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Environmental Risk Limits for several phosphate esters, with possible application as flame retardant

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Rapport in het kort

Milieurisicogrenzen voor enkele fosfaatesters, met mogelijke toepassing als brandvertrager

Voor een aantal fosfaatesters, die mogelijk als vlamvertrager gebruikt worden, zijn Maximaal Toelaatbaar Risiconiveaus (MTR), Verwaarloosbaar Risiconiveaus (VR) en Ernstig Risiconiveaus (ER_{eco}, Engelse afkorting SRC_{eco}) afgeleid. Deze milieurisicogrenzen zijn afgeleid voor de compartimenten water, bodem, en lucht en zijn gebaseerd op ecotoxicologische gegevens voor met name het aquatische milieu. Het gaat om de volgende stoffen: TCEP (tris(2-chloorethyl)fosfaat), TCPP (tris(1-chloor-2-propyl)fosfaat), TDCP (tris(1,3-dichloor-2-propyl)fosfaat), TBP (tri-*n*-butyl fosfaat), TiBP (tri-*iso*-butyl fosfaat), TEP (triethyl fosfaat), TBEP (tris(butoxyethyl) fosfaat), TEHP (tris(2-ethylhexyl) fosfaat), TPP (trifenylfosfaat) en TCP (tricresylfosfaat). Meetgegevens voor Nederland (1989, 1999-2004) laten zien dat voor de meeste fosfaatesters de concentraties in oppervlaktewater rond het VR liggen. Alleen voor TPP blijkt dat concentraties in oppervlaktewater af en toe het MTR overschrijden.

Trefwoorden: milieurisicogrenzen; fosfaatesters; vlamvertragers; maximaal toelaatbaar risiconiveau; ernstig risiconiveau, verwaarloosbaar risiconiveau

Abstract

Environmental Risk Limits for several phosphate esters, with possible application as flame retardant

Maximum Permissible Concentrations (MPC), Negligible Concentrations (NC) and Serious Risk Concentrations (SRC_{eco}) are derived for a number of phosphate esters that are possibly used as flame retardant. These environmental risk limits were derived for the compartments water, soil, and sediment on basis of ecotoxicological data for the aquatic environment in particular. The substances that were evaluated in this study were: TCEP (tris (2-chloroethyl) phosphate), TCPP (tris(2-chloro-1-methylethyl) phosphate), TDCP (tris(1,3-dichloro-2-propyl) phosphate), TBP (tri-*n*-butyl phosphate), TiBP (tri-*iso*-butyl phosphate), TEP (triethyl phosphate), TBEP (tris(2-butoxyethyl) phosphate), TEHP (tris(2-ethylhexyl) phosphate), TPP (triphenyl phosphate), and TCP (tricresyl phosphate). Monitoring data for the Netherlands (1989, 1999-2004) show that for most phosphate esters the concentrations in surface water are around the NC values. It appears that only concentrations of TPP sometimes exceed the MPC value.

Keywords: environmental risk limits; phosphate esters; flame retardants; maximum permissible concentration; serious risk concentration

Contents

Samenvatting

In dit rapport zijn Maximaal Toelaatbaar Risiconiveaus (MTRs), Verwaarloosbaar Risiconiveaus (VRs) en ecotoxicologische Ernstig Risiconiveaus (ER_{eco}s) afgeleid voor fosfaatester verbindingen, die mogelijk gebruikt worden als vlamvertragers.
De genoemde milieurisicogrenzen zijn afgeleid op basis van ecotoxicologische en milieuchemische data en vormen aansluitend de wetenschappelijke basis voor milieukwaliteitsnormen die worden vastgesteld door de Stuurgroep Stoffen.

De onderzochte stoffen zijn: TCEP (tris(2-chloorethyl)fosfaat), TCPP (tris(1-chloor-2-propyl)fosfaat), TDCP (tris(1,3-dichloor-2-propyl)fosfaat), TBP (tri-*n*-butyl fosfaat), TiBP (tri-*iso*-butyl fosfaat), TEP (triethyl fosfaat), TBEP (tris(butoxyethyl) fosfaat), TEHP (tris(2-ethylhexyl) fosfaat), TPP (trifenylfosfaat) en TCP (tricresylfosfaat). Alleen toxiciteitsstudies met eindpunten die gerelateerd zijn aan overleving, groei of reproductie zijn in beschouwing genomen. Voor sediment, en meestal ook voor het compartiment bodem, zijn geen toxiciteitsgegevens gevonden die bruikbaar zijn voor het afleiden van ER_{eco} en MTR-waarden. In dat geval zijn de $ER_{bodem/sediment}$ en $MTR_{bodem/sediment}$ afgeleid met behulp van de evenwichtspartitiemethode. Tabel 1 en tabel 2 tonen de afgeleide milieurisicogrenzen voor de groep fosfaatesters.
Meetgegevens voor Nederland laten zien dat voor de gechloreerde en alkylfosfaatesters de concentraties in oppervlaktewater rond het VR liggen. Alleen voor de arylfosfaatester TPP blijkt dat concentraties in oppervlaktewater af en toe het MTR overschrijden.

Tabel 1. Milieurisicogrenzen voor fosfaatesters in zoet oppervlaktewater en zeewater (marien).

	$ER_{eco,\ opgelost}$ [mg/L]	$ER_{eco,\ totaal}$ [mg/L]	$MTR_{opgelost}$ [µg/L]	MTR_{totaal} [µg/L]	$VR_{opgelost}$ [µg/L]	VR_{totsal} [µg/L]	MTR_{marien} [µg/L]
TCEP	8,6	8,6	[a]	[a]	[a]	[a]	[a]
TCPP	6,5	6,5	[a]	[a]	[a]	[a]	[a]
TDCP	0,52	0,54	[a]	[a]	[a]	[a]	[a]
TBP	1,1	1,1	66	66	0,66	0,66	6,6
TiBP	3,4	3,4	11	11	0,11	0,11	1,1
TEP	110	110	1600	1600	16	16	160
TBEP	2,9	2,9	13	13	0,13	0,13	1,3
TEHP	[b]	[b]	[b]	[b]	[b]	[b]	[b]
TPP	0,060	0,062	0,16	0,17	0,0016	0,0017	0,016
TCP	0,031	0,031	0,032	0,033	0,00032	0,00033	0,0032

Opmerkingen:
a: MTR en VR worden afgeleid na publicatie van de EU-RAR (EC Regulation 793/93) van betreffende stof.
b: milieurisicogrenzen konden niet worden afgeleid

Tabel 2. Milieurisicogrenzen voor fosfaatesters in bodem en sediment.

	$ER_{eco, bodem}$ [mg/kg_{dw}]	MTR_{bodem} [µg/kg_{dw}]	VR_{bodem} [µg/kg_{dw}]	$ER_{eco, sediment}$ [mg/kg_{dw}]	$MTR_{sediment}$ [µg/kg_{dw}]	$VR_{sediment}$ [µg/kg_{dw}]
TCEP	28	[a]	[a]	74	[a]	[a]
TCPP	9,7	[a]	[a]	230	[a]	[a]
TDCP	13	[a]	[a]	380	[a]	[a]
TBP	88	530	53	90	5400	54
TiBP	200	640	6,4	200	660	6,6
TEP	270	4100	41	460	6800	68
TBEP	180	810	8,1	180	830	8,3
TEHP	[b]	[b]	[b]	[b]	[b]	[b]
TPP	35	95	0,95	35	95	0,95
TCP	8,6	8,9	0,089	8,6	9,0	0,090

Opmerkingen:
a: MTR en VR worden afgeleid na publicatie van de EU-RAR (EC Regulation 793/93) van betreffende stof
b: milieurisicogrenzen konden niet worden afgeleid

Summary

In this report Maximum Permissible Concentrations (MPCs), Negligible Concentrations (NCs) and Serious Risk Concentrations for ecosystems (SRC_{eco}s) are derived for phosphate ester compounds that are possibly used as flame retardants. These Environmental Risk Limits (ERLs) are derived using data on (eco)toxicology and environmental chemistry and are the scientific basis for Environmental Quality Standards set by the Steering Committee for Substances.

The following compounds were evaluated: TCEP (tris(2-chloroethyl)phosphate), TCPP (tris(1-chloro-2-propyl)phosphate), TDCP (tris(1,3-dichloro-2-propyl)phosphate), TBP (tri-*n*-butyl phosphate), TiBP (tri-*iso*-butyl phosphate), TEP (triethyl phosphate), TBEP (tris(butoxyethyl) phosphate), TEHP (tris(2-ethylhexyl) phosphate), TPP (triphenylphosphate), and TCP (tricresylphosphate). Only toxicity studies with endpoints related to survival, growth or reproduction are taken into account. For sediment, and in most cases also for soil, no ecotoxicity data were retrieved that could be used for the derivation of MPC of SRC_{eco} values. In that case, the risk limits for soil and sediment were derived by equilibrium partitioning. Table 1 and Table 2 contain an overview of the derived ERLs. Monitoring data for the Netherlands show that for chlorinated and alkyl phosphate ester the concentration in surface water are around the NC values. It appears that only concentrations of the aryl phosphate ester TPP sometimes exceed the MPC value.

Table 1. Environmental risk limits for phosphate esters in surface water.

	$SRC_{eco, dissolved}$ [mg/L]	$SRC_{eco, total}$ [mg/L]	$MPC_{dissolved}$ [µg/L]	MPC_{total} [µg/L]	$NC_{dissolved}$ [µg/L]	NC_{total} [µg/L]	MPC_{marine} [µg/L]
TCEP	8.6	8.6	[a]	[a]	[a]	[a]	[a]
TCPP	6.5	6.5	[a]	[a]	[a]	[a]	[a]
TDCP	0.52	0.54	[a]	[a]	[a]	[a]	[a]
TBP	1.1	1.1	66	66	0.66	0.66	54
TiBP	3.4	3.4	11	11	0.11	0.11	6.6
TEP	110	110	1600	1600	16	16	68
TBEP	2.9	2.9	13	13	0.13	0.13	8.3
TEHP	[b]	[b]	[b]	[b]	[b]	[b]	[b]
TPP	0.060	0.062	0.16	0.17	0.0016	0.0017	0.95
TCP	0.031	0.031	0.032	0.033	0.00032	0.00033	0.090

Notes
a: MPC and NC to be derived when the EU-RAR (EC Regulation 793/93) is published
b: no ERLs could be derived

Table 2. Environmental risk limits for phosphate esters in soil and sediment.

	$SRC_{eco, soil}$ [mg/kg_{dw}]	MPC_{soil} [µg/kg_{dw}]	NC_{soil} [µg/kg_{dw}]	$SRC_{eco, sediment}$ [mg/kg_{dw}]	$MPC_{sediment}$ [µg/kg_{dw}]	$NC_{sediment}$ [µg/kg_{dw}]
TCEP	28	[a]	[a]	74	[a]	[a]
TCPP	9.7	[a]	[a]	230	[a]	[a]
TDCP	13	[a]	[a]	380	[a]	[a]
TBP	88	530	53	90	5400	54
TiBP	200	640	6.4	200	660	6.6
TEP	270	4100	41	460	6800	68
TBEP	180	810	8.1	180	830	8.3
TEHP	[b]	[b]	[b]	[b]	[b]	[b]
TPP	35	95	0.95	35	95	0.95
TCP	8.6	8.9	0.089	8.6	9.0	0.090

Notes
a: MPC and NC to be derived when the EU-RAR (EC Regulation 793/93) is published
b: no ERLs could be derived

1. Introduction

In this report ERLs are derived for several phosphate ester compounds, that are possibly used as flame retardant. This report is a result in the project 'International and National Environmental Quality Standards for Substances in the Netherlands'. Until 1-1-2004 this project was called 'Setting Integrated Environmental Quality Standards', abbreviated with INS. The abbreviation INS is still used as acronym for the project. The most important change with respect to content is that the *guidance* used to derive environmental risk limits is now the Technical Guidance Document (TGD), issued by the European Commission and developed in support of the risk assessment of new notified chemical substances, existing substances and biocides (European Commission, 2003).
The aim of the project INS is to derive environmental risk limits (ERLs) for substances in the environment for the compartments air, (ground)water, sediment and soil. Environmental risk limits (ERLs) serve as advisory values to set environmental quality standards (EQS) by the Steering Committee for Substances for various policy purposes. The term EQS is used to designate all legally and non-legally binding standards that are used in Dutch environmental policy and Table 3 shows the correspondence between ERLs and EQSs. The various ERLs are:

- the negligible concentration (NC) for water, soil, groundwater, sediment and air
- the maximum permissible concentration (MPC) for water, soil, groundwater, sediment and air
- the ecotoxicological serious risk concentration (SRC_{eco}) for water, soil, groundwater and sediment

Table 3. Environmental risk limits (ERLs) and the related environmental quality standards (EQS) that are set by the Dutch government in the Netherlands for the protection of ecosystems.

Description	ERL	EQS
The NC represents a value causing negligible effects to ecosystems. The NC is derived from the MPC by dividing it by 100. This factor is applied to take into account possible combined effects.	NC (for air, water, soil, groundwater and sediment)	Target value (for air, water, soil, groundwater and sediment)
The MPC is the concentration of a substance in air, water, soil or sediment that should protect all species in ecosystems from adverse effects of that substance. A cut-off value is set at the fifth percentile if a species sensitivity distribution of NOECs is used. This is the hazardous concentration for 5% of the species, the $HC5_{NOEC}$.	MPC (for air, water, soil, groundwater and sediment)	MPC (for air, water and sediment)
The SRC_{eco} is the concentration of a substance in the soil, sediment or groundwater at which functions in these compartments will be seriously affected or are threatened to be negatively affected. This is assumed to occur when 50% of the species and/or 50% of the microbial and enzymatic processes are possibly affected, the $HC50_{NOEC}$.	SRC_{eco} (for water, soil, groundwater and sediment)	Intervention value after comparison with SRC_{human} (for soil, sediment and groundwater)

The process of deriving ERLs is shown schematically in Figure 1. ERLs for soil and sediment are calculated for a standardised soil. ERLs for water are reported for dissolved and total concentrations (including a standard amount of suspended matter) and if found significantly different, differentiated to fresh water and salt water. Each of the ERLs and its corresponding EQS represents a different level of protection, with increasing numerical values in the order

NC < MPC[1] < SRC_{eco}. The EQS demand different actions when one of them is exceeded, explained elsewhere (VROM, 2001).
In the series of RIVM reports that were published in the framework of the project 'Setting Integrated Environmental Quality Standards', (now called 'International and National Environmental Quality Standards for Substances in the Netherlands'), ERLs were derived for approximately 250 substances and groups of substances. For an overview of the EQSs set by the Ministry of VROM, see VROM (2001). The Expert Centre for Substances of RIVM has recently launched a website at which all EQSs are available. The web site can be found at: http://www.stoffen-risico.nl.

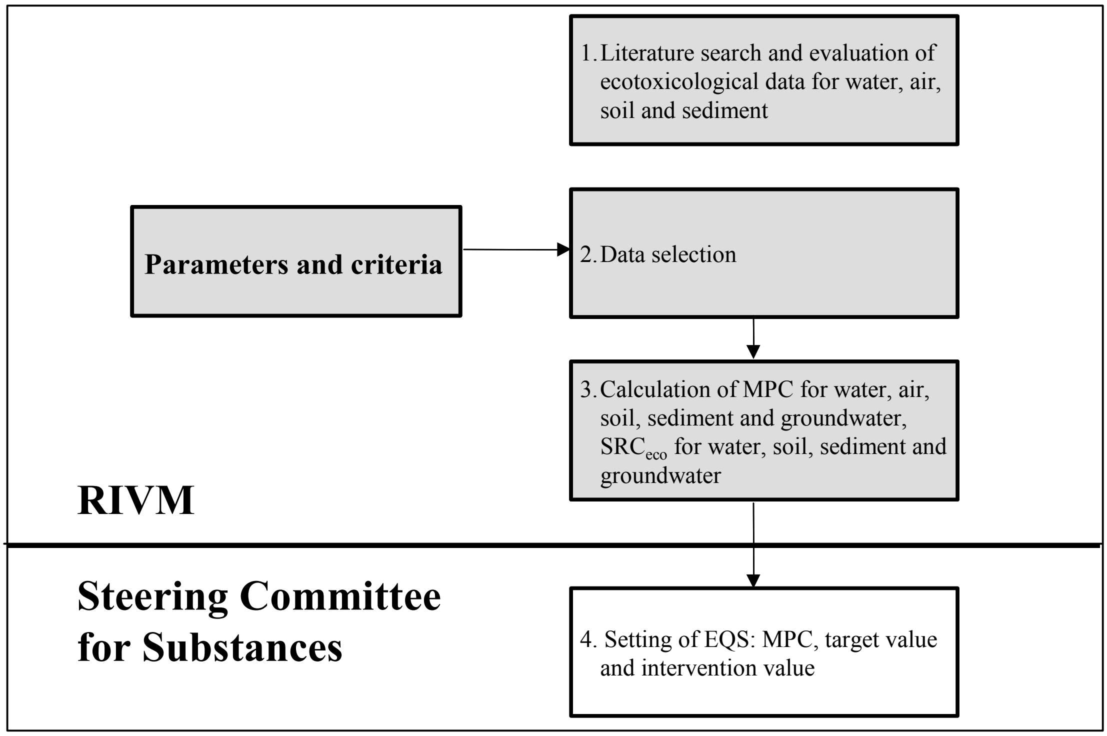

Figure 1. The process of deriving Environmental Risk Limits. Above the line the method to derive ERLs is indicated, i.e. MPC, NC and SRC_{eco}. Below the dashed line the MPC, Target Value and Intervention Value is indicated, set by the Steering Committee for Substances.

For substances, for which toxicity data have been collected and evaluated within the European Existing Substances Regulation (EU-RAR), the ERLs for water, soil and sediment will be derived from the PNEC values mentioned in these reports. In the ecotoxicology part, reference will be made to the EU-RAR documents. If these EU-RARs are already published or finalised, the PNEC will be translated into a Dutch MPC. Otherwise, only data will be presented without reporting an MPC in the summary.
The phosphate ester group can be divided in four major groups, of which the last group, the brominated phosphates, will not be discussed within this report, as they are not longer produced:

- halogenated phosphates (TCEP, TCPP and TDCP),
- alkyl phosphates (TBP, TEP, TBEP and TEHP),
- aryl phosphates (TPP and TCP),
- brominated phosphates (TBPP and BBPP).

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[1] A complicating factor is that the term MPC is used both as an ERL and as an EQS. For historical reasons, however, the same abbreviation is used.

Various organisations are evaluating the toxicity and fate of flame retardants, such as RIVM, the Danish EPA and the European Union under the council's regulations for new and existing substances. Not much is known on the toxicity of phosphate ester flame retardants, although high production volumes, expected low biodegradation rates and high octanol-water partition coefficients indicate that some of these substances are potentially hazardous. Because of the high octanol-water partition coefficients the effects on secondary poisoning are considered, in addition to direct effects on aquatic and terrestrial organisms. This report focuses on a number of phosphate ester flame retardants (PEFRs) that were described earlier in reports of the WHO 'International Programme on Chemical Safety' (IPCS) or of the German program on 'existing chemicals of environmental relevance' (BUA). Many more PEFRs exist that could be studied as well, but data availability is low. It is expected that more information on the group of PEFRs will become available in the next few years through in-depth studies from the EU, the Danish EPA and the Environment Agency UK.

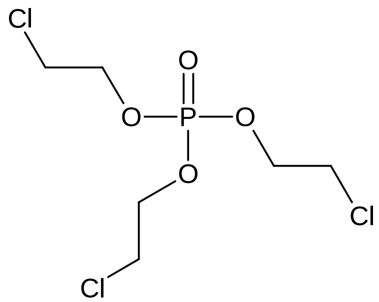
2. Substance properties and use

2.1 Physicochemical properties

In this section an overview of the physicochemical properties is given for the organophosphorus compounds that are considered in this report.

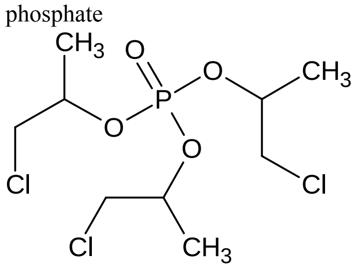
2.1.1 Halogenated phosphates

Table 4. General information and physicochemical properties of tris(2-chloroethyl)phosphate (TCEP)

Properties	Value(s)	Reference
IUPAC Name	Phosphoric acid tris(2-chloroethyl) ester	
Structure		
CAS number	115-96-8	
EINECS number	204-118-5	
Empirical formula	C6 H12 Cl3 O4 P	
Smiles code	O=P(OCCCl)(OCCCl)OCCCl	
Molar Mass (g/mol)	285.49	
n-Octanol/water partition coefficient (log K_{ow})	0.54	Brodsky et al. (1997)
	1.43 (shake-flask)	Sasaki et al. (1981)
	1.44 (exp.)	CITI (1992) in U.S. EPA (2003)
	1.48	Muir (1984)
	1.7	IPCS (1998)
	1.7	Yoshioka et al. (1986a)
	1.78 (exp., shake flask method)	Hazelton (1994b) in European Commission (2004c)
	0.47 (fragment constant estimate)	BioByte (2004)
	1.63 (fragment constant estimate)	U.S. EPA (2003)
Soil/sediment water sorption coefficient (log K_{oc})	2.04	estimated with QSAR for phosphates (Sabljic et al., 1995) and log K_{ow} of 1.78
	2.48 (molecular connectivity estimate)	U.S. EPA (2003)
Vapour pressure (Pa)	6.67	Brodsky et al. (1997)
	2.7 at 90 ºC; 0.25 at 70 ºC; 0.082 at 60 ºC; 0.017 at 46 ºC	Bayer (1980) in GDCh (1987)
	3.7 E-04 at 20 ºC (extrapolated, 7.9 E-04 at 25 ºC)	
	8.22 at 25 ºC (extrapolated; isoteniscope)	Dobry & Keller (1957)
	43 at 136.9 °C	Boerdijk (2000) in European
	1.14E-03 at 20 °C (extrapolated)	Commission (2004c)
	67 at 145 25 ºC	Muir (1984)
	0.0521 at 25 ºC (modified Grain method estimate)	U.S. EPA (2003)
Henry's law constant (Pa. m^3. mol^{-1})	8.07 E-03 at 25 ºC	IPCS (1998)
	4.16E-05	European Commission (2004c)
	1.5E-05 at 20 ºC	GDCh (1987)
	2.58E-03 at 25 ºC (bond method estimate)	U.S. EPA (2003)

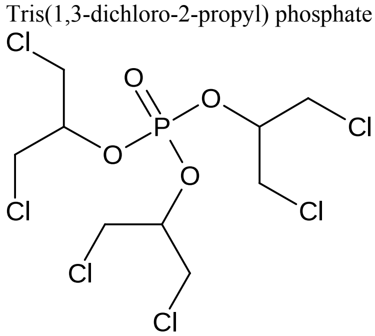
Properties	Value(s)	Reference
Water solubility (mg/L)	5000 at 20 ºC	Hoechst AG (1986) in GDCh (1987)
	6000	Brodsky et al. (1997)
	7000 at 20 ºC	Eldefrawi et al. (1977)
	7000	Muir (1984)
	7820 at 20 ºC	Hazelton (1994a) in European Commission (2004c)
	7900 at 20 ºC (supersaturation over 20 ºC, cooling, filtration)	Yoshioka et al. (1986a)
	8000 at 20 ºC	IPCS (1998)
	7409 at 25 ºC (estimate from log K_{ow} (1.44); liquid assumed)	U.S. EPA (2003)
	5597 (fragment method estimate)	U.S. EPA (2003)

Table 5. General information and physicochemical properties of tris(1-chloro-2-propyl) phosphate (TCPP)

Properties	Value(s)	Reference
EINECS name	Tris(2-chloro-1-methylethyl) phosphate	
Structure		
CAS number	13674-84-5	
EINECS number	237-158-7	
Empirical formula	C9 H18 Cl3 O4 P	
Smiles code	O=P(OC(CCl)C)(OC(CCl)C)OC(CCl)C	
Molar Mass (g/mol)	327.57	
n-Octanol/water partition coefficient (log K_{ow})	2.59 (exp.)	CITI (1992) in U.S. EPA (2003)
	2.59	IPCS (1998)
	2.68 (exp., HPLC method)	Cuthbert and Mullee (2002a) in European Commission (2004b)
	3.33 (exp.)	Robson (1994) in European Commission (2004b)
	1.40 (fragment constant estimate)	BioByte (2004)
	2.89 (fragment constant estimate)	U.S. EPA (2003)
Soil/sediment water sorption coefficient (log K_{oc})	2.44	estimated with QSAR for phosphates (Sabljic et al., 1995) and log K_{ow} of 2.59
	2.76 (exp., HPLC method)	Cuthbert and Mullee (2002b) in European Commission (2004b)
	3.11 (molecular connectivity estimate)	U.S. EPA (2003)
Vapour pressure (Pa)	1.4E-03 at 25 ºC (exp., balance method)	Tremain (2002a) in European Commission (2004b)
	3.3	Krawetz (2000) in European Commission (2004b)
	0.00752 at 25 ºC (modified Grain method estimate)	U.S. EPA (2003)
Henry's law constant (Pa. m^3. mol^{-1})	4.25E-04 at 25 ºC (by calculation from VP and WS results)	European Commission (2004b)
	6.04E-03 at 25 ºC (bond method estimate)	U.S. EPA (2003)
Water solubility (mg/L)	1080 (flask method)	Cuthbert and Mullee (2002a) in European Commission (2004b)
	1100	Muir (1984)
	1200	CITI (1992) in U.S. EPA (2003)
	1600 at 20 ºC	IPCS (1998)

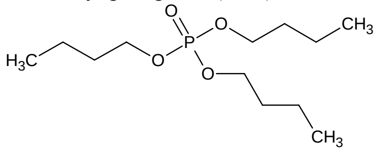
Properties	Value(s)	Reference
	1600	Robson (1994) in European Commission (2004b)
	493.5 at 25 ºC (estimate from log K_{ow} (2.59); liquid assumed)	U.S. EPA (2003)
	740.2 (fragment method estimate)	U.S. EPA (2003)

Table 6. General information and physicochemical properties of tris(1,3-dichloro-2-propyl) phosphate (TDCP)

Properties	Value(s)	Reference
IUPAC Name	Tris(1,3-dichloro-2-propyl) phosphate	
Structure		
CAS number	13674-87-8	
EINECS number	237-159-2	
Empirical formula	C9 H15 Cl6 O4 P	
Smiles code	O=P(OC(CCl)CCl)(OC(CCl)CCl)OC(CCl)CCl	
Molar Mass (g/mol)	430.91	
n-Octanol/water partition coefficient (log K_{ow})	3.65 (exp.)	CITI (1992) in U.S. EPA (2003)
	3.69 (exp., HPLC method)	Cuthbert and Mullee (2002d) in European Commission (2004a)
	3.74	Muir (1984)
	3.76 (shake-flask)	Sasaki et al. (1981)
	3.8	IPCS (1998)
	1.59 (fragment constant estimate)	BioByte (2004)
	3.65 (fragment constant estimate)	U.S. EPA (2003)
Soil/sediment water sorption coefficient (log K_{oc})	2.96	estimated with QSAR for phosphates (Sabljic et al., 1995) and log K_{ow} of 3.65
	4.09 (exp., HPLC method)	Cuthbert and Mullee (2002c) in European Commission (2004a)
	3.96 (molecular connectivity estimate)	U.S. EPA (2003)
Vapour pressure (Pa)	5.6E-06 at 25 ºC (exp., balance method)	Tremain (2002b)
	1.3 at 30 ºC	IPCS (1998)
	3.97E-05 at 25 ºC (modified Grain method estimate)	U.S. EPA (2003)
Henry's law constant (Pa. m^3. mol^{-1})	1.33E-04 (by calculation from VP and WS results)	European Commission (2004a)
	2.65E-04 at 25 ºC (bond method estimate)	U.S. EPA (2003)
Water solubility (mg/L)	100 at 20 ºC	Eldefrawi et al. (1977)
	100 at 30 ºC	IPCS (1998)
	100	Muir (1984)
	7.0 at 24±2 ºC (nephelometry)	Hollifield (1979)
	19.2	Metcalf (1976) in Hollifield (1979)
	7 at 24 ºC	Yalkowsky and Dannenfelser (1992) in U.S. EPA (2003)
	18.1 (flask method)	Cuthbert and Mullee (2002d) in European Commission (2004a)
	29.53 at 25 ºC (estimate from log K_{ow} (3.65); liquid assumed)	U.S. EPA (2003)
	30.17 (fragment method estimate)	U.S. EPA (2003)

2.1.2 Alkyl phosphates

Table 7. General information and physicochemical properties of tributylphosphates

Properties	Value(s)	Reference
IUPAC Name	tri-*n*-butyl phosphate (TBP)	
Structure		
CAS number	126-73-8	
EINECS number	204-800-2	
Empirical formula	C12 H27 O4 P	
Smiles code	O=P(OCCCC)(OCCCC)OCCCC	
Molar Mass (g/mol)	266.32	
n-Octanol/water partition coefficient (log K_{ow})	2.5 (exp.)	MedChem (1989) in GDCh (1995)
	3.4	Yoshioka et al. (1986a)
	3.99 (shake-flask)	Sasaki et al. (1981)
	4.00 (shake-flask)	Saeger et al. (1979)
	4.00	Hansch et al. (1995) in U.S. EPA (2003)
	4.01	Kenmotsu (1980) in IPCS (1991a)
	4.00/4.01	Muir (1984)
	3.46 (fragment constant estimate)	BioByte (2004)
	3.82 (fragment constant estimate)	U.S. EPA (2003)
Soil/sediment water sorption coefficient (log K_{oc})	3.13	estimated with QSAR for phosphates (Sabljic et al., 1995) and log K_{ow} of 4.00
	3.28 (molecular connectivity estimate)	U.S. EPA (2003)
Vapour pressure (Pa)	0.15 at 25 ºC (exp.)	U.S. EPA (2003)
	100 at 114 ºC; 2000 at 160-162 ºC; 0.016 at 25 ºC (extrapolated)	Riddick et al. (1985)
	100 at 97 ºC; 1000 at 144 ºC	Bayer (1987c) in GDCh (1995)
	0.8 at 20 ºC (probably extrapolated; 1.2 at 25 ºC)	
	>66700 at 200 ºC; 973 at 150 ºC	Laham et al. (1984)
	0.904 at 25 ºC (extrapolated; gas saturation method); 133 at 100 ºC	Parker (1980)
	9 at 25 ºC	IPCS (1991a)
	16900 at 177 ºC	Muir (1984)
	0.465 at 25 ºC (modified Grain method estimate)	U.S. EPA (2003)
Henry's law constant (Pa. m^3. mol^{-1})	0.0152 at 25 ºC (exp., calc. from exp. VP and WS)	U.S. EPA (2003)
	0.323 at 25 ºC (bond method estimate)	U.S. EPA (2003)
Water solubility (mg/L)	280 at room temperature	Saeger et al. (1979)
	280	Muir (1984)
	1075 at 3.4 ºC; 1012 at 4.0 ºC; 957 at 5.0 ºC; 640 at 13.0 ºC; 422 at 25.0 ºC; 285 at 50.0 ºC (shake-flask)	Higgins et al. (1959)
	250 at 20 ºC (supersaturation over 20 ºC, cooling, filtration)	Yoshioka et al. (1986a)
	400 at 20 ºC	Bayer (1987c) in GDCh (1995)
	1000 at 25 ºC	Laham et al. (1984)
	27.68 at 25 ºC (estimate from log K_{ow} (4.00); liquid assumed)	U.S. EPA (2003)
	101.0 (fragment method estimate)	U.S. EPA (2003)
Common name	Tri-isobutyl phosphate (TiBP)	
IUPAC Name	Phosphoric acid, tris(2-methylpropyl) ester	

