Substance name: 1,2,4 – Trichlorobenzene
EC number: 204-428-0
CAS number: 120-82-7

MEMBER STATE COMMITTEE
SUPPORT DOCUMENT FOR AGREEMENT ON
1,2,4 - Trichlorobenzene

Adopted on 3 December 2010
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CAS Number: 120-82-1

- It is considered that it is currently not possible to conclude on the identification of 1,2,4 – Trichlorobenzene as a substance of very high concern in accordance with Article 57(f) of Regulation (EC) 1907/2006.

Summary of the evaluation

Based on the data available 1,2,4 – Trichlorobenzene is persistent (P) as the criterion for persistency according to Annex XIII is met and it may be very persistent (vP) in sediments and soil. However, with regard to the bioaccumulation (B) and toxicity (T) criteria, such a conclusion cannot be drawn. Nevertheless the substance still has a significant bioaccumulation and toxicity potential to aquatic organisms.

In addition, results of model calculations have shown a high long-range transport potential of the substance. The potential occurrence of serious effects in biota in remote and sensitive ecosystems was considered, taking into account the intrinsic properties of the substance. However based on the information available it is considered that it is currently not possible to conclude on the identification of 1,2,4 – Trichlorobenzene as a substance of very high concern in accordance with Article 57(f) of Regulation (EC) 1907/2006.
JUSTIFICATION

1 IDENTIFY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Chemical Name: Benzene, 1,2,4-Trichloro-
EC Name: 1,2,4-Trichlorobenzene
EC Number: 204-428-0
CAS Number: 120-82-1
IUPAC Name: 1,2,4-Trichlorobenzene

1.2 Composition of the substance

The detailed composition of the substance is confidential and provided in the technical dossier.

Chemical Name: Benzene, 1,2,4-Trichloro-
EC Number: 204-428-0
CAS Number: 120-82-1
IUPAC Name: 1,2,4-Trichlorobenzene
Molecular Formula: C₆H₃Cl₃
Structural Formula:

Molecular Weight: 181.45 g/mol
Typical concentration (% w/w): Min. > 99 % (w/w)
Concentration range (% w/w): -

1.3 Physico-chemical properties

Table 1: Summary of physico-chemical properties
<table>
<thead>
<tr>
<th>REACH ref Annex, §</th>
<th>Property</th>
<th>IUCLID section</th>
<th>Value</th>
<th>[enter comment/reference or delete column]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII, 7.1</td>
<td>Physical state at 20°C and 101.3 kPa</td>
<td>4.1</td>
<td>liquid</td>
<td>European Communities, 2003</td>
</tr>
<tr>
<td>VII, 7.2</td>
<td>Melting/freezing point</td>
<td>4.2</td>
<td>16-17 °C</td>
<td>European Communities, 2003</td>
</tr>
<tr>
<td>VII, 7.3</td>
<td>Boiling point</td>
<td>4.3</td>
<td>213.5 °C at 1013 hPa</td>
<td>European Communities, 2003</td>
</tr>
<tr>
<td>VII, 7.5</td>
<td>Vapour pressure</td>
<td>4.6</td>
<td>36 Pa at 20 °C</td>
<td>European Communities, 2003</td>
</tr>
<tr>
<td>VII, 7.7</td>
<td>Water solubility</td>
<td>4.8</td>
<td>36 mg/L at 20 °C</td>
<td>European Communities, 2003</td>
</tr>
<tr>
<td>VII, 7.8</td>
<td>Partition coefficient n-octanol/water (log value)</td>
<td>4.7</td>
<td>log K&lt;sub&gt;ow&lt;/sub&gt; 4.05</td>
<td>European Communities, 2003</td>
</tr>
<tr>
<td>XI, 7.16</td>
<td>Dissociation constant</td>
<td>4.21</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>VII, 7.4</td>
<td>Density</td>
<td>4.4</td>
<td>1.456 g/cm³ at 20 °C</td>
<td>European Communities, 2003</td>
</tr>
<tr>
<td>VII, 7.9</td>
<td>Flash point</td>
<td>4.11</td>
<td>110 °C, (close cup)</td>
<td>PTB-AG 3.43, CHEMSAFE, 2009</td>
</tr>
<tr>
<td>VII, 7.10</td>
<td>Flammability</td>
<td>4.13</td>
<td>Pyrophoric properties: The classification procedure need not be applied because the organic substance is known to be stable into contact with air at room temperature for prolonged periods of time (days). Flammability in contact with water: The classification procedure need not to be applied because the organic substance does not contain metals or metalloids. Flammability upon ignition (solids, gases): Testing is technically not possible, substance is a liquid.</td>
<td>BAM, II.2 (2010)</td>
</tr>
<tr>
<td>VII, 7.11</td>
<td>Explosive properties</td>
<td>4.14</td>
<td>The classification procedure needs not to be applied because there are no chemical groups present in the molecule which are associated with explosive</td>
<td>BAM, II.2 (2010)</td>
</tr>
</tbody>
</table>
VII, 7.12  Auto-ignition temperature (Liquids and Gases)  4.12  571 °C  PTB-AG 3.43, CHEMSAFE, 2009

VII, 7.13  Oxidising properties  4.15  The classification procedure need not to be applied because contained chlorine atoms are chemically bonded only to carbon.  BAM, II.2 (2010)

1) The value 17°C is used in the EU risk assessment
2) measured; used for EU risk assessment
2 HARMONISED CLASSIFICATION AND LABELLING

1,2,4-Trichlorobenzene (1,2,4-TCB) entry in Table 3.1 of Annex VI of Regulation (EC) 1272/2008 as amended by the 1st ATP:

Index Number: 602-087-00-6

Acute Tox. 4* H302 (Harmful if swallowed) GHS07
Skin Irrit. 2 H315 (Causes skin irritation) GHS09
Aquatic Acute 1 H400 (Very toxic to aquatic life) Wng H410
Aquatic Chronic 1 H410 (Very toxic to aquatic life with long lasting effects)

1,2,4-TCB entry in Table 3.2 of Annex VI of Regulation (EC) 1272/2008 as amended by the 1st ATP:

Index Number: 602-087-00-6

Xn; R22 (Harmful if swallowed)
Xi; R38 (Irritating to skin)
N; R50-53 (Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment)
3 ENVIRONMENTAL FATE PROPERTIES

3.1 Degradation

A large part of the data presented in this section are quoted from the Risk Assessment Report (European Commission, 2003)

3.1.1 Abiotic degradation

3.1.1.1 Hydrolysis

Based on the experimental data (Korte and Freitag, 1986) on hydrolysis at 50°C, 1,2,4-trichlorobenzene (1,2,4-TCB) is not expected to hydrolyse under normal environmental conditions (Howard, 1989; Schmidt-Bleek et al., 1982).

3.1.1.2 Phototransformation / photolysis

3.1.1.2.1 Phototransformation in air

The atmospheric half-life of 1,2,4-TCB due to photodegradation by hydroxyl radicals is estimated to be in the order of a month. The following table summarises the photodegradation data.

