02 µg/L) (Fromme et al., 2014). TCPP has been detected in the breast milk of Swedish women at concentrations ranging from 22 to 82 ng/g, with a median of 45 ng/g (Sundqvist et al., 2010). See Table 3-9 below for human biomonitoring data.

**Table 3-9. TCPP Biomonitoring Data**

Country	Tissue/fluid	TCPP Concentrations <sup>1</sup>	Reference	Notes
Germany	Urine	Median: <20 ng/L (<0.02 µg/L) Range: <20-8400 ng/L (<0.2-8.4 µg/L)	Fromme et al., 2014	Metabolites of TCPP were found in 21% of urine samples collected from 312 children
Sweden	Human milk lipids	Median: 45 ng/g Range: 22-82 ng/g	Sundkvist et al., 2010	5 Pooled samples (total 285 individuals) from 1997-2003, 1 individual sample 2006, 4 towns

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

Min- minimum; max- maximum

### 3.5 TCPP Exposure Assessments and Estimates

NRC (2000) estimated exposure to TCPP and compared the estimates to toxicity values to characterize risk. ECHA (2008) estimated inhalation and dermal exposure to TCPP as part of its assessment of TDCPP. In addition, several publications were reviewed where the authors estimated exposure levels (Brommer et al., 2012; Yang et al., 2014; Van den Eede et al., 2011; Stapleton et al., 2009).

It should be noted that multiple approaches exist to calculate an average daily intake, each utilizing different values, institutional practices and accepted assumptions about many factors (e.g., safety factors, using high end or average values for intake estimates, assumptions about food intake, and derivation of those values for subpopulations such as children and toddlers). In

an exposure assessment, choices for those values and the assumptions and approaches should be discussed and defended.

The National Research Council (NRC, 2000) conducted an upper bound worst-case screening assessment of the risk and exposure of several flame retardants including Tris monochloropropyl phosphates (TMCPPs), which includes the TCPP isomer, from exposure to upholstered furniture. These estimates used a number of assumptions and scenarios regarding products, air-change rates and emission or release rates. NRC developed risk values for oral and inhalation routes of exposure and calculated hazard indices to provide an indication of potential risk. They estimated an absorbed daily dose of 1.5 mg/kg/day for dermal exposure of adults. No hazard index was calculated due to lack of dermal toxicity data (NRC, 2000). NRC estimated an inhalation short time-average concentration of 0.48  $\mu\text{g}/\text{m}^3$  for adult exposure to particles. The NRC committee also considered possible release of TMCPP vapors from evaporation and estimated a short time-average concentration of 7500  $\text{mg}/\text{m}^3$  for adult exposure to vapors. They thought the results suggest that a vapor inhalation scenario is not realistic. They did not calculate a hazard index for inhalation exposure because no inhalation RfC was available. For oral exposure, NRC estimated a worst case average oral daily dose of 0.14 mg/kg-day but found insufficient data to derive an oral reference dose to compare with the exposure estimate (NRC, 2000).

The European Chemicals Agency (ECHA) looked at occupational and indirect exposures, as well as consumer exposure to TDCPP from flexible foam used in upholstery, cars and bedding (ECHA, 2008). Because information on TDCPP was lacking, they used data on TCPP to estimate average daily human intake from indoor air from PU foam-containing items based upon chamber study data of TCPP and typical human consumption and inhalation rates. A worst-case approach gave a reasonable worst case inhalation exposure value (indoor concentration) of 3.8  $\mu\text{g}/\text{m}^3$  - 24 hours TWA. Using default values of a 70 kg person inhaling 20  $\text{m}^3$  of air per 24-hour day and assuming 100% absorption, the inhalation body burden was 1  $\mu\text{g}/\text{kg}$  (ECHA, 2008). For a typical exposure, ECHA used a concentration of 2.8  $\mu\text{g}/\text{m}^3$  and adjusted the exposure for 18 hours out of 24 hours to estimate a body burden of 0.6  $\mu\text{g}/\text{kg}$ . These inhalation estimates are for exposure from PU foam-containing items and do not include exposure from other sources of exposure.

Brommer et al., 2012 estimated exposure via dust ingestion in subpopulations with various exposure scenarios using TCPP concentrations from their study of cars, offices and residences. Toddler exposure was estimated to range from 0.13 ng/kg bw/day (low, based on 5<sup>th</sup> percentiles) to 1.4 ng/kg bw/day (typical, based on median concentrations), to 4.4 ng/kg bw/day (high, based on 95<sup>th</sup> percentiles), with adult exposure ranging from 0.79 ng/kg bw/day (low, 5<sup>th</sup> percentiles), to 0.25 ng/kg bw/day (typical, medians), to 2.2 ng/kg bw/day (high, 95<sup>th</sup> percentiles). Exposure projections were based on body weights of 12.3 kg and 70 kg and dust ingestion of 200 mg/day and 50 mg/day for toddlers and adults, respectively. Adults were assumed to spend 4.2%, 23.8%,

and 72% of their time in cars, offices, and home, respectively. Toddlers were assumed to spend 4.2% of time in cars and the remainder of the day at home (Brommer et al., 2012).

Yang et al. (2014) measured suspended particulate matter collected from offices for a number of organophosphate flame retardants, including TCPP. The measured concentrations of TCPP in airborne dust were used to estimate inhalation exposure for adults using U.S. EPA and International Commission on Radiological Protection (ICRP) models for deposition efficiency and flux of inhaled particles in the respiratory tract. The authors assumed a dust inhalation rate of 16 m<sup>3</sup>/day, a body weight of 70 kg, and an 8-hour exposure (Yang et al., 2014). The authors reported a median exposure of 0.59 ng/kg/day and a 95<sup>th</sup> percentile exposure of 6.17 ng/kg/day for adults using the U.S. EPA model and a median exposure of 0.35 ng/kg/day and a 95<sup>th</sup> percentile exposure of 3.32 ng/kg/day for adults using the ICRP model (Yang et al., 2014).

Van den Eede et al. (2011) analyzed dust samples from Flemish homes and shops for multiple organophosphate flame retardants, including TCPP (median 2940 ng/g). For adults, the authors assumed 20 mg/day or 50 mg/day (average and high ingestion rates, respectively) and an average body weight of 70 kg. For toddlers they assumed a dust ingestion rate of 50 mg/day (average) and 200 mg/day (high) and an average toddler body weight of 12.3 kg. Using median exposure concentrations, the authors calculated a daily ingestion exposure for toddlers of 5.6 ng/kg/day for average ingestion and 22.4 ng/kg/day for high ingestion. A worst case exposure scenario combined the upper 95<sup>th</sup> percentile concentration with the high ingestion rate resulting in an intake rate of 92.7 ng/kg/day. Using median concentrations for a non-working adult exposure resulted in 0.5 ng/kg/day for average ingestion and 1.2 ng/kg/day for high ingestion; the worst case for working adults was calculated at 10.2 ng/kg/day.

Stapleton et al. (2009) measured concentrations of TDCPP, TCPP, and TPP in house dust extracts from 50 Boston MA homes. They estimated cumulative exposure to these organophosphate flame retardants as well as data on four others (TBB, PBDEs, TBPH, and HCBd) using the geometric mean concentration for each flame retardant and lower bound dust ingestion rates from U.S. EPA (100 mg dust/day for a child; 20 mg dust/day for an adult). For children, the average estimated cumulative exposure was about 1600 ng/day; for the adult it was about 325 ng/day, with a majority of the exposure from TPP, TDCPP and PBDEs (Stapleton et al., 2009).

### **3.6 TCPP Discussion**

Commercial pentaBDE has been banned or phased out around the world over the last 10-20 years. During that period, the use of TCPP has been driven by its identification as a substitute for pentabromodiphenyl ether (pentaBDE). It has been studied and measured in water, dust, consumer products, and indoor and ambient air. The available literature indicates that the relevant concentrations of TCPP are highest in the air and dust of indoor environments.

Breathing contaminated indoor air and contact with dust appears to be the main possible sources of exposures for consumers to TCPP. The highest airborne and dust concentrations of TCPP were measured in homes and other indoor spaces that were presumably proximate to the TCPP treated polymers. Normal hand-to-mouth activity is the primary route of exposure for dust. Incidental hand- to-mouth activity occurs over a person's entire life but it occurs most often and most significantly in children, and therefore, children may have greater exposures than adults. The U.S. EPA estimates daily dust/dirt ingestion rates for children in the range of 50 to 100 mg per day, with adults at a lower but still substantial amount of 30 mg per day (central tendency) in the general population for dust ingested daily (U.S. EPA, 2011).

ECHA estimated a reasonable worst case indoor air concentration for consumers around 3-4  $\mu\text{g}/\text{m}^3$ , which translates to about 80  $\mu\text{g}/\text{day}$  for someone inhaling 20  $\text{m}^3$  per day. This is considerably higher than the estimated exposures of about 1  $\mu\text{g}/\text{day}$  from dust ingestion by Van den Eede et al. (2011) or Brommer et al. (2012). Van den Eede et al. (2011) used a TCPP dust concentration of about 3,000 ng/g. Considerably higher values were seen in other studies, notably work done by researchers in Germany reporting maximum concentrations in house dust of 375,000 ng/g (Ingerowski et al., 2001) and in the dust of a day care center, 47,000 ng/g (Fromme et al., 2014). Using these values would result in orders of magnitude higher estimates of TCPP exposure from dust.

There are limited human biomonitoring data on TCPP, but what is available demonstrates that children and adults take up TCPP. Fromme et al. (2014) measured a metabolite of TCPP in 21% of urine samples collected from 312 children exposed to multiple flame retardants, with median levels of less than 20 ng/L (0.02  $\mu\text{g}/\text{L}$ ). TCPP has also been detected in the breast milk of Swedish women at concentrations ranging from 22 to 82 ng/g, with a median of 45 ng/g (Sundqvist et al 2010).

Worst case exposure from water comes from the assumption of people drinking treated surface water with the maximum amount of TCPP found in the original surface water sample . Here a daily ingestion of 2 liters would result in about 5  $\mu\text{g}$  of TCPP exposure per day from this source (Stepien et al., 2013).

All of the above information and estimates suffer from a considerable amount of uncertainty related to the magnitude, timing and completeness of the monitoring studies and the possible use of overly conservative estimates. In addition, the wide range of values reflects the differences in the products and materials, as well as the wide range of TCPP and flame retardant usages in different countries (and states) based upon prevailing regulations and commerce.

