Common Implementation Strategy for the Water Framework Directive

Environmental Quality Standards (EQS)

Substance Data Sheet

Priority Substance No. 30

Tributyltin compounds (TBT-ion)

CAS-No. 688-73-3 (36643-28-4)

Final version
Brussels, 15 January 2005

Disclaimer

This data sheet provides background information on the setting of the Environmental Quality Standard in accordance with Article 16 of the Water Framework Directive (2000/60/EC). The information was compiled, evaluated and used as outlined in the Manual [4] and has been discussed in a consultative process with the Expert Advisory Forum on Priority Substances and the Expert Group on Quality Standards. Furthermore, it has been peer-reviewed by the SCTEE [15]. The substance data sheet may, however, not necessarily represent the views of the European Commission.

New upcoming information was considered and included up to the date of finalisation of this data sheet. Information becoming available after finalisation of this document will be evaluated in the review process of priority substances according to Art. 16(4) of the Water Framework Directive. If necessary, the Environmental Quality Standard substance data sheets will then be revised in the light of technical and scientific progress.

1 Identity of substance

Priority Substance No: 30	Tributyltin compounds (TBT-ion)
CAS-Number:	688-73-3 (36643-28-4)
Classification WFD Priority List*:	PHS

* PS: priority substance; PHS: priority hazardous substance; PSR: priority substance under review according to Decision 2455/2001.

2 Proposed quality standards

2.1 Overall quality standards

Ecosystem	Quality Standard	Comment
AA-QS all types of surface waters covered by the WFD	0.0002 µg/l	Protection of the pelagic community; see section 8.1 & 8.6
MAC-QS (ECO)	0.0015 µg/l	See section 8.1

2.2 Specific quality standards

Protection Objective	Quality Standard	Comment
Pelagic community all types of surface water covered by the WFD	0.0002 µg/l corresponding conc. in SPM: 0.022 µg/kg (dry wt)	see section 8.1
Benthic community (freshwater & marine sediment)	0.0046 µg/kg wet wt 0.02 µg/kg dry wt	tentative values derived by EP method; see 8.2
Predators (second. poisoning)	230 µg/kg prey (wet wt) corresponding conc. in water: 0.038 µg/l	see 8.3
Food uptake by man	15.2 µg/kg seafood (wet wt) corresponding conc. in water: 0.0025 µg/l	see 8.4
Abstraction of water intended for human consumption (AWIHC)	< 1 µg/l	A1-value for Σpesticides in CD 75/440/EEC; see section 8.5
Water intended for human consumption (WIHC)	0.1 µg/l	Drinking water standard set in CD 98/83/EC

3 Classification

CAS No.	Name	R-Phrases and Labelling	Reference
36643-28-4	(Tributyltin-cation)	Not available for this chemical substance.	[16]
688-73-3	Tri-n-butyltin hydride	This chemical substance is not classified in the Annex I of Directive 67/548/EEC.	[16]
1461-22-9	Tributyltin chloride	This chemical substance is not classified in the Annex I of Directive 67/548/EEC.	[16]
56-35-9	Bis(tributyltin)oxide	This chemical substance is not classified in the Annex I of Directive 67/548/EEC.	[16]

4 Physical and chemical properties

Property	Value	Ref.	Comments
Mol. Weight:			
Water Solubility	18 – 61.4 mg/L (TBTO) 0.75 mg/L (pH 6.6) (TBTO) 31 mg/L (pH 8.1) (TBTO) 30 mg/L (pH 2.6) (TBTO)	[5]	
Vapour Pressure:	3190 mPa	[6]	

5 Environmental fate and partitioning

Property	Value	Ref.	Comments
<u>Abiotic degradation</u>			
Hydrolysis	The C-Sn bonds of TBTO are not subject to hydrolysis under environmental conditions.	[5]	
Photolysis	Undissociated tributyltin may be subject to photolysis	[6]	
<u>Biodegradation</u>	Tributyltin can be biodegraded. In aerobic conditions the degradation may last 1-3 months. Under anaerobic conditions this may last very much longer. Degradation products are dibutyltin and monobutyltin compounds.	[6]	
<u>Partition coefficients</u>			
log Kow	3.1 – 3.8 4.1 3.85 (TBTO 3.2 – 3.8 (TBTO)	[7] [6] [1] [5]	
Koc	log Koc 3 (2.5-6.2) 1030 – 3750 L/kg (sediment)	[6] [5]	
<u>Bioaccumulation</u>			
BCF	6000	[6]	Tributyltin seems not to biomagnify
fish:			
Cyprinodon variegatus	52,000 (liver, TBTO)	[7]	
Cyprinodon variegatus	2600	[5]	
molluscs:			
Crassostrea gigas	11,400 (TBTO)	[7]	
Crassostrea gigas	2,000 – 11,400	[5]	
Ostrea edulis	1,000 – 1,500	[5]	
crustaceans:			
Rhithropanopeus harrisii	500 – 4400	[5]	

6 Effect data (aquatic environment)

Table 6.1: Overview on toxicity data of most sensitive species from different sources (master reference). (The data highlighted in bold are used for the SSD based derivation of the QS, see section 8.1)

