National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

Environmental risk limits for ethyl-benzene and tributylphosphate in water

A proposal for water quality standards in accordance with the Water Framework Directive

RIVM Letter Report 601714019/2011
C.E. Smit | E.M.J. Verbruggen

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This investigation has been performed by order and for the account of Ministry of Infrastructure and Environment, within the framework of Chemical aspects of WFD and RPS

Abstract

Environmental risk limits for ethylbenzene and tributylphosphate in water
A proposal for water quality standards in accordance with the Water Framework Directive

RIVM has derived environmental risk limits (ERLs) for ethylbenzene and tributylphosphate in water. Both compounds are included in the Dutch decree on water quality objectives in the context of the Water Framework Directive (WFD). The standards have to be updated according to the current WFD-methodology. The values in this report serve as a scientific background for the Dutch Steering Committee for Substances, which is responsible for setting those standards. Monitoring data from 2010 indicate that the proposed standards will not be exceeded.

Proposed standards
The proposal for ethylbenzene is based on the European risk assessment report (EU-RAR) for this compound. According to the WFD, two different standards are proposed for fresh- and saltwater. The Maximum Permissible Concentration (MPC) is the level at which no harmful effects are expected, based on annual average concentrations. This MPC is derived for three routes: direct ecotoxicity, secondary poisoning, and consumption of fish by humans. The lowest of these values determines the final MPC (65 microgram per litre for freshwater and 10 microgram per litre for saltwater). The Maximum Acceptable Concentration (MAC_{eco}) is the concentration which protects ecosystems from effects of short term concentration peaks. MAC-values of 220 and 22 microgram per litre are proposed for freshwater and saltwater, respectively.

For tributylphosphate, updated MPC-values have been derived previously (66 and 6.6 microgram per litre for fresh- and saltwater). In addition, MAC-values of 170 and 17 microgram per litre are proposed for the respective water types.

Keywords:
water quality standards; WFD; ethylbenzene; tributylphosphate

Rapport in het kort

Milieurisicogrenzen voor ethylbenzeen and tributylfosfaat in water
Een voorstel voor waterkwaliteitsnormen volgens de Kaderrichtlijn Water

Het RIVM heeft in opdracht van het ministerie van Infrastructuur en Milieu (I&M) milieurisicogrenzen voor ethylbenzeen en tributylfosfaat in water bepaald. De stoffen zijn opgenomen in de Regeling monitoring Kaderrichtlijn Water, waarin staat aan welke eisen oppervlaktewater in Nederland moet voldoen. Voor deze stoffen moeten nieuwe waterkwaliteitsnormen worden vastgesteld, omdat de huidige normen niet zijn afgeleid volgens de meest recente methodiek. Op basis van meetgegevens over 2010 is er geen aanwijzing dat de voorgestelde waterkwaliteitsnormen worden overschreden.

Normvoorstellen
De normvoorstellen voor ethylbenzeen zijn gebaseerd op de Europese risicobeoordeling voor deze stof. De KRW kent voor zoet en zout oppervlaktewater twee typen normen, de Jaargemiddelde Milieukwaliteitsnorm (JG-MKN) en de Maximaal Aanvaardbare Concentratie (MAC-MKN). De JG-MKN is de concentratie in water waarbij geen schadelijke effecten te verwachten zijn, gebaseerd op jaargemiddelde concentraties. Hiervoor zijn drie routes onderzocht: directe effecten op waterorganismen, indirecte effecten op vogels en zoogdieren via het eten van prooidieren en indirecte effecten op mensen via het eten van voedsel. De laagste van deze drie bepaalt de voorgestelde JG-MKN; voor ethylbenzeen is dat 65 microgram per liter voor zoetwater en 10 microgram per liter voor zoutwater. De Maximaal Aanvaardbare Concentratie (MAC-MKN) is de concentratie die het ecosysteem beschermt tegen kortdurende effecten. De voorgestelde MAC-MKN is 220 en 22 microgram per liter voor respectievelijk zoet- en zoutwater.

Voor tributylfosfaat zijn al eerder voorstellen gedaan om de JG-MKN te herzien (66 en 6,6 microgram per liter voor zoet- en zoutwater). In aanvulling daarop wordt nu een MAC-MKN voorgesteld van 170 microgram per liter voor zoetwater en 17 microgram per liter voor zoutwater.

Trefwoorden:
waterkwaliteitsnormen; MKN; Kaderrichtlijn Water; ethylbenzeen; tributylfosfaat

Contents

Summary—9

1 Introduction—11
1.1 Background and aim—11
1.2 Project framework—11
1.3 Data sources—12
1.4 Methodology—12

2 Ethylbenzene—15
2.1 Information on the compound—15
2.2 Current water quality standards—16
2.3 Data sources—16
2.4 Bioconcentration—16
2.5 Ecotoxicity data—16
2.6 Derivation of the MPC_{fw} and MPC_{sw}—17
2.7 $MPC_{dw, hh}$ – surface water for abstraction of drinking water—19
2.8 Derivation of the $MAC_{fw, eco}$ en $MAC_{sw, eco}$—19
2.9 Derivation of the NC_{fw} and NC_{sw}—19
2.10 Derivation of the $SRC_{fw, eco}$ and $SRC_{sw, eco}$—19
2.11 Conclusions—19

3 Tributylphosphate—21
3.1 Information on the compound—21
3.2 Current water quality standards—21
3.3 Relevance of secondary poisoning and human fish consumption—22
3.4 Derivation of the $MAC_{fw, eco}$ and $MAC_{sw, eco}$—22
3.5 $MPC_{dw, hh}$ – surface water for abstraction of drinking water—23
3.6 Conclusion—24

References—25

List of abbreviations—27

Appendix 1. Data on ecotoxicity and bioconcentration of ethylbenzene from the EU-RAR—29

Appendix 2. Relevance of human fish consumption for tributylphosphate—33

Summary

In this report, RIVM presents environmental risk limits (ERLs) for ethylbenzene and tributylphosphate in water. Both compounds are listed as a *specific pollutant* in the context of the Water Framework Directive (WFD). The current water quality standards for chronic exposure are 370 and 13 µg/L, respectively. These values date back to before 2004, and are based on direct ecotoxicity only. Because of the characteristics of the compounds, secondary poisoning and/or human consumption of fishery products have to be considered when deriving water quality standards according to the WFD-guidance. This will potentially lead to lower standards than the current values. In addition, water quality standards for short-term exposure (MAC) have to be derived according to the WFD, as well as quality standards for surface water intended for drinking water abstraction and for the saltwater environment
The proposal for ethylbenzene is based on the European risk assessment report for this compound, while for tributylphosphate information is available from a previous RIVM-report. The methods used are in accordance with the methodology of WFD and INS (International and National environmental quality standards for Substances in the Netherlands). Next to water quality standards required according to the WFD, some additional ERLs are considered in the context of INS, each representing a different protection aim. The following ERLs are derived in this report:

- The Maximum Permissible Concentration (MPC). The MPC represents the concentration that protects man and environment from adverse effects due to chronic exposure. According to the WFD-methodology, three routes have been taken into account for derivation of the MPC: direct exposure of aquatic organisms, secondary poisoning of predatory birds and mammals, and exposure of humans via fish consumption.