<table>
<thead>
<tr>
<th>Rate constant cm$^3$/molecule/s</th>
<th>Half-life (days)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.32 \times 10^{-13}$</td>
<td>18.5</td>
<td>Experimental</td>
<td>(European Commission, 2003)</td>
</tr>
<tr>
<td>$5.32 \times 10^{-13}$</td>
<td>30.2</td>
<td>Measured, 296°C</td>
<td>(Rinke and Zetzsch, 1984)</td>
</tr>
<tr>
<td>$2.82 \times 10^{-13}$</td>
<td>38</td>
<td>Calculated by AOP programme</td>
<td>(AOPWIN, 1995)</td>
</tr>
</tbody>
</table>

The reaction of 1,2,4-TCB with OH radicals was investigated in the presence of helium at pressures from 5 to 800 mbar using a pulsed vacuum UV photolysis-resonance fluorescence apparatus. At 23°C and 133 mbar helium, the rate constant $k$ was observed to be $0.5.10^{12}$ cm$^3$/s (Rinke and Zetzsch, 1984). Assuming an average tropospheric OH radical concentration of $5.10^5$ molecules/cm$^3$, the half-life is about 30 days (BUA, 1987).

In the atmosphere, the estimated vapour phase half-life of 1,2,4-TCB was 18.5 days, estimated as a result of reaction with photochemically produced hydroxyl radicals at $8.10^5$ molecules/cm$^3$, giving a reaction rate of $0.532.10^{12}$ cm$^3$/molecules/s (European Commission, 2003).

The photochemical oxidation was estimated using the structure analysis by the model AOPWIN for comparison (AOPWIN, 1995). The estimated half-life of 38 days is based on an OH-radical concentration of $1.5.10^6$ molecules/cm$^3$ and a 12-hour daylight period. The previous model used $5.10^5$ molecules/cm$^3$ which was a 24-hour average value that included night-time. Using $5.10^5$ molecules/cm$^3$ (24 hours) would result in a DT$_{50}$ of 57 days estimated by AOPWIN.
Using an experimental value for the OH rate constant of $0.55 \times 10^{-12}$ cm$^3$/molecules/s and by setting the OH radical concentration to $5 \times 10^5$ molecules/cm$^3$, a $DT_{50}$ of 29 days would be estimated (Rippen, 1995). The value is based on the geometric mean of the measured absolute $K_{OH}$ value (296 K) $0.5 \times 10^{-12}$ cm$^3$/s and a relative measured $K_{OH}$ value (300 K) $0.6 \times 10^{-12}$ cm$^3$/s.

Measured and calculated OH rate constants are in good agreement and the rate constant of $0.532 \times 10^{-12}$ cm$^3$/molecules/s (European Commission, 2003) is used as input for calculations on the long-range transport potential.

The removal of 1,2,4-TCB from air may be due to degradation by chemical- or sunlight-catalysed reactions or by absorption onto particles that settle or are removed from the atmosphere by rain. A measure of the effectiveness of these factors is the atmospheric residence time. In a field study in California and Arizona, air samples during a two-week period included unspecified trichlorobenzene. The estimated residence time was 116 days, assuming an average daily (24 hours) abundance of OH radicals of $10^6$ molecules/cm$^3$ (Singh et al., 1981).

3.1.1.2.2 Phototransformation in water

Degradation by direct photolysis is not expected to be essential because the maximum absorption value is 286 nm (Bayer spectral data). The half-life for sunlight photolysis in pure surface water at 40° latitude in summer was 450 years (Dulin et al., 1986). The recovery of 1,2,4-TCB from isopropanol solution in Pyrex glass tubing (with a cut-off at 285 nm) irradiated with 300 and 310 nm fluorescent lamps for 30 minutes was 89.4% under anaerobic conditions where O$_2$ was replaced with N$_2$ and 8.1% under aerobic conditions. The products of photodegradation were 1,3- and 1,4-dichlorobenzene (Akermark et al., 1976).

In a laboratory study using artificial light (high pressure mercury vapour lamp at wavelengths > 290 nm), the photodegradation was studied at a concentration of 2-5 ppm. 1,2,4-TCB was dissolved in distilled water and filtered river water. The photolytic half-life was estimated to be 16.7 hours in distilled water and 12.2 hours in river water. The photolysis products in river water were 1,4-dichlorophenol and 4-chlorophenol (Mansour et al., 1989).

The photolysis was studied by exposing 5 ml 1,2,4-TCB at 4 µg/ml at a distance of 30 cm from artificial light (two Fluorochemical lamps 20Wx2) at 25°C. After 144 hours, 0% was degraded (Kondo et al., 1988).

In a test where 1,2,4-TCB was adsorbed on silica gel and irradiated with light at wavelengths >290 nm for 17 hours, 9.8% of the applied amount was degraded to CO$_2$ (Freitag et al., 1985).

In addition to the direct photolysis, the photodegradation may also follow an indirect photolysis by sensitisation or by secondary reactions with OH- and O$_2$-radicals. The photolysis was studied in water solutions (1,2,4-TCB conc.: 4-20 mg/600ml) irradiated for 3 hours. The photoreactivity in solutions in the presence of nitrite was observed to increase the photodegradation rate. The rate constant in pure water was $1.5 \times 10^{-4}$s$^{-1}$ resulting in $DT_{50}$ to be 1.2 hours. In water added nitrite, the rate constant $k$ was $3.1 \times 10^{-4}$s$^{-1}$ and the resulting $DT_{50}$ 0.4 hours (Kotzias et al., 1982). The study was conducted under artificial conditions but indicates that photolysis may be affected by the contents in water. In the study, salts were used but other organic substances and organic matter may also affect the photodegradation rate. Although some photodegradation of 1,2,4-TCB may occur in water it is deemed a very slow process (European Commission 2003) and not expected to be a relevant
degradation process, probably apart from very shallow clear waters in the first few centimetres of the water column. However, the substance is dispersed in the whole water column. Therefore aquatic photodegradation is not considered to have a relevant impact on the overall persistency of 1,2,4-TCB in the environment. In addition, because of the adsorption behaviour of the substance, it will predominantly adsorb to suspended organic matter and sediment (and to soil because of atmospheric washout).

**Summary**

On the basis of the available data, abiotic degradation of 1,2,4-TCB in the atmosphere is expected to be slow (DT$_{50}$ between 18.5 and 38 days). The substance is not expected to hydrolyse under environmental conditions and photodegradation in natural waters is expected to be very slow.

**3.1.2  Biodegradation**

**3.1.2.1  Screening tests**

The ready biodegradability was studied with a method corresponding to the OECD TG 301C, Modified MITI (I) test (MITI-List, 2002). The test concentration was 100 mg/l and activated sludge concentration 30 mg/l. The degradation measured as Biochemical Oxygen Demand (BOD) was 0% after 14 days.

The BOD$_{20}$ value for 1,2,4-TCB was studied using microorganisms from an industrial wastewater treatment plant normally exposed to phenolics and other industrial chemicals (i.e. adapted inoculum) (Simmons et al., 1977). The concentration of 1,2,4-TCB was 1.69 and 2.61 mg/l. Although no apparent biodegradation was indicated by the BOD oxygen uptake until day 10, GC-ECD analysis of the remaining 1,2,4-TCB indicated that the substance began to disappear within 1 to 5 days. 99% and 100% of the 1,2,4-TCB had disappeared in 10 days as determined by the GC-ECD analysis while the BOD test indicated 55% of the theoretical oxygen demand (ThOD). The remaining 45% ThOD was stated to be incompletely oxidised metabolites of 1,2,4-TCB. BOD$_{10}$ and BOD$_{20}$ were 55% and 55% using 1.7 mg/l and 19% and 55% using 2.6 mg/l, respectively. The test with the initial concentration of 2.6 mg/l showed a delayed degradation, which could be an advice for toxicological effects. The ThOD at the test with the initial concentration of 1.7 mg/l was unchanging between day 10 and day 20. Furthermore, it is not clear if volatilization was considered. The study indicated rather disappearance than biodegradation.

