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

1,1,1-Trichloroethane

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Euro Chlor
representing the chlor-alkali industry

EURO CHLOR RISK ASSESSMENT FOR THE MARINE ENVIRONMENT

1,1,1-TRICHLOROETHANE

OSPARCOM Region - North Sea

EXECUTIVE SUMMARY

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

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

In the case of 1,1,1-trichloroethane, 14 data for fish, 9 data for invertebrates and 9 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 appropriate assessment factors have been used to define a final PNEC value of 21 µg/l.

Most of the available monitoring data apply to river and estuary waters and were used to calculate PECs. The most recent data 1990-1996 support a typical PEC for 1,1,1-trichloroethane lower than 0.24 µg/l and a worst case PEC of 0.6 µg/l. The calculated PEC/PNEC ratios give a safety margin of 35 to 1000 between the predicted no effect concentration and the exposure concentration. Dilution within the sea would of course increase these safety margins.

Moreover, as the available data on persistence of 1,1,1-trichloroethane indicate a half-life in water of a few hours or days and as the bioaccumulation in marine organisms can be considered as negligible, it can be concluded that the present use of 1,1,1-trichloroethane does not represent a risk to the aquatic environment. However, 1,1,1-trichloroethane is persistent in the atmosphere and production or imports are restricted for feedstock or essential uses since 1996 under the Montreal Protocol.

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

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

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

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

The exercise consists of the collection and evaluation of data on effects and on environmental concentrations. Basically, the effect data are derived from laboratory toxicity tests and exposure from analytical monitoring programmes.
Where necessary the exposure data are backed up with calculated concentrations based on emission models.

Finally, in the absence of secondary poisoning, the risk is indicated by comparing the "predicted environmental concentrations" (PEC) with the "predicted no effect concentrations" (PNEC), expressed as a hazard quotient for the marine aquatic environment.

2. DATA SOURCES

The data used in this risk assessment activity are primarily derived from the data given in the HEDSET (updated version of June 1995) 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. COMPOUND IDENTIFICATION

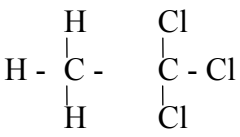
3.1 Description

CAS number	:	71-55-6
EINECS number	:	200-756-3
EEC number	:	602-013-00-2
IUPAC name	:	1,1,1-trichloroethane

1,1,1-trichloroethane is commonly abbreviated to T111. Another synonym which is used is methylchloroform

1,1,1-trichloroethane has the following formula :

$C_2H_3Cl_3$



3.2 EU Labelling

According to Annex I of Directive 93/72/EEC (01.09.93 - 19th TPA), 1,1,1-trichloroethane is classified as: harmful by inhalation (Xn, R20) dangerous for the environment (N) dangerous for the ozone layer (R59).

This classification is applicable for the pure compound.

4. PHYSICO-CHEMICAL PROPERTIES

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

Table 1: Physical and chemical properties of 1,1,1-trichloroethane

Property	**Value**
Molecular weight	133.4 g
Aspect	colourless liquid
Melting point	- 33 °C
Boiling point	73-74 °C at 1013 Pa
Decomposition temperature	≥ 100 °C
Density	1.34 at 20 °C
Vapour pressure	133 - 177 hPa at 20 °C
log octanol-water partition coefficient	2.46 (measured)
Koc	2.2
Water solubility	1.55 g/l at 20 °C
Henry's Law constant	$a.m^3/mol$ at 20 °C

5. COMPARTMENT OF CONCERN BY MACKAY LEVEL I MODEL

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 Mackay level I calculation obtained through the ENVCLASS software distributed by the "Nordic Council of Ministers". This model describes the ultimate distribution of the compound in the environment (Mackay & Patterson, 1990 - Pedersen *et al*., 1994).

The results are valuable particularly in describing the potency of a compound to partition between water, air or sediment. Practically, it is an indicator of the potential compartments of concern.

The results of such a calculation for 1,1,1-trichloroethane are given in Table 2.

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

Compartment	**%**
Air	99.7
Water	0.25
Soil	0.01
Sediment	0.01

(See Appendix 2 for details of calculation)

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

6. PRODUCTION, USE, EMISSIONS

6.1 Production and uses

The world production of 1,1,1-trichloroethane was estimated about 600,000 t in 1995. 1,1,1-trichloroethane was extensively used in metal cleaning (40% of the total consumption) and in aerosols, adhesives, coatings, dry cleaning and textile processing, electronics, etc. (ECSA, 1996).

1,1,1-trichloroethane is being phased out of most uses because of its ozone depletion potential (ODP) in the upper atmosphere. Production for emissive uses has already been phased out end 1995 in Europe and 1996 in the United States, Japan and other industrial countries, according to the Montreal Protocol and its amendments. The ODP (Ozone Depletion Potential) value is 0.12 (based on a value of 1 for CFC 11 and 12).

The main present use of 1,1,1-trichloroethane is as feedstock. 1,1,1-trichloroethane is the feedstock for the manufacture of HCFC 141b and HCFC 142 b and other CFC substitutes. 1,1,1-trichloroethane is also a feedstock for fluoropolymer resins. 1,1,1-trichloroethane is produced generally from ethylene dichloride or 1,1,2-trichlorethane, which is then dehydrochlorinated to 1,1-dichloroethylene and in a further step, 1,1-dichloroethylene is hydrochlorinated to 1,1,1-trichloroethane.