Com-pound *	Species	Taxonomic Group	Medium	Duration	Effect	Endpoint	Value µg/l	Master reference	Reference in master reference	Comments on data reliability in master reference
	Freshwater									
TBTO	*Biomphalaria glabrata*	Mollusca	fw		Significant reduction in egg laying	LOEC	0.001	[7]	Ritchie et al (1974)	Information based on summary data from EHC 1990 study exposed newly-hatched snails to TBTO and looked at the ability to lay eggs following exposure –at 0.001 ug/l egg laying was found to be significantly reduced
TBT	***Poecilia reticula***	**Pisces**	**fw**	**90 d**	**Thymus atrophy, liver vacuolation, hyperplasia of the hemopo-ietic tissue**	**NOEC**	**0.01**	**[5]**	**Wester et al. 1987**	
TBT	*Poecilia reticulata*	Pisces	fw	91 d	Growth	NOEC	0.32	[8]	RIVM Rep. No. 601501002	
TBTC	***Oncorhynchus mykiss***	**Pisces**	**fw**	**110 d**	**Mortality**	**NOEC**	**0.04**	**[6]**	**Stäb & Traas 1996**	
TBT	*Oncorhynchus mykiss*	Pisces	fw	16 w	Growth	NOEC	0.06	[8]	RIVM Rep. No. 601501002	geometric mean (n=2)
TBTO	***Daphnia magna***	**Crustacea**	**fw**	**21 d**	**Reproduction**	**NOEC**	**0.16**	**[5]**	**Kühn et al. 1989**	
TBT	*Daphnia magna*	Crustacea	fw	21 d	Mortality	NOEC	0.16	[8]	RIVM Rep. No. 601501002	
TBT	***Pimephales promelas***	**Pisces**	**fw**	**21 d**	**Growth**	**NOEC**	**0.17**	**[8]**	**RIVM Rep. No. 601501002**	
TBT	*Phoxinus phoxinus*	Pisces	fw	8 d	Mortality	NOEC	0.24	[8]	RIVM Rep. No. 601501002	
TBTC	*Phoxinus phoxinus*	Pisces	fw	7 d	Mortality	NOEC	0.89	[6]	Fent & Meier 1992	
TBT	***Lymnea stagnalis***	**Mollusca**	**fw**	**33 d**	**Mortality**	**NOEC**	**0.32**	**[8]**	**RIVM Rep. No. 601501002**	
TBTC	***Hexagenia sp.***	**Insecta**	**fw**	**21 d**	**Growth**	**NOEC** LOEC IC50	**0.5** 0.9 0.92	**[5]**	**Day et al. 1998**	
TBTC	***Selenastrum capricornutum***	**Algae**	**fw**	**96 h**	**Growth**	**NOEC**	**4**	**[5]**	**Miana et al. 1993**	
TBT	*Selenastrum capricornutum*	Algae	fw	96 h	Growth	NOEC	4	[8]	RIVM Rep. No. 601501002	
TBT	***Chlorella pyrenoïdosa***	**Algae**	**fw**	**4 d**	**Growth**	**NOEC**	**18**	**[8]**	**RIVM Rep. No. 601501002**	