A static culture flask biodegradation screening study was used to determine the biodegradability at two concentrations of 1,2,4-TCB (5 and 10 mg/l), a 7-day static incubation at 25°C followed by three weekly subcultures of yeast and settled domestic wastewater (non-adapted) as microbial inoculum (Tabak et al., 1981). A gradual adaptation process followed by a de-adaptive process in subsequent subcultures (reduced degradation and accumulation of 1,2,4-TCB in the media) was observed. For the original culture 54% and 43% degradation were observed after 7 days at 5 and 10 mg 1,2,4-TCB/l, respectively. This test is less stringent than a standard ready biodegradability test because of the presence of an extra carbon source (yeast) allowing for co-metabolism. Further, it is not clear whether the reported biodegradation percentages are referring to the removal of parent compound or to mineralisation.

On the basis of these three available laboratory biodegradation screening tests, 1,2,4-TCB is not readily biodegradable but biodegradation might occur to a certain degree under conditions favouring biodegradation (adapted sludge as inoculum or presence of an additional carbon source).
3.1.2.2 Simulation tests

In a study by Simmons et al., using $^{14}$C-labelled substance at 0.345 mg/l, the degradation was studied in activated sludge from a textile plant wastewater (i.e. adapted) by measuring $^{14}$CO$_2$ development (Simmons et al., 1977). After 5 days, 56% was recovered as $^{14}$CO$_2$, 23% as polar metabolites, 7% was evaporated and 13% remained as 1,2,4-TCB. The reduced volatilisation is stated to be caused by the high organic sludge environment since 80% was adsorbed to solids and 20% was actually in the water. The amount of $^{14}$C-1,2,4-TCB converted to $^{14}$CO$_2$ was 33% in 1 day and 56% in 5 days. These results indicate that the substance is partly susceptible to biodegradation by adapted micro-organisms.

The removal from seawater was studied in mesocosm studies, which included consideration of volatilisation (Wakeham et al., 1983). The tanks were 5.5 m high and 1.8 m in diameter and contained 13 m$^3$ seawater. In the study, a mixture of volatile organic compounds was added. The dissipation was studied at conditions spring (8-16°C), summer (20-22°C) and winter (3-7°C). The initial concentration of 0.5 $\mu$g/l was equivalent to the concentration measured in a moderately polluted bay. The concentrations were measured during 1-2 months.

**Table 3: Removal of 1,2,4-TCB in mesocosms (Wakeham et al., 1983)**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Initial concentration (mg/l)</th>
<th>Rate constant</th>
<th>DisDT$_{50}$ (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring (Apr. 15-Jun. 18)</td>
<td>8-16</td>
<td>0.5</td>
<td>-0.032</td>
</tr>
<tr>
<td>Summer (Aug. 19-Sep. 8)</td>
<td>20-22</td>
<td>0.2</td>
<td>-0.066</td>
</tr>
<tr>
<td>Winter (Mar. 4-May 4)</td>
<td>3-7</td>
<td>2.2</td>
<td>-0.058</td>
</tr>
<tr>
<td>Water with HgCl$_2$ (Sept. 9th to 15th)</td>
<td>0.2</td>
<td>-0.073</td>
<td>9.5</td>
</tr>
<tr>
<td>Water without HgCl$_2$</td>
<td>0.3</td>
<td>-0.066</td>
<td>10.6</td>
</tr>
</tbody>
</table>

The dissipation was relatively independent of temperature with half-lives of 2-3 weeks regardless of the season. Retardation of the biological activity by adding HgCl$_2$ (2 mg/l) did not increase the summer dissipation time. Therefore, the dissipation was assumed to be primarily dissipation by volatilisation and not biodegradation. Thus, volatilisation dominates the dissipation of 1,2,4-TCB whereas biodegradation is of less importance according to the authors.

Trichlorobenzenes are chemically stable in both aerobic and anaerobic environments. In studies on the degradation in anaerobic sediments, trichlorobenzenes were reductively dechlorinated to monochlorobenzenes via dichlorobenzenes. 1,2,4-TCB was transformed via 1,4-dichlorobenzene (Bosma et al., 1988) and via 1,2- and 1,3- dichlorobenzenes (Peijnenburg et al., 1992). The study by Bosma et al. was performed as a study using 25 cm high and 5.5 cm internal diameter columns wet packed with sediment from the River Rhine near Wageningen. The columns were percolated continuously at a flow rate of 1 cm/h in an upflow mode. It was concluded that the observed removal was due to biological processes because of the long lag-phase preceding the onset of disappearance and because there was no elimination in a batch of anaerobic autoclaved sediment. The study by Peijnenburg et al. was performed in a methanogenic sediment-water system maintained at 22°C in a nitrogen atmosphere. The sediments were taken from a slow flowing river and a eutrophic pond. The anaerobic degradation rates were $\log k = -5.64$ min$^{-1}$ and $\log k = -5.62$ min$^{-1}$ (corresponding to half-lives of 212 days and 202 days), respectively. 1,2-, 1,3- and 1,4-
dichlorobenzenes were formed in ratios of approximately 1.5:1:1.5, as confirmed by GC. Almost immediately after incubation began, monochlorobenzene could be detected.

1,2,4-TCB can be degraded in soil, although very slowly (Marinucci and Bartha, 1979). The aerobic mineralisation was studied using \(^{14}\)C-labelled 1,2,4-TCB and a mineralisation rate measured as CO\(_2\) development/day. In a study using a sandy loam (pH 6.5) added 1,2,4-TCB at a concentration of 50 µg/g soil, the degradation in soil was observed to be slow. The incubation was performed at 20°C for 3 to 12 weeks. 1,2,4-TCB was subject to mineralisation as soil poisoned with 1% HgCl\(_2\) or NaN\(_3\) reduced the CO\(_2\) evolution consistently. Anaerobic conditions either continuously or alternated weekly with aerobic incubation periods markedly depressed the mineralisation. The mineralisation rate was 0.181 µg/day/20 g soil equivalent to 9 µg/d/kg. The turnover rate (% 1,2,4-TCB converted to CO\(_2\)/day = 0.075%) was maximal at 10 µg/g soil and sharply declined at higher concentrations. Haider et al. used 10 µg/g (in 100 g soil) and observed a mineralisation rate about twice as high (Haider et al., 1974).

In addition to the experiments reviewed in the Risk Assessment Report (European Commission, 2003), two other biodegradation studies are available. Bartholomew and Pfaender conducted simulation type of tests measuring mineralisation (\(^{14}\)CO\(_2\) respiration) and uptake of \(^{14}\)C labelled metabolites (Bartholomew and Pfaender, 1983; Pfaender and Bartholomew, 1982). Kinetic values for the total biodegradation of 1,2,4-TCB covering both incorporation of \(^{14}\)C into biomass and \(^{14}\)CO\(_2\) -production, are illustrated in Table 4. The tests have also been reviewed by Battersby (Battersby, 1990).