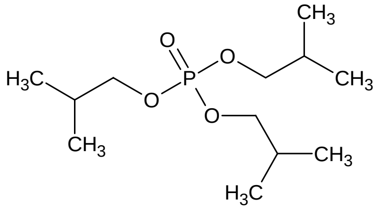
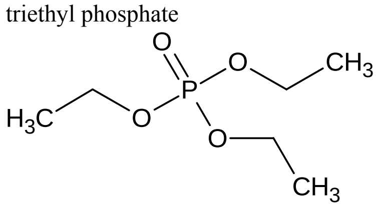
Properties	Value(s)	Reference
Structure		
CAS number	126-71-6	
EINECS number	2064-798-3	
Empirical formula	C12 H27 O4 P	
Smiles code	O=P(OCC(C)C)(OCC(C)C)OCC(C)C	
Molar Mass (g/mol)	266.32	
n-Octanol/water partition coefficient (log K_{ow})	3.72 (exp.)	BASF AG (1990) (IUCLID)
	3.07 (fragment constant estimate)	BioByte (2004)
	3.60 (fragment constant estimate)	U.S. EPA (2003)
Soil/sediment water sorption coefficient (log K_{oc})	2.99	estimated with QSAR for phosphates (Sabljic et al., 1995) and log K_{ow} of 3.72
	3.05 (molecular connectivity estimate)	U.S. EPA (2003)
Vapour pressure (Pa)	100 at 91.74 ºC; 200 at 102.76 ºC; 500 at 118.94 ºC; 1000 at 132.59 ºC; 5000 at 169.85 ºC; 10000 at 118.93 ºC; 50000 at 243.2 ºC	BASF AG (1989) (IUCLID)
	0.95 at 25 ºC (extrapolated)	
	1.71 at 25 ºC (mean of modified Grain and Antoine method estimate)	U.S. EPA (2003)
Henry's law constant (Pa. m^3. mol^{-1})	0.323 at 25 ºC (bond method estimate)	U.S. EPA (2003)
Water solubility (mg/L)	265 at 25 ºC	BASF AG (1990) (IUCLID)
	51.4 at 25 ºC (estimate from log K_{ow} (3.72); liquid assumed)	U.S. EPA (2003)
	475.6 (fragment method estimate)	U.S. EPA (2003)

Table 8. General information and physicochemical properties of triethyl phosphate (TEP)

Properties	Value(s)	Reference
IUPAC Name	triethyl phosphate	
Structure		
CAS number	78-40-0	
EINECS number	201-114-5	
Empirical formula	C6 H15 O4 P	
Smiles code	O=P(OCC)(OCC)OCC	
Molar Mass	182.16	
n-Octanol/water partition coefficient (log K_{ow})	1.11 (exp.)	Radding (1977) in GDCh (1989)
	0.80 (exp.)	Hansch et al. (1995) in U.S. EPA (2003)
	0.28 (fragment constant estimate)	BioByte (2004)
	0.87 (fragment constant estimate)	U.S. EPA (2003)
Soil/sediment water sorption coefficient (log K_{oc})	1.56	estimated with QSAR for phosphates (Sabljic et al., 1995) and log K_{ow} of 0.80
	1.68 (molecular connectivity estimate)	U.S. EPA (2003)
Vapour pressure (Pa)	133 at 39.6 ºC	Sandmeyer and Kirwin (1981) in GDCh (1989)
	133 at 39.6 ºC	Muir (1984)
	17 at 99.2 ºC	Deutsche Chemische

Properties	Value(s)	Reference
		Gesellschaft (1928) in GDCh (1989)
	3300 at 103 ºC; 6700 at 123 ºC; 14900 at 146 ºC; 25100 at 161 ºC; 59300 at 190 ºC; 101300 at 215 ºC;	Deutsche Chemische Gesellschaft (1918) in GDCh (1989)
	60.6 at 25 ºC (extrapolated)	
	52.4 at 25 ºC	U.S. EPA (2003)
	22.0 at 25 ºC (mean of modified Grain and Antoine method estimate)	U.S. EPA (2003)
Henry's law constant (Pa. m^3. mol^{-1})	0.0037 at 25 ºC (20 ºC) (gas-stripping)	Wolfenden and Williams (1983)
	0.0591 at 25 ºC (bond method estimate)	U.S. EPA (2003)
Water solubility (mg/L)	500000 at 25 ºC	Yalkowsky and Dannenfelser (1992) in U.S. EPA (2003)
	41070 at 25 ºC (estimate from log K_{ow} (0.80); liquid assumed)	U.S. EPA (2003)
	115250 (fragment method estimate)	U.S. EPA (2003)

Table 9. General information and physicochemical properties of tris(2-butoxyethyl) phosphate (TBEP)

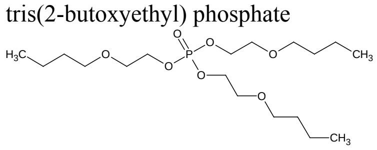
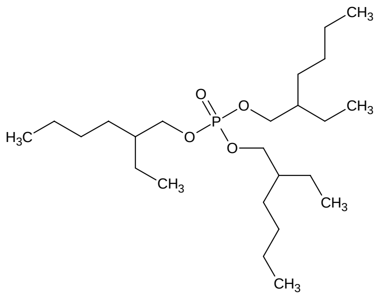
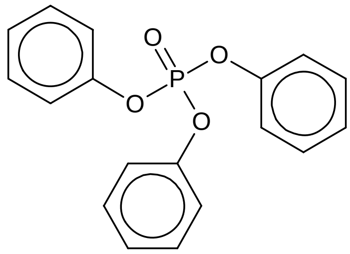
Properties	Value(s)	Reference
IUPAC Name	tris(2-butoxyethyl) phosphate 	
CAS number	78-51-3	
EINECS number	201-122-9	
Empirical formula	C18 H39 O7 P	
Smiles code	O=P(OCCOCCCC)(OCCOCCCC)OCCOCCCC	
Molar Mass	398.48	
n-Octanol/water partition coefficient (log K_{ow})	3.75 (exp.)	CITI (1992) in U.S. EPA (2003)
	3.65 (exp.)	Muir (1984), IPCS (2000)
	4.02 (fragment constant estimate)	BioByte (2004)
	3.00 (fragment constant estimate)	U.S. EPA (2003)
Soil/sediment water sorption coefficient (log K_{oc})	3.01	estimated with QSAR for phosphates (Sabljic et al., 1995) and log K_{ow} of 3.75
	5.67 (molecular connectivity estimate)	U.S. EPA (2003)
Vapour pressure (Pa)	4 at 150 ºC; 1.33 at 20 ºC	Muir (1984)
	4 at 150 ºC; 0.000037 at 25 ºC	IPCS (2000)
	2.8E-05 at 25 ºC (GC-method)	Hinckley (1990)
	2.41E-05 at 25 ºC (extrapolated; effusion method)	Small et al. (1948)
	0.000164 at 25 ºC (modified Grain method estimate)	U.S. EPA (2003)
Henry's law constant (Pa. m^3. mol^{-1})	1.22E-06 at 25 ºC (bond method estimate)	U.S. EPA (2003)
Water solubility (mg/L)	~1100	Muir (1984)
	1100 at 25 ºC	Beilstein Information Systems () in U.S. EPA (2003)
	1100-1300 at 20 ºC	IPCS (2000)
	27.68 at 25 ºC (estimate from log K_{ow} (3.75); liquid assumed)	U.S. EPA (2003)
	604.2 (fragment method estimate)	U.S. EPA (2003)

Table 10. General information and physicochemical properties of tris(2-ethylhexyl) phosphate (TEHP)

Properties	Value(s)	Reference
IUPAC Name	Phosphoric acid, tris(2-ethylhexyl) ester 	
CAS number	78-42-2	
EINECS number	201-116-6	
Empirical formula	C24 H54 O4 P	
Smiles code	CCCCC(CC)COP(=O)(OCC(CC)CCCC)OCC(CC)CCCC	
Molar Mass	434.65	
n-Octanol/water partition coefficient (log K_{ow})	4.1	Ishikawa et al. (1985) in GDCh (1997)
	4.23 (shake-flask)	Saeger et al. (1979)
	4.23	Muir (1984)
	5.04 (exp.)	CITI (1992) in GDCh (1997)
	9.42 (fragment constant estimate)	BioByte (2004)
	9.49 (fragment constant estimate)	U.S. EPA (2003)
Soil/sediment water sorption coefficient (log K_{oc})	5.79	estimated with QSAR for phosphates (Sabljic et al., 1995) and log K_{ow} of 9.42
	6.36 (molecular connectivity estimate)	U.S. EPA (2003)
Vapour pressure (Pa)	1.1E-05 at 25 ºC (exp.)	U.S. EPA (2003)
	1.1E-05 at 25 ºC (GC-method)	Hinckley (1990)
	31 at 150 ºC	Sandmeyer and Kirwin (1981) in Muir (1984)
	53 at 160 ºC; 133 at 180 ºC; 330 at 200 ºC; 0.00294 at 25 ºC (extrapolated)	Bayer AG (1993) in GDCh (1997)
	3.03E-05 at 25 ºC (extrapolated; effusion method)	Small et al. (1948)
	8.09E-05 at 25 ºC (modified Grain method estimate)	U.S. EPA (2003)
Henry's law constant (Pa. m^3. mol^{-1})	0.00796 at 25 ºC (exp., calc. from exp. VP and WS)	U.S. EPA (2003)
	9.69 at 25 ºC (bond method estimate)	U.S. EPA (2003)
Water solubility (mg/L)	1000 (true solubility reported probably to be lower)	Saeger et al. (1979)
	~1000	Muir (1984)
	<100 at 20 ºC	IPCS (2000)
	2	CITI (1992) in GDCh (1997)
	0.600 at 24±2 ºC (nephelometry)	Hollifield (1979)
	0.60 at 24 ºC	Yalkowsky and Dannenfelser (1992) in U.S. EPA (2003)
	<0.5 at 20 ºC	Bayer AG (1993) in GDCh (1997)
	7.161E-05 at 25 ºC (estimate from log K_{ow} (9.49); liquid assumed)	U.S. EPA (2003)
	0.000279 (fragment method estimate)	U.S. EPA (2003)

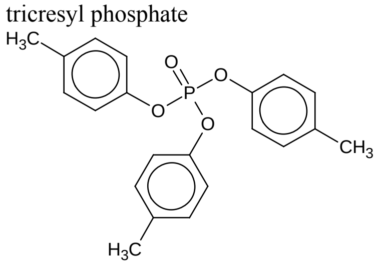
2.1.3 Aryl phosphates

Table 11. General information and physicochemical properties of tri phenyl phosphate (TPP)

Properties	Value(s)	Reference
IUPAC Name	Triphenyl phosphate	
Structure		
CAS number	115-86-6	
EINECS number	204-112-2	
Empirical formula	C18 H12 O4 P	
Smiles code	O=P(Oc(cccc1)c1)(Oc(cccc2)c2)Oc(cccc3)c3	
Molar Mass	326.3	
n-Octanol/water partition coefficient (log K_{ow})	4.59 (exp.)	Hansch et al. (1995) in U.S. EPA (2003)
	4.61	Kenmotsu (1980) in IPCS (1991b)
	4.63 (shake-flask)	Saeger et al. (1979)
	4.61/4.63	Muir (1984)
	4.76 (shake-flask)	Sasaki et al. (1981)
	3.15 (TLC estimate)	Renberg et al. (1980)
	3.40 (HPLC estimate)	Lo & Hsieh (2000)
	3.9	Bengtsson et al. (1986)
	4.46 (fragment constant estimate)	BioByte (2004)
	4.70 (fragment constant estimate)	U.S. EPA (2003)
Soil/sediment water sorption coefficient (log K_{oc})	3.42	estimated with QSAR for phosphates (Sabljic et al., 1995) and log K_{ow} of 4.59
	4.00 at 25 ºC (shake-flask; filtration)	Huckins et al. (1991)
	3.93 at 25 ºC (shake-flask; centrifugation)	
	3.72 (molecular connectivity estimate)	U.S. EPA (2003)
Vapour pressure (Pa)	4.1E-03 at 25 ºC; 2.4E-03 at 20 ºC (extrapolated subcooled liquid)	Environment Agency (2003b)
	2.4E-03 at 25 ºC; 1.2E-03 at 20 ºC (calculated to solid)	
	8.52E-04 at 25 ºC (extrapolated; subcooled liquid; isoteniscope)	Dobry & Keller (1957)
	20 at 150 ºC; 253 at 200 ºC	IPCS (1991b) (Modern Plastics Encyclopedia)
	133 at 193.5 ºC	Sutton et al. (1960) in IPCS (1991b)
	0.0707 at 25 ºC	Midwest Research Institute (1991) in Huckins et al. (1991)
	173 at 200 ºC; 2430 at 250 ºC	Midwest Research Institute (1991) in Muir (1984)
	0.0881 (~0.22 in presented figure) at 100 ºC (effusion method)	Small et al. (1948)
	6.29E-05 at 25 ºC (modified Grain method estimate)	U.S. EPA (2003)
Henry's law constant (Pa. m^3. mol^{-1})	0.335 at 25 ºC (exp., calc. from exp. VP and WS, probably corrected for bond energy)	U.S. EPA (2003)
	0.00403 at 25 ºC (bond method estimate)	U.S. EPA (2003)
Water solubility (mg/L)	1.9 at room temperature	Saeger et al. (1979)

Properties	Value(s)	Reference
	TPP in commercial TCP product: 2.1±0.1 at 25 ºC (generator-column OECD 105)	Ofstad and Sletten (1985)
	0.730 at 24±2 ºC (nephelometry)	Hollifield (1979)
	20	Fordyce & Meyer (1940) in Hollifield (1979)
	3.476 at 25 ºC (estimate from log K_{ow} (4.59); solid assumed, melting point 50.5 ºC)	U.S. EPA (2003)
	4.674 (fragment method estimate)	U.S. EPA (2003)

Table 12. General information and physicochemical properties of tricresyl phosphate (o,m,p-TCP)

Properties	Value(s)	Reference
IUPAC Name	tricresyl phosphate	
Structure	 tri-*p*-cresylphosphate is shown	
CAS number	1330-78-5 (ortho: 78-30-8; meta: 563-04-2; para: 78-32-0)	
EINECS number	215-548-8	
Empirical formula	C21 H21 O4 P	
Smiles code (para)	O=P(Oc1ccc(C)cc1)(Oc2ccc(C)cc2)Oc3ccc(C)cc3	
Molar Mass	368.37	
n-Octanol/water partition coefficient (log K_{ow})	5.11 (shake-flask)	Saeger et al. (1979)
	5.12	Kenmotsu (1980) in IPCS (1990)
	5.1-5.3	Bengtsson et al. (1986)
	5.9	Boethling and Cooper (1985)
	5.93	Environment Agency (2003a)
	3.42 (HPLC estimate)	Veith et al. (1979)
	4.51 (mean of 4.30 and 4.65) (TLC estimate)	Renberg et al. (1980)
	5.95 (fragment constant estimate, equal for all isomers)	BioByte (2004)
	6.34 (fragment constant estimate, equal for all isomers)	U.S. EPA (2003)
Soil/sediment water sorption coefficient (log K_{oc})	3.67	estimated with QSAR for phosphates (Sabljic et al., 1995) and log K_{ow} of 5.11
	1,618±993 (38-2800, estimated from field data)	Environment Agency (2003a)
	o- and *m*-isomers: 4.37 *p*-isomer: 4.35 (molecular connectivity estimate)	U.S. EPA (2003)
Vapour pressure (Pa)	6.6E-05 at 25 ºC; 3.5E-05 at 20 ºC (extrapolated) *o*-isomer: 5.5E-05 at 20 ºC *m*-isomer: 9.9E-05 at 20 ºC *p*-isomer: 4.4E-05 at 20 ºC (extrapolated from boiling point)	Environment Agency (2003a)
	0.001 at 46 ºC; 0.44 at 150 ºC	Environment Agency (2003a)
	0.00019 at 30 ºC	Boethling and Cooper (1985) in Environment Agency (2003a)
	Mixed isomers: <2.7 at 150 ºC; 39 at 200 ºC	Muir (1984)
	m-isomer: 1.84E-06 at 25 ºC (extrapolated; subcooled liquid;	Dobry & Keller (1957)

Properties	Value(s)	Reference
	isoteniscope)	
	o-isomer: 2.26E-04 at 25 ºC (extrapolated; subcooled liquid; isoteniscope)	
	Mixture of isomers: 0.0133 at 20 ºC	Lefaux (1972) in IPCS (1990)
	Technical product: 4.4 at 150 ºC	Great Lakes Chemical Corporation (2003)
	o-isomer: 1333 at 265 ºC	Hine et al. (1981) in IPCS (1990)
	Technical product: 8.76E-06 at 25 ºC	Small et al. (1948)
	m-isomer: 3.74E-06 at 25 ºC (extrapolated; effusion method)	
	m-isomer: 3.94E-06 and 1.21E-05 at 25 ºC (extrapolated; quoted)	
	p-isomer: 2.94E-06 at 25 ºC (extrapolated; quoted)	
	o-isomer: 0.00195 at 25 ºC	U.S. EPA (2003)
	o-isomer: 0.00633	U.S. EPA (2003)
	m-isomer: 1.45E-05	
	p-isomer: 4.65E-6 at 25 ºC (modified Grain method estimate)	
Henry's law constant (Pa. m^3. mol^{-1})	*m*-isomer: 8.38 at 25 ºC (gas sparging)	Muir et al. (1983)
	0.00542 at 25 ºC (bond method estimate)	U.S. EPA (2003)
Water solubility (mg/L)	Mixture: 0.36 at room temperature	Saeger et al. (1979)
	Sum of TCP isomers in commercial TCP product: 0.34±0.04 at 25 ºC (generator-column OECD 105)	Ofstad and Sletten (1985)
	3.4 at 20 ºC	Environment Agency (2003a)
	p-isomer: 0.3 at 25 ºC (extrapolated)	U.S. EPA (2003)
	p-isomer: 0.074 at 24±2 ºC (nephelometry)	Hollifield (1979)
	0.260	Metcalf (1976) in Hollifield (1979)
	o-isomer: 0.246	U.S. EPA (2003)
	m-isomer: 0.243	
	p-isomer: 0.0808 at 25 ºC (estimate from log K_{ow} (5.95); used melting points: 11, 25.5 and 77.5 ºC)	
	0.140 (fragment method estimate)	U.S. EPA (2003)

2.2 Flame retardant properties[2]

Phosphate esters, which usually are used as flame retardant, act in the solid phase of burning materials. When heated, the phosphorus reacts to give a polymeric form of phosphoric acid (PO_4). This acid causes the material to char, inhibiting the pyrolysis process.
Phosphorus based flame retardants are complex P-containing organic molecules offering specific performance properties. Certain products contain both phosphorus and chlorine or bromine. Halogenated flame-retardants mainly act by effectively removing the H· and OH· radicals in the gas phase. This considerably slows or prevents the burning process. When exposed to high temperatures, the flame retardant molecule releases bromine (Br) or chlorine (Cl), as free radicals (Br· or Cl·) which react with hydrocarbon molecules (flammable gases) to give HBr or HCl. These then react with the high-energy H· and OH· radicals to give water and the much lower energy Br· or Cl· radicals, which are then available to begin a new cycle of H· and OH· radical removal. The effectiveness of halogenated flame retardants thus depends on the quantity of the halogen atoms they contain and also, very strongly, on the

[2] This section is based on information taken from the European Flame Retardants Assocation (http://www.cefic-efra.org) and IPCS (1997).

control of the halogen release. Because chlorine is released over a wider range of temperatures than bromine, it is then present in the flame zone at lower concentrations, and so is less effective. Bromine is released over a narrow temperature range, thus resulting in optimal concentrations in the flame zone. Several of the flame-retardants studied in this report thus combine flame retarding mechanisms of phosphorus and halogens. The flame-retardant effects are considered to be additive. For more detail, see IPCS (1997).

2.3 Use, production and discharge

Organophosphorus compounds can be used as flame retardants. Flame retardants can be divided in three main groups of chemicals (IPCS, 1997):
Inorganic flame retardants, representing about 50% by volume of the worldwide flame retardant production. The most important are aluminium trihydroxide, magnesium hydroxide, ammonium polyphosphate and red phosphorus. Some of these chemicals are also used as synergists for other flame retardant, of which antimony trioxide is the most important.
Halogenated products, representing about 25% by volume of the worldwide production. The presence of chlorine and bromine atoms is the main feature of these compounds.
Organophosphorus products, representing about 20% by volume of the worldwide production. These compounds are primarily phosphate esters. An important part of these products contain besides phosphorus also chlorine and/or bromine.

2.3.1 Halogenated phosphates

2.3.1.1 Tris(2-chloroethyl)phosphate (TCEP)

Production and use
According to data from IUCLID for 1991/1992, the European market amounted up to 10,500 tonnes per year (European Commission, 2004c). IPCS (1998) states that global consumption of TCEP peaked at over 9000 tonnes in 1989 but had declined to below 4000 tonnes by 1997. This number is markedly lower today being less than 1000 tonnes. Since the 1980s, TCEP production and use have been decreasing because of substitution by other flame retardants in its historic use in rigid and flexible polyurethane foams and systems (IPCS, 1998).
TCEP is used primarily as a flame retardant for unsaturated polyester resins and no longer much used in polyurethanes. The main industrial branches to use TCEP as a flame-retardant plasticiser are the textile and the building industry (roof insulation). Other utilisation in small volumes of TCEP is represented by flame resistant paints and varnishes, e.g. for polyvinyl acetate or acetyl cellulose.

Release in the environment
In the draft EU-RAR (European Commission, 2004c) an extensive description of the emission scenarios is made. Discharge of tris(2-chloroethyl) phosphate into the environment occurs predominantly via the atmosphere. TCEP is not readily biodegradable (European Commission, 2000). It must be assumed that partial release from polyurethane and other foams to the atmosphere occurs, although volatilisation can be prevented if foams are covered. In the atmosphere, it is quickly degraded abiotically by reaction with photochemically formed hydroxyl radicals. This photochemical degradation in the atmosphere is representing the most important mode of degradation of tris(2-chloroethyl) phosphate. There are further possibilities for elimination in the aquatic environment, in which tris(2-chloroethyl) phosphate enters via the wastewater, as a result of manufacturing processes. It is

degraded extremely slowly by hydrolysis, and there are indications that it may also undergo biotic degradation.

2.3.1.2 Tris(2-chloro-1-methylethyl) phosphate (TCPP)

Production and use

The product TCPP is actually a reaction mixture containing four isomers, of which the individual isomers are not separated or produced as such. The CAS number 13674-84-5 is used for the structure shown in Table 5 and also for the mixture of isomers as commercially produced. The three 1-chloro-2-propyl (2-chloro-1-methylethyl) groups can each be replaced by 2-chloro-1-propyl (i.e. an unbranched hydrocarbon chain). With these two groups, three isomers of the main component are possible, although tris(2-chloro-1-propyl)phosphate is only present in trace levels. Typical percentages of the four isomers in the reaction mixture are: tris(2-chloro-1-methylethyl) phosphate (CAS no. 13674-84-5) about 50 to 85%, bis(2-chloro-1-methylethyl)-2-chloro-1-propyl phosphate (CAS no. 76025-08-6) about 15-40%, bis(2-chloro-1-propyl)-2-chloro-1-methylethyl phosphate (CAS no. 76649-15-5) less than 15% and tris(2-chloro-1-propyl) phosphate (CAS no. 6145-73-9) less than 1% (European Commission, 2004b).

TCPP is produced by the reaction of phosphorus oxychloride with propylene oxide, followed by purification (IPCS, 1998). Both batch and continuous processes can be used in the manufacture of TCPP (UNEP, 1999). The whole process, from reaction to packaging is carried out in closed systems (European Commission, 2004b).

Total EU production of TCPP in the years 1998 to 2000 was 30,000 to 40,000 tonnes, produced at three sites in Germany and one in the UK. Discussions with the Phosphate Ester Flame Retardant Council (PEFRC) indicate that any future increase due to substitution for TCEP is unlikely, because replacement for all the applications for which replacement is possible has been completed (European Commission, 2004b).

TCPP is physically combined with the treated material instead of chemically bonded (additive flame retardant). The amount of flame retardant used depends on the application. The consumption of TCPP in the EU was 37,745 tonnes in 2000. Over 98% of this amount is used as a flame retardant in the production of polyurethane (PUR) for use in construction and furniture. TCPP can be added to polyols, which form PUR in reaction with di-isocyanates (around 60%), or added directly at the point of foaming. Over 80% of PUR is used in rigid PUR foam for construction applications. The remaining PUR (more than 17%) is used in flexible foam for upholstery and bedding, but not for automotive applications (European Commission, 2004b).

Release in the environment

In the draft EU-RAR (2004b) an extensive description of the emission scenarios is made. TCPP is stable in water at pH 4, 7 and 9 at 25 ºC, with a half-life greater than or equal to one year. Based on a prolonged closed bottle test and a SCAS test, TCPP is considered to be inherently biodegradable in the aquatic compartment. No soil degradation data are available (European Commission, 2004b).

2.3.1.3 Tris(1,3-dichloro-2-propyl) phosphate (TDCP)

Production and use

The total production of TDCP in the EU was less than 10,000 tonnes in 2000, produced in Germany and the UK (European Commission, 2004a). In 1997, global TDCP demand was estimated at 8000 tonnes per year (IPCS, 1998). Similar to TCPP, TDCP is a flame retardant of the additive type. The amount of flame retardant used depends on the given application. The consumption of TDCP in the EU was somewhat less than 10,000 tonnes

in 2000. The most important use of TDCP is in the production of flexible polyurethane (PUR) foam. TDCP is added directly at the point of production of flexible foams. Foams containing TDCP are mostly used in the production of motor vehicles. Some of the use is also in furniture (European Commission, 2004a).
TDCP and TCPP are used for similar purposes, but TDCP is used in specific application where TCPP is not adequate. TDCP is not widely used outside the polyurethane industry (European Commission, 2004a).

Release in the environment
In the draft EU-RAR (European Commission, 2004a) an extensive description of the emission scenarios is made.
The estimated half-life for photodegradation is 21.3 hours based on the TGD model for this process and a predicted reaction rate constant by the program AOPWIN (U.S. EPA, 2003). The hydrolysis of TDCP was tested using Fyrol FR2. In the preliminary test, no significant hydrolysis was observed at pH 4 or 7. In the full test carried out at pH 9 and at 50 ºC the half-life was about 14.7 days. In a modified Sturm test no degradation was observed. Therefore, TDCP is considered to be not readily biodegradable. No studies of the degradation of TDCP in soil are available at this moment (European Commission, 2004a).

2.3.2 Alkyl phosphates

2.3.2.1 Tri-n-butyl phosphate (TBP) and Tris(2-methylpropyl) phosphate (TiBP)

Both branched and unbranched butylphosphates are manufactured (Table 7). Most information is available on the unbranched tri-*n*-butyl phosphate (TBP), while no additional information could be found for the branched tris(2-methylpropyl) phosphate (TiBP).

Production and use
The estimated production volume of TBP is 3000 – 5000 tonnes worldwide. TBP is predominantly used in industry as a component of aircraft hydraulic fluid and as a solvent for rare earth metal extraction and purification. This comprises over 80 percent of the volume produced. In smaller amounts, TBP is used as a defoamer additive in cement casings for oil wells, as an anti-air entrainment additive for coatings and floor finishes, and as a carrier for fluorescent dyes. No use of TBP in consumer products is known (UNEP, 2001). Next to the uses mentioned above, TBP is also used as solvent for cellulose ester, lacquers and natural gums (IPCS, 1991a).

Release in the environment
In both soil and water, TBP is expected to adsorb to sediments or particulate matter and to biodegrade. In the atmosphere, TBP will exist as a vapour and will be subject to rapid photodegradation. Bioconcentration is not expected to occur (IPCS, 1991a).
Although usually at low concentrations, TBP has been found widely in air, water, sediment, fish, and several other biota. TBP may enter into the environment by leakage from sites of production or use, as well as by leaching from plastics disposed in landfill sites or aquatic environments. TBP may also be emitted from extraction reagents and solvents, that are continuously emitted to aquatic environments from loss in solvent extraction processes. TBP used in antifoaming agents may be emitted into the environment from manufacturing plants where it is used, such as paper manufacturing sites, where high concentrations of TBP have been detected in river water, fish and air.

2.3.2.2 Triethyl phosphate (TEP)

Production and use

Triethyl phosphate is manufactured by adding phosphorus oxy-chloride to ethanol in excess at low temperature (0-20°C) and reduced pressure. Another method to produce triethyl phosphate is synthesis from ethyl ether and P_2O_5 under pressure (3500 kPa) and at high temperature (180°C) (GDCh, 1989).

1000 – 1600 tonnes of TEP were produced in Germany in the years 1982-1987 and about 2000 tonnes in 1988. About 40 – 50% of TEP used in Germany (ca. 250 tonnes per year) is used in the synthesis of ketene, where the compound is hydrolysed. About 40% (approximately 240 tonnes per year) is used as flame retardant, plasticiser and carrier, where it is available in the matrix. In other industrial branches, a further 10 to 20% is used as solvent, plasticiser, flame retardant or intermediate for the production of pharmaceuticals, pesticides and laquers. In the USA, one company produces about 5000 tonnes per year. Primary uses for TEP in the USA are as an industrial catalyst and as a polymer resin modifier and plasticiser. In small amounts, TEP is used in the USA as solvent, flame retardant, or industrial intermediate for the production of pesticides and other chemicals (UNEP, 1998).

Release in the environment

TEP is not readily biodegradable, but with an industrial inoculum TEP was found to be inherently biodegradable. The bioaccumulation potential is low (measured BCFs are <1.3). Although hydrolytic degradation is possible, the half-life under environmental conditions is estimated to be between five and ten years. Direct photodegradation in water is not possible because TEP doesn't absorb UV light in water. In the atmosphere, the half-life due to photochemical-oxidative degradation is between 7 and 8.8 hours (UNEP, 1998).

The main route for emission of triethyl phosphate into the environment is washing out of plastic materials. Experiments have shown considerable triethyl phosphate migration from PVC materials into water, and that the rate of migration depends upon temperature (GDCh, 1989).

2.3.2.3 Tris(2-butoxyethyl) phosphate (TBEP)

Production and use

TBEP is produced by reaction of phosphorus oxychloride and butoxyethanol (butyl glycol). Another production method uses the sodium salt of the glycol. The world production has been estimated to be 5000-6000 tonnes, with less than 1000 tonnes in Europe (IPCS, 2000).

TBEP is used mainly as self levelling agent in floor polishes. Further TBEP is used as solvent in some resins, as viscosity modifier in plastisols, as antifoam and also as a plasticizer in synthetic rubber, plastics and lacquers (IPCS, 2000). TBEP is not considered a flame retardant and is not used in plastisols and plastic ware applications.

Release in the environment

The input rate of TBEP to the environment cannot be estimated from the available data. It is expected that the emission is mainly to soil, sediments and surface waters from leachates from plastics on landfills, from spillages and from effluents. TBEP appears to be rapidly biodegradable (IPCS, 2000).

2.3.2.4 Tris(2-ethylhexyl) phosphate (TEHP)
Production and use
In 1992, approximately 1000 tonnes of THEP were manufactured in Germany (GDCh, 1997). Data for the world production of TEHP are not available, but the estimated world production is between 1000 and 5000 tonnes/year (IPCS, 2000).
TEHP is produced by reaction of phosphorus oxychloride and 2-ethylhexanol. Technical grade TEHP is usually 99% pure, with 2-ethylhexanol, bis(2-ethylhexyl) phosphate (BEHP) and traces of water as impurities (IPCS, 2000).
TEHP is used in PVC plastisols, as a flame retardant in cellulose acetate and as solvent for certain chemical reactions. It is also used as a flame retardant plasticizer, particularly for PVC, in low temperature application (IPCS, 2000).

Release in the environment
The biodegradation results of TEHP are inconclusive. Some studies show rapid biodegradation, while in other studies no biodegradation is observed during 28 days (IPCS, 2000).

2.3.3 Aryl phosphates

2.3.3.1 Triphenyl phosphate (TPP)
Production and use
Triphenyl phosphate is produced by reaction of phenol with phosphorus oxychloride (IPCS, 1991b). Around 7,250 tonnes of triphenyl phosphate were produced in the United States in 1977 and around 3,750 tonnes were produced in Japan in 1984 (IPCS, 1991b). It can be handled as flakes or as a liquid shipped in heated vessels. The number of companies within the EU that produce triphenyl phosphate is small (Environment Agency, 2003b).
Triphenyl phosphate was initially used as a flame retardant/plasticizer in cellulose acetate safety film. Nowadays, it is applied as flame retardant/plasticizer in cellulose nitrate, various coatings, triacetate film and sheet, and engineering thermoplastics such as polyphenylene-high impact polystyrene and acrylonitrile-styrene-butadiene (ABS)-polycarbonate blends (Environment Agency, 2003b). Further it is used as a non-combustible substitute for camphor in celluloid, as a plasticizer in lacquers and varnishes (IPCS, 1991b). Another application of TPP is as an extreme pressure additive in lubricants and hydraulic fluids (IPCS, 1991b).
In Japan, out of a total of 3,750 tonnes in 1984, 3,200 tonnes were used as a flame retardant in phenolic and phenylene oxide-based resins for the manufacture of electrical and automobile components, around 500 tonnes were used as a flame-retardant plasticizer in cellulose acetate for photographic films and around 50 tonnes were used for other miscellaneous applications (IPCS, 1991b). At present, the major use of triphenyl phosphate in the EU include printed circuit boards, thermoplastic/styrenic polymers and photographic film (Environment Agency, 2003b).

