

Euro Chlor Risk Assessment for the Marine Environment OSPARCOM Region - North Sea

Carbon Tetrachloride

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EURO CHLOR RISK ASSESSMENT FOR THE MARINE ENVIRONMENT

CARBON TETRACHLORIDE

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 in 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 Carbon tetrachloride (CTC) 15 data for fish, 7 data for invertebrates and 5 data for algae have been evaluated according to the 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 $7 \mu g/l$.

Most of the available monitoring data for carbon tetrachloride apply to rivers and estuary waters and were used to calculate PECs. The most recent data (1990-1995) support a typical PEC lower than 0.003 to 0.02 μ g/l and a worst case PEC of 0.10 to 0.31 μ g/l. The calculated PEC/PNEC ratios give a safety margin of 25 to 2500 between the predicted no effect concentration and the exposure concentration. Dilution within the sea would of course increase those safety margins.

Moreover, as the available data on persistence of carbon tetrachloride indicate a half-life in water of days or a maximum of one month, and as the bioaccumulation in marine organisms can be considered as very limited, it can be concluded that the present use of carbon tetrachloride does not represent a risk to the aquatic environment. Due to its persistence in the atmosphere and its significant ozone depletion potential, carbon tetrachloride production and uses have been highly restricted since 1994. This will contribute to further decreases in environmental concentration.

1. <u>INTRODUCTION : PRINCIPLES AND PURPOSES OF EURO</u> <u>CHLOR RISK ASSESSMENT</u>

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 <u>Appendix 1</u>. 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. <u>DATA SOURCES</u>

The data used in this risk assessment activity are primarily derived from the data given in the HEDSET (updated version of 06.06.95) for this compound. Where necessary additional sources have been used. For interested parties, the HEDSET is available at Euro Chlor. The references of the HEDSET and additional sources will be given in Chapter 10.

3. <u>COMPOUND IDENTIFICATION</u>

3.1 Description

CAS Number EINECS Number EEC Number IUPAC Name Synonyms Formula :56-23-5 :200-262-8 :602-008-00-5 :Carbon tetrachloride :Tetrachloromethane, CTC :CCl₄

3.2 EU Labelling

According to Annex I of Directive 93/72/EEC, carbon tetrachloride is classified as carcinogenic category 3: R40 (possible risks irreversible effects) as well as toxic by inhalation in contact with skin and if swallowed (R23/24/25) and danger of serious damage to health by prolonged exposure (R48/23). Environmental labelling of carbon tetrachloride according to the EU criteria is "symbol N" and "risks phrases R52/53 and R59".

4. <u>PHYSICO-CHEMICAL PROPERTIES</u>

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

Property	Value
Molecular weight	153.8 g
Melting point	-23°C
Boiling point	76.7°C
Decomposition temperature	>300°C
Density	1.594 (20°C)
Vapour pressure	119.4 hPa (20°C)
Water solubility	0.8 g/l (20°C)
log Kow	2.6
log Koc	2.0
Henry's Law constant	2300 Pa m ³ /mol at 24.8°C

Table 1 : Chemical and physical properties of carbon tetrachloride (IUCLID, 1996)

5. <u>COMPARTMENT OF CONCERN BY MACKAY LEVEL I MODEL</u>

The risk assessment presented here focuses on the aquatic marine environment, with special attention for 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 carbon tetrachloride are given in Table 2.

Table 2 : Partition of carbon tetrachloride into different environmental compartmentsaccording to Mackay level I calculation (Mackay & Patterson, 1990)

Compartment	%
Air	99.9
Water	0.1
Soil	< 0.01
Sediment	< 0.01

(See <u>Appendix 2</u> for details of calculations).

Due to the very low probability of partitioning to sediment, the risk assessment will focus on the water phase.

6. **PRODUCTION, USES, EMISSIONS**

6.1 <u>Production and uses</u>

Production of carbon tetrachloride in the EU in 1996 was 59,691 tonnes (ECSA, 1998). This is mainly for feedstock for the production of CFC 11 and 12 that are further used as intermediate for the production of other chemicals. Under the Montreal Protocol (Decision IV/12), a controlled substance that undergoes transformation in a process in which it is converted from its original composition is allowed.

Also under the Montreal Protocol and the European Regulation 3093/94 "essential uses" of ozone depleting substances are allowed. In 1996, 233 t of carbon tetrachloride were allocated as essential uses.