- The Maximum Acceptable Concentration for ecosystems (MAC_{eco}). The MAC_{eco} is the concentration that protects aquatic ecosystems from adverse effects of short-term concentration peaks. The MPC and MAC_{eco} are equivalent to the long-term and short-term water quality standards that are indicated as AA-EQS and MAC-EQS in the WFD-guidance. They are derived for both the freshwater and saltwater compartment.

- The Negligible Concentration (NC). The NC is calculated by applying an additional factor of 100 to the MPC. The NC represents the concentration at which effects to ecosystems are expected to be negligible and functional properties of ecosystems are fully safeguarded. In the Dutch policy on substances, the NC is used to define a safety margin that takes combination toxicity into account.

- The Serious Risk Concentration for ecosystems (SRC_{eco}). This is the concentration at which serious ecotoxicological risks might occur in aquatic ecosystems.

- The Maximum Permissible Concentration in water for drinking water abstraction ($MPC_{dw, hh}$). The $MPC_{dw, hh}$ represents the concentration at which surface water can be used for production of drinking water without further treatment.

Where applicable, ERLs are derived for freshwater and saltwater. An overview of the newly derived ERLs is presented in Table 1. Based on monitoring data from 2010, it is not expected that concentrations in freshwater exceed the newly derived MAC-, MPC- or SRC-values. However, NC-values for tributylphosphate in freshwater may be exceeded.

Table 1 Environmental risk limits for ethylbenzene and tributylphosphate in water

Environmental risk limit	**Ethylbenzene**	**Tributylphosphate**
	[µg/L]	**[µg/L]**
Freshwater		
MPC_{fw}	**65**	**66**
NC_{fw}	0.65	0.66
$MAC_{fw, eco}$	**220**	**170**
$SRC_{fw, eco}$	530	1100
Surface water for drinking water production		
$MPC_{dw, hh}$	**300**	**315**
Saltwater		
MPC_{sw}	**10**	**6.6**
NC_{sw}	0.10	0.066
$MAC_{sw, eco}$	**22**	**17**
$SRC_{sw, eco}$	530	1100

1 Introduction

1.1 Background and aim

In this report, a proposal is made for water quality standards for ethylbenzene and tributylphosphate. Ethylbenzene and tributylphosphate are listed in the Dutch decree on monitoring within the context of the Water Framework Directive (WFD), which is further referred to as *Regeling monitoring KRW*. The current water quality standards for ethylbenzene and tributylphosphate were taken over from the decree on surface water quality standards for dangerous substances of 2004 (VROM, 2004), and refer to maximum permissible concentrations (MPC) based on ecotoxicity data alone. The list of so-called "specific pollutants" included in the *Regeling monitoring KRW* is currently being evaluated in view of the second round of river basin management plans for 2015-2021 (Posthuma-Doodeman and Smit, 2009). For those substances remaining on the list, updated water quality standards according to the methodology of the WFD have to be available by the end of 2012. Since both compounds have been detected during routine monitoring by the Waterdienst and RIWA (see www.waterbase.nl and RIWA, 2010), it is expected that ethylbenzene and tributylphosphate belong to this category. Because of the characteristics of the compounds, secondary poisoning and/or human consumption of fishery products have to be considered when deriving water quality standards according to the current WFD-guidance (EC, 2011). This will potentially lead to lower standards than the current values, which are based on ecotoxicity only. In addition, water quality standards for short-term exposure (MAC) have to be derived according to the WFD, as well as quality standards for surface water intended for drinking water abstraction and for the saltwater environment. The aim of the present report is therefore to derive updated environmental risk limits (ERLs) for ethylbenzene and tributylphosphate in water. The ERLs are advisory values that serve as a scientific background for the Dutch Steering Committee for Substances, which is responsible for setting water quality standards in the Netherlands.

1.2 Project framework

The derivation of ERLs is performed in the context of the project Chemical aspects of the Water Framework Directive, which is closely related to the project INS (International and national environmental quality standards for substances in the Netherlands). Next to water quality standards required according to the WFD, some additional ERLs are considered in the context of INS, each representing a different protection aim. The following ERLs are derived in this report:

- Maximum Permissible Concentration (MPC) – defined in VROM (1999, 2004a) as the standard based on scientific data which indicates the concentration in an environmental compartment for which:
    - 1 no effect to be rated as negative is to be expected for ecosystems;
    - 2a no effect to be rated as negative is to be expected for humans (for non-carcinogenic substances);
    - 2b for humans no more than a probability of 10^{-6} per year of death can be calculated (for carcinogenic substances). Within the scope of the Water Framework Directive (WFD), a probability of 10^{-6} on a life-time basis is used.

The MPC for water should not result in risks due to secondary poisoning and/or risks for human health aspects. These aspects are therefore also addressed in the MPC derivation. Separate MPC-values are derived for the freshwater and saltwater environment.

- Negligible Concentration (NC) – the concentration in fresh- and saltwater at which effects are expected to be negligible and functional properties of ecosystems are safeguarded fully. It defines a safety margin which should exclude combination toxicity. The NC is derived by dividing the MPC by a factor of 100.

- Maximum Acceptable Concentration (MAC_{eco}) for aquatic ecosystems – the concentration protecting aquatic ecosystems from effects due to short-term exposure or concentration peaks. The MAC_{eco} is derived for freshwater and saltwater ecosystems.

- Serious Risk Concentration for ecosystems (SRC_{eco}) – the concentration in water at which possibly serious ecotoxicological effects are to be expected. The SRC_{eco} is valid for the freshwater and saltwater compartment.

- Maximum Permissible Concentration for surface water that is used for drinking water abstraction ($MPC_{dw, hh}$). This is the concentration in surface water that meets the requirements for use of surface water for drinking water production. The $MPC_{dw, hh}$ specifically refers to locations that are used for drinking water abstraction.

The quality standards in the context of the WFD refer to the absence of any impact on community structure of aquatic ecosystems. Hence, not the potential to recover after transient exposure, but long-term undisturbed function is the protection objective under the WFD. Recovery in a test situation, after a limited exposure time, is therefore not included in the derivation of the MPC and MAC.

1.3 Data sources

For both compounds, European Risk Assessment Reports (EU-RAR) and/or recent RIVM-reports with ecotoxicological risk limits are available. In addition, information on human toxicological risk limits is available that can be used to derive additional risk limits for human consumption of fishery products, and secondary poisoning. An evaluation of new data sources was therefore not performed.

