**Euro Chlor Risk Assessment for the Marine Environment**

**OSPARCOM Region - North Sea**

# 1,2,4-Trichlorobenzene

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Euro Chlor
representing the chlor-alkali industry

**EURO CHLOR RISK ASSESSMENT FOR THE MARINE ENVIRONMENT**

# 1,2,4-TRICHLOROBENZENE

## OSPARCOM Region - North Sea

## EXECUTIVE SUMMARY

Euro Chlor has voluntarily agreed to carry out risk assessment of 25 chemicals related to the chlorine industry, specifically for the marine environment and according to the methodology laid down in the EU risk assessment Regulation (1488/94) and the Guidance Documents of the EU Existing Substances Regulation (793/93).

The study consists of the collection and evaluation of data on effects and environmental concentrations. Basically, the effect data are derived from laboratory toxicity tests and exposure data from analytical monitoring programs. Finally the risk is indicated by comparing the "predicted environmental concentrations" (PEC) with the "predicted no effect concentrations" (PNEC), expressed as a hazard quotient for the marine aquatic environment.
To determine the PNEC value, three different trophic levels are considered: aquatic plants, invertebrates and fish.

In the case of 1,2,4-trichlorobenzene 27 data for fish, 29 data for invertebrates and 10 data for algae have been evaluated according to the environmental quality criteria recommended by the European authorities. Both acute and chronic toxicity studies have been taken into account and the appropriate assessment factors have been used to define a final PNEC value of 3 µg/l. For sediment a PNEC of 0.12-0.19 mg/kg dry weight is estimated.

The recent typical monitoring concentrations in coastal waters and estuaries are generally below 0.047 µg/l. A worst case value of 0.1 µg/l was determined. Using these values, the calculated PEC/PNEC ratios give a safety margin of about 33 to 63 between the predicted no effect concentration and the exposure concentration. Dilution within the sea will increase those safety margins.

Monitoring data from sediment in rivers and estuaries showed values typically at 40 µg/kg and under worst case at 90 µg/kg dry weight. The corresponding PEC/PNEC ratios give safety margins of 1.3-2.1 to 3-4.8 for the worst-case and typical PEC's, respectively. Based on these margins and in addition to the fact that the PEC's are based on river sediment data, risks for marine sediment organisms are unlikely for 1,2,4-trichlorobenzene.
Moreover, the available data on persistence of 1,2,4-trichlorobenzene indicate a half-life in water of a few days and a significant biodegradation potential. Although bioaccumulation is found in some aquatic organisms, biomagnification in the food chain is not expected due to the relatively high

elimination rate constants. So it can be concluded that the present use of 1,2,4-trichlorobenzene does not represent a risk to the marine environment.

# 1. INTRODUCTION: PRINCIPLES AND PURPOSES OF EURO CHLOR RISK ASSESSMENT

Within the EU a programme is being carried out to assess the environmental and human health risks for "existing chemicals", which also include chlorinated chemicals. In due course the most important chlorinated chemicals that are presently in the market will be dealt with in this formal programme. In this activity Euro Chlor members are cooperating with member state rapporteurs. These risk assessment activities include human health risks as well as a broad range of environmental scenarios.

Additionally Euro Chlor has voluntarily agreed to carry out limited risk assessments for 25 prioritised chemicals related to the chlorine industry. These compounds are on lists of concern of European Nations participating in the North Sea Conference. The purpose of this activity is to explore if chlorinated chemicals presently pose a risk to the marine environment especially for the North Sea situation. This will indicate the eventual necessity for further refinement of the risk assessments and eventually for additional risk reduction programmes.

These risk assessments are carried out specifically for the marine environment according to principles given in *Appendix 1* . The EU methodology is followed as laid down in the EU risk assessment Regulation (1488/94) and the Guidance Documents of the EU Existing Substances Regulation (793/93).

The exercise consists of the collection and evaluation of data on effects and environmental concentrations. Basically, the effect data are derived from laboratory toxicity tests and exposure data from analytical monitoring programs.
Where necessary the exposure data are backed up with calculated concentrations based on emission models. Finally, in the absence of secondary poisoning, the risk is indicated by comparing the "predicted environmental concentrations" (PEC) with the "predicted no effect concentrations" (PNEC), expressed as a hazard quotient for the marine aquatic environment.

# 2. DATA SOURCES

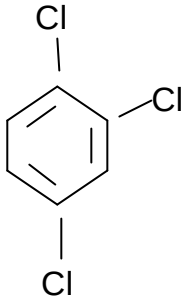
The data used in this risk assessment activity are primarily derived from the data given in the IUCLID (IUCLID, 2000) for this compound. Where necessary additional sources have been used.

# 3. COMPOUND IDENTIFICATION

## 3.1 Description

| | | |
|---|---|---|
| CAS number | : | 120-82-1 |
| EINECS N° | : | 204-428-0 |
| IUPAC name | : | 1,2,4-Trichlorobenzene |
| Appearance | : | liquid |
| Molecular formula | : | $C_6H_3Cl_3$ |

Structural formula:




The purity of the present commercial product is > 99.8 % w/w.
Impurities are:
Chlorobenzene < 0.05 %
p-dichlorobenzene < 0.1 %
1,2,3-trichlorobenzene < 0.1 %

## 3.2 EU Labelling

According to Annex I of Directive 67/548/EEC and its 28 ATP, trichlorobenzene should be labelled harmful (Xn) by oral route (R22) and irritant for the skin (R38). The environmental classification is Dangerous to the environment (N), very toxic to aquatic organisms and may cause long term adverse effects on the aquatic environment (R50/53).

# 4. PHYSICO-CHEMICAL PROPERTIES

Table 1 gives the major chemical and physical properties of the compound which were adopted for the purpose of this risk assessment.

**Table 1 : Physical and chemical properties of 1,2,4-trichlorobenzene**

| Property | Value |
|---|---|
| Molecular weight | 181.45 |
| Appearance | Liquid |
| Melting point | 17°C |
| Boiling point | 213°C |
| Density at 20°C | 1.46 g/cm$^3$ |
| Vapour pressure Pa at 20°C | 36 |
| Log Kow (octanol-water partition coefficient) | 3.9-4.2 |
| log Koc | 3.3-3.5 |
| Water solubility at 20°C | 36 mg/l (up to 48.8 mg/l) |
| Henry's Law constant | 181 Pa.m$^3$/mol (134-181 Pa.m$^3$/mol |

# 5. COMPARTMENT OF CONCERN BY MACKAY LEVEL I MODEL

The risk assessment presented here focuses on the aquatic marine environment, with special attention to the North Sea conditions where appropriate. Although this risk assessment only focuses on one compartment, it should be borne in mind that all environmental compartments are inter-related.

An indication of the partitioning tendency of a compound can be defined using a Mackay level I calculation obtained through the ENVCLASS software distributed by the "Nordic Council of Ministers". This model describes the ultimate distribution of the compound in the environment (Mackay & Patterson, 1990 - Pedersen *et al.*, 1994).
The results are valuable particularly in describing the potency of a compound to partition between water, air or sediment. Practically, it is an indicator of the potential compartments of concern.

The results of such a calculation for 1,2,4-trichlorobenzene are given in Table 2 based on data in *Appendix 2*.

**Table 2 : Partition of 1,2,4-trichlorobenzene into different environmental compartments according to Mackay level I calculation (Mackay & Patterson, 1990)**

| Compartment | % |
|---|---|
| Air | 94.9 |
| Water | 1.5 |
| Soil | 1.9 |
| Sediment | 1.7 |

# 6. PRODUCTION, USES AND EMISSIONS

## 6.1. Commercial trichlorobenzene

The current purity of the product is 99.8%, while the previous commercial trichlorobenzene was a mixture of 2 isomers: 1,2,4 trichlorobenzene (80% to 100%) and 1,2,3 trichlorobenzene (0 to 20%).