Table 4: Biodegradation rates for 1,2,4-trichlorobenzene as derived by Bartholomew and Pfaender and the corresponding half-lives (Bartholomew and Pfaender, 1983)

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>Temperature (°C)</th>
<th>(V_{\text{max}}/K_m=k_1) (d(^{-1}))</th>
<th>(T_{1/2}) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River, upstream</td>
<td>7 Nov .80</td>
<td>12</td>
<td>0.028</td>
<td>24.8</td>
</tr>
<tr>
<td>River, upstream</td>
<td>26 May 81</td>
<td>24</td>
<td>b.d. 2)</td>
<td>-</td>
</tr>
<tr>
<td>Estuary</td>
<td>7 Nov.80</td>
<td>14</td>
<td>b.d. 2)</td>
<td>-</td>
</tr>
<tr>
<td>Estuary</td>
<td>26 May 81</td>
<td>28</td>
<td>0.027</td>
<td>25.7</td>
</tr>
<tr>
<td>Marine</td>
<td>7 Nov.80</td>
<td>17</td>
<td>b.d. 2)</td>
<td>-</td>
</tr>
<tr>
<td>Marine</td>
<td>26 May 81</td>
<td>24</td>
<td>0.012</td>
<td>57.8</td>
</tr>
</tbody>
</table>

1) Original data from Bartholomew and Pfaender (1983); calculations similar to those in Battersby (1990)
2) b.d., below detection limit (\(V_{\text{max}}\) was less than 1 ng liter\(^{-1}\) h\(^{-1}\) and less than the metabolic rate that could be detected by the experimental method)

The data in Table 4 indicate that 1,2,4-TCB is degraded under some conditions with half-lives of approximately 25 days in fresh and estuarine waters and below 60 days in marine water. However, biodegradation rates were too low to be determined in half of the experiments. No explanation for the different results was provided by the authors. The \(^{14}\)CO\(_2\) production was reported to be very low in general (no values provided by the authors), which implies that the \(^{14}\)C incorporated by the biomass consisted of metabolites that were not further degraded during the experiment. It can be assumed, that the results of these two experiments do not change the overall picture provided by the other simulation type of studies available.
The behaviour and fate of chlorobenzenes in spiked and sewage sludge-amended soil was tested by Wang and Jones (Wang and Jones, 1994). For testing the fate, four different experimental conditions were investigated: (1) normal; (2) sterilized; (3) sterilized and shaded; (4) sterilized, shaded and sealed. Under condition (4) no decrease of concentration was observed. Whereas under condition (1)-(3) the concentration of TCB decreased. This indicated volatilization as main loss process. The loss process in soil occurs in two steps (two step first order kinetic model). In the first step the TCB volatilize to the atmosphere over short periods. The second step was much slower and was presumably controlled by the rate of compound desorption from soil. A proportion of the TCB will stay in the soil for much longer periods. The concentration in spiked soil decreased faster than in sludge amended soil.

Table 5: Half-lives of TCB in the sewage sludge-amended soil and standard spiked soil in microcosm experiments (Wang and Jones, 1994)

<table>
<thead>
<tr>
<th>Compound</th>
<th>First step</th>
<th></th>
<th>Second step</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sewage sludge-amended soil</td>
<td>Standard spiked soil</td>
<td>Sewage sludge-amended soil</td>
</tr>
<tr>
<td></td>
<td>Loss (%)</td>
<td>DisDT50 (d)</td>
<td>Loss (%)</td>
<td>DisDT50 (d)</td>
</tr>
<tr>
<td>1,2,4-TCB</td>
<td>83.2</td>
<td>22.5</td>
<td>64.5</td>
<td>12.5</td>
</tr>
<tr>
<td>1,2,3-TCB</td>
<td>88.6</td>
<td>22.2</td>
<td>73.0</td>
<td>15.0</td>
</tr>
<tr>
<td>1,3,5-TCB</td>
<td>85.3</td>
<td>23.7</td>
<td>71.2</td>
<td>10.5</td>
</tr>
</tbody>
</table>

A marine risk assessment on 1,2,4-TCB was carried out by van Wijk et al. (van Wijk et al., 2006). In contrast to the EU risk assessment report (European Commission, 2003) and the results of the EU PBT working group this paper characterised 1,2,4-TCB as non persistent.

The assessment of van Wijk et al. (van Wijk et al., 2006) contains no new tests, but is based on a review of existing data. However, in the majority of cases the experiments showing biodegradability were realized with isolated and enrichment cultures (Adrian et al., 2000; Brunsbach and Reineke, 1994; Nowak et al., 1996; Rapp and Timmis, 1999; Sander et al., 1991; Van der Meer et al., 1987) or the material was pre-exposed (Masunaga et al., 1996). Hence, the respective microorganisms were adapted. Furthermore, the studies showing persistence in soil and sediment (Wang and Jones, 1994; Peijnenburg et al., 1992) are not considered in this assessment.

3.1.3 Summary and discussion on degradation

1,2,4-TCB has a low degradation rate in the atmosphere (DT50 between 18.5 and 38 days) and is not expected to hydrolyse under environmental conditions. Screening studies indicate that 1,2,4-TCB is not readily biodegradable. Further studies show relatively long dissipation time (DisDT50soil = 194 days) and indicate slow degradation in soil. For an evaluation of persistence, the degradation half life is required which is either greater than or equal to the dissipation time. Thus, the degradation half life in soil is considered to be greater than or equal to 194 days. In freshwater sediment, degradation half-lives of more than 200 days were detected. It should be noted that no simulation test performed according to international guidelines is available. However, regarding the available data in a weight of evidence approach, further testing is unlikely to change the overall conclusion.
Based on the data available, 1,2,4-trichlorobenzene is persistent (P) as the criterion for persistency according to Annex XIII is met and it may be very persistent (vP) in sediments and soil.

3.2 Environmental distribution

3.2.1 Adsorption/desorption

Based on model estimates, a Koc of 2400 L/kg has been estimated (ECHA, 2008). Therefore, a high adsorption potential and a low mobility in soil is expected for 1,2,4-Trichlorobenzene. Due to the slow degradation in soil, the substance may contaminate groundwater by leaching through sandy soils with low organic carbon content.

3.2.2 Volatilisation

Calculation of the Henry constant using the equation HENRY=VP*MOLW/SOL from the Guidance document for Chemical Safety Assessment (ECHA, 2008) and the substance properties from table 1 results in a Henry constant of 181.45 Pa*m³*Mol⁻¹. This indicates that the substance is highly volatile from water. Due to the high adsorption potential to organic matter, volatilisation from soil and sludge is expected to be lower.

The distribution coefficient $K_{air,water}$ (Henry coefficient) calculated from the Henry constant is $7.448 \times 10^{-2}$.

3.2.3 Distribution modelling

Distribution in Waste Water Treatment Plant

The modelling of the distribution in a municipal Waste Water Treatment Plant was done with SimpleTreat 3.0 (debugged version, 7 Feb 1997) and the result of the Screening Test on ready biodegradation (substance is not biodegradable; $k=0$/h).

Table 6: Distribution in WWTP (Simple Treat 3.0)

<table>
<thead>
<tr>
<th>Summary of distribution</th>
<th>(Percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>To air</td>
<td>61.8</td>
</tr>
<tr>
<td>To water</td>
<td>20.1</td>
</tr>
<tr>
<td>Via primary sludge</td>
<td>16.1</td>
</tr>
<tr>
<td>Via surplus sludge</td>
<td>1.9</td>
</tr>
<tr>
<td>Degraded</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

The result of the distribution modeling in a WWTP indicates that nearly 62 percent of the 1,2,4-TCB found in the influent waste water is emitted to air.