Use of carbon tetrachloride as a process agent is allowed under the existing European Regulation and the current revision. A process agent is defined as a controlled substance that facilitates an intended chemical reaction and/or inhibits an unintended chemical

reaction. Process agent use is allowed in the EU if emissions are insignificant and the use was established before September 1997. Such applications are extraction of nitrogen trichloride from liquid chlorine, recovery of chlorine from tail gas, chlorinated rubber manufacture and pharmaceuticals processing, etc. Emissions and make up are less than 20 t in the EU. In most of these applications, carbon tetrachloride is completely converted or destroyed, for example in incineration units complying with the UNEP requirements and recovering hydrochloric acid.

Some carbon tetrachloride also appear as by-product in some chemical processes, for example in the manufacture of perchloroethylene or chloromethanes. It is either destroyed by incineration to recover hydrochloric acid, partially dehalogenated into other chloromethanes, or added to feedstocks in the production of other chlorinated compounds, such as tri- or perchloroethylene.

6.2 <u>Applicable regulation</u>

In 1986, carbon tetrachloride was identified as one of several compounds along with CFC 11 and 12 that may deplete the stratospheric ozone layer with an ozone depletion potential (ODP) of 1.098. Consequently, the Montreal Protocol scheduled a phase-out of carbon tetrachloride except for some essential and feedstock uses. In the EU, the use has been phased out by end of 1994 except for small authorized quantities (EU Regulation 3093/94).

6.3 <u>Emissions</u>

Due to its volatility, carbon tetrachloride will be mainly found in the atmosphere. Emissions in air were estimated as 243 t/y in 1995 for about 67 European sites manufacturing or using carbon tetrachloride as a feedstock, process agent or producing it inadvertently. In water, emissions amounted to about 7 t/y for the same period (Euro Chlor, 1996). These figures should have been reduced in 1996 as the main production plants of CFC 11 and 12 and of carbon tetrachloride were closed in Europe.

7. <u>EFFECT ASSESSMENT</u>

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

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

Documented data from all available sources, including company data and data from the open literature, were collected and incorporated into the HEDSET for carbon tetrachloride, including their references (updated version of 06.06.95).

The data are summarised in <u>Appendix 3</u>. In total, there are 15 datapoints for fish, 7 datapoints for invertebrates, and 5 datapoints for algae. Of these, only one datapoint for

crustaceans is fully valid for risk assessment purpose; 5, 2 and 1 should be used with care for the respective taxonomic groups. 10, 4 and 4 were judged as not valid or not assignable for risk assessment, respectively.

It is necessary to distinguish the acute studies (LC50/EC50) from chronic studies (NOEC/LOEC). In <u>Appendix 3</u>, 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).

In the case of carbon tetrachloride, available data in marine species are not sufficient to indicate a similarity in the sensitivity of marine and freshwater species. However, based on other similar chlorinated compounds, no marked difference is expected. Therefore, data from freshwater organisms are regarded as relevant for a risk assessment for the marine compartment and are discussed together with the data from marine species of the respective trophic level. Quantitative structure-activity relationship (QSAR) data were not considered. Due to its high vapour pressure, carbon tetrachloride should be tested under closed conditions (preferably with analytical measurements) to avoid losses by volatilization.

The different trophic levels are reviewed below. The references are listed in the table of <u>Appendix 3</u> and given in <u>Appendix 6</u>.

7.1 <u>Marine fish</u>

Two acute toxicity studies are reported for marine fish. The results for the dab, *Limanda limanda* (Madeley, 1973) are considered valid but are limited and can only be used with care for risk assessment purposes. The flow-through system was designed to minimise volatile losses and is described in detail. Analysis of the solutions was employed, but the results were not reported. Only one concentration (50 mg/l) is reported which caused 100% mortality in 96 hours. The study with *Menidia beryllina* (Dawson *et al.*, 1977) was a static test and the solutions may have been aerated (the text was not specific for individual substances). Considerable loss by volatility may have occurred and therefore the result is not valid.

No chronic toxicity studies are available.

The lowest acute toxicity value for marine fish is observed for *Limanda limanda* with 100% mortality at 50 mg/l after 96 hours.

7.2 Fresh water fish

7.2.1. Acute Toxicity

Ten acute toxicity studies are reported for freshwater fish. The only acute toxicity result from a flow-through system is for the fathead minnow (*Pimephales promelas*) (Kimball, cited in Persoone & Vanhaeke, 1982) with a 96h-LC50 of 43 mg/l. However, only the result is cited, with no details of the methods; the original work may have been part of a

US EPA contract (US EPA, 1978). The validity is therefore "not assignable" (category 4).