1.4 Methodology

The methodology for risk limit derivation is described in detail in the INS-guidance document (Van Vlaardingen and Verbruggen, 2007), which is further referred to as the INS-Guidance. The methodology is based on 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 (EC, 2003) and on the Manual for the derivation of Environmental Quality Standards in accordance with the Water Framework Directive (Lepper, 2005). The European guidance under the framework of WFD has been revised, and the updated guidance has been published recently (EC, 2011). The risk limits in this report will be used for setting water quality standards that will become effective after the new guidance has come in to force. Therefore, the terminology is harmonised as much as possible and the new guidance is followed in the case it deviates from the INS-guidance. This

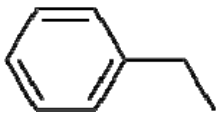
specifically applies to the treatment of data for freshwater and marine species and the derivation of the MAC, for which the new methodology is used (EC, 2011). This also holds for the MPC for surface waters intended for the abstraction of drinking water ($MPC_{dw, hh}$). In the INS-guidance, this is one of the MPCs from which the lowest value should be selected as the general MPC_{fw} (see section 3.1.6 and 3.1.7 of the INS-Guidance). According to the new guidance, the $MPC_{dw, hh}$ is not taken into account for the derivation of the general MPC_{fw}, but specifically refers to locations that are used for drinking water abstraction.

2 Ethylbenzene

2.1 Information on the compound

Ethylbenzene is naturally present in crude oil. Commercially it is mainly produced by alkylating benzene with ethene. The compound is registered under REACH, two summary dossiers are available (ECHA, 2011). According to these dossiers, it is used as an intermediate in industrial processes, as process solvent, and as a component in the production of fuels. The default environmental release rates for these use types indicate that emissions to water, air and soil are to be expected. According to the EU-RAR (EC, 2009), ethylbenzene is primarily used in the manufacture of styrene. In addition, it is a component of "mixed xylenes", which results from gasoline production. The final concentration of ethylbenzene in gasoline is approximately 2 % (by weight). "Mixed xylenes" contains generally about 15 to 20 % ethylbenzene, and is used mainly for blending into gasoline (EC, 2009). The EU-RAR considers environmental releases of ethylbenzene during its production and processing to styrene, and emissions from unintentional use in solvents. Furthermore, emissions from fuel are considered during storage and refuelling, and as constituent of traffic exhaust. The intentional use of ethylbenzene in the solvent sector (e.g. paint industry) is considered only marginal and is not addressed in the EU-RAR. Releases from various sources during combustion processes, e.g. from waste incinerators and power stations, are also not considered further.

Table 2 Identity of ethylbenzene

Name	Ethylbenzene
Other names	ethylbenzol; α-methyltoluene; phenylethane
CAS number	100-41-4
Molecular formula	C8H10
Molar mass	106 g/mol
EC number	202-849-4
Structural formula	
Smiles code	CCc1ccccc1

Physico-chemical characteristics of ethylbenzene are summarised in Table 3

Table 3 Physico-chemical properties of ethylbenzene

Parameter	Unit	Value	Remark	Reference
Water solubility	[mg/L]	160	25 °C	EC, 2009
log K_{ow}		3.13	25 °C	EC, 2009
		3.15		EC, 2009
log K_{oc}		2.64		EC, 2009
Vapour pressure	[Pa]	9300	20 °C	EC, 2009
Henry's law constant	[Pa.m^3/mol]	617	calculated	EC, 2009
Melting point	[°C]	-95		EC, 2009
Boiling point	[°C]	136	1013 hPa	EC, 2009

2.2 Current water quality standards

The current Maximum Permissible Concentration (MPC) for ethylbenzene in the *Regeling monitoring KRW* water is 370 µg/L, based on dissolved concentrations. This value was taken over from the decree on surface water quality standards for dangerous substances of 2004 (VROM, 2004b), and originates from Van de Plassche et al. (1993). The risk limit for ethylbenzene has been derived on the basis of estimated ecotoxicity values by means of a QSAR-approach. In the EU, ethylbenzene has not been classified as carcinogenic (ESIS, 2011). However, the compound is classified as possibly carcinogenic to humans (Group 2B) in IARC (2000). In combination with the potential for bioaccumulation (log K_{ow} 3.13) this requires that human consumption of fishery products and secondary poisoning are considered when deriving water quality standards.

2.3 Data sources

An EU-Risk Assessment Report (EU-RAR) is available for the environment (EC, 2009). The document is indicated as "draft" on the website of the former European Chemicals Bureau (ECB), because the risk assessment for human exposure is not included. However, the environmental risk assessment has been discussed in the Technical Committee for New and Existing Substances (TC NES) and is commented on by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE). The EU-RAR gives sufficient reliable information on direct ecotoxicity and potential for bioconcentration. In addition, REACH-summary dossiers are available via ECHA (2011). One dossier only contains QSAR estimates for ecotoxicity, the other dossier contains the same information as presented in the EU-RAR. A human toxicological threshold limit has been established by RIVM within the framework of the derivation of intervention values for contaminated soil (Baars et al., 2001).

2.4 Bioconcentration

In the EU-RAR, a bioconcentration factor (BCF) for fish of 91 L/kg is calculated from the log K_{ow} of 3.13. No experimental BCF-values are available for ethylbenzene. Some studies have been performed with the water-soluble fraction of crude oil, that contains ethylbenzene. From these studies, BCF-values between 1 and 15 L/kg may be derived for ethylbenzene (see Appendix 1 for a copy of the EU-RAR text on this subject). According to the EU-RAR, the reliability of these values is limited because it is not known if an equilibrium was reached and the organisms have been exposed to a mixture of compounds instead of ethylbenzene alone. Therefore, the EU-RAR uses the estimated BCF-value of 91 L/kg, but concludes that the experimental studies indicate that the actual BCF is most likely lower than this value. A risk assessment for secondary poisoning has not been performed in the EU-RAR. Below in section 2.6.4, a proposal for the $MPC_{fw,\ secpois}$ and $MPC_{sw,\ secpois}$ is made based on the estimated BCF of 91 L/kg.

2.5 Ecotoxicity data

Considering the volatility of ethylbenzene, the EU-RAR only takes into account ecotoxicity studies that are performed using flow-through or closed systems and which include chemical analysis of test concentrations. An overview of the relevant endpoints is presented in Appendix 1. The acute base set (algae, *Daphnia*, fish) is complete, the lowest EC_{50} is 1.8 mg/L for *D. magna*. Two chronic endpoints are available, a 7-days NOEC of 1.0 mg/L for *Ceriodaphnia dubia* and a 96-hours EC_{10} of 3.4 mg/L for *Selenastrum capricornutum* (currently known as *Pseudokirchneriella subcapitata*).