There is some use of 1,3,5 trichlorobenzene but only as intermediate and in low quantities (≈ 200 tonnes per year). There is no PCDD/PCDF in trichlorobenzenes at a sensitivity level of part per billion.

Trichlorobenzenes are obtained by direct chlorination of benzene, together with dichlorobenzenes. Trichlorobenzenes were also produced in the lindane manufacturing process. Lindane is the γ-isomer of hexachlorocyclohexane (HCH). Crude HCH contains only 20% of the γ-isomer. The 80% remaining isomers (α, β,...) are pyrolysed in closed vessels with formation of trichlorobenzenes and hydrochloric acid, which are recovered.

## 6.2. Main Uses

1,2,3 trichlorobenzene is used as an intermediate for the manufacture of pesticides (through the production of 2,3,4 trichloronitrobenzene), as intermediate in several fine chemical products and particularly herbicides, pigments and dyes.

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Both 1,2,3 and 1,2,4 trichlorobenzene are used as process solvents, dye carriers, dielectric fluid. They are also used as solvents in dielectric fluids, but this application has been stopped in Europe.

## 6.3. Production and Sales

About 6,000 tonnes of trichlorobenzenes are produced in Europe, mainly in Belgium and Germany but also in Spain and Italy. Trichlorobenzene uses in Europe are estimated at 1,800 tonnes for 1995 which is used for 100% as intermediates in pesticide production. Imports are estimated at 2,000 tonnes per year. Europe is a net exporter of trichlorobenzenes in the range of 6,200 tonnes per year. Estimated world trichlorobenzenes production for 1995 was about 14,300 tonnes (Srour, 1996; EU final draft RAR, 2000).

## 6.4. Emissions

The main routes by which trichlorobenzene enters the environment during manufacturing, processing and usage are the hydrosphere and atmosphere. Emissions in water and air represent respectively 0.552 t/y and 0.351 t/y in 1997 as based on a survey from about 78 sites from the European chemical industry producing or using trichlorobenzene (Euro Chlor COCEM, 2002). Emissions in water in 1997 have been reduced by 97% as compared to releases from 1985.

Trichlorobenzene is also formed during various combustion processes (Lahaniatis *et al.*, 1981, Linak *et al*., 1987, Panagiotou *et al*., 1996, Jay & Stieglitz, 1995) and industrial cracking or environmental degradation of HCH (Hooftmann & Kreuk, 1982, Fathepure *et al.*, 1988).

## 6.5. Applicable regulations

According to EU Directive 90/415, emission of trichlorobenzenes to water is limited to 0.5 g/t capacity of chlorobenzene production from direct chlorination of benzene and 10 g/t production of trichlorobenzene from HCH pyrolysis. A surface water quality objective of 0.4 µg/l has been set by this Directive. A water quality objective of 0.1 µg/l has been proposed by EU scientific experts (CSTE, 1994).

# 7. EFFECT ASSESSMENT

As a first approach, this chapter only considers the following three trophic levels: aquatic plants, invertebrates and fish.

The evaluation of the data was conducted according to the quality criteria recommended by the European authorities (Commission Regulation 1488/94/EEC). The evaluation criteria are given in *Appendix 1*.

Documented data from all available sources, including company data and data from the open literature, were collected and incorporated into the IUCLID for 1, 2, 4-trichlorobenzene,

including their references (updated version of June 1995). Some additional references were included.

A summary of all data is given in *Appendix 3*. In total 27 data for fish, 29 data for invertebrates and 10 data for algae are given. Respectively 14, 14 and 1 data were considered valid for risk assessment purposes. For the respective taxonomic groups 2, 3 and 1 should be considered with care, and 7, 10 and 4 data, respectively, were judged as not valid for risk assessment. Validity could not be assigned to 4, 2 and 4 datapoints, respectively.

It is necessary to distinguish the acute studies ($LC_{50}$/$EC_{50}$) from chronic studies (NOEC/LOEC). In the tables presented in *Appendix 3*, the data are ranked based on class (fish, invertebrates, algae), criterion (acute, chronic), environment (freshwater/ saltwater) and validity (1, 2, 3, 4) as required by the EU risk assessment process (TGD, 1996).

Due to its relatively low solubility and fairly high volatility, 1,2,4-trichlorobenzene should be tested in closed systems to avoid evaporation.

The three trophic levels are reviewed hereafter. A full summary of toxicity data is given in *Appendix 3*

## 7.1. Marine fish

One acute toxicity result is reported for a marine fish species (*Cyprinodon variegatus*) with a 96 h-$LC_{50}$ of 21 mg/l, plus a study on amphioxus, a marine non-fish chordate. The fish study was not considered valid because it was based on nominal concentrations in a static system, which is not reliable for a substance such as 1,2,4-trichlorobenzene because of likely losses by volatilisation (Heitmüller *et al*., 1981).

The amphioxus study was in a flow-through system with analysis, but cannot be considered valid for these purposes because it is not a fish and the $LC_{50}$ was only reported as being within the range of 1.5-10 mg/l (Clark *et al*., 1987).

One long-term study, an embryo-larval test with *C. variegatus*, is reported. However, the source is secondary (US EPA, 1980) and only gives limited details, citing unpublished US EPA work, and therefore validity cannot be assigned (category 4). A NOEC of 0.15 mg/l is reported.

Therefore, there are no marine fish studies that can be used for risk assessment.

## 7.2. Freshwater fish

Nineteen acute toxicity results are reported for 8 freshwater fish species. Three of these are secondary sources, citing data that is unpublished or could not be traced, and are classified as validity 4.

Of the remaining studies, 5 are classified as category 3 (not valid) because they were run in static (or semi-static) test systems without analysis of the solutions and with no precautions (except one which covered the aquaria with a glass plate) to prevent volatile losses of the test substance. Two studies are assigned to category 2 (use with care), one (Buccafusco *et al.*, 1981) used a static closed system but without analysis. Another study (Knie *et al*., 1983) used an open static system and there is uncertainty about the analysis.
The remaining 9 studies are classified as valid (category 1) and give $LC_{50}$ values ranging from 1.2 to 6.3 mg/l for 5 different species. Seven studies used flow-through systems with analysis. Two studies (Calamari *et al.*, 1983) were conducted under static conditions, but in closed systems to prevent volatility and with analysis of the test solutions. The duration was 24 h (confirmed by Calamari, 2001, checked because of inconsistency in paper between text and table). A 96 hr $LC_{50}$ to *Jordanella floridae* of 1.2 mg/l (Smith *et al.*, 1991) is the lowest valid acute toxicity value for freshwater fish. Even if the value of Knie *et al*. (1983) would have been valid, the PNEC would not change because the value used for its calculation from a crustacean (Clark *et al*., 1987) is lower.

Five long term studies are reported for 2 species. One of these reports (Broecker *et al*., 1984) identified a lowest valid NOEC of 0.04 mg/l for *Brachydanio rerio* in a 21-day test under flow-through condition and measured concentrations. At the next highest concentration (0.18 mg/l) behavioural effects and mortality were reported.

The remaining 4 studies were on the embryo-larval stages of *Pimephales promelas*. All studies were conducted in flow-through systems with analysis (except for McCarty *et al*., 1985) and are considered valid (category 1) with NOECs varying from 0.13 to 0.5 mg/l.