None of the remaining studies employed chemical analysis of the test solutions. A static study with bluegills *(Lepomis macrochirus)* (Buccafusco *et al.*, 1981) used capped vessels to reduce volatilisation but with a headspace of approximately 25% of the total volume. This would limit, but not completely eliminate, losses. The authors reported the presence of a precipitate in the test solution although the 96h-LC50 reported (27 mg/l) would be below the limit of solubility. The final dissolved oxygen concentration in some tests was very low (not necessarily with carbon tetrachloride; not specified for individual substances). The result should be used with care.

The data for *Salmo trutta* (Madeley, 1973)is not valid for these purposes. The procedure used is a screening test which exposes fish in sealed vessels and compares the oxygen remaining in the solution on death. It only provides an indication of the toxic level.

The 14-day LC50 to guppies (*Poecilia reticulata*) was determined in a semi-static study with a closed system (Koenemann, 1981). However, volatile losses would only have been partially controlled and the results should be used with care. It should also be noted that, for the purposes of the risk assessment procedure used here, the 14-day exposure period does not qualify as either an acute or chronic test. All the remaining data (*Lepomis macrochirus, Oryzias latipes* and *Leuciscus idus*) are from static or semi-static tests, without analysis and with no control of volatile losses and are not valid. Although one of these represents the lowest acute toxicity value for fish (48h-LC50 of 13 mg/l for *Leuciscus idus*) (von Knie *et al.*, 1983) and was stated to be performed to the German DIN standard, little detail is given in the paper and the result is significantly lower than those quoted by other authors for the same species to the same method.

The lowest valid acute toxicity value for freshwater fish is observed in *Lepomis macrochirus* with 96 h LC50 of 27 mg/l (Buccafusco *et al.*, 1981).

7.2.2 Chronic Toxicity

Three long-term toxicity studies are reported for freshwater fish. The US Water Quality Criteria document (US EPA, 1978) quotes a longer-term (embryo-larval) study with *Pimephales promelas* giving a NOEC of 3.4 mg/l. However, only the result is cited, with no details of the methods. The validity is therefore "not assignable" (category 4).

Embryo-larval studies using *Pimephales promelas* and *Salmo gairdneri* (subsequently renamed *Oncorhynchus mykiss*) are reported by Black & Birge (1982). These studies have been criticised for testing widely spaced concentrations and giving few details of control performance (UK Department of the Environment, 1994) and the methods were non-standard and not well validated. However, they were conducted under flow-through conditions, with control of volatile loss and with analysis. Therefore, the long-term LC50 values quoted can be used with care. The 9 day-LC50 (4 days post-hatch) for *P. promelas* was 4 mg/l; for *S. gairdneri*, the 27 day-LC50 (4 days post-hatch) was 1.97 mg/l. A NOEC (which is required for the PNEC calculation) is not cited in the paper. The lowest concentration tested which had no discernible effect on survival of *S. gairdneri* (0.07 mg/l) is not valid as a NOEC, because of the wide interval between concentrations.

The conclusion is that the apparent NOEC was within the range 0.07 to 1.1 mg/l. However, the lower end of this range is approximately the same as the NOEC for freshwater algae (see section 7.6). Therefore, the *S. gairdneri* study is sufficient to demonstrate that fish are no more sensitive than other trophic levels and the study can be used for that purpose without needing to define a NOEC for PNEC calculation.

Therefore, the lowest chronic toxicity value is observed for *Salmo gairdneri* with a 27day embryo-larval LC50 of 1.97 mg/l, with an uncertain NOEC within the range 0.07 -1.1 mg/l (Black & Birge, 1982).

7.3 <u>Marine invertebrates</u>

One study on *Artemia salina* should be handled with care as this occurred was performed in a closed system under static conditions. A <u>24h-LC50 of 31 mg/l</u> was found (<u>Abernethy *et al.*, 1988</u>) which represents the only acute toxicity value for marine invertebrates. No chronic studies are reported.

7.4 <u>Freshwater invertebrates</u>

7.4.1 Acute toxicity

Five <u>acute toxicity</u> values are reported for freshwater invertebrates. EC50 values for *Daphnia magna* range from 28 to >770 mg/l; both these extreme values were from 24hour studies with no control of volatile losses, and are not valid. The lower value was from the same authors who derived the lowest acute value for fish (von Knie *et al*, 1983). A more reliable EC50 was obtained from a 48-hour study (Le Blanc, 1980) which used plastic wrapped vessels, although the headspace was approximately 25% of the total volume and losses may have occurred into or through the plastic. Therefore the value obtained (35 mg/l) should be used with care. All other data for *Daphnia* are considered not valid due to probable volatile loss. Although one of these employed stoppered vessels for *Daphnia* and also for *Tubifex* worms (Havelka & Albertova, 1970), the headspace volume was not reported.