Two endpoints based on nominal concentrations are included in the data table of the EU-RAR. According to the EU-RAR, these values should be used with care because actual concentrations have not been determined. The LC_{50} for *D. magna* of 2.1 mg/L is in close agreement with the other endpoints reported for this species (1.8-2.9 mg/L). The LC_{50} for *Artemia salina* of 15.9 mg/L is higher than the other value for this species (48-hours EC_{50} 9.2 mg/L), but this may also be due to the longer exposure time and the fact that mobility rather than mortality was studied in the latter experiment. Based on the data presented in Appendix 1, the aggregated endpoints per species are presented below in Table 4 and 5. The lowest endpoints in the EU-RAR are also included as key-studies in one of the REACH dossiers. The other dossier only contains ecotoxicity data based on QSAR estimates.

Table 4 Aggregated data for toxicity of ethylbenzene: freshwater species

Chronic		**Acute**	
Taxon/*species*	**EC_{10}/NOEC [mg/L]**	**Taxon/***species*	**L/EC_{50} [mg/L]**
algae		**algae**	
Pseudokirchneriella subcapitata	3.4	*Pseudokirchneriella subcapitata*	5.0[a]
crustacea		**crustacea**	
Ceriodaphnia dubia	1.0	*Ceriodaphnia dubia*	3.2
		Daphnia magna	2.2[b]
		pisces	
		Oncorhynchus mykiss	4.2
		Pimephales promelas	12.1
		Poecilia reticulata	9.6

a: most sensitive test duration (96-hours E_rC_{50}; geometric mean of 72-hours values is 5.2 mg/L)

b: geometric mean of 48-hours L/EC_{50} values of 2.38, 2.41, 1.81, 1.93, 1.81, 2.1, 2.9 mg/L

Table 5 Aggregated data for toxicity of ethylbenzene: marine species

Chronic		**Acute**	
Taxon/*species*	**EC_{10}/NOEC [mg/L]**	**Taxon/***species*	**L/EC_{50} [mg/L]**
algae/diatomea		**algae/diatomea**	
Skeletonema costatum	4.5	*Skeletonema costatum*	7.7
		crustacea	
		Artemia salina	9.2[a]
		Mysidopsis bahia	2.6
		pisces	
		Menidia menidia	5.1

a: most sensitive test duration and endpoint (48-hours immobility)

2.6 Derivation of the MPC_{fw} and MPC_{sw}

2.6.1 Treatment of data for freshwater and marine species

According to the new WFD-guidance, statistical testing should be performed to detect whether there are differences in sensitivity between the freshwater and marine species. Where a lack of data makes a sound statistical analysis unworkable, the datasets for organic substances should be pooled. This is the case for ethylbenzene. Similar to the EU-RAR, the combined dataset is used for risk limit derivation.

2.6.2 *$MPC_{fw, eco}$ and $MPC_{sw, eco}$ –direct ecotoxicity*

According to the schemes of the Technical Guidance Document (EC, 2003) and WFD-guidance (EC, 2011), an assessment factor of 50 to the lowest NOEC/EC_{10} of 1.0 mg/L is applicable, since no chronic data are available for fish. However, ethylbenzene belongs to the category of "neutral organics" that act via narcosis. the TC NES has therefore agreed upon a lower assessment factor of 10, in line with the assessment of similar compounds. The $PNEC_{aquatic}$ has been established as 1.0 / 10 = 0.1 mg/L = 100 µg/L. Both REACH-dossiers present the same value of 0.1 mg/L as PNEC for freshwater (ECHA, 2011). This value can be considered as the $MPC_{fw, eco}$, which according to the new WFD-guidance refers to dissolved concentrations.

For the marine environment, a $PNEC_{marine}$ of 10 µg/L has been derived in the EU-RAR by applying an additional assessment factor of 10 to the $PNEC_{aquatic}$. This is in accordance with the WFD-methodology in case no typical marine species are present in the dataset. This value is also mentioned in one of the REACH dossiers. The other registrant, however, presents the same PNEC of 0.1 mg/L for freshwater and marine species, probably based on the QSAR estimates for chronic toxicity to fish. The derivation of the $PNEC_{marine}$ in the EU-RAR is in accordance with the WFD-methodology, and the value of 10 µg/L is considered as the $MPC_{sw, eco}$.

2.6.3 *$MPC_{water, hh food}$ – human exposure*

The human toxicological threshold limit of 136 µg/kg_{bw}.d from Vermeire et al. (1991) has been revised by Baars et al. (2001). Starting point for both values is the NOAEL of 136 mg/kg_{bw}.d from a 6-months study with rats. In the 2001-revision, a correction has been made for the exposure from five days a week to seven days a week. With a safety factor of 1000, the (rounded) TDI is reported as 100 µg/kg_{bw}.d = 0.1 mg/kg_{bw}.d by Baars et al. (2001). Using the unrounded TDI of 97 µg/kg_{bw}.d and assuming a body weight of 70 kg, a daily fish consumption of 0.115 kg, a contribution of fish consumption to the total TDI of 10%, and the BCF of 91 L/kg, the risk limit for human consumption of fish is calculated (0,97 x 70 x 0,1)/(0,115 x 91) = 0.065 mg/L = 65 µg/L. This value applies to freshwater as well as to saltwater. The $MPC_{water, hh food}$ is 65 µg/L.

2.6.4 *$MPC_{fw, secpois}$ and $MPC_{sw, secpois}$ – secondary poisoning*

Starting point is the above mentioned NOAEL of 136 mg/kg_{bw}.d, corrected for exposure from five to seven days a week this is equivalent to 97 mg/kg_{bw}.d. With a conversion factor of 20, the food-based NOAEC is 1943 mg/kg_{fd}. Applying an assessment factor of 90 and using the BCF of 91 L/kg, the risk limit for secondary poisoning $MPC_{fw, secpois}$ is 0.237 mg/L = 237 µg/L. Since an additional factor for bioaccumulation by marine top-predators is not necessary, this value is also valid as $MPC_{sw, secpois}$.

2.6.5 *Selection of the MPC_{fw} and MPC_{sw}*

The $MPC_{fw, eco}$ is 100 µg/L, the $MPC_{water, hh food}$ is 65 µg/L and the $MPC_{fw, secpois}$ is 237 µg/L. The lowest of these values determines the final MPC_{fw}, which is set to 65 µg/L.

The $MPC_{sw, eco}$ is 10 µg/L, the $MPC_{water, hh food}$ is 65 µg/L and the $MPC_{sw, secpois}$ is 237 µg/L. The lowest of these values determines the final MPC_{sw}, which is set to 10 µg/L.

2.7 $MPC_{dw, hh}$ – surface water for abstraction of drinking water

According to the WFD-guidance, guideline values published by the World Health Organization (WHO) can be used as a basis for derivation of the $MPC_{dw, hh}$. The WHO guideline value is 300 µg/L (WHO, 2011). A substance specific removal rate should be considered to derive the $MPC_{dw, hh}$. At present, such information is not available and water treatment is not taken into account. The $MPC_{dw, hh}$ is set 300 µg/L. It is noted that lower concentrations may affect the appearance, taste or odour of the water, leading to consumer complaints.