It would appear that homes with TCPP treated carpet, carpet backing, or wall coverings could present the highest potential for TCPP exposure to consumers. The large surface-area-to-volume

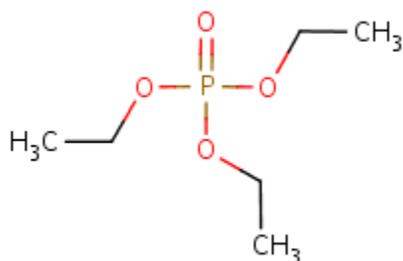
ratio of these products could ultimately produce the highest indoor air and dust concentrations, with concomitant exposure via hand-to-mouth dust ingestion and inhalation of re-entrained dust, along with the greatest potential for dermal exposure. On the other hand, estimates of exposure as generated by the National Academies (NRC, 2000) risk assessment reflect a severe lack of data and the use of very high default assumptions as a result of the dearth of available information.

## 4 Triethyl Phosphate (TEP) (CAS 78-40-0)

### 4.1 TEP Chemical and Physical Properties

Triethyl phosphate (TEP) (CAS 78-40-0) is a clear, liquid with a pleasant odor (HSDB, 2013). The water solubility value of  $5 \times 10^5$  mg/L at 25 °C indicates that TEP is completely miscible in water. It is also soluble in most solvents and is not expected to adsorb to solids and sediments in water based on an estimated soil-water coefficient ( $K_{oc}$ ) value of 65 (HSDB, 2013). An estimated vapor pressure of  $3.93 \times 10^{-1}$  torr at 25 °C indicates that TEP will exist as a vapor in the atmosphere (HSDB, 2013). Significant volatilization from water surfaces is not expected based on an estimated Henry's Law constant of  $3.6 \times 10^{-8}$  atm-m<sup>3</sup>/mol at 20 °C (HSDB, 2013).

**Figure 4-1. Molecular Structure of TEP** (ChemIDPlus, 2014)



**Table 4-1. CAS Registry Number and Synonyms for TEP** (ChemIDPlus, 2014; CalEPA, 2011)

CAS registry/RN	78-40-0
Synonyms	4-01-00-01339 (Beilstein Handbook Reference), AI3-00653, BRN 1705772, CCRIS 4882, EINECS 201-114-5, Ethyl phosphate ((EtO) <sub>3</sub> PO), Ethyl phosphate (VAN), HSDB 2561, NSC 2677, Phosphoric acid, triethyl ester, TEP, Triethoxyphosphine oxide, Triethyl phosphate, Triethylfosfat Triethylfosfat [Czech], Triethylphosphate, Tris(ethyl) phosphate, UNII-QIH4K96K7

**Table 4-2. Physical and Chemical Properties of TEP** (ChemIDPlus, 2014; HSDB, 2013; OECD, 2005)

Molecular Formula	C <sub>6</sub> H <sub>15</sub> O <sub>4</sub> P
Molecular Weight	182.1545

Melting Point	-56.4 °C
Boiling Point	215.5 °C
Density	1.0695 g/cm <sup>3</sup> (at 20 °C)
Solubility (in water)	5.00 x 10 <sup>5</sup> mg/L (at 25 °C)
Log K <sub>ow</sub>	0.8
Vapor Pressure	3.93 x 10 <sup>-1</sup> torr (at 25 °C) (HSDB, 2013) 2.92 x 10 <sup>-1</sup> torr (at 20 °C) (OECD, 2005)
Henry's Law Constant	3.60 x 10 <sup>-8</sup> atm-m <sup>3</sup> /mole (at 20 °C)

Many flame retardants are typically characterized by relatively high molecular weight, low vapor pressure/volatility, low or moderate solubility in water and a high octanol-water partition coefficient (K<sub>ow</sub>). The properties of TEP are quite different. Its molecular weight compared to other flame retardants is relatively low, while its vapor pressure and water solubility are quite high. To a significant degree, these properties determine the fate of TEP in the environment, which impacts the potential for human exposure. The relatively low K<sub>ow</sub> means it will not be strongly lipophilic and thus not partition into any sediment layers in an environmental water column. It will tend to remain in the water column. If it exists in the indoor environment, it will be present in the air as a vapor. To a lesser extent, TEP can also partition into and be present in available organic rich substrates like house dust.

Because of its properties and predicted fate in the indoor environment, the vapor pressure (VP) of pure TEP can be used in estimating its potential to become airborne as a vapor. Taking the highest measured vapor pressure at room temperature of 20°C (68°F) results in the following estimation of a maximum or saturated airborne concentration:

$$(0.393\text{torr}/760\text{torr}) (1,000,000) (430.9/24.4) = 3860 \text{ mg/m}^3$$

All monomers (including monomeric flame retardants) embedded within polymer matrices will move out of that matrix into surrounding media following classic laws of diffusion. Given a time frame of many months or a few years, a significant portion of the monomer will diffuse out of the polymer. Because of its relatively low partitioning coefficient into organics, TEP would be expected to diffuse from any polymer matrix relatively quickly. At least initially, TEP would not be expected to exist as a pure liquid indoors. Initially, it would be present in a polymer matrix of a material and, after it diffuses out of the matrix, it comes to the surface. Once on or near the surface, TEP, because of its relatively high vapor pressure, could then partition as a vapor into the indoor air or it may become associated with house dust on the polymer. Exposure would then be via inhalation of the vapor or dermal or hand-to-mouth ingestion of the TEP on the surface or in dust.

## 4.2 TEP Uses

TEP is a high production volume chemical in Europe (OECD, 2009). In the U.S., the production rate of TEP is less than 5000 tons/year, and primary uses are as an industrial catalyst, a polymer resin modifier and plasticizer, and an intermediate in the production of pharmaceuticals and ketene synthesis. Smaller amounts of TEP are used as a solvent, flame retardant, or an industrial intermediate for the production of pesticides and other chemicals (OECD, 2005, HSDB, 2013). TEP is registered as a component of a car paint repairing product (12–18 % w/w) and as a flame retardant in PU-polymers (3% w/w) in Finland (OECD, 2005).

## 4.3 TEP Human Exposure

TEP has been measured in indoor and ambient air, surface and drinking waters, food, and food packaging. It has been found in dust in houses and other indoor environments in the U.S., Japan, Belgium, Romania, and Spain. TEP is found in consumer electronics (laptop components and LCD TVs), and small concentrations have been measured in curtains, electrical outlets, insulation boards and wallpaper. Concentrations of TEP in the various media found in the literature are presented below.

OECD (2005) reports that some TEP passes diffusely into the environment through migration from plastics and from the use of TEP as a solvent and degradation of the pesticide parathion but do not specify amounts. Saito et al. (2007) measured the migration of TEP from walls and ceilings of a new home in Japan. TEP passed into effluent after treatment in a waste water treatment plant in Germany; in the U.S. it is processed for removal from one manufacturing waste stream (concentration of TEP in the resulting effluent is not known) (OECD, 2005). TEP is released into the air from industrial production in Germany, but in the U.S., atmospheric releases are minimal due to a closed manufacturing process (OECD, 2005).

### 4.3.1 TEP in Indoor and Ambient Air

TEP is anticipated to become airborne as a vapor after diffusing out of indoor matrices, such as treated plastics. Diffused TEP can also become associated with house dust, which is quite mobile, and can become airborne. Thus, TEP could be distributed within the indoor environment as a vapor and as dust on surfaces with a lesser amount of the TEP containing dust being airborne. An exception to this rule of low airborne levels from dust would be relatively “dusty” rooms where the dust has been allowed to accumulate and/or activities occur that tend to continually entrain the dust into the air. In these indoor environments, relatively high levels of airborne TEP as a free vapor or dissolved in dust may be found.

TEP air concentrations have been measured indoors in houses, offices, other workplaces, electronic dismantling center, vehicles, and various public places (Kanazawa et al., 2010;

Rothweiler et al., 1992; Saito et al., 2007; Staaf and Ostman, 2005a,b). The TEP concentrations measured in indoor air range from not detected to several hundred ng/m<sup>3</sup> in most studies (Kanazawa et al., 2010; Saito et al., 2007; Staaf and Ostman, 2005a,b). However, Rothweiler et al. (1992) reported measurement of 60,000 ng/m<sup>3</sup> in the air of renovated buildings in Switzerland (authors did not indicate how many of the 10 buildings or whether 60,000 ng/m<sup>3</sup> represents a maximum concentrations). The authors noted that TEP is used as a softening agent in carpet polyurethane foam backing (Rothweiler et al., 1992). TEP-treated foam in flooring, wall-covering or furniture appear to represent a significant source of TEP in indoor air; with these products' large surface area, they could represent a significant subset of relatively high exposure to this compound indoors. See Table 4-3.

**Table 4-3. TEP Concentrations in Indoor Air**

Country	Location	Media	TEP Concentrations <sup>1</sup>	Reference	Notes
Sweden, Stockholm	House, transport vehicles, offices, workshops, shops, and health care facilities	Indoor air	House: 1-21 ng/m <sup>3</sup> Transport: 1-220 ng/m <sup>3</sup> Offices: 1-2 ng/m <sup>3</sup> Workshops: 1-23 ng/m <sup>3</sup> Shops: 1-19 ng/m <sup>3</sup> Health care: 7 ng/m <sup>3</sup>	Staaf and Ostman, 2005a	Stationary sampler with SPE cartridge containing an aminopropyl silica phase (25 mg, 1 ml)
	Electronic dismantling facility (n=5)	Indoor air	5 ng/m <sup>3</sup>	Staaf and Ostman, 2005b	Glass fibre filter
23 ng/m <sup>3</sup>			SPE cartridge		
Switzerland	Renovated buildings	Indoor air	60,000 ng/m <sup>3</sup> (60 µg/m <sup>3</sup> )	Rothweiler et al., 1992	Sampled on Tenax TA and analyzed with GC-MS
Japan, Tokyo	Houses and offices	Indoor air	House Median: 2.4 ng/m <sup>3</sup> Range: ND-58.2 ng/m <sup>3</sup> Office Median: 3.2 ng/m <sup>3</sup> Range: 0.44-8.8 ng/m <sup>3</sup> Lab range: 0.60-0.67 ng/m <sup>3</sup>	Saito et al., 2007	MDL = 0.26 ng/m <sup>3</sup> ; Sampled using quartz fiber Filter (47 mm), first stage and a solid phase extraction disk (empore <sup>tm</sup> Disk C18, 47mm), second stage.

Country	Location	Media	TEP Concentrations <sup>1</sup>	Reference	Notes
Japan	Sapporo, Houses	Indoor air	Median: 62.3 ng/m <sup>3</sup> Range: 18.1-511 ng/m <sup>3</sup>	Kanazawa et al., 2010	Sampling at 1-1.5 m from floor and 1 m from floor; empore <sup>tm</sup> Disk C18, 47mm

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

ND – not detected; MDL – method detection limit; SPE – Solid Phase Extraction

One ambient air study in Tokyo reported TEP concentrations ranging from not detected to 1.4 ng/m<sup>3</sup> (Saito et al., 2007).