Therefore, the lowest valid acute toxicity value for freshwater invertebrates is reported for *Daphnia magna* with a 48h-EC50 of 35 mg/l (Le Blanc, 1980).

7.4.2 Chronic toxicity

A recent study determined effects on reproduction, survival and growth (length) of *Daphnia magna* over 21 days (Thompson *et al.*, 1997). The semi-static test was carried out in closed, fully-filled vessels, with analysis of the test solutions which confirmed that no significant volatile loss of the carbon tetrachloride had occurred. The study was considered valid and found no effect on reproduction, final length of the parent or survival at 3.1 mg/l. At 5.7 mg/l, there was a significant decrease in reproduction and length.

Therefore, the only valid chronic toxicity value for freshwater invertebrates is a 21day NOEC for *Daphnia magna* of 3.1 mg/l (Thompson *et al.*, 1997).

7.5 <u>Marine algae</u>

Data for 3 species of diatom (Tadros *et al.*, 1995) were not considered valid due to a high test temperature and no control of volatile losses. Only an approximate EC50 could be estimated, because the test concentrations were derived by dilution of a "saturated solution" which was not analysed. A further 4 species were tested in the same study but showed less than 50% inhibition at the highest concentration. For these latter, EC50 could not be estimated (and therefore they are not included in Appendix 3).

7.6 <u>Freshwater algae</u>

A study with Haematococcus pluvialis (von Knie et al., 1983) is considered not valid since no precautions were taken to prevent loss of the substance. Two remaining studies (Bringmann & Kühn, 1978a,b) used capped vials although the headspace volume was approximately 66% of the total, which would have allowed considerable volatile loss. The more sensitive species, *Microcystis aeruginosa*, was reported to show a "toxicity threshold" at 105 mg/l and therefore the EC50 would be >105 mg/l. This, and the result for Scenedesmus aquadricauda (>600 mg/l) were considered not valid. Recent data for Chlamydomonas reinhardtii (Brack & Rottler, 1994) tested in a closed system with confirmatory analysis, suggest much greater sensitivity with an EC50 of 0.246 mg/l and an EC10 of 0.072 mg/l. Caution is needed in interpreting these results because of the non-standard methodology which was necessary in order to prevent volatility. The method boosted the carbon dioxide level in the headspace to provide a "reservoir" for the test period. It is uncertain whether this would have affected the result; the authors did not compare the modified system with a standard test using non-volatile chemicals. However, the concentration-response relationship was convincing and the EC10 can be taken as a reasonable approximation of the NOEC. The data are considered usable but with care.

Therefore the lowest valid toxicity values for freshwater algae are a 72 h EC50 of 0.246 mg/l and a 72 h EC10 for *Chlamydomonas reinhardtii* of 0.072 mg/l (Brack & Rottler, 1994).

7.7 **<u>PNEC for marine environment</u>**

There is insufficient data to conclude whether the sensitivity of marine and freshwater organisms to carbon tetrachloride is similar, but this is a reasonable assumption based on the data for other, similar, chlorinated compounds.

A summary of the valid data used for the derivation of the PNEC values at different levels is given in Table 3.

The final PNEC which is calculated for this risk assessment is 7 mg/l. Moreover, if all data are taken into account (see <u>Appendix 3</u>), no effect is observed below 72 μ g/l.

It is also interesting to point out that the Water Quality Objective for carbon tetrachloride has been set by EU Directive 86/280 at a level of 12 μ g/l and at a level of 10 μ g/l by the EU Draft Water Quality Objectives for 132 substances of List I (CSTE, 1994).

Data set	Assigned Assessment Factor	Lowest Toxicity values
At least 1 short-term LC50 from each trophic level	1000 PNEC = 0.25 mg/l	 Lepomis macrochirus, 96 h LC50 = 27 mg/l (Buccafusco et al., 1981) Artemia salina, 24 h EC50 = 31 mg/l (Abernethy et al., 1988) Daphnia magna, 48 h EC50 = 35 mg/l (Le Blanc, 1980) Chlamydomonas reinhardtii, 72 h EC50 = 0.246 mg/l (Brack & Rottler, 1994)
3 long-term NOEC from species of 3 trophic levels	10	 Salmo gairdneri, 27-day embryo-larval NOEC (tentative): 0.07 - 1.1 mg/l (Black et al., 1982) Daphnia magna, 21-day; NOEC = 3.1 mg/l (Thompson et al., 1997) Chlamydomonas reinhardtii, 72 h EC10 = 0.072 mg/l (Brack & Rottler, 1994)
	PNEC = 7 ng/l	

