Australian Government
Department of Health and Aged Care
Australian Industrial Chemicals Introduction Scheme

Triphenyl phosphate and diphenyl phosphate

Evaluation statement

26 June 2023

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AICIS evaluation statement

Subject of the evaluation

Triphenyl phosphate and diphenyl phosphate

Chemicals in this evaluation

Name	CAS registry number
Phosphoric acid, triphenyl ester	115-86-6
Phosphoric acid, diphenyl ester	838-85-7

Reason for the evaluation

Evaluation Selection Analysis indicated a potential environmental risk.

Parameters of evaluation

This evaluation considers the environmental risks associated with the industrial uses of the organophosphate flame retardant (OPFR) triphenyl phosphate (TPHP, CAS No. 115-86-6) and its metabolite diphenyl phosphate (DPHP, CAS No. 838-85-7). These chemicals are listed on the Australian Inventory of Industrial Chemicals (the Inventory) and have been assessed for their risks to the environment according to the following parameters:

- default domestic introduction volumes of 100 tonnes per annum
- industrial uses listed in the 'Summary of Use' section
- expected emission into sewage treatment plants (STPs) and soil due to consumer and commercial use.

The evaluation of these substances has been conducted as a group because DPHP is a degradation product of TPHP.

Summary of evaluation

Summary of introduction, use and end use

There is currently no specific information about the introduction of the chemicals in Australia. TPHP is used as a flame retardant and plasticiser in a variety of commercial and household products worldwide. It is used in the following products according to reported domestic and international use data:

- Adhesive and sealant products
- Lubricant and grease products
- Personal care products – limited environmental release
- Paint and coating products

- Plastic and polymer products
- Construction products
- Fabric, textile and leather products
- Electronic products
- Paper products
- Photographic products.

The reported uses of DPHP include as an intermediate in the manufacture of other chemicals and as an additive in commercial paints and coatings.

Chemicals in this group have non-industrial uses in veterinary products.

There are no specific domestic introduction volume data available for these chemicals. TPHP is an Organisation for Economic Co-operation and Development (OECD) High Production Volume (HPV) chemical.

Environment

Summary of environmental hazard characteristics

Based on the information presented in this evaluation and according to the environmental hazard thresholds stated in the Australian Environmental Criteria for Persistent, Bioaccumulative and/or Toxic Chemicals (DCCEEW n.d.), TPHP is:

- Not Persistent (not P)
- Not Bioaccumulative (not B)
- Toxic (T).

DPHP is:

- Not Persistent (not P)
- Not Bioaccumulative (not B)
- Not Toxic (not T).

Environmental hazard classification

The chemical TPHP satisfies the criteria for classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) for environmental hazards as follows. This does not consider classification of physical hazards and health hazards.

Environmental Hazard	Hazard Category	Hazard Statement
Hazardous to the aquatic environment (acute / short-term)	Aquatic Acute 1	H400: Very toxic to aquatic life
Hazardous to the aquatic environment (long-term)	Aquatic Chronic 1	H410: Very toxic to aquatic life with long-lasting effects

DPHP satisfies the criteria for classification according to the GHS for environmental hazards as follows. This does not consider classification of physical hazards and health hazards.

Environmental Hazard	Hazard Category	Hazard Statement
Hazardous to the aquatic environment (acute / short-term)	Aquatic Acute 3	H402: Harmful to aquatic life

Based on the available acute endpoint, and considering the substance is rapidly degradable and not potentially bioaccumulative, DPHP is not classified for long term hazard.

Summary of environmental risk

The chemical TPHP is used as a flame retardant and plasticiser in a range of products and articles. DPHP is the principal degradant of TPHP as well as a number of other phosphate flame retardant chemicals. DPHP has limited industrial use as an intermediate or additive in paints and coatings. Both chemicals are expected to be released to the environment through diffuse emissions from products and articles, with the main source of emissions to the aquatic environment from STP effluent.

These chemicals are not persistent in the environment and have a low potential for bioaccumulation. TPHP is highly toxic to aquatic organisms and may induce endocrine effects in some species of fish, but effect concentrations are typically above those expected to be found in the Australian environment.

Based on measured domestic and international concentrations in STP effluent these chemicals are expected to be present in Australian surface waters at concentrations below the level of concern. Calculated risk quotient values (RQ) are less than 1. Therefore, current use of these chemicals is not expected to pose a significant risk to the environment.

Conclusions

The conclusions of this evaluation are based on the information described in this statement.

The Executive Director is satisfied that the identified environment risks can be managed within existing risk management frameworks. This is provided that all requirements are met under environmental, workplace health and safety and poisons legislation as adopted by the relevant state or territory.

Note: Obligations to report additional information about hazards under *Section 100 of the Industrial Chemicals Act 2019* apply.

Supporting information

Grouping rationale

This evaluation considers the environmental risks associated with the industrial uses of TPHP and DPHP, two structurally related organophosphate esters. The evaluation of these substances has been conducted as a group because DPHP is a degradation product of TPHP.

The chemical TPHP belongs to a larger group of chemicals known as organophosphate triesters. It represents a general structure for the subgroup of triaryl phosphates, which all have similar industrial uses. Organophosphate flame retardants (OPFRs) were developed to replace other types of additive flame retardants, such as polybrominated diphenyl esters (PBDEs) (Cristale et al. 2013a; Lee JS et al. 2020; Pakalin et al. 2007).

The evaluation selection analysis (ESA) of TPHP highlighted a high volume of use globally and potential toxic (T) hazard characteristics, which indicate a high concern for the environment.