1,1,1-trichloroethane is also produced from EDC via vinyl chloride, which is reacted catalytically with hydrogen chloride to produce 1,1-dichloroethane. This material is then converted to 1,1,1-trichloroethane by chlorination.

6.2 Applicable regulations

In 1986, 1,1,1-trichloroethane was identified as one of several compounds along with CFC 11 and 12, that may deplete the stratospheric ozone layer. However, 1,1,1-trichloroethane was shown to have only one tenth of the ozone depletion potential of CFC 11 or 12 (ODP=0.12). As a result, 1,1,1-trichloroethane was excluded from the 1987 Montreal Protocol. The Protocol was amended in London in June 1990 calling for a scheduled phase out on 1,1,1-trichloroethane (along with some other candidates) with total elimination by 2005. Further initiatives from USA and EU brought forward the 2005 date to 1996 for USA and 1995 for EU.

Since January 1996, in Europe, 1,1,1-trichloroethane can only be produced or imported for feedstock and “essential uses” where an alternative substance bas not been found effective or safe, for example in US space shuttle used by NASA, laboratory or analytical uses and some pharmaceutical uses are still permitted.

6.3 Emissions

The total of emissions of 1,1,1-trichloroethane to water from sites using 1,1,1-trichloroethane as feedstock is estimated in 1995 to be 810 kg/y (Euro Chlor, 1996). This figure should have been reduced in 1996 as the main production plants were closed in Europe.

7. EFFECT ASSESSMENT

As a first approach, this chapter only considers the following three trophic levels: aquatic plants, invertebrates and fish. The effects on other organisms are only discussed when indicated.

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

Documented data from all available sources, including company data and data from the open literature, were collected and incorporated into the HEDSET for 1,1,1-trichloroethane, including their references (version of June 1995).

A summary of all data is given in *Appendix 3*. In total 14 data for fish, 9 data for invertebrates and 9 data for algae are given. Respectively 4, 3 and 1 data were considered valid for risk assessment purposes. For the respective taxonomic groups, 8, 4 and 3 should be considered with care, and 2, 2 and 5 data respectively were judged as not valid or not assignable for the risk assessment.

It is necessary to distinguish the acute studies (LC50/EC50) from chronic studies (NOEC/LOEC). In the tables presented in *Appendix 3*, the data are ranked based on class (fishes, 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 1,1,1-trichloroethane, only a few valid acute toxicity data and no results from long-term studies in marine species are available. Available data in marine species do not indicate a marked difference in the sensitivity of marine and freshwater species towards 1,1,1-trichloroethane exposure. 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, 1,1,1-trichloroethane should be tested under closed conditions (preferably with analytical measurements) to avoid losses by volatilization.

The different trophic levels are reviewed below. The reference numbers are those listed in the table of *Appendix 3* and given in *Appendix 6*.

7.1 Marine fish

Two studies report acute toxicity values but they should be considered with care although one is a flow-through study. The lowest 96 h-LC50 was 33 mg/l for *Limanda limanda* is found in this flow-through study but there is some uncertainty on the isomer used (Pearson & McConnell, 1975).

No studies were found on the long term toxicity of 1,1,1-trichloroethane to marine fish.

7.2 Freshwater fish

Eleven studies report on the short term toxicity for three species of freshwater fish. From the three available valid studies, the lowest 96h-LC50 was 42.3 mg/l for *Pimephales promelas* (Brooke *et al.,* (1985-1988). The lowest 96 h-EC50 (loss of equilibrium) was 11.1 mg/l (Alexander *et al.*, 1978).

Two studies report on the long-term toxicity for fish. Only one valid study is found showing a 14d-NOEC for *Cyprinus carpio* at 7.7 mg/l (Thompson & Carmichael, 1989). One lower NOEC is 3.4 mg/l for *Brachydanio rerio* (Röderer,1990), however this experiment could not be checked and the data was judged not assignable for the risk assessment (validity 4).

7.3 Marine invertebrates

Three studies report on the short term toxicity for crustaceans. The lowest 48 h-LC50 was 7.5 mg/l for *Elminius modestus* (Australian Barnacle) (Pearson & McConnell, 1975) in a study which should be considered with care. In another 24h-acute study (Sanchez-Fortun *et al*., 1997) various life stages *of Artemia salina* were evaluated from 24h- to 72h-stages. Results of the 24h-stage was considered valid with care (24h EC50 of 113 mg/l). However the results obtained from the 48h- and 72h-stages (respectively 24h EC50 of 44 and 8 mg/l) cannot be considered as relevant as starvation may have influenced the results. Additionally, control data are not described. A higher value of 31.2 mg/l was found for *Mysidopsis bahia* but the validity cannot be checked (USEPA, 1980).

No studies were found on the long term toxicity of 1,1,1-trichloroethane to marine invertebrates.

7.4 Freshwater invertebrates

Four short term studies on *Daphnia magna* were reported. The only valid study showed a lowest 48 h-LC50 of 57.6 mg/l (Bobra *et al.*,1984). Other less valid values were between 59.6 and 2,400 mg/l. Two valid studies report on the long-term toxicity for *D. magna*. The lowest NOEC for *D. magna* was 1.3 mg/l (Thompson & Carmichael, 1989). This includes effects on reproduction and mortality. The other NOEC is found at 7.9 mg/l (Wolf *et al.,*1986).