Release in the environment (EHC 111 and UK environment agency, 2003)
In the draft report from the Environment Agency (2003b) the emission scenarios for TPP are discussed in detail. Triphenyl phosphate undergoes hydrolysis to form diphenyl phosphate, which is more stable to hydrolysis than the parent compound. The rate of hydrolysis increases with pH. The half-lives found from several studies typically carried out at 20-30 ºC are generally <3 days at pH of 9 and above, 7.5-24 days at pH around 8 and 19 days or longer at pH around 7. Because of the generally lower temperatures, the rate of hydrolysis in the environment may be longer than these values (Environment Agency, 2003b).

The hydrolysis rates of triaryl phosphates with alkyl substituents on the aromatic ring (such as tricresyl phosphate) should be lower than those for triphenyl phosphate due to the electron-donating character of these alkyl groups (Boethling and Cooper, 1985). Several studies have shown that photolytic degradation of TPP by UV radiation is a possible route of degradation as well. The half-life of atmospheric photooxidation of triphenyl phosphate by hydroxyl radicals is estimated to be around 36 hours (Environment Agency, 2003b).
Aryl phosphates in general are most likely biodegraded by initial hydrolysis of the phosphate ester to orthophosphate and the corresponding phenolic compounds or alcohols (from alkyl groups), which then themselves undergo further biodegradation (Saeger et al., 1979).
Although triphenyl phosphate is readily biodegradable in standard tests, it is not clear from many other studies if the half-life is less than 10 days (Environment Agency, 2003b).
TPP has, because of its hydrophobicity, a high potential for bioaccumulation. Laboratory studies of continuous exposure to high concentrations of radiolabelled TCP have shown high bioconcentration factors (BCF), although the BCFs from studies that are considered reliable are all below 2000, probably due to metabolism. Further, accumulation factors from food to fish are all very much less than 1 (Environment Agency, 2003b).

2.3.3.2 Tricresyl phosphate (TCP)

Production and use
Tricresyl phosphate is made by the reaction of a mixture of meta- and para-cresol with phosphorus oxychloride. The amount of ortho-cresol in this production process is minimised due to the toxicity of the *o*-isomer. The most important isomers in the product are tri-*m*-cresyl phosphate, bis-*m,p*-cresyl phosphate and bis-*p,m*-cresyl phosphate (Environment Agency, 2003a). Commercial TCP may contain considerable amounts of other compounds such as triphenyl phosphate and other tri-aryl phosphates (Environment Agency, 2003a; Ofstad and Sletten, 1985).
33,000 tonnes were produced in 1984 in Japan. 10,400 tonnes of TCP were produced in 1977 in the USA. In China about 800-1000 tonnes TCP per year were produced at the end of the eighties. No information on the total production worldwide is available. In the USA, triphenyl, tricresyl, and trixylenyl phosphates from petroleum-based feedstocks are replaced by aryl phosphates derived from synthetic precursors. Further, mixed tri-alkyl/aryl phosphates are replacing TPP and TCP as a plasticizer (IPCS, 1990).
Tricresyl phosphate is produced by only a small number of companies within the EU. The major current uses of the substance in the EU are in PVC, in rubber, in polyurethane in textile coating, as additives in lubricants and in photographic film (Environment Agency, 2003a; Ofstad and Sletten, 1985).
TCP is applied as a flame retardant in flexible PVC, cellulose nitrate, ethylcellulose coatings, lacquers, adhesives and various rubber products. These products are used vinyl tarpaulins, mine conveyor belts, air ducts, cable insulation and vinyl films. TCP is also used as an extreme pressure additive in lubricants, as fire-resistant hydraulic fluid and a petrol/diesel fuel anti-preignition additive, and as a clarifying agent in casein polymer production (Environment Agency, 2003a).

Release in the environment
Tricresyl phosphate can be hydrolysed. The hydrolysis rate increases with increasing pH. The products from the hydrolysis reaction are likely to be cresol and dicresyl phosphate, which probably is more stable to hydrolysis than the parent compound. However, the estimated hydrolysis reaction rate is only rapid at very high pHs (e.g. the estimated half-life at 25 ºC is 1,100-2,200 days at pH 7 and 30-40 days at pH 8). Several studies have shown that UV radiation may lead to photolytic degradation of tricresyl phosphate. The estimated half-life for

atmospheric photooxidation of tricresyl phosphate by hydroxyl radicals is around 27.5 hours (Environment Agency, 2003a).
Initial hydrolysis of the TCP to orthophosphate and cresols, which then themselves undergo further biodegradation is the most likely path for biodegradation (Saeger et al., 1979). Many studies show that tricresyl phosphate is readily biodegradable in a variety of aerobic test systems. When released into water TCP is readily adsorbed by sediment particles (Environment Agency, 2003a).
TCP has, because of its physicochemical properties, a high potential for bioaccumulation. Laboratory studies of continuous exposure to high concentrations of radiolabelled TCP have shown high bioconcentration factors (BCF) of up to around 2700 although most values are smaller than 2000. However, these studies failed to show that the isotope was still associated with the original compound. Taking into account the ready biodegradability of TCP, these data should be viewed as probable overestimates, and it is suggested that little bioaccumulation would occur with environmentally realistic TCP exposure. Further, accumulation factors from food to fish are all very much less than 1 (Environment Agency, 2003a).

3. Methods

3.1 Literature search and data selection

For the studied compounds a lot of literature has already been collected in different frameworks. In the series 'Environmental Health Criteria' of IPCS the following compounds were regarded: Tris(2-chloroethyl) phosphate, tris(1-chloro-2-propyl) phosphate and tris(1,3-dichloro-2-propyl) phosphate (1998), tri-*n*-butyl phosphate (1991a), tris(2-butoxyethyl) phosphate and tris(2-ethylhexyl) phosphate (2000), triphenyl phosphate (1991b), and tricresyl phosphate (1990). For the following compounds BUA reports of the GDCh are available: Tris(2-chloroethyl) phosphate (1987; 2001), triethyl phosphate (1989), tri-*n*-butyl phosphate (1995), and tri(2-ethylhexyl) phosphate (1997; 2000). Further, the Environment Agency of the UK has almost completed their risk assessment reports on triphenyl phosphate (2003b) and tricresyl phosphate (2003a). For the chlorinated alkyl phosphate esters risk assessment reports are being prepared by the European Commission in the framework of the existing chemicals legislative: Tris(2-chloroethyl) phosphate (European Commission, 2004c), tris(1-chloro-2-propyl) phosphate (European Commission, 2004b), tris(1,3-dichloro-2-propyl) phosphate (European Commission, 2004a).
These sources have been used to collect data from. For the compounds considered in the risk assessment reports of the European Commission (EU-RAR) additional data were not searched for. Further, a literature search was performed to collect additional data. Some literature was found from retrospective searching. As far as possible, original publications were checked. Data were considered reliable if the experimental set-up is in accordance with internationally accepted guidelines, such as the OECD guidelines. For other studies that deviate from these guidelines, the Technical Guidance Document of the EU (European Commission, 2003) gives information on the requirements these studies should fulfil with regards to the test substance, test species, exposure, water quality and so on (Appendix III). Toxicity data based on QSAR studies and data based on methods, which are considered not reliable, are not taken into consideration to the derivation of ERLs. This also applies for data that are unpublished or that can not be verified and for 'higher or lower than' values. Although not used for the derivation of ERL, these data are however shown in the tables of the Appendix 1.
The effects that are considered as relevant for the derivation of environmental risk limits are those that affect the population dynamics, such as survival, immobilisation, growth, reproduction. Other effects such reburial or photosynthesis might be considered relevant as well, if they are strongly related to one of the above effects. Toxicity studies with endpoints such as biochemistry or animal behaviour are not taken into account for the derivation of ERLs, as they do not have a clear relationship with population dynamics.
Special attention was paid to the experiments with algae, because algae appeared one of the most sensitive groups for the studied phosphate esters. The most relevant parameter for algae is the growth rate of the population. If a result was available for growth rate, this was preferred above other endpoints, for example biomass. If the raw data were presented, growth rate was deduced from these data if it was not presented. To determine the growth rate, algae should be in a phase of exponential growth. If mentioned in the study, the growth rate was selected for the exposure time for which exponential growth could be assumed.
When more data for the same species and the same endpoint are available, a geometric mean of these data is taken. In the TGD (European Commission, 2003), the use of a geometric mean is explicitly recommended for acute toxicity data and for chronic toxicity data when a statistical extrapolation technique is applied. The TGD does not mention this topic in the case

that assessment factors are used. Here, in all cases a geometric mean is used when toxicity data are available for the same species and endpoint.

3.2 Derivation of environmental risk limits

3.2.1 Derivation of maximum permissible concentrations (MPCs)

For the derivation of the MPCs the procedures to derive the PNECs from aquatic, terrestrial and benthic toxicity data as documented in the TGD (European Commission, 2003) are followed. Concentrations in soil from the toxicity tests are normalised to standard soil, by taking the organic matter content of both test and standard soil into account (European Commission, 2003). The environmental risk limits for soil and sediment in the Netherlands are based on a standard soil with 10% organic matter, in the TGD standard soil has 3.4% organic matter. Because environmental risk limits for the Netherlands are derived in this report, a normalisation to 10% organic matter has been applied to the terrestrial data.
For the derivation of the PNECs the assessment factors as mentioned in the TGD are used. According to the TGD, statistical extrapolation techniques may only be applied if chronic toxicity data for at least 10 species from 8 different taxonomic groups are available (European Commission, 2003)
For the derivation of ERLs salt and freshwater data are combined if there are no (statistical) reasons to keep the data separated. This means that the ERLs are derived using the combined dataset. However, according to the TGD separate PNECs, and thus MPCs, are derived for fresh water and marine water. Only if enough additional toxicity data for specific marine species are available, the same assessment factor as for the derivation of the PNEC for fresh water may be applied to derive the PNEC for marine water.

3.2.2 Derivation of serious risk concentrations ($SRCs_{eco}$)

The $SRCs_{eco}$ are derived in accordance with the procedures introduced with the updated proposals of the first series of compounds of Intervention Values (Verbruggen et al., 2001). In general the minimum of the geometric mean of the acute toxicity data divided by a factor of 10 and the geometric mean of the chronic toxicity data is taken. In the case of terrestrial (and benthic) toxicity data a comparison with the value derived by equilibrium partitioning is also made. In the case that chronic toxicity data are available for at least 4 different taxonomic groups, the geometric mean of the chronic toxicity data is directly used as SRC_{eco} without comparison.

3.2.3 Derivation of negligible concentrations (NCs)

Negligible concentrations (NCs) are derived by dividing the MPCs by a factor of 100. The NC represents a value causing negligible effects to ecosystems. This factor is supposed to function as protection against mixture toxicity, since species are always exposed in the environment to mixtures of chemicals and complex mixtures of chemicals are generally best described as concentration-additive (Van Leeuwen et al., 1996; Deneer, 2000).

3.3 Equilibrium Partitioning (EqP)

If no data are available for benthic or terrestrial organisms, the ERLs for sediment and soil are calculated by equilibrium partitioning according to the TGD. If only acute toxicity data are available for benthic organisms or only one number for acute toxicity of terrestrial organisms, equilibrium partitioning is also used in comparison with the direct toxicity data.

The PNECs calculated according to the TGD are for bulk (wet weight) sediment and soil. In the framework of INS, sediment and soil concentrations are normalised to dry weight, with the organic matter content of 10% for Dutch standard soil and sediment. This recalculation is performed according to the equations as documented in the guidance document for deriving Dutch Environmental Risk Limits from EU-Risk Assessment Reports (Janssen et al., 2004). According to the TGD, PNECs for sediment are calculated with the characteristics of suspended matter. In this report, not only the fraction water and solids but also the organic carbon content of suspended matter is used in the recalculation of concentrations based on wet weight suspended matter to Dutch standard sediment. This results in concentrations for standard sediment, which are twice as low as calculated according to Janssen et al. (2004), according to which the density and composition of suspended matter must be used for the recalculation to dry weight, but at the same time the organic carbon content of sediment for the normalisation to Dutch standard sediment.
Due to the amount of a substance that is present in the (pore)water phase of sediment and soil, small differences between the ERLs for sediment and soil may occur for less hydrophobic chemicals. This reflects the fact that although expressed as concentrations normalised to dry weight of sediment, the total amount of the substance in bulk sediment or soil is determined by means of common extraction techniques.

3.4 Secondary poisoning

The group of organophosphorus flame retardants are compounds with low to very high hydrophobicity (log K_{ow} 1 - 9) and therefore, some of these compounds have a potential for secondary poisoning. However, for several compounds bioconcentration factors appear to be lower than the trigger value of 100 L/kg (for TCEP, TCPP, TDCP, TBP, TEHP, see Table A4.1). For some compounds no experimental data on bioaccumulation are available (TEP, TiBP, and TEBP). Given the low hydrophobicity of TEP, the intermediate hydrophobicity of TBEP and structural similarity of TiBP to TBP, no high bioconcentration factors are expected for these compounds as well. The bioconcentration factors for TPP and TCP are higher, with values up to 2000 L/kg or above. However, the concentration in the tests resulting in the highest BCF values were determined by liquid scintillation counting (LSC). With this technique no distinction is made between the parent compound and metabolites. However, the aryl phosphate esters are rapidly metabolised. BCF values expressed on basis of the concentration of the parent compound, are lower than that. BCF values for TPP are generally in the order of 271 to 420 L/kg (Environment Agency, 2003b) and around 310-800 L/kg for TCP (Environment Agency, 2003a).
Further, for TPP and TCP, the uptake from food by minnows (*Phoxinus phoxinus*) appeared to be very low, with biomagnification factors (BMF) far below 1 (i.e. 0.001 and less) (Bengtsson et al., 1986).
Based on the information given above, it was decided not to incorporate secondary poisoning in the risk assessment. This seems indeed to be justified, because on the draft risk assessment reports of the Environment Agency of the UK secondary poisoning led to lower values than direct toxicity, even with the used default biomagnification factors of 1 (Environment Agency, 2003b; Environment Agency, 2003a).

4. Toxicity data and derivation of ERLs

In this chapter the derived environmental risk limits for the phosphate ester are presented. The risk limits are presented per compartment.

4.1 Derivation of ERLs for water

The aquatic toxicity data that are found for the phosphate esters considered in this report are presented in Appendix 2. The selected toxicity data that were used for the derivation of the ERLs, are given in separated tables shown in Appendix 1.

4.1.1 Halogenated phosphate esters

4.1.1.1 Tris (2-chloroethyl)phosphate (TCEP)

A draft EU-RAR is available for TCEP (European Commission, 2004c). Aquatic toxicity data presented in the EU-RAR are reported in Table A2.1 (acute data) and Table A2.2 (chronic data). Additional aquatic toxicity data, that were found but are not presented in the EU-RAR, are reported in Table A2.3 (fresh water, acute and chronic) and Table A2.4 (salt water).
Acute toxicity data are available for bacteria, algae, crustaceans, invertebrates and fish. Especially algae appear to be a sensitive taxonomic group. The most sensitive species is *Scenedesmus subspicatus* (algae) and the least sensitive is *Moina macropoda* (crustacea). Chronic toxicity was tested for algae and crustacea. The most sensitive species is *Scenedesmus subspicatus* (algae) and the least sensitive is *Daphnia magna* (crustacea).
In the draft EU-RAR the lowest number for the growth rate of *Scenedesmus subspicatus* of 0.65 mg/L is used as basis for the PNEC. For compounds that are evaluated within the Existing Substances Regulation the environmental quality standards will be derived following the PNEC estimated in the EU-RAR. An MPC will thus be derived when the EU-RAR is finalised and published.
The SCR_{eco} is derived from the data set in the EU-RAR. Additional data are not considered. The selected data from the EU-RAR are tabulated in Table A1.1. The geometric mean of the acute and chronic toxicity data are 186 and 8.6 mg/L, respectively. As the geometric mean of the NOECs is lower than the geometric mean of the acute values divided by 10, the **SRC_{eco}** for water is equivalent to the geometric mean of NOEC values resulting in **8.6 mg/L**.

4.1.1.2 Tris (2-chloro-1-methylethyl) phosphate (TCPP)

A draft EU-RAR is available for TCPP (European Commission, 2004b). Aquatic toxicity data presented in the EU-RAR are reported in Table A2.6 (acute data), Table A2.7 (chronic data), and Table A2.8 (saltwater data, acute). Additional aquatic toxicity data that are not presented in the EU-RAR are reported in Table A2.9 (saltwater).
Acute toxicity data are available for bacteria, algae, crustaceans and fish. Chronic toxicity are available for algae and crustaceans. For compounds that are evaluated within the Existing Substances Regulation the environmental quality standards will be derived following the PNEC estimated in the EU-RAR. An MPC will be derived when the EU-RAR is finalised and published. It is concluded in the EU-RAR, that at present it is not possible to determine a PNEC, as a full base set of acceptable ecotoxicity data is not available and the results for the fish and algal tests suggest that *Daphnia magna* may not represent the most sensitive taxonomic group and therefore the chronic test data for *Daphnia magna* cannot be used as the basis of the PNEC. However, according to the TGD an assessment factor of 100 should be applied to the lowest NOEC or EC10 in such a case.
For the derivation of the SRC_{eco} for aquatic species, the selected data from the draft EU-RAR are presented in Table A1.3 (fresh water) and Table A1.4 (saltwater). The geometric mean of the two chronic toxicity data is 14 mg/L. One acute value is available for the marine

bacterium *Vibrio fischeri*. This number seems to be rather high in comparison with the other toxicity data. However, when examining the other phosphate esters bacteria seem to be rather insensitive, regardless whether these are fresh water or saltwater species (see tris(*iso*-butyl)phosphate, §4.1.2.2 and data on microbial activity in sludge: Table A2.5, Table A2.10, Table A2.14, Table A2.19, Table A2.23, Table A2.26, Table A2.30, and Table A2.41). Therefore, all data are combined. The geometric mean of the acute toxicity data is 65 mg/L. The **SRC_{eco}** for water is therefore based on the acute toxicity data and is **6.5 mg/L**.

4.1.1.3 Tris (1,3-dichloro-2-propyl) phosphate (TDCP)

Aquatic toxicity data for tris (1,3-dichloro-2-propyl) phosphate are reported in Table A2.11 (acute data) and Table A2.12 (chronic data). There are reliable acute toxicity data on algae, crustaceans and fish and chronic toxicity data on algae. In the draft EU-RAR, the PNEC is based on the lowest acute value. In this case, the lowest of two LC50s values for rainbow trout (*Oncorhynchus mykiss*) is used. For compounds that are evaluated within the Existing Substances Regulation the environmental quality standards will be derived following the PNEC estimated in the EU-RAR. An MPC will be derived when the EU-RAR is finalised and published. However, it is concluded in the EU-RAR, that currently a PNEC can be derived from the acute data. There are insufficient data to determine a PNEC from chronic test results. Currently a chronic *Daphnia* reproduction study is being conducted as part of an industry programme of further work. With this study available, the assessment factor would be 100 according to the TGD, applied to the lowest NOEC.
For the derivation of the SRC_{eco}, the selected values are reported in Table A1.6. The **SRC_{eco}** for water is derived from the geometric mean of the acute toxicity data divided by a factor of 10 and is **0.52 mg/L**.

4.1.2 Alkyl phosphate esters

4.1.2.1 Tri-n-butyl phosphate (TBP)

Aquatic toxicity data for tri-*n*-butyl phosphate are reported in Table A2.15 (freshwater, acute), Table A2.16 (freshwater, chronic), Table A2.17 (saltwater, acute), and Table A2.18 (saltwater, chronic). Acute toxicity data are available for algae, crustaceans, fish, bacteria, flatworms and protozoans. The most sensitive species was the crustacean *Gammarus pseudolimnaeus* and the least sensitive marine bacterium *Vibrio fischeri*. Chronic toxicity data are available for algae, crustaceans, fish, bacteria, cyanophyta, protozoans, and rotifers. The most sensitive species tested was *Scenedesmus subspicatus* (algae), the least sensitive species is *Pseudomonas putida*. The selected toxicity data for freshwater and saltwater species are reported in Table A1.8 and Table A1.9. Although chronic toxicity data are available for seven taxonomic groups, statistical extrapolation may not be applied according to the TGD, because chronic toxicity data for insects and higher plants are missing. Because chronic toxicity data are available for algae, *Daphnia*, and fish, an assessment factor of 10 can be applied to the lowest NOEC. This is the NOEC of 0.66 mg/L for the growth rate (48-h) of *Scenedesmus subspicatus*. The resulting **MPC** for **freshwater** is **0.066 mg/L**. No additional data are available for typical marine organisms. Therefore, the applied assessment factor is 100 and the **MPC** for the **marine** environment is consequently **0.0066 mg/L**.
For the derivation of the SRC_{eco} the chronic toxicity to *Vibrio fischeri* has been taken into account as well. Although the TGD mentions that for the derivation of the PNEC using assessment factors, these tests may not be considered as chronic, the test for tri-*n*-butyl phosphate is a real chronic test for bacteria (22 hour) which covers several cell multiplications times (Radix et al., 1999). The geometric mean of the acute and chronic toxicity data are 11 and 5.3 mg/L, respectively. Therefore, the **SRC_{eco}** is **1.1 mg/L**.

4.1.2.2 Tris(2-methylpropyl) phosphate (TiBP)

Aquatic toxicity data for TiBP are available for algae, crustaceans, fish, and bacteria. Data for freshwater species are reported in Table A2.20 (acute) and Table A2.21 (chronic). Acute toxicity to saltwater species is reported in Table A2.22. The selected toxicity data for the derivation of the ERLs are reported in Table A1.10 (freshwater) and Table A1.11 (saltwater). Because only one NOEC for algae is available, the MPC is based on the acute toxicity data. In such a case an assessment factor of 1000 is applied. The lowest EC50 is 11 mg/L for *Daphnia* magna. The resulting **MPC** for **freshwater** is **0.011 mg/L**. For the **marine** environment, the assessment factor is 10000 and the resulting **MPC** is **0.0011 mg/L**. The **SRC_{eco}** is also based on the combined acute toxicity data sets for freshwater and saltwater. The geometric mean of these data divided by a factor of 10 is **3.4 mg/L**.

4.1.2.3 Triethyl phosphate (TEP)

Selected aquatic toxicity data for triethyl phosphate are reported in Table A2.24 (freshwater, acute), Table A2.25 (freshwater, chronic), Table A2.27 (saltwater, acute). Acute toxicity data are given for the base-set (algae, *Daphnia*, fish). In brackish water one additional species of crustaceans and one species of fish were tested. The most sensitive species was *Daphnia magna* (crustacean) and the least sensitive species was *Alburnus alburnus* (fish).
Chronic toxicity data are available for *Scenedesmus subspicatus* (algae) and *Daphnia magna* (crustacean).
For *Daphnia magna* an acute toxicity tests and a reproduction study are available. The EC50 for immobility from the acute toxicity studies ranges from 900-2700 mg/L for an exposure time of 24 hours, while for 48 and 96 hours exposure the EC50 is 350 mg/L. For the 21-d reproduction study, the EC50 is 729 mg/L. A NOEC could however not be established. The lowest tested concentration of 10 mg/L was still statistically different from the control. The presented data follow a clear dose-response relationship. Therefore, the derived EC10 of 190 mg/L from this relationship is used in the risk assessment (Figure 2).

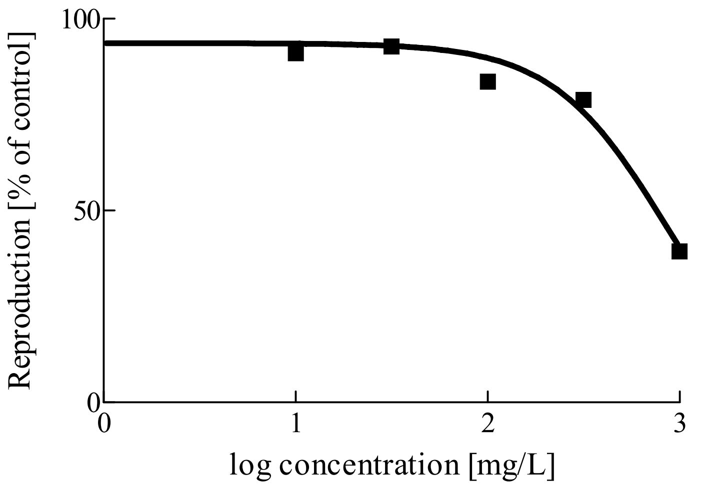


Figure 2. Dose-response relationship for the 21-d reproduction test with Daphnia magna. *Control reproduction of 100% was used as well in establishing the top of the dose-response curve.*

The base-set for triethyl phosphate is complete. The lowest EC50 is 350 mg/L for *Daphnia magna*. For this species a chronic study is available too, together with an EC10 for growth of the algae *Scenedesmus subspicatus*. Therefore, an assessment factor of 50 can be applied to the lowest chronic value, which is the EC10 of 80.3 mg/L for *Scenedesmus subspicatus*. The **MPC** for **freshwater** thus becomes **1.6 mg/L**. No additional data are available for typical

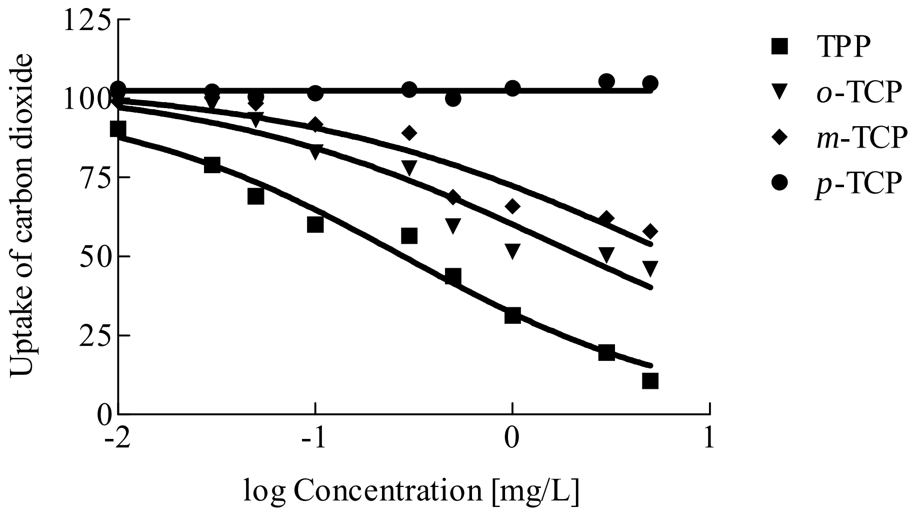
marine organisms. Therefore, the applied assessment factor is 500 and the **MPC** for the **marine** environment is consequently **0.16 mg/L**.
The geometric mean of all acute toxicity data (fresh and brackish water combined) is 1070 mg/L. The geometric mean value for the chronic data is 123 mg/L. The SRC_{eco} is determined by the mean LC50 value divided by an assessment factor of 10, leading to an **SRC_{eco}** of **110 mg/L**.

4.1.2.4 Tris (2-butoxyethyl) phosphate (TBEP)
Selected aquatic toxicity data for tris (2-butoxyethyl) phosphate are reported in Table A2.28. The only available toxicity data are acute toxicity data for crustaceans (*Daphnia*) and fish. The least sensitive species is *Daphnia magna* (crustacea). In cases where the base-set is not complete (but at the most the acute toxicity for *Daphnia* is determined), the PNEC should be calculated with a factor of 1000 (European Commission, 2003: Note a to Table 16). The lowest LC50 is 13 mg/L for the fathead minnow (*Pimephales promelas*). The resulting **MPC** for **freshwater** is **0.013 mg/L**. A factor of 10000 is applied for the **marine** environment and the resulting **MPC** is **0.0013 mg/L**.
The **SRC_{eco}** is calculated from the geometric mean of all data with an assessment factor of 10 resulting in a value of **2.9 mg/L**.

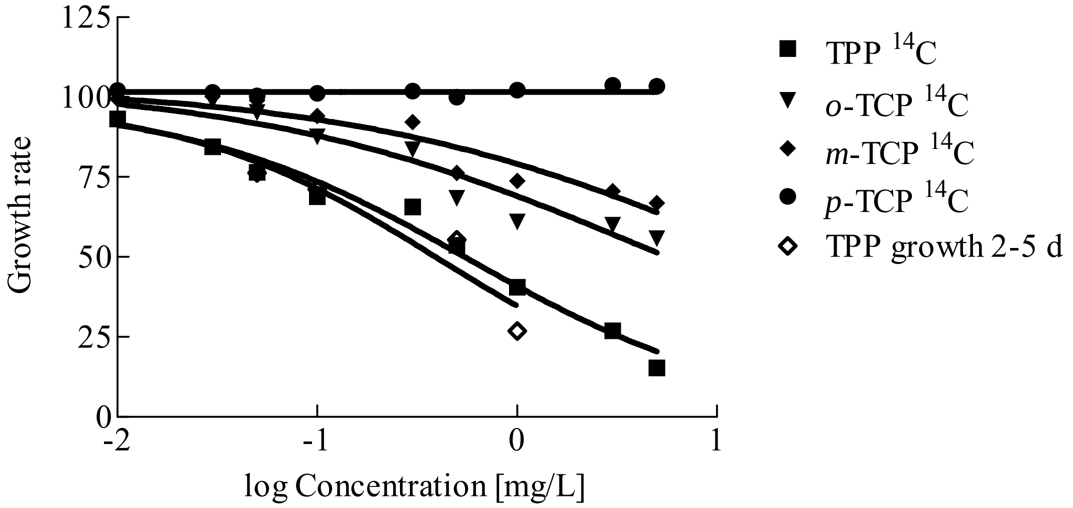
4.1.2.5 Tris (2-ethylhexyl) phosphate (TEHP)
The only available toxicity data for tris(2-ethylhexyl) phosphate with fish show no effects at all (Table A2.29). Up to the aqueous solubility no effects are observed. However, the true solubility of this compound is not clear (Table 10). The measured concentration in the study with *Daphnia magna* was 0.074 mg/L. However, calculated values for solubility still are much lower. Because of the lack of suitable data no MPC can be derived for TEHP.