Com-pound *	Species	Taxonomic Group	Medium	Duration	Effect	Endpoint	Value µg/l	Master reference	Reference in master reference	Comments on data reliability in master reference
TBTO	*Daphnia magna*	Crustacea	fw	24 h	Immobilization	EC50	0.03	[5]	Kuhn 1988	
TBTO	*Chironomus plumosus*	Insecta	fw	96 h	Mortality	LC50	0.05	[5]	Fargasova 1997	
TBTO	*Chironomus plumosus*	Insecta	fw	96 h	Mortality	LC50	0.05	[6]	Ohtsubo 1999	
TBTO	*Tubifex tubifex*	Annelida	fw	96 h	Mortality	LC50	0.1	[6]	Ohtsubo 1999	
TBTC	*Phoxinus phoxinus*	Pisces	fw	6 d	Malformation	EC50	0.69	[6]	Fent 1992	
TBTO	*Oncorhynchus mykiss*	Pisces	fw	96 h	Mortality	LC50	1.28	[5]	Martin et al. 1989	
TBTO	*Oncorhynchus mykiss*	Pisces	fw	48 h	Mortality	LC50	21	[7]	Alabaster (1969)	
TBTO	*Rana temporaria*	Amphibia	fw	96 h	Mortality	LC50	1.65	[5]	Rana temporaria 1989	
TBTF	*Lebistis reticulatus*	Pisces	fw	90 d	Mortality	LC52	3.5	[7]	Cardarelli (1973)	
TBTO	*Ankistrodesmus falcatus*	Algae	fw	8 d	Inhibition of reproduction	EC50	5	[7]	Wong et al (1982)	
TBTC	*Azolla filiculoides*	Cormophyta	fw	96 h	Growth	EC50	8.3	[6]	Lyman et al. 1990	
TBTF	*Ictalurus punctatus*	Pisces	fw	96 h	Mortality	LC50	12	[7]	Slesinger (1979) cited in Argaman et al (1984)	
TBTO	*Anabaena flos aquae*	Algae	fw	4 h	Inhibition of primary prod.	EC50	13	[7]	Wong et al (1982)	
TBTH	*Lemna minor*	Cormophyta	fw	96 h	Reproduction	IC50	30.83	[5]	Zhihui et al. 1998	
TBTC	*Lemna minor*	Cormophyta	fw	96 h	Growth	EC50	30.8	[6]	Lyman et al. 1990	
	Saltwater									
TBTO	***Nucella lapillus***	**Mollusca**	**sw**	**360 d**	**Imposex**	**NOEC**	**0.001**	**[5], [1]**	**IPCS 1990**	
TBTO	***Mercenaria mercenaria***	**Mollusca**	**sw**	**14 d**	**Growth**	**NOEC**	**0.0024**	**[5]**	**Laughlin et al. 1988**	
TBT	*Mercenaria mercenaria*	Mollusca	sw	4 d	Growth	NOEC	0.0024	[8]	RIVM Rep. No. 601501002	
TBT	***Buccinum undatum***	**Mollusca**	**sw**	**19 m**	**Growth**	**NOEC**	**0.0028**	**[8]**	**RIVM Rep. No. 601501002**	
TBTO	*Crassostrea gigas*	Mollusca	sw	360 d	Growth	NOEC	< 0.005	[5]	Nell et al. 1992	
TBT	***Crassostrea gigas***	**Mollusca**	**sw**	**28 d**	**Growth**	**NOEC**	**0.005**	**[8]**	**RIVM Rep. No. 601501002**	
TBT	*Crassostrea gigas*	Mollusca	sw	21 d	Mortality	NOEC	0.025	[8]	RIVM Rep. No. 601501002	
TBT	***Saccostrea commercialis***	**Mollusca**	**sw**	**28 d**	**Growth**	**NOEC**	**0.005**	**[8]**	**RIVM Rep. No. 601501002**	
TBTH	***Mytilus edulis***	**Mollusca**	**sw**	**14 d**	**Growth & survival of larvae**	**NOEC**	**0.006**	**[5]**	**Lapota et al. 1993**	
TBT	*Mytilus edulis*	Mollusca	sw	33 – 66 d	Growth	NOEC	0.05	[8]	RIVM Rep. No. 601501002	geometric mean (n=3)
TBT	*Mytilus edulis*	Mollusca	sw	6 d	Survival	NOEC	0.1	[8]	RIVM Rep. No. 601501002	
TBT	***Nucella lima***	**Mollusca**	**sw**	**4 m**	**Imposex**	**NOEC**	**0.0064**	**[8]**	**RIVM Rep. No. 601501002**	
TBT	***Eurytemora affinis***	**Crustacea**	**sw**	**13 d**	**Reproduction**	**NOEC**	**0.01**	**[8]**	**RIVM Rep. No. 601501002**	

Com-pound *	Species	Taxonomic Group	Medium	Duration	Effect	Endpoint	Value µg/l	Master reference	Reference in master reference	Comments on data reliability in master reference
TBTO	***Ophioderma brevispina***	**Echino-dermata**	**sw**	**28 d**	**Regeneration**	**NOEC**	**0.01**	**[9]**	**Walsh et al. 1986**	
TBT	***Palaemonetes pugio***	**Crustacea**	**sw**	**21 d**	**Mortality**	**NOEC**	**0.033**	**[8]**	**RIVM Rep. No. 601501002**	
TBTO	*Palaemonetes pugio*	Crustacea	sw	21 d	Sloughing	NOEC	0.1	[5]	Khan et al. 1993	
TBT	***Dunaliella tertiolecta***	**Algae**	**sw**	**18 d**	**Growth**	**NOEC**	**0.05**	**[8]**	**RIVM Rep. No. 601501002**	
TBT	***Neanthes arenaceodentata***	**Annelida**	**sw**	**70 d**	**Growth**	**NOEC**	**0.05**	**[8]**	**RIVM Rep. No. 601501002**	
TBT	***Acartia tonsa***	**Crustacea**	**sw**	**6 d**	**Survival**	**NOEC**	**0.1**	**[8]**	**RIVM Rep. No. 601501002**	
TBT	***Gasterosteus aculeatus***	**Pisces**	**sw**	**225 d**	**Reproduction**	**NOEC**	**0.1**	**[8]**	**RIVM Rep. No. 601501002**	
TBT	***Gammarus oceanicus***	**Crustacea**	**sw**	**8 w**	**Mortality**	**NOEC**	**0.3**	**[8]**	**RIVM Rep. No. 601501002**	
TBT	***Cyprinodon variegatus***	**Pisces**	**sw**	**28 d**	**Growth**	**NOEC**	**0.34**	**[8]**	**RIVM Rep. No. 601501002**	
TBT	*Arenicola cristata*	Annelida	sw	7 d	Mortality	NOEC	2.5	[8]	RIVM Rep. No. 601501002	
TBTC	*Acartia tonsa*	Crustacea	sw	8 d	Larvae survival retarded larvae development	LC50 EC50	0.0015 0.003	[5]	Kusk et al. 1997	
TBTC	*Acartia tonsa*	Crustacea	sw	48 h	Mortality	LC50	0.24	[5]	Kusk et al. 1997	
TBTO	*Acartia tonsa*	Crustacea	sw	96 hour	Mortality	LC50	1	[7]	Uren (1983)	
TBTB	*Enteromorpha intestinalis*	Algae	sw	5 d	Inhibition of spore germination	EC50	0.027	[7]	Davies et al (1984)	TBTB in acetone used Information based on summary data from EHC 1990
TBTO	*Crassostrea virginica*	Mollusca	sw	96 h		EC50	0.13	[5]	US-EPA 1995	
TBTO	*Skeletonema costatum*	Algae	sw	72 h	Growth	EC50	0.33	[5]	Walsh et al. 1985	
TBTO	*Solea solea (larvae)*	Pisces	sw	96 hour	Mortality	LC50	2.1	[7]	Thain (1983)	