## 7.3. Marine invertebrates

Four acute toxicity studies are reported for 4 marine invertebrate species. One of these (US EPA, 1980) cites unpublished data and is classified as category 4, due to insufficient information on the test conditions. One (Bengtsson *et al.*, 1983) was conducted under static conditions with no analysis of the test solutions, and the result has been classified as category 3, invalid. One study on *Artemia salina* should be handled with care as this occurred in a closed system under static conditions and no analysis. A 24h-$LC_{50}$ of 3.3 mg/l was found (Abernethy *et al*., 1988). The remaining study was conducted in a flow-through system with analysis, and was considered valid. It gives a 96h $LC_{50}$ value to *Palaemonetes pugio* of 0.54 mg/l (Clark *et al.*, 1987), which represents the lowest valid acute toxicity for marine invertebrates.

One valid long-term toxicity study is reported for *Mysidopsis bahia* conducted under flow-through conditions with analyses (US EPA, 1988). The most sensitive endpoint was reproduction, which gave a NOEC of 0.033 mg/l, with a LOEC of 0.064 mg/l.

## 7.4. Freshwater invertebrates

Nineteen acute values are reported for 7 species of freshwater invertebrates. One of these is secondary sources (Nendza & Klein, 1990) and is classified as category 4. Eight studies

were not considered valid because they are based upon nominal concentrations in static tests. One of the studies with *Daphnia magna* was considered valid with restrictions (Richter *et al.*, 1983); although the result was based on measured concentrations, the animals were fed during the test which is not allowed in standard methods. However, the same authors also reported results with unfed animals.

Nine studies conducted with 4 species were considered valid, being carried out with analysis of the solutions. The $LC/EC_{50}$ values ranged from 0.93 to 3.16 mg/l. The lowest value for *D. magna* was 1.2 mg/l. However, a slightly lower value is reported for the midge, *Tanytarsus dissimilis* (Holcombe *et al.*, 1987) with a 96-hour $LC_{50}$ of 0.93 mg/l, which is the lowest valid acute toxicity for freshwater invertebrates.

Five long-term toxicity results are reported for the freshwater invertebrate, *D. magna*. One paper (Yoshioka & Ose, 1993) gives little information of the test method but is presumed to have been carried out without analysis and is classified as invalid. One study quotes a 14 day $EC_{16}$ of 0.32 mg/l (Calamari *et al.*, 1983). From this study a NOEC of 0.16 mg/l (NOEC = LOEC/2 if LOEC between 10 to 20% of effects) can be derived (TGD, 1996). This study can be used with care. Three results with *D. magna* are considered valid (Hermens *et al.*, 1984; Richter *et al.*, 1983; Broecker et al., 1984). All were carried out under semi-static test conditions with analysis of the solutions. The lowest long-term value for freshwater invertebrates is a 16-day NOEC for *D. magna* of 0.06 mg/l (Hermens *et al.*,1984).

## 7.5. Marine algae

One report (US EPA, 1980) provides 2 datapoints for the marine alga, *Skeletonema costatum*, but is a secondary source citing unpublished US EPA data (96-hour $EC_{50}$ values of 8.75 and 8.93 mg/l for chorophyll and cell number, respectively). There was insufficient detail to validate the results (category 4).

NOEC values were not reported for these studies.

## 7.6. Freshwater algae

Nine toxicity studies are reported for 5 species of freshwater algae. Two values were from a secondary source (US EPA, 1980) citing unpublished data and validity could not be assigned. Four studies were carried out without chemical analysis and were considered not valid. One study (Broecker *et al*., 1984) is classified as category 3 because the test method is not well described and is based on nominal concentrations in a static system. One study (Calamari *et al.*, 1983) employed analysis and a closed system but was of short duration (3 hours), with an endpoint of radio-carbon fixation, and could be used with care. Only one study was classified as valid, using a closed system, with analysis, and measuring growth. This quotes a 96-hour $EC_{50}$ to *Selenastrum capricornutum* of 1.4 mg/l, which is the lowest acute toxicity value for freshwater algae (Calamari *et al.*, 1983).

The same study provides a valid 96-hour NOEC to *S. capricornutum* of 0.37 mg/l, which is the lowest NOEC value for freshwater algae (Calamari *et al.*, 1983).

## 7.7. Field study

In addition to the data for single-species laboratory studies described above, a freshwater outdoor model-ecosystem study has been reported (Lay *et al*, 1985). A natural pond was compartmentalised to provide 200 litre sediment-water columns. Three compartments were dosed with a nominal 250 µg/l of 1,2,4-trichlorobenzene and three others served as controls. After treatment, microalgal diversity and numbers did not differ significantly from the controls. Daphnid numbers declined to less than 10% of the controls, but numbers increased again after 21 days, when measured aqueous concentrations had declined to 50 - 100 µg/l.

Macrobenthic animal communities in sand-filled aquaria established by planktonic larvae entrained in continuously supplied unfiltered seawater for 50 days were exposed to waterborne 1,2,4-trichlorobenzene for 6 days. The lowest 1,2,4-trichlorobenzene concentration (measured) that affected average numbers of individuals exposed via the water were 0.04 mg/l for molluscs, 0.4 mg/l for arthropods, and 4 mg/l for annelids. Average number of species was significantly lower than the control at 4 mg/l. (Tagatz *et al.*, 1985).

Although the results cannot be used directly for risk assessment, they are in general agreement with the laboratory data (*Daphnia* NOEC of 60 µg/l, Hermens *et al.*, 1984).

## 7.8. PNEC for marine environment

Although there is more valid information on freshwater toxicity, it seems reasonable to conclude that the sensitivity of marine and freshwater organisms to 1,2,4-trichlorobenzene is similar.

A summary of the valid data selected for the derivation of PNEC values at different levels is given in Table 3. This table summarises the PNEC values derived from acute and chronic studies. When chronic studies are available, it is generally acknowledged that they are closer to real world than acute tests (TGD, 1996). As far as the North Sea is concerned, acute exposure is not relevant because of the absence of local sources.

**Table 3: Summary of ecotoxicity data selected for the PNEC derivation, with the appropriate assessment factors for 1,2,4-trichlorobenzene**

| Available valid data | Assigned assessment factor | Lowest toxicity values |
|---|---|---|
| At least 1 short-term $LC_{50}$ from three trophic levels (fish, invertebrates, algae) | 1000 | - *J. floridae*, $LC_{50}$, 96h = 1.2 mg/l (Smith *et al.*, 1991)<br>-*P. pugio*, $EC_{50}$, 48h = 0.54 mg/l (Clark *et al.*, 1987))<br>- *S. capricornutum*, $LC_{50}$, 96h = 1.4 mg/l (Calamari *et al.*, 1983) |
| | **PNEC = 0.54 mg/l** | |
| Long-term NOEC from 3 species representing three trophic level (fish, invertebrates, algae) | 10 | - *B. rerio*, NOEC, 21d = 0.04 mg/l (Broecker et al., 1984)<br>- *M.bahia*, NOEC, 28d = 0.03 mg/l (US EPA, 1988)<br>- *S. capricornutum*, NOEC, 96h = 0.37 mg/l (Calamari *et al.*, 1983) |
| | **PNEC = 3 mg/l** | |

**The final $PNEC_{water}$ which is calculated for this risk assessment of 1,2,4-trichlorobenzene is 3 mg/l.**

The quality objective for surface waters of the European Union for substances of List I of Directive 76/464 corresponds to a value of 0.1 µg/l for 1,2,4-trichlorobenzene (CSTE, 1994). The EU Directive 90/415 gives a surface water quality objective of 0.4 µg/l.