7.5 Marine Algae

For the marine algae *Phaeodactylum tricornutum* the EC_{50} was 5 mg/l. This study has to be considered with care due to uncertainty for the isomer used and unsual methodology ($^{14}CO_2$ uptake) (Pearson & McConnell, 1975).

7.6 Fresh Water Algae

Valid or nearly valid values are available for three freshwater algae species. The lowest 72 h-EC_{50} is found at 0.54 mg/l for *Chlamydomonas reinhardtii* (Brack & Rottler, 1994). The NOEC (EC10) for this species is 0.21 mg/l.

7.7 PNEC for marine environment

From an evaluation of the available toxicity data for aquatic organisms, it is reasonable to conclude that the sensitivity of both marine and freshwater organisms to 1,1,1-trichloroethane is quite similar.

A summary of the valid data selected for the derivation of PNEC values at different levels is given in Table 3. This table summarises the PNEC values derived from acute and chronic studies. When these studies are available, it is generally considered that the latter are closer to real world than the former. Therefore the more reliable value should be in the lower end of the table. As far as the North Sea is concerned, acute effect studies are not relevant because of the absence of local sources.

The $PNEC_{aquatic}$ was derived on the basis of data for both freshwater and marine organisms. The lowest data are presented per major taxonomic group. Acute EC/LC_{50} -values are available for the three trophic levels of the base-set and therefore an assessment factor of 1000 to the lowest value may be applied. Prolonged toxicity studies were found for fish, invertebrates and algae, implying that an assessment factor of 10 can be used to the lowest NOEC.

Application of an assessment factor of 1000 to the lowest EC_{50} results in a PNEC of 0.54 µg/l, whereas application of an assessment factor of 10 to the lowest NOEC results in a PNEC for aquatic organisms of 21 µg/l.
The final PNEC which is calculated for this risk assessment is 21 µg/l.

Table 3: Summary of ecotoxicity data selected for the PNEC derivation, with the appropriate assessment factors for 1,1,1- trichloroethane.

Available valid data	Assigned assessment factor	Lowest toxicity values
At least 1 short-term LC50 from each trophic level (fish, daphnia , algae)	1000	- *Pimephales promelas,* 96h LC50 = 42.3 mg/l (Brooke, *et al.,* 1985-1988) - *Limanda limanda*, 96h LC50 = 33 mg/l (Pearson & McConnell, 1975) - *Daphnia magna,* 48h LC50 = 57.6 mg/l (Bobra, *et al.,* 1984) - *Elminius modestus*, 48h LC50 7.5 mg/l (Pearson & McConnell, 1975) - *Chlamydomonas reinhardtii*, 72h EC50 = 0.54 mg/l (Brack & Rottler, 1994) - *Phaeodactylum tricornutum*, EC50 = 5 mg/l (Pearson & McConnell, 1975)
	PNEC = 0.54 µg/l	
Long-term NOEC for 3 species representing three trophic levels (fish, daphnia, algae)	10	- *Cyprinus carpio*, 14d NOEC growth = 7.7 mg/l (Thompson & Carmichael, 1989) - *Daphnia magna*, 17d NOEC mortality, reproduction = 1.3 mg/l (Thompson & Carmichael, 1989) - *Chlamydomonas reinhardtii*, 72h EC10 = 0.21 mg/l (Brack & Rottler, 1994)
	PNEC = 21 µg/l	

According to the EU Directive 90/415/CEE, the surface water quality objective for 1,1,1-trichloroethane was set at 10 µg/l for freshwaters, estuaries and marine waters.

7.8 Bioaccumulation

Bioaccumulation of 1,1,1-trichloroethane in aquatic species is unlikely in view of its physical and chemical properties. A bioconcentration factor of 8.9 was found for bluegill sunfish in a 28 day test (Davies & Dobbs, 1984). A measured log P_{ow} of 2.46 and observed Bioconcentration factor (BCF) below 100 for fishes allow the conclusion that bioaccumulation would be negligible in marine organisms.

7.9 Persistence in water

As indicated by the Henry's law constant (1500 Pa.m_3/mol at 20 °C), 1,1,1-trichloroethane entering aquatic systems would be rapidly transferred to the atmosphere through volatilization. Half-life will range from hours to a few weeks depending on wind and mixing conditions, water velocity, rivers or lakes.

In laboratory experiments, a half-life in water ranges from a fraction of an hour to several hours (Dilling *et al*, 1976). Using the Henry's Law constant, one would calculate a half-life of 3.7 hour from a model river 1 m deep with a 1 m/sec current and a 3 m/sec wind (Lyman *et al*, 1982); in the same way, by using the oxygen reaeration coefficients for various bodies of water, one calculates that the volatilization half-lives range from 5.1-10.6 days for ponds, 3-29 hours for rivers and 3.8-12 days for lakes (Lyman *et al*, 1982).

Half-lives in a mesocosm simulating the conditions in Narragansett Bay were 24, 12 and 11 days under spring, summer and winter conditions, respectively (Wakeham *et al*, 1983).

Such values show that 1,1,1-trichloroethane will rapidly disappear from water to atmosphere by volatilization.

