Common Implementation Strategy for the Water Framework Directive

Environmental Quality Standards (EQS)

Substance Data Sheet

Priority Substance No. 31

Trichlorobenzenes

CAS-No. 12002-48-1

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 [12]. 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: 31	Trichlorobenzenes (1,2,3-TCB; 1,2,4-TCB; 1,3,5-TCB)
CAS-Number:	12002-48-1 (1,2,3-TCB: 87-61-6; 1,2,4-TCB: 120-82-1; 1,3,5-TCB: 108-70-3)
Classification WFD Priority List *:	PSR

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

2 Proposed quality standards

As commercial trichlorobenzene consists predominantly of 1,2,4-TCB and the individual uses of the 1,2,3-and 1,3,5- isomers appear to be very limited it is proposed to derive the required quality standards not for the individual isomers but for trichlorobenzenes as Σ of individual isomers. For the reasons given in section 8.2 of this data sheet it is further suggested to use the quality standard derived for 1,2,4-trichlorbenzene as overall standard for trichlorobenzenes.

2.1 Overall quality standards for trichlorobenzenes

Ecosystem	Quality Standard	Comment
AA-QS all surface waters covered by the WFD	**0.4 µg/l**	An overall QS of 0.4 µg/l, as already set by Council Directive 86/280/EEC for all surface waters, is suggested. The proposal is covered by Article 4(9) of the Water Framework Directive. This Article stipulates that it must be ensured that new provisions guarantee at least the same level of protection as the existing Community legislation, see 8.1.6 & 8.2
MAC-QS (ECO) *	**50 µg/l**	see section 8.1.1

* The proposal by the Commission may include a MAC-QS value which is based on the calculation of 12 * AA-EQS. This derivation is based on the minimum annual frequency of monitoring of priority substances in accordance with the Water Framework Directive. The derivation of such a MAC-QS is based on monitoring, compliance and reporting considerations rather than derived from effect data as presented in this EQS datasheet.

2.2 Specific quality standards (based on data for 1,2,4-trichlorobenzene)

Protection Objective #	Quality Standard	Comment:
Pelagic community (freshwater)	4 µg/l	see section 8.1.1
Pelagic community (saltwater)	0.4 µg/l	see section 8.1.1
Benthic community (sediment)	derivation of QS not required (tentative value 90 µg/kg wet wt)	trigger value not met; see section 8.1.2
Predators (secondary poisoning)	4 mg/kg (tissue of prey, wet wt) corresponding conc. in water: 2 µg/l	see section 8.1.3
Food uptake by man	3.65 mg/kg (seafood, wet wt); corresponding conc. in water 1.83 µg/l	see section 8.1.4
Abstraction of water intended for human consumption (AWIHC)	no DW abstraction standard set in CD 75/440/EEC; derivation of such a standard is not required	see section 8.1.5
Water intended for human consumption (WIHC)	no standard set in CD 98/83/EC	

If justified by substance properties or data available, QS for the different protection objectives are given independently for freshwater environments, transitional waters or coastal and territorial waters

3 Classification

CAS-No.		R-Phrases and Labelling	Ref.
12002-48-1	Trichlorobenzene	This chemical substance is not classified in the Annex I of Directive 67/548/EEC.	[13]
87-61-6	1,2,3-Trichlorobenzene	This chemical substance is not classified in the Annex I of Directive 67/548/EEC.	[13]
120-82-1	1,2,4-Trichlorobenzene	Xn; R22 - Xi; R38 - N; R50-53	[13]
108-70-3	1,2,5-Trichlorobenzene	This chemical substance is not classified in the Annex I of Directive 67/548/EEC.	[13]

4 Physical and chemical properties

Table 4.1: 1,2,4-Trichlorobenzene

Property	Value	Ref.	Comments
Water Solubility	36 mg/l at 20°C 48.8 mg/l at 20°C	[1]	(BUA 1987, Bayer 1986) (Chiou *et al.* 1983)
Vapour Pressure:	21.5 Pa at 20°C 36 Pa at 20°C 38.6 Pa at 25°C 46.8 Pa at 25°C 80 Pa at 30°C	[1]	(BUA 1987, Bayer) (Bayer 1994) (US-EPA 1980) (DIPPR 1998) (Bayer 1994)
Henry's Law constant	101 Pa m^3/mol (20ºC) 290 Pa m^3/mol (25ºC) 181 Pa m^3/mol (20ºC)	[1]	(ten Hulscher *et al.* 1992) (EPIWIN 1995, est) (calc. according to TGD)

5 Environmental fate and partitioning

Table 5.1: 1,2,4-Trichlorbenzene

Property	Value	Ref.	Comments
Abiotic degradation Hydrolysis Photolysis	 not expected to hydrolyse under normal environmental conditions Photodegradation in water is very slow and is therefore not included in the risk assessment	 [1] [1]	
Biodegradation	half life water: 150 d half live sediment: 300d	[1]	1,2,4-TCB can be regarded as inherently biodegradable
Partition coefficients Octanol – Water Koc (organic carbon-water) $Kp_{(susp(}$ (suspended matter) $K_{susp-water}$ (sediment)	 log Kow: 4.2 log Kow: 4.05 (used in RAR) log Kow: 4.02 log Kow: 3.93 1400 (used in the RAR) 35.9	 [1] [1] [1]	 (BUA 1987) (Bruijn et al. 1989) (Hansch & Leo 1985) (Meylan & Howard 1995, calc) The average Koc value from the data mentioned in the RAR is 1424 see section 6.1.2 of this data sheet
Bioaccumulation Bioconcentration Factor (BCF) Fish	 120 – 3200 (whole body; several tests in different fish	 [1]	 studies regarded as reliable in [1]

Property	**Value**	**Ref.**	**Comments**
	species)		
	2000 (whole body)	[1]	[1]: used in the risk assessment
Crustaceans:			
Daphnia	142	[1]	
Penaeus duorarum	69	[1]	
Algae	250	[1]	