4.1.3 Aryl phosphate esters
4.1.3.1 Triphenyl phosphate (TPP)
The UK Environment Agency prepared in cooperation with industry a risk assessment of TPP in an EU-RAR like manner (2003b). Aquatic toxicity data for TPP from this draft risk assessment report are reported in Table A2.31 (freshwater, acute), Table A2.32 (fresh water, chronic), and Table A2.33 (saltwater, acute). Additional data to this report are tabulated in Table A2.34 (freshwater) and Table A2.35 (saltwater). Because risk assessment report of the Environment Agency is not a report of the European Union and the additional data are decisive for the derivation of the ERLs, these data have been used as well for the derivation of the ERLs. The selected data for TPP are shown in Table A1.15 (freshwater) and Table A1.16 (saltwater). The lowest acute EC50s are for the crustaceans *Gammarus pseudolimnaeus* (freshwater, 0.25 mg/L) and *Mysidopsis bahia* (saltwater, 0.24 mg/L). Other groups of species for which the EC50s lie below or around the aqueous solubility of 0.7-2.1 mg/L are algae (lowest EC50 of 0.26 mg/L), insects (lowest EC50 of 0.36 mg/L) and fish (lowest EC50 of 0.42 mg/L for three species).
The lowest EC50 of 0.26 mg/L for algae comes from a study with *Ankistrodesmus falcatus* in which the uptake of radiolabelled carbon dioxide is studied for 4 hour after an incubation time with TPP of 24 hour (Wong and Chau, 1984). The presented results show a strong dose-response relationship (Figure 3). Also tri-*o*-cresyl phosphate and tri-*m*-cresyl phosphate inhibited the carbon uptake to a lesser extent in this test while tri-*p*-cresyl phosphate induced no effects. The uptake of carbon dioxide is considered as a measure of primary productivity, which is the amount of biomass formed by photosynthesis over time (dB/dt). Because the carbon uptake is preceeded by an incubation time of 24 hours, the initial number of cells when the uptake experiment started was different for each concentration. The growth rate of algae is

the amount of biomass (or cells) formed over time relative to the biomass initially present (dB/dt*1/B). Therefore, the carbon uptake between 24 and 28 hours is not a good measure of the growth rate, because the initial amount of biomass after 24 hours differs for each exposure concentration.
The same authors (Wong and Chau, 1984) performed also a growth test during 22 days for TPP with *Ankistrodesmus falcatus*. However, the results of this test, based on biomass, were inconclusive, also when only the first period of the exponential growth phase is considered. The first two concentrations of 0.05 mg/L and 0.10 mg/L had higher biomass than the control, while significant inhibition was observed from 0.50 mg/L onward. This is explained by stimulation, but such an effect was not observed for any other phosphate ester studied in this report. Further, stimulation is very unlikely, because the algae are initially in an exponential growth phase and cultivated in a growth medium (CHU-10 in this case). In this case, limitation by nutrients seems not very plausible. When expressed as growth rate (by taking the logarithm of the cell density) this effect of stimulation is not observed. Although the concentrations of 0.05 and 0.10 mg/L show a lower growth rate than the control (12 and 18% over 3 days, respectively), the irregular growth of in particular the 0.50 mg/L sample over the first few days does not allow the calculation of a dose-response relationship over 72 hours, based on growth rate. If on the other hand, the growth rate between 2 and 5 days of exposure is calculated, a clear dose-response relationship is obtained with an EC10 of 0.016 mg/L and an EC50 of 0.41 mg/L (Figure 3).
The exponential growth rate of the control from the growth test (0.017 h^{-1}, r^2=0.95) can also be assumed for the carbon uptake experiment, which was performed under the same conditions. Then, the relative amount of biomass formed in the four hours of the carbon uptake experiment in comparison with the initial amount of biomass can be calculated. From this value, the growth rate for all of the exposure concentrations of the carbon uptake experiment can be calculated. For TPP, the EC10 and EC50 for the growth rates are 0.016 mg/L and 0.57 mg/L, respectively. It can be concluded that the these numbers are accordance with the numbers, determined for the growth rate between day 2 and 5 of that experiment. Therefore, these numbers are used in the risk assessment.



a



b

Figure 3. Dose-response relationship for a) the carbon dioxide uptake by the algae Ankistrodesmus falcatus *inhibited by triphenyl phosphate and the three isomers (o, m, p) of tricresyl phosphate and b) the growth rates deduced from these values and directly determined. Control productivity and growth rate of 100% was used as well in establishing the top of the dose-response curves.*

The most sensitive species in acute experiments are crustaceans. Chronic toxicity data are available for fish, algae and cyanophyta. Therefore, according to the TGD an assessment factor of 100 must be applied to the lowest NOEC or EC10. This is the EC10 of 0.016 mg/L for *Ankistrodesmus falcatus*. The resulting **MPC** for **freshwater** is thus **0.16 µg/L**. The assessment factor for the **marine** environment is 1000 and the resulting **MPC** is **0.016 µg/L**. In the draft risk assessment report of the UK an assessment factor of 50 is applied, although it is recognised that crustaceans might be the most sensitive species, based on an evaluation of the available long-term invertebrate data for triaryl phosphates as a whole. Further, the data for *Ankistrodesmus falcatus* are not studied in more detail. So, applying a factor of 50 to the lowest EC10 of 0.037 mg/l obtained for fish, results in a PNEC of 0.74 µg/L in this draft report.

The geometric mean of the acute toxicity data for the combine data set for of freshwater and saltwater species is 0.60 mg/L. The geometric mean of the chronic toxicity data is 0.13 mg/L. The **SRC_{eco}** is therefore equivalent to the geometric mean of the acute toxicity values divided by an assessment factor of 10 resulting in **60 µg/L**.

4.1.3.2 Tricresyl phosphate (TCP)
Also for tricresyl phosphate a draft risk assessment report is available from the UK Environment Agency (Environment Agency, 2003a). In Table A2.36 (freshwater, acute), Table A2.37 (freshwater, chronic), and Table A2.38 (saltwater, acute) the data from this report are tabulated. Additional data were retrieved and these data are tabulated in Table A2.39 (freshwater) and Table A2.40 (saltwater). Also in this case, these data have been used as well for the derivation of the ERLs. The selected data for TCP are shown in Table A1.17 (only freshwater). Values more than three times the aqueous solubility of 0.074-0.34 mg/L were discarded, so only values lower than 1 mg/L are selected. Tricresylphosphate is produced as technical mixtures (see §2.3.3.2). Since too few data are available to distinguish toxicity between the different isomers, all data are taken together. Acute and chronic toxicity data are selected for algae, crustaceans (*Daphnia*) and fish. All acute toxicity data are rather close to each other, varying from 0.11 mg/L (*Lepomis macrochirus*) up to the aqueous solubility. From the chronic studies it appears that algae and especially fish are the most sensitive taxonomic groups.
The MPC will be derived based on the available chronic data. As data are available for three different trophic levels, an assessment factor of 10 is appropriate. Thus applying this factor to the lowest NOEC of 0.32 µg/l for fish gives a **MPC** for **freshwater** of **0.032 µg/L**. No data are available for saltwater species. Therefore, the assessment factor for the **marine** environment is 100, resulting in an **MPC** of **0.0032 µg/L**. The PNEC from the draft risk assessment report of the UK Environment Agency is derived in the same way.
The geometric mean of the selected acute values is 0.36 mg/L. The geometric mean of the chronic toxicity data is 0.029 mg/L. As the geometric mean of the acute values divided by 10 is higher as the geometric mean of the chronic values, the **SRC_{eco}** is equivalent to the geometric mean of the chronic values of **31 µg/L**.

4.2 Derivation of ERLs for soil

The terrestrial toxicity data that are found for the phosphate esters considered in this report are presented in Appendix 2. The selected toxicity data are given in separated tables shown in Appendix 1.

4.2.1 Halogenated phosphate esters
4.2.1.1 Tris (2-chloroethyl)phosphate (TCEP)
For soil, appropriate data are available for plants, springtails, earthworms and dehydrogenase activity (Table A3.1). The study with the terrestrial plant *Avena sativa* includes germination and two weeks growth. According to the OECD guideline 208 this is an acute study. Moreover, a NOEC could not be established statistically. Therefore, this test is only included as acute test. For earthworms (*Eisenia andrei*) no acute toxicity was observed at concentrations up to 1000 mg/kg. However, in the same 14-d study a NOEC for growth of 577 mg/kg_{dw} (10% o.m.) was found. For the springtail *Folsomia candida* a chronic reproduction test was performed. The EC10 for reproduction was 44.6 mg/kg_{dw} (1.21% o.m.). In the same test an LC50 of 66.5 mg/kg_{dw} was found for the parent generation. However, this value is not selected as an acute value, because in the acute test (24-h) the LC50 was higher than 1000 mg/kg_{dw} with the first signs of mortality at this concentration. For dehydrogenase

activity, a 28-d study was performed with two types of soil (1.53 and 3.74% o.m.). In the soil with the lower organic matter content, inhibition of dehydrogenase activity was observed at both concentrations, while in the soil with the higher organic matter content only the highest concentration of 50 mg/kg_{dw} lead to significant effects. Normalised to standard soil with an organic matter content of 10%, an EC10 of 28 mg/kg_{dw} could be derived from these three data.
In the draft EU-RAR, the PNEC for soil is based on the NOEC for *Folsomia candida*, because the information on chronic toxicity to *Folsomia* covers a broader spectrum of effects than the 28-d study with bacteria (dehydrogenase activity). No normalisation was applied to the data to correct for the percentage organic matter in the soil, although this should be done according to the TGD. In the draft EU-RAR this subject is not discussed at all.
Similar to the MPC for water, an MPC for soil will be derived when the EU-RAR is finalised and published. The SCR_{eco} is derived from the data set in the EU-RAR. The selected data from the EU-RAR are tabulated in Table A1.2. The geometric mean of the two normalised chronic EC10s is 68 mg/kg_{dw}. The EC50 value divided by 10 is 28 mg/kg_{dw}. This value for the SRC_{eco} for soil derived directly from the terrestrial data has to be compared with a value for equilibrium partitioning, because of the limited amount of terrestrial data. The value derived by equilibrium partitioning recalculated to dry weight is 59 mg/kg_{dw}. The value derived from terrestrial toxicity data is lower and therefore, the **SRC_{eco}** for soil is **28 mg/kg_{dw}**.

4.2.1.2 Tris (2-chloro-1-methylethyl) phosphate (TCPP)

Terrestrial toxicity data for TCPP are available for earthworms and plants (Table A3.2). In the draft EU-RAR, the PNEC is based on the NOEC for emergence of lettuce (*Lactuca sativa*). This is the lowest value for TCPP. However, in the draft EU-RAR only the numbers for the studies with earthworms (*Eisenia fetida*) are normalised to organic matter content (10% o.m.). The study with three species of terrestrial plants, performed with a soil with an organic matter content of 1.4%, is not normalised to standard soil, because this would only lead to higher values.
Similar to the MPC for water, an MPC for soil will be derived when the EU-RAR is finalised and published. The SCR_{eco} is derived from the data set in the EU-RAR. If all data are normalised to standard soil, the lowest value is the NOEC of 33 mg/kg_{dw} for mortality of *Eisenia fetida* from an acute 14-d study. The NOEC for reproduction of *Eisenia fetida* from a 56-d chronic study is 53 mg/kg_{dw}. This value is selected as chronic value, together with the three NOEC for terrestrial plants, normalised to the Dutch standard soil with 10% organic matter (Table A1.5). The geometric mean of these data is 120 mg/kg_{dw}. The acute LC50 for *Eisenia fetida* is 97 mg/kg_{dw}. This value divided by a factor of 10 is the SRC_{eco} for soil derived directly from the terrestrial data. Because of the limited amount of terrestrial data, this value has to be compared with a value for equilibrium partitioning. The value derived by equilibrium partitioning recalculated to dry weight is 222 mg/kg_{dw}. The value derived from terrestrial toxicity data is lower and therefore, the **SRC_{eco}** for soil is **9.7 mg/kg_{dw}**.

4.2.1.3 Tris (1,3-dichloro-2-propyl) phosphate (TDCP)

Only one terrestrial toxicity study is available for TDCP (Table A3.3). The PNEC from the draft EU-RAR is based on this value. Similar to the MPC for water, an MPC for soil will be derived when the EU-RAR is finalised and published. The SCR_{eco} is derived from the data set in the EU-RAR. The selected data from the EU-RAR are tabulated in Table A1.7. The LC50 value divided by 10 is 13 mg/kg_{dw}. This value for the SRC_{eco} for soil derived directly from the terrestrial data has to be compared with a value for equilibrium partitioning, because of the limited amount of terrestrial data. The value derived by equilibrium partitioning recalculated to dry weight is 376 mg/kg$_{dw}$. The value derived from terrestrial toxicity data is lower and therefore, the **SRC$_{eco}$** for soil is **13 mg/kg$_{dw}$**.

4.2.2 Alkyl phosphate esters

4.2.2.1 Tri-n-butyl phosphate (TBP)

No terrestrial toxicity data for TBP are available. Therefore, the ERLs have to be derived by equilibrium partitioning. The used log K_{oc} value for TBP of 3.13 was calculated from the log K_{ow} value (4.00). The Henry coefficient was estimated from the experimental solubility of 280 mg/L and vapour pressure of 0.904 Pa (gas saturation method). The resulting **MPC** for soil recalculated to dry weight for standard soil (10% o.m.) is **5.3 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **88 mg/kg$_{dw}$**.

4.2.2.2 Tris(2-methylpropyl) phosphate (TiBP)

No terrestrial toxicity data for TiBP are available. Therefore, the ERLs have to be derived by equilibrium partitioning. The used log K_{oc} value for TiBP of 2.99 was calculated from the log K_{ow} value. The Henry coefficient was estimated from the experimental solubility of 265 mg/L and vapour pressure of 0.95 Pa. The resulting **MPC** for soil recalculated to dry weight for standard soil (10% o.m.) is **0.64 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **200 mg/kg$_{dw}$**.

4.2.2.3 Triethyl phosphate (TEP)

Only one terrestrial toxicity study is available for TEP for *Eisenia fetida* (Table A3.4). In this acute toxicity study, the LC50 was higher than 1000 mg/kg$_{dw}$. The NOEC for mortality in this 14-d study was 100 mg/kg$_{dw}$. Although no organic matter content is given, it is likely that this will be the same as in the study for tris(2-ethylhexyl) phosphate, also performed by Bayer AG, in which an OECD soil was used with 10% organic matter (Bayer AG, 1998). However, because this is an acute toxicity study, the use of this value is limited. Therefore, the ERLs have to be derived by equilibrium partitioning. The used log K_{oc} value for TEP of 1.56 was calculated from the log K_{ow} value (0.80). The Henry coefficient was experimentally determined by gas-stripping and is 0.0037 Pa·m^3/mol. The resulting **MPC** for soil recalculated to dry weight for standard soil (10% o.m.) is **4.1 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **270 mg/kg$_{dw}$**.

4.2.2.4 Tris (2-butoxyethyl) phosphate (TBEP)

No terrestrial toxicity data for TBEP are available. Therefore, the ERLs have to be derived by equilibrium partitioning. The used log K_{oc} value for TEBP of 3.01 was calculated from the experimental log K_{ow} value (3.75). The Henry coefficient was estimated from the experimental solubility of 1100 mg/L and vapour pressure of 2.8·10^{-5} Pa (GC-method). The resulting **MPC** for soil recalculated to dry weight for standard soil (10% o.m.) is **0.81 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **180 mg/kg$_{dw}$**.

4.2.2.5 Tris(2-ethylhexyl) phosphate (TEHP)

Only one terrestrial toxicity study is available for TEHP for *Eisenia fetida* (Table A3.5). In this acute toxicity study, the LC50 was higher than 1000 mg/kg$_{dw}$. The NOEC for weight loss in this 14-d study was 562 mg/kg$_{dw}$ in a soil with 10% organic matter. However, because this is an acute toxicity study, the use of this value is limited. Because no ERLs for water could be determined, the derivation of ERLs for soil by equilibrium partitioning is not possible. Therefore, no MPC and SRC$_{eco}$ for soil are derived.

4.2.3 Aryl phosphate esters

4.2.3.1 Triphenyl phosphate (TPP)

No terrestrial toxicity data for TPP are available. Therefore, the ERLs have to be derived by equilibrium partitioning. The experimental log K_{oc} value for TPP of 4.00 was used. The Henry coefficient was estimated from the experimental solubility of 1.9 mg/L and vapour pressure of $2.4 \cdot 10^{-3}$ Pa. The resulting **MPC** for soil recalculated to dry weight for standard soil (10% o.m.) was **0.095 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **35** mg/kg$_{dw}$.

4.2.3.2 Tricresyl phosphate (TCP)

No terrestrial toxicity data for TCP are available. Therefore, the ERLs have to be derived by equilibrium partitioning. The used log K_{oc} value for TCP of 3.67 was calculated from the experimental log K_{ow} value (5.11). The Henry coefficient was estimated from the experimental solubility of 0.34 mg/L (generator-column method) and vapour pressure of $6.6 \cdot 10^{-5}$ Pa. The resulting **MPC** for soil recalculated to dry weight for standard soil (10% o.m.) is **0.0089 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **8.6** mg/kg$_{dw}$.

4.3 Derivation of ERLs for sediment

No toxicity data for benthic organisms are available. Therefore, all environmental risk limits will be derived by equilibrium partitioning.

4.3.1 Halogenated phosphate esters

4.3.1.1 Tris (2-chloroethyl)phosphate (TCEP)

Similar to the MPC for water and soil, an MPC for soil will be derived when the EU-RAR is finalised and published. According to the TGD, equilibrium partitioning is applied using the characteristics of suspended matter. The derived **SRC$_{eco}$** for sediment, recalculated to dry weight, is **74 mg/kg$_{dw}$**.

4.3.1.2 Tris (2-chloro-1-methylethyl) phosphate (TCPP)

Similar to the MPC for water and soil, an MPC for soil will be derived when the EU-RAR is finalised and published. According to the TGD, equilibrium partitioning is applied using the characteristics of suspended matter. The derived **SRC$_{eco}$** for sediment, recalculated to dry weight, is **230 mg/kg$_{dw}$**.

4.3.1.3 Tris (1,3-dichloro-2-propyl) phosphate (TDCP)

Similar to the MPC for water and soil, an MPC for soil will be derived when the EU-RAR is finalised and published. According to the TGD, equilibrium partitioning is applied using the characteristics of suspended matter. The derived **SRC$_{eco}$** for sediment, recalculated to dry weight, is **380 mg/kg$_{dw}$**.

4.3.2 Alkyl phosphate esters

4.3.2.1 Tri-n-butyl phosphate (TBP)

Similar to soil, the ERLs are derived by equilibrium partitioning with the same log K_{oc} value of 3.13. The resulting **MPC** for sediment recalculated to dry weight for standard sediment (10% o.m.) is **5.4 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **90 mg/kg$_{dw}$**.

4.3.2.2 Tris(2-methylpropyl) phosphate (TiBP)
Similar to soil, the ERLs are derived by equilibrium partitioning with the same log K_{oc} value of 2.99. The resulting **MPC** for sediment recalculated to dry weight for standard sediment (10% o.m.) is **0.66 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **200 mg/kg$_{dw}$**.

4.3.2.3 Triethyl phosphate (TEP)
Similar to soil, the ERLs are derived by equilibrium partitioning with the same log K_{oc} value of 1.56. The resulting **MPC** for sediment recalculated to dry weight for standard sediment (10% o.m.) is **6.8 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **460 mg/kg$_{dw}$**.

4.3.2.4 Tris (2-butoxyethyl) phosphate (TBEP)
Similar to soil, the ERLs are derived by equilibrium partitioning with the same log K_{oc} value of 3.01. The resulting **MPC** for sediment recalculated to dry weight for standard sediment (10% o.m.) is **0.83 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **180 mg/kg$_{dw}$**.

4.3.2.5 Tris(2-ethylhexyl) phosphate (TEHP)
Because no ERLs for water could be determined, the derivation of ERLs for sediment by equilibrium partitioning is not possible. Therefore, no MPC and SRC$_{eco}$ for sediment are derived.

4.3.3 Aryl phosphate esters
4.3.3.1 Triphenyl phosphate (TPP)
Similar to soil, the ERLs are derived by equilibrium partitioning with the same log K_{oc} value of 4.00. The resulting **MPC** for sediment recalculated to dry weight for standard sediment (10% o.m.) is **0.095 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **35 mg/kg$_{dw}$**.

4.3.3.2 Tricresyl phosphate (TCP)
Similar to soil, the ERLs are derived by equilibrium partitioning with the same log K_{oc} value of 3.67. The resulting **MPC** for sediment recalculated to dry weight for standard sediment (10% o.m.) is **0.0090 mg/kg$_{dw}$**. The corresponding **SRC$_{eco}$** is **8.6 mg/kg$_{dw}$**.

4.4 Summary of derived ERLs
The derived ERLs for water, sediment, and soil are that were derived are summarised below. In Table 13 the derived risk limits for water are reported. For the calculation of the total concentration in water, 30 mg/L for the concentration of suspended solids in water, consisting for 20% of organic matter. These values are the standard values within the framework of INS (Traas, 2001). The values for marine water (only dissolved) are all 1/10th of the values for fresh water. Due to the absence of suitable toxicity data, no ERLs have been derived for TEHP.
In Table 14, the derived risk limits for soil and sediment are presented. The data are normalised to an organic matter content of 10%. This is the standard organic matter content for soil and sediment within the framework of INS (Traas, 2001).

Table 13. Environmental risk limits for phosphate esters in water.

	$SRC_{eco, dissolved}$ [mg/L]	$SRC_{eco, total}$ [mg/L]	$MPC_{dissolved}$ [µg/L]	AF	MPC_{total} [µg/L]	$NC_{dissolved}$ [µg/L]	NC_{total} [µg/L]
TCEP	8.6	8.6	[a]		[a]	[a]	[a]
TCPP	6.5	6.5	[a]		[a]	[a]	[a]
TDCP	0.52	0.54	[a]		[a]	[a]	[a]
TBP	1.1	1.1	66	10	66	0.66	0.66
TiBP	3.4	3.4	11	1000	11	0.11	0.11
TEP	110	110	1600	50	1600	16	16
TBEP	2.9	2.9	13	1000	13	0.13	0.13
TPP	0.060	0.062	0.16	100	0.17	0.0016	0.0017
TCP	0.031	0.031	0.032	10	0.033	0.00032	0.00033

Notes
a: MPC and NC to be derived when the EU-RAR is published

Table 14. Environmental risk limits for phosphate esters in soil and sediment.

	$SRC_{eco, soil}$ [mg/kg_{dw}]	MPC_{soil} [$µg/kg_{dw}$]	NC_{soil} [$µg/kg_{dw}$]	$SRC_{eco, sediment}$ [mg/kg_{dw}]	$MPC_{sediment}$ [$µg/kg_{dw}$]	$NC_{sediment}$ [$µg/kg_{dw}$]
TCEP	28 [a]	[b]	[b]	74	[b]	[b]
TCPP	9.7 [a]	[b]	[b]	230	[b]	[b]
TDCP	13 [a]	[b]	[b]	380	[b]	[b]
TBP	88	5300	53	90	5400	54
TiBP	200	640	6.4	200	660	6.6
TEP	270	4100	41	460	6800	68
TBEP	180	810	8.1	180	830	8.3
TPP	35	95	0.95	35	95	0.95
TCP	8.6	8.9	0.089	8.6	9.0	0.090

Notes
a: derived from terrestrial toxicity data
b: MPC and NC to be derived when the EU-RAR is published

5. Preliminary risk analysis

The data that were found for the Dutch environment date back to before 1990. In 1974, TCEP was found in the Dutch river Waal (IPCS, 1998). In 1979, TCEP was detected in water from the River Rhine at Lobith in the Netherlands at a level of 1 µg/L and at lower levels from 0.16 to 0.35 µg/L in 1986. In 1989 samples were taken at several points in the Rhine delta (Hendriks et al., 1994). After sedimentation of suspended matter, the organic matter in the water was extracted with XAD resin. The compounds that were reported were TEP, TDCP (with possible interference of TCPP), and TCEP. The concentration ranges from not detected to 0.422 µg/L for TEP, from not detected to 0.055 for TDCP, and from 0.048 to 0.172 µg/L for TCEP (Table 15).

Table 15. Monitoring data from the Rhine delta in 1989 (Hendriks et al., 1994).

Compound	Location	Date	Concentration [µg/L]
TCEP	Markermeer	24/01/1989	0.05
TCEP	Kampen	21/04/1989	0.056
TCEP	Lobith	17/03/1989	0.129
TCEP	Lobith	15/09/1989	0.056
TCEP	Werkendam	29/09/1989	0.172
TCEP	Maassluis	26/05/1989	0.067
TCEP	Maassluis	22/09/1989	0.092
TCEP	Haringvliet	19/05/1989	0.048
TDCP	Markermeer	24/01/1989	0
TDCP	Kampen	21/04/1989	0
TDCP	Lobith	17/03/1989	0
TDCP	Lobith	15/09/1989	0
TDCP	Werkendam	29/09/1989	0.038/0.055
TDCP	Maassluis	26/05/1989	0.024
TDCP	Maassluis	22/09/1989	0.026
TDCP	Haringvliet	19/05/1989	0.025
TEP	Markermeer	24/01/1989	0.079
TEP	Kampen	21/04/1989	0.042
TEP	Lobith	17/03/1989	0
TEP	Lobith	15/09/1989	0.077
TEP	Werkendam	29/09/1989	0
TEP	Maassluis	26/05/1989	0.422
TEP	Maassluis	22/09/1989	0.079
TEP	Haringvliet	19/05/1989	0.05

More recent monitoring data are available for several of the phosphate esters. From data for the river Meuse and tributaries in 2002/2003 (see Table 16) it appears that the concentration of TCEP in the river Meuse at Keizersveer itself is much higher than in the tributaries Dieze and Niers (Jeuken and Barreveld, 2004). Concentrations of TCEP in water from the river Lek in 2002 (Table 17) show similar concentrations as those in the Meuse (RIWA, 2003). Concentrations of TCEP in STP effluents that discharge into the river Meuse have much higher concentrations (Berbee et al., 2004). The concentrations of TCEP in STP effluents in Friesland is similar to that in the STP effluents discharging into the river Meuse (Berbee et al., 2004). From a comparison of concentrations of TCEP in surface water in 1989 (Table 15) with the concentrations in 2002 (Table 16 and Table 17), it can be concluded that the concentrations of TCEP remained relatively constant over the period of 13 years. Concentrations of TDCP from STP effluents in 2002/2003 (Table 16) were in the same order of magnitude as concentrations in surface water in 1989 (Table 15). Maximum concentrations

of TEBP from STP effluents in 2003 (Table 16) were higher than concentrations in surface water in 2002/2003 (Table 16 and Table 17).
For TCPP, TBP, and TPP more monitoring data are available from the internet-database Waterbase (V&W,). The concentrations of TCPP at Amsterdam, Belfeld, Eemmeerdijk, Eijsden, Haringvlietsluit, IJmuiden, Lobith, Maassluis, Schaar van Ouden Doel, and Steenbergen in 2002 and 2003 were all lower than the detection limit of 5 µg/L. However, this limit seems rather high and lower have been reported. The average values are 1.93 µg/L in the effluents of STPs discharging into the river Meuse (Table 16) and 0.27 and 0.55 µg/L for two isomers in water of from the river Lek (Table 17). The 90th percentiles were 0.07 µg/L in the river Roer (tributary of the river Meuse) in 2002/2003 (Table 16) and 0.31 and 0.61 µg/L for two isomers in water of from the river Lek at Nieuwegein in 2002 (Table 17).
The concentrations of TBP at seven of the sixteen locations were always below the detection limit of 0.1 µg/L at all sampling times (Table 18). The highest average concentrations in the period 2002-2004 are found at two locations in the river Meuse (Eijsden and Belfeld). At both locations highest average and maximum concentrations were found in 2004. Although the concentrations at Nieuwegein in 2002 (Table 17) are similar to the concentrations in Belfeld in 2002 and 2003, the concentrations in 2004 were below the detection limit as well (Table 18). The concentrations in effluents to STP (Table 16) are higher than these concentrations in surface waters. However, the average (0.93 µg/L) and maximum (4.5 µg/L) of the concentrations measured at Eijsden in 2004 (Table 18) approach those of the effluents (1.11 and 6.48 µg/L, respectively).

Table 16. Monitoring data for several phosphate ester in the river Meuse and tributaries (data from Jeuken and Barreveld (2004)) and discharging effluents in comparison with effluents in Friesland (data from Berbee et al. *(2004)).*

Compound	Location	Date	Max [µg/L]	90th P [µg/L]	Avg [µg/L]	Med [µg/L]	Min [µg/L]
TCEP	STP effluents (5) Meuse basin	12/2002-3/2003	0.83		0.42	0.58	
TCEP	STP effluents Friesland (NL)	end of the 90s	0.6				
TCEP	Keizersveer	3/2002-2/2003		0.14			
TCEP	Dieze	3/2002-2/2003		0.01			
TCEP	Niers	3/2002-2/2003		0.02			
TCPP	STP effluents (5) Meuse basin	12/2002-3/2003	4.2		1.93	1.57	0.11
TCPP	Roer	3/2002-2/2003		0.07			
TDCP	STP effluents (5) Meuse basin	12/2002-3/2003	0.45				0.15
TBP	STP effluents (5) Meuse basin	12/2002-3/2003	6.48		1.11	0.16	0.01
TBP	STP effluents Friesland (NL)	end of the 90s	8				
TBP	River Meuse (6 locations)	3/2002-2/2003	7.21				
TBEP	STP effluents (5) Meuse basin	12/2002-3/2003	1.12				0.05
TBEP	STP effluents Friesland (NL)	end of the 90s	2				

Table 17. Monitoring data for several phosphate ester near the river Lek at Nieuwegein (data from RIWA (2003))

Compound	Location	Date	Max [µg/L]	90th P [µg/L]	Avg [µg/L]	10th P [µg/L]	Min [µg/L]
TCEP	Nieuwegein	4/2002-6/2002	0.24	0.20	0.14	0.11	0.11
TCPP 1st isomer	Nieuwegein	4/2002-6/2002	1.72	0.31	0.27	0.09	0.05
TCPP 2nd isomer	Nieuwegein	4/2002-6/2002	0.62	0.61	0.55	0.49	0.48
TEP	Nieuwegein	4/2002-6/2002	0.44	0.25	0.16	0.10	0.10
TBP	Nieuwegein	4/2002-6/2002	0.51	0.44	0.24	0.09	0.05
TiBP	Nieuwegein	4/2002-6/2002	0.15	0.15	0.12	0.10	0.09
TBEP	Nieuwegein	4/2002-6/2002	0.40	0.32	0.22	0.17	0.16

*Table 18. Monitoring data for tri-*n*-butyl phosphate (TBP) at several places in the Netherlands in the period 1999-2004 (data from Waterbase (V&W,)).*

Location	Date	Max [µg/L]	90th P [µg/L]	Avg [µg/L]	Med [µg/L]	Min [µg/L]
Amsterdam km 25	2002	<0.1	<0.1	<0.1	<0.1	<0.1
Amsterdam km 25	2003	<0.1	<0.1	<0.1	<0.1	<0.1
Amsterdam km 25	2004	<0.1	<0.1	<0.1	<0.1	<0.1
Belfeld boven	2002	0.72	0.52	0.23	0.14	<0.1
Belfeld boven	2003	0.56	0.29	0.14	<0.1	<0.1
Belfeld boven	2004	3.8	0.68	0.49	0.19	<0.1
Eemmeerdijk km 23	2002	<0.1	<0.1	<0.1	<0.1	<0.1
Eemmeerdijk km 23	2003	<0.1	<0.1	<0.1	<0.1	<0.1
Eemmeerdijk km 23	2004	<0.1	<0.1	<0.1	<0.1	<0.1
Eijsden ponton	2002	2.7	1.2	0.48	0.25	<0.1
Eijsden ponton	2003	2.6	0.58	0.39	0.15	<0.1
Eijsden ponton	2004	4.5	2.4	0.93	0.6	<0.1
Haringvlietsluis	2002	0.13	<0.1	<0.1	<0.1	<0.1
Haringvlietsluis	2003	0.13	<0.1	<0.1	<0.1	<0.1
Haringvlietsluis	2004	0.12	0.12	<0.1	<0.1	<0.1
IJmuiden km 2	2002	0.34	0.32	0.13	<0.1	<0.1
IJmuiden km 2	2003	0.13	<0.1	<0.1	<0.1	<0.1
IJmuiden km 2	2004	0.21	0.17	<0.1	<0.1	<0.1
Lobith ponton	2002	0.11	<0.1	<0.1	<0.1	<0.1
Lobith ponton	2003	0.11	<0.1	<0.1	<0.1	<0.1
Lobith ponton	2004	<0.1	<0.1	<0.1	<0.1	<0.1
Maassluis	2002	0.37	<0.1	<0.1	<0.1	<0.1
Maassluis	2003	<0.1	<0.1	<0.1	<0.1	<0.1
Maassluis	2004	0.13	<0.1	<0.1	<0.1	<0.1
Schaar van Ouden Doel	2002	0.16	0.12	<0.1	<0.1	<0.1
Schaar van Ouden Doel	2003	0.22	0.13	<0.1	<0.1	<0.1
Schaar van Ouden Doel	2004	0.25	<0.1	<0.1	<0.1	<0.1
Steenbergen	2002	<0.1	<0.1	<0.1	<0.1	<0.1
Steenbergen	2003	<0.1	<0.1	<0.1	<0.1	<0.1
Steenbergen	2004	<0.1	<0.1	<0.1	<0.1	<0.1
Brienenoord km 996.5	2004	<0.1	<0.1	<0.1	<0.1	<0.1
Keizersveer	2004	0.21	0.18	<0.1	<0.1	<0.1
Ketelmeer west	2004	<0.1	<0.1	<0.1	<0.1	<0.1
Nieuwegein	2004	<0.1	<0.1	<0.1	<0.1	<0.1
Puttershoek	2004	<0.1	<0.1	<0.1	<0.1	<0.1
Vrouwenzand	2004	0.13	<0.1	<0.1	<0.1	<0.1

The concentrations of triphenyl phosphate are highest at Steenbergen. The maximum concentrations found was 0.99 µg/L in 1999. For all locations and dates except one the median of the concentrations is below the detection limit of 0.05 µg/L. This means that in more than half of the samples TPP is not detected. Only in Eijsden in 2003, TPP was measured in 9 of the 13 samples. Only for a few locations, maximum concentrations exceed the concentration of 0.1 µg/L. These location are Eijsden, IJmuiden, Steenbergen, and Schaar van Ouden Doel.
When the reported concentrations are compared with the derived risk limits, it can be concluded that for TEP the reported concentrations do not exceed any of the risk limits. For the chlorinated TCEP, TCPP, and TDCP no MPCs and NCs are derived until the EU RARs are published, but for these compounds the NC will probably lie in the range of measured concentrations, but might be exceeded. However, concentrations remain well below the MPC. This is also true for the alkyl phosphate esters TBP, TiBP and TEBP. Only for TPP the measured concentrations might exceed the MPC of 0.17 µg/L as well. A comparison with the

NC is difficult for TPP, because the detection limit is 0.05 µg/L, only three times lower than the MPC.