* TBT tributyltin compounds
TBTA tributyltin acetate
TBTB tributyltin benzoate
TBTC tributyltin chloride
TBTF tributyltin fluoride
TBTH tributyltin hydride
TBTO bis tributyltin oxide

Table 6.2: Mammalian oral toxicity data relevant for the assessment of non compartment specific effects relevant for the food chain (secondary poisoning) [13]

Species	Study type	Effects investigated	Endpoint	Ref.
Rat	2 year carcinogenicity / chronic toxicity study. Oral administration of TBTO in food.	Increased water consumption and urine production. Decreased urine osmolarity and the changes in water intake and urinary indices are suggestive of impaired renal concentrating capacity and may be associated with age-related degenerative changes in the kidney	Based on the constellation of changes observed at the highest dose, the LOAEL for chronic toxicity is 2.1 mg/kg-day, and the **NOAEL is 0.19 mg/kg-day**	1)
Rat	Two generation reproduction study. Oral administration of TBTO in food.	Decreased pup weight	LOAEL for developmental toxicity is 3.43 mg/kg-day and the **NOAEL is 0.34 mg/kg-day**	2)

1) Wester, P.W., E.I. Krajnc, F.X.R. van Leeuwen et al. 1990. Chronic toxicity and carcinogenicity of bis(tri-n-butyltin)oxide (TBTO) in the rat. Fd. Chem. Toxic. 28: 179-196.

2) Schroeder, R.E. 1990. A two-generation reproduction study in rats with bis(tri-n-butyltin)oxide. Unpublished report by Bio/dynamics, Inc., prepared for Schering AG and M&T Chemicals, Inc. MRID No. 416938-01. Available from EPA. Write to FOI, EPA, Washington, DC 20460.

Summary on endocrine disrupting potential

CAS No.	Substance		Reference
688-73-3	Tributyltin compounds	Substance with evidence of ED or evidence of potential ED	[2]

It is well known that tributyltin compounds affect the endocrine system of certain marine as well as freshwater mollusc species at very low concentrations (1 ng/l onwards). This results in different types of malformation of the genital system known as „imposex“ and „intersex“ which lead, depending on the severity of malformations, to an impairment or eventually a complete loss of the ability to reproduce. The severity of malformations is positively correlated with TBT concentrations.

7 Effect data (human health)

No oral toxicity data (NOAELs) that could be used for the calculation of quality standards referring to human health were provided by Member States or other stakeholders. However, the World Health Organization (WHO) has proposed a Tolerable Daily Intake (TDI) of 0.25 µg/kg bw/d bis tributyltin oxide and a drinking water guideline value of 2 µg/l [10] with a justification as follows:

> *TBTO is not genotoxic. One carcinogenicity study has been reported in which neoplastic changes were observed in endocrine organs, but the significance of these changes is considered questionable. The most sensitive end-point appears to be immunotoxicity, with a lowest NOAEL of 0.025 mg/kg of body weight per day in a 17-month feeding study in rats related to suppression of resistance to the nematode Trichinella spiralis. The significance to humans of this finding is not completely clear, but this NOAEL is consistent, within an order of magnitude, with other NOAELs for long-term toxicity.*
>
> *A TDI of 0.25 µg/kg of body weight was calculated by applying an uncertainty factor of 100 (for inter- and intraspecies variation) to the NOAEL of 0.025 mg/kg of body weight per day for suppression of resistance to T. spiralis. The guideline value for TBTO is 2 µg/litre (rounded figure) based on an allocation of 20% of the TDI to drinking-water.*

The Reference Dose for Chronic Oral Exposure (RfD) derived by the US-EPA is 0.3 µg TBTO /kg bw $*d^{-1}$ [13]. This RfD is based on a 10% immunosuppression benchmark dose of 0.03 mg/kg bw $*d^{-1}$ seen in a 18 months immunotoxicity study with rats and an uncertainty factor of 100 (factors of 10 each are applied for uncertainty associated with extrapolating from a laboratory animal species to humans and to protect sensitive humans).

8 Calculation of quality standards

8.1 Quality standards for water

There are many long-term no effect and short-term acute toxicity data for a broad range of species from different taxonomic groups available (see table 6.1). Molluscs appear to be the most sensitive taxonomic group. However, the difference to the most sensitive species of other taxonomic groups such as fish, invertebrates and algae is only gradual on a very low exposure level (lowest reported NOECs for molluscs 1ng/l and 10 – 50 ng/l for the other taxonomic groups mentioned).

Although it is stated in the section on marine risk assessment of the TGD [3] that marine and freshwater species of the same taxonomic groups might differ in sensitivity to organotin compounds this is obviously not the case for tributyltin compounds, as can be seen from the data listed in table 6.1. It is therefore suggested to derive the qualtiy standards applicable to freshwater or saltwater environments from the same data set (i.e. the data reported in tab. 6.1).