Table 5.2: 1,2,3-Trichlorbenzene

Property	**Value**	**Ref.**	**Comments**
Abiotic degradation Hydrolysis Photolysis			
Biodegradation	Not ready biodegradable	[5]	
Partition coefficients Octanol – Water	log Kow 4.14 log Kow 3.75 –4.22	[7], [5] [6]	
Koc (organic carbon-water)	log Koc 3.71	[7]	
Bioaccumulation Bioconcentration Factor (BCF)			
Fish			
Salmo gairdneri (whole body)	1100 – 1600 (4.3 ng/l 1,2,3-TCB)	[6]	Oliver & Niimi 1983
Salmo gairdneri (whole body)	2300 – 2900 (72 ng/l 1,2,3-TCB)	[6]	Oliver & Niimi 1983
Insects:			
Chironomus decorus	140 – 230 (whole body)	[9]	Knezovich and Harrison (1988)

Table 5.3: 1,3,5-Trichlorbenzene

Property	**Value**	**Ref.**	**Comments**
Abiotic degradation Hydrolysis Photolysis			
Biodegradation	Not ready biodegradable	[5]	
Partition coefficients Octanol – Water	log Kow 4.49 log Kow 4.14 log Kow 4.19	[7] [6] [5]	
Koc (organic carbon-water)	log Koc 3.71	[7]	
Bioaccumulation Bioconcentration Factor (BCF)			
Fish:			
Poecilia reticulata	1350 (whole body, 5% fat)	[9]	Opperhuizen et al (1988)
Salmo gairdneri	1400 – 2000 (2.3 ng/l 1,3,5-TCB)	[6]	Oliver & Niimi 1983
Salmo gairdneri	3700 – 8400 (45 ng/l 1,3,5-TCB)	[6]	Oliver & Niimi 1983

6 Effect data (aquatic environment)

The quality standards proposed in this data sheet are based on the data evaluation and the effects assessment of the draft risk assessment report (RAR) on 1,2,4-trichlorobenzene[1]. Full bibliographic details of the cited references may be found in the RAR.

Aquatic toxicity data assessed and used in the risk assessment report for 1,2,4-trichlorobenzene [1] are listed in annex 1 to this data sheet.

Aquatic toxicity data for 1,2,3-trichlorobenzene and 1,3,5-trichlorobenzene are listed in annex 2 to this data sheet.

6.1 Predicted no-effect concentrations (aquatic environment) for 1,2,4-TCB

Table 6.1: PNECs (1,2,4-TCB)

Compartment	**Value**	**Reference**
Surface water	4 µg/l	[1]
Sediment	0.09 mg/kg wet weight	[1]
$PNEC_{oral}$ (secondary poisoning)	0.6 mg/kg bw/d	[1]

6.1.1 Calculation of PNEC surface water for 1,2,4-TCB [1]

The data on aquatic organisms include acute toxicity data on fish, daphnia and algae plus several other aquatic animals. Valid long-term studies on both fish and Daphnia and a NOEC for algae are also present. According to TGD, an assessment factor of 10 applied to the lowest long term NOEC may therefore be used. The lowest NOEC (21d) on Daphnia is 0.06 mg/l and the lowest NOEC (21 d) on fish is 0.04 mg/l, that is within the same long-term toxicity range.

The $PNEC_{aquatic\ organisms}$: 0.04 / 10 = 0.004 mg/l or 4 µg/l

6.1.2 Calculation of PNEC sediment for 1,2,4-TCB [1]

Clark *et al.*(1987) studied the waterborne and sediment-source toxicities to grass shrimp and amphioxus. The test sediment was 9:1 washed beach sand and sediment dredged from Santa Rosa Sound. The mixture contained 0.5-1% organic matter. The measured concentrations were 75-95% of nominal concentrations in waterborne studies and 60-95% in sediment exposures. Sediments containing 1,2,4-TCB at 10 mg/kg were not lethal to grass shrimp during 10 days of flow-through and no higher concentration were tested (Clark *et al.* 1987).

For amphioxus (*Branchiostoma caribaeum*), the 96 h LC_{50} for waterborne 1,2,4-TCB was between 1.5 (0% mortality) and 10 mg/kg sediment (100% mortality). In the 10 days sediment test, LC_{50} was observed to be 200 mg/kg (NOEC: 75 mg/kg). Both tests were performed under flow through conditions and results based on nominal values (Clark *et al.* 1987).

The effects of 1,2,4-TCB on estuarine macrobenthic communities exposed via water and sediments were studied in laboratory study (Tagatz *et al.* 1985) using sand-filled aquaria (clean silica sand at 5.5 cm height) under flow-through conditions. In one test, communities established by planktonic larvae entrained in continuously supplied unfiltered seawater for 50 days were exposed to 1,2,4-TCB for 6 days at the nominal concentrations 0.05, 0.5 and 5 mg/l. The lowest measured concentrations that affected the average numbers of individuals exposed via water were 0.04 mg/l for molluscs, 0.4 mg/l for arthropods and 4 mg/l for annelids, and the average number of species was significant lower than the control at 4 mg/l.

In a second test, 1,2,4-TCB was added to the sediment 8 weeks before colonisation. The concentrations in the sediment fluctuated during the exposure period: The nominal concentrations were 10, 100 and 1000 mg/kg, the measured ranges were 4.3-<0.01 mg/kg, 97-2.1 mg/kg and 790-519 mg/kg sediment. After 8 weeks, the measured concentrations were <0.01, 6.1 and 519 mg/kg, respectively, for sediment and 0.51, 12 and 74 µg/l, respectively, for water. The lowest nominal concentration that affected the average numbers of individuals was 100 mg/kg for molluscs and echinoderms and 1000 mg/kg sediment for arthropods and annelids. The average number of species was significantly lower than the control at ≥100 mg/kg sediment. Concentrations that affected community structure were usually two orders of magnitude lower for waterborne 1,2,4-TCB than for sediment-bound 1,2,4-TCB, but the same types of organisms were affected by each route of exposure. Most 1,2,4-TCB persisted in the sediment but some leached into the water throughout the 8-week exposure period (Tagatz *et al.* 1985).