Hydrolysis in water is a small, but significant degradation process, dissolved 1,1,1-trichloroethane having a half-life of approximately 6 months (Callahan *et al*, 1979; Dilling *et al*, 1975). 1,1,1-trichloroethane is also resistant to photolysis.

7.10 Persistence in air

Direct photolysis is not important in the troposphere since 1,1,1-trichloroethane does not absorb light above 290 nm.

In the troposphere 1,1,1-trichloroethane is photochemically oxidized by hydroxyl radicals abstracting H atoms. This reaction is slow and the atmospheric life-time towards OH oxidation is approximately 5 years, which requires a globally averaged OH radical concentration of $9.7.10^5$ radicals/cm^3 (Prinn *et al.,* 1995).

When the loss due to hydrolysis in oceans is included, the same authors calculated the total atmospheric life-time to be 4.6 ± 0.3 years. This value corresponding to a half-life of about 3.2 years, is now accepted as the standard life-time (IPCC, 1996).

The final products of atmospheric oxidation of 1,1,1-trichloroethane are carbon dioxide and hydrogen chloride.

A small fraction of the emissions of 1,1,1-trichloroethane will survive degradation in the troposphere and be transported to the stratosphere, this has resulted in 1,1,1-trichloroethane being controlled under the 1990 amendment to the Montreal Protocol. It has been assigned an Ozone Depletion Potential of 0.12 and consumption within developed nations was phased out in 1996 except for feedstock and essential uses (WMO, 1994).

7.11 Degradation in biological systems

In the aquatic environment, biodegradation will not be a significant sink due to the volatility of 1,1,1-trichloroethane.

1,1,1-trichloroethane can be slowly biodegraded in water and soil by acclimated aerobic cultures (Bouwer *et al*, 1983; Bouwer *et al*, 1981; Tabak *et al*, 1981; Wilson *et al*, 1983).

In seawater, a half-life of 9 months has been determined based on hydrolysis in closed system (Pearson *et al*, 1975).

Under anaerobic conditions, 1,1,1-trichloroethane was completely removed by methanogenic bacteria after 8 to 10 weeks exposure. Field evidence of biodegradation in aquifers was obtained by following the concentration of 1,1,1-trichloroethane in a confined aquifer after it was infected with reclaimed ground water. The half-life of 1,1,1-trichloroethane was 231 days with biodegradation given as the probable cause of loss (McCarthy *et al*, 1984). This value is comparable to the one obtained under laboratory conditions in closed system (Pearson *et al*., 1975).

7.12 Conclusion

Although 1,1,1-trichloroethane is persistent in the atmosphere (ODP 0.12), it should not be considered as bioaccumulable. It can be deduced from the above information that 1,1,1-trichloroethane is not a "toxic, persistent and liable to bioaccumulate" substance as mentioned by the Oslo and Paris Conventions for the Prevention of Marine Pollution (OSPARCOM) according to the criteria currently under discussion and especially those defined by UN-ECE, Euro Chlor and CEFIC.

8. EXPOSURE ASSESSMENT

The exposure assessment is essentially based on exposure data from analytical monitoring programmes. 1,1,1-trichloroethane has been measured in a number of water systems. These levels in surface waters (river water and marine waters) are detailed in *Appendix 4*. References of the available monitoring data can be found in HEDSET Data Sheet for 1,1,1-trichloroethane (version of June 1995). Additional sources have been also used. 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 Marine waters and estuaries

In coastal waters and estuaries from Germany, the Netherlands and United Kingdom, observed concentrations are in a range from below 0.005 µg/l up to 7.6 µg/l although values higher than 1 µg/l are generally outliers. Typical recent monitoring data for 1,1,1-trichloroethane in coastal waters and estuaries which are part of the OSPARCOM region are given in *Appendix 4* and illustrated on the North Sea map in *Appendix 5*.

A recent survey (1990-1992) of the UK and NL estuaries and coastal waters (n=39 data) shows a geometric mean concentration (typical) of 0.024 µg/l and a worst case mean value of 0.206 µg/l (WRc, 1998).

8.2 River waters

Background levels of 1,1,1-trichloroethane in typical big rivers coming into the North Sea are in general lower than 0.1 µg/l.

In the Rhine river water and other adjacent industrialized rivers, up to 0.6 µg/l is measured with an outlier value of 1.1 µg/l in the Mersey river. Monitoring data from the river Seine at 100 km or less from the sea was under the detection limit of 1 µg/l in 1995 (see *Appendix 4*).

8.3 Other monitoring data

Only few data on 1,1,1-trichloroethane levels measured in aquatic organisms are available.

As already stated (see 7.8: log P_{ow} below 2.47 and observed BCF below 100 for fishes) we can consider that bioaccumulation is negligible in marine organisms.

9. RISK ASSESSMENT CONCLUSION

In the risk characterization of 1,1,1-trichloroethane for the aquatic organisms, the PNEC is compared to the PEC.

A PNEC of 21 µg/l was obtained for the aquatic species exposed to 1,1,1-trichloroethane.

In coastal waters and estuaries, 1,1,1-trichloroethane is observed up to 2.79 µg/l (worst case) but the concentrations measured support a typical water concentration of less than 0.1 µg/l.