2.8 Derivation of the $MAC_{fw, eco}$ en $MAC_{sw, eco}$

A PNEC for intermittent release or short-term toxicity has not been derived in the EU-RAR. The acute base set (algae, *Daphnia*, fish) is available, L/EC_{50} values range from 1.8 to 15.4 mg/L (see Table 4 and 5 and Appendix 1). According to the WFD-guidance (EC, 2011), an assessment factor of 10 can be applied to the lowest endpoint for chemicals without a specific mode of action if the variation between species is relatively low, as shown by a standard deviation of the log-transformed L/EC_{50}-vaues of <0.5. The standard deviation of the aggregated acute data is 0.25. Therefore, an assessment factor of 10 is applied to the lowest endpoint of 2.2 mg/L for *D. magna*. The $MAC_{fw, eco}$ is 0.22 mg/L = 220 µg/L.

For the derivation of the $MAC_{sw, eco}$, a similar approach is followed as for the $MPC_{fw, eco}$. With an additional assessment factor of 10, the $MAC_{sw, eco}$ is 22 µg/L.

2.9 Derivation of the NC_{fw} and NC_{sw}

The NC_{fw} and NC_{sw} are derived as 1/100 of the respective MPC-values. The NC_{fw} is 0.65 µg/L, the NC_{sw} is 0.10 µg/L.

2.10 Derivation of the $SRC_{fw, eco}$ and $SRC_{sw, eco}$

Two long-term NOECs are available for two of the specified taxa (algae, *Daphnia*, fish). The geometric mean of the L/EC_{50} values presented in Table 4 and 5 is 5.3 mg/L, the geometric mean of the $NOEC/EC_{10}$-values is 2.5 mg/L. In this case, the $SRC_{fw, eco}$ is derived as the geometric mean of all available L/EC_{50}-values with an assessment factor of 10. Therefore, the $SRC_{fw, eco}$ is 0.53 mg/L (530 µg/L). This value is also valid as $SRC_{sw, eco}$.

2.11 Conclusions

The following environmental risk limits were derived for ethylbenzene in water (Table 6). Risk limits that are equivalent to the water quality standards according to the WFD are indicated in bold. All values refer to dissolved concentrations.
As indicated in the introduction, ethylbenzene is included in the monitoring programmes of Waterdienst and RIWA. For the majority of sampling stations, including those in the coastal zone, concentrations were below the reporting limit (0.01 µg/L) on most sampling dates. Occasionally, concentrations between 0.01 and 0.04 µg/L were found (www.waterbase.nl). An exception is the RIWA sampling point in the Amsterdam-Rijnkanaal at Nieuwersluis, where concentrations of 3 and 0.13 µg/L were detected in February and August 2010, respectively. The yearly average was 0.252 µg/L (RIWA, 2010). Note that reported levels refer to total concentrations, whereas the proposed risk limits are expressed as dissolved concentrations. However, taking into account the default suspended matter concentration of 30 mg/L for Dutch surface waters, and a log K_{oc} of 2.64 (EC, 2009), total and dissolved concentrations are the

same. This also holds for a lower suspended matter concentration of e.g. 15 mg/L. Based on these data, it is not expected that the newly derived ERLs for ethylbenzene will be exceeded.

Table 6 Environmental risk limits for ethylbenzene in water

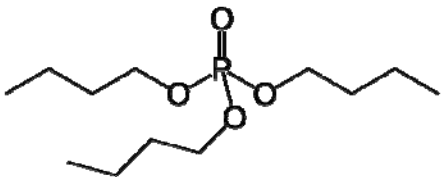
Environmental risk limit	**Value [µg/L]**
Freshwater	
$MPC_{fw, eco}$	100
$MPC_{fw, secpois}$	237
$MPC_{water, hh\ food}$	65
MPC_{fw}	**65**
NC_{fw}	0.65
$MAC_{fw, eco}$	**220**
$SRC_{fw, eco}$	530
Surface water for drinking water production	
$MPC_{dw, hh}$	**300**
Saltwater	
$MPC_{sw, eco}$	10
$MPC_{sw, secpois}$	237
$MPC_{water, hh\ food}$	65
MPC_{sw}	**10**
NC_{sw}	0.10
$MAC_{sw, eco}$	**22**
$SRC_{sw, eco}$	530

3 Tributylphosphate

3.1 Information on the compound

Tributylphosphate is registered under REACH, two summary dossiers are available (ECHA, 2011). According to these dossiers, it is used in hydraulic fluids, as an anti-foam agent in chemical synthesis and in the manufacture and use of concrete, as an extracting agent, in pigments and paints, in PUR coatings and adhesives. The default environmental release rates for these use types indicate that emissions to water, air and soil are to be expected. According to Verbruggen et al. (2005), the uses as a component of aircraft hydraulic fluid and as a solvent for rare earth metal extraction and purification comprise over 80 percent of the volume produced. Except for paints, adhesives, and PUR coatings, no specific consumer use is known. Verbruggen et al. (2005) also mention the use of tributylphosphate as solvent for cellulose ester, lacquers and natural gums.

Table 7 Identity of tributylphosphate

Name	Tributylphosphate
Other names	Tri-*n*-butylphosphate
CAS number	126-73-8
Molecular formula	$C_{12}H_{27}O_4P$
Molar mass	266.32 g/mol
EC number	204-800-2
Structural formula	
Smiles code	O=P(OCCCC)(OCCCC)OCCCC

A summary of the physico-chemical characteristics of tributylphosphate reported by Verbruggen et al. (2005) is presented in Table 8.

Table 8 Physico-chemical properties of tributylphosphate

Parameter	Unit	Value	Remark
Water solubility	[mg/L]	250-280	20 °C
log K_{ow}		2.5-4.01	exp.
log K_{oc}		3.13	QSAR
Vapour pressure	[Pa]	0.15-1.2	25 °C
Henry's law constant	[Pa.m^3/mol]	0.0152	calculated

3.2 Current water quality standards

The current Maximum Permissible Concentration for tributylphosphate in water as listed in the *Regeling monitoring KRW* is 13 µg/L, based on dissolved concentrations. This value was taken over from the decree on surface water quality standards for dangerous substances of 2004 (VROM, 2004b), and originates from Beek (2002). Updated water quality standards (MCP_{fw} 66 µg/L, NC_{fw} 0.66 µg/L, MPC_{sw} 6.6 µg/L) have been approved by the Steering Committee on Substances on 17 March 2007. These values were derived on the basis of the

report by Verbruggen et al. (2005). In the REACH dossiers, PNEC-values for freshwater are reported of 0.035 and 0.082 mg/L, respectively. The first dossier contains only QSAR estimates for ecotoxicity, the PNEC is probably based on the estimated long-term NOEC for fish. The second dossier contains experimental data. A chronic study with *Daphnia magna* with a NOEC of 1.3 mg/L is indicated as key-study, this value is also reported by Verbruggen et al. (2005). The updated MPC-values have been based on a NOEC of 0.66 mg/L for algae, which is also included in the second REACH dossier. In view of this, it is not clear how the PNEC of 0.082 mg/L has been derived.