In the study by Tagatz *et al.* (1985), the lowest measured concentration influencing the average number of individuals exposed via the water was 0.04 mg/l. (This figure is an order of magnitude higher than the estimated $PNEC_{aquatic\ organisms}$). With exposure via the sediment, the lowest nominal concentration affecting average number of individuals was 100 mg/kg sediment which after 8 weeks was measured to 6 mg/kg in sediment. The concentration in water was measured to be 12 to 74 µg/l at the end of the study.

However, due to the uncertainties in these two studies, data can not be used directly in the risk assessment for the sediment compartment, although especially the data from Tagatz *et al*. (1985) may indicatively be compared with the estimated $PNEC_{sed}$ obtained by employing the equilibrium partitioning method of the TGD.

According to TGD equation 54: $PNEC_{sed} = (K_{sed\text{-}water}/RHO_{sed})*PNEC_{water}*1000 = 0.218$ mg/kg ww. using $Foc_{(sed)}$ 0.1 (as recommended by technical recommendations, Doc. ECB4/TR2/97 based on discussions at TMIV 1997).

Use of an organic fraction (Foc) of 0.05 according to the TGD results in a PNECsed: 0.11 mg/kg ww (EUSES).

Another method is use of $K_{susp\text{-}water}$ and RHO_{susp} which results in:

$PNEC_{sed} = (K_{susp\text{-}water}/RHO_{susp})*PNEC_{water}*1000 = (35.9/1150)*0.004*1000 = 0.09$ mg/kg ww.

The difference PNECs according to these two methods is caused by slight differences of the fraction of solids and water.

In the latter method, sediments are more dominated by the superficial layer of suspended matter, i.e. according to this method the sediment has a higher content of water (and thus less content of solids).

There seems to be different viewpoints regarding which method actually to employ when performing a risk assessment for the sediment compartment. According to the availability of experimental test data for sediment organisms and knowledge regarding their preferred type of sub-compartmental habitat within the sediment, it may be possible to make a justifiable decision on which of the above methods to employ.

In this case where the derivation of PNEC is based on application of the equilibrium partitioning method and available experimental data on pelagic organisms, the right choice of method seems to be application of the latter. If this method is used, the PNEC/PEC ratios for sediment will be virtually the same as those for water.

Thus $PNEC_{sediment}$ = 0.09 mg/kg ww

This $PNEC_{sed}$ is three orders of magnitude lower than the lowest reported nominal and around two orders below the lowest reported measured effect concentration in the experimental study by Tagatz *et al.* (1985) referred to above.

6.1.3 Calculation of the PNEC for non compartment specific effects of 1,2,4-TCB relevant for the food chain (secondary poisoning) [1]

A bioaccumulation potential is present and the BCFs in fish is approximately 2000 based on whole body wet weight. Also possibility for 1,2,4-TCB being an animal carcinogen exists and therefore assessment of secondary poisoning is warranted. There are no results on bird toxicity and therefore the effect on fish-eating birds can not be considered.

As for fish-eating mammals, it is assumed that the available mammalian toxicity data can give an indication on the possible risks of 1,2,4-TCB to fish eating mammals.

NOAEL oral for rat is 100 ppm in the diet (6 mg/kg bw/d) after 2 years of exposure (cf. section 4.1.2.6 (of [1]) on conclusion of repeated dose toxicity). An assessment factor of 10 should be applied according to the TGD:

$PNEC_{oral}$ = 100/10 ppm = 10 ppm (~0.6 mg/kg bw/d).

6.2 Summary on endocrine disrupting potential

Trichlorobenzenes are rated (in [2]) as substances with insufficient data (in the BKH Report) to assess their potential for interfering with endocrine regulation.

According to the risk assessment report, 1,2,4-TCB does not show oestrogenic or anti-androgenic activity [1]. However, during metabolism of 1,2,4-TCB, 2,4-dichlorophenol may be formed. The latter is suspected to be an environmental endocrine disrupter.

7 Effect data (human health)

Table 7.1: Summary effect data of 1,2,4-trichlorobenzene relevant for human health [1]

Effect	Value	Comment
Chronic Toxicity: The target organs are the liver, the kidney and the adrenals.	Oral administration: **NOAEL: 5.5 – 6.7 mg/kg/d** LOAEL: 19 – 23 mg/kg/d species: rat reference: Moore, 1994b [1]: For the purpose of the risk characterisation the oral NOAEL is taken as 6 mg/kg bw/d	Ten studies have been performed. Duration: 14 d 104 weeks. The NOAEL and LOAEL values have been taken from a 104 weeks feeding study. The LOAEL is based on renal papillary mineralisation and fatty liver changes in the liver. The LOAEL is the lowest of all values found in the repeated dose toxicity studies.
Reproduction:	The data on the effects of 1,2,4-TCB is inadequate to properly evaluate the possible effects on reproductive toxicity. The data on the effects of 1,2,4-TCB are inadequate to establish a LOAEL for reproductive effects. A NOAEL for effects on the foetus based on a 2-generation study can be established as greater or equal to 33 mg/kg bw/d for males and 53 mg/kg bw/day for females, which is at a level of 5 to 10 times the NOAEL chosen for repeated dose toxicity. It is considered unlikely that further testing will lead to a lower NOAEL/NOAEC for reproduction. The data presented here do not suggest that classification for reproductive toxicity is appropriate.	
Mutagenicity & Carcinogenicity:	The database for genotoxicity is complicated and does not lead to a clear conclusion.… On balance, 1,2,4-TCB is not considered to express systemic genotoxic effects in vivo. In spite of the uncertainties associated with the evaluation of both the genotoxicity and the carcinogenicity of the substance, it is considered unlikely that additional guideline testing would provide further information that would lead to either a change in the conclusion for the mutagenicity or the carcinogenicity of the substance. Based upon the present data, classification as either a category 3 carcinogen or a category 3 mutagen is not considered appropriate.	