**Table 4-4. TEP Concentrations in Ambient Air**

Country	Location	Media	TEP Concentrations <sup>1</sup>	Reference	Notes
Japan	Tokyo, Eight different locations	Outdoor air	Median: ND Range: ND-1.4 ng/m <sup>3</sup>	Saito et al., 2007	MDL = 0.26 ng/m <sup>3</sup>

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

ND – non detect; MDL – method detection limit

### 4.3.2 TEP in Water

No studies of TEP measurements in U.S. drinking water were located. TEP has been detected in finished drinking water in Canada and has also been detected in surface waters in Japan, Spain, Italy, and the Netherlands. TEP concentrations measured in finished drinking water in Canada ranged from 1.1-27.1 ng/L (Williams and Lebel, 1981; Williams et al., 1982; Lebel et al., 1981 as cited in HSDB, 2013).

In surface waters, OECD (2005) reports maximum concentrations for the Rhine River and tributaries in Europe ranging from <100 – 6500 ng/L, and a maximum concentration of 1,000 ng/L was measured in bank-filtered water from the Rhine River in the Netherlands (Piet and Morra, 1983, as cited in HSDB, 2013). The mean concentration of TEP in Osaka City Rivers in Japan from 1976-1990 was 1,500 ng/L (Fukushima et al., 1992). OECD (2005) does not provide citations for these concentrations but notes “The 90-percentile of the listed highest concentrations recorded over the last years is 2.4 µg/l, which is very close to the calculated background concentration of 1.1 µg/l. As more confidence can be put upon the measured values

in this case, a regional background concentration of  $PEC_{regional} = 2.4 \mu\text{g/l}$  is used in the risk characterization” (OECD, 2005 page 9).

TEP has been qualitatively detected in groundwater at U.S. Superfund sites and the River Waal in Brakel Netherlands (Maney et al., 1995; Meijer and VanderLeer, 1976 as cited in HSDB, 2013). Information on concentrations of TEP before and after drinking water treatment was not found in the available literature. See Table 4-5 below.

**Table 4-5. TEP Concentrations in Water**

Country	Location	Media	TEP Concentrations <sup>1</sup>	Reference	Notes
Canada	12 municipalities	Finished drinking water	Range: 10.3-13.0 ng/L	Williams et al., 1982	Source water from the Great Lakes
	6 Ontario municipalities	Finished drinking water	Range: 17.2-27.1 ng/L	Lebel et al., 1981 as cited in HSDB, 2013	Detected in 2 of the 6 Ontario water treatment plants
	29 municipalities	Finished drinking water	Range: 1.1-23 ng/L	Williams and Lebel, 1981	Water treatment plants, sources include rivers, lakes and ground water
Netherlands	Rhine River	Bank-filtered water	Max: 1,000 ng/L	Piet and Morra, 1983 as cited in HSDB, 2013	Surface water
Spain	Northwest area	Surface water	Median: 3 ng/L	Rodil et al., 2012	
Italy	River Tiber	River	Mean: 45 ng/L (June) Mean: 27 ng/L (Nov)	Bacaloni et al., 2007	
Japan	Osaka	Surface water	Mean: 1,500 ng/L (1.5 $\mu\text{g/L}$ )	Fukushima et al., 1992	Trend of concentration from 1976-1990

Country	Location	Media	TEP Concentrations <sup>1</sup>	Reference	Notes
Europe	River Rhine and tributaries	Surface water	Range: <100-6500 ng/L ( <0.1-6.5 µg/L)	OECD, 2005	Highest concentrations recorded between 1987 and 1992. DL = 100 ng/L (0.1 µg/L)

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

Max – maximum; DL – detection limit

### 4.3.3 TEP in Food

No reports of TEP measurements in food in the U.S. were located. Tomizawa et al. (2004) measured TEP in several foods, concentrations ranged from 80 to 270 ng/g, and food packaging concentrations ranged from 130 to 4,700 ng/g (Tomizawa et al., 2004; abstract available in English). The authors assumed that TEP leached into the food from the packaging, but note that TEP has also been found in cereal (with fat) that has been stored for a long time (Tomizawa et al., 2004). See Table 4-6.

**Table 4-6. TEP Concentrations in Food**

Country	Study Type	Food	TEP Concentrations <sup>1</sup>		Reference	Notes
UK	Pesticide residue analysis	Oatmeal	Food: 270 ng/g (0.27 µg/g)	Package: 470 ng/g (0.47 µg/g)	Tomizawa et al., 2004	Japanese study measured TEP values in products and their packaging from various countries
Italy		Pasta	Food: 90 ng/g (0.09 µg/g)	Package: 150 ng/g (15 µg/g)	Tomizawa et al., 2004	
France		Pasta	Food: 80 ng/g (0.08 µg/g)	Package: 4,700 ng/g (4.7 µg/g)	Tomizawa et al., 2004	
France		Pasta	Food: 90 ng/g (0.09 µg/g)	Package: 130 ng/g (13 µg/g)	Tomizawa et al., 2004	

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

NA – not available

### 4.3.4 TEP in Dust

TEP has been measured in dust in a variety of settings, including houses, a carpenter workshop, a second-hand store, electronics stores, and a laboratory. TEP levels in dust measured in California houses ranged from <20-410 ng/g (Dodson et al., 2012). Japanese studies reported a range of less than the method detection limit of 520 ng/g to 3,310 ng/g from floor and multi-surface house dust in that country (Araki et al., 2014; Kanazawa et al., 2010). In Belgium, TEP levels in house dust ranged from less than the quantification limit of 30 ng/g to 50 ng/g and levels in shops ranged from 50-370 ng/g (Van den Eede et al., 2011, 2012). Levels of TEP measured in dust are significantly lower than what has been reported for other flame retardants. This is a result of its significantly lower octanol-water partitioning coefficient ( $K_{ow}$ ) compared to most other flame retardants. Common house dust is made up in large part of human skin cells that have been shed, and it is essentially organic in nature. Flame retardants with a high  $K_{ow}$  will partition into dust particles to a much higher extent than TEP. Adsorption that does occur for TEP into dust may be more associated with any water content of the dust. Also, any molecular water layers on an indoor surface will absorb TEP. See Table 4-7 below.

**Table 4-7. TEP Concentrations in Dust**

Country	Location	Media	TEP Concentrations <sup>1</sup>		Reference	Notes
United States	California houses	Dust	2006 sampling Median: 28 ng/g Range: <20 - 410 ng/g	2011 sampling Median: <20 ng/g Range: <20-250 ng/g	Dodson et al., 2012	2006 and 2011 collection, vacuum cleaner with cellulose extraction thimble.
Japan	182 single family houses	Floor, multi surface dust	Floor All: <MDL Range: <MDL-2,800 ng/g (<MDL-2.8 µg/g)	Multi surface dust Median: <MDL Range: <MDL-3,310 ng/g (3.31 µg/g)	Araki et al., 2014	Hand held vacuum cleaner; MDL = 520 ng/g (0.52 µg/g)

Country	Location	Media	TEP Concentrations <sup>1</sup>		Reference	Notes
Japan	Sapporo House	Dust	Floor Median: <MDL Range: <MDL-2,100 ng/g (<MDL- 2.1 mg/kg)	Multi surface dust Median: <MDL Range: <MDL-2,100 ng/g (<MDL- 2.1 mg/kg)	Kanazawa et al., 2010	Vacuum cleaner collection; MDL = 520 ng/g (0.52 mg/kg)
Belgium, Flemish region	House	Dust	Mean: 50 ng/g (<0.05 µg/g)	Median: same as mean	Van den Eede et al., 2011	Vacuum dust samples
	Carpenter workshop, second-hand store, electronics stores, laboratory	Dust	Mean: 130 ng/g (0.13 µg/g) Median: 60 ng/g (0.06 µg/g)	Range: 50- 370 ng/g (<0.05-0.37 µg/g)		
Belgium, Romania, Spain	Houses	Dust	All: <LOQ		Van den Eede et al., 2012	LOQ = 30 ng/g; Vacuum dust samples

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

max – maximum; min – minimum; MDL – method detection limit; LOQ – level of quantification

### 4.3.5 TEP in Consumer Products

Only a few studies were located measuring concentrations of TEP in consumer products. See Table 4-8 below.

#### 4.3.5.1 Furniture and Household Products

An analysis of carpet samples determined that TEP was a major component of carpet tested, but the quantitative amount was not determined (Pleil et al., 1990). Scientists in China created a novel polyurethane rigid foam that has a high percentage of castor oil phosphate flame-retarded polyol (COFPL) derived from renewable castor oil (Zhang et al., 2013). The addition of expandable graphite (EG) and TEP to the COFPL polyurethane rigid foam increases the flame retardant efficiency (Zhang et al., 2013). TEP was measured in curtains (<0.1 ng/g), electrical outlets (<0.5-1.4 ng/g), insulation boards (5.7-11 ng/g), and wallpaper (1.1-4.0 ng/g) (Kajiwara et al., 2011). Saito and colleagues (2007) measured the migration of TEP from walls and ceilings in a new home in Japan. TEP migrated at a rate of 130 ng/m<sup>2</sup>-hr for walls and 160 ng/m<sup>2</sup>-hr for ceilings (Saito et al., 2007).

### 4.3.5.2 Electronic Products

Kajiwara et al. (2001) measured the levels of TEP using the wipe method from various computer and LCD TV components in Japan; levels of TEP ranged from 0.3-190 ng/g.

**Table 4-8. TEP Concentrations in Consumer Products**

Country	Item	Media	TEP Concentrations <sup>1</sup>	Reference	Notes	
Japan	Laptop computer	Chassis	6.0 ng/g	Kajiwara et al., 2011		
		Keyboard top	17 ng/g			
		PC boards	56 ng/g			
		Cooling fan and speakers	30 ng/g			
		AC adapter	1.1 ng/g			
		LCD panel	13 ng/g			
	LCD TVs; purchased new in Japan in 2008	Rear cover	0.5 ng/g TV1 0.40 ng/g TV2		Two TVs sampled	
		Front cover	3.0 ng/g TV1 0.40 ng/g TV2			
		Power board	3.6 ng/g TV1 190 ng/g TV2			
		PC board for power and fluorescent	1.1 ng/g TV1 0.40 ng/g TV2			
		Other PC boards	0.70 ng/g TV1			
		LCD panel	6.3 ng/g TV1 0.30 ng/g TV2			
	Other products; purchased new in Japan in 2008	Curtains	<0.1 ng/g		Two samples	
		Electrical outlets	Range: <0.5-1.4 ng/g		Two samples	
		Insulation boards	Range: 5.7-11 ng/g		Two samples	
		Wallpaper	Range: 1.1-4.0 ng/g		Four samples	
	Newly built house	Wall	130 ng/m <sup>2</sup> /hr (0.13 µg/m <sup>2</sup> /hr)		Saito et al., 2007	Migration from interior surface to solid extraction disk
		Ceiling	160 ng/m <sup>2</sup> /hr (0.16 µg/m <sup>2</sup> /hr)			
		Floor	ND			MDL = 90 ng/m <sup>2</sup> /hr (0.09 µg/m <sup>2</sup> /hr)

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

ND- non detect; AC- alternating current; LCD- liquid crystal display; PC- personal computer; ND – not detected; MDL – method detection limit

#### 4.4 TEP ADME and Biomonitoring Studies

No *in vivo* human data for absorption, distribution, metabolism, or elimination of TEP by any route of exposure were located. TEP administered orally or by intraperitoneal injection at doses of 100 or 1,000 mg/kg to rats and mice is eliminated rapidly and comprehensively via the urine (90% within 16 hours, 100% within 96 hours) as the metabolite, diethyl phosphate (OECD, 2005; Jones, 1970 as cited in Berdasco et al., 2011). A skin penetrating study using human anterior forearm stratum corneum conjunctum found a maximum steady-state dermal penetration rate of 0.288  $\mu\text{mol}/\text{cm}^2/\text{min}$ . Acute dermal toxicity studies indicate a low order of systemic toxicity (Jones, 1970 as cited in Berdasco et al., 2011). This low acute dermal toxicity supports that absorption via dermal exposure is much less than via oral administration (OECD, 2005).