3.3 Relevance of secondary poisoning and human fish consumption

In the report of Verbruggen et al. (2005), it was already concluded that secondary poisoning is not relevant because the BCF of tributylphosphate is lower than the trigger value of 100 L/kg.
Regarding the relevance of human fish consumption for derivation of water quality standards, an internal memorandum was prepared by Janssen and Verbruggen (2007), the relevant part of which is copied in Appendix 2. They derived a risk limit for water based on human fish consumption, using a TDI of 0.09 mg/kg_{bw}.d, a body weight of 70 kg, a daily fish consumption of 0.115 kg, a maximum contribution of fish consumption to the total TDI of 10%, and a BCF of 49 L/kg. Since the resulting $MPC_{water,\ hh\ food}$ of 112 µg/L is higher than that for direct ecotoxicity (66 µg/L and 6.6 µg/L for fresh- and saltwater), human fish consumption is not critical for the final MPC_{fw} and MPC_{sw}. The above mentioned decision of the Steering Committee on Substances was taken on the basis of this memorandum.

3.4 Derivation of the $MAC_{fw,\ eco}$ and $MAC_{sw,\ eco}$

The available ecotoxicity data for freshwater and marine species used by Verbruggen et al. (2005) are copied below in Table 9 an 10. For organic chemicals, the datasets for freshwater and marine species can be combined unless there is evidence for a difference in sensitivity between the two groups (EC, 2011). There are not enough marine data to make a sound statistical comparison, but the data do not indicate that there is a difference for crustacea. The combined dataset is used for risk limit derivation, but different assessment schemes are used for freshwater and saltwater.

The acute base set (algae, *Daphnia*, fish) is available, L/EC_{50} values range from 1.7 to 68 mg/L. The lowest value is for *Gammarus pseudolimnaeus*, the highest for *Daphnia pulex*, both species are crustacea. For chemicals without a specific mode of action, an assessment factor of 10 can be applied to the lowest acute endpoint if the variation between species is relatively low (EC, 2011). This is considered to be the case if the standard deviation of the log-transformed L/EC_{50}-vaues is <0.5. The standard deviation of the present dataset is 0.51. However, it appears that the variation between species within the most sensitive taxonomic group (crustacea) is even larger, the standard deviation of the log transformed L/EC_{50}-values is 0.64. The variation among the other species is smaller, when the crustacea are left out of consideration, the standard deviation of the log transformed L/EC_{50}-values is 0.46. Because of the relatively large dataset and the number of different taxa included, it is considered justified to put an assessment factor of 10 to the lowest EC_{50} of 1.7 mg/L, leading to a $MAC_{fw,\ eco}$ of 0.17 mg/L = 170 µg/L.

To derive the $MAC_{sw,\ eco}$, an additional factor of 10 is applied because data for typical marine species are not available. The $MAC_{sw,\ eco}$ is 17 µg/L.

Table 9 Aggregated toxicity data for tributylphosphate: freshwater species (copied from table A1.8 in Verbruggen et al., 2005)

Chronic		**Acute**	
Taxon	**EC_{10}/NOEC [mg/L]**	**Taxon**	**L/EC_{50} [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
		Pisces	8.8
		Pisces	7.6
		Pisces	8.3 [c]
		Pisces	13 [d]
		Pisces	6.6 [e]
		Platyhelminthes	4
		Protozoa	20

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: gometric 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 10 Aggregated toxicity data for tributylphosphate: marine species (copied from table A1.9 in Verbruggen et al., 2005)

Chronic		**Acute**	
Taxon	**EC_{10}/NOEC [mg/L]**	**Taxon**	**L/EC_{50} [mg/L]**
Bacteria	2.62	Bacteria	80.7
		Crustacea	54.6

3.5 $MPC_{dw, hh}$ – surface water for abstraction of drinking water

No official guideline value is available for tributylphosphate. A provisional $MPC_{dw, hh}$ of 315 µg/L is mentioned in the table in Appendix 2, using the TDI of 0.09 mg/kg_{bw}.d and assuming a body weight of 70 kg, a daily water consumption of 2 L and a maximum contribution of water consumption to the total TDI of 10%. According to the WFD-guidance, a substance specific removal rate should be considered to derive the $MPC_{dw, hh}$. At present, such information is not available and water treatment is not taken into account. The $MPC_{dw, hh}$ is 315 µg/L.

3.6 Conclusion

The environmental risk limits for tributylphosphate that were derived in this report or have been established earlier are presented in Table 11. Risk limits that are equivalent to the water quality standards according to the WFD are indicated in bold. All values refer to dissolved concentrations.

In 2010, tributylphosphate was detected at several sampling stations of the Waterdienst on various occasions, for instance, Belfeld (0.17-0.81 µg/L), Eijsden (0.16-0.82 µg/L), Keizersveer (0.13-0.47 µg/L), Nederweert (0.13-0.92 µg/L), and Stevensweert (0.14-0.75 µg/L). The highest concentration was 1.8 µg/L on April, 19 2010 at Puttershoek (www.waterbase.nl). Note that reported levels refer to total concentrations, whereas the proposed risk limits are expressed as dissolved concentrations. However, taking into account the default suspended matter concentration of 30 mg/L for Dutch surface waters, and a log K_{oc} of 3.13 (Verbruggen et al., 2005), total and dissolved concentrations are the same. This also holds at a lower suspended matter concentration of e.g. 15 mg/L. Based on these data, it is not expected that the MAC-, MPC-, or SRC-values will be exceeded. It is possible, however, that the yearly average is higher than the NC-values.

Table 11 Environmental risk limits for tributylphosphate in water

Environmental risk limit	**Value [µg/L]**
Freshwater	
$MPC_{fw, eco}$	66[a]
$MPC_{fw, secpois}$	n.r.
$MPC_{water, hh\ food}$	112[b]
MPC_{fw}	**66**[a]
NC_{fw}	0.66[a]
$MAC_{fw, eco}$	**170**
$SRC_{fw, eco}$	1100[a]
Surface water for drinking water production	
$MPC_{dw, hh}$	**315**[b]
Saltwater	
$MPC_{sw, eco}$	6.6[a]
$MPC_{sw, secpois}$	n.r.
$MPC_{water, hh\ food}$	112[b]
MPC_{sw}	**6.6**[a]
NC_{sw}	0.066[a]
$MAC_{sw, eco}$	**17**
$SRC_{sw, eco}$	1100[a]

a: ERLs reported by, or based on Verbruggen et al. (2005)
b: Janssen and Verbruggen (2007; Appendix 2)
n.r.: not relevant