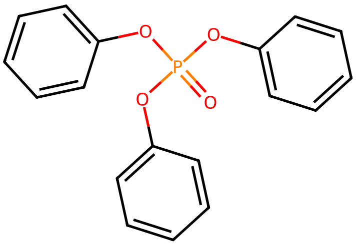
Environmental risks resulting from the use of other organophosphate compounds as flame retardants and plasticisers in Australia have previously been assessed by the former National Industrial Chemicals Notification and Assessment Scheme (NICNAS). A ‘Priority Existing Chemical Assessment Report’ for triphosphates (No. 17) is available (NICNAS 2001).

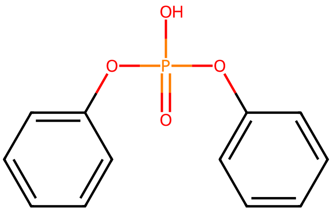
Chemical identity

The chemical TPHP is a phosphate ester where the phosphorus atom is linked to three phenol moieties. The substance is generally produced through the reaction of phenol with phosphorus oxychloride (UK EA 2009a).

Under environmentally relevant conditions, TPHP hydrolyses forming DPHP and phenol (CAS No. 108-95-2). DPHP is also the main metabolite of several other phosphate esters, such as 2-isopropylphenyl diphenyl phosphate (CAS No. 64532-94-1) and bisphenol A bis(diphenyl phosphate) (CAS No. 5945-33-5).

Non-halogenated OPFRs, such as TPHP and DPHP, prevent fire mainly through reactions in the solid phase. Thermal degradation of TPHP forms phosphoric acid and pyrophosphoric acid, which extract water from the substrate and char the material to form a glassy layer. This hinders passage of combustible gases and exposure of carbon, while simultaneously establishing a heat transfer barrier (Brommer 2014; EFRA 2007; Lassen 1999; van der Veen and de Boer 2012):

Chemical name	Phosphoric acid, triphenyl ester
CAS No.	115-86-6
Synonyms	TPHP TPP triphenyl phosphate phenyl phosphate triphenoxyphosphine oxide Celluflex TPP Disflamoll TP Phosflex TPP Kronitex TPP
Molecular formula	C18H15O4P
Molecular weight (g/mol)	326.28
SMILES	C1=CC=C(C=C1)OP(=O)(OC2=CC=CC=C2)OC3=CC=CC=C3
Chemical description	-
Structural formula	

Chemical name	Phosphoric acid, diphenyl ester
CAS No.	838-85-7
Synonyms	diphenyl phosphate DPHP
Molecular formula	C12H11O4P
Molecular weight (g/mol)	250.19
SMILES	C1=CC=C(C=C1)OP(=O)(O)OC2=CC=CC=C2
Chemical description	-
Structural formula	

Relevant physical and chemical properties

Measured physical and chemical property data for TPHP were retrieved from the registration dossier for the chemical submitted under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation in the European Union (EU) (REACH n.d.). The melting point and acid dissociation constant (pKa) values for DPHP were retrieved from the databases in EPISuite or the scientific literature, respectively (Funk et al. 2019; US EPA 2017). Calculated values were estimated using EPI Suite (US EPA 2017).

Chemical	TPHP	DPHP
Physical form	solid	solid
Melting point	50°C (exp.)	67.5°C (exp.)
Boiling point	413.5°C (exp.)	397°C (calc.)
Vapour pressure	8.5×10^{-4} Pa (25°C, exp.)	1.22×10^{-5} Pa (calc.)
Water solubility	1.9 mg/L (25°C, exp.)	143.6 mg/L (calc.)
Henry's law constant	0.15 Pa·m^3/mol (calc.)	1.08×10^{-5} Pa·m^3/mol (calc.)
Ionisable in the environment?	No	Yes
pKa	-	3.88 (exp.)
log K_{OW}	4.6 (20°C, exp.)	2.88 (calc.)

The chemical TPHP is a slightly volatile organic chemical with a slight solubility in water based on measured physicochemical properties. The moderate measured K_{OW} indicates that it is lipophilic.

Limited experimental physical and chemical property data are available for DPHP. However, estimated data suggest that the chemical is more water soluble and less lipophilic than TPHP. DPHP is a weak organic acid and, based on the measured pKa, is expected to be ionised in the pH range of environmental surface waters (pH 4–9).

Introduction and use

Australia

No specific Australian import or manufacturing information has been identified for TPHP and DPHP.

The chemical TPHP has reported domestic use in (NICNAS 2018; SCA n.d.; SWA 2020):

- polymer products
- lubricants
- hydraulic fluids
- construction materials,

- vehicle upholstery
- cosmetics (manicure products)
- industrial sealants.

The chemical is also used as a plasticiser for cellulose acetate films (NFSA n.d.).

The chemical TPHP is a component in the fire retardant Firemaster 550, which may be available in Australia (NICNAS 2018). Based on information in the public domain, TPHP is available for use in cosmetic products (at concentrations of 0.1–1.6%) in Australia (SCA n.d.). As recently as 2015, the substance was detected in around 1500 nail polish ingredient labels, including some brands available in Australia (EWG n.d.).

International

Available information indicates that TPHP is used as a flame retardant and plasticiser in a range of industrial and consumer products worldwide. DPHP is used as an intermediate in the manufacture of other chemicals.

The world-wide production volume of TPHP in the year 2000 was thought to be around 20000–30000 tonnes (OECD 2002). Annual production volume in China for the year 2020 was estimated to be 14493 tonnes (Huang J et al. 2022). The worldwide production volume of DPHP was suggested to be at least 2409 tonnes in 2021 (Liu Y et al. 2021).