Kim et al. (2014) tested human breast milk for organophosphate flame retardants in women in the Philippines, Vietnam, and Japan. TEP levels in Filipino women ranged from not detected to 1.5 ng/g, Vietnamese women ranged from not detected to 18 ng/g, and Japanese women ranged from not detected to 15 ng/g (detection limits between 0.01 and 0.08 ng/g lipid weight) (Kim et al., 2014). See Table 4-9.

**Table 4-9. TEP Biomonitoring Data**

Country (location)	Tissue/fluid	Concentrations <sup>1</sup>	Reference	Notes
Philippines (Payatas and Malate)	Human breast milk	<i>Overall</i> Median: ND <i>Payatas</i> Median: ND Range: ND-1.2 ng/g <i>Malate</i> Median: ND Range: nd-1.5 ng/g	Kim et al., 2014	MDL = 0.01-0.08 ng/g lipid weight (2.7-7.9% lipid weight)
Japan (Kanagawa)	Human breast milk	Median: ND Range: nd-15 ng/g	Kim et al., 2014	MDL = 0.01-0.08 ng/g lipid weight (2.7-7.9% lipid weight)

Country (location)	Tissue/fluid	Concentrations <sup>1</sup>	Reference	Notes
Vietnam (Hanoi, Bui Dau, Trang Minh)	Human breast milk	<i>Overall</i> Median: ND <i>Bui Dau</i> Median: ND Range: ND -0.80 ng/g <i>Hanoi and Trang Minh</i> Median: ND Range: ND	Kim et al., 2014	MDL = 0.01-0.08 ng/g lipid weight (2.7-7.9% lipid weight)

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

ND – not detected; MDL – method detection limit

#### 4.5 TEP Exposure Assessments and Estimates

Little information on exposure estimates was located for TEP. OECD prepared a SIDS Initial Assessment Profile on TEP and concluded that “the chemical is of low current priority for further work in the SIDS context” (OECD, 2005, page 2). To reach this conclusion OECD considered production, releases to the environment, toxicity and estimated human exposures. They calculated a predicted environmental concentration (PEC) of 194 µg/L for a realistic worst case situation for release into water at production. Using specific data for a German production site, they calculated a concentration of 0.2 µg/L to the Rhine River. Concentrations to water from inclusion of TEP into a polymeric matrix was calculated using German data, and a PEC of 196 µg/L was calculated for a worst case scenario that assumes all TEP used as a flame retarder or plasticizer in Germany is processed at one site. In addition, they calculated regional PEC concentrations based on diffuse release sources using the regional distribution model SIMPLEBOX and worst case assumptions for the release rate of TEP in Germany with the following results:

- Water: 1.1 µg/L
- Soil: 0.075 ng/kg dry weight
- Sediment: 0.71 µg/kg dry weight
- Air: 4.3 x 10<sup>-12</sup> g/m<sup>3</sup>

OECD notes that, although they used German specific exposure data, the assumed emitted amounts are considered worst case, and exposures should be similar in other countries when production volumes and use patterns are comparable. They also concluded that the measured data probably reflect mostly background concentrations with the exception of sediments.

For consumer exposure, OECD thought that exposure concentrations are probably very low because of TEP's low vapor pressure. They concluded that the highest exposure for the general population would be through drinking water (processed from surface water) and that removal of significant amounts of TEP would not be expected during processing due to TEP's physical and chemical properties. OECD reported the "90<sup>th</sup> percentile of the listed highest concentrations recorded over the last years is 2.4 µg/L" (OECD, 2005, page 9).

OECD noted that data are not available on consumer exposure, but they did not rule out that products containing TEP might give off small amounts into the environment. They thought that exposure to consumers would be low due to TEP's low vapor pressure, rapid degradation in the body, and limited dermal uptake (OECD, 2005).

#### **4.6 TEP Discussion**

It would appear from the limited available data and physical properties of this flame retardant, that the primary mode of exposure for U.S. consumers to TEP in products is from treated polymers used indoors. Because of its relatively high affinity for water and air versus organic matter, TEP is expected to ultimately appear in air or possibly in the ambient moisture present in house dust. The available data suggest relatively little human exposure potential for the places that have been monitored; however, the use and properties profile for this chemical suggest that the potential for human exposure (inhalation, dermal, hand-to-mouth oral) could be relatively high in indoor environments that have large surface areas of TEP treated polymer in such products as carpet, carpet backing, furniture or wall covering.

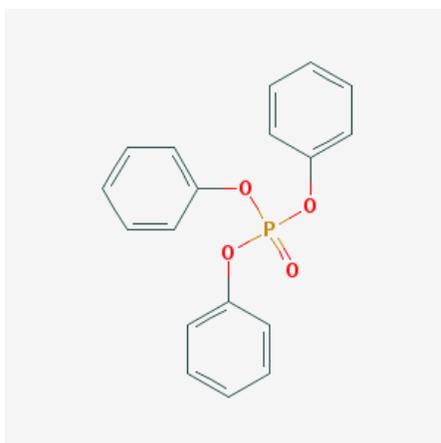
The literature search did not reveal if these circumstances of product use are common, rare, or essentially non-existent in the U.S.; thus, it may or may not hold the key to significant consumer exposure to TEP. However, Kim et al. (2014) tested human breast milk for organophosphate flame retardants in women in the Philippines, Vietnam, and Japan and found levels up to 18 ng/g (Kim et al., 2014), giving evidence that people are exposed to TEP and it is absorbed by the body.

## 5 Triphenyl Phosphate (TPP) (CAS 115-86-6)

### 5.1 TPP Chemical and Physical Properties

Triphenyl phosphate (TPP) is a colorless crystalline powder with a phenol-like odor (HSDB, 2013). TPP has a water solubility ranging from 0.2 mg/L (river water) to 1.9 mg/L (distilled water) at 20°C (OECD, 2002; HSDB, 2013). TPP is expected to adsorb to solids and sediments in water based on an estimated soil-water coefficient ( $K_{oc}$ ) range of 2,514 to 3,561 and is expected to volatilize from water surfaces based on an estimated Henry's Law constant of  $3.6 \times 10^{-8}$  atm-m<sup>3</sup>/mol at 25°C (HSDB, 2013). An estimated vapor pressure of  $6.3 \times 10^{-6}$  torr at 25°C indicates that TPP will exist as a vapor and particulate in the atmosphere (HSDB, 2013).

**Figure 5-1. Molecular Structure of TPP** (ChemIDPlus, 2014)



**Table 5-1. CAS Registry Number and Synonyms for TPP** (ChemIDPlus, 2014; HSDB, 2013)

CAS registry/RN	115-86-6
Synonyms	Disflamoll TP; Phosphoric acid, triphenyl ester; Celluflex TPP; Phosflex TPP; Triphenoxyphosphine oxide; Triphenylphosphate; Phosphoric Acid Triphenyl Ester; Triphenyl Phosphate TPP; Phenyl phosphate ((PhO) <sub>3</sub> PO); Trifenylfosfat; Trifenylfosfat [Czech]; NSC 57868; UNII-YZE19Z66EA; CCRIS 4888; HSDB 2536; EINECS 204-112-2; EC 204-112-2; BRN 1888236; AI3-04491

**Table 5-2. Physical and Chemical Properties of TPP** (ChemIDPlus, 2014; HSDB, 2013)

Molecular Formula	C <sub>18</sub> H <sub>15</sub> O <sub>4</sub> P
Molecular Weight	326.29 g/mol
Melting Point	50.5°C (HSDB, 2013) 49-50 °C (ICSC, 2000)
Boiling Point	370°C (ICSC, 2000)
Density	1.2055 g/cu cm at 50°C (HSDB, 2013)
Solubility (in water)	0.2 mg/L at 20°C (OECD, 2002) 1.9 mg/L at 20°C (HSDB, 2013)
Log K <sub>ow</sub>	4.59 (HSDB, 2013; Babich, 2006)
Vapor Pressure	6.28 x 10 <sup>-6</sup> torr at 25°C (HSDB, 2013; Babich, 2006)
Henry's Law Constant	3.31 x 10 <sup>-6</sup> atm·m <sup>3</sup> /mol at 25°C (HSDB, 2013)

Semi-Volatile Organic Compounds (SVOCs), such as TPP, are typically characterized by a relatively high molecular weights, low vapor pressure/volatility, low or moderate solubility in water and a high octanol-water partition coefficient. To a significant degree, these properties determine the fate of TPP in the environment, which impacts the potential for human exposure. The high octanol-water partition coefficient means it will be lipophilic or “fat loving;” that is, it will partition into any sediment layers in an environmental water column. Unless there are large areas of volatilizing surface in the indoor environment, it will not be highly present in the air as a vapor but will ultimately partition out of treated objects and into and be present in available organic rich substrates like house dust. If associated with food packaging it could partition into the food.

Because of its properties and fate in the indoor environment, the vapor pressure (VP) of pure TPP can be misleading in estimating its potential to become airborne as a vapor. Using the measured vapor pressure at typical room temperature of 25°C (73°F) results in the following estimation of a maximum or saturated airborne concentration:

$$(6.3 \times 10^{-6} \text{ torr} / 760 \text{ torr}) (1,000,000) (326.3 / 24.4) = 111 \mu\text{g}/\text{m}^3$$

All monomers (including monomeric flame retardants) embedded within polymer matrices will move out of that matrix into surrounding media following classic laws of diffusion. Given a time frame of many months or a few years, a significant portion of the monomer will diffuse out of the polymer. In reality, TPP would never be expected to exist as a pure material indoors. Initially, it is in the polymer (typically PVC and PUR) matrix and, after it diffuses out of the matrix, it comes to the surface. TPP is then associated with house dust, which is primarily composed of human skin cells that have been shed. As such, house dust is essentially an organic

substrate. In this case, an estimated  $6.3 \times 10^{-6}$  mmHg VP at 25°C (73°F) of pure TPP is highly attenuated via what is known as Raoult's Law:

(VP of Pure TPP)(Mole Fraction of TPP in substrate) = VP over the substrate

This is for "ideal mixtures" of TPP in various substrates (e.g., PVC film, polyurethane foam or typical house dust). For real world mixtures a thermodynamic activity coefficient ( $AC \ll 1$ ) is added.