In non-industrialized areas, a typical river water concentration below 0.01 µg/l was derived from the measured levels; a worst case was also identified in industrialized zone with measured levels up to 0.6 µg/l.

These monitoring values allow to calculate the ratios PEC/PNEC which are summarized in Table 4.

Table 4: Calculation of PEC/PNEC ratios for 1,1,1-trichloroethane

Type of water	PEC level	PEC/PNEC
Coastal waters/Estuaries		
• worst case	0.206 µg/l	0.01
• typical case	0.024 µg/l	0.001
River waters		
• worst case	0.6 µg/l	0.03
• typical water	< 0.1 µg/l	< 0.005

These calculated ratios, **which do not take into account any dilution factor within the sea,** correspond to a safety margin of 35 to 1000 between the aquatic effect and the exposure concentration so that the present use of 1,1,1-trichloroethane should not represent a risk to the aquatic environment. Moreover, current restrictions on the use of 1,1,1-trichloroethane since 1996 would further reduce the environmental levels.

In addition, as stated previously, there is no sign of accumulation neither in the biosphere nor in the hydrosphere.

10. REFERENCES

10.1 General references

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10.2 References for ecotoxicity data : see *Appendix 6*

Those references are used in Appendix 3.

10.3 References for monitoring data: see Appendix 7

Those references are used in Appendix 4.

APPENDIX 1

Environmental quality criteria for assessment of ecotoxicity data

The principal quality criteria for acceptance of data are that the test procedure should be well described (with reference to an official guideline) and that the toxicant concentrations must be measured with an adequate analytical method.
Four cases can be distinguished and are summarized in the following table (according to criteria defined in IUCLID system).

Table: Quality criteria for acceptance of ecotoxicity data

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

The selected validated data LC50, EC50 or NOEC are divided by an assessment factor to determine a PNEC (Predicted No Effect Concentration) for the aquatic environment.
This assessment factor takes into account the confidence with which a PNEC can be derived from the available data: interspecies- and interlaboratory variabilities, extrapolation from acute to chronic effects,...
Assessment factors will decrease as the available data are more relevant and refer to various trophic levels.

APPENDIX 2

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

Fugacity Level I calculation

Chemical: 1,1,1-trichloroethane

Temperature (C)	20
Molecular weight (g/mol)	133.40
Vapor pressure (Pa)	13300
Solubility (g/m3)	1550
Solubility (mol/m3)	11.62
Henry's law constant (PA.m3/mol)	1144.66
Log octanol water part. coefficient	2.46
Octanol water part. coefficient	288.40
Organic C-water part. coefficient	118.25
Air-water partition coefficient	0.47
Soil-water partition coefficient	3.55
Sediment-water partition coefficient	7.09
Amount of chemical (moles)	1
Fugacity (Pa)	.40515735E-6
Total VZ products	2468176.84

Phase properties and compositions:

Phase	Air	Water	Soil	Sediment
Volume (m3)	.6000E+10	.70000E+7	.45000E+5	.21000E+5
Density(kgm3)	.12056317E+2	.10000E+4	.15000E+4	.15000E+4
Frn org carb.	.00000E+0	.00000E+0	.20000000E-1	.40000000E-1
Z mol/m3.Pa	.41029864E-3	.87362333E-3	.30990553E-2	.61981107E-2
VZ mol/Pa	.24617918E+7	.61153633E+4	.13945749E+3	.13016032E+3
Fugacity	.40515735E-6	.40515735E-6	.40515735E-6	.40515735E-6
Conc mol/m3	.16623551E-9	.35395492E-9	.12556050E-8	.25112101E-8
Conc g/m3	.22175817E-7	.47217586E-7	.16749771E-6	.33499543E-6
Conc ug/g	.18393524E-5	.47217586E-7	.11166514E-6	.22333029E-6
Amount mol	.99741307E+0	.24776844E-2	.56502228E-4	.52735413E-4
Amount %	99.74	0.25	0.01	0.01

APPENDIX 3

SUMMARY TABLE OF ECOTOXICITY DATA ON 1,1,1-TRICHLOROETHANE

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							
Pimephales promelas	96 h	A,F-T	EC50 LC50	11.1 52.8	1	loss of equilibrium	Alexander *et al,* 1978
Pimephales promelas	96 h	A,F-T	EC50 LC50	28.8 42.3	1	respiration, loss of equilibrium; effects prior to death	Brooke *et al,* 1985
Pimephales promelas	96 h	A,F-T	LC50	52.9	1		Brooke *et al,* 1985
Lepomis macrochirus	96 h	N,S	LC50	72	2		Buccafusco *et al*, 1981
Oryzias latipes	48 h	F-T	LC50	73	2		CITI, 1992
Pimephales promelas	96 h	N,S	LC50	105	2		Alexander *et al*, 1978
Leuciscus idus melanotus	48 h	N,S	LC50	123	2		Juhnke & Lüdemann, 1978
Poecilia reticulata	7 d	N,SS,C	LC50	133	2		Könemann, 1981
Poecilia reticulata	96 h	S	LC50	148	2		Könemann, 1981
Lepomis macrochirus	96 h	S	LC50	69.7	4		US EPA, 1980
2. Saltwater							
Limanda limanda	96 h	A,F-T	LC50	33	2	no explicit confirmation of the isomer tested	Pearson & McConnell, 1975
Cyprinodon variegatus	96 h	N,S	LC50	71	2		Heitmuller *et al,* 1981

