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

Dichloromethane

February 1999

Euro Chlor
representing the chlor-alkali industry

EURO CHLOR RISK ASSESSMENT FOR THE MARINE ENVIRONMENT

DICHLOROMETHANE

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 dichloromethane, 23 data for fish, 17 data for invertebrates and 6 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 830 µg/l.

Most of the available monitoring data apply to river and estuary waters and were used to calculate PECs. The most recent data (1983-1995) support a typical PEC for dichloromethane lower than 0.2 µg/l and a worst case PEC of 13.6 µg /l. The calculated PEC/PNEC ratios give a safety margin of 60 to 4000 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 dichloromethane 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 dichloromethane does not represent a risk to the aquatic environment.

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

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

Additionally Euro Chlor has voluntarily agreed to carry out limited risk assessments for 25 prioritised chemicals related to the chlorine industry. These compounds are on lists of concern of European Nations participating in the North Sea Conference. The purpose of this activity is to explore if chlorinated chemicals presently pose a risk to the marine environment especially for the North Sea situation. This will indicate the 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. The references of the HEDSET and additional sources will be given in chapter 10.

3. COMPOUND IDENTIFICATION

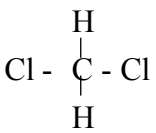
3.1 Description

CAS number	:	75-09-2
EINECS number	:	200-838-9
EEC number	:	602-004-00-3
IUPAC name	:	dichloromethane

Dichloromethane is also known as methylene chloride and is commonly abbreviated to DCM. Another synonym which is used includes methylene dichloride.

Dichloromethane has the following formula :

CH_2Cl_2



3.2 EU labelling

According to Annex I of Directive 93/72/EEC (01.09.93 - 19th TPA), dichloromethane is classified as carcinogenic category 3 : Xn, R40.

Dichloromethane is not classified as dangerous for the environment.

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 dichloromethane

Property	**Value**
Molecular weight	84.9 g
Aspect	liquid
Melting point	- 94.9 °C
Boiling point	39 - 40 °C at 1013 hPa
Decomposition temperature	120 °C
Density	1.33 at 20 °C
Vapour pressure	475 hPa at 20 °C
log octanol-water partition coefficient	1.3 (calculated)
log Koc	1.68
Water solubility	13.7 g/l at 20 °C
Henry's Law constant	270 $Pa.m^3/mol$ 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 - Pederson *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 dichloromethane are given in Table 2.

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

Compartment	%
Air	99.04
Water	0.96
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

Dichloromethane is mainly produced together with other chloromethanes e.g. methyl chloride and chloroform. The raw materials are methanol and chlorine and, to a lesser extent, methane and chlorine.

In the methanol hydrochlorination process, hydrogen chloride reacts with methanol to form methylchloride. In a second step, methyl chloride is chlorinated to heavier chloromethanes through thermal, catalytic, or photolytic chlorination. Direct chlorination – either thermal or catalytic – of methane is also used, but the methanol hydrochlorination process, where no net hydrogen chloride is generated, is usually favoured, except when a near-by use of HCl is possible (e.g. vinyl chloride production).

The European sales of dichloromethane were in 1996 about 138,000 tonnes per year, down from 200,000 tonnes in 1984. More efficient use, increasing recycling, and replacement in some applications, are the reasons of such decrease. Dichloromethane is produced in Germany, France, Italy, Spain, The Netherlands, United Kingdom in 8 plants. Exports out of Europe are estimated at the level of 100,000 tonnes per year (ECSA, 1997).

6.2. Main Uses

According to the European Chlorinated Solvent Association (ECSA, 1997), the uses of dichloromethane are:

- **For the pharmaceutical industry** (30%): where dichloromethane is used as solvent for chemical reactions, purification and isolation of intermediates or products.
  In this area, dichloromethane has some good advantages:
  - poorly miscible with water (2% weight)
  - non flammable, high auto-ignition temperature (556°C)

- easy to remove from the products
- low freezing point (-97°C)

- **For paint stripping** (19%): Dichloromethane based paint strippers normally consist of 70-90% dichloromethane along with other organic solvents, e.g. ethanol, surfactants, emulsifiers and alkaline and/or acid activators. These products have several crucial advantages over other coating removal methods, as example, non flammable, reasonable price, universally suitable for all types of coatings, fast acting at room temperature, etc.
- **For aerosols** (9%): This application began in the mid-1970 to replace CFC. Dichloromethane is not a propellant itself, but contributes to package homogeneity through its good solvency and reduces the flammability of the propellant hydrocarbon mixture.
- **For adhesives** (10%): This application uses dichloromethane as a replacement of 1,1,1-trichloroethane as a solvent.
- **For other applications** (32%) including metal degreasing, foam blowing, chemical processing (polyurethanes, polycarbonates), secondary refrigerant medium, etc.