Table 3 : Summary of ecotoxicity data selected for the PNEC derivation, with the appropriate assessment factors for carbon tetrachloride

7.8 <u>Bioaccumulation</u>

Bioaccumulation of carbon tetrachloride in aquatic species is unlikely in view of its physical, chemical and biological properties. The log Kow is in the range of 2.6 to 2.83 and a bioaccumulation factor of 30 for *Lepomis macrochirus* (Veith *et al.*, 1980) and of 17.7 for *Salmo gairdneri* (Neely *et al.*, 1974) are reported in the literature. Bioaccumulation through the food chain is unlikely.

7.9 <u>Persistence</u>

Due to the value of the Henry's law constant, carbon tetrachloride entering aquatic systems would be transferred to the atmosphere through volatilization. A half life of 3.7 hours can be calculated from this constant. The half life of carbon tetrachloride in river water is estimated at a level between 0.3 and 3 days, depending upon the water movement. In lakes, the half life is estimated at 30 days (BUA report, 1990).

In the troposphere, carbon tetrachloride is very stable mainly because the reaction rate with ambient hydroxyl radicals is very low. The atmospheric lifetime is calculated to be 42 years with photolytic decomposition through shortwave UV rays representing the main degradation pathway (WMO, 1994). As a result, the substance is controlled with an Ozone Depleting Potential of 1.1 by the 1990 Amendment to the Montreal Protocol. Consumption in the developed countries was phased out in 1994 except for essential uses and feedstock (see section 6.2).

Carbon tetrachloride is not listed as a greenhouse gas under the Kyoto Protocol (UN-FCCC, 1997; IPCC, 1997). Carbon tetrachloride has a negligible tropospheric ozone creation potential (UN-ECE, 1994).

7.10 Conclusion

Although carbon tetrachloride is persistent in the atmosphere, it should not be considered as persistent in water, nor bioaccumulable. It can be deduced from the above information that carbon tetrachloride is not a "toxic, persistent and liable to bioaccumulate" substance as mentioned by the Oslo and Paris Convention 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. <u>EXPOSURE ASSESSMENT</u>

The exposure assessment is essentially based on exposure data from analytical monitoring programs. Carbon tetrachloride has been measured in a number of water systems. These levels in surface waters (river water and marine waters) are detailed in *Appendix 4*. All the references are given in *Appendix 7*.

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 the background "regional" concentrations and the higher to contaminated areas, or "local" concentrations, considered as worst cases.

8.1 <u>Marine waters and estuaries</u>

In coastal waters and estuaries from Denmark, France, Germany, The Netherlands, Sweden and United Kingdom, observed concentrations are in a range from below 0.0005 μ g/l up to 0.31 μ g/l. Typical recent monitoring data for carbon tetrachloride in coastal waters and estuaries which are part of the OSPARCOM region are illustrated on the North Sea map in <u>Appendix 5</u>.

In a review study (WRc, 1998) evaluating data on coastal waters and estuaries along the North Sea/Irish Sea from 1990 to 1994, the geometric mean concentration was found as $0.003 \ \mu g/l$ with a maximum level of $0.030 \ \mu g/l$ (n = 37 data)

<u>Remark</u>: The uses of carbon tetrachloride having been strongly reduced in the last years, the measured concentrations will further decrease in surface waters.

8.2 <u>River waters</u>

In a review study (WRc, 1998) evaluating data on main rivers in Europe coming into the North Sea/Irish Sea from 1980 to 1994, the geometric mean concentration was 0.043 μ g/l (n = 101 data).

Taking typical levels from 1990 onwards leads to a concentration of 0.02 μ g/l (geometric mean). On the same period, a worst case situation was found in the Mersey river with a level of 23.6 μ g/l but this value appears as an outlier as all other data were lower than 0.1 μ g/l. This latter value is considered as a realistic worse case.

9. <u>RISK ASSESSMENT CONCLUSION</u>

In the risk assessment of carbon tetrachloride for aquatic organisms, the PNEC is compared to the PEC.

A PNEC of 7 μ g/l was obtained for aquatic species exposed to carbon tetrachloride.