Long-range Transport

An important indicator for the spatial range of chemicals can be the long-range transport to remote areas. For the calculation of the long-range transport potential of 1,2,4-Trichlorobenzene two different multimedia models have been used. On the one hand the OECD $P_{ov}$ and LRTP Screening Tool (OECD, 2006) has been used and on the other hand the model ChemRange (Scheringer, 1996).
Both models require only a few input parameters. These are the partition coefficients octanol/water, Kow, the dimensionless Henry’s Low Constant, Kaw and the environmental degradation half-lives in air, water and soil.

Unfortunately only very few measured half-lives are available for 1,2,4-Trichlorobenzene. These are the half-life in air and a measured DisT50 in soil. Although, it is well known that this DisT50 represents not only degradation this value was used in the calculation. 1,2,4-Trichlorobenzene is benchmarked as “non-biodegradable”. According to TGD (ECHA 2008) the half-lives in soil and water have to be considered as infinite. However the models require a discrete value for the simulation. Due to this fact the half-lives according to the TGD for inherent biodegradation in water of 150 d and 3000 d in soil have been used. Furthermore, the half-lives in water have been calculated on the one hand according to Arnot (Arnot et al., 2005) and on the other hand using the QSAR-model CATALOGIC (OASIS Catalogic v5.10.7, 2009). Finally, four calculations with different half-lives for water and soil has been carried out to show the influence of these half-lives on the long-range transport potential of 1,2,4-Trichlorobenzene.

Table 7: Input parameters for both models

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>1,2,4-TCB (TGD)</th>
<th>1,2,4-TCB (Arnot)</th>
<th>1,2,4-TCB (Catalogic)</th>
<th>1,2,4-TCB (measured soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>logKow</td>
<td>4.05</td>
<td>4.05</td>
<td>4.05</td>
<td>4.05</td>
</tr>
<tr>
<td>logKaw</td>
<td>-1.128</td>
<td>-1.128</td>
<td>-1.128</td>
<td>-1.128</td>
</tr>
<tr>
<td>t½ (air) [d]</td>
<td>18.5</td>
<td>18.5</td>
<td>18.5</td>
<td>18.5</td>
</tr>
<tr>
<td>t½ (water) [d]</td>
<td>150</td>
<td>91.025</td>
<td>82</td>
<td>150</td>
</tr>
<tr>
<td>t½ (soil) [d]</td>
<td>3000</td>
<td>273.075</td>
<td>246</td>
<td>194</td>
</tr>
</tbody>
</table>

Results using the OECD Po and LRTP Screening Tool:

Figure 1 shows that all four calculations yield nearly the same values for characteristic travel distance (CTD) and overall persistency (Po). Substances with CTD and Po values of this magnitude are considered to show a high long-range transport potential.
In order to benchmark the calculated long-range transport potential of 1,2,4-Trichlorobenzene the results have been compared with the long-range transport potential of the well known POPs PCB 28, PCB 101 and PCB 153, regulated under the Stockholm Convention. In Table 8, the characteristic travel distances (CTD) calculated with the OECD $P_{ov}$ and LRTP Screening Tool are listed:

**Table 8: Characteristic Travel Distances [km]**

<table>
<thead>
<tr>
<th>Substance</th>
<th>CTD [km]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,4-Trichlorobenzene (Arnot)</td>
<td>9018</td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene (Catalogic)</td>
<td>9010</td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene (measured soil)</td>
<td>9050</td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene (TGD)</td>
<td>9053</td>
</tr>
<tr>
<td>PCB 153</td>
<td>12629</td>
</tr>
<tr>
<td>PCB 101</td>
<td>8595</td>
</tr>
<tr>
<td>PCB 28</td>
<td>3298</td>
</tr>
</tbody>
</table>

Figure 2 illustrates that the long-range transport potential of 1,2,4-Trichlorobenzene is in the same order of magnitude as the long-range transport potential of all three PCBs.
Furthermore, a sensitivity analysis has been carried out using the Monte Carlo method. The atmospheric half-life in air turned out to be the most relevant parameter; its contribution to the overall variance in CTD is about 98.6%.

**Results using ChemRange:**
In contrast to the OECD P_{ov} and LRTP Screening Tool, ChemRange calculates the spatial range of a chemical. The spatial range is calculated as the fraction of earth circumference which can be reached by a substance. The long-range transport is calculated for the surface compartments soil, water and air. In order to benchmark the calculated long-range transport potential of 1,2,4-Trichlorobenzene the results have been compared with the long-range transport potential of the well known POPs PCB 28, PCB 101 and PCB 153 regulated under the Stockholm Convention. Using a release scenario to air the calculated spatial ranges are listed in **Table 9**:

**Table 9: Spatial ranges**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Range soil (Fraction of earth circumference)</th>
<th>Range water (Fraction of earth circumference)</th>
<th>Range air (Fraction of earth circumference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,4-Trichlorobenzene (Arnot)</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene (Catalogic)</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Comparison of results
The calculated spatial ranges for 1,2,4-TCB using a release scenario to soil are very similar. The high long-range transport potential of 1,2,4-Trichlorobenzene and PCB 28 is illustrated by Figure 3 and Figure 4: Both diagrams are similar and show a shape which is characteristic for substances with a high long-range transport potential. In case of a substance with a low long-range transport potential the shape of the plot would show just a sharp peak at the source point.

![Relative steady-state concentration distribution of 1,2,4-TCB](image)

Figure 3: Relative steady-state concentration distribution of 1,2,4-Trichlorobenzene.
Conclusions:
Due to its high volatility (Henry constant of 181.45 Pa*m³*Mol⁻¹), 1,2,4-TCB is expected to be distributed from water to air. In the air, 1,2,4-TCB is persistent (estimated half lives between 18.5 and 38 days) and may be transported via air for several thousand kilometres. Distributed by this pathway also to remote areas, 1,2,4-TCB will be deposited there again to soil or water where it may be even more persistent e.g. due to lower temperatures.
Model calculations confirm the expected potential for long-range transport, as both the OECD POP and LRTP Screening Tool and ChemRange yield a long-range transport potential that is in the same order of magnitude for 1,2,4-Trichlorobenzene and for the POPs PCB 101, 153 and PCB 28.
Thus, it can be concluded that 1,2,4-Trichlorobenzene is persistent in air and has a high long-range transport potential.

3.3 Bioaccumulation

3.3.1 Aquatic bioaccumulation

3.3.1.1 Bioaccumulation estimation

The log $K_{ow}$ of 4.05 is indicating that bioconcentration in aquatic organisms may occur due to high lipophilicity.
### Measured bioaccumulation data