Table 7.2: Summary effect data of 1,2,3- and 1,3,5--trichlorobenzenes relevant for human health [5]

1,2,3-trichlorobenzene	
(Sub)chronic Toxicity:	No suitable studies available
Teratogenicity & Reproduction:	No teratogenic or fetotoxic effects were produced in rats by gavage of up to 600 mg/kg bw on days 6 to 15 of gestation. Reproduction studies are not available.
Mutagenicity & Carcinogenicity:	Available data too limited to classify the compound as genotoxic. No suitable carcinogenicity studies are available.
1,3,5-trichlorobenzene	
(Sub)chronic Toxicity:	Inhalation studies have been performed in mice and rats. The lowest NOAEL is 100 mg/m^3 (DCV: 17.9 mg/m^3).
Teratogenicity & Reproduction:	No studies available.
Mutagenicity & Carcinogenicity:	It is provisionally concluded that the data are too limited to suggest that 1,3,5-TCB is genotoxic. No suitable carcinogenicity studies are available..

8 Calculation of quality standards

Trichlorobenzenes are obtained by direct chlorination of benzene and were also produced in the lindane manufacturing process by pyrolysis of the remaining hexachlorocyclohexane isomers (α, β,...). They are also formed during various combustion processes and environmental degradation of HCH. [10]

The current purity of commercial trichlorobenzene[1] is 99.8% 1,2,4-TCB, while the previous commercial trichlorobenzene was a mixture of 2 isomers: 1,2,4 TCB-(80% to 100%) and 1,2,3-TCB (0 to 20%) [10]. According to the RAR for 1,2,4-TCB [1] the impurities in the commercial product comprise usually 0.1-0.4% 1,2,3-TCB and <2% 1,3,5-TCB (percentages on w/w basis).

As commercial trichlorobenzene consists predominantly of 1,2,4-TCB and the individual uses of the 1,2,3-and 1,3,5- isomers appear to be very limited it is proposed to derive the required quality standards not for the individual isomers but for trichlorobenzenes as sum of individual isomers. For the reasons given in section 8.2 of this data sheet it is further suggested to use the quality standard derived for 1,2,4-trichlorbenzene as overall standard for trichlorobenzenes.

8.1 Calculation of quality standards for 1,2,4-Trichlorobenzene

8.1.1 Quality standards for water

Freshwater

The PNEC (4 µg/l) derived in the risk assessment report for 1,2,4-TCB [1] (see section 6.1.1 of this data sheet) is proposed as quality standard referring to the protection of the pelagic community in freshwater:

$QS_{freshwater}$ = 4 µg 1,2,4-Trichlorobenzene /l

The log Kp_{susp} is <3[2] and therefore the calculation of the concentration in SPM corresponding to the $QS_{freshwater}$ is not required (see section 4.3.1 of the Manual [4]).

Transitional, coastal and territorial Waters

In the EU risk assessment report [1] only acute toxicity tests with marine crustaceans are available in addition to the freshwater data. In the Euro Chlor risk assessment for the marine environment [10] some further short- or long-term tests with fish and algae are listed but rated as unreliable. Based on the available reliable data it is concluded in the RAR [1] that 1,2,4-TCB is apparently more toxic to marine crustaceans than to freshwater species of that group. As a full data set of short-term and long-term toxicity data is available for at least 3 trophic levels, but no additional toxicity data for additional marine taxonomic groups, it is suggested in accordance with the provisions of the TGD regarding marine effects assessment to use an assessment factor of 100 on the lowest NOEC (40 µg/l, *Brachydanio rerio*) for the derivation of the $QS_{saltwater}$ (see section 4.3.2.2 of the Manual [4]).

$QS_{saltwater}$ = 40 µg/l / AF 100 = 0.4 µg 1,2,4-Trichlorobenzene /l

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1 There is some use of 1,3,5 trichlorobenzene but only as intermediate and in low quantities ($\approx$ 200 tonnes per year) [10].

2 Kp_{susp} can be calculated based on the Koc as described in the TGD (section 2.3.5.3):
Kp_{susp} [l/kg] = foc (0.1) * Koc (1,400) = 140 l/kg (log 2.15)

The log Kp_{susp} is <3 and therefore the calculation of the concentration in SPM corresponding to the $QS_{freshwater}$ is not required.

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

Acute toxicity data are available for algae, invertebrates, and fish. The lowest short-term acute toxicity values identified as valid in the risk assessment [1] are in the range of 0.5 to 1 mg/l for both crustaceans and fish (see tables in annex 1 to this data sheet). The MAC-QS is derived on the basis of this value and the guidance given in the TGD on the effects assessment for intermittent releases (section 3.3.2 of part II of [3]). As the acute toxic effects of 1,2,4-TCB are due to non specific narcosis (Veith et al. 1983, cited in [1]) a reduced assessment factor of 10 is considered as appropriate (as it is not deemed very probable that acute toxic effects may occur in other taxa at significantly lower concentrations than in crustaceans and fish).

MAC-QS = 500 µg/l / AF (10) = 50 µg 1,2,4-Trichlorobenzene / l

8.1.2 Quality standard for sediment

As the log Kp_{susp} is <3, the calculation of a quality standard for sediment is normally not required (see table 1a of the Manual [4]).

A $PNEC_{sediment}$ of 90 µg 1,2,4-TCB per kg sediment (wet wt) has been calculated in the risk assessment with the equilibrium partitioning method.

This $PNEC_{sediment}$ may be used as indicative value for the assessment of sediment quality.

8.1.3 Secondary poisoning of top predators

A BCF_{fish} of 2000 is considered as realistic worst case in the risk assessment [1]. Hence, the derivation of a quality standard referring to secondary poisoning is required as the trigger value for the derivation of a quality standard referring to secondary poisoning of top predators is met (BCF ≥100; see table 1a of the Manual [4]).

There is only a NOAEL for mammals available (chronic study with rats, 6 mg/kg $bw.d^{-1}$); see section 6.1.3 of this data sheet). From this NOAEL a $PNEC_{oral}$ is calculated according to the procedure described in section 5.1.4.2 of the final report [4] (based on section 3.8.3.5 of the TGD [3]).