## 7.9. PNEC for sediment

Some studies on the effects of 1,2,4-TCB on sediment organisms have been reported, but these are not valid studies. One study (Clark *et al*., 1987) used contaminated sediment diluted with beach sand containing organic matter between 0.5 and 1%. A 10-day test was performed on grass shrimps (*P. pugio*) and amphioxus (*Branchiostoma caribaeum*) in a flow-through system. NOEC for mortality was 10 mg/kg sediment for grass shrimp (no higher concentration tested) and 75 mg/kg sediment for amphioxus based on nominal values. Measured concentrations varied between 60-95% of nominal values.

Macrobenthic animal communities that colonized sand-filled aquaria were exposed to 1,2,4-TCB. In a first test, communities established by planktonic larvae entrained in continuously supplied unfiltered seawater for 50 days were exposed to waterborne TCB for 6 days. In a second test, macrobenthic animals were exposed for 8 weeks to sediment contaminated with 1,2,4-TCB. In the second test, sediments concentrations were 10, 100 and 1000 mg/kg (nominal concentrations). Number of individuals were affected from 100mg/kg for Mollusca and Echinodermata, and from 1000 mg/kg for Arthropoda and Annelida. No significant effect on the number of individuals was observed for Chordata, Cnidaria and Rhynchocoela.

This test is not validated for two reasons. Firstly, the mortality of macrobenthic animals was not measured. Effects were determined by comparing communities that developed in aquaria containing contaminated and uncontaminated sand. Larvae may have avoided settling or failed to develop in the contaminated sediment. NOEC for mortality cannot be established. Secondly, the results are based on nominal concentrations although leaching from sediment to water was observed.

Due to the lack of measured values, a PNEC was calculated according to the TGD equation:

| | | |
|---|---|---|
| $PNEC_{sed}$ d.m. | = | $K_{oc}$ x $F_{oc}$ x $PNEC_{aqua}$ mg/l + (1.6 x $PNEC_{aqua}$ mg/l) |
| $PNEC_{aqua}$ | = | 0.003 mg/l |
| $K_{oc}$ | = | 1920 - 3177 |
| $F_{oc}$ | = | 0.02 (fraction of organic carbon in estuarine sediment) |

$PNEC_{sed}$ is calculated as 0.12-0.19 mg/kg d.w.

A final **$PNEC_{sed}$ of 0.12 – 0.19 mg/kg d.w.** is used for this risk assessment of 1,2,4-trichlorobenzene.

## 7.10. Bioaccumulation

Due to the average log $K_{ow}$ value of 4, limited bioaccumulation can be expected, which is confirmed by measured bioconcentration factors (BCFs). Log BCF values for fish ranged from 2.28 (Carp. 2.2% lipid, Geyer *et al.*, 1985) to around 3 for green sunfish, rainbow trout, bluegill sunfish, guppy, zebra fish (Veith *et al.*, 1979; Oliver & Niimi, 1983; Barrows *et al.*, 1980; Geyer *et al.*, 1985; Van Eck *et al.*, 1997). Heitmüller et al. (1995) studied bioaccumulation of 1,2,4-TCB from food and the marine fish *Leiostomis xanthums.* They found negligible accumulation from contaminated food and moderate accumulation from water, with BCF values of 69-135.

At other trophic levels bioconcentration seems to occur at a similar extent. Log BCF values for algae are reported from 2.4 to 2.90 by Geyer *et al.* (1984); Freitag (1985) and Halfon & Reggiani (1986). Log BCF values for bacteria are reported to be 3.15 by Freitag *et al.* (1984), Halfon & Reggiani, (1986) (activated sludge) and 3.52 by Mabey (1982).

Knezovitch and Harrison (1988) used a closed flow-through bio-assay to investigate the bioavailability to chironomid midge larvae of sediment-bound 1,2,4 trichlorobenzene. A Log BCF of 2.4 was reported, but under non-equilibrium conditions.

Uptake and elimination rate constants are reported by Könemann & Van Leeuwen (1980) and Smith *et al.* (1990) for guppy and American flagfish. $K_2$ values of 0.45 $day^{-1}$ and 0.57 $day^{-1}$ suggest a half life in the fish (CT50 Clearance time) of 1.54 day or 1.21 day, indicating a rather high elimination rate.

The similar values of BCF reported for different trophic levels and the relatively high elimination rate constants suggest that concentrations of trichlorobenzenes do not increase as

they move up the food chain. No studies were found against the validity of this assessment (IPCS, 1991).

In conclusion, 1,2,4-trichlorobenzene has moderate bioaccumulation potential with cited measured values mainly in the range of 100-1000 and for marine fish of approx. 100. Based on its combination of environmental characteristics it is unlikely to expect any risks via accumulation in the food chain. This is based on the environmental distribution characteristics (mainly to air), the low persistency in water and the high elimination rates from biota of 1,2,4-trichlorobenzene.

## 7.11. Persistence in water

As indicated by the Henry's law constant, trichlorobenzenes entering aquatic systems would be transferred to the atmosphere through volatilisation. The MacKay Level 1 repartition (see Section 5) indicates that more than 94% of the 1,2,4 trichlorobenzene entering the environment will be transferred to the atmosphere which is the primary compartment for trichlorobenzene.

For 1,3,5 trichlorobenzene, the half-life for a river model of 1 m depth with a water current of 1 m/sec and wind velocity of 3 m/sec at 20°C is given as 4.5 hours by Lyman *et al.* (1982) or 5.1 hrs by SRC's EPIWIN. In the same model, the half-life for a lake (1 m depth, 0.05 m/sec water current and 0.5 m/sec wind velocity) would be 136.1 hrs.

Longer volatilisation half life can be expected for marine waters compared to river waters. Wakeham *et al.* (1983) reported half-lives from marine mesocosms for 1,2,4 trichlorobenzene: 22 days at 8-16°C in the spring, 11 days at 20-22°C in summer. These data are experimental and include some microbial degradation.

Using data from an ecosystem study from Lay *et al.* (1985), a half-life of 10 days (geometric mean) is calculated based on measured data.

Bartholomew (1983) and Battersby (1990) gave the following data:

| | $K_B$ ($day^{-1}$) | Half lives(days) |
|---|---|---|
| river water | 0.029 | 23.8 |
| estuary water | 0.026 | 26.5 |
| marine water | 0.012 | 57.5 |

These data should be compared with field measurements made by Zoeteman *et al.* (1980) in river waters (0.3-3 days) and lake (3-30 days).

## 7.12. Persistence in air

Photoxidation half-life in air is given from 128.4 to 1284 hours (5 to 53 days), based on a rate constant for vapour phase reaction with hydroxy radicals in air of 5.32 $10^{-13}$ $cm^3$/mole.sec (Atkinson., 1988). A half-life of about 38 days is obtained with SRC's EPIWIN software.

No significant effect of trichlorobenzenes can be expected on stratospheric ozone depletion and global warming, as a half life of at least one year is necessary to expect such effects.

## 7.13. Degradation in biological systems

Several data are given for degradation rate constants in water.

Tabak *et al.* (1981) and Mills (1982) reported a $K_B$ rate constant of 0.05 $day^{-1}$ which, assuming first order kinetics, will give a half life of 13.8 days.

While in laboratory tests on waste water treatment over 90% elimination of 1,3,5 trichlorobenzene was obtained by Hoechst (1992, quoted by BUA Report 16), some other standard tests indicated no degradation and MITI (1986) lists trichlorobenzenes as non-biodegradable.

Simmons *et al.* (1977) reported on other studies on activated sludge with 56% converted to $CO_2$ after 5 days, 23% converted to polar metabolites and 7% evaporated.