In coastal waters and estuaries, carbon tetrachloride is observed up to 0.31 μ g/l (worst case) but typical values are generally lower than 0.003 μ g/l (geometric mean of recent data)

In non-industrialised areas, a typical river water concentration lower than 0.02 μ g/l was derived from the levels measured in the 1990's; worst cases were also identified in industrialised zones with measured levels up to 0.1 μ g/l (reasonable worst case).

These selected values allow calculation of the PEC/PNEC ratios which are summarised in Table 4.

Type of water	PEC level	PEC/PNEC
Coastal waters/estuaries worst case	0.21	0.04
	0.31 μg/l	0.04
typical	0.003 µg/l	0.0004
<u>River waters</u> worst case typical	0.10 μg/l 0.02 μg/l	0.014 0.003

Table 4 : Calculation of PEC/PNEC ratios for carbon tetrachloride

These calculated ratios **which do not take into account any dilution factor within the sea** correspond to a safety margin of 25 to 2500 between the aquatic effect and the exposure concentration so that the present restricted use of carbon tetrachloride should not represent a risk to the aquatic environment.

10. <u>REFERENCES</u>

10.1 General References

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10.2. <u>References for ecotoxicity data</u> : see <u>Appendix 6</u>

Those references are used in Appendix 3.

10.3. <u>References for monitoring data</u> : see <u>Appendix 7</u>

Those references are used in Appendix 4

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 summarized in the following table (according to criteria defined in IUCLID system).

Case	Detailed description of the test	Accordance with scientific guidelines	Measured concentration	Conclusion: reliability level
Ι	+	+	+	[1] : valid without restriction
п	±	±	±	[2] : valid with restrictions; to be considered with care
III	insufficient or -	-	-	[3] : invalid
IV	the inform	[4] : not assignable		

Table : Quality criteria for acceptance of ecotoxicity data

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.

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

Chemical: Perchlorethylene Temperature (C)	
Temperature (C)	
Log octanol water part. coefficient Octanol water part. coefficient Organic C-water part. coefficient Air-water partition coefficient Soil-water partition coefficient Sediment-water partition coefficient Amount of chemical (moles)	20 165.80 1900 150 0.90 2100.13 2.53 338.84 138.93 0.86 4.17 8.34 1 53053E-6

Phase properties and compositions:

Phase	:	Air	Water	Soil	Sediment
Volume (m3) Density(kgm3) Frn org carb. Z mol/m3.Pa VZ mol/Pa Fugacity Conc mol/m3 Conc g/m3 Conc ug/g Amount mol		.6000E+10 .12056317E+2 .00000E+0 .41029864E-3 .24617918E+7 .40563053E-6 .16642965E-9 .27594037E-7 .22887615E-5 .99857795E+0	.70000E+7 .10000E+4 .00000E+0 .47616024E-3 .3331217E+4 .40563053E-6 .19314513E-9 .32023463E-7 .32023463E-7 .13520159E-2	.45000E+5 .15000E+4 .20000000E-1 .19845326E-2 .89303968E+2 .40563053E-6 .80498703E-9 .13346684E-6 .88977899E-7 .36224416E-4	.21000E+5 .15000E+4 .40000000E-1 .39690652E-2 .83350370E+2 .40563053E-6 .16099740E-8 .26693369E-6 .17795579E-6 .33809455E-4
Amount %	:	99.86	0.14	.36224416E-2	.33809455E-2

SUMMARY TABLE OF ECOTOXICITY DATA ON CARBONTETRACHLORIDE

1. FISH

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (mg/l)	Validity	Comments	Reference
ACUTE STUDIES							
1. FRESHWATER							
Lepomis macrochirus	96 h	S,C,N	LC50	27	2	Precipitate? Low oxygen?	Buccafusco <i>et al.</i> (1981)
Poecilia reticulata	14 d	SS,C,N	LC50	67	2	Neither acute nor chronic	Koenemann (1981)
Salmo gairdneri	14 d	SS,N	LC50	> 80	3		Statham et al. (1978)
Lepomis macrochirus	96 h	S,N	LC50	125	3	Aeration "if required", 24 h	Dawson et al. (1977)
Leuciscus idus	48 h	S,N	LC50	13	3		von Knie et al. (1983)
Leuciscus idus	48 h	S,N	LC50	95-472	3		Juhnke & Luedemann (1978)
Leuciscus idus	48 h	S,N	LC50	47	3		Scheubel (1980)
Salmo trutta	6 h	S,C,N	LC50	24-56	3	Residual oxygen test	Madeley (1973)
Oryzias latipes	48 h	SS,N	LC50	45	3		CITI (1992)
Pimephales promelas	96 h	FT,N?	LC50	43	4	Insufficient detail	Kimball quoted in Persoone & Vanhaecke, 1982
2. SALT WATER							
Limanda limanda	96 h	F-T,C,A	LC50	< 50	2	100% mortality at 50 mg/l	Madeley (1973)
Menidia beryllina	96 h	S,N	LC50	150	3	Aeration "if required", 24 h	Dawson et al. (1977)