APPENDIX 3

SUMMARY TABLE OF ECOTOXICITY DATA ON 1,1,1-TRICHLOROETHANE

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50, NOEC)	Concentration (mg/l)	Validity	Comments	Reference
CHRONIC STUDIES							
1. Freshwater							
Cyprinus carpio	14 d	A,F-T,C	NOEC	7.7	1	gain of weight	Thompson & Carmichael, 1989
Brachydanio rerio	14 d		NOEC	3.4	4		Röderer, 1990
2. Saltwater							
no data available							

APPENDIX 3

SUMMARY TABLE OF ECOTOXICITY DATA ON 1,1,1-TRICHLOROETHANE

2 CRUSTACEANS

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	AS,C	LC50	57.6	1		Bobra *et al*, 1984
Daphnia magna	48 h	N,S,C	EC50	59.6	2	immobility	Abernethy *et al,* 1986
Daphnia magna	48 h	N,S,C	LC50	> 530	2	NOEC: 530 mg/l	LeBlanc, 1980
Daphnia magna	24 h	N,S	EC50	2400	3	immobility; isomer not given	Bringmann & Kühn, 1982
2. Saltwater							
Elminius modestus	48 h	N,S,C	LC50	7.5	2	no explicit confirmation of the isomer tested	Pearson & McConnell, 1975
Artemia salina	24 h	S,N	EC50-24h stage EC50-48h stage EC50-72h stage	113 44 8	2 (3) (3)	lack of reported control data	Sanchez-Fortun *et al*., 1997
Mysidopsis bahia	96 h	N,S	LC50	31.2	4		US EPA, 1980
CHRONIC STUDIES							
1. Freshwater							
Daphnia magna	17 d	A,SS(2 d),C	NOEC	1.3	1	reproduction, mortality	Thompson & Carmichael, 1989
Daphnia magna	21 d	A,SS,C	NOEC	7.9	1	growth	Wolf *et al,* 1986
2. Saltwater							
no data available							

APPENDIX 3

SUMMARY TABLE OF ECOTOXICITY DATA ON 1,1,1-TRICHLOROETHANE

3 AQUATIC PLANTS, INCLUDING ALGAE

Species	Duration d (days) h (hours	Type of study	Criterion (LC50/EC50, NOEC)	Concentration (mg/l)	Validity	Comments	Reference
1. Freshwater							
ALGAE							
Chlamydomonas reinhardtii	72 h	A,S,C	EC10 EC50	0.213 0.536	1	growth (biomass)	Brack & Rottler, 1994
Chlorella vulgaris	3 h	S,C	EC50	153	2	$^{14}CO_2$-uptake	Hutchinson *et al,* 1980
Chlamydomonas angulosa	3 h	S,C	EC50	280	2	$^{14}CO_2$-uptake	Hutchinson *et al,* 1980
Microcystis aeruginosa	8 d	S	LOEC	350	3	growth; pH 7; artificial medium; isomer unknown	Bringmann & Kühn, 1978
Scenedesmus quadricauda	8 d	S	LOEC	430	3	growth; isomer unknown	Bringmann & Kühn, 1978
Selenastrum capricornutum	96 h		EC50	> 669	3		US EPA, 1978
Chlorococcales (mixed)	24 h		EC10	100	4	oxygen production	Krebs, 1985
2. Saltwater							
ALGAE							
Phaeodactylum tricornutum	?		EC50	5	2	$^{14}CO_2$-uptake; no explicit confirmation of the isomer tested	Pearson & McConnell, 1975
Skeletonema	?		EC50	> 669	3	growth	US EPA, 1978

APPENDIX 3

SUMMARY TABLE OF ECOTOXICITY DATA ON 1,1,1-TRICHLOROETHANE

ABBREVIATIONS

A	=	analysis
C	=	closed system or controlled evaporation
h	=	hour(s)
d	=	day(s)
MATC	=	maximum acceptable toxicant concentration
N	=	nominal concentration
S	=	static
SS	=	semi static
F-T	=	flow-through
Validity column		1 = valid without restriction
		2 = valid with restrictions: to be considered with care
		3 = invalid
		4 = not assignable
NOEC		No-observed effect concentration
LOEC		Lowest observed effect concentration

APPENDIX 4

ENVIRONMENTAL MONITORING LEVELS OF 1,1,1-TRICHLOROETHANE IN NATURAL SURFACE WATER

1. Open sea

Location	Year of measurement	Mean concentration (µg/l)	Reference
North Sea, open sea	1983 - 84	0.005	van de Graaff, 1988
Arctic Sea :			
- Svalbard area (South of Spitzberg)	1980	0.0025	Fogelqvist, 1985
- Open sea	1987	< 0.00005	Krijsell & Wallace, 1988