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List of abbreviations

BCF	Bioconcentration Factor
EC_x	Concentration at which x% effect is observed
ERL	Environmental Risk Limit
EU-RAR	European Union Risk Assessment Report
INS	International and National Environmental Quality Standards for Substances in the Netherlands
LC_{50}	Concentration at which 50% mortality is observed
MAC_{eco}	Maximum Acceptable Concentration for ecosystems
$MAC_{fw, ecor}$	Maximum Acceptable Concentration for ecosystems in freshwater
$MAC_{sw, eco}$	Maximum Acceptable Concentration for ecosystems in the saltwater compartment
Marine species	Species that are representative for marine and brackish water environments and that are tested in water with salinity > 0.5 ‰.
MPC	Maximum Permissible Concentration
MPC_{fw}	Maximum Permissible Concentration in freshwater
MPC_{sw}	Maximum Permissible Concentration in the saltwater compartment
$MPC_{fw, eco}$	Maximum Permissible Concentration in freshwater based on ecotoxicological data
$MPC_{sw, eco}$	Maximum Permissible Concentration in the saltwater compartment based on ecotoxicological data
$MPC_{fw, secpois}$	Maximum Permissible Concentration in freshwater based on secondary poisoning
$MPC_{sw, secpois}$	Maximum Permissible Concentration in the saltwater compartment based on secondary poisoning
$MPC_{water, hh food}$	Maximum Permissible Concentration in freshwater and saltwater based on consumption of fish and shellfish by humans
$MPC_{dw, hh}$	Maximum Permissible Concentration in water used for abstraction of drinking water
NC	Negligible Concentration
NC_{fw}	Negligible Concentration in freshwater
NC_{sw}	Negligible Concentration in the saltwater compartment
NOEC	No Observed Effect Concentration
NOAEC	No Observed Adverse Effect Concentration
NOAEL	No Observed Adverse Effect Level
SRC_{eco}	Serious Risk Concentration for ecosystems
$SRC_{fw, eco}$	Serious risk concentration for freshwater ecosystems
$SRC_{sw, eco}$	Serious risk concentration for saltwater ecosystems
TDI	Tolerable Daily Intake
TGD	Technical Guidance Document
WFD	Water Framework Directive (2000/60/EC)

Appendix 1. Data on ecotoxicity and bioconcentration of ethylbenzene from the EU-RAR

Ecotoxicity of ethylbenzene

The following table is copied from the EU-RAR.

Table 3.18 Most relevant results of acute toxicity tests with aquatic organisms

Test organism/ source	duration	test design/ remarks	analytical data	effect concentration [mg/l]	effect
Vertebrates, short-term toxicity					
Menidia menidia (Boeri, 1987a)	96 h	flow-through saltwater	y	96 h-LC_{50} = 5.1	mortality
Pimephales promelas (Geiger et al., 1986)	96 h	flow–through freshwater	y	96 h-LC_{50} = 12.1	mortality
Oncorhynchus mykiss (Galassi et al., 1988)	96 h	semi-static, closed bottles OECD 203 freshwater	y	96 h-LC_{50} = 4.2	mortality
Morone saxatilis (Benville and Korn, 1977)	96 h	static, open system more than 99% of test substance was lost within 24 h saltwater	y	96 h-LC_{50} = 4.3 a)	mortality
Poecilia reticulata (Galassi et al., 1988)	96 h	semi-static, closed bottles OECD 203 freshwater	y	96 h-LC_{50} = 9.6	mortality
Invertebrates, short-term and long-term toxicity					
Mysidopsis bahia (Boeri, 1988)	96 h	flow-through saltwater	y	96 h-LC_{50} = 2.6	mortality
Daphnia magna (Vigano, 1993)	24 h 48 h	static, EPA method F closed system freshwater	y	24 h-LC_{50} = 2.3-2.9 48 h-LC_{50} = 1.8-2.4	immobilization
Ceriodaphnia dubia (Niederlehner et al., 1998)	7 d	semi-static, EPA Whole Effluent Testing Program method, modified to minimize volatilization freshwater	y	7 d-LC_{50} = 3.6 7 d-IC_{50} = 3.3 (repro) 7 d-LOEC = 1.7 (repro) 7 d-NOEC = 1.0 (repro) 48 h-LC_{50} = 3.2	mortality / reproduction
Daphnia magna (Abernethy et al., 1986; Bobra et al., 1983)	48 h	static, closed system freshwater	n	48 h-LC_{50} = 2.1 b)	mortality
Artemia salina (Abernethy et al., 1986)	24 h	static, closed system saltwater	n	24 h-LC_{50} = 15.4 b)	mortality
Daphnia magna (MacLean and Doe, 1989)	48 h	static, closed system freshwater	y	48 h-EC_{50} = 2.9	immobilization

Test organism/ source	duration	test design/ remarks	analytical data	effect concentration [mg/l]	effect
Artemia salina (MacLean and Doe, 1989)	48 h	static, closed system saltwater	y	48 h-EC_{50} = 9.2	immobilization
Crago franciscorum (Benville and Korn, 1977)	24 h 96 h	static, open system more than 99% of test substance was lost within 24 h saltwater	y	24 h-EC_{50} = 2.2 a) 96 h-EC_{50} = 0.49 a)	y
Daphnia magna (Galassi et al., 1988)	24 h	OECD 202 effect: immobilization freshwater	y	24 h-IC_{50} = 2.2	immobilization
Plants					
Selenastrum capricornutum (Boeri, 1987b)	96 h	TSCA 797.1050 freshwater	y	72 h-E_RC_{50} = 5.9 72 h-NOEC = 3.4 96 h-E_RC_{50} = 5.0 96 h-E_RC_{10} = 3.4	growth rate
Skeletonema costatum (Boeri, 1987c)	96 h	TSCA 792.1050, static saltwater	y	72 h-E_RC_{50} = 7.7 b) 72 h-NOEC = 4.5 b)	growth rate
Selenastrum capricornutum (Galassi et al., 1988)	72 h	growth inhibition test freshwater	y	72 h-E_RC_{50} = 4.6	growth rate

a) test result is not valid b) exponential growth in the control only over 72 h

Note concerning data on *Daphnia magna* from Vigano (1993):
Inspection of the original publication learns that the range of EC_{50}-values of 1.8-2.4 mg/L reported in the EU-RAR refers to separate tests with five different feeding regimes. A copy of the results table from Vigano (1993) is included below. Food ratios were 0.6, 1, 1.8, 3, and 5 x 10^5 cells/mL per day for treatment A to E, respectively, diet consisted of an equal mixture of algae and yeast. There seems to be a tendency towards decreasing EC_{50}-values with increasing food levels, but the relationship is not consistent and 95% confidence intervals of the respective treatments overlap. Feeding is normally not allowed in acute ecotoxicity tests. However, the 48-hours EC_{50}-values are similar to the data of other authors. It is therefore considered justified to calculate a geometric mean value for *D. magna* using all data: 2.38, 2.41, 1.81, 1.93, 1.81, 2.1, 2.9 mg/L, resulting value is 2.2 mg/L.