Table 19. Monitoring data for triphenyl phosphate (TPP) at several places in the Netherlands in the period 1999-2004 (data from Waterbase (V&W,)).

Location	Date	Max [µg/L]	90^{th} P [µg/L]	Avg [µg/L]	Med [µg/L]	Min [µg/L]
Amsterdam km 25	1999	<0.05	<0.05	<0.05	<0.05	<0.05
Amsterdam km 25	2000	0.05	<0.05	<0.05	<0.05	<0.05
Amsterdam km 25	2001	<0.05	<0.05	<0.05	<0.05	<0.05
Amsterdam km 25	2002	<0.05	<0.05	<0.05	<0.05	<0.05
Amsterdam km 25	2003	<0.05	<0.05	<0.05	<0.05	<0.05
Belfeld boven	2002	0.06	<0.05	<0.05	<0.05	<0.05
Belfeld boven	2003	0.08	<0.05	<0.05	<0.05	<0.05
Eemmeerdijk km 23	2002	<0.05	<0.05	<0.05	<0.05	<0.05
Eemmeerdijk km 23	2003	0.05	<0.05	<0.05	<0.05	<0.05
Eijsden ponton	2002	0.21	0.08	<0.05	<0.05	<0.05
Eijsden ponton	2003	0.15	0.14	0.07	0.06	<0.05
Haringvlietsluis	1999	0.09	0.05	<0.05	<0.05	<0.05
Haringvlietsluis	2000	<0.05	<0.05	<0.05	<0.05	<0.05
Haringvlietsluis	2001	<0.05	<0.05	<0.05	<0.05	<0.05
Haringvlietsluis	2002	<0.05	<0.05	<0.05	<0.05	<0.05
Haringvlietsluis	2003	<0.05	<0.05	<0.05	<0.05	<0.05
IJmuiden km2	1999	<0.05	<0.05	<0.05	<0.05	<0.05
IJmuiden km2	2000	0.15	0.08	<0.05	<0.05	<0.05
IJmuiden km2	2001	<0.05	<0.05	<0.05	<0.05	<0.05
IJmuiden km2	2002	<0.05	<0.05	<0.05	<0.05	<0.05
IJmuiden km2	2003	0.1	0.06	<0.05	<0.05	<0.05
Lobith ponton	2002	<0.05	<0.05	<0.05	<0.05	<0.05
Lobith ponton	2003	<0.05	<0.05	<0.05	<0.05	<0.05
Maassluis	2002	<0.05	<0.05	<0.05	<0.05	<0.05
Maassluis	2003	0.09	<0.05	<0.05	<0.05	<0.05
Schaar van Ouden Doel	2002	0.13	0.12	0.05	<0.05	<0.05
Schaar van Ouden Doel	2003	0.09	0.07	<0.05	<0.05	<0.05
Steenbergen (Roosendaalse Vliet)	1999	0.99	0.63	0.23	<0.05	<0.05
Steenbergen (Roosendaalse Vliet)	2000	0.07	<0.05	<0.05	<0.05	<0.05
Steenbergen (Roosendaalse Vliet)	2001	0.14	0.11	0.06	<0.05	<0.05
Steenbergen (Roosendaalse Vliet)	2002	0.06	<0.05	<0.05	<0.05	<0.05
Steenbergen (Roosendaalse Vliet)	2003	0.1	0.08	<0.05	<0.05	<0.05

6. Conclusions and recommendations

In this report environmental risk limits were derived for some phosphate esters, of which several are used as flame retardants. Within the framework of INS these compounds were not regarded yet, and consequently no comparison with former ERLs can be made. In general the number of aquatic toxicity data was sufficient to derive environmental risk limits. However, many of the data had to be retrieved from summaries from IUCLID (European Commission, 2000) or other secondary sources. Otherwise, the number of data would be very limited. Only for two compounds, an assessment factor of 10 could be used to derive the MPCs. In all other cases, chronic toxicity data were not available for all three trophic levels. For TEHP the number of suitable data was insufficient to derive ERLs. This fact is probably connected with the fact that the toxicity of this compounds is limited by its aqueous solubility. For TCEP, TCPP, and TDCP no MPCs and NCs were derived. These values are derived when the final EU RAR on these substances are finished with the PNEC as basis for the MPC.
For soil and sediment, the number of toxicity data was very limited. For TCEP, TCPP, TDCP, TEP, and TEHP terrestrial studies were retrieved. However, for TEP and TEHP these studies showed no suitable endpoint with no acute toxicity and only NOECs from an acute study. Therefore, for all these compounds the ERLs for soil are derived by equilibrium partitioning as well. For the three chlorinated phosphate esters, for which no MPC and NC are derived pending the publication of the final EU RAR on these substances, the terrestrial toxicity data lead to lower SRC_{eco} values than those derived by equilibrium partitioning. For benthic organisms no data were found for any of the compounds. It can be concluded that data for terrestrial and benthic organisms would be useful to get more insight in the vulnerability of species in these compartments.
Monitoring data for the phosphate esters in the Netherlands are scarce and only for a few compounds. Moreover, the data date back from before 1990. From these data it can be concluded that the compounds do not pose a direct risk for the aquatic environment. However, the studied compounds were not the most toxic among the studied phosphate esters and the concentrations at present are unknown. Therefore, it would be useful to have new monitoring data available, covering all studied compounds.

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Appendix 1. Selected toxicity data used for derivation of ERLs

Legend
NOEC/EC10 refers to chronic toxicity data
E(L)C50 refers to acute toxicity data

Table A1.1. Selected toxicity data for tris(2-chloroethyl)phosphate (TCEP) to freshwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
Algae	5	Algae	117
Algae	9.8 [a]	Algae	51 [b]
Crustacea	13	Crustacea	330 [c]
		Crustacea	1000
		Pisces	90
		Pisces	200
		Pisces	249
		Pisces	190 [d]
		Platyhelminthes	158

Notes
a: Geometric mean of 0.65 and 148 mg/L for *Scenedesmus subspicatus*
b: Geometric mean of 5.0 and 522 mg/L for *Scenedesmus subspicatus*
c: Geometric mean of 451, 340 and 235 mg/L for *Daphnia magna*
d: Geometric mean of 210 and 170 mg/L for *Oryzias latipes* exposed for 96 h between 20 and 25 ºC

Table A1.2. Selected toxicity data for tris(2-chloroethyl)phosphate (TCEP) to terrestrial species

Taxonomic group	NOEC/EC10 [mg/kg_{dw}]	Taxonomic group	E(L)C50 [mg/kg_{dw}]
Insecta	160	Macrophyta	279
Microbial activity	28		

Table A1.3. Selected toxicity data for tris(2-chloro-1-methylethyl)phosphate (TCPP) to freshwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
Algae	6	Algae	73
Crustacea	32	Algae	45
		Crustacea	91 [a]
		Pisces	56
		Pisces	84
		Pisces	54
		Pisces	51
		Pisces	30

Notes
a: Geometric mean of 63 and 131 mg/L for *Daphnia magna*

Table A1.4. Selected toxicity data for tris(2-chloro-1-methylethyl)phosphate (TCPP) to saltwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
		Bacteria	172

Table A1.5. Selected toxicity data for tris(2-chloro-1-methylethyl)phosphate (TCPP) to terrestrial species

Taxonomic group	NOEC/EC10 [mg/kg_{dw}]	Taxonomic group	E(L)C50 [mg/kg_{dw}]
Annelida	53	Annelida	97
Macrophyta	157		
Macrophyta	207		
Macrophyta	121		

Table A1.6. Selected toxicity data for tris(2-chloro-1-(chloromethyl)ethyl)phosphate (TDCP) to freshwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
Algae	6	Algae	39
		Crustacea	4.2 [a]
		Pisces	5.1
		Pisces	1.2 [b]
		Pisces	3.6 [c]

Notes
a: Geometric mean of 3.8 and 4.6 mg/L for *Daphnia magna*
b: Geometric mean of 1.4 and 1.1 mg/L for *Oncorhynchus mykiss*
c: Geometric mean of 3.7 and 3.6 mg/L for *Oryzias latipes*

Table A1.7. Selected toxicity data for tris(2-chloro-1-(chloromethyl)ethyl)phosphate (TDCP) to terrestrial species

Taxonomic group	NOEC/EC10 [mg/kg_{dw}]	Taxonomic group	E(L)C50 [mg/kg_{dw}]
		Annelida	130

Table A1.8. Selected toxicity data for tris(n-butyl)phosphate (TBP) to freshwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
Algae	4.7	Algae	25
Algae	3.2	Algae	58
Algae	0.66	Algae	4.4
Algae	2.2	Algae	4.2
Crustacea	1.4 [a]	Crustacea	3.65 [b]
Pisces	13.5	Crustacea	68
Pisces	8.3	Crustacea	1.7
Cyanophyta	4.1	Crustacea	2.4
Protozoa	42	Crustacea	63
Protozoa	14	Crustacea	34.6
Protozoa	21	Crustacea	32.8
Rotifera	6.4	Crustacea	21.8
		Pisces	11.4

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
		Pisces	8.8
		Pisces	7.6
		Pisces	8.3 [c]
		Pisces	13 [d]
		Pisces	6.6 [e]
		Platyhelminthes	4
		Protozoa	20

Notes
a: Geometric mean of 1.3, 0.73 and 3 mg/L for *Daphnia magna*
b: Only value for *Daphnia magna* with the standard exposure time of 48 hours
c: Geometric mean of all values for *Oncorhynchus mykiss* with the standard exposure time of 96 hours, but with different ages of fish and different temperatures (13, 9.4, 11.8, 8.2, 4.2, and geometric mean of 5 and 9).
d: Geometric mean of 9.6 and 17 mg/L for *Oryzias latipes*
e: Geometric mean of 11, 8.18, and the geometric mean of 1 and 10 mg/L for *Pimephales promelas*

Table A1.9. Selected toxicity data for tris(n-butyl)phosphate (TBP) to saltwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
Bacteria	2.62	Bacteria	80.7
		Crustacea	54.6

Table A1.10. Selected toxicity data for tris(isobutyl)phosphate (TiBP) to freshwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
Algae	25	Algae	34
		Crustacea	11
		Pisces	20 [a]
		Pisces	23
		Pisces	20
		Bacteria	440

Notes
Geometric mean of 17.8 and 21.5 for *Leuciscus idus*

Table A1.11. Selected toxicity data for tris(isobutyl)phosphate (TiBP) to saltwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
		Bacteria	129

Table A1.12. Selected toxicity data for triethyl phosphate (TEP) to freshwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
Algae	80.3	Algae	900
Crustacea	190	Crustacea	350 [a]
		Pisces	2140

Notes
a: Only value for *Daphnia magna* with the standard exposure time of 48 hours

Table A1.13. Selected toxicity data for triethyl phosphate (TEP) to saltwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
		Crustacea	950
		Pisces	2200 [a]

Notes
a: Geometric mean of 2100 and 2400 mg/L for *Alburnus alburnus*

Table A1.14. Selected toxicity data for tris(2-butoxyethyl)phosphate (TBEP) to freshwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
		Crustacea	75
		Pisces	24
		Pisces	30 [a]
		Pisces	13 [b]

Notes
a: Only value for *Oryzias latipes* with the standard exposure time of 96 hours and normal temperature of 20 ºC
b: Geometric mean of 11.2 and 16 mg/L for *Pimephales promelas*

Table A1.15. Selected toxicity data for triphenyl phosphate (TPP) to freshwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
Algae	0.016 [a]	Algae	0.57 [a]
Algae	1	Algae	1.0 [e]
Algae	0.46 [b]	Algae	0.5
Algae	0.37 [c]	Crustacea	1.1 [f]
Pisces	0.037	Crustacea	0.25
Pisces	0.087	Pisces	0.70
Cyanophyta	0.076	Pisces	0.42
		Pisces	0.78
		Pisces	0.42 [g]
		Pisces	1.2
		Pisces	0.83 [h]
		Insecta	0.36
		Insecta	1.60

Notes
a: EC10 and EC50 for the growth rate determined from primary productivity experiment with *Ankistrodesmus falcatus*
b: Geometric mean of 0.53 and 0.40 mg/L determined for EC10 of the growth rate of *Pseudokirchneriella subcapitata* exposed for 72 h in two different growth media
c: Geometric mean of 0.1, 1, and 0.5 mg/L for the NOEC for the growth rate and area under the curve for *Scenedesmus subspicatus* exposed for 72 h in three different growth media
d: EC50 for primary productivity of *Ankistrodesmus falcatus*
e: Geometric mean of 1.0 and 1.1 mg/L determined for EC50 of the growth rate of *Pseudokirchneriella subcapitata* exposed for 72 h in two different growth media
f: Geometric mean of 1.35, 1.0, and 1.0 mg/L for *Daphnia magna*
g: Geometric mean of 0.37, 0.4, 0.85, 0.32, and 0.31 mg/L for mortality of *Oncorhynchus mykiss* varying from sac-fry to 45 d
h: Geometric mean of 0.87, 1.0, and 0.66 mg/L for *Pimephales promelas*

Table A1.16. Selected toxicity data for triphenyl phosphate (TPP) to saltwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
		Crustacea	0.24 [a]
		Pisces	0.42 [b]

Notes
a: Geometric mean of 0.18 and 0.32 mg/L for *Mysidopsis bahia*
b: Geometric mean of 0.32 and 0.56 mg/L for *Cyprinodon variegatus*

Table A1.17. Selected toxicity data for tricresyl phosphate (TCP) to freshwater species

Taxonomic group	NOEC/EC10 [mg/L]	Taxonomic group	E(L)C50 [mg/L]
Algae	0.052 [a]	Algae	0.29
Algae	0.42 [b]	Crustacea	0.27 [d]
Algae	0.056	Pisces	0.40 [e]
Crustacea	0.1	Pisces	0.80
Pisces	0.0072 [c]	Pisces	0.44
Pisces	0.00032	Pisces	0.11 [f]
Pisces	0.01	Pisces	0.43 [g]
Pisces	0.9	Pisces	0.50
Pisces	0.01		

Notes
a: Geometric mean 0.029 and 0.094 mg/L for the EC10 for the growth rate determined from primary productivity experiment with *Ankistrodesmus falcatus* to respectively the *ortho* and the *meta* isomer
b: Geometric mean of 0.32 and 0.56 mg/L for *Scenedesmus pannonicus*
c: Geometric mean of 0.018, 0.0056, 0.0056, 0.0056, 0.01, 0.01, and 0.0032 for the NOEC for mortality of *Brachydanio rerio* in an ELS test
d: Only value for immobility of *Daphnia magna* below the aqueous solubility
e: Only value for mortality of *Brachydanio rerio* (1-2 d) below the aqueous solubility
f: Geometric mean of 0.15 and 0.082 mg/L for mortality of *Lepomis macrochirus* in water with different hardness
g: Geometric mean of 0.26, 0.40, and 0.75 mg/L for mortality of *Oncorhynchus mykiss*

Appendix 2. Aquatic toxicity data

Legend

Species	species used in the test, if available followed by age, size, weight or life stage
Analysed	Y = test substance analysed in test solution N = test substance not analysed in test solution or no data
Test type	S = static, Sc = static with closed test vessels, R = static with renewal, F = flow through
Substance purity	percentage active ingredient, or chemical grade of purity.
Hardness/salinity	freshwater: hardness expressed as mg $CaCO_3$/L saltwater: salinity expressed in ‰
Test water	am = artificial medium, dtw = dechlorinated tap water, dw = dechlorinated water, nw = natural water, rw = reconstituted water (+additional salts), tw = tap water
Exposure time	h = hours, d = days, w = weeks, m = months, min. = minutes
Criterion	L(E)Cx = test result showing x% mortality (LCx) of effect (ECx). LC50s and EC50s are usually determined for acute effects, EC10s are for chronic effects; NOEC = no observed effect concentration, statistically determined

Table A2.1. Acute toxicity data for tris(2-chloroethyl)phosphate (TCEP) to freshwater organisms. All data are from the draft EU-RAR (European Commission, 2004c). Additional information on the tests was retrieved from IUCLID (European Commission, 2000) , EHC 209 (IPCS, 1998) and BUA 20 (GDCh, 1987)

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Algae														
Pseudokirchneriella subcapitata	-	N	-	-	-	-	-		96 h	EC50	growth rate	117		Akzo Chemicals (1992)
Pseudokirchneriella subcapitata	-	N	-	-	-	-	-		96 h	EC50	biomass	38		Akzo Chemicals (1992)
Scenedesmus subspicatus	-	-	-	-	-	8	-		48 h	EC50	biomass	2		Kühn et al. (1989)
Scenedesmus subspicatus	-	-	-	-	-	8	-		72 h	EC50	biomass	1.1	a	Kühn et al. (1989)
Scenedesmus subspicatus	-	-	-	-	-	8	-		96 h	EC50	biomass	1.2	a	Kühn et al. (1989)
Scenedesmus subspicatus	-	-	-	-	-	8	-		48 h	EC50	growth rate	5.0		Kühn et al. (1989)
Scenedesmus subspicatus	-	-	-	-	-	8	-		72 h	EC50	growth rate	3.6	a	Kühn et al. (1989)
Scenedesmus subspicatus	-	Y	-	-	-	7.5	-		72 h	EC50	biomass	271	b	Hoechst AG (1988)
Scenedesmus subspicatus	-	Y	-	-	-	7.5	-		72 h	EC50	biomass	278	b	Hoechst AG (1988)
Scenedesmus subspicatus	-	-	-	-	-	8	-		72 h	EC50	growth rate	522	c	Nyholm & Kusk (2003)
Scenedesmus subspicatus	-	-	-	-	-	-	-		-	EC50	-	67.9	d	Akzo Chemicals (1993)
Scenedesmus subspicatus	-	-	-	-	-	-	-		72 h	EC50	-	1.1	d	Akzo Chemicals (1993)
Crustacea														
Daphnia magna	-	-	-	-	-	-	-		24 h	EC0	mobility	186		Kühn et al. (1989)
Daphnia magna	-	-	-	-	-	-	-		24 h	EC50	mobility	451		Kühn et al. (1989)
Daphnia magna	-	Y	-	-	-	-	-		24 h	EC0	mobility	100		Hoechst AG (1989)
Daphnia magna	-	Y	-	-	-	-	-		24 h	EC50	mobility	340		Hoechst AG (1989)
Daphnia magna	-	Y	-	-	-	-	-		24 h	EC100	mobility	1000		Hoechst AG (1989)
Daphnia magna	-	-	-	-	-	-	-		24 h	EC50	mobility	235		Bayer AG (1991)
Moina macropoda	5 d	N	S	-	am	-	-	20±1	3h	LC50	mortality	1000	e	Yoshioka et al. (1986a)
Pisces														
Carassius auratus	3 inch	N	S					20	7 d	LC0	mortality	5		Eldefrawi et al. (1977)
Carassius auratus	0.8-2.8 g	N	S	-	dtw	-	-	25	96 h	LC50	mortality	90		Sasaki et al. (1981)
Leuciscus idus melanotus		-	S	-	-	-	-		48 h	LC0	mortality	ca. 100		Hoechst AG (1978)
Leuciscus idus melanotus		-	S	-	-	-	-		48 h	LC50	mortality	ca. 200		Hoechst AG (1978)
Leuciscus idus melanotus		-	S	-	-	-	-		48 h	LC100	mortality	300		Hoechst AG (1978)
Oncorhynchus mykiss	-	N	S	-	-	7.49-8.52	198-204	13.8-14.8	96 h	LC0	mortality	100		Akzo Chemicals (1990b)
Oncorhynchus mykiss	-	N	S	-	-	7.49-8.52	198-204	13.8-14.8	96 h	LC50	mortality	249		Akzo Chemicals (1990b)
Oncorhynchus mykiss	-	N	S	-	-	7.49-8.52	198-204	13.8-14.8	96 h	LC100	mortality	400		Akzo Chemicals (1990b)
Oryzias latipes	-	N	R	-	-	-	-		48 h	LC50	mortality	300		CITI (1992)
Oryzias latipes	0.1-0.2 g	N	S	-	dtw	-	-	25	96 h	LC50	mortality	210		Sasaki et al. (1981)
Oryzias latipes	2 cm, 0.2 g	N	S	-		7.2	40	10	48 h	LC50	mortality	230		Tsuji et al. (1986)

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Oryzias latipes	2 cm, 0.2 g	N	S	-		7.2	40	20	48 h	LC50	mortality	190		Tsuji et al. (1986)
Oryzias latipes	2 cm, 0.2 g	N	S	-		7.2	40	30	48 h	LC50	mortality	66		Tsuji et al. (1986)
Oryzias latipes	-	N	R	-	dtw	7.2	40	20±1	96 h	LC50	mortality	170		Yoshioka & Ose (1993)
Platyhelminthes														
Dugesia japonica	-	N	S	-	am	~7	-	20±1	7d	LC50/ EC50	mortality / regeneration	158	e	Yoshioka et al. (1986a)

Notes

a: Between day 2 and day 3 the pH increased from 8 to 9.4.

b: Two separate tests.

c: This is a recalculation of the results by Hoechst AG (1988).

d: No original data or reference given. Probably one of the numbers is the same study as that from Kühn et al. (1989).

e: In this study the compound trichloroethyl phosphate is mentioned. In the EU-RAR (European Commission, 2004c) this is considered as tris(2-chloroethyl)phosphate. In AQUIRE (U.S. Environmental Protection Agency, 2002) however, this compound is interpreted as 2,2,2-trichloroethyl phosphate (triclofos).

Table A2.2. Chronic toxicity data for tris(2-chloroethyl)phosphate (TCEP) to freshwater organisms. All data are from the draft EU-RAR (European Commission, 2004c). Additional information on the tests was retrieved from IUCLID (European Commission, 2000).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
algae														
Scenedesmus subspicatus	-	-	-	-	-	-	-		48 h	EC10	biomass	0.29		Kühn et al. (1989)
Scenedesmus subspicatus	-	-	-	-	-	-	-		72 h	EC10	biomass	0.2	a	Kühn et al. (1989)
Scenedesmus subspicatus	-	-	-	-	-	-	-		96 h	EC10	biomass	0.3	a	Kühn et al. (1989)
Scenedesmus subspicatus	-	-	-	-	-	-	-		48 h	EC10	growth rate	0.65		Kühn et al. (1989)
Scenedesmus subspicatus	-	-	-	-	-	-	-		72 h	EC10	growth rate	0.55	a	Kühn et al. (1989)
Scenedesmus subspicatus	-	Y	-	-	-	-	-		72 h	NOEC	growth rate	100		Hoechst AG (1988)
Scenedesmus subspicatus	-	-	-	-	-	-	-		72 h	EC10	growth rate	148	b	Nyholm & Kusk (2003)
Scenedesmus subspicatus	-	-	-	-	-	-	-		-	EC10	-	15.9	c	Akzo Chemicals (1993)
Scenedesmus subspicatus	-	-	-	-	-	-	-		72 h	EC10	-	0.2	c	Akzo Chemicals (1993)
Pseudokirchneriella subcapitata	-	N	-	-	-	-	-		96 h	LOEC	growth rate	15		Akzo Chemicals (1992)
Pseudokirchneriella subcapitata	-	N	-	-	-	-	-		96 h	NOEC	growth rate	5	d	Akzo Chemicals (1992)
Crustacea														
Daphnia magna	-	-	-	-	-	-	-		21 d	NOEC	reproduction	13		Kühn et al. (1989)

Notes

a: Between day 2 and day 3 the pH increased from 8 to 9.4.

b: This is a recalculation of the results by Hoechst AG (1988).
c: No original data or reference given. Probably one of the numbers is the same study as that from Kühn et al. (1989).
d: In the range-finding test, no growth inhibition was observed up to 100 mg/L

Table A2.3. Toxicity data for tris(2-chloroethyl)phosphate (TCEP) to freshwater organisms, additional to data from the draft EU-RAR (European Commission, 2004c).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Algae															
Pseudokirchneriella subcapitata	-	N	-	-	-	-	-		96 h	EC20	growth rate	68	a	European Commission (2000)	Akzo Chemicals (1992)
Pseudokirchneriella subcapitata	-	N	-	-	-	-	-		96 h	EC20	biomass	17	a	European Commission (2000)	Akzo Chemicals (1992)
Crustacea															
Daphnia magna										EC50		340		GDCH (2001)	Noack (1989)
Daphnia magna									24 h	EC50	immobility	7.1	b	Yoshioka & Ose (1993)	
Daphnia magna									14 d	NOEC	reproduction	0.01	c	Yoshioka & Ose (1993)	
Pisces															
Oryzias latipes	~3 cm, 0.3 g	N	S		dtw		80	20±1	48 h	LC50	mortality	251		Yoshioka et al. (1986a)	
Oryzias latipes	-	N	R	-	dtw	7.2	40	20±1	48 h	LC50	mortality	260	d	Yoshioka & Ose (1993)	
Bacteria															
Pseudomonas putida										LC50		>5000		IPCS (1998)	Bayer (1986)
Insecta															
Culex tarsalis	4th instar, malathion resistant strain	N	S	-	dw	-	-	-	24 h	LC50	mortality	>1	4	Plapp & Tong (1966)	
Protozoa															
Tetrahymena pyriformis		N	S		am			30	24 h	EC50	proliferation	115	e	Yoshioka et al. (1985)	

Notes
a: With a log-logistic dose-response relationship and the reported EC50s this corresponds to EC10s of 50 mg/L for growth rate and 11 mg/L for biomass
b: According to OECD guideline 202. The value was calculated from reported environmental concentration/effect concentration and environmental concentration values. The compound is referred to as tris(chloroethyl) phosphate. The reported value for Oryzias latipes is in accordance with that given elsewhere in the paper for 2-tris(chloroethyl) phosphate
c: The value was calculated from reported environmental concentration/effect concentration and environmental concentration values. The compound is referred to as tris(chloroethyl) phosphate. The reported value for Oryzias latipes is in accordance with that given elsewhere in the paper for 2-tris(chloroethyl) phosphate. Although this value is extremely low, calculated values for other compounds seem to be in the same range with other studies. The environmental concentration of 90 ng/L might be erroneous.
d: This compound is referred as to tri(chloroethyl) phosphate. Next to this compound also tris(2-chloroethyl) phosphate is included.

e: The presented number for trichloroethyl phosphate is given in mg/L and µmol/L. The used molecular weight is that of (2,2,2-trichloroethyl)phosphate (triclofos). In Yoshioka et al. (1986a) the same test with this compound is presented but now with a different number in mg/L, according to the molecular weight of tris(2-chloroethyl)phosphate. The value in mg/L is taken from Yoshioka et al. (1986a).

Table A2.4. Toxicity data for tris(2-chloroethyl)phosphate (TCEP) to saltwater organisms, additional to data from the draft EU-RAR (European Commission, 2004c).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Bacteria															
Vibrio fischeri	-	N	-	-	am	-	20	15	15 min	EC50	luminescence	323		Guzzella & Galassi (1993)	
Vibrio fischeri	-	N	-	-	am	-	20	15	15 min	EC10	luminescence	46	a	Guzzella & Galassi (1993)	

Notes

a: EC10 was determined from EC50 and slope of log gamma versus log concentration mentioned in the study.

Table A2.5. Toxicity data for tris(2-chloroethyl)phosphate (TCEP) to fresh water microbiological processes and enzyme activity. All data are from the draft EU-RAR (European Commission, 2004c).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Bacteria														
activated sludge bacteria	-	-	-	-	-	-	-		3 h	EC20	respiration	1400	a	Akzo (1990a)
activated sludge bacteria	-	-	-	-	-	-	-		3 h	EC50	respiration	3200	a	Akzo (1990a)
activated sludge bacteria	-	-	-	-	-	-	-		3 h	EC90	respiration	7800	a	Akzo (1990a)
activated sludge bacteria	-	-	-	-	-	-	-		-	EC50	aerobic degradation	>500	b	Hoechst (1978)
anaerobic microorganisms	-	-	-	-	-	-	-		-	EC50	gas evolution	>250	c	Hoechst (1978)
anaerobic microorganisms	-	-	-	-	-	-	-		24 h	EC0	gas evolution	1500	c	Hoechst (1985)
anaerobic microorganisms	-	-	-	-	-	-	-		24 h	EC50	gas evolution	10-100	c	Hoechst (1994)

Notes

a: According to OECD guideline 109; with a log-logistic dose-response model and the three ECx values the calculated EC10 is 1000 mg/L

b: Up to 10000 mg/L inhibition was compensated for after one day of adaptation

c: ETAD fermentation tube method

Table A2.6. Acute toxicity data for tris(2-chloro-1-methylethyl)phosphate (TCPP) to freshwater organisms. All data are from the draft EU-RAR (European Commission, 2004b). Additional information on the tests was retrieved from (European Commission, 2000).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
algae														
Pseudokirchneriella subcapitata	-	N	S	-	-	-	-	-	96 h	EC50	biomass	47	a	Kroon & van Ginkel (1992b)
Pseudokirchneriella subcapitata	-	N	S	-	-	-	-	-	96 h	EC50	growth rate	73	a	Kroon & van Ginkel (1992b)
Scenedesmus subspicatus	-	N	S	-	-	-	-	-	72 h	EC50	chlorophyll content	45	b, c	Griebenow (1998)
Scenedesmus subspicatus	-	N	S	-	-	-	-	-	72 h	EC20	chlorophyll content	25	b, c	Griebenow (1998)
crustacea														
Daphnia magna	-	N	S	-	-	-	-	-	48 h	EC50	mobility	63	b, d	Griebenow (1998)
Daphnia magna		Y	S	-	-	-	-	-	48 h	EC50	mobility	131	e	Meeks (1985)
Daphnia magna	-	N	S	-	-	-	-	-	48 h	EC20	mobility	51	b, d	Griebenow (1998)
Daphnia magna		Y	S	-	-	-	-	-	48 h	NOEC	mobility	33.5	e	Meeks (1985a)
pisces														
Brachydanio rerio	-	Y	S	97.9%	-	-	-	-	96 h	LC50	mortality	56	f, g	Kanne (1990)
Brachydanio rerio	-	Y	S	97.9%	-	-	-	-	96 h	LC0	mortality	32	f	Kanne (1990)
Lepomis macrochirus	-	Y	S	-	-	-	-	-	96 h	LC50	mortality	84	h	Meeks (1985b)
Lepomis macrochirus	-	Y	S	-	-	-	-	-	96 h	NOEC	mortality	6.3	h	Meeks (1985b)
Oryzias latipes	-	-	-	-	-	-	-	-	48 h	LC50	mortality	54	b, i	CITI (1992)
Pimephales promelas	-	Y	S	-	-	-	-	-	96 h	LC50	mortality	51	h	Meeks (1985c)
Pimephales promelas	-	Y	S	-	-	-	-	-	96 h	NOEC	mortality	6.6	h	Meeks (1985c)
Poecilia reticulata	-	N	S	-	-	-	-	-	96 h	LC50	mortality	30	b, h	Griebenow (1998)

Notes

a: OECD guideline 201, marked in the draft EU RAR as invalid study due to dilution of stock suspension without chemical analysis

b: marked as unassignable study due to incompleteness of submitted data

c: DIN 38412/L33, from the reported EC50 and EC20 the EC10 estimated with a log-logistic model is 18 mg/L

d: DIN 38412/L11

e: OECD guideline 202

f: UBA (Berlin) method

g: geometric mean between LC0 and LC100

h: OECD guideline 203

i: Japanese Industrial Standard method (JIS K0102-1986-71)

Table A2.7. Chronic toxicity data for tris(2-chloro-1-methylethyl)phosphate (TCPP) to freshwater organisms. All data are from the draft EU-RAR (European Commission, 2004b). Additional information on the tests was retrieved from (European Commission, 2000).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
algae														
Pseudokirchneriella subcapitata	-	N	S	-	-	-	-	-	96 h	NOEC	growth	6	a	Kroon & van Ginkel (1992b)
Crustacea														
Daphnia magna	-	Y	R	-	-	-	-	-	21 d	NOEC	reproduction	32	b	Sewell et al. (1995)
Daphnia magna	-	Y	R	-	-	-	-	-	21 d	NOEC	mortality	32	b	Sewell et al. (1995)
Daphnia magna	-	Y	R	-	-	-	-	-	21 d	EC50	reproduction	32-56	b	Sewell et al. (1995)
Daphnia magna	-	Y	R	-	-	-	-	-	21 d	EC50	immobilisation	40	b	Sewell et al. (1995)

Notes

a: OECD guideline 201, invalid study due to dilution of stock suspension without chemical analysis

b: OECD 202 guideline, based on nominal concentration, which were close to measured concentrations

Table A2.8. Toxicity data for tris(2-chloro-1-methylethyl)phosphate (TCPP) to saltwater organisms. All data are from the draft EU-RAR (European Commission, 2004b).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Bacteria														
Vibrio fischeri	-	N	S	-	am	-	20	15	15 min	EC50	luminescence	172	a	Guzzella & Galassi (1993)

Notes

a: LUMIStox test, marked in the EU RAR as invalid, because the species is not representative for micro-organisms in sewage treatment plants. However, according to the TGD (European Commission, 2003, p. 100), the EC50s for non-adapted pure cultures of micro-organisms may be used for the derivation of the PNEC for the aquatic compartment.