The main commercial uses of TPHP are as a flame retardant and plasticiser for polymers such as polyvinyl chloride (PVC), polyurethanes and polycarbonate/acrylonitrile butadiene styrene (PC/ABS) blends, that are used for electronic products, cable insulation, circuit boards, water pipes, insulating foams, and automotive and furniture upholstery (Marklund et al. 2003; NICNAS 2018). Concentrations of TPHP in computer covers can range between 0.3–10% (w/w) (Marklund et al. 2003), and the chemical has been detected in various electronic products at up to 1.4% w/w (Ballesteros-Gómez et al. 2014; Kajiwara et al. 2011). TPHP was a frequently detected chemical in polyurethane foam (PUF) samples from US household sofas, with measured concentrations of up to 1.5% w/w in foam (Hammel et al. 2017). The substance is a non-flammable plasticiser additive in cellulose acetate used to make photographic film (WHO 1991), and both a flame retardant and plasticiser in protective triacetyl cellulose films for LCD panels (Kajiwara et al. 2011).

The chemical TPHP is used as an extreme pressure additive or antiwear agent in hydraulic fluids, lubricants, and transmission and motor oils to prevent surface damage (Marklund et al. 2005a). In hydraulic fluids for aircraft, it may be present at up to 5% (Marklund 2005; Schindler et al. 2014), although historically it was a major additive in commercial products such as Pydraul 50E (36% TPHP) and Phosflex 31P (28–30% TPHP) (Cleveland et al. 1986). Other applications are as a non-combustible additive for impregnating roofing paper (WHO 1991), to regulate pore sizes in concrete (Meyer and Bester 2004). It is also used as an additive in adhesives and textiles (Danish EPA 2016), fillers (US EPA 2020), paints and coatings (NCBI n.d.).

The chemical TPHP has cosmetic uses as a plasticiser in manicuring preparations such as nail polish and polish strips, where it can make up 1–14.5% of the product (CIR 2018; CPID n.d.). It has been found at up to 1.68% w/w in a survey of nail polish sold in the United States of America even in products that did not declare this as an ingredient (Mendelsohn et al. 2016).

Commercial fire retardants frequently contain TPHP, such as Firemaster 550 where it makes up 18–20% by weight (Kajiwara et al. 2011; Phillips et al. 2017), and Reofos 35 that contains 35% of the substance (UK EA 2009b). TPHP may be present as an impurity in other OPFR mixtures such as cresyl diphenyl phosphates (e.g. CAS No. 26444-49-5), isopropylphenyl diphenyl phosphates (e.g. CAS No. 28108-99-8) and tert-butylphenyl diphenyl phosphates (e.g. CAS No. 56803-37-3) (UK EA 2009a), trixylyl phosphate (CAS No. 25155-23-1) and isodecyl diphenyl phosphate (CAS No. 29761-21-5) (WHO 1991). It may also be present at up to 6% in trade products of resorcinol bis(diphenylphosphate) (CAS No. 57583-54-7) that have been used as a substitute for TPHP (Brommer 2014; Lassen 1999; Leisewitz et al. 2001), and which are sometimes used in a mixture with more TPHP (Leisewitz et al. 2001).

The chemical DPHP may be used as a catalyst in polymerisation processes (Zhao J and Hadjichristidis 2015), and as an additive (<1%) in paints and coatings (Björnsdotter et al. 2018; US EPA 2016). It is also used as an intermediate in the manufacture of TPHP and other phosphate triesters such as (Fisher Scientific n.d.):

- trixylyl phosphate (CAS No. 25155-23-1)
- isodecyl diphenyl phosphate (CAS No. 29761-21-5)
- cresyl diphenyl phosphate (CAS No. 26444-49-5)
- isopropylphenyl diphenyl phosphate (CAS No. 28108-99-8).

Existing Australian regulatory controls

Environment

The use of the chemicals in this group is not subject to any specific national environmental regulations.

International regulatory status

United Nations

The chemicals TPHP and DPHP are not currently identified as persistent organic pollutants (POPs) (UNEP 2001), ozone depleting substances (UNEP 1987), or hazardous substances for the purpose of international trade (UNEP & FAO 1998).

OECD

The chemical TPHP is listed as an OECD High Production Volume (HPV) chemical (OECD n.d.). The substance has been sponsored for assessment under the Cooperative Chemicals Assessment Programme (CoCAP). A Screening Information Data Sheet (SIDS) Initial Assessment Report (SIAR) has also been published (OECD 2002). Further exposure and environmental risk assessments were recommended.

European Union

The chemical TPHP is listed on the community rolling action plan (CoRAP) of the EU due to potential for endocrine disruption, high aggregated tonnage and wide dispersive use. The substance is currently undergoing an endocrine disruptor assessment (ECHA n.d.).

Environmental risk limits (maximum permissible concentrations, MPCs) for TPHP in Holland are 170 ng/L for surface water, 950 ng/L for marine water, and 95 µg/kg dry weight (dw) for soil and sediment (Verbruggen EMJ et al. 2006).

The chemical TPHP is listed on the SIN list, a database of chemicals that have been identified as being Substances of Very High Concern by the Swedish NGO ChemSec. The listing is due to the chemical's suspected endocrine disrupting properties (ChemSec n.d.).

Canada

On the basis of a draft screening assessment conducted under the Canadian Environmental Protection Act, 1999 (CEPA), it was recommended that TPHP is added to the List of Toxic Substances in Schedule 1 of the Act (Government of Canada 2021). TPHP was found to meet one or more of the criteria set out in section 64 of CEPA.

Environmental exposure

Industrial uses of TPHP and DPHP are expected to result in both diffuse and point source emissions into the environment.

Triphenyl phosphate is a synthetic compound used as flame retardant and plasticiser in plastic articles. It is an additive that is not chemically bonded to the materials in which it is included. Emissions of the chemical to the environment are expected from the migration of this chemical onto the surface of rubber and plastic articles as well as from abrasion and wear of these articles during their normal use (Lassen 1999; Regnery and Püttmann 2010). These emissions may occur to air, water, and soil. Leaching of the chemical may occur to any immediate environment from plastics including from PVC pipes or cladding on buildings as well as microplastics in the environment (Schmidt et al. 2021; van der Veen and de Boer 2012).