$NOEC_{oral} = NOAEL_{mammal.chronic}$ (6 * 10^{-6} kg/kg bw.d) * $CONV_{mammal}$ (20 kg bw.d/kg food)

$PNEC_{oral}$ = $NOEC_{oral}$ (120 (mg/ kg food) / AF (30) = 4 mg/kg food

with:
$CONF_{mammal}$: conversion factor from NOAEL to NOEC for the species (20 for rat >6 weeks)
AF: assessment factor for the extrapolation to PNEC, depending on duration of test (30 for chronic study with mammals)

Thus, the $QS_{secpois.biota}$ (contaminant level in prey of top predators) is:

$QS_{secpois.biota}$ = 4 mg 1,2,4-Trichlorobenzene / kg (wet weight)

1,2,4-TCB has been shown to bioaccumulate. The BCF_{fish} used in the RAR [1] (2000) is taken to calculate the concentration in water that corresponds to the $QS_{secpois.biota}$.

According to the guidance given in the TGD [3] regarding the assessment of secondary poisoning of top predators, biomagnification factors (BMF) should be taken into account for the calculation of the PEC_{oral} of top predators. The use of default BMFs as proposed in the TGD is recommended, if the bioconcentration factor of the substance concerned exceeds a level of 2000 and measured BMFs are not available (see sections 4.3.2.5 and 4.3.2.6 of the Manual [4]).

However, according to studies[3] mentioned in the RAR [1] the uptake via the oral route seems to be negligible for 1,2,4-TCB. Therefore, it appears not justified to use default BMF values for the calculation of the quality standard referring to secondary poisoning.

The $QS_{secpois.water}$ is therefore calculated as follows:

$$\mathbf{QS_{secpois.water} = QS_{secpois.biota}\ (4\ [mg/kg]) * BCF^{-1}\ ((2000\ [kg/l])^{-1}) = 2\ \mu g\ 1,2,4\text{-Trichlorbenzene}\ /l}$$

The protection of top predators from secondary poisoning does require a lower QS_{water} than the protection of the pelagic community in freshwater.

8.1.4 Quality standard referring to food uptake by humans

1,2,4-TCB is classified as "Harmful if swallowed" (R22) and has a bioaccumulation potential (BCF >100). Thus the trigger values for the derivation of a quality standard referring to food uptake by humans are met (see table 8.1 of the final report [4]).

The lowest relevant $NOAEL_{oral}$ identified in the risk assessment [1] is 6 mg/kg bw.d for effects on kidney and liver in a 104 weeks study with rats (see table 7.1). If the usual safety factor of 100 is applied to extrapolate from laboratory mammal to human individuals the relevant threshold level for humans is 60 µg/kg bw.d (≈ 4.2 $mg.d^{-1}$ for a person with 70 kg body weight).

In the Manual (section 4.3.2.6) [4] it is suggested that the relevant threshold level may not be exhausted for more than 10% by consumption of food originating from aquatic sources (i.e. 0.42 $mg.d^{-1}$).

The average fish consumption of an EU citizen is 115 $g.d^{-1}$ (TGD [3]). Thus, 115 g fish (or seafood) must not contain more than 0.42 mg 1,2,4-TCB.

$$\mathbf{QS_{hh.food}} = \frac{0.42\ \text{mg 1,2,4-TCB}}{115\text{g seafood consumption}} * 1000\ \text{g} = \mathbf{3.65\ mg\ 1,2,4\text{-}TCB\ /\ kg\ seafood}$$

The same approach and assumptions as described in section 8.1.3 of this data sheet are used to calculate the water concentration that corresponds to the $QS_{hh.food}$::

$$\mathbf{QS_{hh.food.water}} = \frac{3.65\ [mg/kg]}{BCF\ (2000\ [l/kg])} = 1.83\ \mu g\ \text{1,2,4-Trichlorobenzene}\ /\ l$$

Thus, the quality standard required to protect human health from adverse effects due to ingestion of food originating from aquatic environments is lower than the level required to protect the freshwater community. Though slightly lower, it is comparable to the standard required to safeguard top predators from secondary poisoning.

3 The studies of Heitmüller and Clark 1989, Oliver 1987 and Burkhard *et al.* 1997 described in section 3.1.1.4 (bioaccumulation) of [1].

8.1.5 Quality standard for drinking water abstraction

An "A1 value" for drinking water has not been set for 1,2,4-TCB in Council Directive 75/440/EEC and also no drinking water standard has been derived in the context of Council Directive 98/83/EC. In this case the methodological framework for the derivation of quality standards requires the calculation of a provisional drinking water standard based on the recommendations given in the TGD [3] (see section 8.4.4 of the final report [4]).

The lowest relevant $NOAEL_{oral}$ identified in the risk assessment [1] is 6 mg/kg bw.d. If the usual assessment factor of 100 is applied to extrapolate from animal to man the $NOAEL_{oral.human}$ is 60 µg/kg bw.d (≈ threshold level for human health).

The provisional quality standard for drinking water is calculated with the provision that uptake by drinking water should in any case not exceed 10% of the threshold level for human health [3].

$$QS_{DW.provisional} = \frac{0.1 * TL_{HH} * BW}{Uptake_{DW}} = \mathbf{210\ \mu g\ 1,2,4\text{-}Trichlorobenzene\ /l}$$

with:

$QS_{DW.provisional}$	provisional quality standard for drinking water (µg/l)
TL_{HH}	threshold level for human health (60 µg 1,2,4-TCB / kg bw per day)
BW	body weight (70 kg)
$Uptake_{DW}$	uptake drinking water (2 l per day)

The provisional drinking water quality standard is by far higher than the standard required to protect human health form adverse effects by food uptake or the aquatic community. It is therefore not necessary to derive a quality standard for drinking water abstraction.