Table A2.9. Toxicity data for tris(2-chloro-1-methylethyl)phosphate (TCPP) to saltwater organisms, additional to data from the draft EU-RAR

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Bacteria															
Vibrio fischeri	-	N	S	-	am	-	20	15	15 min	EC10	luminescence	16	a	Guzzella & Galassi (1993)	
Vibrio fischeri	-	-	S	-	-	-	-	-	30 min	EC50	luminescence	295	b	European Commission (2000)	Griebenow (1998)

Notes

a: LUMIStox test, EC10 determined from EC50 and slope of the dose-response relationship

b: DIN 38412/L34

Table A2.10. Toxicity data for tris(2-chloro-1-methylethyl)phosphate (TCPP) to fresh water microbiological processes and enzyme activity. All data are from the draft EU-RAR (European Commission, 2004b).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
activated sludge bacteria	-	N	S	97.9%	-	-	-	-	3 h	EC50	oxygen consumption	784	a	Bayer (1990)

Notes
a: ISO 8192, marked use with care

Table A2.11. Acute toxicity data for tris(2-chloro-1-(chloromethyl)ethyl)phosphate (TDCP) to freshwater organisms. All data are from the draft EU-RAR (European Commission, 2004a).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Algae														
Scenedesmus subspicatus		N	S	-	-	-	-	-	72 h	EC50	biomass	≥10	a, b	Sewell (1994)
Scenedesmus subspicatus		N	S	-	-	-	-	-	72 h	EC50	growth rate	≥10	a, b	Sewell (1994)
Pseudokirchneriella subcapitata		N	S	-	-	-	-	-	96 h	EC50	biomass	12	a, b	Kroon & van Ginkel (1992a)
Pseudokirchneriella subcapitata		N	S	-	-	-	-	-	96 h	EC50	growth rate	39	a, b	Kroon & van Ginkel (1992a)
Crustacea														
Daphnia magna		Y	F	>95%	-	-	-	-	48 h	EC50	mobility	3.8	c	Drottar et al. (1999)
Daphnia magna		N	S	-	-	-	-	-	48 h	EC50	mobility	4.6	c, d	Sewell (1993a)
Daphnia magna		Y	F	>95%	-	-	-	-	48 h	NOEC	mobility	1.6	c	Drottar et al. (1999)
Daphnia magna		N	S	-	-	-	-	-	48 h	NOEC	mobility	1.8	c, d	Sewell (1993a)
Pisces														
Carassius auratus	0.8-2.8 g	N	S	-	dtw	-	-	25	96 h	LC50	mortality	5.1	d	Sasaki et al. (1981)
Oncorhynchus mykiss		N	S	-	-	-	-	-	96 h	LC50	mortality	1.4	d, e	Jenkins (1990a)
Oncorhynchus mykiss		N	S	-	-	-	-	-	96 h	LC50	mortality	1.1	b, e	Sewell (1993b)
Oncorhynchus mykiss		N	S	-	-	-	-	-	96 h	NOEC	mortality	<0.63	d, e	Jenkins (1990a)
Oncorhynchus mykiss		N	S	-	-	-	-	-	96 h	NOEC	mortality	0.56	b, e	Sewell (1993b)
Oryzias latipes		N	-	-	-	-	-	-	48 h	LC50	mortality	3.7	d, f	CITI (1992)
Oryzias latipes	0.1-0.2 g	N	S	-	dtw	-	-	25	96 h	LC50	mortality	3.6	d	Sasaki et al. (1981)

Notes
a: OECD 201 guideline
b: marked as use with care
c: OECD 202 guideline
d: marked as invalid study, due to the absence of measured exposure concentrations
e: OECD 203 guideline
f: Japanese Industrial Standard method (JIS K0102-1986-71)

Table A2.12. Chronic toxicity data for tris(2-chloro-1-(chloromethyl)ethyl)phosphate (TDCP) to freshwater organisms. All data are from the draft EU-RAR (European Commission, 2004a).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Algae														
Scenedesmus subspicatus	-	N	S	-	-	-	-	-	72 h	NOEC		≥10	a	Sewell (1994)
Pseudokirchneriella subcapitata	-	N	S	-	-	-	-	-	96 h	NOEC		6	a	Kroon & van Ginkel (1992a)

Notes
a: OECD 201 guideline; marked as use with care

Table A2.13. Toxicity data for tris(2-chloro-1-(chloromethyl)ethyl)phosphate (TDCP) to freshwater organisms, additional to data from the draft EU-RAR.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Pisces														
Carassius auratus	3 inch	N	S	-	-	-	-	20	7 d	LC0	mortality	1		Eldefrawi et al. (1977)
Carassius auratus	3 inch	N	S	-	-	-	-	20	7 d	LC100	mortality	5		Eldefrawi et al. (1977)
Oryzias latipes	-	N	R	-	dtw	7.2	40	20±1	96 h	LC50	mortality	2		Yoshioka & Ose (1993)

Table A2.14. Toxicity data for tris(2-chloro-1-(chloromethyl)ethyl)phosphate (TDCP) to fresh water microbiological processes and enzyme activity. All data are from the draft EU-RAR (European Commission, 2004a).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
sewage sludge bacteria										NOEC		>10000	a	Jenkins (1990b)

Notes
a: OECD guideline 209

Table A2.15. Acute toxicity data for tris(n-butyl)phosphate (TBP) to freshwater organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Algae															
Bumilleriopsis filiformis	Vischer CCAP 809/2	N	S	-	am	-	-	20±1	14 d	EC100	biomass	25-≥100	a	Blanck et al. (1984)	
Chlamydomonas dysosmos	Moewus CCAP 11/36	N	S	-	am	-	-	20±1	14 d	EC100	biomass	25-≥100	a	Blanck et al. (1984)	
Chlorella emersonii	Emerson CCAP 211/8h	N	S	-	am	-	-	20±1	14 d	EC100	biomass	25-≥100	a	Blanck et al. (1984)	
Chlorella emersonii	strain 211/8h	N	S	-	am	-	-	25±0.5	48 h	EC50	biomass	5-10	b	Dave et al. (1979)	

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Chlorella emersonii	strain 211/8h	N	S	-	am	-	-	25±0.5	72 h	EC50	growth rate	10-50	b	Dave et al. (1979)	
Chlorella emersonii	strain 211/8h	N	S	-	am	-	-	25±0.5	48 h	EC50	growth rate	25	c	Dave et al. (1979)	
Chlorella vulgaris		-	S	-	-	-	-	-	7 d	EC50	growth inhibition	58	d	Yoshioka & Ose (1993)	
Kirchneriella contorta	Schmidle	N	S	-	am	-	-	20±1	14 d	EC100	biomass	25-≥100	a	Blanck et al. (1984)	
Klebsormidium marinum	Deason UTEX 1706	N	S	-	am	-	-	20±1	14 d	EC100	biomass	25-≥100	a	Blanck et al. (1984)	
Monodus subterraneus	Petersen CCAP 848/1	N	S	-	am	-	-	20±1	14 d	EC100	biomass	25-≥100	a	Blanck et al. (1984)	
Monoraphidium pusillum	Printz	N	S	-	am	-	-	20±1	14 d	EC100	biomass	25-≥100	a	Blanck et al. (1984)	
Pseudokirchneriella subcapitata	Printz CCAP 278/4	N	S	-	am	-	-	20±1	14 d	EC100	biomass	25-≥100	a	Blanck et al. (1984)	
Pseudokirchneriella subcapitata	-	-	S	-	-	-	-	24	96 h	EC50	growth rate	4.4		GDCh (1995)	Burgess & Wirth (1990)
Raphidonema longiseta	Vischer UTEX 339	N	S	-	am	-	-	20±1	14 d	EC100	biomass	25-≥100	a	Blanck et al. (1984)	
Scenedesmus obtusiusculus	Chod.	N	S	-	am	-	-	20±1	14 d	EC100	biomass	25-≥100	a	Blanck et al. (1984)	
Scenedesmus subspicatus	8681 SAG	N	Sc	-	am	8.0-9.3	55	24±1	48 h	EC50	AUC	1.3	e	Kühn & Pattard (1990)	
Scenedesmus subspicatus	8681 SAG	N	Sc	-	am	8.0-9.3	55	24±1	48 h	EC50	growth rate	4.2	e	Kühn & Pattard (1990)	
Scenedesmus subspicatus	8681 SAG	N	Sc	-	am	8.0-9.3	55	24±1	72 h	EC50	AUC	1.1	e	Kühn & Pattard (1990)	
Scenedesmus subspicatus	8681 SAG	N	Sc	-	am	8.0-9.3	55	24±1	72 h	EC50	growth rate	2.8	e	Kühn & Pattard (1990)	
Crustacea															
Daphnia magna	<24 h, 0.315-0.630 mm	N	S		tw	7.6-7.7	286	20-22	24 h	EC50	immobility	33		Bringmann and Kühn (1977a)	
Daphnia magna	<24 h, Strauss, IRCHA	N	S		am	8.0±0.2	250.2	20	24 h	EC50	immobility	30		Bringmann & Kühn (1982)	
Daphnia magna	-	N	S	-	-	-	-	-	24 h	EC50	mortality	5.8	f	GDCh (1995)	Bayer AG data
Daphnia magna	-	-	-	-	-	-	-	-	6 h	EC50	mortality	52		GDCh (1995)	Wakabayashi et al (1988)
Daphnia magna	-	-	-	-	-	-	-	-	24 h	EC50	mortality	35		GDCh (1995)	Wakabayashi et al (1988)
Daphnia magna	< 24 h	N	S	-	am	7.8-8.2	202	20	24 h	LC50	mortality	12.8	g	Dave et al. (1981)	
Daphnia magna	< 24 h	N	S	-	am	7.8-8.2	202	20	48 h	LC50	mortality	3.65	g	Dave et al. (1981)	
Daphnia magna	< 24 h	N	S	-	am	7.8-8.2	202	20	72 h	LC50	mortality	2.1	g	Dave et al. (1981)	
Daphnia magna	<24 h, IRCHA	Y	S	-	am	8.0±0.2	250	25±1	24 h	EC50	mortality	35	h	Kühn et al. (1989)	
Daphnia magna	-	-	-	-	-	-	-	-	24 h	EC50	immobility	9.2	i	Yoshioka & Ose (1993)	
Daphnia magna	<24 h, 0.315-0.630 mm	N	S		tw	7.6-7.7	286	20-22	24 h	EC0	immobility	7		Bringmann and Kühn (1977a)	
Daphnia magna	<24 h, Strauss, IRCHA	N	S		am	8.0±0.2	250.2	20	24 h	EC0	immobility	5		Bringmann & Kühn (1982)	
Daphnia magna	-	N	S	-	-	-	-	-	24 h	EC0	mortality	2.5	f	GDCh (1995)	Bayer AG data
Daphnia magna	<24 h, IRCHA	Y	S	-	am	8.0±0.2	250	25±1	24 h	EC0	mortality	9.3	h	Kühn et al. (1989)	
Daphnia pulex	-	-	-	-	-	-	-	-	6 h	EC50	mortality	93		GDCh (1995)	Wakabayashi et al (1988)

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Daphnia pulex	-	-	-	-	-	-	-	-	24 h	EC50	mortality	68		GDCh (1995)	Wakabayashi et al (1988)
Gammarus pseudolimnaeus	2-3 mm	Y	F	-	-	-	-	-	96 h	LC50	mortality	1.7		GDCh (1995)	England & Cramer (1991)
Gammarus pseudolimnaeus	2-3 mm	Y	F	-	-	-	-	-	96 h	NOEC	mortality	0.52		GDCh (1995)	England & Cramer (1991)
Hyalella azteca	1-2 mm	Y	F	-	-	-	-	-	96 h	LC50	mortality	2.4		GDCh (1995)	England & Schrier (1990)
Hyalella azteca	1-2 mm	Y	F	-	-	-	-	-	96 h	NOEC	mortality	<1.9		GDCh (1995)	England & Schrier (1990)
Moina macropoda	5 d	N	S	-	am	-	-	20±1	3h	LC50	mortality	63		Yoshioka et al. (1986a)	
Streptocephalus proboscideus	cysts	N	S	ag	am	-	-	25±0.5	24 h	LC50	mortality	34.6	j	Crisinel et al. (1994)	
Streptocephalus rubricaudatus	cysts	N	S	ag	am	-	-	25	24 h	LC50	mortality	32.8		Crisinel et al. (1994)	
Streptocephalus texanus	cysts	N	S	ag	am	-	-	20	22 h	LC50	mortality	21.8		Crisinel et al. (1994)	
Pisces															
Brachydanio rerio	-	-	-	-	-	-	-	-	96 h	LC0	mortality	10	f	GDCh (1995)	Bayer AG data
Brachydanio rerio	-	-	-	-	-	-	-	-	96 h	LC100	mortality	14	f	GDCh (1995)	Bayer AG data
Brachydanio rerio	juvenile 0.25 g	N	S	-	rw	7.3-8.5	100	25	96 h (24, 48, 144 h)	LC50	mortality	11.4	k	Dave et al. (1981)	
Carassius auratus	0.8-2.8 g	N	S	-	dtw	-	-	25	96 h	LC50	mortality	8.8		Sasaki et al. (1981)	
Leuciscus idus melanotus		N	S	-	tw	7—8	255	20±1	48 h	LC50	mortality	7.6	l	Juhnke and Lüdemann (1978)	
Leuciscus idus melanotus		N	S	-	tw	7—8	255	20±1	48 h	LC0	mortality	5.8	l	Juhnke and Lüdemann (1978)	
Oncorhynchus mykiss		Y	F					12	96 h	LC50	mortality	13	m	GDCh (1995)	Bowman & Schrier (1990)
Oncorhynchus mykiss	fry, 0.15 g	N	S	-	tw	7.0	45	5	96 h	LC50	mortality	9.4		Dave et al. (1979)	
Oncorhynchus mykiss	fry, 0.15 g	N	S	-	tw	7.0	45	10	96 h	LC50	mortality	11.8		Dave et al. (1979)	
Oncorhynchus mykiss	fry, 0.15 g	N	S	-	tw	7.0	45	15	96 h	LC50	mortality	8.2		Dave et al. (1979)	
Oncorhynchus mykiss	fry, 0.15 g	N	S	-	tw	7.0	45	20	96 h	LC50	mortality	4.2		Dave et al. (1979)	
Oncorhynchus mykiss	fry, 0.15 g	N	S	-	tw	7.0	45	5	120 h	LC50	mortality	6.8		Dave et al. (1979)	
Oncorhynchus mykiss	fry, 0.15 g	N	S	-	tw	7.0	45	10	120 h	LC50	mortality	10.5		Dave et al. (1979)	
Oncorhynchus mykiss	fry, 0.15 g	N	S	-	tw	7.0	45	15	120 h	LC50	mortality	7.2		Dave et al. (1979)	
Oncorhynchus mykiss	fry, 0.15 g	N	S	-	tw	7.0	45	20	120 h	LC50	mortality	4.2		Dave et al. (1979)	
Oncorhynchus mykiss	20 g	Y	S	-	-	8.5 (7.0-9.4)	43.4	15±1	96 h	LC50	mortality	5-9		IPCS (1991a); GDCh (1995)	Dave & Lidman (1978)
Oncorhynchus mykiss	20 g	N	S	-	-	8.5 (7.0-9.4)	43.4	15±1	96 h	LC50	mortality	11.5-13.5		GDCh (1995)	Dave & Lidman (1978)
Oncorhynchus mykiss	-	Y	F	-	-	-	-	12	96 h	LC0	mortality	4.3	m	GDCh (1995)	Bowman & Schrier (1990)
Oryzias latipes	-	-	-	-	-	-	-	-	48 h	LC50	mortality	14.2	n	European Commission (2000)	CITI (1992)
Oryzias latipes	0.1-0.2 g	N	S	-	dtw	-	-	25	96 h	LC50	mortality	9.6		Sasaki et al. (1981)	

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Oryzias latipes	~3 cm, 0.3 g	N	S		dtw		80	20±1	48 h	LC50	mortality	18	o	Yoshioka et al. (1986a)(1986b; 1986a)	
Oryzias latipes	-	N	R	-	dtw	7.2	40	20±1	96 h	LC50	mortality	17	p	Yoshioka & Ose (1993)	
Pimephales promelas	32 d, 18.5 ± 2.309 mm, 0.101 ±0.0371 g	Y	F	99%	nw/ dtw	7.84± 0.05	45.1±0.25	26.7±0.20	96 h	LC50	mortality	11		Geiger et al. (1986)	
Pimephales promelas	31 d, 18.6 ± 1.981 mm, 0.113 ±0.0385 g	Y	F	99%	nw/ dtw	7.82± 0.05	42.6±1.80	25.9±0.20	96 h	LC50	mortality	8.18		Geiger et al. (1986)	
Pimephales promelas	32 d, 18.5 ± 2.309 mm, 0.101 ±0.0371 g	Y	F	99%	nw/ dtw	7.84± 0.05	45.1±0.25	26.7±0.20	96 h	LC0	mortality	8.6		Geiger et al. (1986)	
Pimephales promelas	31 d, 18.6 ± 1.981 mm, 0.113 ±0.0385 g	Y	F	99%	nw/ dtw	7.82± 0.05	42.6±1.80	25.9±0.20	96 h	LC0	mortality	6.0		Geiger et al. (1986)	
Pimephales promelas	1.20 g	-	S	-	-	7.4	44	17	96 h	LC50	mortality	1-10		Mayer & Ellersieck (1986)	
Bacteria															
Thiobacillus ferroxidans		Y	S	-	am	2.3	-	35	90 min	EC39	oxygen uptake	218	q	Torma & Itzkovitch (1976)	
Cyanophyta															
Oscillatoriales sp.	PCC 6402	N	S	-	am	-	-	20±1	14 d	EC100	biomass	50-≥100	r	Blanck et al. (1984)	
Synechococcus leopoliensis	Racib. UTEX 625	N	S	-	am	-	-	20±1	14 d	EC100	biomass	50-≥100	r	Blanck et al. (1984)	
Platyhelminthes															
Dugesia japonica	-	N	S	-	am	~7	-	20±1	7d	LC50	mortality	10		Yoshioka et al. (1986a)	
Dugesia japonica	-	N	S	-	am	~7	-	20±1	7d	EC50	regeneration	4		Yoshioka et al. (1986a)	
Protozoa															
Tetrahymena pyriformis		N	S		am			30	24 h	EC50	proliferation	20		Yoshioka et al. (1985) Yoshioka et al. (1986b)	

Notes

a: continuous lighting at 10±1 W/m^2 with cool fluorescent light between 400 and 700 nm

b: continuous lighting at 10 W/m^2 with cool fluorescent light; initial density 0.16 $\mu g/cm^3$

c: continuous lighting at 10 W/m^2 with cool fluorescent light; initial density 0.16 $\mu g/cm^3$; determined from data in figure between 12 and 48 h with a log-logistic dose-response curve; exponential growth up to 48 h

d: According to OECD guideline 203. The value was calculated from reported environmental concentration/effect concentration and environmental concentration values.

e: fluorescent light with 17.0 W/m^2; initial cell density: $1 \cdot 10^4$ cells/L, exponential growth up to 48 h; DIN 38412 part 9

f: UBA draft method

g: 12 h photoperiod, illumination by diffuse light

h: photoperiod 9:15 light:dark with fluorescent light; result based on nominal values

i: According to OECD guideline 202. The value was calculated from reported environmental concentration/effect concentration and environmental concentration values.

j: Streptoxkit F

k: ISO method (1975)

l: test according to Mann (1976)
m: EPA method 40 CFR part 797
n: Japanese Industrial Standard method (JIS K0102-1986-71)
o: 16:8 light:dark
p: According to OECD 203
q: one concentration tested
r: continuous lighting at 10±1 W/m^2 with cool fluorescent light between 400 and 700 nm

Table A2.16. Chronic toxicity data for tris(n-butyl)phosphate (TBP) to freshwater organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Algae															
Chlorella emersonii	strain 211/8h	N	S	-	am	-	-	25±0.5	72 h	NOEC	growth rate	<5	a	Dave et al. (1979)	
Chlorella emersonii	strain 211/8h	N	S	-	am	-	-	25±0.5	48 h	EC10	growth rate	4.7	b	Dave et al. (1979)	
Scenedesmus quadricauda		N	Sc		am	7.0	55	27	8 d	NOEC	growth	3.2	c	Bringmann and Kühn (1977b) (1978a; 1978b; 1979; 1980)	
Scenedesmus subspicatus	8681 SAG	N	Sc	-	am	8.0-9.3	55	24±1	48 h	EC10	AUC	0.44	d	Kühn & Pattard (1990)	
Scenedesmus subspicatus	8681 SAG	N	Sc	-	am	8.0-9.3	55	24±1	48 h	EC10	growth rate	0.66	d	Kühn & Pattard (1990)	
Scenedesmus subspicatus	8681 SAG	N	Sc	-	am	8.0-9.3	55	24±1	72 h	EC10	AUC	0.37	d	Kühn & Pattard (1990)	
Scenedesmus subspicatus	8681 SAG	N	Sc	-	am	8.0-9.3	55	24±1	72 h	EC10	growth rate	0.92	d	Kühn & Pattard (1990)	
Pseudokirchneriella subcapitata	-	-	S	-	-	-	-	24	96 h	NOEC	growth inhibition	2.2		GDCh (1995)	Burgess & Wirth (1990)
Crustacea															
Daphnia magna	<24 h, IRCHA	Y	R	-	am	8.0±0.2	250	25±1	21 d	NOEC	reproduction	1.3	e	Kühn et al. (1989)	
Daphnia magna	-	-	-	-	-	-	-	-	14 d	NOEC	reproduction	0.73	f	Yoshioka & Ose (1993)	
Daphnia magna	-	-	-	-	-	-	-	-	21 d	NOEC	-	3		Radix et al. (1999)	Roman (1996)
Pisces															
Brachydanio rerio	eggs	N	R	-	rw	7.3-8.5	100	25	10 d	NOEC	survival time	13.5	g	Dave et al. (1981)	
Oncorhynchus mykiss	eggs	N	R	-	rw	7.3-8.5	100	8±1	48 d	NOEC	survival time	8.3	g	Dave et al. (1981)	
Bacteria															
Pseudomonas putida	-	N	Sc	-	am	7.0	81.2	25	16 h	NOEC	growth	>100	h	Bringmann & Kühn (1976; 1977b; 1979; 1980)	
Cyanophyta															
Microcystis aeruginosa	-	N	Sc	-	am	7.0	55	27	8 d	NOEC	growth	4.1	i	Bringmann (1975); Bringmann and Kühn (1976; 1978b; 1978a)	
Protozoa															
Chilomonas paramaecium	-	N	Sc	-	am	6.9	74.6	20	48 h	NOEC	growth	42		Bringmann et al. (1980)	

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Entosiphon sulcatum	Stein	N	Sc	-	am	6.9	75.1	25	72 h	NOEC	growth	14		Bringmann (1978) Bringmann and Kühn (1979; 1980)	
Uronema parduczi	Chatton-Lwoff	N	Sc	-	am	6.9	75.1	25	20 h	NOEC	growth	21		Bringmann and Kühn (1980)	
Rotifera															
Brachionus calyciflorus	neonates 0-2 h old	N	S	-	am	7.5	moderately hard	25	48 h	NOEC	reproduction	3	j	Radix et al. (1999)	
Brachionus calyciflorus	neonates 0-2 h old	N	S	-	am	7.5	moderately hard	25	48 h	EC10	reproduction	6.4	j	Radix et al. (1999)	
Brachionus calyciflorus	neonates 0-2 h old	N	S	-	am	7.5	moderately hard	25	48 h	EC20	reproduction	8.2	j	Radix et al. (1999)	
Brachionus calyciflorus	neonates 0-2 h old	N	S	-	am	7.5	moderately hard	25	48 h	EC50	reproduction	12.5	j	Radix et al. (1999)	

Notes

a: continuous lighting at 10 W/m^2 with cool fluorescent light; initial density 0.16 $\mu g/cm^3$

b: continuous lighting at 10 W/m^2 with cool fluorescent light; initial density 0.16 $\mu g/cm^3$; determined from data in figure between 12 and 48 h with a log-logistic dose-response curve; exponential growth up to 48 h

c: light intensity 2800 lm; toxicity threshold is used as a NOEC

d: fluorescent light with 17.0 W/m2; initial cell density: $1 \cdot 10^4$ cells/L, exponential growth up to 48 h; DIN 38412 part 9

e: photoperiod 9:15 light:dark with fluorescent light; result based on nominal values

f: The value was calculated from reported environmental concentration/effect concentration and environmental concentration values.

g: 12 h photoperiod; NOEC from by authors from graphical interpolation; no feeding during test

h: toxicity threshold is used as a NOEC

i: light intensity 2800 lm; toxicity threshold is used as a NOEC

j: test performed in dark

Table A2.17. Acute toxicity data for tris(n-butyl)phosphate (TBP) to saltwater organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Bacteria														
Vibrio fischeri	-	N	S	-	am	-	20	15	15 min	EC50	bioluminescence	80.7	a	Guzzella & Galassi (1993)
Vibrio fischeri	-	N	S	-	am	-	20	15	15 min	EC10	bioluminescence	5.4	b	Guzzella & Galassi (1993)
Crustacea														
Artemia salina	cysts	N	S	ag	rw	-	35	25±0.5	24 h	LC50	mortality	54.6	c	Crisinel et al. (1994)

Notes

a: LUMIStox test

b: LUMIStox test, EC10 determined from EC50 and slope of the dose-response relationship

c: Artoxkit M; performed in the dark

Table A2.18. Chronic toxicity data for tris(n-butyl)phosphate (TBP) to saltwater organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Bacteria														
Vibrio fischeri	-	-	-	-	am	7.5	35	27	22 h	NOEC	bioluminescence	3	a	Radix et al., 1999
Vibrio fischeri	-	-	-	-	am	7.5	35	27	22 h	EC10	bioluminescence	2.62	a	Radix et al., 1999
Vibrio fischeri	-	-	-	-	am	7.5	35	27	22 h	EC20	bioluminescence	2.97	a	Radix et al., 1999
Vibrio fischeri	-	-	-	-	am	7.5	35	27	22 h	EC50	bioluminescence	3.69	a	Radix et al., 1999

Notes
a: Microtox test

Table A2.19. Toxicity data for tris(n-butyl)phosphate (TBP) to fresh water microbiological processes and enzyme activity.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
activated sludge bacteria	-	-	-	-	-	-	-	-	3 h	EC50	oxygen consumption	300	a	GDCh (1995)	Bayer Ag data
activated sludge bacteria	-	-	-	-	-	-	-	-	3 h	EC50	respiration	100	b	GDCh (1995)	Yoshioka et al. (1986b)

Notes
a: ISO 8192
b: OECD guideline 209

Table A2.20. Acute toxicity data for tris(iso-butyl)phosphate (TiBP) to freshwater organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Algae														
Scenedesmus subspicatus	-	-	-	98%	-	-	-	-	72 h	EC50	biomass	33	a	BASF AG (1989)
Scenedesmus subspicatus	-	-	-	98%	-	-	-	-	72 h	EC50	growth rate	34	a	BASF AG (1989)
Scenedesmus subspicatus	-	-	-	98%	-	-	-	-	96 h	EC50	biomass	30	a	BASF AG (1989)
Scenedesmus subspicatus	-	-	-	98%	-	-	-	-	96 h	EC50	growth rate	18	a	BASF AG (1989)
Crustacea														
Daphnia magna	-	-	-	98%	-	-	-	-	48 h	LC50	mortality	11	b	BASF AG (1989)
Daphnia magna	-	-	-	98%	-	-	-	-	48 h	LC0	mortality	5.8	b	BASF AG (1989)
Pisces														
Leuciscus idus	-	Y	S	90%	-	-	-	-	96 h	LC50	mortality	17.8-21.5	c	BASF AG (1978)
Oncorhynchus mykiss	-	Y	F	-	-	-	-	-	96 h	NOEC	mortality	9.4	d	TSCATS (1993)
Oncorhynchus mykiss	-	Y	F	-	-	-	-	-	96 h	LC50	mortality	23	d	TSCATS (1993)
Oryzias latipes	-	Y	S	90%	-	-	-	-	48 h	LC50	mortality	20	e	BASF AG (1978)
Bacteria														
Pseudomonas putida	-	-	-	98%	-	-	-	-	30 min	EC50	respiration	440	f	BASF AG (1989)
Pseudomonas putida	-	-	-	98%	-	-	-	-	30 min	EC10	respiration	280	f	BASF AG (1989)

Notes
a: DIN 38412 part 9
b: DIN 38412 part 11
c: DIN 38412, part 15
d: US EPA method
e: Japanese Industrial Standard, K 0102
f: DIN 38412, part 27

Table A2.21. Chronic toxicity data for tris(iso-butyl)phosphate (TiBP) to freshwater organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Algae														
Scenedesmus subspicatus	-	-	-	98%	-	-	-	-	72 h	EC10	biomass	24	a	BASF AG (1989)
Scenedesmus subspicatus	-	-	-	98%	-	-	-	-	72 h	EC10	growth rate	25	a	BASF AG (1989)
Scenedesmus subspicatus	-	-	-	98%	-	-	-	-	96 h	EC10	biomass	22	a	BASF AG (1989)
Scenedesmus subspicatus	-	-	-	98%	-	-	-	-	96 h	EC10	growth rate	13	a	BASF AG (1989)

Table A2.22. Acute toxicity data for tris(iso-butyl)phosphate (TiBP) to saltwater organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Bacteria														
Vibrio fischeri	-	N	S	-	am	-	20	15	15 min	EC50	bioluminescence	129	a	Guzzella & Galassi (1993)
Vibrio fischeri	-	N	S	-	am	-	20	15	15 min	EC10	bioluminescence	15	b	Guzzella & Galassi (1993)

Notes

a: LUMIStox test

b: LUMIStox test, EC10 determined from EC50 and slope of the dose-response relationship

Table A2.23. Toxicity data for tris(iso-butyl)phosphate (TiBP) to fresh water microbiological processes and enzyme activity. All data are from IUCLID (European Commission, 2000).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
activated sludge bacteria	-	-	-	-	-	-	-	-	30 min	EC10	oxygen consumption	390	a	BASF AG (1984)