The chemical TPHP is routinely detected in house dust. In Australia, TPHP levels in dust were reported to be up to 51 µg/g in different indoor settings (Banks et al. 2020; He et al. 2018; Huang Y et al. 2020), while DPHP was found present at up to 316 µg/g (Huang Y et al. 2020; Van den Eede et al. 2015). Dust may reach the environment through ventilation, flushing of dust particles collected during wet cleaning and disposal of vacuum cleaner dust (Marklund et al. 2003) and contribute to emissions of the chemical to air, soil and STP effluent.

The chemical TPHP can enter the environment from industrial activities such as the chemicals production, formulation and the recycling of plastic articles that contain the chemical. Emissions may contribute to levels of the chemical in STP influents or to soil nearby areas of manufacture or recycling (Wang Y et al. 2018).

When used in textiles and clothing, TPHP may be transferred to wastewater and become a source of contamination in STP influent (Schreder and La Guardia 2014). Depending on degradation and partitioning processes of chemicals in sewage treatment plants (STPs), some fraction of the quantity of chemicals in wastewater entering STPs can be emitted to the air compartment, to rivers or oceans in treated effluent, or to soil through application of biosolids to agricultural land (Struijs 1996).

Another major source of contamination is leakages from hydraulic machinery (Anderson et al. 1993), such as excavators and digging equipment, aircraft hydraulic systems and automobile braking and transmission fluids. It has been estimated that up to 80% of trialkyl/aryl phosphate hydraulic fluid is used to replace losses from leakage (David and Seiber 1999). Emissions from these uses occur in soil near the operation of hydraulic machinery. The chemical is routinely detected in soils near airports (David and Seiber 1999; Yadav and Devi 2020) and has been detected in water runoff from roads in Australia (Pantelaki and Voutsa 2019).

The release of DPHP occurs predominately via the degradation of triphenyl phosphate in the environment, although some may occur from manufacturing and processing activities that use DPHP as an intermediate or catalyst (Björnsdotter et al. 2018). DPHP is also a degradation product from other aryl phosphate flame retardants.

Environmental fate

Partitioning / Dissolution, speciation and partitioning

The chemical TPHP is expected to partition to sediments and soil when released into the environment. DPHP is an ionised chemical that will predominantly transfer to or remain in the water compartment.

The chemical TPHP is a neutral organic chemical that is slightly soluble in water. An estimated Henry's Law constant (0.15 $Pa \cdot m^3/mol$) indicates it will be moderately volatile from water and moist soil. The substance is a lipophilic chemical with a high log K_{OW} value (4.6) and soil adsorption coefficients (K_{OC} >2000) that indicate it will be immobile in different types of soil (Anderson et al. 1993) and preferentially adsorb to phases in the environment with high organic carbon content (including sediment and soil).

The chemical DPHP is moderately soluble in water where it exists as an anion at neutral pH, with a pKa of 3.88. It is expected to have medium mobility through soil.

The chemicals in this group are expected to be released to the environment through STP effluent and diffuse emissions from plastic articles. The chemicals are released to surface waters in STP effluent as a result of their use and released to the soil compartment through application of STP biosolid residues to land. Release to soil may also occur from the operation of hydraulic machinery. Fugacity calculations (Level III approach) assuming equal release to the water, soil and air compartments (1000 kg/h) predict that TPHP will predominately remain in soil (75.3%), some will partition to water (14.8%), and small quantities to sediment (9.23%) and air (0.619%) (US EPA 2017). DPHP is a charged species that will predominantly be found in the water compartment. Elimination rates of TPHP in STPs are generally thought to be around 56–87% (Meyer and Bester 2004), and 70–80% has been suggested for two Norwegian STPs (Green et al. 2008).

Degradation

Based on available evidence, the chemicals in this group are not expected to be persistent in the environment.

In distilled water, TPHP undergoes pH dependent hydrolysis to form DPHP and phenol, with measured half-lives of 3–19 days at pH 7–9 (OECD 2002; REACH n.d.). DPHP appears resistant to further hydrolysis under neutral and basic conditions, possibly due to deprotonation of its free hydroxy group that forms the corresponding conjugate base (Su et al. 2016).

The chemical TPHP is biodegradable in water under both aerobic and anaerobic conditions. Over 28 days, the substance was shown to degrade to 83–94% in a biological oxygen demand (BOD) test (OECD Test Guideline (TG) 301C), and to 82% through CO_2 evolution (EPA OTS 796.3260, similar to OECD TG 301B) at the same time passing the 10 d window (REACH n.d.). An STP simulation test following OECD TG 303A protocol recorded a degradation of 93.8% after 20 days (REACH n.d.). In mineral salt solution, TPHP (and DPHP that formed during the experiment) was shown to degrade under biotic conditions with 99% mineralisation after 28 d (OECD TG 310), and a DT50 value of 2.8 d (Jurgens et al. 2014).

The chemical TPHP is not expected to be persistent in soils. A non-guideline soil degradation study with TPHP using a loamy sand standard soil (organic carbon 2.22%) revealed ultimate degradation half-lives of around 100 days. Primary half-lives of 37 days (aerobic conditions) and 21 days (anaerobic conditions) were observed (Anderson et al. 1993; REACH n.d.).

The chemicals TPHP and DPHP are expected to degrade in the atmosphere through reaction with photogenerated hydroxyl radicals. The rate of this degradation may be influenced by the association of the chemicals to particles in the air. Calculations performed assuming a typical hydroxyl radical concentration of 1.5×10^6 molecules/cm^3 and 12 hours of sunlight per day resulted in a half-life of 11.8 h for TPHP and 17.4 h for DPHP (US EPA 2017). However, when TPHP and DPHP were deposited on $(NH_4)_2SO_4$ particles, the mean lifetime was found to be 3.4–8.5 days for TPHP (corresponding to a half-life of 2.4–5.9 days) and 3.1–7.6 days for DPHP (half-life of 2.1–5.3 days) (Liu Q et al. 2019).