SUMMARY TABLE OF ECOTOXICITY DATA ON CARBONTETRACHLORIDE

1. FISH

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (mg/l)	Validity	Comments	Reference
CHRONIC STUDIES							
1. FRESHWATER							
Pimephales promelas	9 d	F-T,C,A	LC50	4	2		Black & Birge (1982)
			NOEC	0.07-0.72	(4)	Widely spaced concns.	
Salmo gairdneri	27 d	F-T,C,A	LC50 NOEC	2 0.07-1.1	2 (4)	Widely spaced concns.	Black & Birge (1982)
Pimephales promelas	?	F-T?,A?	NOEC	3.4	4	Insufficient detail	US EPA (1978a,b)
Pimephales promelas 2. SALTWATER (NO DATA AVAILABLE)	?	F-T?,A?					US EPA (1978a

SUMMARY TABLE OF ECOTOXICITY DATA ON CARBONTETRACHLORIDE

2. INVERTEBRATES

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (mg/l)	Validity	Comments	Reference
ACUTE STUDIES							
1. FRESHWATER							
Daphnia magna	48 h	S,C,N	LC50	35	2	Partial volatility control	Le Blanc (1980)
Daphnia magna	24 h	S,N	LC50	> 770	3		Bringmann & Kuehn (1977)
Daphnia magna	24 h	S,N	EC50	28	3		Von Knie <i>et al.</i> (1983)
Daphnia magna	24 h	S,C,N	EC50	50-100	3	Partial volatility control	Havelka & Albertova (1970)
Tubifex tubifex	24 h	S,C,N	EC50	500-750	3	Partial volatility control	Havelka & Albertova (1970)
2. SALTWATER				-			
Artemia salina	24 h	S,C,N	LC50	31	2	Partial volatility control	Abernethy <i>et al.</i> (1988)
CHRONIC STUDIES				-			
2. FRESHWATER							
Daphnia magna	21 d	SS/C/A	NOEC (rep) LOEC (rep)	3.1 5.7	1	Fully filled vessels	Thompson <i>et al.</i> , 1997
2. SALTWATER (no data available)			• • • • • • •				

SUMMARY TABLE OF ECOTOXICITY DATA ON CARBONTETRACHLORIDE

3. AQUATIC PLANTS

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (mg/l)	Validity	Comments	Reference
1. FRESHWATER							
Chlamydomonas reinhardtii	72 h	S,C,A	EC50 EC10	0.246 0.072	2	Elevated CO ₂ level – EC10 equivalent to NOEC	Brack & Rottler (1994)
Haematococcus pluvialis	4 h	S,N	EC50	> 136	3	Toxicity threshold	von Knie et al. (1983)
Microcystis aeruginosa	8 d	S,C,N	EC50	> 105	3	Partial volatility control	Bringmann & Kuehn. (1978a)
Scenedesmus quadricauda	8 d	S,C,N	EC50	> 600	3	Partial volatility control	Bringmann & Kuehn (1978b)
2. SALTWATER							
Diatoms (3 species)	96 h	S,N	EC50	Approx 20 to 40	3	High temp (30°C) – 200 to 400 dilution of "saturated solution"	Tadros <i>et al.</i> (1995)

LIST OF ABBREVIATIONS USED IN TABLES

А	=	Analysis
С	=	Closed system or controlled evaporation
0	=	Open vessel
h	=	hour(s)
d	=	day(s)
s MATC	=	Maximum acceptable toxicant concentration
Ν	=	nominal concentration
S	=	static
SS	=	semistatic
F-T	=	flowthrough
Validity	colum	n: 1 = valid without restriction 2 = valid with restrictions: to be considered with care 3 = invalid 4 = not assignable