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

APPENDIX 4

ENVIRONMENTAL MONITORING LEVELS OF 1,1,1-TRICHLOROETHANE IN NATURAL SURFACE WATER

2. Coastal waters and estuaries

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

Location	Year of measurement	Mean concentration (µg/l)	Reference
Great-Britain :			
- English Channel (Plymouth)	1993	0.015	WRc, 1998
- North Sea coast (various)	1993	0.015-0.137	WRc, 1998
- Solent estuary	1990	< 0.005 - 2.79	Bianchi *et al*, 1991
- Humber estuary	< 1993	0.0051 - 0.053	Krijsell & Nightingale, 1993
	1992	0.010-0.049	Dawes *et al*., 1994
- Tees estuary (Redcar Jetty)	1996	< 0.1	UK Environmental Agency, 1997
	1992	0.206	WRc, 1998
- Wear estuary	1992	< 0.010 - 0.064	Dawes & Waldock, 1994
- Tyne estuary	1992	< 0.010 - 0.089	Dawes & Waldock, 1994
- Liverpool bay	1992	< 0.010 - 0.040	Dawes & Waldock,1994
- Poole	1992	< 0.010 - 0.015	Dawes& Waldock, 1994
- Various sites around UK (Southampton, Bristol channel, North Minch, ...)	1992	< 0.010	Dawes & Waldock, 1994
- Mersey estuary	1989	0.7 - 7.6	Rogers *et al*, 1992
	1993	0.167	Wrc, 1998
France :			
- Loire estuary	1983 – 84	0.048 - 0.068	Marchand *et al*, 1986

APPENDIX 4

ENVIRONMENTAL MONITORING LEVELS OF 1,1,1-TRICHLOROETHANE IN NATURAL SURFACE WATER

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

Location	Year of measurement	Mean concentration (µg/l)	Reference
Netherlands:			
- Rhine / Maas estuary	1983 - 84	max. 0.029	van de Graaff, 1988
	1994	0.020	WRc, 1998
- Ijsselmeer, Andijk	1989 - 92	< 0.1	RIWA, 1992, 1993, 1994
- North Sea coasts	1983 - 84	0.007	van de Meent *et al*, 1986
	1990	< 0.1	RIWA, 1992
Germany, Schleswig – Holstein			
- Baltic sea, Glücksburg	1981	max. 0.145	Atri, 1985
- Schlei estuary, Kappeln	1981	max. 0.005	Atri, 1985
- North Sea coasts, Außeneider	1981	max. 0.025	Atri, 1985
- Weser estuary	1993	< 0.1	Weser Güteberich, 1993
Sweden:			
- Stenungsund, Skagerrak	1988	0.0024 - 0.0030	Abrahamsson & Klick, 1989

APPENDIX 4

ENVIRONMENTAL MONITORING LEVELS OF 1,1,1-TRICHLOROETHANE IN NATURAL SURFACE WATER

3. River waters

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

Location	Year of measurement	Mean concentration (µg/l)	Reference
Belgium:			
- Scheldt, Doel	1994	0.17 (max. 0.49)	Rijkswaterstaat, 1994
- Scheldt, Baasrode	1995	0.097	Dewulf et al, 1997
- Meuse, Tailfer	1992 - 94	0.03	RIWA, 1994, 1995, 1996 a
	1995	<0.1	RIWA, 1996 b
Netherlands :			
- Rhine	1983	< 0.005 - 0.080	van de Graaff, 1988
- Rhine, Lobith	1990	max. 0.1	IAWR, 1991
	1991	0.05	RIVM, 1993; RIWA, 1993
	1993	0.05	WRc, 1998
- Rhine, Hagestein	1991 - 92	< 0.1	RIWA, 1993, 1994
- Maas, Eijsden	1991	0.15	RIVM, 1993
	1992	0.19	RIWA, 1994
	1993	0.17	RIWA, 1995
	1994	0.26	RIWA, 1996 a
	1995	0.08	RIWA, 1996 b
- Maas, Keizersveer	1992	0.02	RIWA, 1994
	1993	0.01	RIWA, 1995
	1994 - 95	< 0.01	RIWA, 1996 a, 1996 b

APPENDIX 4

ENVIRONMENTAL MONITORING LEVELS OF 1,1,1-TRICHLOROETHANE IN NATURAL SURFACE WATER

4. River waters

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

Location	Year of measurement	Mean concentration (µg/l)	Reference
France:			
- Seine	1995	< 1	Agence de Bassin, 1995
Switzerland :			
- Northern part, 155 samples from 45 river sites	1981 - 83	0.064	Fahrni, 1984
- Rivers and lakes in general	1984	0.063	Fahrni, 1984
Germany, various rivers:			
- Neckar, Heilbronn	1982 - 83	< 0.1	Ballschmiter et al, 1988
	1988	0.03 (max. 0.06)	AWBR, 1988
- Rodau, Hessen	1985 - 89	< 0.2 - 1.0	Ott, 1990
- Unterweser (km 362 - 28)	1985 - 87	0.1	Bohlen et al, 1989
- Elbe, Schnackenburg	1980 - 82	0.022	Ballschmiter et al, 1988; Atri, 1985
- Elbe, Stade	1981 - 82	0.030	Ballschmiter et al, 1988
- Elbe, Hamburg, Nordostsee kanal at Brunsbüttel	1981	max. 0.057	Atri, 1985
- Elbe profile	1992	< 0.01 - 0.04	ARGE Elbe, 1993
- Main	1989 - 90	0.01 - 0.03	Trapp et al, 1992