(VP of Pure TPP)(Mole Fraction of TPP in substrate)(AC) = VP over the substrate

Thus, one would not expect but a small portion of the above saturation airborne concentration to occur in indoor air. Indeed, most of the measured indoor air values agree with this expectation. The one possible exception is a value reported by Makinen et al. (2009) in which a maximum value of  $10.3 \mu\text{g}/\text{m}^3$  was reported. This is slightly less than 10% of the above calculated saturation concentration of pure TPP and may be the result of the volatilization of essentially pure TPP after diffusion from very large areas of TPP surfaces in the home such as curtains or wall paper. Migration rates of TPP have been measured from a computer video display unit (Carlsson et al., 2000).

## 5.2 TPP Uses

TPP is utilized as an additive flame retardant in PVC (where it also has plasticizing properties), other polymers, textiles, polyurethane (PU) foam, rubbers, electronic circuit boards, photo films, and building materials (HSDB, 2013; OECD, 2002). TPP is also used to a lesser degree in hydraulic fluid, lubricating oil, lacquers, paint, ink, adhesives and some coatings (OECD, 2002; Marklund et al., 2003).

## 5.3 TPP Human Exposure

TPP has been measured in outdoor and indoor air; surface, ground, bottled, and drinking waters; and food packaging. It has been found in dust in houses and other indoor environments in the U.S., Canada and other countries. TPP concentrations have been measured in baby products, toys, electronics, and some building materials. Concentrations of TPP in various media and found in the literature are presented below.

Most human exposure is expected to come from the diffusion of TPP from treated objects used indoors, which ultimately results in inhalation, dermal and oral exposure from hand-to-mouth ingestion of dust. Migration rates of TPP have been measured from computer monitors and TV sets (Saito et al., 2007; Carlsson et al., 2000). Exposure may also come from ingestion of some foods that were packaged in TPP containing material. Andresen and Bester (2006) found drinking water treatment removed much of TPP from water.

### **5.3.1 TPP in Indoor and Ambient Air**

Like TEP, TPP is anticipated to become airborne as a vapor after diffusing out of indoor matrices, such as treated plastics. Diffused TPP can also become associated with house dust, which is quite mobile, and can become airborne. Thus, TPP could be distributed within the indoor environment as a vapor/condensed solid in air, in dust on surfaces with a lesser amount of the TPP containing dust being airborne. An exception to this rule of low airborne levels from dust would be relatively “dusty” rooms where the dust has been allowed to accumulate and/or activities occurs that tend to continually entrain the dust into the air. In these indoor environments, because of its relatively low VP, relatively low levels of airborne TPP as both a free vapor and dissolved in dust have been found. An exception is in possible scenarios with large surface areas of TPP-treated objects, such as curtains or wall paper.

TPP air concentrations have been measured in homes, offices, other workplaces, an electronic dismantling center, cars, and various public places (Hartmann et al., 2004; Kanazawa et al., 2010; Makinen et al., 2009; Otake et al., 2004; Saito et al., 2007; Staaf and Ostman, 2005a,b; Tollback et al., 2010; Yang et al., 2014; Wensing et al., 2005 cited in Weschler and Nazaroff, 2008). TPP concentrations in indoor air generally ranged from not detected to 1,000 ng/m<sup>3</sup> (Table 5-3) (Hartmann et al., 2004; Kanazawa et al., 2010; Otake et al., 2004; Saito et al., 2007; Staaf and Ostman, 2005a,b; Tollback et al., 2010; Yang et al., 2014; Wensing et al., 2005 cited in Weschler and Nazaroff, 2008). OECD (2002) reported maximum TPP concentrations of 100 ng/m<sup>3</sup> in Sweden, Germany, and Japan from indoor air monitoring in residential and public buildings from several studies (Carlsson et al., 1997; Hansen et al., 2001; Otake et al., 2001, respectively; as cited in OECD, 2002). Weschler and Nazaroff (2008) reported indoor air concentrations in a range of 0.1-1 ng/m<sup>3</sup> from Wensing et al. (2005) (as cited in Weschler and Nazaroff, 2008).

Carlsson and colleagues (2000) measured the TPP air concentration in the breathing zone of a computer video display unit for an operator in a small office from the first day of new operation through 2 years of operation. The initial concentration of TPP was measured at 100 ng/m<sup>3</sup>; following 1 week of operation, the level decreased by half, and was 10 ng/m<sup>3</sup> at the end of two years.

Makinen et al. (2009) measured much higher levels in the air of an electronics dismantling facilities in Finland, with a maximum concentration of 10,300 ng/m<sup>3</sup> reported. Measured air concentrations in a TPP manufacturing plant ranged from 500-29,600 ng/m<sup>3</sup> (0.5-29.6 mg/m<sup>3</sup>) (Sutton et al., 1960). TPP was only detected occasionally in oil aerosol/vapor and total volatile organic compounds for aviation workers exposed to hydraulic and turbine oils (Solbu et al., 2010). See Table 5-3 below.

**Table 5-3. TPP Concentrations in Indoor Air**

Country	Location	Media	TPP Concentrations	Reference	Notes	
Sweden	Stockholm House, transport vehicles, offices and shops	Indoor air	House: ND Transport: 1-3 ng/m <sup>3</sup> Offices: ND-3 ng/m <sup>3</sup> Workshops: ND-17	Staaf and Ostman, 2005a	LOD = <0.3 ng/m <sup>3</sup> ; stationary sampler with SPE cartridge containing an aminopropyl silica phase (25 mg, 1 ml)	
	Stockholm Electronic dismantling facility (n=5)	Indoor air	18 ng/m <sup>3</sup>	Staaf and Ostman, 2005b	Glass fibre filter	
			17 ng/m <sup>3</sup>		SPE cartridge	
	Lecture hall, computer hall	Indoor air	ND 3 ng/m <sup>3</sup>		LOD = <0.3 ng/m <sup>3</sup> ; stationary sampler with SPE cartridge containing an aminopropyl silica phase (25 mg, 1 ml)	
	Car	Indoor air	Range: 0.36* - 0.90* ng/m <sup>3</sup>		Hartmann et al., 2004	*indicates below quantification limit; MDL = 1.5 ng/m <sup>3</sup> ; air sample taken with polyurethane foam plugs
	Office	Indoor air	Range: 0.97* - 3.1 ng/m <sup>3</sup>			
	Public areas: theater, furniture and electronic stores	Indoor air	Range: 0.19* - 5.7 ng/m <sup>3</sup>			
	Laboratory and lecture hall	Indoor air	7-8 ng/m <sup>3</sup>		Tollback et al., 2010	Dynamic non-equilibrium Solid-phase microextraction (SPME) for air sampling

Country	Location	Media	TPP Concentrations	Reference	Notes
Sweden	Computer	Indoor air around video display units	94 ng/m <sup>3</sup>	Carlsson et al., 2000	Detected in air samples in the breathing zone of a computer user.
	Residential and public buildings	Indoor air	Max: 100 ng/m <sup>3</sup> (0.1 ug/m <sup>3</sup> )	Carlsson et al., 1997, as cited in OECD, 2000	Sampling not specified
Germany	Residential and public buildings	Indoor air	Max: 100 ng/m <sup>3</sup> (0.1 ug/m <sup>3</sup> )	Hansen et al., 2001, as cited in OECD, 2000	Sampling not specified
Finland	Circuit board factory, furniture workshop	Indoor air	Geo means: 9-50 ng/m <sup>3</sup> Range: <3-530 ng/m <sup>3</sup>	Makinen et al., 2009	Stationary and personal air sampling; glass Fiber filter placed in an IOM sampler and OVS Sampler (SKC Ltd.)
	Electronics Dismantling facilities	Indoor air	Geo means: 20-850 ng/m <sup>3</sup> Range: <4-10,300 ng/m <sup>3</sup>		
China	Hangzhou, Offices	Indoor air	Mean: 2.09 ng/m <sup>3</sup> Median: 1.41 ng/m <sup>3</sup> Range: 0.25-10.21 ng/m <sup>3</sup>	Yang et al., 2014	Particulate matter filter
Japan	Residential and public buildings	Indoor air	Max: 100 ng/m <sup>3</sup> (0.1 ug/m <sup>3</sup> )	Otake, et al., 2001, as cited in OECD, 2000	Sampling not specified
	Tokyo, houses and offices	Indoor air	House Median: ND Range: ND-5.4 ng/m <sup>3</sup> Offices Median: ND Range: ND-0.60 ng/m <sup>3</sup>	Saito et al., 2007	MDL = 0.69 ng/m <sup>3</sup> ; Sampled using quartz fiber Filter (47 mm), first stage and a solid phase extraction disk (empore <sup>tm</sup> Disk C18, 47mm), second stage.

Country	Location	Media	TPP Concentrations	Reference	Notes
Japan	Tokyo, houses	Indoor air	Mean: 10 ng/m <sup>3</sup> (0.01 µg/m <sup>3</sup> ) Median: <1 ng/m <sup>3</sup> (<0.001 µg/m <sup>3</sup> ) Range: <1-70 ng/m <sup>3</sup> (<0.001-0.07 µg/m <sup>3</sup> )	Otake et al., 2004	Charcoal tube filtration
	Sapporo, Houses	Indoor air	Median: < MDL Range: < MDL- 32.1 ng/m <sup>3</sup>	Kanazawa et al., 2010	MDL = 15.6 ng/m <sup>3</sup> ; Sampling at 1- 1.5 m from floor and 1 m from floor; empore™ Disk C18, 47mm
Not Specified	Not specified	Indoor air	Range of 0.1-1 ng/m <sup>3</sup>	Wensing et al., 2005, as cited in Weschler and Nazaroff, 2008	Sampling not specified

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

ND – not detected; max – maximum; geo mean – geometric mean ; LOD – limit of detection; MDL – method detection limit

Fewer data were located regarding TPP in ambient air, and measured concentrations were lower than those seen in indoor environments. TPP was measured outside areas where hydraulic fluids are used (airports, newly constructed homes and buildings) at a concentration of 1.9 ng/m<sup>3</sup> in Japan (Haraguchi et al., 1985). See Table 5-4 below.