#### Table 10: Available bioconcentration factors (BCF) as measured in aquatic organisms and normalized on lipid content

<table>
<thead>
<tr>
<th>Organism</th>
<th>Exposure mg/L</th>
<th>Exposure days</th>
<th>BCF whole body</th>
<th>Lipid content</th>
<th>BCF 5% lipids</th>
<th>Reference</th>
<th>Rel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Jordanella floridae</em></td>
<td>0.0038</td>
<td>28</td>
<td>2026 (kin.)</td>
<td>11.4%</td>
<td>888</td>
<td>(Smith et al., 1990)</td>
<td>2</td>
</tr>
<tr>
<td><em>Cyprinus carpio</em></td>
<td>0.005</td>
<td>42</td>
<td>120-1320 (ss)</td>
<td>not given</td>
<td>-</td>
<td>(MITI-List, 2002)</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>42</td>
<td>420-1140 (ss)</td>
<td>not given</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Salmo gairdneri</em></td>
<td>3.2 *10^-6</td>
<td>119</td>
<td>1300 (ss)</td>
<td>8.3%</td>
<td>783</td>
<td>(Oliver and Niimi, 1983)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>52 *10^-6</td>
<td>105</td>
<td>3200 (ss)</td>
<td>8.8%</td>
<td>1818</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Cyprinus carpio</em></td>
<td>0.004</td>
<td>56</td>
<td>830</td>
<td>4.8%</td>
<td>864</td>
<td>(Broecker et al., 1984)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>56</td>
<td>805</td>
<td>4.8%</td>
<td>838</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Brachydanio rerio</em></td>
<td>0.0085</td>
<td>28</td>
<td>1412</td>
<td>not given</td>
<td>-</td>
<td>(Ballhorn et al., 1984)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>0.2141</td>
<td>28</td>
<td>574</td>
<td>not given</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Poecilia reticulata</em></td>
<td>0.136</td>
<td>17</td>
<td>1139 (ss)</td>
<td>not given</td>
<td>-</td>
<td>(van Eck et al., 1997)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1142 (kin.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Salmo gairdneri</em></td>
<td>note(^1)</td>
<td>note(^3)</td>
<td>not given</td>
<td>124(^2)</td>
<td>344</td>
<td>(Geyer et al., 1985)</td>
<td>4</td>
</tr>
<tr>
<td><em>Pimephales promelas</em></td>
<td>note(^1)</td>
<td>note(^3)</td>
<td>not given</td>
<td>2100(^2)</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crustaceans:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Daphnia</em></td>
<td>0.003</td>
<td>not given</td>
<td>142</td>
<td>not given</td>
<td>-</td>
<td>(Callahan et al., 1979)</td>
<td>4</td>
</tr>
<tr>
<td>Algae:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Chlorella fusca</em></td>
<td>0.05</td>
<td>1</td>
<td>250</td>
<td>not given</td>
<td>-</td>
<td>(Geyer et al., 1984)</td>
<td>4</td>
</tr>
</tbody>
</table>

Reliability scores: 1) reliable without restriction, 2) reliable with restriction, 3) not reliable, 4) not assignable.

\(^1\) A mixture of three isomeric trichlorobenzenes was administered and the individual BCF were calculated. There is no further information given on lipid normalization of BCF;
\(^2\) This study was rated not reliable because fish were exposed simultaneously to 12 substances and the overall concentration may have elicited adverse effects on fish (conc. of 1,2,4-trichlorobenzene = 3.2 / 52 ng/L, overall conc. = 116 / 2544 ng/L);
\(^3\) Comparison of literature-reported BCF values for diverse fish species and varying lipid contents. Original literature not reviewed.

There is a moderate number of studies available, investigating the bioaccumulation potential of 1,2,4-trichlorobenzene. Most of these studies have already been evaluated in the TC NES subgroup on identification of PBT and vPvB substances and the EU Risk Assessment (European Commission, 2003).

In the study on juvenile American flagfish (*Jordanella floridae*) conducted in compliance with ASTM 1978 guideline juvenile fish, four to six month old and with a lipid content of 11.4% were kept in a flow through system at 25°C. After being exposed to a test concentration of 3.8 µg/L for 28 days, a BCF of 2026 was measured (lipid normalized 888). The elimination time half-life was calculated to be 1.2 days (Smith et al., 1990).

The MITI database provides BCF values for 1,2,4-trichlorobenzene determined for carp using a standard test system. Though, a mixture of all three isomeric trichlorobenzenes was administered in
two different overall concentrations and individual concentrations of each isomer in exposure medium as well as in fish were analyzed. The reported maximum BCF values range between 1140 and 1320. Unfortunately no information on lipid content or lipid normalization is explicitly given. Nevertheless, the reliability was assigned with scoring 2 because before listing a substance normally a set of prerequisites regarding the reliability of the result need to be met.

In a study conducted by Oliver and Niimi (1983) trout with an initial weight of about 250 g were exposed to 2 different overall concentrations of a mixture containing 12 chlorinated benzenes and aliphatic compounds. The uptake period was extended to 119 days and 105 days, respectively, and the trout reached a final weight of about 400 g. Food was also analyzed for contamination with trichlorobenzenes and blank values were considered in BCF calculation. For the higher exposure concentration a BCF of 3200 was measured (normalized to a lipid content of 5%: 1818). However, this study was deemed with reliability score 3 because 12 substances were simultaneously administered and effects regarding mixture toxicity influencing bioaccumulation can not be excluded due to the elevated background level of additional contaminants.

The relationship between lipid content of fish and their bioconcentration potential was investigated by Geyer et al. (1985). Within a selection of 23 literature data BCF for 1,2,4-trichlorobenzene ranged from 124 (trout with 1.8% lipid, normalized 344) to 2100 (fathead minnow with 10.5% lipid, normalized 1000). Unfortunately further information on exposure conditions is not listed.

A study on carp (Cyprinus carpio) was performed as a flow through test according to OECD 305 C (Broecker et al., 1984). The fish showed a lipid content of 4.8%. For the two exposure regimes, BCF of 830 and 805 (lipid normalized 864 and 838) were calculated. No time dependent increase was observed and the steady state is expected to be attained within seven days. However, the report also noted that a great variation in exposure concentrations of 1,2,4-trichlorobenzene was observed due to the inappropriate test design and the substance’s volatility. Equally, great variations of concentrations in fish were also observed due to individual variability. The authors thus suggested a modification in test design and the usage of smaller fish such as Zebrafish (Brachydanio rerio) to better maintain constant exposure concentration and to enhance the number of test fish per vessel.

The study on Zebrafish (Brachydanio rerio) was performed as a semi-static test (daily water renewal) almost following the OECD 305 B guideline (Ballhorn et al., 1984). The concentrations were measured initially and at water changes. The recovery rate was determined for 50-90% of the initial test concentration after two days. Additionally, a reverse dependency of BCF values on exposure concentration occurred showing higher BCF at lower exposure concentration. The BCF are reported for 1412 and 574, although no lipid content is provided.

Studies on invertebrates and algae revealed a low bioaccumulation of 1,2,4-trichlorobenzene for these species (Callahan 1979 and Geyer 1984).

In summary it can be stated that measured maximum BCF values with the highest reliability (scoring 2) range from 888 (normalized to 5% lipids) (Smith 1990) to 1320 (MITI-List).

Field-measured bioaccumulation factors (BAF):

The bioaccumulation of several chlorinated benzenes and butadienes was investigated in a field-study by Burkhard (Burkhard et al., 1997). Within the study site area sediment and water samples were taken at three representative locations in an effluent water channel ending in an adjacent river, at one location upstream and at two locations downstream the adjacent river. Biota samples were collected for four species (1 crustacean and 3 fish) and body concentrations were reported on basis of lipid normalization to 100% lipids. The bioaccumulation endpoints, in the study referred to as
BAF, were calculated by division of normalized concentration in biota by averaged concentration in water while sediment concentrations were not used for calculation.

The BAF reported in table 11 (referred to 100% lipid) were recalculated to 5% lipid content. Although the actual exposure pathways remain unknown and additional uptake via sediment was disregarded, these BAF indicate a significant uptake and high accumulation of 1,2,4-trichlorobenzene in biota ranging from 2100-3600.