6.3. Applicable regulations

The 3rd North Sea Conference held in The Hague in 1990 did not include dichloromethane in Annex 1A – chemicals where emission reductions were needed. It was included in Annex 1D which contains 170 chemicals that might need to be considered for prioritisation for reduction initiatives. The 4th North Sea Conference (Esjberg, Denmark) (1995) has called for OSPARCOM to develop Best Available Techniques and Best Environmental Practices for all chlorinated solvents by 2000.

6.4. Emissions

The main route by which dichloromethane enters the environment during manufacturing, processing and usage is the atmosphere and to a lesser extent the hydrosphere. Emissions in water from the manufacturing and use represented 44.6 t/y in 1995 based on a survey from about 77 sites from the European industry (Euro Chlor, 1996). This value represents a reduction of 52% compared with releases from 1985. This emission value does not include diffuse emissions coming from some uses and applications (see section 6.2.).

7. EFFECT ASSESSMENT

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

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

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

A summary of all data is given in *Appendix 3*. In total 23 data for fish, 17 data for invertebrates and 6 data for algae are given. Respectively 7, 1 and 0 data were considered valid for risk assessment purposes. For the respective taxonomic groups 1, 4 and 0 should be considered with care, and 15, 11 and 6 data respectively were judged as not valid for the risk assessment or could not be assigned due to lack of information.

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 (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 dichloromethane, 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 dichloromethane 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, dichloromethane 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 acute toxicity studies are reported for 2 marine fish species. The study with *Cyprinodon variegatus* (Heitmüller *et al*, 1981) is not considered valid because it was a static test without analysis and with no apparent measures to prevent volatile loss of the substance. LeBlanc (1980) and US Department of Commerce (1978) appear to be secondary sources for the same study, although the LC50 quoted is slightly different (331 mg/l rather than 330 mg/l).

The study with *Fundulus heteroclitus* was expressed as measured concentrations and provided some information on the decline in concentration with time. The salinity for the study was 10‰, approximately 30% full seawater. The study is valid and gave a 96h LC50 of 97 mg/l which is the lowest toxicity value for marine fish (Burton and Fisher, 1990).

No long-term studies are available.

7.2. Freshwater fish

Eleven acute toxicity studies are reported for 5 freshwater fish species. Three studies were conducted using a flow-through system with analysis of the test solutions, on *Pimephales promelas*. The results were based on measured concentrations and are considered valid, with 96h LC50s of 193 mg/l (Alexander *et al.*, 1978) 330 mg/l (Geiger *et al.*, 1986) and 502 mg/l (Dill *et al*, 1987); a 192 h LC50 of 471 mg/l was also reported (Dill *et al*, 1987). Although there is some difference between the different 96h LC50 values, they appear equally reliable. An EC50 based on loss of equilibrium was also reported (Geiger *et al.*, 1986) but was identical to the LC50, which suggests there were no such effects at concentrations below those that caused mortality.

A study with *Lepomis macrochirus* (Buccafusco *et al.*, 1981) was carried out as a static test in a closed system but without analysis. The result could be used with restrictions, but was not lower than the lowest valid LC50.

Other studies were static tests and all of them were conducted without analysis of the test concentrations, and were considered not valid.

The lowest acute toxicity value for freshwater fish was the 96h LC50 for *Pimephales promelas* which was 193 mg/l (Alexander *et al.*, 1978).

Four long-term studies have been conducted with early lifestages of 4 different freshwater fish species. Only 1 of these was conducted to recognised guidelines, with analysis, and considered valid. This study was performed with eggs and larvae of *Pimephales promelas* in a flow-through system, giving a 28d NOEC for growth of the larvae of 83 mg/l based on measured concentrations (Dill *et al*, 1987). Hatchability and survival were less sensitive, with 28d NOECs of 321 and 142 mg/l, respectively.