APPENDIX 4

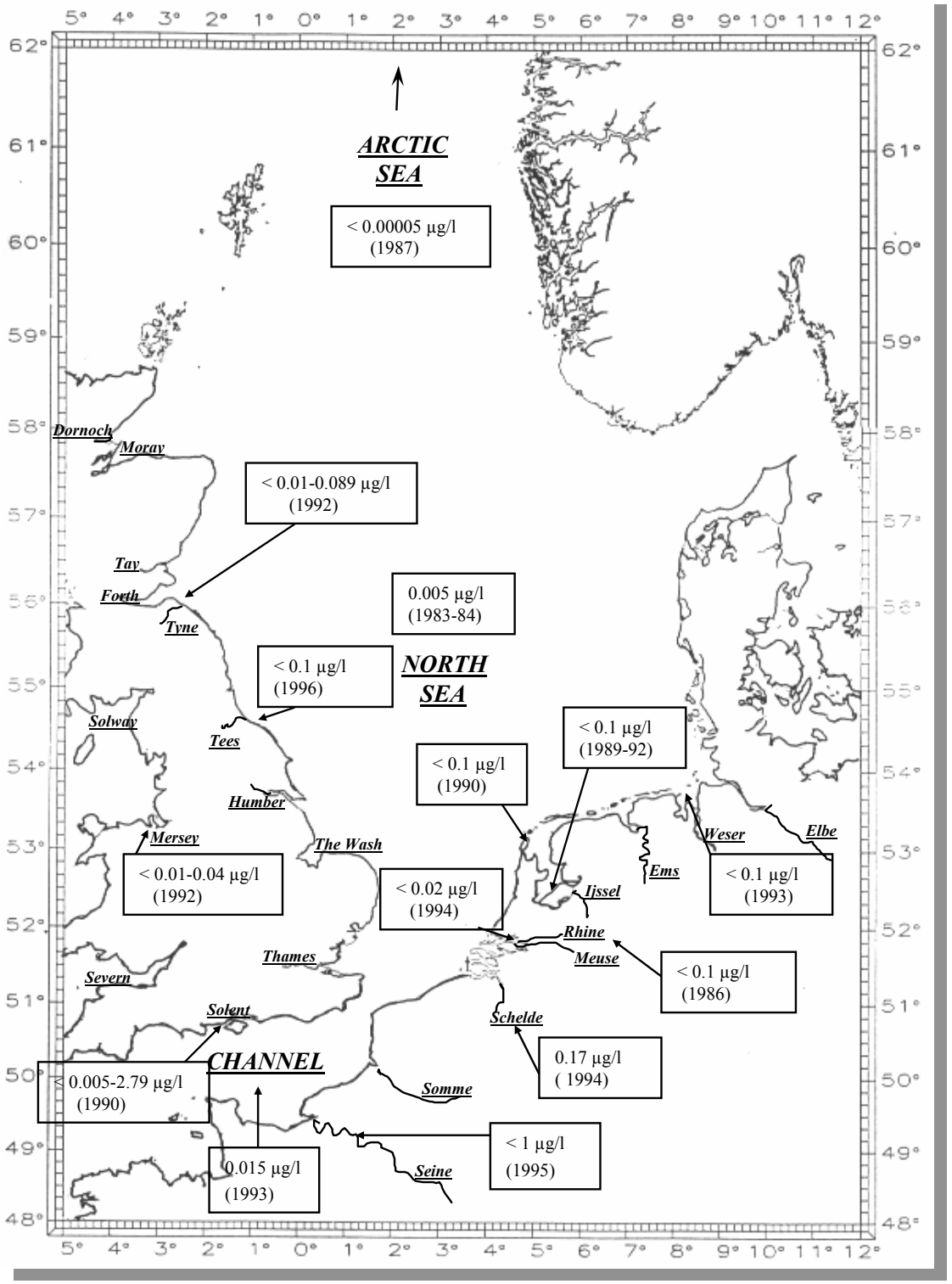
ENVIRONMENTAL MONITORING LEVELS OF 1,1,1-TRICHLOROETHANE IN NATURAL SURFACE WATER

5. River waters

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

Location	Year of measurement	Mean concentration (µg/l)	Reference
Germany, Rhine at various sites			
- Bad Honnef	1990	< 0.05 - 0.08	LWA, 1991
- Köln	1991	0.03 (max. 0.21)	ARW, 1991
- Düsseldorf	1986	max. 0.1	Gewässergütebericht, 1986
- Niederrhein	1985	0.140	Ballschmiter et al, 1988
- Karlsruhe	1988	0.02 (max. 0.09)	AWBR, 1988
- G/NL borderline, km 865	1986	< 0.1	Malle, 1987; Gewässergütebericht, 1986
Germany, Rhine tributaries			
- Sieg	1986 - 90	< 0.1 - 0.1	LWA, 1987 - 92
- Wupper	1986 - 91	0.6 - < 0.05	LWA, 1987 - 92
- Erft	1986 - 91	< 0.1 - 0.2	LWA, 1987 - 92
- Ruhr	1986 - 90	0.6 - < 0.05	LWA, 1987 - 92
- Emscher	1986 - 91	0.5 - 2.4	LWA, 1987 - 92
- Lippe	1986 - 91	0.1 - 0.53	LWA, 1987 – 92
Great Britain			
- Humber	1990	0.053	WRc, 1998
- Mersey	1991	1.1	WRc, 1998

APPENDIX 5 : NORTH SEA monitoring data on 1,1,1-trichloroethane



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