Table 11: Measured bioaccumulation factors BAF for 1,2,4-trichlorobenzene

<table>
<thead>
<tr>
<th>Organism</th>
<th>Environmental concentrations</th>
<th>Concentration in biota (mg/kg lipids)</th>
<th>BAF (100% lipids)</th>
<th>BAF* (5% lipids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crab: <em>Callinectes sapidus</em> (Blue crab)</td>
<td>Concentration in water 296 ng/L (82-382)</td>
<td>10.0 (4.0-19.1)</td>
<td>41700</td>
<td>2080</td>
</tr>
<tr>
<td>Fish: <em>Fundulus heteroclitus</em> (Mummichog)</td>
<td>Concentration in water 15.8 (3.7-35.1)</td>
<td>47900</td>
<td>2390</td>
<td></td>
</tr>
<tr>
<td><em>Micropogania undulatus</em> (Atlantic croaker)</td>
<td>Concentration in sediment 10.0 (3.1-17.0)</td>
<td>56200</td>
<td>2810</td>
<td></td>
</tr>
<tr>
<td><em>Brevoortia patronus</em> (Gulf menhaden)</td>
<td>Concentration in sediment 13.2 (8.8-15.8)</td>
<td>72400</td>
<td>3620</td>
<td></td>
</tr>
</tbody>
</table>

* The BAF were recalculated for 5% lipid content

Interpretation is not straightforward as the study is not conducted according to standard laboratory conditions. Furthermore, this study has a number of shortcomings. For example, the presence of particulate organic carbon and an unusually high content of dissolved organic carbon complicate the analysis of results.

It is therefore questionable whether such a study is reliable enough to be used as supporting evidence that the B criterion is met according to Annex XIII of REACH.

3.3.2 Terrestrial bioaccumulation

No data.

3.3.3 Summary and discussion of bioaccumulation

1,2,4-trichlorobenzene has a log \( K_{ow} \) of 4.05 indicating a significant bioaccumulation potential. The bioaccumulation potential is confirmed by several bioconcentration tests using different fish species. Reliable measured BCF values range from 888 up to 1320.

The B criterion according to Annex XIII of REACH is therefore not met as none of the reliable lipid normalized BCF values in aquatic organisms is higher than 2000.
4 ENVIRONMENTAL HAZARD ASSESSMENT

4.1 Aquatic compartment (including sediment)

4.1.1 Toxicity data.

In this section only test results of long-term studies are reported as those are relevant for comparison with the aquatic T-criterion of Annex XIII of the Reach Regulation. Acute toxicity data can be found in the Risk Assessment Report (European Commission, 2003).

4.1.1.1 Fish

4.1.1.1.1 Long term toxicity to fish

Valid studies on long-term toxicity to fish are available for five fish species (see Table 11). All results are based on measured concentrations.

Table 11: Valid data on long-term ecotoxicity to fish. For details and references, see European Commission (2003)

<table>
<thead>
<tr>
<th>Species</th>
<th>Duration</th>
<th>EC\textsubscript{50} (mg l\textsuperscript{-1})</th>
<th>NOEC (mg l\textsuperscript{-1})</th>
<th>Method, conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pimephales promelas</em></td>
<td>32 days</td>
<td>0.29</td>
<td>0.5</td>
<td>Flow-through, ESF (egg and sac fry)-test</td>
<td>(McCarty and Reinhard, 1980; U.S.EPA, 1985)</td>
</tr>
<tr>
<td><em>Pimephales promelas</em></td>
<td>32 days</td>
<td>0.5</td>
<td>0.5</td>
<td>Flow-through, ELS-test, measured conc.</td>
<td>(Ahmad et al., 1984)</td>
</tr>
<tr>
<td><em>Pimephales promelas</em></td>
<td>32 days</td>
<td>0.50</td>
<td>2.4</td>
<td>Lake water, flow-through, ELS-test, EPA</td>
<td>(Carlson and Kosian, 1987)</td>
</tr>
<tr>
<td><em>(Brachy)danio rerio</em></td>
<td>21 days</td>
<td>2.4</td>
<td>0.04</td>
<td>Flow-through, mortality, behaviour, OECD 204</td>
<td>Broecker et al. (1984)</td>
</tr>
<tr>
<td><em>Salmo gairdneri</em></td>
<td>85 days</td>
<td>0.13</td>
<td>0.13</td>
<td>ELS (fry)</td>
<td>(Carlson and Kosian, 1987)</td>
</tr>
<tr>
<td><em>Poecilia reticulata</em></td>
<td>14 days</td>
<td>2.4</td>
<td>0.11</td>
<td>Semi-static (daily renewal), juvenile fish: growth</td>
<td>(Könemann, 1981)</td>
</tr>
<tr>
<td><em>Cyprinodon variegatus</em></td>
<td>-</td>
<td>0.11</td>
<td>0.222 mg l\textsuperscript{-1}</td>
<td>ESF-test, MATC = 0.222 mg l\textsuperscript{-1}</td>
<td>Suter and Rosen (1988)</td>
</tr>
</tbody>
</table>

Abbreviations: ESF-test (Egg and Sac Fry) embryo-larvae test. ELS: Early Life Stage test

The most sensitive species seems to be *Danio rerio* with a NOEC of 0.04 mg/L for the endpoint behaviour in a prolonged toxicity test (Broecker et al. 1984). Tests using *Poecilia reticulata* and *Salmo gairdneri* delivered NOEC-values of 0.11 and 0.13 mg/L (Carlson and Kosian, 1987) and (Könemann, 1981).
4.1.1.2 Aquatic invertebrates

4.1.1.2.1 Long term toxicity to aquatic invertebrates

Valid studies on long-term toxicity to invertebrates are available for *Daphnia magna* and *Mysidopsis bahia* (see Table 12). Results of *Daphnia magna* are based on measured concentrations.

**Table 12: Valid data on long-term toxicity to aquatic invertebrates. For details and references, see European Commission (2003)**

<table>
<thead>
<tr>
<th>Species</th>
<th>Duration</th>
<th>EC$_{50}$ (mg l$^{-1}$)</th>
<th>NOEC (mg l$^{-1}$)</th>
<th>Method, conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Daphnia magna</em></td>
<td>14 days</td>
<td>0.45</td>
<td>(0.32)</td>
<td>Semi-static, (closed)</td>
<td>(Calamari et al., 1983)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(NOEC = EC16)</td>
</tr>
<tr>
<td><em>Daphnia magna</em></td>
<td>16 days</td>
<td>0.16 (reproduction)</td>
<td>0.06 (reproduction)</td>
<td>Semi-static (3 times a week);</td>
<td>(Hermens et al. 1984)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.32 (mortality)*</td>
<td>0.19 (mortality)*</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Daphnia magna</em></td>
<td>21 days</td>
<td>0.4</td>
<td></td>
<td>Semi-static, EEC-Ann.V-c; reproduction</td>
<td>(Broecker et al. 1984)</td>
</tr>
<tr>
<td><em>Daphnia magna</em></td>
<td>28 days</td>
<td>0.36</td>
<td></td>
<td>Semi-static (closed), ASTM 1980</td>
<td>(Richter et al. 1983)</td>
</tr>
<tr>
<td><em>Mysidopsis bahia</em></td>
<td>28 days</td>
<td>≤0.064</td>
<td></td>
<td>Flow-through, measured, EPA standard</td>
<td>(US EPA 1988)</td>
</tr>
</tbody>
</table>

* from RAR2003: EC$_{50}$ values and NOECs are corrected values of the Rapporteur.