Another study with eggs and larvae of *Pimephales promelas* was carried out in a flow-through system with analysis (Black *et al.*, 1982). However, the interval between concentrations was wide (up to a factor of 10) and there was no information provided concerning control effects. Furthermore, the 9-day LC50 (34 mg/l) was several times lower than the 28d NOEC described above. The study is therefore not considered valid. The similar early lifestage study with *Onchorhynchus mykiss* by the same authors (Black *et al.*, 1982) giving a 27d LC50 of 13.16 mg/l is also considered non-valid for the same reasons.

The lowest NOEC value for freshwater fish is from an early life stage (28-day) test with *Pimephales promelas* which was 83 mg/l.

7.3. Marine invertebrates

Five acute toxicity studies are reported for 3 marine invertebrate species. All of them were conducted under static conditions, but only 1 (*Palaemonetes pugio*) had analysis

of the test solutions (Burton and Fisher, 1990). 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 122 mg/l). However the results obtained from the 48h- and 72h-stages (respectively 24h EC50 of 99 and 87.5 mg/l) cannot be considered as relevant as starvation may have influenced the results. Additionally, control data are not described. On the same species, Abernethy et al. (1988) found a 24 h LC50 of 510 mg/l. As only partial volatility control has been taken in this study, results should be handled with care. Without analysis of the test compound or sufficient precautions to prevent volatile losses, the *Artemia salina* study (Calleja *et al.*, 1994) should be considered not valid. Only secondary sources giving the data for *Mydidopsis bahia* could be located.
The 48h LC50 for *Palaemonetes pugio* was 109 mg/l (Burton and Fisher, 1990) which is the lowest acute toxicity value for marine invertebrates.

No long-term toxicity study is reported for marine invertebrates.

7.4. Freshwater invertebrates

Twelve acute values are reported for freshwater invertebrates. None of these meet the criteria to be classified as valid without restriction, and only 3 are considered to be valid with restrictions and should be used with care. Of these, the lowest measured 48h LC50 to *Daphnia magna* was 220 mg/l (LeBlanc, 1980). The test was performed in a system where a control of volatile losses was provided. The higher values provided in the other two studies (Kuhn *et al*, 1989. Lilius *et al.,* 1994) suggest that, although these were stated to be closed vessels, these did not fully prevent volatile loss, possibly due to a large headspace.

Two studies which report LC50/EC50 values lower than the value selected above were considered invalid. An LC50 of 136 mg/l was obtained (Abernethy *et al.*, 1986) using a closed system but the *Daphnia* appear to have been cultured and tested in distilled water, were 4 to 6 days old (normally <1 day) and were tested at 23ºC (rather than 20ºC). Furthermore, the test concentrations were estimated from the published solubility data, after preparation of a saturated solution. The value given in Knie (1988) (*Daphnia* 24h EC50 of 12.5 mg/l) was over an order magnitude lower than the lowest valid result and over two orders of magnitude lower than similar studies (24 hours, open system eg Bringmann and Kuhn, 1977). The data are therefore considered unreliable. A 48h EC50 of 27 mg/l is quoted for *Daphnia* (Daniels *et al*., 1985) but the paper does not describe original work and no citation is given (validity not assignable).

The remaining studies were invalid because of the lack of precautions to avoid volatile losses and the lack of analysis.
The lowest valid acute toxicity value for freshwater invertebrates is a 48h LC50 to *Daphnia magna* of 220 mg/l (Leblanc, 1980).
No long-term toxicity study is reported for freshwater invertebrates.

7.5. Marine algae

One acute toxicity study is reported for marine algae (*Skeletonema costatum*), the validity of which cannot be determined due to lack of information. However, the EC50

value cited, >662 mg/l, is sufficient to indicate that this species is not more sensitive than other trophic levels.

7.6. Freshwater algae

Five studies are reported for freshwater algae. None are considered valid, either because of short duration (Kuhn *et al.*, 1989), the use of a non standard endpoint (toxicity threshold, Bringmann, 1978) or because of lack of information (Bayard *et al.*, 1985), and all were based on nominal concentrations. Although some of the studies used closed vessels, there was a significant headspace which would allow loss by volatility. However, the toxicity threshold values reported for *Microcystis* and *Scenedesmus* are approximately equivalent to NOEC values and are sufficient to indicate that algae are probably less sensitive to dichloromethane than fish or invertebrates. Therefore, the lowest value (550 mg/l for *Microcystis*) has been included in the PNEC derivation (Table 3).

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 dichloromethane 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, chronic and ecosystem studies. When these studies are available, it is generally acknowledged 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 exposure is not relevant because of the absence of local sources.