A guide value of 20 µg/l for the total of the 3 isomers is proposed by WHO for drinking water. This value is based on a TDI of 7.7 µg/kg body weight per day. It has to be noted that the olfactory detection limit of TCBs in water is only 5 µg/l. [11]

8.1.6 Overall quality standard for 1,2,4-Trichlorobenzene

An overall annual average QS of 0.4 µg/l, as already set by Council Directive 86/280/EEC for all surface waters, is suggested. The proposal is covered by Article 4(9) of the Water Framework Directive. This Article stipulates that it must be ensured that new provisions guarantee at least the same level of protection as the existing Community legislation.

8.2 Overall Quality Standard for Trichlorobenzene (1,2,3-, 1,2,4- & 1,3,5-isomers)

It is suggested to use the quality standard derived for 1,2,4-trichlorbenzene as overall standard for trichlorobenzes (Σ 1,2,3-, 1,2,4- and 1,3,5- isomers).

Reasons for this proposal are:

1. Commercial trichlorobenzene consists predominantly of 1,2,4-TCB (>97.5%) and the individual uses of the 1,2,3-and 1,3,5- isomers appear to be very limited [1, 10]. Hence, 1,2,4-TCB should be the prevailing isomer occurring in the environment (all isomers appear to have a comparable environmental stability).
2. From the toxicity data of the 1,2,3- and 1,3,5- isomers (table A2.1 in annex 2 to this data sheet) it can be concluded that 1,2,3-TCB is as toxic to aquatic organisms as the 1,2,4-isomer

whereas 1,3,5-TCB is apparently less toxic (however, it has to be kept in mind that the data base for 1,3,5-TCB is very limited).

3. The bioconcentration potential of 1,2,3-TCB and 1,2,4-TCB appears to be comparable whereas the potential of the 1,3,5-isomer for bioconcentration may be slightly higher (see available BCF data in section 5 of this data sheet). Hence, it may be concluded that the hazard potential (toxic potential * bioaccumulation potential) of the individual isomers for predators and humans might be of the same magnitude.

9 References

[1] European Union Risk Assessment Report: 1,2,4-Trichlorobenzene (CAS No.: 120-82-1, EINECS-No.: 204-428-0), Final Report, March 2001, Danish Environmental Protection Agency (file: R039_0103_env_hh_final.doc). The draft report is available at the internet site of the European Chemicals Bureau: http://ecb.jrc.it/existing-chemicals/ ⇒ tick ESIS button, then enter CAS or EINECS number of substance.

[2] COM(2001)262 final: Communication from the Commission to the Council and the European Parliament on the implementation of the Community Strategy for Endocrine Disrupters – a range of substances suspected of interfering with the hormone system of humans and wildlife.

[3] Technical Guidance Document on Risk Assessment in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances and Directive 98/8/EC of the European Parliament and the Council Concerning the placing of biocidal products on the market. Part II. European Commission Joint Research Centre, EUR 20418 EN/2, © European Communities 2003. Available at the internet-site of the European Chemicals Bureau: http://ecb.jrc.it/existing-chemicals/

[4] Manual of the Methodological Framework Used to Derive Environmental Quality Standards for Priority Substances of the Water Framework Directive. Peter Lepper, Fraunhofer-Institute Molecular Biology and Applied Ecology, 15 November 2004. Available at the internet-site of the European Commission: http://europa.eu.int/comm/environment/water/water-dangersub/pri_substances.htm

[5] De Bruijn, J. et al.: Environmental Risk Limits in The Netherlands. National Institute of Public Health and the Environment (RIVM), Bilthoven. Parts I-III, data for trichlorobenzenes

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[8] International Commission for the Protection of the Rhine. Rhine Action Programme. Data Sheets for Quality Objectives. Trichlorobenzenes. RIZA, NL-Lelystad, 1994

[9] UK response to request for information relating to quality standards for the Priority List. Submission of data on toxicity, persistence and bioaccumulation by DETR (e-mail of 23 May 2001 by Natasha Robinson)

[10] 1,2,4-Trichlorobenzene. EURO CHLOR Risk Assessment for the Marine Environment. OSPARCOM Region – North Sea. Final Draft, March 2002

[11] Information provided by EURO CHLOR. Personal communication (e-mail Prof. André Lecloux, 22 June 2001)

[12] Opinion of the Scientific Committee on Toxicity, Ecotoxicity and the Environment (SCTEE) on “The Setting of Environmental Quality Standards for the Priority Substances included in Annex X of Directive 2000/60/EC in Accordance with Article 16 thereof”, adopted by the CSTEE during the 43rd plenary meeting of 28 May 2004, European Commission Health & Consumer Protection Directorate General, Brussels. http://europa.eu.int/comm/health/ph_risk/committees/sct/documents/out230_en.pdf

[13] ESIS: European Chemicals Bureau – ESIS (European Substances Information System), January 2005. http://ecb.jrc.it/existing-chemicals/ ⇒ tick ESIS button, then enter CAS or EINECS number of substance.

ANNEX 1: Aquatic toxicity data assessed and used in the risk assessment report for 1,2,4-trichlorobenzene [1]

Short term toxicity to aquatic organisms

Table A1.1: Short term toxicity to fish according to valid studies (Table 3.35 of [1]).