Sander *et al.* (1991) demonstrated the enrichment, isolation and characterization of bacterial strains capable of using 1,2,4-trichlorobenzene as the sole source of carbon and energy and in an aerobic process.
In recent studies Masunaga *et al.* (1996) investigated the reductive dechlorination of trichlorobenzenes in an anaerobic estuarine sediment. In laboratory tests the transformation of the substance and appearance of its intermediate metabolites were analysed. The overall loss of parent compound followed pseudo first order reaction kinetics. The rate constants and subsequent half lives are summarised in Table 4:

**Table 4: Rate constants and half lives of 1,2,4-trichlorobenzene in anaerobic estuarine sediment and its intermediates**

| | Rate constant $day^{-1}$ | Half life in sediment days | Intermediates |
|---|---|---|---|
| 1,2,3-TCB | 0.0299 | 23.2 | 1,3-DCB, 1,2-DCB, MCB |
| 1,2,4-TCB | 0.0170 | 40.8 | 1,4-DCB, 1,2-DCB, 1,3-DCB, MCB |
| 1,3,5-TCB | 0.0198 | 35.0 | 1,3-DCB, MCB |

TCB = trichlorobenzene
DCB = dichlorobenzene
MCB = monochlorobenzene

## 7.14. Conclusion

1,2,4-trichlorobenzene is very toxic to aquatic organisms and has a limited bioaccumulation potential. It is not considered as persistent in the aquatic compartment mainly due to its volatility but also due to its susceptibility to degration. It can be deduced from the above information that 1,2,4-trichlorobenzene is not a „toxic, persistent and liable to bioaccumulate“ substance as mentioned by the Oslo and Paris Conventions for the Prevention of Marine

Pollution (OSPARCOM) according to the criteria currently under discussion and especially those defined by UN-ECE, Euro Chlor and CEFIC.

# 8. EXPOSURE ASSESSMENT

Trichlorobenzenes have been measured in several water systems. As the specific isomer is not always mentioned, data are given as trichlorobenzenes.
The distribution of the concentrations in the river waters or sediments have been mainly obtained from the COMMPS database (EU COMMPS, 1998), by a statistical analysis. This latter, first disregards the outliers, then estimates the parameters of a log-normal distribution at each location (by applying the maximum likelihood approach) and finally aggregates all the local distributions into a regional one. The curves provided are the aggregated ones. More details on the method are given by Govaerts *et al*. (2001). The data also include some heavily polluted areas which are not representative of the regional mean. The 90-percentile of the distribution is clearly the worst case for the marine environment, which does not take into account further dilution into the sea.
As it is generally not specified if the location of sampling is close to a source of emission (production or processing), it is assumed that the lower levels correspond to background "regional" concentrations and the higher to contaminated areas, or "local" concentrations, considered as worst cases.
To better illustrate the exposure in the marine environment, in the COMMPS database, the concentrations corresponding to the locations situated at estuaries or in coastal areas have been identified and reported in *Appendix 4*, as well as additional information from other literature sources.

## 8.1. Concentration of trichlorobenzenes measured in water

As previously indicated, the exposure assessment is essentially based on exposure data from analytical monitoring programs.

### 8.1.1. Marine waters and estuaries

A summary of the available monitoring data of trichlorobenzene levels in the marine environment is shown in Appendix 4a. The data came from: the Rhine estuary (Netherlands); Elbe estuary (Germany); Tees estuary (UK); coastal waters (Netherlands); North Sea coast (Germany); and the Seine estuary (France).These data indicate that in coastal waters and estuaries concentrations of TCB range from less than 0.0004 µg/l to 0.4 µg/l. Some higher concentrations are locally observed (Mersey Estuary in UK for example), but these are considered as outliers and treated at a local level. **Typical** more recent data (1994-1996) suggest that marine and estuarine concentrations of TCB are mostly below 0.1 µg/l, which is the limit of detection in most locations. Realistic regional worst case could be up to 0.1 µg/l.

### 8.1.2 River waters

Background levels in big rivers in Germany, The Netherlands, France and UK are in general lower than 0.4 µg/l. Surface waters from Germany, the Netherlands and France in the 1990's gave levels below the detection limits (between 0.01 and 0.4 µg/l). Similarly, in the COMMPS database covering rivers from D, E, F, GR, LUX, NL and UK, only 15 % of the measured concentrations are above the detection limit.The statistical analysis shows a 90-percentile value of the distribution at 0.1 µg/l and a mean typical value at 0.047 µg/l. The distribution of concentrations is illustrated in Figure 1.

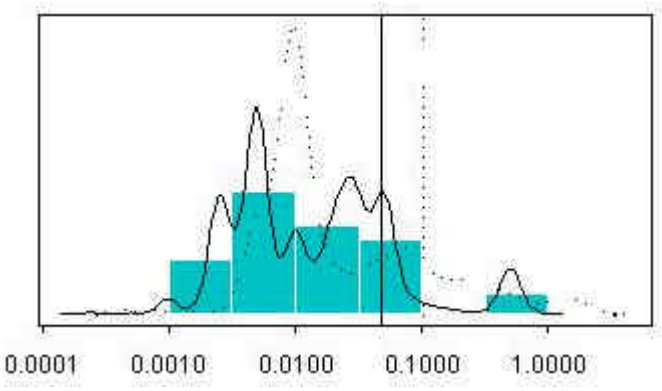


Figure 1: Distribution of 1,2,4-trichlorobenzene in European river waters, in µg/l

### 8.1.3 Predicted environmental concentrations of TCB in marine environment

The calculation of $PEC_{(marine)}$ is based on monitoring data which indicate that the levels of TCB in marine waters are usually below 0.1 µg/l and limited by detection levels. We consider the mean value of 0.047 µg/l for river water as a typical $PEC_{(marine)}$. The value of 0.1 µg/l representing the 90-percentile of the distribution of concentrations observed in river water is used as a conservative worst case $PEC_{(marine)}$.

## 8.2. Concentrations of TCB measured in sediments

Due to the Log $K_{ow}$ of about 4, it is necessary to consider the amount of 1,2,4-trichlorobenzene adsorbed on sediment. A consolidation of TCB measurements in river sediments has been presented in the COMMPS report from (EU COMMPS, 1998). The concentrations have been measured in freshwater sediment of rivers in Germany, Denmark, France and The Netherlands from 1994 to 1997. The values vary from < 0.5 to 400 µg/kg, with a mean value of 40 µg/kg d.w. The highest values are observed in the river Elbe in particularly contaminated sites which should not be considered as representative of the marine environment. It is suggested to use a worst case $PEC_{sediment}$ of 90 µg/kg d.w. corresponding to the 90-percentile of the concentration distribution. The distribution of concentrations is illustrated in Fig. 2. This figure shows that there are several high local concentrations in European rivers but the levels of TCB in main estuarine sediments as reported in Appendix 4b do not exceed 83 µg/kg, with a mean value varying with the locations from 1 to 24 µg/kg.

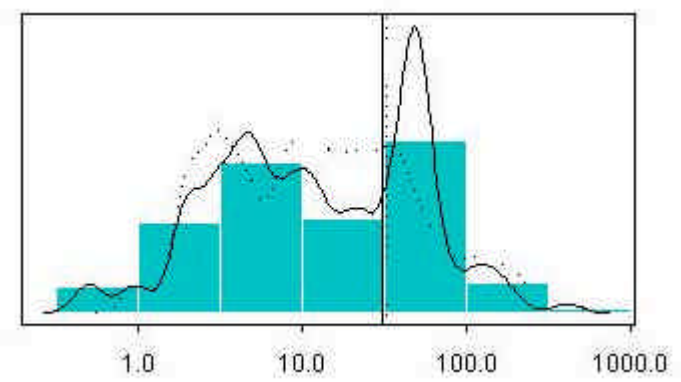


Figure 2: Distribution of 1,2,4-trichlorobenzene in European river sediments, in µg/kg

### 8.2.1 Predicted environmental concentration of TCB in sediment

For the purpose of the risk assessment for the marine sediment typical and worst case $PEC_{(sediment)}$ values of 40 and 90 µg/kg dw, respectively, have been used in the calculations.