Table 2. Toxicity test results obtained for ethylbenzene with the young daphnid produced by *D. magna* fed five food levels. Neonate weight and length refer to the specific brood used to run the test

Food ration*	24-h EC_{50} (mg/l)	95% C.I.	Slope	95% C.I.
A	2.69	2.45–3.00	10.85	6.21–15.49
B	2.89	2.61–3.27	10.53	5.69–15.34
C	2.27	1.93–2.68	8.11	4.40–11.82
D	2.45	2.09–2.86	9.08	4.81–13.35
E	2.37	2.04–2.76	10.04	5.23–14.86

	48-h EC_{50} (mg/l)	95% C.I.	Slope	95% C.I.	Neonate weight (μg)	Neonate length (mm)	Brood number
A*	2.38	2.16–2.63	10.72	6.39–15.05	12.3	0.978	11
B	2.41	2.15–2.67	11.14	5.46–16.82	12.2	0.976	10
C	1.81	1.51–2.14	7.44	3.91–10.97	12.9	0.982	9
D	1.93	1.63–2.28	7.93	4.16–11.69	12.5	0.985	9
E	1.81	1.47–2.18	5.97	3.25–8.70	11.9	0.977	9

*Capital letters indicate increasing food levels. See methods.

Bioconcentration of ethylbenzene

The following text is copied from the EU-RAR, section 3.1.3.3:

Accumulation and metabolism
The log Kow of 3.13 indicates a potential for bioaccumulation. According to the TGD a BCF of 91 can be estimated from this value.

No bioaccumulation studies performed with pure ethylbenzene are available. In several studies the water-soluble fraction (WSF) of crude oil that contains ethylbenzene was tested. Roubal et al. (1978) investigated the bioconcentration of ethylbenzene from the WSF of crude oil by Coho salmon (Oncorhynchus kitutsch) and starry flounder (Platichthys stellatus). The fish were exposed for 6 weeks (salmon) and 2 weeks (flounder) in a flow-through system to a mean WSF concentration of 0.9 mg/l containing a mean ethylbenzene concentration of 0.005 mg/l. At the end of the exposure periods, both species were transferred to clean sea water for 2 weeks to study the depuration. Bioconcentration factors for C2-substituted benzenes (related to dry weight) were 1.1, 2.4, 2 and 1 after 2, 3, 5 and 6 weeks of exposure for Coho salmon (muscle tissue). For the starry flounder the bioconcentration factors for C2- substituted benzenes in muscle tissues were determined to be 20 and 4 after 1 and 2 weeks of exposure. Depuration of the accumulated ethylbenzene to concentrations below the detection limit (0.05 mg/kg) occurred within 1 week for salmon and within 2 weeks for the flounder. Manila clams (Tapes semidecussata) were exposed for 8 days in a flow-through system to the water-soluble fraction of crude oil containing a mixture of 6 monoaromatics (Nunes and Benville, 1979). The amount of aromatics in water was measured three times a day. The mean ethylbenzene concentration was 0.08 mg/l. Every 48 h a sub-sample of 10 test organisms was pooled and analyzed for aromatic content by GC. After 2 days of exposure the ethylbenzene concentration in the tissue (related to wet weight) was 0.34 mg/kg and after 8 days 0.37 mg/kg. After transfer of the clams into clean water, depuration of the ethylbenzene to concentrations below the detection limit (0.13 mg/kg) occurred within 7 days. In a poorly documented study Ogata et al. (1984) determined a log BCF of 1.19 (BCF = 15) for ethylbenzene in goldfish. From the description of the study it is not clear whether the fish were exposed to pure ethylbenzene or to a mixture of alkyl benzenes. No information is given on the exposure duration or whether steady state conditions had been achieved. Therefore, the study is not regarded as valid and the result is not used for the risk assessment.

The validity of the available bioconcentration studies is limited as for all tests there is no information whether steady state was reached. In addition, the test organisms were not exposed to pure ethylbenzene but to a mixture of oil components. However, the available study results can be used as an indication that the bioaccumulation potential of ethylbenzene may be lower than predicted from the log Kow. The predicted BCF of 91 is used further in the risk assessment.

(end of citation)

Appendix 2. Relevance of human fish consumption for tributylphosphate

Milieukwaliteitsnormen op basis van humane blootstellling voor de fosfaatesters uit RIVM rapport 601501024

P.J.C.M. Janssen & E.J.M. Verbruggen, 24 januari 2007

Voor de fosfaatbrandvertragers uit RIVM-rapport 601501024 zijn geen ADI, TDI of vergelijkbare waarden gevonden. Daarom is in beperkte tijd onderstaand overzicht van de aanwezige toxiciteitsgegevens gemaakt voor zoogdieren. Op basis van het overzicht werd een schatting gemaakt van de hoogte van de TDI en de normen voor drinkwater en visconsumptie. Deze zijn in onderstaande tabel weergegeven.

Stof	Afgeleide norm ecotoxiciteit [ug/l]	TDI niveau [mg/kg$_{bw}$/d]	Schatting van norm voor drinkwater [µg/l]	Maximale BCF [l/kg]	Schatting van norm voor visconsumptie [µg/l]
TBP	66	0.09	315	49	112
TBiP	11			<100	
TEP	1600	0.125	437.5	<100	
TBEP	13	0.015	52.5	<100	
TEHP		0.357	1249.5	22	52
TPP	0.16	0.161	563.5	420	23
TCP	0.032	0.0375	131.25	800	2.9

Normen berekend voor visconsumptie komen hoger uit dan de normen voor aquatische ecotoxiciteit. Normen voor de inname van drinkwater komen in de meeste gevallen ook hoger uit dan de normen voor ecotoxiciteit. Een uitzonder hierop is de waarde voor triethylphosphate. De waarde voor drinkwater komt lager uit. Hierin is nog niet verwerkt dat deze norm gedeeld mag worden door de niet eenvoudig fractie met simpele reinigingstechnieken. Echter vanwege de stofeigenschappen van TEP moet er volgens de OECD-SIDS geen significante verwijdering verwacht worden. De norm voor TEP zou op basis hiervan kunnen worden herzien in een voorlopige norm van 440 µg/l op basis van inname voor drinkwater.

Tributylphosphates 126-73-8 (n-butyl) en 126-71-6 (isobutyl)

Tributylfosfaat (CAS 126-73-8) is beoordeeld in het kader van OECD-SIDS (2001). Volledig pakket aan data beschikbaar (inclusief chronische tox, genotoxiciteit, reproductietox, teratogeniteit). Overall- NOAEL 9 mg/kg lg/dag (rat chronisch).

Tri-isobutylfosfaat is minder uitgebreid onderzocht. De enige beschikbare evalautie is door de Duitse BG-Chemie uit 2004. Op basis van subchronische studie in rat lijkt stof minder toxisch dan tributyl-analoog. Stof lijkt wel sensibiliserend bij huidcontact.

Conclusie: geen bestaande TDI beschikbaar. Wel waarde voorlopige afleidbaar (voldoende data).

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