**Table 5-4. TPP Concentrations in Ambient Air**

Country	Location	Media	TPP Concentrations <sup>1</sup>	Reference	Notes
Japan	Kitakyushu District	Outdoor ambient air,	2.2 ng/m <sup>3</sup>	Haraguchi et al., 1985	High-volume sampler -glass fiber filter and XAD-7 resins (20g)

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

### 5.3.2 TPP in Water

TPP has been detected in drinking water in the U.S., Canada, the Netherlands, and China; it has also been detected in surface waters in the U.S., Japan, Germany, Italy, Poland, and the Netherlands (Andresen and Bester, 2006; Andresen et al., 2004; Bacaloni et al., 2007, 2008; Barnes et al., 2008; DeLeon et al., 1986; Fukushima et al., 1992; Haggard et al., 2006; Keith et al., 1976 as cited in HSDB, 2013; Kolpin et al., 2002; Kowalski et al., 2014; Lebel et al., 1981 as cited in HSDB, 2013; Lee and Rasmussen, 2006; Li et al., 2014; Lucas, 1984; Mayer et al., 1981 as cited in HSDB, 2013; Sheldon et al., 1978 as cited in HSDB, 2013; Williams and Lebel, 1981; Williams et al., 1982).

Limited reports of TPP concentrations in drinking water in the U.S. were located. TPP was not detected (reporting level of 500 ng/L) in a U.S. Geological Survey that sampled water from a drinking water treatment facility (Barnes et al., 2008). Keith and colleagues measured concentrations ranging from 30-120 ng/L in New Orleans drinking water (Keith et al., 1976 as cited in HSDB, 2013). TEP concentrations measured in finished drinking water in Canada ranged from 0.2-2.6 ng/L (Williams and Lebel, 1981; Lebel et al., 1981 as cited in HSDB, 2013) and from 19.8-84.1 ng/L with a mean of 40 ng/L in China (Li et al., 2014).

Wastewater and drinking water treatments have shown removal of significant levels of TPP (85-92%) (Fukushima and Kawai, 1986, as cited by OECD, 2002; Sheldon and Hites, 1979 as cited by OECD, 2002). Andresen and Bester (2006) measured a concentration of TPP before drinking water treatment at 7.2 ng/L and after drinking water treatment at <0.3 ng/L. See Table 5-5.

**Table 5-5. TPP in Water**

Country	Location	Media	TPP Concentrations <sup>1</sup>	Reference	Notes
United States	Arkansas	Surface Water	Median: 34 ng/L (0.034 µg/L) (estimated) Range: 9-63 ng/L (0.009-0.063 µg/L)	Haggard et al., 2006	Levels estimated at or below the reporting limit
	Mississippi Rive	Surface Water	ND-11 ng/L	DeLeon et al., 1986	Detection limit not specified
	USGS, 18 States	Groundwater	<RL	Barnes et al., 2008	RL = 0.5 µg/L; found in 4.3% of 47 samples
	Johnson County, Kansas	Surface water	ND	Lee and Rasmussen, 2006	LOD = 0.5 µg/L

Country	Location	Media	TPP Concentrations <sup>1</sup>	Reference	Notes
United States	30 states	Surface water	Median: 40 ng/L (0.04 µg/L)	Kolpin et al., 2002	139 streams sampled in 30 states 1999-2000
	New Orleans	Finished drinking water	30 ng/L (0.03 µg/L) 120 ng/L (0.12 µg/L)	Keith et al., 1976 as cited in HSDB, 2013	Study details not available
	Rivers in MO, MS, WV, CA	Surface water	Range: 100-7,900 ng/L (0.1-7.9 µg/L)	Mayer et al., 1981 as cited in HSDB, 2013	Study details not available
	Delaware River	Surface water	Range: 0.1-0.4 ppb	Sheldon et al., 1978 as cited in HSDB, 2013	Study details not available
Canada	6 Ontario municipalities	Finished drinking water	Range: 0.2-2.6 ng/L	Lebel et al., 1981 as cited in HSDB, 2013	Detected in 2 of the 6 Ontario water treatment plants
	29 municipalities	Finished drinking water	Range: 0.2-2.6 ng/L	Williams and Lebel, 1981	Water treatment plants, sources include rivers, lakes and ground water
Germany	River Ruhr	Surface Water	Range: < LOQ - 80 ng/L	Andresen et al., 2004	LOQ = 10 ng/L; July and Sept 2002 sampling
	River Ruhr	Surface Water, reservoir	Source Mean: 7.2 ng/L Finished water mean: <0.3 ng/L	Andresen and Bester, 2006	
Italy	Volcanic Lakes	Surface water	Means: 2-21 ng/L	Bacaloni et al., 2008	Detection limit not reported
	Near Vico Lake	Well Water	Range: ND-164 ng/L		
	River Tiber	Surface water	Mean: 11,165 ng/L	Bacaloni et al., 2007	
Japan	Well Water	Surface water	Mean: 500 ng/L (< 0.5 µg/L)	Fukushima et al., 1992	Trend of concentration from 1976-1990

Country	Location	Media	TPP Concentrations <sup>1</sup>	Reference	Notes
China	Various cities, inland and coastal, developed and less developed	Tap water	Mean: 40 ng/L Range: 19.8-84.1 ng/L	Li et al., 2014	Boiling water increased the TPP concentration by 5.72 ng/L
	Various brands (n=8)	Bottled water	Range: 2.57-14.8 ng/L		
Poland, Gliwice, Ruda Slaska, Zabrze	Klodnica River	Surface water	300 ng/L (0.30 µg/L)	Kowalski et al., 2014	New method to identify flame retardants using ultra-HPLC equipment and UV detection
	Kokotka Lake	Surface water	120 ng/L (0.12 µg/L)		
	Pileckiego Lake	Surface water	30 ng/L (0.03 µg/L)		

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

Max – maximum; ND – not detected; DL – detection limit; RL – reporting limit; LOD – limit of detection; LOQ – limit of quantification; USGS – U.S. Geological Service

### 5.3.3 TPP in Food

TPP was measured in food in an U.S. FDA market basket survey of 234 food items from 1982-1991 (U.S. FDA, 2006 as cited by ATSDR, 2009). TPP was found in caramel, margarine, and baby food at levels of 0.02-0.04 ppm (U.S. FDA, 2006 as cited by ATSDR, 2009). Food packaging was tested in the United Kingdom; taco trays were the only product found with TPP (concentration of 98.4 ng/g) (Bradley, 2013). See Table 5-6 below.

Gunderson (1995a) calculated mean daily intake per unit body weight per day for TPP from food. It ranged from a low of 0.0014 ug/kg/day (60-65 year old females) to 0.0348 ug/kg/day (2 year olds).

**Table 5-6. TPP in Food and Food Packaging**

Country	Food	TPP Concentrations <sup>1</sup>	Reference	Notes
United States	Caramel	40 ng/g (0.04 ppm)	U.S. FDA, 2006 as cited by ATSDR 2009	U.S. FDA's Total Diet Study, market basket survey, 234 food items evaluated over a 10-year period from 1982-1991
	Margarine	40 ng/g (0.04 ppm)		
	Baby food	20 ng/g (0.02 ppm)		

Country	Food	TPP Concentrations <sup>1</sup>	Reference	Notes
United Kingdom	Taco tray	98.4 ng/g (98.4 µg/kg) in packaging	Bradley, 2013	Study of migration of inks in packaging to foods. 350 foods packaged in printed paper/board from UK retail outlets. TPP in one packaging material

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

### 5.3.4 TPP in Dust

TPP has been measured in dust in a variety of indoor settings. Given TPP properties and the data found on dust, it would appear that a dominant mechanism for human exposure is diffusion of TPP out of materials to the surface where it can partition into dust, which can then be ingested. TPP levels in house dust measured in U.S. homes in California and Massachusetts ranged from <150-1,798,100 ng/g, with means around 7000 ng/g in the Massachusetts homes and medians around 3000 ng/g in the California homes (Dodson et al., 2012; Meeker and Stapleton, 2010; Stapleton et al., 2009). Canadian house dust levels ranged from non detect to 63,000 ng/g (Fan et al., 2014). In Europe, TPP levels in dust in homes ranged from 40-29,800 ng/g (Van den Eede et al., 2011, 2012, Brommer et al., 2012; Marklund et al., 2003; Garcia et al., 2007). Levels measured in several other countries were lower. Weschler and Nazaroff (2008) reported dust concentrations in a range of 2,000-20,000 ng/g (2-20 µg/g) from Wensing et al. (2005)

TPP dust concentrations have been measured in day care centers in Germany ranging from less than 300 to 64,500 ng/g (Fromme et al., 2014). Dust in cars has also been tested for TPP in several countries, with the highest level reported of 43,000 ng/g in the Netherlands (Brandsma et al., 2014). Concentrations of TPP have also been measured at varying levels in dust around electronics and in other indoor spaces, including offices, hospitals, mosques, prison, university, laboratory, and other public buildings. In addition, Marklund et al. (2003) measured concentrations of TPP from wipe samples on a computer screen and a cover of up to 4000 µg/m<sup>3</sup> in the Netherlands. Makinen et al. (2009) used a dermal patch test to measure the amount of TPP transferred to hands of people in a circuit board factory and furniture workshop.

Compared to other media, given incidental ingestion dust rates of between the range of 50 to 100 mg per day, dust appears to be a dominant environmental conduit for potential human exposure to TPP. See Table 5-7 below.