The RAR 2003 treats the data of a study by Hermens et al. (1984) on the sublethal toxicity to *Daphnia magna* in the following way: the 16-day LC$_{50}$ on mortality was 0.56 mg/l and the EC$_{50}$ on reproduction was 0.27 mg/l (reported as µmol/l in the reference). In an identical 16-day experiment, measurements of the test concentrations are stated to average 58% of nominal (Hermens et al., 1985) and the 16-day EC$_{50}$ was 0.52 mg/l. The results are not corrected for the measured concentrations. Assuming the average concentration was the same in the two experiments, the 16-day LC$_{50}$ was 0.32 mg/l, EC$_{50}$ 0.16 mg/l and the NOEC on mortality and reproduction 0.19 mg/l and 0.06 mg/l, respectively.

4.1.1.3 Algae and aquatic plants

Results of four standard ecotoxicity tests on algae are available.

**Table 13: Toxicity to algae (see European Commission 2003)**

<table>
<thead>
<tr>
<th>Species</th>
<th>Duration</th>
<th>EC$_{50}$ (mg l$^{-1}$)</th>
<th>NOEC (mg l$^{-1}$)</th>
<th>Method, conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Some of the tests did not consider the volatility of the substance. Thus, the real values are probably lower than most of the mentioned. It may be assumed that results from static and open system tests underestimate the toxicity due to evaporation and photolysis, respectively. Therefore, only the results from the test using a closed system are accepted to be used in the risk assessment procedure: Algae EC$_{50}$ (96 h): 1.4 mg/l and NOEC (96 h): 0.37 mg/l.

### 4.1.1.4 Sediment organisms

Two studies have looked at the effects of 1,2,4-TCB on benthos. In an 8-week study employing macrobenthos community and spiked sediment, the lowest concentration influencing the number of animals was 100 mg kg$^{-1}$ sand (ww) (added 1,2,4-TCB, nominal) for molluscs, echinoderms and the most abundant arthropod Corophium acherusicum corresponding to 6 mg kg$^{-1}$ measured at the end of exposure. In the same study planktonic larvae of macrobenthos were exposed 6 days to 1,2,4-TCB via water under flow-through conditions. The lowest effect concentration (mortality) of 0.04 mg l$^{-1}$ was observed for mollusc larvae. In another study, grass shrimp (Palaemonetes pugio) and amphioxus (Branchiostoma caribaeum) were tested via water and sediment exposure, respectively. During a 10-day sediment exposure, no mortality was observed for grass shrimp at 10 mg kg$^{-1}$ sand (wet weight). For amphioxus LC$_{50}$ was observed to be 200 mg kg$^{-1}$ sand (ww) and NOEC 75 mg kg$^{-1}$ sand (ww).

### 4.1.1.5 Other aquatic organisms

Results from ecotoxicity tests with Tetrahymena poryformis (protozoa), Tanytarsus dissimilis (chironomid) and Aplexa hypnorum (snail) gave EC$_{50}$ values between 0.91-3.16 mg l$^{-1}$.
Table 14: Short-term toxicity to other aquatic organisms (see European Commission 2003)

<table>
<thead>
<tr>
<th>Species</th>
<th>Duration</th>
<th>EC₅₀ (mg l⁻¹)</th>
<th>Method, conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Tetrahymena pyriformis</em></td>
<td>24 h</td>
<td>0.91</td>
<td>30°C, 2% protease peptone medium, growth inhibition</td>
<td>(Yoshioka et al., 1985)</td>
</tr>
<tr>
<td><em>Tanytarsus dissimilis</em></td>
<td>48 h</td>
<td>0.93</td>
<td>Flow through, lake water, 17°C, 43 mg CaCO₃/l measured conc.</td>
<td>(Holcombe et al., 1987)</td>
</tr>
<tr>
<td><em>Aplexa hypnorum</em></td>
<td>96 h</td>
<td>3.16</td>
<td>Flow through, lake water, 17°C, 43 mg CaCO₃/l measured conc.</td>
<td>(Holcombe et al., 1987)</td>
</tr>
</tbody>
</table>

* These ciliate data are also included in the section below because they are regarded representative for ciliate species in sewage treatment plants.
5 CONCLUSIONS ON THE SVHC PROPERTIES

5.1 PBT, vPvB assessment

See section 5.3.

5.2 CMR assessment

Not relevant for this dossier.

5.3 Substances of equivalent level of concern assessment

5.3.1 Assessment of PBT/vPvB properties

5.3.1.1 Persistence

1,2,4-trichlorobenzene (1,2,4-TCB) is hydrolytically stable. The screening biodegradation tests indicate that 1,2,4-TCB is not readily biodegradable. Based on data from soil and sediment simulation tests on degradability half-lives of more than 200 days have been determined.

Due to its high volatility (Henry constant of 181.45 Pa*m³*Mol⁻¹), 1,2,4-TCB is expected to be distributed from water to air. In the air, 1,2,4-TCB is persistent (estimated half lives between 18.5 and 38 days) and may be transported by air for several thousand kilometres. Distributed by this pathway also to remote areas, 1,2,4-TCB will be deposited again to soil or water being even more persistent in regions with low temperatures.

Thus, considering all information available, 1,2,4 – trichlorobenzene is persistent (P) as the criterion for persistency according to Annex XIII is met and it may be very persistent (vP) in sediments and soil.

5.3.1.2 Bioaccumulation

1,2,4-trichlorobenzene has a log $K_{ow}$ of 4.05 indicating a significant bioaccumulation potential. The significant bioaccumulation potential is confirmed by several fish bioconcentration tests and a field study.

Reliable measured BCF values in aquatic organisms (fish) range from 888 to 1320. The B criterion according to Annex XIII of REACH is therefore not met.

5.3.1.3 Toxicity

Aquatic ecotoxicity tests with chronic exposure are available for fish, aquatic invertebrates and algae. The lowest NOEC is 0.04 mg l⁻¹ for zebra fish. The NOECs measured for invertebrates and algae are in the same order of magnitude. Although these NOECs indicate a high toxicity for aquatic organisms on the long-term, the T-criterion is formally not fulfilled.

5.3.1.4 Further supporting evidence

*Long-range transport potential:* Due to its volatility and persistence to atmospheric degradation, 1,2,4-TCB has a very high potential for long-range atmospheric transport, which is comparable to
the long-range transport potential of persistent organic pollutants like PCBs. Based on model calculations, estimated travelling distances are several thousand kilometres.

5.3.2 Summary and overall conclusions on the properties leading to an equivalent level of concern

Based on the data available 1,2,4-trichlorobenzene is persistent (P) as the criterion for persistency according to Annex XIII is met and it may be very persistent (vP) in sediments and soil. However, with regard to the bioaccumulation (B) and toxicity (T) criteria, such a conclusion cannot be drawn. Nevertheless the substance still has a significant bioaccumulation and toxicity potential to aquatic organisms.

In addition, results of model calculations have shown a high long-range transport potential of the substance. The potential occurrence of serious effects in biota in remote and sensitive ecosystems was considered, taking into account the intrinsic properties of the substance. However based on the information available it is considered that it is currently not possible to conclude on the identification of 1,2,4-trichlorobenzene as a substance of very high concern in accordance with Article 57(f) of Regulation (EC) 1907/2006.
REFERENCES


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van Eck JMC, Koelmans AA, Deneer JW. 1997. Uptake and elimination of 1,2,4-trichlorobenzenein the guppy (Poecilia reticulata) at sublethal and lethal aqueous concentrations. Chemosphere 34(11): 2259-2270.