Notes

a: ISO 8192

Table A2.24. Acute toxicity data for triethyl phosphate (TEP) to fresh water organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Algae															
Scenedesmus subspicatus	-	-	S	99.8%	-	-	-		72 h	EC50	growth	900.8	a	GDCh (1989), European Commission (2000)	Bayer AG (1987b)
Pseudokirchneriella subcapitata	-	-	S	-	-	-	-		7 d	EC0	growth rate	1000	b	European Commission (2000)	Boatman (1983)
Crustacea															
Asellus intermedius	0.012 g	N	S	-	nw	6.5-8.5	130	20±1	96 h	EC50	mobility	>100		Ewell et al. (1986)	
Daphnia magna	<24 h, Strauss, IRCHA	N	S		am	8.0±0.2	250.2	20	24 h	EC50	immobility	900		Bringmann & Kühn (1982)	
Daphnia magna	Straus	N	S		am		250	20	24 h	EC50	immobility	950	c	Knie et al. (1983)	
Daphnia magna	-	-	S	-	-	-	-		24 h	EC50	mobility	2705	d	GDCh (1989), European Commission (2000)	Bayer AG (1987a)
Daphnia magna	-	-	S	-	-	-	-		96 h	EC50	mobility	350		GDCh (1989)	Daugherty (1985)
Daphnia magna	-	-	S	-	-	-	-		48 h	LC50	mortality	350	e	European Commission (2000)	Boatman (1983)
Daphnia magna	first and second larval instar	N	S	-	nw	6.5-8.5	130	20±1	96 h	EC50	mobility	>100		Ewell et al. (1986)	
Daphnia magna	<24 h, Strauss, IRCHA	N	S		am	8.0±0.2	250.2	20	24 h	EC0	immobility	603	f	Bringmann & Kühn (1982)	
Daphnia magna	Straus	N	S		am		250	20	24 h	EC0	immobility	500	c	Knie et al. (1983)	
Gammarus fasciatus	0.007 g	N	S	-	nw	6.5-8.5	130	20±1	96 h	EC50	mobility	>100		Ewell et al. (1986)	
Pisces															
Leuciscus idus	-	-	-	-	-	-	-	-	48 h	LC50	mortality	>1000		GDCh (1989)	Bayer AG (1978)
Leuciscus idus	L.	N	S	-	-	-	-	-	48 h	LC50	mortality	2140	g	Knie et al. (1983)	
Leuciscus idus	L.	N	S	-	-	-	-	-	48 h	LC0	mortality	1926	g	Knie et al. (1983)	
Oryzias latipes	-	-	S	-	-	-	-	-	48 h	LC50	mortality	>500	h	European Commission (2000)	CITI (1992)
Pimephales promelas	-	N	S	-	-	-	-	-	96 h	EC50	mobility	>1070	i	European Commission (2000)	Boatman (1983)
Pimephales promelas	0.2-0.5 g	N	S	-	nw	6.5-8.5	130	20±1	96 h	LC50	mortality	>100		Ewell et al. (1986)	
Annelida															
Lumbriculus variegatus	0.006 g	N	S	-	nw	6.5-8.5	130	20±1	96 h	EC50	mobility	>100		Ewell et al. (1986)	
Bacteria															
Escherichia coli		N	Sc						16-18 h	EC0		100000		GDCh (1989)	Bayer AG (1978)
Pseudomonas fluorescens		N	Sc						16-18 h	EC0		100000	j	GDCh (1989), European Commission (2000)	Bayer AG (1978)
Pseudomonas putida		N	Sc		am	7			30 min	EC10	oxygen consumption	2985	k	Knie et al. (1983)	
Mollusca															
Helisoma trivolvis	0.180 g	N	S	-	nw	6.5-8.5	130	20±1	96 h	EC50	mobility	>100		Ewell et al. (1986)	
Platyhelminthes															
Dugesia tigrina	0.006 g	N	S	-	nw	6.5-8.5	130	20±1	96 h	EC50	mobility	>100		Ewell et al. (1986)	

Notes
a: according to DIN 38412 part 9, draft 1987
b: according to OECD guideline 201
c: according to DIN 38412 Teil 11
d: according to OECD guideline 202
e: according to method of Ewell et al. (1986)
f: photoperiod 16:8 h light:dark with 50 ft-c cool-white fluorescent light; species test in multi-species test (7)
g: according to DIN 38412 Teil 15
h: according to Japanese Industrial Standard (JIS K 0102-1986-71)
i: similar to OECD guideline 203
j: method DEV part 8, (1968)
k: Robra test (1976)

Table A2.25. Chronic toxicity data for triethyl phosphate (TEP) to fresh water organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Algae															
Scenedesmus subspicatus	-	-	S	99.8%	-	-	-		72 h	EC10	growth	80.3	a	GDCh (1989), European Commission (2000)	Bayer AG (1987b)
Crustacea															
Daphnia magna	-	-	-	99.8%	-	-	-		21	NOEC	reproduction	<10	b	GDCh (1989),	Bayer AG (1987a)
Daphnia magna	-	-	-	99.8%	-	-	-		21	EC50	reproduction	729	b	GDCh (1989), European Commission (2000)	Bayer AG (1987a)
Daphnia magna	-	-	-	99.8%	-	-	-		21	EC50	reproduction	830	c	GDCh (1989),	Bayer AG (1987a)
Daphnia magna	-	-	-	99.8%	-	-	-		21	EC10	reproduction	190	c	GDCh (1989),	Bayer AG (1987a)

Notes
a: according to DIN 38412 part 9, draft 1987
b: according to OECD guideline 202
c: according to OECD guideline 202; determined from presented data with log-logistic dose-response model

Table A2.26. Toxicity data for triethyl phosphate (TEP) to fresh water microbiological processes and enzyme activity. All data are from IUCLID (European Commission, 2000).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
activated sludge bacteria	-	-	-	-	-	-	-	-	5 h	EC50	respiration	>5000	a	Boatman (1983)

Notes
a: OECD guideline 209

Table A2.27. Acute toxicity data for triethyl phosphate (TEP) to salt water organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Crustacea														
Nitroca spinipes	adult, 3-6 w	N	S	98%	nw	7.8	7	10	96 h	EC50	mobility	950		Lindén et al. (1979)
Pisces														
Alburnus alburnus	~8 cm	N	S	98%	nw	7.8	7	10	96 h	LC50	mortality	2100-2400		Lindén et al. (1979)

Table A2.28. Acute toxicity data for tris(2-butoxyethyl)phosphate (TBEP) to fresh water organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
crustacea															
Daphnia magna	-	-	-	-	-	-	-		24 h	LC50	mortality	84		IPCS (2000), European Commission (2000)	Monsanto (1984b)
Daphnia magna	-	-	-	-	-	-	-		48 h	LC50	mortality	75		IPCS (2000), European Commission (2000)	Monsanto (1984b)
Daphnia magna	-	-	-	-	-	-	-		48 h	NOEC	mortality	32		IPCS (2000)	Monsanto (1984b)
pisces															
Oncorhynchus mykiss									96 h	LC50	mortality	24	a	IPCS (2000)	Wetton & Handley (1998)
Oncorhynchus mykiss									96 h	NOEC	mortality	10	a	IPCS (2000)	Wetton & Handley (1998)
Oryzias latipes	-	-	-	-	-	-	-	30	48 h	LC50	mortality	6.8		IPCS (2000), European Commission (2000)	Tsuji et al. (1986)
Oryzias latipes	-	-	-	-	-	-	-	20	48 h	LC50	mortality	27		IPCS (2000), European Commission (2000)	Tsuji et al. (1986)
Oryzias latipes	-	-	-	-	-	-	-	10	48 h	LC50	mortality	44		IPCS (2000), European Commission (2000)	Tsuji et al. (1986)
Oryzias latipes	-	N	R	-	dtw	7.2	40	20±1	96 h	LC50	mortality	30		Yoshioka & Ose (1993)	
Pimephales promelas	31 d, 19.6±2.010 mm, 0.119±0.0465 g	Y	F	98%	nw/ dtw	7.84±0.05	45.4±0.75	26.2±0.45	96 h	LC50	mortality	11.2		Geiger et al. (1986)	
Pimephales promelas	31 d, 19.6±2.010 mm, 0.119±0.0465 g	Y	F	98%	nw/ dtw	7.84±0.05	45.4±0.75	26.2±0.45	96 h	LC10	mortality	9.29		Geiger et al. (1986)	
Pimephales promelas								22	96 h	LC50	mortality	16		IPCS (2000), European Commission (2000)	Monsanto (1984a)
Insecta															
Culex tarsalis	4th instar, malathion resistant strain	N	S	-	dw	-	-	-	24 h	LC50	mortality	>1		Plapp & Tong (1966)	

Notes

a: according to OECD guideline 203

Table A2.29. Acute toxicity data for tris(2-ethylhexyl)phosphate (TEHP) to fresh water organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
crustacea															
Daphnia magna		Y	S	-	-	-	-	-	-	LC0	mortality	≥0.074	a	GDCh (2000)	Bayer AG (1998)
fish															
Brachydanio rerio		-	S	-	-	8.1-8.5	-	21.2-23.2	96 h	LC0	mortality	≥100	b	GDCh (1997), IPCS (2000), European Commission (2000)	Bayer AG (1982a)
Oryzias latipes		-	S	-	-	-	-	-	48 h	LC50	mortality	>500	c	European Commission (2000)	CITI (1992)
Insecta															
Culex tarsalis	4th instar, malathion resistant strain	N	S	-	dw	-	-	-	24 h	LC50	mortality	>1		Plapp & Tong (1966)	
Protozoa															
Tetrahymena pyriformis		N	S	-	am	-	-	30	24 h	EC50	proliferation	20	d	GDCh (1997)	Yoshioka et al. (1985)

Notes
a: according to guideline 67/548/EEC; one concentrations testes at the solubility limit of the compound; measured concentration is the geometric mean of the concentration at the begin and end of the test (0.11 and 0.05 mg/L)
b: UBA draft method (1982)
c: Japanese Industrial Standard (JIS K 0102-1986-71)
d: in the original study this compound is indicated as trioctyl phosphate.

Table A2.30. Toxicity data for tris(2-ethylhexyl)phosphate (TEHP) to fresh water microbiological processes and enzyme activity.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
activated sludge	-		S	-	-	8.2-8.3	-	22.5	3 h	IC50	respiration inhibition	>100	a	GDCh (1997), IPCS (2000), European Commission (2000)	Bayer AG (1982b)

Notes
a: inhibition test E3002

Table A2.31. Acute toxicity data for triphenylphosphate (TPP) to freshwater organisms. Data are reported in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003b).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Algae															
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	28 h	EC50	carbon uptake	0.26	a	Wong & Chau (1984)	
Pseudokirchneriella subcapitata	-	N	S	-	-	-	-	-	96 h	EC50	cell density	2	b	Mayer et al. (1981)	
Scenedesmus quadricauda	-	-	S	pure	am	8	-	20	28 h	EC50	carbon uptake	0.5	a	Wong & Chau (1984)	

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
natural algal community	Hamilton, Lake Ontario	-	S	pure	nw	-	-	20	28 h	EC50	carbon uptake	0.2	c	Wong & Chau (1984)	
Crustacea															
Daphnia magna	-	N	S	-	-	-	-	-	48 h	EC50	mobility	1.35	d, e	European Commission (2000)	Ciba-Geigy Limited (1981a)
Daphnia magna	-	N	S	-	-	-	-	-	48 h	EC50	mobility	1.0		Mayer et al. (1981)	
Daphnia magna	< 24 h	N	S						48 h	EC50	mobility	1.0	f	Ziegenfuss et al. (1986)	
Gammarus pseudolimnaeus	mid-instar, 60-90 d	N	S	99%	nw	7.6	73	17	96 h	EC50	mobility	0.25		Huckins et al. (1991)	
Pisces															
Carassius auratus	0.8-2.8 g	N	S	-	dtw	-	-	25	96 h	LC50	mortality	0.70		Sasaki et al. (1981)	
Ictalurus punctatus	0.23 g	Y	S	-	-	7.5	38	22	96 h	LC50	mortality	0.42	d	Mayer & Ellersieck (1986)	
Gambusia affinis	~0.2-0.26	-	S	≥99%	tw	-	-	23	96 h	NOEC	mortality	0.2		Environment Agency (2003b)	Solomon et al. (1999)
Lepomis macrochirus	33-75 mm	N	S	-	nw	7.6-7.9	55	23	96 h	LC50	mortality	290	g	Dawson et al. (1975-1977)	
Lepomis macrochirus	0.5-1.0 g	N	S	99%	nw	7.6	73	22	96 h	LC50	mortality	0.78		Huckins et al. (1991)	
Leuciscus idus	-	-	-	-	-	-	-	-	96 h	LC50	mortality	>5	e	Environment Agency (2003b)	Bayer (2002)
Oncorhynchus mykiss	fry, 12 d past swim-up, 0.11 g, 24 mm	-	S	99%	nw	7.5	272	-	96 h	LC50	mortality	0.36	h	Palawski et al. (1983)	
Oncorhynchus mykiss	fry, 12 d past swim-up, 0.11 g, 24 mm	-	S	99%	nw	7.5	272	-	96 h	EC50	immobility	0.30	h	Palawski et al. (1983)	
Oncorhynchus mykiss	0.6 g	Y	S	-	-	7.4	40	12	96 h	LC50	mortality	0.37	d	Mayer & Ellersieck (1986)	
Oncorhynchus mykiss	fry	N	S	-	-	7.2	272	12	96 h	LC50	mortality	0.4	d	Mayer et al. (1981)	
Oncorhynchus mykiss	0.94 g	N	S	-	tw	7.8-8.1	172	15	96 h	LC50	mortality	0.85	i	European Commission (2000)	Ciba-Geigy Limited (1981b)
Oncorhynchus mykiss	fingerling, 45 d	N	S	-	rw	7.0-7.2	40-48	12	96 h	LC50	mortality	0.32		Environment Agency (2003b)	Sitthichaikasem (1978)
Oncorhynchus mykiss	fingerling, 45 d	Y	F	-	nw	7.4-7.5	295-305	12	96 h	LC50	mortality	>0.45		Environment Agency (2003b)	Sitthichaikasem (1978)
Oncorhynchus mykiss	sac fry, 10 d	N	S	-	rw	7.0-7.2	40-48	12	96 h	LC50	mortality	0.31		Environment Agency (2003b)	Sitthichaikasem (1978)
Oncorhynchus mykiss	sac fry, 10 d	Y	F	-	nw	7.4-7.5	295-305	12	96 h	LC50	mortality	>0.45		Environment Agency (2003b)	Sitthichaikasem (1978)
Oryzias latipes	0.1-0.2 g	N	S	-	dtw	-	-	25	96 h	LC50	mortality	1.2		Sasaki et al. (1981)	
Pimephales promelas	29 d, 17.0 ± 1.395 mm, 0.071±0.0245 g	Y	F	98%	nw/dtw	7.78± 0.04	45.6±0.75	24.5±0.38	96 h	LC50	mortality	0.87	j	Geiger et al. (1986)	
Pimephales promelas	1.00 g	Y	S	-	-	7.3	44	22	96 h	LC50	mortality	1.0	d	Mayer & Ellersieck (1986)	
Pimephales promelas	-	N	S	-	-	-	-	-	96 h	LC50	mortality	0.66	d	Mayer et al. (1981)	
Bacteria															
Escherichia coli	-	-	-	-	-	-	-	-	24 h	EC0	-	200		Environment Agency (2003b)	OECD (2002)
Pseudomonas fluorescens	-	-	-	-	-	-	-	-	24 h	EC0	-	200		Environment Agency (2003b)	OECD (2002)

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Cyanophyta															
Anabaena flos-aquae	-	-	S	pure	am	-	-	20	4 h	EC16	nitrogenase activity	0.1	k	Wong & Chau (1984)	
Anabaena flos-aquae	-	-	S	pure	am	-	-	20	4 h	EC23	nitrogenase activity	1	k	Wong & Chau (1984)	
Anabaena flos-aquae	-	-	S	pure	am	-	-	20	4 h	EC32	nitrogenase activity	5	k	Wong & Chau (1984)	
Fungi															
Aspergillus niger	-	-	-	-	-	-	-	30	24 h	NOEC	spore germination	>1631	l	Environment Agency (2003b)	Eto et al. (1975)
Aspergillus niger	-	-	-	-	-	-	-		30 min	EC9	oxygen uptake	163		Environment Agency (2003b)	OECD (2002)
Insecta															
Chironomus riparius	4th instar	N	S	99%	nw	7.6	73	22	48 h	EC50	mobility	0.36		Huckins et al. (1991)	
Chironomus tentans	2nd instar, 10-14 d		S						48 h	EC50	mobility	1.6	f	Ziegenfuss et al. (1986)	
Mollusca															
Pomacea canaliculata	L., 35-40 d		S	98%	nw	7.5		26	72 h	LC50	mortality	38.2	g	Lo & Hsieh (2000)	
Protozoa															
Tetrahymena pyriformis	-	N	S	>95%	-	-	-	-	40 h	EC50	growth inhibition	5.05		Sinks & Schultz (2001)	

Notes
a: $4.7 \cdot 10^4$ cells/mL; photoperiod 16:8 light:dark at 5000 lux
b: US EPA method
c: photoperiod 16:8 light:dark at 5000 lux
d: EPA-660/3-75-009 method
e: marked as not assignable in the draft risk assessment report
f: ASTM method
g: marked as invalid in the draft risk assessment report
h: extrapolated LC50. For immobility the effect percentages were 4, 7 and 34, for mortality 0, 5 and 6. Such a value is assigned as **invalid** in the framework of INS
i: OECD 203 method
j: cited in the draft environmental risk assessment report as Sinks and Schultz (2001). Here the original reference is given.
k: nitrogenase activity was measured with the acetylene reduction technique. Test performed at 5000 lux.
l: $2.5 \cdot 10^5$ cells/mL

Table A2.32. Chronic toxicity data for triphenylphosphate (TPP) to freshwater organisms. Data are reported in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003b).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Algae															
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	72 h	NOEC	growth rate, biomass	0.1	a	Wong & Chau (1984)	
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	22 d	NOEC	growth rate, biomass	0.1	a	Wong & Chau (1984)	
Chlorella vulgaris	CCAP 211/11b	N	S	-	am	-	47	22	72 h	NOEC	biomass (AUC)	1	b	Millington et al. (1988)	
Chlorella vulgaris	CCAP 211/11b	N	S	-	am	-	18	22	72 h	NOEC	biomass (AUC)	1	c	Millington et al. (1988)	
Chlorella vulgaris	CCAP 211/11b	N	S	-	am	-	22	22	72 h	NOEC	biomass (AUC)	1	d	Millington et al. (1988)	
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	47	22	72 h	NOEC	biomass (AUC)	0.1	b	Millington et al. (1988)	
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	18	22	72 h	NOEC	biomass (AUC)	1	c	Millington et al. (1988)	
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	22	22	72 h	NOEC	biomass (AUC)	0.5	d	Millington et al. (1988)	
Scenedesmus subspicatus	CCAP 276/20	N	S	-	am	-	47	22	72 h	NOEC	biomass (AUC)	0.1	b	Millington et al. (1988)	
Scenedesmus subspicatus	CCAP 276/20	N	S	-	am	-	18	22	72 h	NOEC	biomass (AUC)	1	c	Millington et al. (1988)	
Scenedesmus subspicatus	CCAP 276/20	N	S	-	am	-	22	22	72 h	NOEC	biomass (AUC)	0.5	d	Millington et al. (1988)	
Pisces															
Oncorhynchus mykiss	sac fry	Y	F	-	nw	7.2	272	12±1	90 d	NOEC	mortality, growth, development	≥0.0014		Mayer et al. (1981)	
Oncorhynchus mykiss	sac fry, 10 d	-	F	-	nw	7.4-7.5	295-305	12	30 d	EC10	growth	0.037		Environment Agency (2003b)	Sitthichaikasem (1978)
Oncorhynchus mykiss	sac fry, 10 d	-	F	-	nw	7.4-7.5	295-305	12	30 d	NOEC	growth	<0.055		Environment Agency (2003b)	Sitthichaikasem (1978)
Oncorhynchus mykiss	fingerling, 45 d	-	F	-	nw	7.4-7.5	295-305	12	30 d	NOEC	growth (length)	0.055		Environment Agency (2003b)	Sitthichaikasem (1978)
Oncorhynchus mykiss	sac fry, 10 d	-	F	-	nw	7.4-7.5	295-305	12	30 d	LC50	growth	0.24		Environment Agency (2003b)	Sitthichaikasem (1978)
Oncorhynchus mykiss	fingerling, 45 d	-	F	-	nw	7.4-7.5	295-305	12	30 d	LC50	growth	0.26		Environment Agency (2003b)	Sitthichaikasem (1978)
Pimephales promelas	ELS	Y	F	-	-	-	-	-	30 d	NOEC	hatchability, growth, development	≥0.23		Mayer et al. (1981)	
Pimephales promelas	ELS	Y	F	-	-	-	-	-	30 d	NOEC	mortality	0.087		Mayer et al. (1981)	

Notes
a: $4.7 \cdot 10^4$ cells/mL; photoperiod 16:8 light:dark at 5000 lux
b: OECD 201 method; 10^4 cells/mL; Bold's basal medium; continuous light
c: OECD 201 method; 10^4 cells/mL; OECD medium; continuous light
d: OECD 201 method; 10^4 cells/mL; US EPA medium; continuous light

Table A2.33. Acute toxicity data for triphenylphosphate (TPP) to saltwater organisms. Data are reported in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003b).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [°C]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Crustacea														
Mysidopsis bahia	-	N	S	-	-	-	-	-	96 h	LC50	mortality	0.18-0.32	a	Mayer et al. (1981)
Pisces														
Menidia beryllina	40-100 mm	N	S	-	rw	-	-	20	96 h	LC50	mortality	95	b	Dawson et al. (1975-1977)
Cyprinodon variegatus	-	N	S	-	-	-	-	-	96 h	LC50	mortality	0.32-0.56	a	Mayer et al. (1981)

Notes
a: EPA-660/3-75-009 method
b: marked as invalid in the draft risk assessment report

Table A2.34. Additional toxicity data for triphenylphosphate (TPP) to fresh water organisms not included in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003b).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [°C]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Algae														
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	28 h	EC50	growth rate	0.57	a	Wong & Chau (1984)
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	28 h	EC10	growth rate	0.016	a	Wong & Chau (1984)
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	5 d	EC50	growth rate	0.41	b	Wong & Chau (1984)
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	5 d	EC10	growth rate	0.016	b	Wong & Chau (1984)
Chlorella vulgaris	CCAP 211/11b	N	S	-	am	-	47	22	96 h, 5 d	NOEC	biomass (AUC) and growth rate	1	c	Millington et al. (1988)
Chlorella vulgaris	CCAP 211/11b	N	S	-	am	-	18	22	96 h, 5 d	NOEC	biomass (AUC) and growth rate	1	d	Millington et al. (1988)
Chlorella vulgaris	CCAP 211/11b	N	S	-	am	-	22	22	96 h, 5 d	NOEC	biomass (AUC) and growth rate	1	e	Millington et al. (1988)
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	47	22	96 h, 5 d	NOEC	biomass (AUC) and growth rate	0.1	c	Millington et al. (1988)
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	18	22	96 h, 5 d	NOEC	biomass (AUC) and growth rate	1	d	Millington et al. (1988)
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	22	22	96 h, 5 d	NOEC	biomass (AUC) and growth rate	0.1	e	Millington et al. (1988)
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	47	22	72 h, 96 h	EC50	growth rate	1.0	f	Millington et al. (1988)
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	47	22	72 h	EC10	growth rate	0.53	f	Millington et al. (1988)
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	47	22	96 h	EC10	growth rate	0.76	f	Millington et al. (1988)
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	18	22	72 h, 96 h	EC50	growth rate	>5	g	Millington et al. (1988)
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	22	22	72 h, 96 h	EC50	growth rate	1.1	h	Millington et al. (1988)
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	22	22	72 h	EC10	growth rate	0.40	h	Millington et al. (1988)

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Pseudokirchneriella subcapitata	CCAP 278/4	N	S	-	am	-	22	22	96 h	EC10	growth rate	0.45	h	Millington et al. (1988)
Scenedesmus subspicatus	CCAP 276/20	N	S	-	am	-	47	22	96 h, 5 d	NOEC	biomass (AUC) and growth rate	0.1	c	Millington et al. (1988)
Scenedesmus subspicatus	CCAP 276/20	N	S	-	am	-	18	22	96 h	NOEC	biomass (AUC) and growth rate	0.5	d	Millington et al. (1988)
Scenedesmus subspicatus	CCAP 276/20	N	S	-	am	-	18	22	5 d	NOEC	biomass (AUC) and growth rate	1	d	Millington et al. (1988)
Scenedesmus subspicatus	CCAP 276/20	N	S	-	am	-	22	22	96 h, 5 d	NOEC	biomass (AUC) and growth rate	1	e	Millington et al. (1988)
Pisces														
Lepomis macrochirus	33-75 mm	N	S	-	nw	7.6-7.9	55	23	96 h	LC50	mortality	380	j	Dawson et al. (1975-1977)
Lepomis macrochirus	33-75 mm	N	S	-	nw	7.6-7.9	55	23	96 h	LC10	mortality	180	k	Dawson et al. (1975-1977)
Oncorhynchus mykiss	fry, 12 d past swim-up	-	-	-	-	-	-	-	96 h	EC50	immobility	0.24	l	Palawski et al. (1983)
Pimephales promelas	29 d, 17.0 ± 1.395 mm, 0.071±0.0245 g	Y	F	98%	nw/dtw	7.78± 0.04	45.6±0.75	24.5±0.38	96 h	EC10	mortality	0.75		Geiger et al. (1986)
Cyanophyta														
Anabaena flos-aquae	-	-	S	pure	am	-	-	20	4 h	EC10	nitrogenase activity	0.01	m	Wong & Chau (1984)
Anabaena flos-aquae	-	-	S	pure	am	-	-	20	4 h	EC50	nitrogenase activity	120	m	Wong & Chau (1984)
Anabaena flos-aquae	-	-	S	pure	am	-	-	20	28 h	EC10	nitrogenase activity	0.076	m	Wong & Chau (1984)
Anabaena flos-aquae	-	-	S	pure	am	-	-	20	28 h	EC50	nitrogenase activity	15	m	Wong & Chau (1984)
Insecta														
Chironomus riparius	4th instar	N	S	99%	nw	7.6	73	22	48 h	EC50	mobility	0.44	j	Huckins et al. (1991)
Chironomus riparius	4th instar	N	S	99%	nw	7.6	73	22	48 h	EC10	mobility	0.20	k	Huckins et al. (1991)
Culex tarsalis	4th instar, malathion resistant strain	N	S	-	dw	-	-	-	24 h	LC50	mortality	>1		Plapp & Tong (1966)

Notes
a: $4.7 \cdot 10^4$ cells/mL; photoperiod 16:8 light:dark at 5000 lux; determined with log-logistic model, growth rate determined from presented data on carbon uptake
b: $4.7 \cdot 10^4$ cells/mL; photoperiod 16:8 light:dark at 5000 lux; determined with log-logistic model from presented data after log-transformation; data from 2-5 days of exposure used, lag-time 2 d
c: OECD 201 method; 10^4 cells/mL; Bold's basal medium; continuous light
d: OECD 201 method; 10^4 cells/mL; OECD medium; continuous light
e: OECD 201 method; 10^4 cells/mL; US EPA medium; continuous light
f: OECD 201 method; 10^4 cells/mL; Bold's basal medium; continuous light; determined from presented data with a log-logistic model
g: OECD 201 method; 10^4 cells/mL; OECD medium; continuous light; determined from presented data with a log-logistic model
h: OECD 201 method; 10^4 cells/mL; US EPS medium; continuous light; determined from presented data with a log-logistic model
j: LC50 recalculated with log-logistic equation
k: LC10 calculated from original data with log-logistic equation
l: mean value from 5 acute toxicity studies performed at Columbia National Fisheries Research Laboratory

m: test performed at 5000 lux; determined with a log-logistic model from presented data

Table A2.35. Additional toxicity data for triphenylphosphate (TPP) to saltwater organisms not included in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003b).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Pisces														
Menidia beryllina	40-100 mm	N	S	-	rw	-	-	20	96 h	LC50	mortality	98	a	Dawson et al. (1975-1977)
Menidia beryllina	40-100 mm	N	S	-	rw	-	-	20	96 h	LC10	mortality	92	b	Dawson et al. (1975-1977)

Notes
a: LC50 recalculated with log-logistic equation
b: LC10 calculated from original data with log-logistic equation

Table A2.36. Acute toxicity data for tricresylphosphate (TCP) to freshwater organisms. Data are reported in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003a).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Algae															
Ankistrodesmus falcatus	-	-	S	pure	am	8	-	20	28 h	EC50	carbon uptake	2.5	a,d	Wong & Chau (1984)	
Ankistrodesmus falcatus	-	-	S	pure	am	8	-	20	28 h	EC50	carbon uptake	>5	b,d	Wong & Chau (1984)	
Ankistrodesmus falcatus	-	-	S	pure	am	8	-	20	28 h	EC50	carbon uptake	>5	c,d	Wong & Chau (1984)	
Scenedesmus pannonicus	-	-	S	pract.	am	-	-	23±2	96 h	EC50	growth	1.5	e	Adema et al. (1981)	
Scenedesmus quadricauda	-	-	S	pure	am	8	-	20	28 h	EC50	carbon uptake	4.2	a,d	Wong & Chau (1984)	
Scenedesmus quadricauda	-	-	S	pure	am	8	-	20	28 h	EC50	carbon uptake	>5	b,d	Wong & Chau (1984)	
Scenedesmus quadricauda	-	-	S	pure	am	8	-	20	28 h	EC50	carbon uptake	>5	c,d	Wong & Chau (1984)	
Natural algal community	-	-	S	pure	nw	-	-	20	28 h	EC50	carbon uptake	1.7	a,d	Wong & Chau (1984)	
Natural algal community	-	-	S	pure	nw	-	-	20	28 h	EC50	carbon uptake	4.1	b,d	Wong & Chau (1984)	
Natural algal community	-	-	S	pure	nw	-	-	20	28 h	EC50	carbon uptake	>5	c,d	Wong & Chau (1984)	
Crustacea															
Daphnia magna	-	-	S	pract.	am	-	-	-	48 h	EC50	immobility	5.6	f	Adema et al. (1981; 1983)	
Daphnia magna	-	-	S	pract.	am	-	-	-	48 h	NOEC	immobility	0.18	f	Adema et al. (1981; 1983)	
Daphnia magna	-	N	S	-	-	-	-	-	48 h	EC50	immobility	0.27		European Commission (2000)	Union Carbide (1979)
Daphnia magna	-	N	S	-	-	-	-	-	48 h	NOEC	immobility	0.1		European Commission (2000)	Union Carbide (1979)

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Pisces															
Brachydanio rerio	4-5 w and 1-2 d	N	-	-	-	-	-	-	96 h	LC50	mortality	>1.0		van den Dikkenberg et al. (1989)	
Brachydanio rerio	4-5 w and 1-2 d	N	-	-	-	-	-	-	96 h	NOEC	behaviour	0.18		van den Dikkenberg et al. (1989)	
Ictalurus punctatus	1.3 g	Y	F	-	-	7.4	44	12	96 h	LC50	mortality	0.80		Mayer & Ellersieck (1986)	
Jordanella floridae	4-5 w	N	R	pract.	am	-	-	23±2	96 h	LC50	mortality	5.0		van den Dikkenberg et al. (1989)	
Jordanella floridae	4-5 w	N	R	pract.	am	-	-	23±2	96 h	NOEC	behaviour	1.0		van den Dikkenberg et al. (1989)	
Gasterosteus aculeatus	4-5 w	Y	R	pract.	am	8.2±0.2	208	19±1	96 h	LC50	mortality	0.44	g	van den Dikkenberg et al. (1989)	
Gasterosteus aculeatus	4-5 w	Y	R	pract.	am	8.2±0.2	208	19±1	96 h	NOEC	behaviour	0.16	g	van den Dikkenberg et al. (1989)	
Lepomis macrochirus	33-75 mm	N	S	-	nw	7.6-7.9	55	23	96 h	LC50	mortality	7000		Dawson et al. (1975-1977)	
Lepomis macrochirus	0.02 g	N	S		rw	7.0-7.2	40-48	22	96 h	LC50	mortality	>100	c	Environment Agency (2003a)	Sitthichaikasem (1978)
Lepomis macrochirus	0.60 g	Y	F	-	-	7.4	44	12	96 h	LC50	mortality	0.15		Mayer & Ellersieck (1986)	
Lepomis macrochirus	0.60 g	Y	F	-	-	7.6	314	12	96 h	LC50	mortality	0.082		Mayer & Ellersieck (1986)	
Oncorhynchus mykiss	0.23 g	Y	F	-	-	7.4	44	12	96 h	LC50	mortality	0.26		Mayer & Ellersieck (1986)	
Oncorhynchus mykiss	0.50 g	Y	F	-	-	7.4	44	12	96 h	LC50	mortality	0.40		Mayer & Ellersieck (1986)	
Oncorhynchus mykiss	-	N	S	-	-	7.4	42	-	96 h	LC50	mortality	0.75		European Commission (2000)	Union Carbide (1978a)
Oryzias latipes	-	N	R	-	dtw	7.2	40	20±1	96 h	LC50	mortality	6.7		Yoshioka & Ose (1993)	
Oryzias latipes	4-5 w	N	R	pract.	am	-	-	23±2	96 h	LC50	mortality	4.9		van den Dikkenberg et al. (1989)	
Oryzias latipes	4-5 w	N	R	pract.	am	-	-	23±2	96 h	NOEC	behaviour	1.8		Adema et al. (1981);; van den Dikkenberg et al. (1989)	
Perca flavescens	0.70 g	Y	F	-	-	7.4	242	12	96 h	LC50	mortality	0.50		Mayer & Ellersieck (1986)	
Pimephales promelas	-	N	S	-	-	7.23	44	-	96 h	LC50	mortality	>100		European Commission (2000)	Union Carbide (1978b)
Poecilia reticulata	3-4 w	N	R	pract.	am	-	-	23±2	96 h	LC50	mortality	4.0	h	Adema et al. (1981; 1983)	
Poecilia reticulata	3-4 w	N	R	pract.	am	-	-	23±2	96 h	NOEC	behaviour	1.0	h	Adema et al. (1981; 1983); van den Dikkenberg et al. (1989)	
Poecilia reticulata	3-4 w	N	R	pract.	am	-	-	23±2	96 h	LC50	mortality	5.5	h	Adema et al. (1981); van den Dikkenberg et al. (1989)	