No specific biodegradation data for DPHP in water or soil are available. As TPHP will hydrolyse to form DPHP, and TPHP is shown to be readily biodegradable, it is assumed that DPHP will also be readily biodegradable in these environmental compartments.

Bioaccumulation

The chemicals in this group exhibit a low potential to bioconcentrate in aquatic organisms. Experimentally determined bioconcentration factors (BCFs) for both chemicals are below the Australian categorisation threshold for bioaccumulation hazards in aquatic organisms (DCCEEW n.d.).

Identified experimental BCF values for TPHP in various fish species (zebrafish, killifish, goldfish, bleak, trout, fathead minnow) and the mussel *Mytilus galloprovincialis*, based on concentrations per wet weight of organism are below 2000 (Mata et al. 2022; REACH n.d.; Verbruggen EMJ et al. 2006; Wang G et al. 2016; Wang G et al. 2017; WHO 1991). Depuration half-lives of TPHP in rainbow trout, zebrafish and fathead minnows were in the range 1–50 h (Wang G et al. 2017; WHO 1991). However, a study involving zebrafish found relatively high concentrations and slow depuration of TPHP in roe (semi-static conditions, OECD TG 305), which may indicate a potential for the substance to be transferred to the next generation (Wang G et al. 2017).

Bioaccumulation factor (BAF) values from dietary exposure were found to be 158.5 for fish, 512.9 for invertebrates and 354.8 for plankton (Wang X et al. 2019). These values are below 2000, which suggests that TPHP has low potential for bioaccumulation from food sources in aquatic organisms. In addition, biota-sediment accumulation factors (BSAFs) for catfish were below 0.642, indicating minimal uptake of TPHP from sediment (Peng et al. 2021).

Biotransformation experiments with TPHP in aquatic species comprising several trophic levels and microbes identified a total of 29 degradation products, with DPHP generated in all test species (Choi et al. 2021). Metabolism of TPHP to DPHP is thought to be mediated by cytochrome P450 (CYP) enzymes (Mitchell et al. 2019). TPHP may be able to cross the blood-brain barrier, whereas its metabolites cannot (Wang G et al. 2016).

The only available experimental BCF value for DPHP is 0.29 L/kg (Muir and Grift 1981). A study that exposed rainbow trout fry to DPHP found that accumulation of the chemical in these fish occurs rapidly (within 20 min). Depuration in clean water led to a 90% reduction of body burden in 1.5 hours (Muir and Grift 1981).

Studies of organisms of different trophic levels have found no or low biomagnification of TPHP, such as between the fish capelin (*Mallotus villosus*) and different seabirds and mammals in the Arctic (Hallanger et al. 2015), and between ringed seal and polar bears (BMF = 0.88) (Strobel et al. 2018). Trophic magnification of TPHP was not significant in a food web involving sediment, suspended matter and 12 different organisms or their eggs found in a Dutch estuary (Brandsma et al. 2015) and in 17 species from a Chinese freshwater lake (Zhao H et al. 2018). In both cases, the observed trophic dilution was attributed to rapid metabolism.

The chemical TPHP has been detected in birds. Great Lakes herring gull (*Larus argentatus*) eggs held TPHP at 0.89 ng/g wet weight (ww) in yolk and at up to 4.18 ng/g ww in albumen (Greaves and Letcher 2014), whereas whole eggs of black-tailed gull (*Larus crassirostris*) contained up to 1.78 ng/g ww (Choo et al. 2022). Australian chicken egg albumen contained 0–3.1 ng/g TPHP and 0–9.7 ng/g DPHP, while yolks held only DPHP at 0.26–34 ng/g (Li Z et al. 2020). TPHP levels in bald eagle (*Haliaeetus leucocephalus*) eggs were 0–742 ng/g ww and in nestling plasma 0.22–1.61 ng/g ww (Guo et al. 2018).

Acute dermal exposure of Indian Blue Earthworms (*Perionyx excavates*) to sublethal concentrations of TPHP led to minor uptake and rapid biotransformation of the substance, while chronic exposure resulted in low BAF values of 0.075–0.319. Metabolism of the substance in P. excavates resulted in formation of DPHP, and hydroxyl, thiol and glucoside isomers of TPHP (Wang L et al. 2018).

Several studies indicate that accumulation of TPHP and DPHP in plants will be low, and that metabolism of TPHP is fast. A BCF of 43 L/kg was obtained for duckweed (*Lemna minor*) exposed to TPHP in water (US EPA n.d.), while wheat (*Triticum aestivum* L.) seedlings had a maximum root concentration factor (RCF) of 1300 L/kg in the presence of TPHP, and 180 L/kg with DPHP (Gong X et al. 2020). Another study found that wheat seedlings absorbed TPHP in roots and shoots. DPHP and monophenyl phosphate were found in both after 12 h, indicating rapid metabolism of TPHP (Wan et al. 2017).

Environmental transport

The chemicals in this group may undergo long range transport by adhesion to atmospheric particles. However, some monitoring studies in remote regions have been complicated by potential local contamination sources.

In the air compartment, organophosphorus flame retardants such as TPHP predominantly exist adsorbed to airborne particles. They have been found in the particulate phase of both urban and marine air (Brommer 2014). Adsorption to particles may increase a substance’s resistance to degradation, which in turn increases its atmospheric half-life and may make it prone to long range transport. An experimental study of particle (ammonium sulfate) bound OPFRs determined a half-life of 2.4–5.9 days for TPHP and 2.1–5.3 days for DPHP (Liu Q et al. 2019). The lifetime for TPHP increased to 14 days (a half-life of 9.7 days) when the particles were further coated with oxalic acid to simulate complex mixtures (Liu Y et al. 2014).