**Table 5-7. TPP in Dust**

Country	Location	Media	TPP Concentrations <sup>1</sup>		Reference	Notes
United States	Massachusetts houses	Dust	Mean: 7,400 ng/g	Range: <173-1,798,100 ng/g	Meeker and Stapleton, 2010	Dust collected from vacuum bags
	California, houses	Dust, 2006	Median: 3,000 ng/g	Range: 580-14,000 ng/g	Dodson et al., 2012	Dust collected with vacuum with Teflon collector
		Dust, 2011	Median: 2,800 ng/g	Range: 790-36,000 ng/g		
Boston, MA houses	Dust	Geo mean: 7,360 ng/g	Range: <150-1,798,000 ng/g	Stapleton et al., 2009	Household vacuum cleaner bag collection	
Canada	House	Dust	Median: 1,700 ng/g (1.7 µg/g)	Range: 260-63,000 ng/g (0.26-63 µg/g)	Fan et al., 2014	Fresh/active dust method
	House	Dust	Median: 1,600 ng/g (1.6 µg/g)	Range: MDL-9,500 ng/g (MDL-95 µg/g)		Household vacuum cleaner method; MDL = 0.2 µg/g (200 ng/g)
Belgium, Flemish region	House	Dust	Mean: 2,020 ng/g (2.02 µg/g) Median: 500 ng/g (0.50 µg/g)	Range: 40-29,800 ng/g (0.04-29.8 µg/g)	Van den Eede et al., 2011	Vacuum dust samples
	Carpenter workshop, second-hand store, electronics stores, laboratory	Dust	Mean: 4,700 ng/g (4.70 µg/g) Median: 1,970 ng/g (1.97 µg/g)	Range: 50-370 ng/g (0.15-34.2 µg/g)		
Belgium, Romania, Spain	House	Dust	Range: 105-3,750 ng/g		Van den Eede et al., 2012	Vacuum dust samples
Egypt	House	Dust	Avg: 101 ng/g Median: 67 ng/g	Range: 8-289 ng/g	Abdallah and Covaci, 2014	Samples were sieved through a 500 µm mesh size sieve

Country	Location	Media	TPP Concentrations <sup>1</sup>		Reference	Notes
Egypt	Offices	Dust	Avg: 94 ng/g Median: 73 ng/g	Range: 11-337 ng/g		
	Cars	Dust	Avg: 392 ng/g Median: 135 ng/g	Range: 26-1872 ng/g		
	Public Micro-Environments	Dust	Avg: 959 ng/g Median: 629 ng/g	Range: 116-2357 ng/g		
Germany	Daycare center	Dust	Mean: 2,560 ng/g (2.56 mg/kg) Median: 500 ng/g (0.5 mg/kg)	Range <300-64,500 ng/g (<0.3-64.5 mg/kg)	Fromme et al., 2014	Cartridge with glass fiber filter
	Car	Dust	Mean: 3,000 ng/g	Range: 500-11,000 ng/g	Brommer et al., 2012	
	House	Dust	Mean: 380 ng/g	Range: 180-1,300 ng/g		
	Office	Dust	Mean: 2,500 ng/g	Range: 470-4,800 ng/g		
Netherlands	Around Electronics	Dust	Median: 820 ng/g	Range: 6,80-11,000 ng/g	Brandsma et al., 2014	Vacuum cleaner bags
	On Electronics	Dust	Median: 6,500 ng/g	Range: 1,600-21,000 ng/g		
	Car Dashboards	Dust	Median: 1,700 ng/g	Range: 360-14,000 ng/g		
	Car Seats	Dust	Median: 2400 ng/g	Range: 670-43,000 ng/g		
	Homes	Dust	Range: 850-990 ng/g (0.85-0.99 mg/kg)		Marklund et al., 2003	Vacuum cleaner bag collection and wipe test samples from computer screens and covers
	Work (daycare, hospital, radio and textile shop, office)	Dust	Range: 930-6,800 ng/g (0.93-6.8 mg/kg)			

Country	Location	Media	TPP Concentrations <sup>1</sup>		Reference	Notes
Netherlands	Public Places (hotel, prison, university lobby, aircraft, library, cinema, dance hall)	Dust	Range: 1,100-110,000 ng/g (1.1-110 mg/kg)			
	Computer screen and cover (wipe test)	Dust	Screen: 3,300 ng/m <sup>2</sup> Cover: 4,000 ng/m <sup>2</sup>			
Finland	Circuit board factory, furniture workshop	Dust	Hand Geo mean: 3,300 ng/hand Range: 1,300-8,700 ng/hand	Patch Geo mean: <0.08 ng/cm <sup>2</sup>	Makinen et al., 2009	Hand washing samples – rinsed hands with ethanol; dermal patch test
	Electronics dismantling facilities	Dust		Patch Geo mean: 3.1-6.7 ng/cm <sup>2</sup> Range: <0.08-160 ng/cm <sup>2</sup>		Dermal patch test
Spain	Northwest of Spain, homes	Dust	Mean: 2,600 ng/g (2.6µg/g)	Range: 290-9,500 ng/g (0.29-9.5 µg/g)	Garcia et al., 2007	Household vacuum cleaner bag collection
Japan	Home, multi-surface	Dust	Median: 14,300 ng/g (14.3 mg/kg)	Range: <MDL-17,500 ng/g (<MDL-175 mg/kg)	Kanazawa et al., 2010	MDL = 1.6 mg/g; vacuum cleaner bag collection
	Home, floor	Dust	Median: 5,400 ng/g (5.4 mg/kg) median	Range: <MDL-78,400 ng/g (<MDL-78.4 mg/kg)		

Country	Location	Media	TPP Concentrations <sup>1</sup>		Reference	Notes
Japan	182 single family homes, floor	Dust	Median: 4,510 ng/g (4.51 µg/g)	Range: <MDL-245,080 ng/g (<MDL-245.08 µg/g)	Araki et al., 2014	MDL = 1,600 ng/g (1.60 µg/g); Handheld vacuum with paper filter
	182 single family homes, multi-surface	Dust	Median: 11,540 ng/g (11.54 µg/g)	Range: <MDL-889,180 ng/g (<MDL-889.18 µg/g)		
	Homes, floor	Dust	Median: 870 ng/g (0.87 µg/g)	Max: 23,350 ng/g (23.35 µg/g)	Tajima et al., 2014	Vacuum cleaner bag collection
	Homes, upper surfaces	Dust	Median: 3,130 ng/g (3.13 µg/g)	Max: 27,470 ng/g (27.47 µg/g)		
Philippines	Malate, homes	Dust	Median: 89 ng/g	Range: 8.5-2,100 ng/g	Kim et al., 2013	Household vacuum cleaner bag collection
	Payatas, homes	Dust	Median: 71 ng/g	Range: 13-440 ng/g		
Pakistan	Gujrat, homes	Dust	90 ng/g (estimated from graph)		Ali et al., 2012	Dust collected using a brush, 31 residential samples, 12 mosque samples
	Gujrat, Mosques	Dust	75 ng/g (estimated from graph)			
Not Specified	Not specified	Not specified	Range of 2,000 -20,000 ng/g (2-20 µg/g)		Wensing et al., 2005, as cited in Weschler and Nazaroff, 2008	Sampling not specified

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

geo mean – geometric mean; max – maximum; min – minimum; MDL – method detection limit

### 5.3.5 TPP in Consumer Products

Various investigators have tested a variety of consumer products for the presence of TPP and some have reported percent content or concentrations. These studies are consistent with TPP's use as a flame retardant and/or plasticizer in various products.

Concentrations of TPP measured in consumer products cannot be used directly as a proxy for concentration levels to which consumers are exposed. To develop realistic consumer exposure concentrations, the flame retardant levels in these products would need to be paired with experimental or monitoring results that reflect the availability of the compound to leave these products and enter the body. For TPP, there are limited emission or migration rates to estimate actual exposure concentrations. See Table 5-8.

#### **5.3.5.1 Children and Baby Products**

TPP was found in baby product samples, such as car seats, changing table pads, portable crib mattresses, nursery rocking chairs/glidens, car seat pillow, and in miscellaneous bathroom items (Stapleton et al., 2011). Stapleton and colleagues (2011) reported TPP in the range of 1,000,000-9,500,000 ng/g (1-9.5 mg/g) with a mean of 3,800,000 ng/g (3.8 mg/g) in these various baby products. This suggested that infants may have a greater exposure than adults given the prevalence of TPP in baby products. The Center for Environmental Health (2013) found TPP in 18 of 24 children's foam nap mats that were purchased in 2012 (no concentrations provided). Ionas and colleagues (2014) qualitatively identified TPP in 52% of 114 toy samples with concentrations ranging from 2,000 ng/g to 12,800,000 ng/g.

#### **5.3.5.2 Furniture and Household Products and Materials**

Stapleton et al. (2012) collected and analyzed 102 PU foam samples from residential couches purchased from 1985-2010 (samples were collected and donated by individuals from numerous cities in the U.S.). Flame retardants were detected in 85% of the samples. TPP was found in several of the flame retardants measured in this study, including Firemaster550, which was found in 5% of the samples purchased between 1985-2005 and 18% of the samples purchased after 2005 (Stapleton et al., 2012). The study listed only one TPP specific measurement (average level of TPP in the MPP mixture of 3.23 mg/g). In 2009, Stapleton and colleagues analyzed 26 PU foam samples from chairs, pillows, couches, mattress pads, and a futon (samples were collected and donated by individuals from numerous cities in the U.S. (Stapleton et al., 2009). FireMaster 550 was found in 1 of the 26 samples with a percent by weight of 4.5% (Stapleton et al., 2009). In Japan, concentrations of TPP have been measured in curtains (840,000 ng/g), electrical outlets (up to 12,000 ng/g), insulation boards (up to 8700 ng/g), wallpaper (up to 1,800 ng/g), and cushions (4,700-23,300 ng/g) (Kajiwara et al., 2001; Nagase et al., 2003).

#### **5.3.5.3 Electronic Products**

Kajiwara et al. (2011) measured concentrations of TPP in computer and LCD TV components; concentrations ranged from 560-14,000,000 ng/g. Saito and colleagues (2007) measured the migration of TPP from computer monitors and TV sets at a rate of 690 ng/m<sup>2</sup>-hour for computer monitors and 330 ng/m<sup>2</sup>-hour for TV sets (Saito et al., 2007). TPP levels were measured at 10% w/w in computer video display units; a concentration of 94 ng/m<sup>3</sup> was measured in the breathing

zone of a potential operator (see discussion in Section 5.3.1 above) (Carlsson et al., 2000). TPP was qualitatively identified in plastic products such as electrical power boards, electrical adaptors, heat sealers, televisions, and printers (Ballestros-Gomez et al., 2014).