Species	Duration (hours)	LC_{50} (mg/l)	Method, conditions	Ref.
Lepomis macrochirus Bluegill sunfish	96	3.02	Flow through, lake water, 17°C, 45 mg $CaCO_3$/l, pH 7.4, measured conc.	Holcombe *et al.* 1987
Pimephales promelas Fathead minnow	96	3.01	Flow through, lake water, 17°C, 45 mg $CaCO_3$/l, pH 7.4, measured conc.	Holcombe *et al.* 1987
Pimephales promelas Fathead minnow (fry)	96	2.76	Flow through, lake water, 25°C, 44 mg $CaCO_3$/l, pH 7.6, ASTM 1980	Broderius & Kahl 1985
Pimephales promelas Fathead minnow (fry)	96	2.8	Flow through, lake water, 25°C, 45 mg $CaCO_3$/l, pH 7.5, ASTM 1975	Carlson & Kosian 1987
Pimephales promelas Fathead minnow	96	2.99	Flow through, lake water, 45.5 mg $CaCO_3$, pH 7.5, 25°C, measured conc.	Geiger *et al.* 1990, Veith *et al.* 1983
*Salmo gairdneri** Rainbow trout	24/48*	1.95	Static (closed), 15°C, 320 mg $CaCO_3$ pH 7.4, OECD TG 203	Calamari *et al* 1983
*Salmo gairdneri** Rainbow trout	96	1.32	Flow through, lake water, 17°C, 45 mg $CaCO_3$/l, pH 7.4, measured conc.	Holcombe *et al.* 1987
Jordanella floridae American flagfish	96	1.217	Flow through, lake water, 25°C, 48 mg $CaCO_3$, US-EPA 1975, measured conc.	Smith *et al.* 1991
Brachydanio rerio Zebra fish	24/48**	6.3	Static (closed), 23°C, pH 7.3, OECD TG 203	Calamari *et al* 1983
Leuciscus idus Golden ide	48	0.7	Static, DIN 38412-15, measured conc.	Knie *et al.* 1983
Oryzias latipes Orange red killifish	48	12.3	static, 20°C. ***	MITI 1992

* Now *Oncorhynchos mykiss*. **: In the study method is mentioned that 24 h LC_{50} is used due to the volatility of the substance but 48 h is stated in the tables of the study. ***: MITI (1992) does not clearly specify whether the values represent measured or nominal concentrations.

1,2,4-TCB has an acute non-specific toxic effect via narcosis (Veith *et al.* 1983). Regarding the acute toxicity to fish, a value from the lower end of tests with measured concentrations is **used in the risk assessment: *LC_{50} (96h) 1.0 mg/l***.

Table A1.2: Short term toxicity to crustaceans according to valid studies Table 3.36 of [1]).

Species	Duration hours	L(E)C_{50} (mg/l)	Method, conditions	Ref.
Daphnia magna	48	3.39	Flow through, lake water, 20°C, 45 mg $CaCO_3$/l, measured conc.	Holcombe *et al.* 1987
		2.68 1) 1.55 2)	Semi-static, Daphnids <2 days old, 22ºC, pH 7, NEN6502	Hermens *et al.* 1984
		2.72	Static (closed system), Daphnids 4-6 days old, 23°C, pH 7, US-EPA 1975. Nominal conc.	Bobra *et al.* 1983
		1.7 2.1	Static (closed), ASTM 1980, measured conc. Results from fed and unfed daphnids	Richter *et al.* 1983, US-EPA 1984
	24	1.2	Static, closed systems, measured conc. AFNOR	Calamari *et al.* 1983
		2.0-2.4	Static, OECD TG 202-I, measured (EC_0: 0.3-0.3, EC_{100}: 6.5-7.5)	Broecker *et al.* 1984
Orconectes immunis crayfish	96	3.02	Flow through, lake water, 20°C, 45 mg $CaCO_3$/l, measured conc.	Holcombe *et al.* 1987
Palaemonetes pugio (Mature grass shrimp)	96	0.54	Flow through, seawater, pH 8, 22°C, (APHA 1985), nominal conc (75-95% of actual)	Clark *et al.* 1987
Mysidopsis bahia (shrimp)	96	0.45	Static, US-EPA	Clark *et al.* 1987
	96	0.49	Flow-through, measured concentrations, (US-EPA standard CFR797.1930). NOEC= 0.19 mg/l, LC_{100} = 0.99 mg/l	US-EPA 1988
Nitocra spinipes (copepod)	96	2.6	Static, 21°C, 0,7% salinity, pH 7.8 initial conc.	Bengtsson & Tarkpea 1983

1) : based on nominal concentration. 2) : based on measured concentrations

1,2,4-TCB is apparently more toxic to species living in salt water but the TGD does not include assessment for marine environment and therefore effect concentrations with these organisms are not included. **The geometric mean of the accepted studies on *Daphnia magna* is an *EC_{50} (48h) of 2.1 mg/l* which is used in the risk assessment**.

Table A1.3: Toxicity to algae (table 3.37 of [1]).

Species	Duration	EC_{50} (mg/l)	NOEC (mg/l)	Method, conditions	Ref.	Valid
Selenastrum capricornutum	96 h	1.4	0.37	Static, closed system, US-EPA, measured conc.	Calamari *et al.* 1983, Galassi & Vighi 1981	yes
Scenedesmus subspicatus	96 h	18.9	2.2 (EC_{10})	Static (open system), 22°C, UBA guideline 1982, nominal conc.	Broecker *et al.* 1984	no
		8.4	3.0 (EC_{10})	Static (open system), 22°C, UBA guideline 1982, initial conc.	Geyer *et al.* 1985	no
Chlorella vulgaris	7 d	5.6		OECD TG 201 *	Yoshioka & Ose 1993	no
Cyclotella meneghiniana (diatom)	48 h	2.83		Static, 15°C (effects on DNA content reduction)	Figueroa & Simmons 1991	no

*: Stated to be carried out according to OECD guideline, However, OECD recommends 72 h tests to consider the growth inhibition within the exponential growth stage.

The results from the tests using closed system are accepted for use in the risk assessment procedure: **Algae EC_{50} (96 h): 1.4 mg/l and NOEC (96 h): 0.37 mg/l**.

Table A1.4: Short term toxicity to other aquatic organisms (Table 3.38 in [1]).

Species	Duration	EC_{50} (mg/l)	Method, conditions	Ref.
Tetrahymena pyriformis * (freshwater aquatic protozoa)	24 h	0.91	30°C, 2% protease peptone medium, growth inhibition	Yoshioka *et al.* 1985
Tanytarsus dissimilis (chironomid midge)	48 h	0.93	Flow through, lake water, 17°C, 43 mg $CaCO_3$/l measured conc.	Holcombe *et al.* 1987
Aplexa hypnorum Snail	96 h	3.16	Flow through, lake water, 17°C, 43 mg $CaCO_3$/l measured conc.	Holcombe *et al.* 1987

*: This ciliate data is also included in the section below because the data is regarded representative for ciliate species in sewage treatment plants.