In line with the TGD the Manual [4] offers the option to support the effects assessment performed with the assessment factor method by a statistical extrapolation method if the database is sufficient for its application. The TGD requires reliable NOECs from chronic/long-term studies for a minimum of 10 and preferably more than 15 different species from at least 8 taxonomic groups. In the TBT database long-term/chronic NOECs are only available for 7 different taxonomic groups (freshwater & saltwater together). However, of the minimum species requirement mentioned in section 3.3.1.2 of the TGD, only tests with higher plant species are not available. As, on the other hand, many tests for the taxonomic group deemed most sensitive to TBT are available (molluscs) the method of Aldenberg & Jaworska has been applied in order to explore to which extent the result of this method differs from the outcome of the standard TGD assessment factor method. Details of application and the result of the SSD method are described in section 8.1.1.

Freshwater

Long-term toxicity data as well as short-term acute data are available across 3 trophic levels for the "standard" representatives fish, crustaceans and algae. In addition, long-term toxicity data are available for molluscs (snails and clams), annelid worms, insects, and echinoderms (see table 6.1).

Based on the available information the mollusc species *Nucella lapillus* (Dog Whelk) is the species most sensitve to tributyltin compounds. The NOEC is 0.001 µg/l based on effects on the endocrine system leading to "imposex". The appropriate assessment factor according to the Manual (section 4.3.2.1) [4] is 10 (long-term toxicity data across at least 3 trophic levels for 3 different taxonomic groups are available and the species for which the lowest acute result has been obtained belongs to that groups):

$QS_{freshwater}$ = 0.001 µg/l / AF (10) = 0.0001 µg TBT-Compounds /l

Transitional, coastal and territorial waters

As there is a comprehensive data base on marine species available it is suggested in accordance with the section on marine risk assessment of the Manual (section 4.3.2.2) [4] to apply a safety factor of 10 on the lowest reported NOEC. Hence, the suggested qualtiy standard for the saltwater pelagic communitiy is equal to that calculated for freshwater.

$QS_{saltwater}$ = $QS_{freshwater}$ = 0.0001 µg TBT-Compounds /l

Quality standard accounting for transient concentration peaks (MAC-QS)

It is suggested to derive the MAC-QS on the basis of the lowest acute toxicity test available. This is a 8 days test with the marine crustacean species *Acartia tonsa.* The EC50 for retarded larvae development is reported as 0.003 µg/l whereas the LC50 for larvae survival is 0.015 µg/l. The lowest toxicity test result reported for a freshwater species is the 24 hour EC50 of 0.03 µg/l for *Daphnia magna*. Thus, pelagic crustacean species appear to be most sensitive to TBT-compounds in saltwater as well as in freshwater. It seems reasonable to use the *Arcatia tonsa* LC50 of 0.015 µg/l as the relevant value for the derivation of the MAC-QS (the *Daphnia* EC50 may be lower for a standard exposure time of 48 h, the significance of the retarded development on the population of *Arcatia* is unclear and it may not occur at short term concentration peaks).

Based on the guidance given in the TGD on the effects assessment for intermittent releases (section 4.3.6 of the Manual [4]) it is suggested to apply a reduced assessment factor of 10 on the selected LC50 in order to derive the MAC-QS. This appears justified as acute test results are available for a very broad spectrum of freshwater and marine taxonomic groups showing that these groups do not have a higher acute sensitivity to TBT-compounds.

MAC-QS = 0.015 µg/l / AF (10) = 0.0015 µg TBT-Compounds /l

8.1.1 Calculation of the quality standard for water using statistical extrapolation

The 5th-percentile cut-off value was calculated with the method of Aldenberg & Jaworska [12] (for details see also section 4.3.4 of the Manual [4]). The program ETX-2000 [14] was used for the calculation and for assessing the fit of the input data to the supposed log-normal distribution.

The toxicity tests highlighted in bold in table 6.1 were used as input-data. The selected data fit very well to the expected distribution curve (see figure 8.1). The Kolomogorov-Smirnov and Anderson-Darling tests for goodness of fit are passed on the highest level of significance.

The calculated 5th-percentile cut off-value is 0.00083 µg/l (see table 8.1).

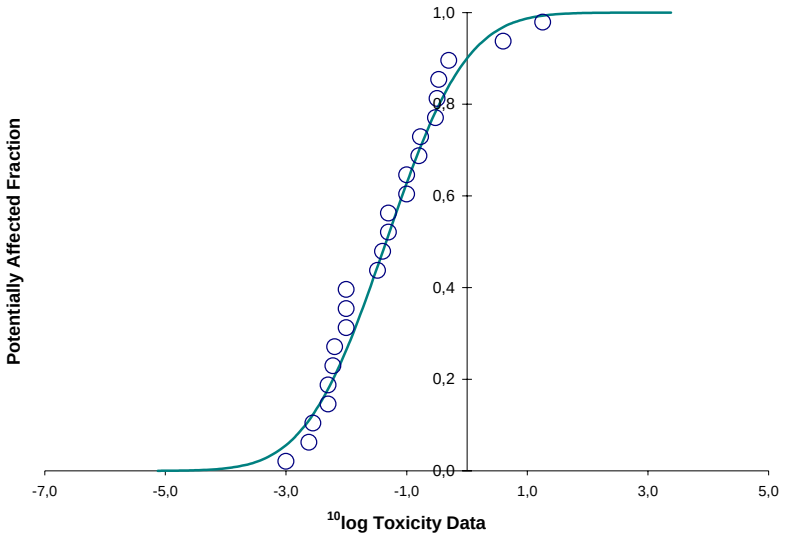

Figure 8.1: Cumulative frequency distribution of the combined freshwater and saltwater data set used for the derivation of the 5th-percentile cut-off value by the method of Aldenberg and Jaworska [12]