Notes
a: ortho-isomer
b: meta-isomer
c: para-isomer
d: $4.7 \cdot 10^4$ cells/mL; photoperiod 16:8 h light:dark at 5000 lux
e: in line with OECD 201; ~5000 lux; 10^4 cells/mL
f: in line with OECD 202
g: photoperiod 16:8 h light:dark
h: in line with OECD guidelines (203); results from tests performed at two laboratories; NOEC is the same for both tests

Table A2.37. Chronic toxicity data for tricresylphosphate (TCP) to freshwater organisms. Data are reported in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003a). Additional information for the fish toxicity tests is retrieved from Canton et al. (1984)

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [°C]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Algae															
Scenedesmus pannonicus	-	-	S	pract.	am	-	-	23±2	4 d	NOEC	growth	0.32	a	Adema et al. (1981; 1983)	
Crustacea															
Daphnia magna	<1 d	-	R	pract.	am	-	-	19±1	21 d	NOEC	reproduction	0.1	b	Adema et al. (1981; 1983)	
Pisces															
Brachydanio rerio	embryo-larval	-	-	-	-	-	-	-	-	NOEC	mortality, development, growth	0.0056	c	van den Dikkenberg et al. (1989)	
Brachydanio rerio	embryo-larval	-	-	-	-	-	-	-	-	NOEC	embryonic development, hatching time	0.32	c	van den Dikkenberg et al. (1989)	
Gasterosteus aculeatus	<6 h eggs	N	R	pract.	am	8.2±0.2	208	19±1	35 d	NOEC	mortality and sublethal effects	0.0010	d	van den Dikkenberg et al. (1989)	
Gasterosteus aculeatus	<6 h eggs	N	R	pract.	am	8.2±0.2	208	19±1	35 d	LC50	mortality	0.0017	d	van den Dikkenberg et al. (1989)	
Gasterosteus aculeatus	<6 h eggs	N	R	pract.	am	8.2±0.2	208	19±1	35 d	EC50	mortality and sublethal effects	0.0013	d	van den Dikkenberg et al. (1989)	
Gasterosteus aculeatus	<6 h eggs	N	R	pract.	am	8.2±0.2	208	19±1	35 d	NOEC	embryo stage	0.0032	d	van den Dikkenberg et al. (1989)	
Gasterosteus aculeatus	<6 h eggs	N	R	pract.	am	8.2±0.2	208	19±1	35 d	NOEC	growth	0.00032	d	van den Dikkenberg et al. (1989)	
Jordanella floridae	eggs, <6 h, ELS	-	R	pract.	am	-	-	23±2	42 d; max 28 post-hatching	NOEC	development	0.01	c,e	Adema et al. (1983); van den Dikkenberg et al. (1989)	
Jordanella floridae	eggs, <6 h, ELS	-	R	pract.	am	-	-	23±2	42 d; max 28 post-hatching	NOEC	embryonic development, hatching time	1.0	c	van den Dikkenberg et al. (1989)	
Oncorhynchus mykiss	yearling	-	F	~75%	-	-	-	-	120 d	NOEC	sublethal effects	0.9		Environment Agency (2003a)	Lockhart et al. (1975)
Oryzias latipes	embryo-larval	-	-	-	-	-	-	-	-	NOEC	mortality	0.01	c	van den Dikkenberg et al. (1989)	
Oryzias latipes	embryo-larval	-	-	-	-	-	-	-	-	NOEC	embryonic development, hatching time	0.032	c	van den Dikkenberg et al. (1989)	
Poecilia reticulata	3-4 w	-	R	pract.	am	-	-	23±2	28 d	NOEC	mortality and growth	1.0	c,f	Adema et al. (1981; 1983); van den Dikkenberg et al. (1989)	

Notes
a: in line with OECD 201; ~5000 lux; 10^4 cells/mL
b: same results from two laboratories; in line with OECD guidelines (202)
c: data from Adema et al.
d: photoperiod 16:8 h light:dark
e: according to OECD procedures (OECD 210)
f: according to OECD procedures (OECD 204)

Table A2.38. Acute toxicity data for tricresylphosphate (TCP) to saltwater organisms. Data are reported in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003a).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Pisces														
Menidia beryllina	40-100 mm	N	S	-	rw	-	-	20	96 h	LC50	mortality	8700	a	Dawson et al. (1975-1977)

Notes
a: marked as invalid in the draft risk assessment report

Table A2.39. Additional toxicity data for tricresylphosphate (TCP) to freshwater organisms not included in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003a).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Algae															
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	28 h	EC50	growth rate	4.6	a,d	Wong & Chau (1984)	
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	28 h	EC10	growth rate	0.029	a,d	Wong & Chau (1984)	
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	28 h	EC50	growth rate	15	b,d	Wong & Chau (1984)	
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	28 h	EC10	growth rate	0.094	b,d	Wong & Chau (1984)	
Ankistrodesmus falcatus	*acicularis*	-	S	pure	am	8	-	20	28 h	EC10	growth rate	>5	c,d	Wong & Chau (1984)	
Scenedesmus pannonicus	-	-	S	pract.	am	-	-	23±2	4 d	EC50	growth	3.8, 1.3	e, f	Adema et al. (1981)	
Scenedesmus pannonicus	-	-	S	pract.	am	-	-	23±2	4 d	NOEC	growth	0.56	e, f	Adema et al. (1981)	
Scenedesmus pannonicus	-	-	S	pract.	am	-	-	23±2	14 d	EC50	growth	1.5	e	Adema et al. (1981)	
Scenedesmus pannonicus	-	-	S	pract.	am	-	-	23±2	14 d	NOEC	growth	0.32	e	Adema et al. (1981)	
Chlorella pyrenoïdosa	-	-	S	pract.	am	-	-	23±2	4 d	NOEC	growth	>1.0	e	Adema et al. (1981)	
Euglena gracilis	-	-	S	pract.	am	-	-	23±2	4 d	NOEC	growth	>1.0	e	Adema et al. (1981)	
Pseudokirchneriella subcapitata	-	-	S	pract.	am	-	-	23±2	4 d	NOEC	growth	<1.0	g	Adema et al. (1981)	
Pseudokirchneriella subcapitata	-	-	S	pract.	am	-	-	23±2	4 d	EC50	growth	>1.0	g	Adema et al. (1981)	
Stephanodiscus hantzschii	-	-	S	pract.	am	-	-	17±2	4 d	NOEC	growth	0.056	h	Adema et al. (1981)	
Stephanodiscus hantzschii	-	-	S	pract.	am	-	-	17±2	4 d	EC50	growth	0.29	h	Adema et al. (1981)	
Crustacea															
Daphnia magna	-	-	S	pract.	am	-	-	-	48 h	EC50	immobility	3.6		Adema et al. (1981)	
Daphnia magna	-	-	S	pract.	am	-	-	-	48 h	EC50	immobility	1.0		Adema et al. (1981)	
Daphnia magna	<1 d	-	R	pract.	am	-	-	19±1	21 d	EC50	immobility	>0.1 <0.32, >0.32 <1.0	f	Adema et al. (1981)	
Daphnia magna	<1 d	-	R	pract.	am	-	-	19±1	21 d	NOEC	immobility	0.1, 0.32	f	Adema et al. (1981)	

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Pisces															
Brachydanio rerio	4-5 w	N	-	-	-	-	-	-	96 h	LC50	mortality	5.9	f	Canton et al. (1984)	
Brachydanio rerio	4-5 w	N	-	-	-	-	-	-	96 h	NOEC	mortality	0.56, 3.2	f	Canton et al. (1984)	
Brachydanio rerio	4-5 w	N	-	-	-	-	-	-	96 h	NOEC	behaviour	0.32	f	Canton et al. (1984)	
Brachydanio rerio	1-2 d	N	-	-	-	-	-	-	96 h	LC50	mortality	0.4	f	Canton et al. (1984)	
Brachydanio rerio	1-2 d	N	-	-	-	-	-	-	96 h	NOEC	mortality	0.24, 0.10	f	Canton et al. (1984)	
Brachydanio rerio	embryo-larval	-	-	-	-	-	-	-	-	NOEC	mortality	0.018;0.0056;0.0056;0.0056;0.01;0.01;0.0032	i	Canton et al. (1984)	
Brachydanio rerio	embryo-larval	-	-	-	-	-	-	-	-	NOEC	egg development	≥0.056;≥0.056;0.32;≥0.18;≥0.18;0.18;0.32)	i	Canton et al. (1984)	
Brachydanio rerio	embryo-larval	-	-	-	-	-	-	-	-	NOEC	growth	0.018;≥0.018;0.016;0.056;≥0.1;0.032;0.018	i	Canton et al. (1984)	
Carassius auratus	3 inch	N	S	technical	-	-	-	20	7 d	LC50	mortality	<1	a	Eldefrawi et al. (1977)	
Gasterosteus aculeatus	4-5 w	N	R	pract.	am	8.2±0.2	208	19±1	96 h	LC50	mortality	0.51	j	van den Dikkenberg et al. (1989)	
Gasterosteus aculeatus	4-5 w	N	R	pract.	am	8.2±0.2	208	19±1	96 h	NOEC	mortality and behaviour	0.18	j	van den Dikkenberg et al. (1989)	
Jordanella floridae	1-2 d	N	R	pract.	am	-	-	23±2	96 h	LC50	mortality	2.1		Adema et al. (1981)	
Jordanella floridae	1-2 d	N	R	pract.	am	-	-	23±2	96 h	NOEC	mortality	1.0		Adema et al. (1981)	
Jordanella floridae	1-2 d	N	R	pract.	am	-	-	23±2	96 h	NOEC	behaviour	0.56		Adema et al. (1981)	
Jordanella floridae	4-5 w	N	R	pract.	am	-	-	23±2	96 h	NOEC	mortality	1.8		Adema et al. (1981); Canton et al. (1984)	
Jordanella floridae	<36 h	N	R	pract.	am	-	-	23±2	28 d	LC50	mortality	>0.01 <0.032		Adema et al. (1981)	
Jordanella floridae	<36 h	N	R	pract.	am	-	-	23±2	28 d	NOEC	mortality and growth	0.01		Adema et al. (1981)	
Jordanella floridae	<36 h	N	R	pract.	am	-	-	23±2	28 d	NOEC	egg development	1.0		Adema et al. (1981)	
Lepomis macrochirus	33-75 mm	N	S	-	nw	7.6-7.9	55	23	96 h	LC50	mortality	6500	k	Dawson et al. (1975-1977)	
Lepomis macrochirus	33-75 mm	N	S	-	nw	7.6-7.9	55	23	96 h	LC10	mortality	3900	l	Dawson et al. (1975-1977)	
Oncorhynchus mykiss		N	S			7.4	42		96 h	NOEC	mortality	<0.56		European Commission (2000)	Union Carbide (1978a)
Oryzias latipes	1-2 d	N	R	pract.	am	-	-	23±2	96 h	LC50	mortality	13		Adema et al. (1981)	
Oryzias latipes	1-2 d	N	R	pract.	am	-	-	23±2	96 h	NOEC	mortality	3.2		Adema et al. (1981)	
Oryzias latipes	1-2 d	N	R	pract.	am	-	-	23±2	96 h	NOEC	behaviour	0.32		Adema et al. (1981)	

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference	Original reference
Oryzias latipes	4-5 w	N	R	pract.	am	-	-	23±2	96 h	LC50	mortality	>3.2 <10		Adema et al. (1981); Canton et al. (1984)	
Oryzias latipes	4-5 w	N	R	pract.	am	-	-	23±2	96 h	NOEC	mortality	3.2		Adema et al. (1981); Canton et al. (1984)	
Oryzias latipes	< 36 h	N	R	pract.	am	-	-	23±2	7 d	LC50	mortality	0.08		Adema et al. (1981)	
Oryzias latipes	< 36 h	N	R	pract.	am	-	-	23±2	7 d	NOEC	mortality	0.032		Adema et al. (1981)	
Oryzias latipes	< 36 h	N	R	pract.	am	-	-	23±2	28 d	NOEC	mortality	<0.032		Adema et al. (1981)	
Oryzias latipes	< 36 h	N	R	pract.	am	-	-	23±2	28 d	NOEC	egg development	0.1		Adema et al. (1981)	
Oryzias latipes	embryo-larval	-	-	-	-	-	-	-	-	NOEC	growth	0.032		Canton et al. (1984)	
Pimephales promelas		N	S			7.2	44		96 h	NOEC	mortality	56		Union Carbide 1978	
Poecilia reticulata	3-4 w	N	R	pract.	am	-	-	23±2	96 h, 1 w	NOEC	mortality	1.8, 1.0	f	Adema et al. (1981; 1983); van den Dikkenberg et al. (1989)	
Poecilia reticulata	3-4 w	-	R	pract.	am	-	-	23±2	7 d	LC50	mortality	3.7, 3.5	f	Adema et al. (1981)	
Poecilia reticulata	3-4 w	-	R	pract.	am	-	-	23±2	14 d	LC50	mortality	2.8, 2.5	f	Adema et al. (1981)	
Poecilia reticulata	3-4 w	-	R	pract.	am	-	-	23±2	28 d	LC50	mortality and growth	2.6, 2.2	f	Adema et al. (1981)	
Poecilia reticulata	3-4 w	-	R	pract.	am	-	-	23±2	28 d	NOEC	mortality and growth	1.0, 1.0	f	Adema et al. (1981)	
Cyanophyta															
Microcystis aeruginosa	-	-	S	pract.	am	-	-	23±2	4 d		growth	>1.0	m	Adema et al. (1981)	
Insecta															
Culex tarsalis	4th instar, malathion resistant strain	N	S	-	dw	-	-	-	24 h	LC50	mortality	>1	n	Plapp & Tong (1966)	

Notes
a: ortho-isomer
b: meta-isomer
c: para-isomer
d: $4.7 \cdot 10^4$ cells/mL; photoperiod 16:8 h light:dark at 5000 lux; determined with log-logistic model; growth rate determined from presented data on carbon uptake
e: in line with OECD 201; ~5000 lux; 10^4 cells/mL
f: results from tests performed at two laboratories
g: in line with OECD 201; ~2500 lux; ca. $5 \cdot 10^4$ cells/mL
h: in line with OECD 201; ~1500 lux; ca. 10^4 cells/mL
i: data from seven tests
j: photoperiod 16:8 h light:dark
k: LC50 recalculated with log-logistic equation
l: LC10 calculated from original data with log-logistic equation
m: in line with OECD 201; ~2500 lux; ca. $5 \cdot 10^5$ cells/mL
n: all isomers tested

Table A2.40. Additional toxicity data for tricresylphosphate (TCP) to saltwater organisms not included in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003a).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Salinity [‰]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
Pisces														
Menidia beryllina	40-100 mm	N	S	-	rw	-	-	20	96 h	LC50	mortality	9100	a	Dawson et al. (1975-1977)
Menidia beryllina	40-100 mm	N	S	-	rw	-	-	20	96 h	LC10	mortality	5600	b	Dawson et al. (1975-1977)

Notes
a: LC50 recalculated with log-logistic equation
b: LC10 calculated from original data with log-logistic equation

Table A2.41. Toxicity data for tricresylphosphate (TCP) to fresh water microbiological processes and enzyme activity. Data are reported in the draft risk assessment report of the UK Environment Agency (Environment Agency, 2003a).

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg/L $CaCO_3$]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Value [mg/L]	Notes	Reference
activated sludge bacteria										NOEC		>1000	a	Bayer (2002)

Notes
a: OECD guideline 209
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Appendix 3. Terrestrial toxicity data

Legend

Species/process/activity	species used in the test, if available followed by age, size, weight or life stage, or microbial processes and enzymatic activity of the soil
Soil type	description of the used type of soil
o.m.	organic matter content of the soil
Clay	clay content of the soil
Temperature	temperature during exposure
Exposure time	h = hours, d = days, w = weeks, m = months, min. = minutes
Criterion	L(E)Cx = test result showing x% mortality (LCx) of effect (ECx). LC50s and EC50s are usually determined for acute effects, EC10s are for chronic effects; NOEC = no observed effect concentration, statistically determined
Result test soil	Concentration in the used test soil corresponding to the L(E)Cx or NOEC
Result standard soil	Concentration corresponding to the L(E)Cx or NOEC normalised to standard soil (containing 10% organic matter and 25% clay)

Table A3.1. Terrestrial toxicity data for tris(2-chloroethyl)phosphate (TCEP). All data are from the draft EU-RAR (European Commission, 2004c).

Species/process/activity	Species properties	Soil type	pH	o.m. [%]	Clay [%]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Result test soil [mg/kg$_{dw}$]	Result standard soil [mg/kg$_{dw}$]	Notes	Reference
Macrophyta													
Avena sativa		loamy sand, LUFA 2.2	5.6	2.29		20	16 d	NOEC	growth	10	44	a, b	Römbke et al. (1995)
Avena sativa		loamy sand, LUFA 2.2	5.6	2.29		20	16 d	EC50	growth	64	279	a	Römbke et al. (1995)
Annelida													
Eisenia andrei		OECD artificial soil	6±0.5	10	30	20 ± 2	14 d	NOEC	mortality	≥1000	≥1000	c	Römbke et al. (1995)
Eisenia andrei		OECD artificial soil	6±0.5	10	30	20 ± 2	14 d	NOEC	growth	577	577	c	Römbke et al. (1995)
Insects													
Folsomia candida	≥3 mm	loamy sand, LUFA 2.1	5.9-6.4	1.21		20 ± 2	24 h	LC50	mortality	>1000	>2860	d	Römbke et al. (1995)
Folsomia candida		loamy sand, LUFA 2.1	5.9-6.4	1.21		20 ± 2	28 d	LC50	mortality	66.5	550	d	Römbke et al. (1995)
Folsomia candida		loamy sand, LUFA 2.1	5.9-6.4	1.21		20 ± 2	28 d	LC10	mortality	19.3	160	d	Römbke et al. (1995)
Folsomia candida		loamy sand, LUFA 2.1	5.9-6.4	1.21		20 ± 2	28 d	EC50	reproduction	131.9	1090	d	Römbke et al. (1995)
Folsomia candida		loamy sand, LUFA 2.1	5.9-6.4	1.21		20 ± 2	28 d	EC10	reproduction	44.6	369	d	Römbke et al. (1995)
Poecilus cupreus		quartz sand				20 ± 2	14 d	EC28	feeding rate	5		e	Römbke et al. (1995)
Pardosa		quartz sand				22	14 d	LC42	mortality	5		f	Römbke et al. (1995)
Microbial activity and enzymatic activity													
Dehydrogenase activity		natural sandy soil		1.53	6.9	20 ± 2	28 d	EC15		5	33	g	Römbke et al. (1995)
Dehydrogenase activity		natural sandy soil		1.53	6.9	20 ± 2	28 d	EC42		50	327	g	Römbke et al. (1995)
Dehydrogenase activity		natural loamy soil		3.74	29.5	20 ± 2	28 d	EC20		50	134	g	Römbke et al. (1995)

Notes

a: According to OECD guideline 208, slightly modified; two days of seed germination and seedling emergence followed by 14 d exposure, photoperiod 16:8 h light:dark at least 7000 lux

b: Due to heterogeneity of the data, the NOEC could not be established statistically, NOEC is therefore considered not valid according to INS guidance

c: According to a BBA guideline (very similar to OECD guideline 207); constant light at 400-800 Lux

d: According to a BBA guideline (Riepert, 1991) which corresponded to the analogous ISO draft; constant light at 250-500 Lux

e: Bait-lamina test (BBA guideline VI, 23-2.1.8, 1991). One concentration tested, no mortality or any behavioral effects.

f: BBA guideline (draft, 1992), one concentration tested; 22 ºC in the dark

g: From these two effect percentages an EC10 of 2.4 mg/kg would be estimated and the EC50 85 mg/kg. This corresponds to concentrations in standard soil of 15 and 550 mg/kg. With the third value for the second soil included the EC10 and EC50 in standard soil are 28 and 590 mg/kg in standard soil.

Table A3.2. Terrestrial toxicity data for tris(2-chloro-1-methylethyl)phosphate (TCPP). All data are from the draft EU-RAR (European Commission, 2004b).

Species/process/activity	Species properties	Soil type	pH	o.m. [%]	Clay [%]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Result test soil [mg/kg_{dw}]	Result standard soil [mg/kg_{dw}]	Notes	Reference
annelida													
Eisenia foetida	-	-	-	10	-	-	14 d	LC50	mortality	97	97	a	Wetton (1996a)
Eisenia foetida	-	-	-	10	-	-	14 d	NOEC	mortality	32	32	a	Wetton (1996a)
Eisenia fetida	-	-	-	10	-	-	56 d	NOEC	mortality	≥196	≥196	b	Servajean (2003b)
Eisenia fetida	-	-	-	10	-	-	56 d	NOEC	biomass	116	116	b	Servajean (2003b)
Eisenia fetida	-	-	-	10	-	-	56 d	NOEC	reproduction	53	53	b	Servajean (2003b)
Eisenia fetida	-	-	-	10	-	-	56 d	EC50	reproduction	71	71	b	Servajean (2003b)
macrophyta													
Triticum aestivum				1.4				NOEC	emergence	≥98	≥700	c	Servajean (2003a)
Triticum aestivum				1.4				NOEC	dry weight	22	157	c	Servajean (2003a)
Sinapsis alba				1.4				NOEC	emergence	30	214	c	Servajean (2003a)
Sinapsis alba				1.4				NOEC	dry weight	29	207	c	Servajean (2003a)
Lactuca sativa				1.4				NOEC	emergence	17	121	c	Servajean (2003a)
Lactuca sativa				1.4				NOEC	dry weight	18	129	c	Servajean (2003a)

Notes

a: OECD guideline 207, result based on nominal concentrations, labelled use with care

b: OECD draft guideline, result based on nominal concentrations

c: OECD guideline 208, result based on nominal concentrations

Table A3.3. Terrestrial toxicity data for tris(2-chloro-1-(chloromethyl)ethyl)phosphate (TDCP). All data are from the draft EU-RAR (European Commission, 2004a).

Species/process/activity	Species properties	Soil type	pH	o.m. [%]	Clay [%]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Result test soil [mg/kg_{dw}]	Result stand. soil [mg/kg_{dw}]	Notes	Reference
annelida													
Eisenia foetida	-	-	-	10	-	-	14 d	LC50	mortality	130	130	a	Wetton (1996b)
Eisenia foetida	-	-	-	10	-	-	14 d	NOEC	mortality	100	100	a	Wetton (1996b)

Notes

a: OECD guideline 207; result based on nominal concentrations

Table A3.4. Terrestrial toxicity data for triethyl phosphate (TEP). All data are from IUCLID (European Commission, 2000).

Species/process/activity	Species properties	Soil type	pH	o.m. [%]	Clay [%]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Result test soil [mg/kg$_{dw}$]	Result standard soil [mg/kg$_{dw}$]	Notes	Reference
annelida													
Eisenia foetida	-	artificial soil	-	-	-	-	14 d	LC50	mortality	>1000		a	Bayer AG data
Eisenia foetida	-	artificial soil	-	-	-	-	14 d	NOEC	mortality	100		a	Bayer AG data

Notes

a: OECD guideline 207; concentrations measured

Table A3.5. Terrestrial toxicity data for tri(2-ethylhexyl)phosphate (TEHP). All data are from GDCh (2000).

Species/process/activity	Species properties	Soil type	pH	o.m. [%]	Clay [%]	Temperature [ºC]	Exposure time	Criterion	Test endpoint	Result test soil [mg/kg$_{dw}$]	Result standard soil [mg/kg$_{dw}$]	Notes	Reference
annelida													
Eisenia foetida	-	-	-	10	20	-	14 d	NOEC	weight loss	562	562	a	Bayer AG (1998)
Eisenia foetida	-	-	-	10	20	-	14 d	LC0	mortality	>1000	>1000	a	Bayer AG (1998)

Notes

a: OECD guideline 207

Appendix 4. Bioconcentration factors

Legend

Species	species used in the test, if available followed by age, size, weight or life stage
Analysed	Y = test substance analysed in test solution N = test substance not analysed in test solution or no data
Test type	S = static, Sc = static with closed test vessels, R = static with renewal, F = flow through
Substance purity	percentage active ingredient, or chemical grade of purity.
Hardness/salinity	freshwater: hardness expressed as mg $CaCO_3$/L saltwater: salinity expressed in ‰
Test water	am = artificial medium, dtw = dechlorinated tap water, dw = dechlorinated water, nw = natural water, rw = reconstituted water (+additional salts), tw = tap water
Exposure time	h = hours, d = days, w = weeks, m = months, min. = minutes
Depuration half-life	half-life of the compound in the organisms, equal to ln(2)/k2
BCF	Bioconcentration factor
Method	k1/k2: BCF calculated as the quotient of uptake rate (k1) and depuration rate (k2), mostly determined independently during an uptake and a depuration phase. equilibrium: BCF determined as the quotient of the concentrations in fish and water at equilibrium

Table A4.1. Bioconcentration factors for the studies phosphate esters.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness/ Salinity	Temperature [ºC]	Exposure time	(Initial) exposure concentration [mg/L]	Depuration half-life (h)	BCF [L/kg]	Method	Reference	Original reference
TCEP															
Carp (*Cyprinus carpio*)			S						42 d	1		0.6-0.8		European Commission (2004c)	CITI (1992)
Carp (*Cyprinus carpio*)			S						42 d	0.1		<1.2-5.1		European Commission (2004c)	CITI (1992)
Goldfish (*Carassius auratus*)		GC-FID	S					25	96 h	2.1		0.9		Sasaki et al. (1981)	
Killifish (*Oryzias latipes*)		GC-FID	S					25	96 h	2.1		2.2		Sasaki et al. (1981)	
Killifish (*Oryzias latipes*)			S						96 h	0.3-8.5		1.4-2.2		Sasaki (1982)	
Killifish (*Oryzias latipes*)			F						5 d	12.7	0.7 h	1.1		Sasaki (1982)	
Killifish (*Oryzias latipes*)			F						11 d	2.3	0.7 h	1.3		Sasaki (1982)	
TCPP															
Carp (*Cyprinus carpio*)			S						42 d	0.2		0.8-2.8		European Commission (2004b)	CITI (1992)
Carp (*Cyprinus carpio*)			S						42 d	0.02		<1.9-4.6		European Commission (2004b)	CITI (1992)
TDCP															
Carp (*Cyprinus carpio*)			S						42 d	0.02		0.3-3.3		European Commission (2004a)	CITI (1992)
Carp (*Cyprinus carpio*)			S						42 d	0.002		<2.2-22		European Commission (2004a)	CITI (1992)
Goldfish (*Carassius auratus*)		GC-FID	S					25	96 h	1		3-5		Sasaki et al. (1981)	
Killifish (*Oryzias latipes*)		GC-FID	S					25	96 h	1		77-113		Sasaki et al. (1981)	
Killifish (*Oryzias latipes*)			S						96 h	0.3-1.2		47-107		Sasaki (1982)	
Killifish (*Oryzias latipes*)			F						3-32 d	0.04-0.4	1.65 h	31-59		Sasaki (1982)	
TBP															
Goldfish (*Carassius auratus*)		GC-FID	S					25	96 h	4		6-11		Sasaki et al. (1981)	
Killifish (*Oryzias latipes*)		GC-FID	S					25	96 h	4		30-35		Sasaki et al. (1981)	
Killifish (*Oryzias latipes*)			S							0.2-0.06		11-49		Sasaki (1982)	
Killifish (*Oryzias latipes*)			F							0.84-0.1	1.25	16-27		Sasaki (1982)	
TEHP															
Carp (*Cyprinus carpio*)			S							2		2.4-6.5		GDCh (1997)	CITI (1992)
Carp (*Cyprinus carpio*)			S							0.2		9.2-22		GDCh (1997)	CITI (1992)
TPP															
Bleak (*Alburnus alburnus*)	5 g	GC-N/P	F	technical product	nw	7.6-7.9	7‰	10	14 d+14 d			400		Bengtsson et al. (1986)	
Goldfish (*Carassius auratus*)		GC-FID	S					25	96 h	0.25		110-150		Sasaki et al. (1981)	

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness/ Salinity	Temperature [ºC]	Exposure time	(Initial) exposure concentration [mg/L]	Depuration half-life (h)	BCF [L/kg]	Method	Reference	Original reference
Killifish (*Oryzias latipes*)		GC-FID	S					25	96 h	0.25		250-500		Sasaki et al. (1981)	
Killifish (*Oryzias latipes*)			F					25	18 d	0.009-0.01	1.2	84		Sasaki (1982)	
Killifish (*Oryzias latipes*)			S					25				157-390		Sasaki (1982)	
Killifish (*Oryzias latipes*)			F	in mixture				25	32-35 d			189-193		Sasaki (1982)	
Lake trout (*Salvelinus namaycush*)	eggs		F	technical product					120 d	0.0026-0.016		886±521		Environment Agency (2003b)	Mayer et al. (1993)
Fathead minnow (*Pimephales promelas*)			F	technical product						0.001-0.176		1482±702 (1007-1958)		Environment Agency (2003b)	Cleveland et al. (1986)
Rainbow trout (*Oncorhynchus mykiss*)				technical product					90 d			180-280		Environment Agency (2003b)	Lombardo & Egry (1979)
Rainbow trout (*Oncorhynchus mykiss*)			S					12				271		IPCS (1991b)	Sitthichaikasem (1978)
Rainbow trout (*Oncorhynchus mykiss*)	fry	GC-FID	F					12	90 d	0.00022-0.0014	13	271±80		Mayer (1981)	
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	42.5	1368±329	k1/k2 independent	Muir et al. (1983)	
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	42.5	573±97	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	42.5	931±122	k1/k2, k1 non-linear regression	Muir et al. (1983)	
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	hexane, GC-N/P	S		dtw			10	24 h+18 d	0.005, 0.050	20.7	324±99	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	49.6	1743±282	k1/k2 independent	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	49.6	561±115	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	49.6	218±55	k1/k2, k1 non-linear regression	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	hexane, GC-N/P	S		dtw			10	24 h+18 d	0.005, 0.050	30.0	420±25	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
***m*-TCP**															
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	30.3	1162±313	k1/k2 independent	Muir et al. (1983)	
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	30.3	784±82	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	30.3	1102±137	k1/k2, k1 non-linear regression	Muir et al. (1983)	
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	hexane, GC-N/P	S		dtw			10	24 h+18 d	0.005, 0.050	25.8	310±52	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	59.2	1653±232	k1/k2 independent	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	59.2	596±103	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	59.2	385±92	k1/k2, k1 non-linear regression	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	hexane, GC-N/P	S		dtw			10	24 h+18 d	0.005, 0.050	53.3	462±3	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
***p*-TCP**															
Daphnia magna		LSC	IF					22	24 h	0.00015		722		Boethling & Cooper (1985)	Sitthichaikasem (1978)

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness/ Salinity	Temperature [ºC]	Exposure time	(Initial) exposure concentration [mg/L]	Depuration half-life (h)	BCF [L/kg]	Method	Reference	Original reference
Lepomis macrochirus	0.64 g, 36.4 mm	LSC	IF					22	4 w	0.00015		1589		Environment Agency (2003a)	Sitthichaikasem (1978)
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	72.2	2768±641	k1/k2 independent	Muir et al. (1983)	
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	72.2	1420±42	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	72.2	1466±138	k1/k2, k1 non-linear regression	Muir et al. (1983)	
Rainbow trout (*Oncorhynchus mykiss*)	0.75 g	hexane, GC-N/P	S		dtw			10	24 h+18 d	0.005, 0.050	65.4	770±24	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	90.0	2199±227	k1/k2 independent	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	90.0	928±78	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	LSC	S		dtw			10	24 h+18 d	0.005, 0.050	90.0	588±129	k1/k2, k1 non-linear regression	Muir et al. (1983)	
Fathead minnow (*Pimephales promelas*)	2.5 g	hexane, GC-N/P	S		dtw			10	24 h+18 d	0.005, 0.050	73.7	709±76	k1/k2, k1 implied by fitted k2	Muir et al. (1983)	
TCP															
Oncorhynchus mykiss	yearling	hydrolysis to cresols	F	Technical, 2% *o*-TCP, 42% *m*-TCP, and 31% *p*-TCP					4 m	0.9		10 (muscle) 169 (gut)		Environment Agency (2003a)	Lockhart et al. (1975)
Bleak (*Alburnus alburnus*)	5 g	GC-N/P	F	technical product	nw	7.6-7.9	7‰	10	14 d+14 d			400-800		Bengtsson et al. (1986)	
Pimephales promelas	6 m		F		nw	7..49±0.15	45.5±0.97 mg/L	25	32 d	0.0316		165		Veith et al. (1979)	