## 9. RISK ASSESSMENT CONCLUSIONS

In the risk characterisation of 1,2,4-trichlorobenzene for the marine environment, the PNEC is compared to the PEC for the aquatic and for the sediment compartment. A PNEC of 3 µg/l was obtained for the aquatic species exposed to 1,2,4-trichlorobenzene. A PNEC of 0.12-0.19 mg/kg d.w. was obtained for sediment species.

### 9.1. PEC/PNEC ratios

For marine coastal waters and river estuaries, a typical $PEC_{(marine)}$ for trichlorobenzenes of 0.047 µg/l and a worst case $PEC_{(marine)}$ of 0.1 µg/l have been proposed even if due to the volatility of 1,2,4-trichlorobenzene and its evaporation from the water compartment, the concentration in the North Sea will be lower than the measured concentration in estuaries. Monitoring data for marine sediments are not available, but sediments in rivers show typical and worst case $PEC_{sediment}$ values of 40 µg/kg and 90 µg/kg, respectively. Overall, both values can be considered as worst-case for the marine environment.

These values allow to calculate the PEC/PNEC ratios which are summarised in table 5:

**Table 5: Calculation of PEC/PNEC ratios for 1,2,4-trichlorobenzene**

| Compartment | PEC level | PEC/PNEC |
|---|---|---|
| Water | | |
| • worst case | 0.1 µg/l | 0.03 |
| • typical | 0.047 µg/l | 0.016 |
| Sediment | | |
| • worst case | 90 µg/kg d.w. | 0.75-0.47 |
| • typical | 40 µg/kg d.w. | 0.33-0.21 |

## 9.2. Safety margins

These calculated ratios which do not take into account any dilution factor within the sea correspond to a safety margin of 33 to 63 between the aquatic effect and the exposure concentration in water, so that the present use of 1,2,4-trichlorobenzene should not represent a risk to the aquatic environment. The safety margins for the sediment are 1.3-2.1 and 3-4.8 for the worst-case and typical PEC's, respectively. Based on these safety factors and additionally the fact that the PEC's are based on river sediment data, any risks to marine sediment organisms are unlikely for 1,2,4-trichlorobenzene.

Although moderate bioaccumulation is found with 1,2,4-trichlorobenzene in aquatic organisms (BCF mainly between 100 and 1000), biomagnification in the food chain is not expected due to the volatility, low aquatic persistency and relatively high elimination rate constants.

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**APPENDIX 1**

## Environmental quality criteria for assessment of ecotoxicity data

The principal quality criteria for acceptance of data are that the test procedure should be well described (with Reference to an official guideline) and that the toxicant concentrations must be measured with an adequate analytical method.

Four cases can be distinguished and are summarised in the following table according to criteria defined in IUCLID system).

Table: Quality criteria for acceptance of ecotoxicity data

| Case | Detailed description of the test | Accordance with scientific guidelines | Measured concentration | Conclusion: reliability level |
|---|---|---|---|---|
| **I** | **+** | **+** | **+** | **[1] : valid without restriction** |
| **II** | ± | ± | ± | **[2] : valid with restrictions; to be considered with care** |
| **III** | **insufficient or -** | **-** | **-** | **[3] : invalid** |
| **IV** | **the information to give an adequate opinion is not available** | | | **[4] : not assignable** |

The selected validated data LC50, EC50 or NOEC are divided by an assessment factor to determine a PNEC (Predicted No Effect Concentration) for the aquatic environment.

This assessment factor takes into account the confidence with which a PNEC can be derived from the available data: interspecies- and interlaboratory variabilities, extrapolation from acute to chronic effects.

Assessment factors will decrease as the available data are more relevant and Refer to various trophic levels.

**APPENDIX 2**

**Ultimate distribution in the environment according to Mackay level I model**
(details of calculation)

Fugacity Level I calculation

Chemical: 1,2,4-trichlorobenzene

| | |
|---|---|
| Temperature (C) | 20 |
| Molecular weight (g/mol) | 181.45 |
| Vapor pressure (Pa) | 36 |
| Solubility (g/m3) | 36 |
| Solubility (mol/m3) | 0.20 |
| Henry's law constant (PA.m3/mol) | 181 |
| Log octanol water part. coefficient | 4.20 |
| Octanol water part. coefficient | 15848.93 |
| Organic C-water part. coefficient | 6498.06 |
| Air-water partition coefficient | 0.07 |
| Soil-water partition coefficient | 194.94 |
| Sediment-water partition coefficient | 389.88 |
| Amount of chemical (moles) | 1 |
| Fugacity (Pa) | .38552894-6 |
| Total VZ products | 2593838.94 |

Phase properties and compositions:

| Phase | Air | Water | Soil | Sediment |
|---|---|---|---|---|
| Volume (m3) | .6000E+10 | .70000E+7 | .45000E+5 | .21000E+5 |
| Density(kgm3) | .12056317E+2 | .10000E+4 | .15000E+4 | .15000E+4 |
| Frn org carb. | .00000E+0 | .00000E+0 | .20000000E-1 | .40000000E-1 |
| Z mol/m3.Pa | .41029864E-3 | .55111600E-2 | .10743558E+1 | .21487116E+1 |
| VZ mol/Pa | .24617918E+7 | .38578120E+5 | .48346011E+5 | .45122944E+5 |
| Fugacity | .38552894E-6 | .38552894E-6 | .38552894E-6 | .38552894E-6 |
| Conc mol/m3 | .15818200E-9 | .21247117E-8 | .41419526E-6 | .82839053E-6 |
| Conc g/m3 | .28702124E-7 | .38552894E-6 | .75155731E-4 | .15031146E-3 |
| Conc ug/g | .23806708E-5 | .38552894E-6 | .50103820E-4 | .10020764E-3 |
| Amount mol | .94909202E+0 | .14872982E-1 | .18638787E-1 | .17396201E-1 |
| Amount % | 94.91 | 1.49 | 1.86 | 1.74 |

**APPENDIX 3**

## SUMMARY TABLE OF ECOTOXICITY DATA ON 1, 2, 4-TRICHLOROBENZENE

### 1. FISH

| Species | Duration h (hours)/ d (days) | Type of Study | Criterion (LC50/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| **ACUTE STUDIES** | | | | | | | |
| **1. FRESHWATER** | | | | | | | |
| *Jordanella floridae* | 96h | A,F-T | LC50 | 1.2 | 1 | | Smith *et al*., 1991 |
| *Oncorhynchus mykiss* | 96h | A,F-T | LC50 | 1.32 | 1 | | Sulaiman, 1993; Holcombe *et al*., 1987 |
| *Oncorhynchus mykiss* | 96h | A,F-T | LC50 | 1.53 | 1 | Also 192h LC50 of 1.28 mg/l. | Call *et al*., 1983 |
| *Pimephales promelas* | 96h | A,F-T | LC50 | 2.76 | 1 | | Carlson, 1987; Broderius & Kahl, 1985 |
| *Pimephales promelas* | 96h | A,F-T | LC50 | 3.01 | 1 | | Sulaiman, 1993; Holcombe *et al*., 1987 |
| *Pimephales promelas* | 96h | A,F-T | LC50 | 2.9 | 1 | | Veith *et al*., 1983 |
| *Lepomis macrochirus* | 96h | A,F-T | LC50 | 3.0 | 1 | . | Holcombe *et al*., 1987 |
| *Leuciscus idus* | 48h | A,S | LC50 | 0.7 | 2 | | Knie *et al*., 1983 |
| *Lepomis macrochirus* | 96h | N,S,C | LC50 | 3.4 | 2 | Undissolved chemical observed. | Buccafusco *et al*., 1981 |
| *Brachydanio rerio* | 24h | A,S,C | LC50 | 6.3 | 1 | 24h exposure. Calamari, pers. comm. | Calamari *et al*., 1983 |
| *Oncorhynchus mykiss* | 24h | A,S,C | LC50 | 1.95 | 1 | 24h exposure. Calamari, pers. comm. | Calamari *et al*., 1983 |
| *Oryzias latipes* | 48h | N,S | LC50 | 12.3 | 3 | | Yoshioka *et al*., 1986; MITI, 1992 |
| *Oryzias latipes* | 96h | N,S,S | LC50 | 8.4 | 3 | | |
| *Jordanella floridae* | 96h | N,S,S | LC50 | 4.0 | 3 | | Smith *et al*., 1991 |
| *Oryzias latipes* | 24h | N,S | LC50 | 8.5 | 3 | | Ikemoto *et al*., 1992 |
| *Poecilia reticulata* | 14d | N,S,S | LC50 | 2.39 | 3 | Closed with glass plate, with air gap. | Konemann, 1981 |