Table 8.1: Results of the SSD calculation (NOEC data; n = 24)

		90 % Confidence Interval	
Data set	**5-Percentile Cut-Off Value (50% confidence)**	5P-COV (95% conf.)	5P-COV (5% conf.)
NOECs highlighted bold in table 6.1	0.00083 µg/l	0.00018 µg/l	0.00248 µg/l

In order to derive the PNEC (≈ Quality Standard) it is suggested in the TGD to divide the 5-percentile cut off value by an appropriate assessment factor between 1 and 5, reflecting further uncertainties identified.

The exact value of the AF must depend on an evaluation of the uncertainties around the derivation of the 5th percentile. As a minimum, the following points have to be considered when determining the size of the assessment factor:

- The overall quality of the database and the endpoints covered, e.g., if all the data are generated from “true” chronic studies (e.g., covering all sensitive life stages).

  Many of the studies included in the SSD are no “true” chronic studies covering all sensitive life stages of the species examined. Exceptions are the algae studies.

- The diversity and representativity of the taxonomic groups covered by the database, and the extent to which differences in the life forms, feeding strategies and trophic levels of the organisms are represented.

  The database is rather comprehensive. Although some important (marine) taxonomic groups are not covered, the species requirements of the TGD are fulfilled with the exception of higher plants. A broad spectrum of life forms and feeding strategies is covered. Trophic levels from primary producers to secondary consumers are included.

- Knowledge on presumed mode of action of the chemical (covering also long-term exposure).

  It is widely believed that tributyltin compounds affect cell metabolism by, e.g., uncoupling mitochondrial oxidative phosphorylation, inhibition of ion transport, damaging of cell membranes and inhibition of enzyme systems. Further the compounds interfere with the endocrine regulation and are known to be immunosuppressive and neurotoxic in mammals. Mollusks are among the aquatic organisms most sensitive towards the endocrine mediated toxicity of TBT compounds. This group is well covered by the database.

- Statistical uncertainties around the 5th percentile estimate, e.g., reflected in the goodness of fit or the size of confidence interval around the 5th percentile, and consideration of different levels of confidence (e.g. by a comparison between the 5% of the SSD (50%) with the 5% of the SSD (95%)).

  The fit of the log-transformed data to the assumed normal distribution is very good. The spread of the 5th-percentile estimate between the 5% and the 95% confidence level is ≈14 (i.e. the figure of the 5th-percentile 95% confidence level is eleven times lower than the figure of the respective 5% confidence level).

- Comparisons between field and mesocosm studies, where available, and the 5th percentile and mesocosm/field studies to evaluate the laboratory to field extrapolation.

  Field or meso/microcosm data are not available.

On the one hand, the database used for the calculation of the 5-percentile cut-off value does not comprise very many "true" chronic studies covering all sensitive life stages of the species examined. Further, the spread between the 5% and 95% confidence levels of the 5th-percentile is larger than one order of magnitude (≈14) and therefore considered quite high. On the other hand, mollusks as particular sensitive organisms towards the endocrine disrupting effects of the chemical are well covered by the database and it is unlikely that aquatic organisms from taxonomic groups not covered by the database are significantly more susceptible than molluscs.

Based on the above considerations an assessment factor of 4 is suggested for the derivation of the water quality standard.

$QS_{water.SSD}$ = 5th-percentile cut-off (0.00083 µg/l) / AF (4) = 0.0002 µg tributyltin /l

It is suggested to use the value derived by statistical extrapolation according to the method of Aldenberg & Jaworska as water quality standard as this value is based on a rather broad range of NOEC data covering 7 different taxonomic groups.

Koc values between approximately 1,000 and more than 1,500,000 have been reported (see section 5 of this data sheet), however, the average range appears to be 1,000 – 3,750. Hence, the log Kp_{susp}[1] is between 2 and 2.57 and the trigger criterion to calculate the corresponding concentration to the $QS_{freshwater}$ in SPM is met (see section 4.3.1 of the Manual [4]). It is proposed to use a Kp_{susp} of 108[2] for the calculation. The $QS_{SPM.freshwater}$ is derived as follows:

$$\mathbf{QS_{SPM.freshwater}} = \frac{QS_{water.SSD}\ [0.0002\ \mu g/l]}{C_{SPM}\ [15\ mg/l] * 10^{-6}\ [kg/mg] + Kp^{-1}\ [(108\ l/kg)^{-1}]} = \mathbf{0.022\ \mu g/kg\ SPM\ (dry\ wt)}$$

[1] Kp_{susp} is the partition coefficient solid-water in suspended matter = Koc * foc (with foc 0.1; see TGD section 2.3.5.3 [3]).