The chemical TPHP has been detected in polar regions and other remote areas. While detected levels in air are generally below 250 pg/m^3 (Han et al. 2020; Wei et al. 2015), 12 ng/m^3 of the substance were measured in a remote area of northern Finland (Marklund et al. 2005a). TPHP has been detected within Arctic animals such as polar bears and ringed seals (Hallanger et al. 2015; Strobel et al. 2018).

Experimental results confirm that TPHP and DPHP could be transported to remote areas through air ($t_{1/2}$ >2 days) (Liu Q et al. 2019) and from there reach aquatic and terrestrial systems via precipitation. Although an investigation of TPHP in Antarctic lakes suggests that this substance may be present due to human activity in the area (Gao X et al. 2018), findings of TPHP in air and precipitation (Bacaloni et al. 2008; Pantelaki and Voutsa 2019; Wu et al. 2020) may support long range atmospheric transport as a possible mechanism of distribution for TPHP (Möller et al. 2011; Wei et al. 2015).

Predicted environmental concentration (PEC)

The PECs for TPHP and DPHP have been selected based on international monitoring of the chemicals in surface water, soil and sediments. The PECs for TPHP are 9.1 µg/kg in soil, 11 µg/kg in sediment, 293 ng/L in STP effluent, and 25 ng/L in surface water. Available PECs for DPHP are 252 ng/L in STP effluent and 70 ng/L for surface water.

In Australia, TPHP has been detected in water samples on two occasions at low concentrations or not at all. The substance was observed in rainwater at 2.59 ng/L and road runoff water at 50 ng/L (Pantelaki and Voutsa 2019). A survey of 11 STPs across four eastern states (11 in Queensland, two in South Australia, one in the ACT and one in Tasmania) found no TPHP in STP influents up to the limit of detection at 0.2 µg/L (O'Brien et al. 2015).

Frequent detections of TPHP in environmental compartments have occurred throughout different parts of the world. Lake water samples collected in Antarctica, Canada, China, Italy and Korea had average TPHP concentrations of 0.77–25 ng/L (Andresen et al. 2007; Bacaloni et al. 2008; Chen M-H and Ma 2021; Gao X et al. 2018; Wang X et al. 2019). Relatively high concentrations of 10.6 and 18.8 ng/L in one of three Antarctic lakes are thought to be due to nearby human activity (Gao X et al. 2018). Average values of 0.35–22.3 ng/L TPHP were seen in ground, river and surface water throughout Europe, Asia, the USA, and Arctic regions (Bacaloni et al. 2008; Chen M-H and Ma 2021; Cristale et al. 2013a; Cristale et al. 2013b; Gao X et al. 2020; Haggard et al. 2006; Martínez-Carballo et al. 2007; Wei et al. 2015). DPHP concentrations have been reported for surface waters on two occasions, with observed values between 0–70 ng/L (Grigoriadou et al. 2008; Liu Y et al. 2021).

High maximal concentrations of TPHP have been detected in areas near industrial activity and waste disposal. In Italy, concentrations up to 165 ng/L TPHP was measured in river water (Wei et al. 2015) and 164 ng/L in ground water possibly contaminated through illegal dumping (Bacaloni et al. 2008). Elevated median values for TPHP were observed in US streams considered susceptible to contamination from human, industrial, and agricultural wastewater, with TPHP concentrations up to 220 ng/L (Kolpin et al. 2002). In the Netherlands ten river sites had an average maximum of 81.6 ng/L with the highest value of 990 ng/L seen at one site in 1999 (Verbruggen EMJ et al. 2006).

Measurements from highly disturbed locations are not considered to be representative of the expected concentrations in the environment. As such, the PECs of TPHP and DPHP in surface waters are 25 ng/L and 70 ng/L, respectively, in line with the highest average values from typical surface water measurements.

Concentrations of TPHP in STP wastewater vary globally but concentrations are typically in the range of 0–491 ng/L in influent and 0–293 ng/L in effluent (Kim U-J et al. 2017; Marklund 2005; Marklund et al. 2005b; Martínez-Carballo et al. 2007; Meyer and Bester 2004; O'Brien et al. 2015; Wei et al. 2015). Concentrations ≥3000 ng/L were found in STP effluent in Sweden, Norway, and China. However, most of these STPs were receiving influent that included landfill leachate or were in highly industrialised areas (Chen M-H and Ma 2021; Green et al. 2008; Wei et al. 2015). Slightly elevated values were obtained in a USA study, where STP influent contained on average 491 ng/L TPHP and 263 ng/L DPHP, and secondary treated effluent contained average concentrations of 293 ng/L TPHP and 252 ng/L DPHP (Kim U-J et al. 2017). As this STP receives mainly residential wastes, these effluent values are taken as conservative PEC values for STP effluent.

The chemical TPHP has been found in STP biosolids samples from Europe, China and the US at average concentrations of 15–133 µg/kg dw (Kim U-J et al. 2017; Marklund et al. 2005b; Pantelaki and Voutsa 2019; Wang Y et al. 2019), often with high maximum values of up to 1170 µg/kg dw (Wang Y et al. 2019). These elevated values can be due to local contamination such as landfill (Green et al. 2008). DPHP was detected in a few studies conducted in the USA and China, where average values were between 18–41 µg/kg dw (Gao L et al. 2016; Kim U-J et al. 2017; Wang Y et al. 2019). Biosolids from a USA STP that contained very high TPHP concentrations, was found to have even higher levels of DPHP at up to 1680 µg/kg dw (Wang Y et al. 2019).