**APPENDIX 3**

## SUMMARY TABLE OF ECOTOXICITY DATA ON 1, 2, 4-TRICHLOROBENZENE

| Species | Duration h (hours)/ d (days) | Type of Study | Criterion (LC50/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| *Leuciscus idus* | ? | ? | LC50 | 20 - 50 | 4 | Secondary data. | Bayer, 1987 |
| *Pimephales promelas* | 96h | ? | LC50 | 3.08 | 4 | Secondary data. | Nendza & Klein, 1990 |
| *Pimephales promelas* | ? | ? | LC50 | 1.8 | 4 | Secondary data. | Zhao *et al.*, 1995 |
| **2. SALTWATER** | | | | | | | |
| *Cyprinodon variegatus* | 96h | N,S | LC50 | 21 | 3 | Seawater 10-31‰. | Heitmuller *et al.*, 1981 |
| *Branchiostoma caribaeum* | 96h | A,F-T | LC50 | >1.5 - <10 | 3 | Amphioxus, a chordate but not fish. | Clark *et al.*, 1987 |

**APPENDIX 3**

## SUMMARY TABLE OF ECOTOXICITY DATA ON 1, 2, 4-TRICHLOROBENZENE

| Species | Duration h (hours)/ d (days) | Type of Study | Criterion (LC50/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| **CHRONIC STUDIES** | | | | | | | |
| **1. FRESHWATER** | | | | | | | |
| *Brachydanio rerio* | 21d | A,F-T | NOEC | 0.04 | 1 | Next highest concn (0.18 mg/l) stated to cause behavioural effects and mortality. | Broecker *et al.*, 1984 |
| *Pimephales promelas* | 30d (post-hatch) | A,F-T | NOEC | 0.21 | 1 | Hatching, survival & growth. | LeBlanc, 1984 |
| *Pimephales promelas* | 32d | A,F-T | NOEC | 0.5 | 1 | Hatching, survival & growth. | Carlson, 1987 |
| *Pimephales promelas* | 85d (post-hatch) | A,F-T | NOEC | 0.13 | 1 | Fry | Carlson, 1987 |
| *Pimephales promelas* | 32d (post-hatch) | F-T | NOEC | 0.29 | 1 | ESF test | McCarty *et al.*, 1985 |
| **2. SALTWATER** | | | | | | | |
| *Cyprinodon variegatus* | ? | ? | NOEC | 0.15 | 4 | Secondary data (unpublished) | US EPA, 1980 |

**APPENDIX 3**

**SUMMARY TABLE OF ECOTOXICITY DATA ON 1, 2, 4-TRICHLOROBENZENE**

## 2. INVERTEBRATES

| Species | Duration h (hours)/ d (days) | Type of Study | Criterion (LC50/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| **ACUTE STUDIES** | | | | | | | |
| **1. FRESHWATER** | | | | | | | |
| *Daphnia magna* | 24h | A,S,C | EC50 | 1.2 | 1 | | Calamari *et al.*, 1983 |
| *Daphnia magna* | 24h | A,S,C | EC50 | 2.0 | 1 | | Bazin *et al.*, 1987 |
| *Daphnia magna* | 48h | A,S,C | LC50 | 2.09 | 1 | | Richter *et al.*, 1983 |
| *Daphnia magna* | 48h | A,F-T | EC50 | 3.39 | 1 | | Holcombe *et al.*, 1987 |
| *Tanytarsus dissimilis* | 48h | A,F-T | LC50 | 0.93 | 1 | (Midge larvae) | Holcombe *et al.*, 1987 |
| *Orconectes immunis* | 96h | A,F-T | LC50 | 3.02 | 1 | (Crayfish) | Holcombe *et al.*, 1987 |
| *Aplexa hypnorum* | 96h | A,F-T | LC50 | 3.16 | 1 | (Mollusc) | Holcombe *et al.*, 1987 |
| *Daphnia magna* | 48h | A,S | EC50 | 2.5 | 1 | | Hermens, *et al.*, 1984 |
| *Daphnia magna* | 24h | A,S | EC50 | 2.0-2.4 | 1 | | Broecker *et al.*, 1984 |
| *Daphnia magna* | 48h | A,S,C | LC50 | 1.68 | 2 | Fed during test, otherwise ASTM (1980). | Richter *et al.*, 1983 |
| *Daphnia magna* | 24h | N,S | EC50 | 4.1 | 3 | | Yoshioka & Ose, 1993 |
| *Daphnia magna* | 24h | N,S | EC50 | 5.7 | 3 | | Zhao & Wang, 1995 |
| *Daphnia magna* | 48h | N,S,(C) | LC50 | 50 | 3 | Vessels closed by plastic wrap. | LeBlanc, 1980 |
| *Daphnia magna* | 48h | N,S | LC50 | 7.69 | 3 | | Oikari *et al.*, 1992 |

**APPENDIX 3**

**SUMMARY TABLE OF ECOTOXICITY DATA ON 1, 2, 4-TRICHLOROBENZENE**

| Species | Duration h (hours)/ d (days) | Type of Study | Criterion (LC50/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| *Daphnia magna* | 24h | N,S | EC50 | 21 | 3 | | Bringmann & Kuhn, 1982 |
| *Daphnia pulex* | 24h | N,S | LC50 | 2.2 | 3 | | Ikemoto *et al.*, 1992 |
| *Moina macrocopa* | 3h | N,S | LC50 | 12.6 | 3 | | Yoshioka & Ose, 1986 |
| *Dugesia japonica* | 7d | N,S | LC50 | 25 | 3 | (Planarian) Same value for EC50 based on head regeneration. | Yoshioka & Ose, 1986 |
| *Daphnia magna* | 48h | ? | EC50 | 4.9 | 4 | Secondary data. | Nendza & Klein, 1990 |
| **2. SALTWATER** | | | | | | | |
| *Palaemonetes pugio* | 96h | A,F-T | LC50 | 0.54 | 1 | | Clark *et al.*, 1987 |
| *Artemia Salina* | 24h | N,S,C | LC50 | 3.3 | 2 | Larvae | Abernethy *et al.*, 1988 |
| *Nitocra spinipes* | 96h | N,S | LC50 | 2.6 | 3 | (copepod) | Bengtsson & Tarkpea, 1983 |
| *Mysidopsis bahia* | 96h | N,S | LC50 | 0.45 | 4 | | US EPA, 1980 |