[2] For the calculation of the Kp_{susp} it is suggested to use a Koc of 1,084. This value is the geometric mean of the reported lower log Koc range of 2.5 – 3.57 and is deemed a realistic worst case assumption.

As the SPM concentration in marine waters is significantly lower than in freshwater (discussed in the context of the marine risk assessment: approx. 3 mg/l as standard concentration), the quality standard is additionally calculated for a SPM concentration of 3 mg/l:

$$\mathbf{QS_{SPM.saltwater}} = \frac{QS_{water.SSD}\ [0.0002\ \mu g/l]}{C_{SPM}\ [3\ mg/l] * 10^{-6}\ [kg/mg] + Kp^{-1}\ [(108\ l/kg)^{-1}]} = \mathbf{0.022\ \mu g/kg\ SPM\ (dry\ wt)}$$

It should be kept in mind that because of the large reported Koc range there is considerable uncertainty associated with the calculation of a reliable $QS_{SPM.freshwater}$. Therefore, if it is intended to base the compliance monitoring on monitoring of SPM, special care must be taken to choose a partition coefficient that is representative for the water body concerned.

8.2 Quality standard for sediment

Koc values between approximately 320 and more than 1,500,000 have been reported (see section 5 of this data sheet), resulting in log Kp_{susp} values between 1.5 and 5.2 (see footnote 1). Hence, the trigger for the derivation of a sediment quality standard is met, although not unequivocally.

According to the Manual (sections 4.3.2.3 and 4.3.2.4) [4], the $PNEC_{sediment}$ ($\approx QS_{sediment}$) may be calculated using the equilibrium partitioning method in the absence of toxicity data for sediment dwelling organisms.

The equilibrium partitioning approach only considers uptake via the water phase. However, uptake may also occur via other exposure pathways like ingestion of sediment and direct contact with sediment. There is evidence from studies in soil that the proportion of the total dose remains low for chemicals with a log Kow up to 5. The log Kow of tributyltin is <5 (see section 5 of this data sheet). Therefore, exposure routes other than direct uptake via the water phase need not to be considered and the $QS_{sediment}$ is calculated as follows:

$$QS_{sed.wet\_weight}\ [mg.kg^{-1}] = \frac{Kp_{SPM\text{-}water}\ [27\ m^3/m^3]}{bulk\ density_{SPM.wet}\ [1{,}150\ kg/m^3]} * 1{,}000 * QS_{water}\ [mg/l]$$

with:

$K_{SPM\text{-}water}$ = f_{solid} (0.1) * Kp_{susp} (108 l/kg) / 1,000 * RHO_{solid} (2,500 kg/m^3) = 27 m^3/m^3 (sect 2.3.5 of [3])

bulk $density_{SPM.wet}$ = 1,150 kg/m^3

1000 = conversion factor m^3/kg to l/kg

QS_{water} = 0.0000002 mg/l

The TGD defines wet SPM as 90% vol/vol water (density 1 kg/l) and 10% vol/vol solids (density 2.5 kg/l), thus giving a wet density of (0.9 × 1) + (0.1 × 2.5) = 1.15 kg/l. The dry weight of solids is therefore 0.25 kg (per litre wet SPM) and thus the wet:dry ratio is 1.15/0.25 = 4.6.

This results in the following quality standards for sediment (wet and dry weight):

$QS_{sediment.water}$	0.0046 µg/kg (wet wt)	0.02 µg/kg (dry wt)

The values derived by the EP-method should only be considered as tentative standards. In order to refine the quality standards for the sediment compartment long term tests conducted with benthic organisms are required. For the time being no reliable effects based $QS_{sediment}$ can be derived.

8.3 Secondary poisoning of top predators

Tributyltin has a BCF >> 100. Thus the trigger criterion to derive a quality standard referring to the protection of top predators from secondsary poisoning is met (see table 1a of the final report [4]).

Oral toxicity data such as NOECs in food or (sub)chronic NOAELs from feeding studies with mammals and birds were not provided to the consultant by Member States or industry. However, data could be found in the IRIS database of the U.S.-EPA [13] (see table 6.2).

Two NOAELs from long term studies with rats are available. It is suggested to use the NOAEL of 0.34 mg/kg bw/d obtained for adverse effects on reproduction (decreased pup weight) as starting point for the QS derivation because the ecological significance of the NOAEL of 0.19 mg/kg bw/d derived in the second study for slight effects on the renal system is questionable.

According to the Manual (sections 4.3.2.5 and 4.3.2.6) [4], the appropriate conversion factor from a $NOAEL_{rat}$ (>6weeks) to the corresponding concentration in food ($NOEC_{food}$) is 20:

$NOEC_{food}$ = NOAEL (0.34 mg/kg) * 20 = 6.8 mg TBT /kg food

Based on this $NOEC_{food}$, the $QS_{secpois.biota}$ ($PNEC_{oral}$) is derived by dividing it with the assessment factor of 30 that is recommended in the TGD for extrapolation from chronic mammalian toxicity data.