ENVIRONMENTAL MONITORING LEVELS OF CARBONTETRACHLORIDE IN NATURAL SURFACE WATER

Area	Year of measurement	Mean concentration (µg/l)	Reference
1. Coastal waters and Estuaries			
Germany:			
- Ostsee	1983	0.01-0.05	Hellmann, 1984
- Nordsee	1983	0.01-0.27	Hellmann, 1984
	1990	<0.00096	WRc, 1998
- Elbe estuary	1993	< 0.01-0.02	IKSE, 1993
- Weser estuary	1993	< 0.05	ARGE-Weser, 1993
Sweden :			
- Stenungsund	1988	0.0008-0.001	Abrahamsson et al., 1989
Denmark :			
- Skagerrak	1991-1993	0.00091-0.00097	Abrahamsson & Ekdahl, 1996
France:			
- Seine	1995	< 0.1	Agence de Bassin, 1995
United-Kingdom :			
- English channel (Plymouth)	1993	0.0025	WRc, 1998
- Solent estuary	1990	< 0.01-0.311	Bianchi et al., 1991
- Humber estuary	1993	< 0.0031-0.018	Krijsell et al., 1993
- Tees estuary	1993	< 0.025-0.029	Dawes & Waldock, 1994
- Tyne (coast)	1993	0.0025	WRc, 1998
- Wear estuary	1993	< 0.025-0.102	Dawes & Waldock, 1994
- UK rivers estuaries	1993	< 0.0005-0.038	MAFF, 1995
The Netherlands :			
- Coastal waters	1983	0.0005-0.001	Van de Meent et al., 1986
- Rhine estuary	1993	0.00096-0.0081	Krijsell & Nightingale, 1993
	1993	< 0.03	RIZA, 1995
	1994	0.005	WRc, 1998

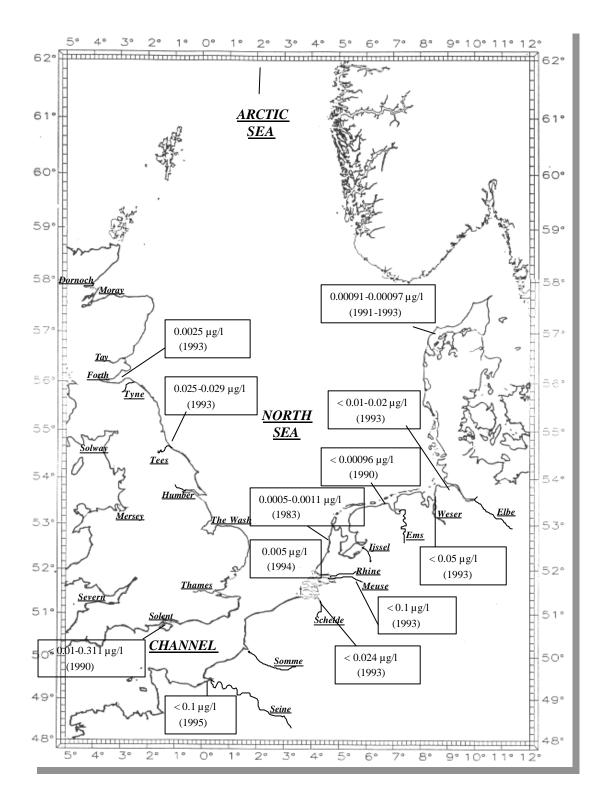
The symbol < indicates that the value is under the detection limit of the analytical method

ENVIRONMENTAL MONITORING LEVELS OF CARBONTETRACHLORIDE IN NATURAL SURFACE WATER

Area	Year of measurement	Mean concentration (µg/l)	Reference
2. River waters			
~			
Germany:			
- Rhine – Karlsruhe	1984	0.01	ARW, 1984-1986
- Rhine – Düseldorf	1986	< 0.1	ARW, 1986
- Rhine – Lobith	1993	< 0.1	WRc, 1998
- Rhine D/NL border	1993	< 0.02-0.13	Deutsche Kommission, 1995
			WRc, 1998
- Mosel, Koblenz	1994	0.005	
The Netherlands:			
- Rhine, Maasshuis	1992	0.01	WRc, 1998
- Rhine, Andijk	1985	< 0.1	RIWA, 1985
- Rhine, Lobith	1993	< 0.02	RIZA, 1995
- Meuse, Eysden	1992	< 0.05	RIZA, 1994
- Meuse, Keijserveer	1993	< 0.1	WRc, 1998
- Scheldt, Doel	1993	0.024	WRc, 1998
Switzerland:			
- Binnensee	1984	0.25	Fahrni, 1985
Belgium:			
- Meuse, Tailfer	1193	0.01	WRc, 1998
United-Kingdom:			
- Mersey	1991	23.6	WRc, 1998
- Humber	1990	0.0054	WRc, 1998

The symbol < indicates that the value is under the detection limit of the analytical method





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