Detections of TPHP have occurred in river, lake and sea sediment samples, and average concentrations are generally between 0.023 and 20 µg/kg dw (Chen M-H and Ma 2021; Cristale et al. 2013a; Lee S et al. 2018; Sühring et al. 2021; Wang X et al. 2019; Wei et al. 2015; Wolschke et al. 2018). Higher concentrations of up to 316.5 µg/kg dw are occasionally measured and are usually due to known or suspected contamination from airports (Martínez-Carballo et al. 2007; Yadav and Devi 2020), heavy traffic (Yadav and Devi 2020) and industrial areas (Lee S et al. 2018). 20 µg/kg dw has been chosen as a conservative PEC for TPHP in sediments as it is the highest average value from locations that weren't highly disturbed.

Soil samples from different environments show typical average TPHP concentrations of 1.8–9.1 µg/kg dw, with most of the samples collected in areas of human activity (Gong S et al. 2021; Han et al. 2020; Mihajlović et al. 2011; Wang Y et al. 2018). A notably higher average was observed in Nepal at 26.2 µg/kg, which reflects a high level of commercial activity and close proximity to heavy traffic and an airport (Yadav and Devi 2020). High maximum values were also reported in China at 111 and 303 µg/kg, both from industrial areas (Gong S et al. 2021; Wang Y et al. 2018). 9.1 µg/kg dw has been chosen as a conservative representative PEC for TPHP in soils, despite potential disturbance from commercial areas.

TPHP has been detected in outdoor air in different environments around the world. In urban areas averages were found to be in the range of <60–200 pg/m^3 (Brommer 2014; Green et al. 2008; Wu et al. 2020). Concentrations of TPHP are generally lower in remote areas. Averages of 0.6–55 pg/m^3 have been measured in polar and other remote areas (Brommer 2014; Möller et al. 2012; Wang C et al. 2020; Wu et al. 2020), with occasional maximum values at up to 239 pg/m^3 (Han et al. 2020). A notable exception is one air sample collected in remote northern Finland that contained 12 ng/m^3 TPHP, presumable due to air traffic through the area (Marklund et al. 2005a). For Australia, only one indoor air study is available. TPHP was detected in all samples from 15 fire stations, at a range of 0.85–3.8 ng/m^3 (Banks et al. 2020).

The chemical TPHP has been detected in fat, muscle and whole-body samples of living and stranded species including Arctic mammals and various marine organisms, at concentrations up to 7.2 ng/g ww (Brandsma et al. 2015; Papachlimitzou et al. 2015; Sala et al. 2021; Strobel et al. 2018).

Environmental effects

Effects on aquatic life

Acute toxicity

The following measured median lethal concentration (LC50) and effective concentration (EC50) values for TPHP and DPHP were retrieved from the scientific literature (Chen J-Y et al. 2022; Funk et al. 2019) and the registration dossier for TPHP submitted to ECHA under REACH legislation (REACH n.d.):

Taxon	Endpoint	Method
Fish	TPHP: 96 h LC50 = 0.36 mg/L	*Oncorhynchus mykiss* (rainbow trout) static, nominal concentrations EPA 660/3-75-009
	DPHP: 96 h LC50 = 49.98 mg/L	*Danio rerio* (embryo zebrafish) mortality semi static nominal concentrations
Invertebrate	TPHP: 48 h EC50 = 0.55 mg/L	*Daphnia magna* (water flea) mortality static, measured concentrations OECD TG 202
Algae	TPHP: 72 h EC50 = 2.45 mg/L*	*Raphidocelis subcapitata* (green algae) biomass static, nominal concentrations OECD TG 201
Amphibians	TPHP: 96 h EC50 = 2.89 mg/L*	*Hoplobatrachus rugulosus* (Chinese edible frog) mortality semi-static, measured concentrations

* Toxicity endpoint above solubility limit

The toxicity of TPHP towards other freshwater organisms has been evaluated. A 72 h LC50 (mortality) value for the aquatic mollusc Pomacea canaliculate was determined to be 38.2 mg/L (Lo and Hsieh 2000), and a 40 h growth inhibition EC50 for the protozoa *Tetrahymena pyriformis* of 5.05 mg/L was obtained (Sinks and Schultz 2001). It should be noted that these endpoints are all above the solubility limit of TPHP and their relevance is uncertain.

Chronic toxicity

The following measured 10% lethal concentration (LC10), no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC) values for TPHP in model organisms across three trophic levels were retrieved from the registration dossier under REACH legislation (REACH n.d.) and the literature (Yuan et al. 2018):

Taxon	Endpoint	Method
Fish	30 d LC10 = 37 µg/L	*Oncorhynchus mykiss* (rainbow trout fry) mortality flow-through, nominal concentrations EPA 660/3-75-009
	73 d LC10 = 4.8 µg/L	*Danio rerio* (zebrafish) mortality flow-through, measured concentrations OECD TG 234
Invertebrates	21 d NOEC = 254 µg/L	*Daphnia magna* (water flea) reproduction semi-static, measured concentrations OECD TG 211
Algae	72 h EC10/NOEC = 250 µg/L	*Raphidocelis subcapitata* (green algae) growth static, nominal concentrations OECD TG 201

In addition to the above results, a two week sub-chronic toxicity experiment involving Chinese edible frog tadpoles (*Hoplobatrachus rugulosus*) showed decreased survival at TPHP concentrations of ≥50 µg/L and delayed metamorphosis at ≥100 µg/L (Chen J-Y et al. 2022).

Effects on terrestrial Life

No studies demonstrating adverse effects of TPHP to terrestrial organisms have been identified. An OECD TG 207 test on the effects of TPHP on the earthworm *Eisenia andrei* gave no observed adverse effects under 1000 mg/kg soil dw during the 14-day test period (REACH n.d.).

Endocrine effects/activity

TPHP may cause endocrine effects in fish based on laboratory studies on transgenic fish. However, the exposure concentrations are typically greater than reported mortality values.