$QS_{secpois.biota}$ = $NOEC_{food}$ (6.8 mg/kg) / AF (30) = **230 µg TBT /kg prey** (biota tissue wet wt)

In the TGD approach for the assessment of secondary poisoning (see sections 4.3.2.5 and 4.3.2.6 of the Manual [4]) it is foreseen to consider bioconcentration and biomagnification as relevant factors affecting body burdens and the PEC, respectively. If no information on BMF values is available, it is proposed in the TGD to use default BMFs for substances with a BCF_{fish} >2000.

As the BCF of TBT-compounds is in the range of 500 – 11400 biomagnification could be a relevant process. Biomagnification of tributyltin compounds through the food chain may not occur as a study by Stäb et al. [11] and the studies cited therein indicate. The authors investigated TBT body burdens in species representing different levels of the trophic net in a Dutch inland water ecosystem. Birds as top-predators in this ecosystem showed lower TBT body burdens as species lower in the food chain. It therefore seems realistic to assume that biomagnification does not significantly contribute to the accumulation of TBT in biota. As regards bioconcentration, it seems that TBT is accumulated to a slightly larger extent in invertebrates than in fish. It is therefore proposed to use a BCF of 6000 as a realistic worst case mean (see section 5) for the calculation of the concentration in water corresponding to the $QS_{secpois.biota}$, which is calculated as follows:

$QS_{secpois.water}$ = $QS_{secpois.biota}$ (0.23 mg/kg prey) / BCF (6000) = 0.038 µg TBT-compounds /l

Hence, the specific QS required to protect predators from secondary poisoning is not as low than the standard derived for the pelagic communities in surface waters[3].

[3] Use of the highest reported BCF of 11,400 would not change this conclusion as the $QS_{secpois.water}$ in this case would be 0.02 µg/l.

8.4 Quality standard referring to food uptake by humans

Tributyltin compounds are classified as toxic and may cause adverse health effects by prolonged exposure. Further the compounds are subject to bioaccumulation. Therefore the derivation of a quality standard referring to ingestion of food from aquatic environments by humans is required.

The WHO has proposed a tolerable daily intake for bis-tributyltin oxide of 0.25 µg/kg bw/d [10]. This TDI is used for the calculation.

In the Manual (section 4.3.2.6) [4] it is suggested that the ADI may not be exhausted for more than 10% by consumption of food originating from aquatic sources. For a person weighing 70 kg this results in an acceptable daily intake of 1.75 µg tributyltin per day.

The average fish consumption of an EU citizen is 115 g d-1 (TGD [3]). Thus, 115 g edible fishery products must not contain more than 1.75 µg TBT.

$$\mathbf{QS_{hh.food}} = \frac{1.75\ \mu g\ TBT}{115 g\ fishery\ product\ consumption} * 1000\ g = \mathbf{15.2\ \mu g\ TBT\ /\ kg\ fishery\ product}$$

In the TGD approach for the assessment of secondary poisoning (see sections 4.3.2.5 and 4.3.2.6 of the Manual [4]) it is foreseen to consider bioconcentration and biomagnification as relevant factors affecting body burdens and the PEC, respectively. If no information on BMF values is available, it is proposed in the TGD to use default BMFs for substances with a BCF_{fish} >2000.

As the BCF of TBT-compounds is in the range of 500 – 11,400 biomagnification could be a relevant process. However, according to the available studies [11 and references therein] addressing this issue, it seems more realistic to assume that biomagnification does not significantly contribute to the accumulation of TBT in biota. As regards bioconcentration, it seems that TBT is accumulated to a larger extent in molluscs than in fish. It is therefore proposed to use a BCF of 6000 as a realistic worst case mean for the calculation of the concentration in water corresponding to the $QS_{hh.food}$, which is calculated as follows:

$$\mathbf{QS_{hh.food.water}} = \frac{QS_{hh.food}\ (15.2\ [\mu g/kg])}{BCF\ \ (6000\ [kg/l])} = \mathbf{0.0025\ \mu g\ TBT\text{-}Compounds\ /\ l}$$

Thus, the protection of the pelagic community does require a more than 10-fold lower QS than the protection of human health from adverse effects by oral uptake of food from aquatic environments[4].

8.5 Quality standard for drinking water abstraction

The imperative A1 value referring to drinking water abstraction by simple treatment is 1 µg/l for the total amount of pesticides (Council Directive 75/440/EEC). The drinking water standard set in CD 98/83/EC is 0.1 µg/l for individual pesticides. The WHO guidance value for drinking water is 2 µg/l [10].

The DWS is a limit value never to be exceeded at the tap. The MAC-QS (ECO) derived for the protection of the freshwater community (0.0015 µg/l) is therefore sufficient to allow for compliance with the DWS. Hence, it is not necessary to set a specific MAC-QS referring to abstraction of water intended for human consumption (AWIHC) as objective of protection.

[4] Use of the highest reported BCF of 11,400 would not change this conclusion as the $QS_{hh.food.water}$ in this case would be 0.0013 µg/l.

8.6 Overall quality standard

The quality standards derived for the protection of the pelagic communities in freshwater and saltwater environments are the lowest and are therefore suggested as overall annual average quality standards.

Lack of data for sediment dwelling organisms was the reason that only a tentative standard based on the equilbrium partitioning method could be derived for the sediment compartment.

9 References

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