Long term toxicity to aquatic organisms

Long term studies on fish and daphnia are all based on measured concentrations.

Table A1.5: Long term toxicity to aquatic organisms according to valid studies (Table 3.40 in [1]).

Species	Duration	EC_{50} mg/l	NOEC mg/l	Method, conditions	Ref.
Fish:					
Pimephales promelas	32 d		0.29	Flow-through, ESF-test	A
Pimephales promelas	32 d		0.50	Lake water, flow-through, ESF-test, EPA	B
Brachydanio rerio	21 d		0.04	Flow-through, mortality, behaviour	C
Salmo gairdneri	85 d		0.13	ELS (fry)	B
Poecilia reticulata	14 d	2.4		Semi-static (daily renewal), growth	E
Cyprinodon variegatus	-		0.11	ESF-test, MATC = 0.222 mg/l	F
Crustaceans:					
Daphnia magna	14 d	0.45	(0.32)	Semi-static, (closed)	H
Daphnia magna (mortality)	16 d	0.32*	0.19*	Semi-static (3 times a week)	I
Daphnia magna (repro)	16 d	0.16*	0.06*	Semi-static (3 times a week)	I
Daphnia magna (repro)	21 d		0.4	Semi-static, EEC-Ann.V-c	C
Daphnia magna	28 d		0.36	Semi-static (closed), ASTM 1980	J
Mysidopsis bahia	28 d		≤0.064	Flow-through, measured, EPA standard	K

A: US-EPA 1985, McCarty *et al.* 1985. B: Carlson & Kosian 1987. C: Broecker *et al.* 1984. E: Könemann 1981. F: Suter & Rosen 1988. H: Calamari *et al.* 1983 (NOEC = EC_{16}). I: Hermens *et al.* 1984 (*: refer to text below). J: Richter *et al.* 1983. K: US-EPA 1988 (LOEC = 0.033 mg/l).
Abbreviations: ESF-test (Egg and Sac Fry) embryo-larvae test. ELS: Early Life Stage test

The lowest NOEC in long term studies was 0.04 mg/l (mortality and behaviour, Zebra fish).

ANNEX 2: Aquatic toxicity data for 1,2,3-trichlorobenzene and 1,3,5 trichlorobenzene

Table A2.1: Overview on toxicity data of sensitive species from different sources (master reference)

Isomer	Species	Taxonomic Group	Medium *	Duration	Effect	Endpoint	Value	Unit	Master reference	Reference in master reference
1,2,3-TCB	Daphnia magna	Crustacea	fw	21 d	Reproduction	NOEC LOEC	30 § 60	µg/l	[7]	Kuhn *et al* (1989a)
1,2,3-TCB	Selenastrum capricornutum	Algae	fw	96 h	Growth	NOEC	220	µg/l	[7], [9]	Galassi et Vighi (1981)
1,2,3-TCB	Daphnia magna	Crustacea	fw	21 d		NOEC	630 §	µg/l	[8]	Kühn et al. (1989)
1,2,3-TCB	Brachydanio rerio	Fish	fw	14 d		NOEC	900	µg/l	[8]	Hahn et al. 1989
1,2,3-TCB	Selenastrum capricornutum	Algae	fw	96 h		EC0	220	µg/l	[8]	Galassi et al. 1981
1,2,3-TCB	Daphnia magna	Crustacea	fw	14 d	Reproduction	EC16	80	µg/l	[9], [8]	Calamari et al (1983)
1,2,3-TCB	Daphnia magna	Crustacea	fw	48 h	Immobilisation	EC50	330	µg/l	[9]	WRc (1988)
1,2,3-TCB	Daphnia magna	Crustacea	fw	24 h	Immobilisation	EC50	350	µg/l	[7]	Calamari *et al* (1983)
1,2,3-TCB	Poecilia reticulata	Fish	fw	96 h	Mortality	LC50	350	µg/l	[9]	Van Hoogen and Opperhuizen (1988)
1,2,3-TCB	Oncorhynchus mykiss	Fish	fw	48 h		LC50	710	µg/l	[8]	Calamari et al (1983)
1,2,3-TCB	Oncorhynchus mykiss	Fish	fw	24 h	Mortality	LC50	710	µg/l	[9]	Calamari et al (1983)
1,2,3-TCB	Selenastrum capricornutum	Algae	fw	96 h	Growth	EC50	900	µg/l	[7]	Galassi et Vighi (1981)
1,2,3-TCB	Brachydanio rerio	Fish	fw	48 h		LC50	3100	µg/l	[7]	Calamari *et al* (1983)
1,3,5-TCB	Daphnia magna	Crustacea	fw	21 d		NOEC	200 - 250	µg/l	[8]	Hahn et al. 1989
1,3,5-TCB	Brachydanio rerio	Fish	fw	14 d		NOEC	>410	µg/l	[8]	Hahn et al. 1989
1,3,5-TCB	Mercenaria mercenaria	Mollusca	sw			NOEC	1000	µg/l	[5]	RIVM Report 679101008
1,3,5-TCB	Scenedesmus subspicatus	Algae	fw	72 h		EC10	>2000	µg/l	[8]	Hahn et al. 1989
1,3,5-TCB	Daphnia magna	Crustacea	fw	48 h	Mortality	LC50	400	µg/l	[9]	WRc (1988)
1,3,5-TCB	Daphnia magna	Crustacea	fw	48 h	Immobilisation	EC50	1700	µg/l	[7]	WRc (1988)
1,3,5-TCB	Poecilia reticulata	Fish	fw	14 d		LC50	3300	µg/l	[7]	Konemann (1981)

*: fw = freshwater, sw = saltwater

§ One of the NOECs given by [7] and [8] may be incorrect as for both figures the same reference is given: Kühn, R, Pattard, M., Pernak, K. et Winter, A. (1989a) Results of the harmful effects of water pollutants to *Daphnia magna* in the 21 day reproduction test, *Water Research*, 23, 501-510.