The high chronic toxicity of TPHP to fish may interfere with the results of endocrine activity investigations. An OECD TG 234 fish sexual development test observed no endocrine related effects at TPHP concentration of 3 µg/L (REACH n.d.). Mortality was observed at exposures greater than 4.8 µg/L.

In vivo studies in transgenic fish indicate decreased ovarian function in females and increased intersex in males. However, these effects were mostly observed at exposure concentrations greater than reported mortality endpoints. A 100 day exposure of female Japanese medaka to TPHP resulted in retardation of ovaries (reduced number of mature follicles) in 12% of tested fish at nominal concentrations of 1.6 µg/L. At exposures of 8 µg/L, a 39% decreased egg production rate was observed (Li Y et al. 2019). A 100 day exposure of male Japanese medaka to 40 µg/L of TPHP altered the reproductive behaviour of the fish and induced a 26% increase of gonadal intersex (Li Y et al. 2018).

In female Japanese medaka, TPHP caused a decrease in the number of total and fertilised eggs at 44.9 µg/L after 21 days (Kawashima et al. 2022). A 7 day exposure of zebrafish embryos to TPHP increased levels of thyroid hormones T3 and T4, with a LOEC of 40 µg/L, and at concentrations above 200 µg/L influenced the expression of several genes associated with the thyroid system (Kim S et al. 2015). Exposure of zebrafish to TPHP over 21 days (semi-static exposure, nominal concentrations) caused transcriptional changes for some regulatory and steroidogenic genes of the hypothalamus-pituitary-gonadal (HPG) axis in both sexes, for example the VTG1 gene in males exposed to as low as 40 µg/L (Liu X et al. 2013).

Predicted no-effect concentration (PNEC)

A PNEC for TPHP of 0.48 µg/L was derived from the measured fish chronic ecotoxicity endpoint (73 d LC10 = 4.8 µg/L) using an assessment factor of 10. This assessment factor was selected, as reliable chronic ecotoxicity data are available over three trophic levels.

This PNEC is considered protective as TPHP shows potential endocrine activity that may impact fish at concentrations greater than 1.6 µg/L.

For DPHP, a PNEC of 49.98 µg/L was obtained from the measured fish acute ecotoxicity endpoint (96 h LC50 = 49.98 mg/L) and using an assessment factor of 1000 to reflect the fact that only one ecotoxicity endpoint is available for this substance.

Categorisation of environmental hazard

The categorisation of the environmental hazards of the assessed chemical according to Australian Environmental Criteria for Persistent, Bioaccumulative and/or Toxic Chemicals (DCCEEW n.d.) is presented below:

Persistence

Not Persistent (Not P). Based on measured biodegradation studies showing ready biodegradability, TPHP and DPHP are categorised as Not Persistent.

Bioaccumulation

Not Bioaccumulative (Not B). Based on low measured bioconcentration factors (BCF) in fish, and evidence of rapid biotransformation, TPHP and DPHP are categorised as Not Bioaccumulative.

Toxicity

TPHP: Toxic (T). Based on available acute ecotoxicity values below 1 mg/L and evidence of high chronic toxicity, TPHP is categorised as Toxic.

DPHP: Not Toxic (Not T). Based on available ecotoxicity values above 1 mg/L, DPHP is categorised as Not Toxic.

Environmental risk characterisation

Based on the PEC and PNEC values determined above, the following Risk Quotient (RQ = PEC ÷ PNEC) have been calculated for release of TPHP and DPHP into freshwater and soil:

Compartment	Chemical	PEC	PNEC	RQ
Water (freshwater)	TPHP	0.025 µg/L	0.48 µg/L	0.052
	DPHP	0.07 µg/L	50 µg/L	0.001
STP effluent	TPHP	0.29 µg/L	0.48 µg/L	0.60
	DPHP	0.25 µg/L	49.98 µg/L	0.005

Given that the calculated RQ values are less than 1, the chemicals are not expected to pose a significant risk to the aquatic environment, as environmental concentrations are below levels likely to cause harmful effects in typical environmental conditions.

While the highest environmental concentration values were found in highly disturbed areas (e.g., landfills, airports, industrial areas) they are not expected to be representative of the risk of the chemicals to the environment. Instead, average environmental concentrations from international monitoring studies have been considered for risk calculations.

While the chemicals in this evaluation are frequently found in soils and sediment, little information is known regarding the toxicity of these substances to soil or sediment dwelling organisms. As a result, no RQ for the release of the chemicals to soil or sediment has been calculated. If more information becomes available, a risk characterisation of the chemicals in this group for these compartments may be possible.

TPHP may induce endocrine effects in some species of fish, but effect concentrations are typically above those found in the environment. The PNEC derived in this assessment is considered protective for the endocrine effects described by currently available evidence. The endocrine activity of the chemical is an active area of research, and the risk will need to be re-evaluated if new information becomes available.

Uncertainty

This evaluation was conducted based on a set of information that may be incomplete or limited in scope. Some relatively common data limitations can be addressed through use of conservative assumptions (OECD 2019) or quantitative adjustments such as assessment factors (OECD 1995). Others must be addressed qualitatively, or on a case-by-case basis (OECD 2019).

The most consequential areas of uncertainty for this evaluation are:

- Limited Australian monitoring information was available for the chemicals in this evaluation. The outcomes of this evaluation may change if new monitoring information become available to indicate that environmental concentrations of these chemicals in Australia are higher than currently assessed.

- Insufficient information is available to characterise the terrestrial and sediment toxicity of the chemicals in this evaluation. The outcomes of the evaluation may change if additional information becomes available.
- There is limited ecotoxicity information available for DPHP. The outcomes of the evaluation may change if additional information becomes available to suggest that the ecotoxicity of DPHP has been underestimated.

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