**APPENDIX 3**

## SUMMARY TABLE OF ECOTOXICITY DATA ON 1, 2, 4-TRICHLOROBENZENE

| Species | Duration h (hours)/ d (days) | Type of Study | Criterion (LC50/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| **CHRONIC STUDIES** | | | | | | | |
| **1. FRESHWATER** | | | | | | | |
| *Daphnia magna* | 28d | A,SS,C | NOEC | 0.36 | 1 | Parameters: Reproduction and length. | Richter *et al.*, 1983 |
| *Daphnia magna* | 16d | A,SS,C | NOEC | 0.06 | 1 | Test parameter: Reproduction. NOEC for mortality = 0.19 mg/l. | Hermens *et al.*, 1984 |
| *Daphnia magna* | 21d | A,SS | NOEC | 0.4 | 1 | | Broecker *et al.*, 1984 |
| *Daphnia magna* | 14d | A,SS,C | EC16 | 0.32 | 2 | Test parameter: Reproduction. EC16 approx = NOEC. | Calamari *et al.*, 1983 |
| *Daphnia magna* | 14d | ? | NOEC | 3.4 | 3 | No description of test method. | Yoshioka *et al.*, 1993 |
| **2. SALTWATER** | | | | | | | |
| Mysidopsis bahia | 28d | A,F-T | NOEC<br>LOEC | 0.033<br>0.064 | 1 | Test parameter: Reproduction GLP – EPA/OTS guidelines – ASTM 1985 | US EPA, 1988 |

**APPENDIX 3**

**SUMMARY TABLE OF ECOTOXICITY DATA ON 1, 2, 4-TRICHLOROBENZENE**

## 3. AQUATIC PLANTS

| Species | Duration h (hours)/ d (days) | Type of Study | Criterion (LC50/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| **1. FRESHWATER** | | | | | | | |
| *Selenastrum capricornutum* | 96h | A,S,C | EC50<br>NOEC | 1.4<br>0.37 | 1 | Parameter: Growth<br>Max conc. for zero effect | Calamari et al, 1983 |
| *Selenastrum capricornutum* | 3h | A,S,C | EC50 | 3.9 | 2 | Parameter: Radiocarbon fixation | Calamari et al, 1983 |
| *Scenedesmus subspicatus* | 96h | N,S,C | EC50<br>EC10 | 8.4<br>3.0 | 3 | | Geyer *et al.*, 1985 |
| *Chlorella vulgaris* | 7d | N,S | EC50 | 5.6 | 3 | | Yoshioka & Ose 1993 |
| *Cyclotella meneghiniana* | 48h | N,S | EC50 | 2.83 | 3 | Parameter: DNA content. | Figueroa & Simmons, 1991 |
| *Ankistrodesmus falcatus* | 4h | N,S,C | EC50 | 6.0 | 3 | Parameter: Carbon fixation. | Wong *et al.*, 1984 |
| *Scenedesmus subspicatus* | 96h | N,S,O | EC50 | 18.9 | 3 | Insufficient description of test system | Broecker *et al.*, 1984 |
| *Selenastrum capricornutum* | 96h | ? | EC50 | 35.3 | 4 | Secondary data. Parameter: Chlorophyll A. | US EPA, 1980 |
| *Selenastrum capricornutum* | 96h | ? | EC50 | 36.7 | 4 | Secondary data. Parameter: cell number. | US EPA, 1980 |
| **2. SALTWATER** | | | | | | | |
| *Skeletonema costatum* | 96h | ? | EC50 | 8.75 | 4 | Secondary data. Parameter: Chlorophyll A. | US EPA, 1980 |
| *Skeletonema costatum* | 96h | ? | EC50 | 8.93 | 4 | Secondary data. Parameter: cell number. | US EPA, 1980 |

**APPENDIX 3**

## LIST OF ABBREVIATIONS USED IN TABLES

A = Analysis

C = Closed system or controlled evaporation

h = hour(s)

d = day(s)

N = nominal concentration

S = static

SS = semistatic

FT = flowthrough

Validity column:
1 = valid without restriction
2 = valid with restrictions: to be considered with care
3 = invalid
4 = not assignable

**APPENDIX 4**

## ENVIRONMENTAL MONITORING LEVELS OF TRICHLOROBENZENES IN SURFACE WATER

| Area | Year of Measurement | Average or median concentration (µg/l) | Reference |
|---|---|---|---|
| **Germany** | | | |
| Rhine - NL border | 1993 | < 0.2 | Deutsche Kommission zur Rheinhaltung des Rheins (DKR) 1995 |
| | 1994 | < 0.2 | DKR, 1996 |
| | 1995-1996 | <0.01 | COMMPS |
| Elbe - estuary | 1993 | < 0.001-0.005 | IKSE, 1993 |
| Hamburg | 1993 | 0.001-0.002 | IKSE, 1993 |
| estuary | 1994-1995 | from <0.0004 to 0.02 | COMMPS |
| Emsher | 1989 | < 0.1 | NRW, 1990 |
| North Sea coast | 1983 | 0.00003-0.00059 | BUA, 1987 |
| German Bay | 1989 | 0.0002-0.0074 | UBA, 1989 |
| **The Netherlands** | | | |
| Rhine – border | 1990 | < 0.1 | RIWA, 1993 |
| estuary | 1983 | 0.002-0.03 | Van de Meent *et al.*, 1986 |
| Maassluis | 1996-1997 | <0.01 | COMMPS |
| Schelde-Schaar Van Ouden Doel | 1996-1997 | from <0.01 to 0.07 | COMMPS |
| Coastal waters | 1983 | 0.0007-0.0016 | Van de Meent *et al.*, 1986 |
| Meuse - border | 1990 | < 0.1 | RIWA, 1993 |
| **United Kingdom** | | | |
| Tees estuary | 1996 | < 0.01 | UK Environmental Agency, 1997 |
| Forth estuary | 1990 | < 0.0012-0.084 | Harper *et al.*, 1992 |
| Kent estuary | 1994-1996 | <0.1 | COMMPS |
| Lune estuary | 1994-1996 | <0.1 | COMMPS |
| Mersey estuary | 1994-1996 | from<0.1 to 9 | COMMPS |
| Ribble estuary | 1994-1996 | <0.1 | COMMPS |
| **France** | | | |
| Seine River - Honfleur | 1995 | < 0.4 | Agence de Bassin, 1996 |
| Seine estuary | 1995 | <0.02 | COMMPS |
| **Denmark** | | | |
| Aarhus county | 1997 | <0.01 | COMMPS |

1. The symbol < indicates that the value is under the detection limit of the analytical method
2. COMMPS refers to the database developed in the Fraunhofer study (1998)

**APPENDIX 4**

## ENVIRONMENTAL MONITORING LEVELS OF TRICHLOROBENZENES IN RIVER WATER SEDIMENT

| Area | Year of Measurement | Average or median concentration (µg/kg w.w.) | Reference |
|---|---|---|---|
| **Germany** | | | |
| Rhine - Bimmen | 1994-1995 | from < 1 to 83 | COMMPS |
| Lobith | 1995 | from 7 to 18 | COMMPS |
| Maassluis | 1995 | from 18 to 30 | COMMPS |
| Elbe - estuary | 1994-1995 | from <1 to 5 | COMMPS |
| **The Netherlands** | | | |
| Rhine – Maassluis | 1996-1997 | from <5 to 36 | COMMPS |
| Schelde-Schaar Van Ouden Doel | 1996-1997 | from <2 to 24 | COMMPS |
| **Denmark** | | | |
| Aarhus county | 1997 | from<0.5 to 3.3 | COMMPS |

1. The symbol < indicates that the value is under the detection limit of the analytical method
2. COMMPS refers to the database developed in the Fraunhofer study (1998)

## APPENDIX 1

**NORTH SEA MONITORING DATA ON 1,2,4-TRICHLOROBENZENE**