**Table 5-8. TPP in Consumer Products**

Country	Item	Media	TPP Concentrations <sup>1</sup>	Reference	Notes
United States	Baby products	car seats, changing table pads, mattresses, rocking chairs; car seat pillow	Mean: 3,800,000 ng/g (3.8 mg/g) Range: 1,000,000-9,500,000 ng/g (1-9.5 mg/g)	Stapleton et al., 2011	Donated PU foam samples from numerous cities in U.S.
	Furniture	PU foam	Mean TPP in MPP mixture: 3230 ng/g (3.23 mg/g)	Stapleton et al., 2012	Donated PU foam samples from numerous cities in U.S. TPP quantified only for MPP mixture, which was detected in 2 of 102 samples
Belgium	Toys	Overall	Median: 2,000 ng/g (2 µg/g) Max: 12,800,000 ng/g (12,800 µg/g)	Ionas et al., 2014	TPP found in 52% of 114 toys sampled
		Hard plastic (n=50)	Median: 2,000 ng/g (2 µg/g) Max: 12,800,000 ng/g (12,800 µg/g)		
		Soft plastic and rubber (n=31)	Median: 2,000 ng/g (2 µg/g) Max: 940,000 ng/g (940 µg/g)		

Country	Item	Media	TPP Concentrations <sup>1</sup>	Reference	Notes
Belgium		Wood (n=8)	Median: 35,000 ng/g (35 µg/g) Max: 70,000 ng/g (70 µg/g )		
		Foam and textiles (n=25)	Median: 1,000 ng/g (1 µg/g) Max: 120,000 ng/g (120 µg/g )		
Sweden	Computer	Air around video display units	94 ng/m <sup>3</sup>	Carlsson et al., 2000	Detected in air samples in the breathing zone of a computer user.
Japan	Laptop computer	Chassis	170,000 ng/g	Kajiwara et al., 2011	Items purchased new in Japan in 2008.
		Keyboard top	500,000 ng/g		
		PC boards	560 ng/g		
		Cooling fan and speakers	42,000 ng/g		
		AC adapter	1,800 ng/g		
		LCD panel	2,600,000 ng/g		
	LCD TV; Purchased new in Japan in 2008	Rear cover	1,100 ng/g TV1 600,000 ng/g TV2	Kajiwara et al., 2011	Two TVs sampled
		Front cover	2,400 ng/g TV1 40,000 ng/g TV2		
		Power board	6,700,000 ng/g TV1		
		PC board for power and fluorescent	320,000 ng/g TV1 14,000,000 ng/g TV2		
		Other PC boards	870 ng/g TV1 1,600,000 ng/g TV2		
		LCD panel	1,200,000 ng/g TV1&2		

Country	Item	Media	TPP Concentrations <sup>1</sup>	Reference	Notes
Japan	Other products; Purchased new in Japan in 2008	Curtains	820,000 - 840,000 ng/g	Kajiwara et al., 2011	Two samples
		Electrical outlets	630 - 12,000 ng/g		Two samples
		Insulation boards	5,300 - 8,700 ng/g		Two samples
		Wallpaper	140-1800 ng/g		Four samples
	Household products	Cushion	Range: 4,700-23,300 ng/g (4.7-23.3 µg/g)	Nagase et al., 2003	
	Electronics	Computer monitors	Median: 690 ng/m <sup>2</sup> -hr (0.69 µg/m <sup>2</sup> -hr) Range: ND-20,700 ng/m <sup>2</sup> -hr (ND-20.7 µg/m <sup>2</sup> -hr)	Saito et al., 2007	ND = 240 ng/m <sup>2</sup> -hr (0.24 µg/m <sup>2</sup> -hr); migration from outer case surface to solid extraction disk
TV sets		Median: 330 ng/m <sup>2</sup> -hr (0.33 µg/m <sup>2</sup> -hr) Range: ND-6,700 ng/m <sup>2</sup> -hr (ND-6.7 µg/m <sup>2</sup> -hr)			

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

max – maximum; ND – not detected

## 5.4 TPP ADME and Biomonitoring Studies

No *in vivo* human data for absorption, distribution, metabolism, or elimination of TPP by any route of exposure were located. Only one valid *in vitro* study on the metabolism of TPP was found in the literature (Sasaki et al., 1984). Metabolism of TPP was investigated using microsomes and soluble fractions prepared from rat liver homogenates. Decomposition of TPP was catalyzed by the microsomal fraction in the presence of NADPH, and to a lesser extent without NADPH. The only major metabolite, as identified by gas chromatography, was diphenyl-phosphate. Diphenyl-phosphate did not undergo additional decomposition by microsomes. The metabolic reactions were inhibited almost completely by SKF-525A and carbon monoxide and the absence of NADPH, whereas KCN, NaN<sub>3</sub>, dipyriddy and EDTA showed little effect. It was concluded that, arylesterase and mixed function oxidase (MFO) in the microsomes play a central role in the metabolism of triphenyl phosphate. TPP is degraded by hydrolysis in rat liver homogenate to diphenyl phosphate as the major metabolite (OECD, 2002).

In the U.S., Meeker and colleagues investigated the relationship between urinary metabolites of TPP and TDCPP, and each flame retardant's respective concentrations in house dust (Meeker et al., 2013). The authors detected DPP in 96% of urine samples but found no correlation in paired house dust and urine samples for urinary DPP and dust concentrations of TPP. The authors concluded that, for TPP, household dust is not likely to be an important source of exposure (Meeker et al., 2013).

Kim et al. (2014) tested human breast milk for organophosphate flame retardant levels in women in the Philippines, Vietnam, and Japan; TPP was not detected in any of the breast milk samples. Sundqvist and colleagues (2010) measured a range of 3.2-11 ng/g (median 8.5 ng/g) of TPP in human breast milk from women in Sweden. TPP was measured at 11.2 ng/g and 13.6 ng/g in two human adipose tissue samples in Canada (Lebel and Williams, 1986)

**Table 5-9. TDCPP Biomonitoring Data**

Country (location)	Tissue/fluid	Concentrations	Reference	Notes
United States	Urinary metabolite, DPP	Geo mean: 0.31 ng/ml Range: 0.07-9.84 ng/ml	Meeker et al., 2013	9 repeated urine samples from 7 men over 3 months. DPP detected in 96% of samples
Canada	Human adipose tissue	11.2 ng/g 13.6 ng/g	Lebel and Williams, 1986 as cited in HSDB, 2013	Two samples reported in HSDB, 2013
Sweden	Human breast milk	Median: 8.5 ng/g Range: 3.2-11 ng/g	Sundqvist et al., 2010	Based on average lipid content

<sup>1</sup>For ease of comparison, all units are converted to ng equivalent. Original study units, if different, are shown in parentheses.

geo mean – geometric mean

## 5.5 TPP Exposure Assessments and Estimates

Few exposure assessments or estimates were located for TPP. The U.S. CPSC staff prepared a preliminary risk assessment on TPP in upholstered furniture foam and calculated an Average Daily Dose (ADD) of  $1.8 \times 10^{-3}$  mg/kg/day for adults and  $4.8 \times 10^{-3}$  mg/kg/day for children (Babich, 2006). The exposure estimate was dominated by vapor inhalation (>95%), which was based on a mathematical model. The authors note that to more accurately estimate TPP exposures, empirical data are needed (Babich, 2006).

Stapleton et al. (2009) measured concentrations of TDCPP, TCPP and TPP in house dust extracts from 50 Boston homes. They estimated cumulative exposure to these organophosphate flame retardants, as well as data on four others (TBB, PBDEs, TBPH, and HCBDD), using the geometric mean concentration for each flame retardant and lower bound dust ingestion rates from U.S. EPA (100 mg dust/day for a child; 20 mg dust/day for an adult). For children, the average estimated cumulative exposure was about 1600 ng/day; for the adult it was about 325 ng/day, with a majority of the exposure from TPP, TDCPP and PBDEs (Stapleton et al., 2009).

Mean levels of TPP from foods in the U.S. FDA Total Diet Study appear to be increasing over time (from 1982 to 1991); the highest levels are for 2-year olds, indicating they could have exposures from food of >30 ng/kg/day of TPP (Gunderson, 1988, 1995a, 1995b).

## 5.6 TPP Discussion

TPP has been detected in various media including outdoor and indoor air, surface water, groundwater, house dust, food, and consumer products. The primary sources of exposure to TPP for consumers appear to be dust and inhalation of vapors and particulates in indoor air. Drinking treated surface water contaminated with TPP could also represent a significant source of exposure if the TPP is not removed during treatment. As is often the case, there are limited U.S. data for these exposure sources. There are data from other countries, but use of these data may introduce uncertainty into exposure estimates because TPP levels in other countries may not be representative of U.S. levels. However, in this review of available literature, the highest concentration of TPP in house dust was found in Massachusetts.

Human biomonitoring demonstrates some level of uptake of TEP by humans. In the U.S., Meeker and colleagues detected DPP in 96% of urine samples but found no correlation in paired house dust and urine samples for urinary DPP and dust concentrations of TPP. The authors concluded that for TPP, household dust is not likely to be an important source of exposure to TPP (Meeker et al., 2013). Kim et al. (2014) did not detect TPP in human breast milk in women in the Philippines, Vietnam, and Japan, although Sundqvist and colleagues (2010) measured a range of 3.2-11 ng/g (median 8.5 ng/g) of TPP in human breast milk from women in Sweden. TPP was measured in two human adipose tissue samples in Canada (Lebel and Williams, 1986)

There are limited data available to perform an exposure assessment. Most notably, information on migration and degradation from indoor media and dermal exposure factors are lacking. However, reasonable worst case estimates of exposure can be made using the media concentrations presented herein along with age-specific estimates of inhalation or ingestion rates of these media.

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## Appendix A – Flame Retardant Exposure Literature Search Strategy

TERA conducted a thorough literature search that included: Pubmed, Google Scholar, Science Direct, TOXNET (including Toxline), CAB abstracts databases and a general web search. The search terms that were used are listed below.

### Search terms

Chemical name OR CAS number AND exposure  
Chemical name OR CAS number AND human  
Chemical name OR CAS number AND children  
Chemical name OR CAS number AND consumer  
Chemical name OR CAS number AND consumers  
Chemical name OR CAS number AND residential  
Chemical name OR CAS number AND residential AND children  
Chemical name OR CAS number AND residential AND consumers  
Chemical name OR CAS number AND dust  
Chemical name OR CAS number AND "hand to mouth"  
Chemical name OR CAS number AND mouthing  
Chemical name OR CAS number AND dislodgeable residue  
Chemical name OR CAS number AND dermal  
Chemical name OR CAS number AND oral  
Chemical name OR CAS number AND inhalation  
Chemical name OR CAS number AND ingestion  
Chemical name OR CAS number AND indoor air  
Chemical name OR CAS number AND products  
Chemical name OR CAS number AND toys  
Chemical name OR CAS number AND pillows  
Chemical name OR CAS number AND baby carriers  
Chemical name OR CAS number AND baby products  
Chemical name OR CAS number AND human exposure assessment  
Chemical name OR CAS number AND human risk assessment  
Chemical name OR CAS number AND migration  
Chemical name OR CAS number AND electronics  
Chemical name OR CAS number AND plastic  
Chemical name OR CAS number AND food  
Chemical name OR CAS number AND air  
Chemical name OR CAS number AND soil  
Chemical name OR CAS number AND water  
Chemical name OR CAS number AND bedding  
Chemical name OR CAS number AND mattress

Chemical name OR CAS number AND foam  
Chemical name OR CAS number AND carpet  
Chemical name OR CAS number AND furniture  
Chemical name OR CAS number AND biomonitoring  
Chemical name OR CAS number AND breast milk

**Inclusion criteria**

According to the SOW, exposure should be human with an emphasis on residential or consumer exposures. herefore, preference will be given to those articles that describe residential or consumer exposures. Articles will be included if human exposures or children’s exposures to other sources are included. Articles will also be included if they describe levels in the environment and /or other media because they represent potential sources of exposure. If found, biomonitoring data will be included as they are represented of an exposed population. Also to be included is "grey" literature, such as white papers, poster, or presentations. More focus will be placed on references published two to three years prior to and after the publication of any identified major secondary references (i.e., ATSDR, EPA) for flame retardants because it is assumed that they did a thorough literature search. We will not apply any time exclusions.