The final PNEC which is calculated for this risk assessment of dichloromethane is 830 µg/l.

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

Available valid data	Assigned assessment factor	Lowest toxicity values
At least 1 short-term LC50 from 3 trophic levels (fish, invertebrates, algae)	1000	- *Fundulus heteroclitus*, LC50, 96h = 97 mg/l, (Burton and Fisher, 1990) - *Pimephales promelas*, LC50, 96h = 193 mg/l (Alexander *et al.,* 1978) - *Palaemonetes pugio*, LC50, 48h = 109 mg/l, (Burton and Fisher, 1990) - *Daphnia magna*, LC50, 48h = 220 mg/l, (LeBlanc, 1980) - *Microcytis aeruginosa* Toxicity threshold = 550 mg/l, (Bringmann, 1978)
	PNEC = 97 µg/l	
One Long-term NOEC from fish	100	- *Pimephales promelas*, NOEC, 28d = 83 mg/l, (Dill *et al,* 1987)
	PNEC = 830 µg/l	

A surface water quality objective for methylene chloride has been set at 10 µg/l by a European expert committee (CSTE, 1994) based on lack of data in 1987.

7.8. Bioaccumulation

Bioaccumulation of dichloromethane in aquatic species is unlikely in view of its physical and chemical properties. A bioconcentration factor of 6.4 to 40 was found for Cyprinus carpio exposed to 25 µg dichloromethane/l for 42 days (MITI, 1992). A measured log P_{ow} of 1.25 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 (270 Pa.m^3/mol at 20 °C), dichloromethane entering aquatic systems would be rapidly transferred to the atmosphere through volatization.

In laboratory experiments, a half-life in water of a few hours has been reported (Rathbun, Tai (1981); Lyman *et al.,* 1982; Dilling (1977).

In a controlled outdoor experiment the half-life for the disappearance from Rhine river water was found to be about 35 days (Zoeteman *et al*, 1980).

When released into an estuarine bay, all the chemical dissipated within 4 km of the release point in the spring and within 8 km in the winter under ice (Helz and Hsu, 1978).

Such values show that dichloromethane will rapidly disappear from water to atmosphere by volatilization.

Hydrolysis in water is not an important process under normal environmental conditions.

7.10 Persistence in air

Since dichloromethane does not absorb light above 290 nm, it will not degrade by direct photolysis in the troposphere (Hubrich and Stuhl, 1980).

In the troposphere dichloromethane is photochemically oxidized by hydroxyl radicals abstracting H atoms. Consequently, its atmospheric lifetime is 5 to 6 months based on the latest kinetic data and as assessed by IPCC (1996), UNEP (1991) and WMO (1994). This corresponds to a half-life of about 3.5 to 4.1 months. This life-time would preclude accumulation in the troposphere and transport to the stratosphere, hence dichloromethane does not exert any significant impact on the stratospheric ozone layer. Furthermore, the primary degradation products, formyl chloride and formic acid, have high solubility in water so that they are removed from the troposphere by rain-out. Final decomposition products are carbon dioxide and hydrogen chloride. With a POCP of 0.009, dichloromethane is not a precursor of tropospheric ozone (Derwent *et al.*, 1996, UN ECE, 1994).

7.11. Degradation in biological systems

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

Dichloromethane is reported to completely biodegrade under aerobic conditions with sewage seed or activated sludge between 6 hours to 7 days (Davis *et al.*, 1981; Klecka, 1982; Rittmann & McCarthy, 1980; Stover & Kincannon, 1983, Tabak *et al.*, 1981). 86-92 % conversion to CO_2 will occur after a varying acclimation period using anaerobic digestion in wastewater (Bouwer *et al.*, 1981).

7.12. Conclusion

It can be deduced from the above information that dichloromethane 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. dichloromethane 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 dichloromethane (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 and United Kingdom, observed concentrations are in a range from below 0.015 µg/l up to 1 µg/l. Typical recent monitoring data for dichloromethane 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*.

8.2. River waters

Background levels of dichloromethane in typical river in non-industrialized areas are in general lower than 0.1 µg/l.

In Seine and the Rhine river water or other adjacent industrialized rivers, up to a maximum of 13.6 µg/l is measured (see *Appendix 4*).

8.3. Other monitoring data

Only few data on dichloromethane levels measured in aquatic organisms are available.

As already stated (see section 7.8: log P_{ow} below .125 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 dichloromethane for the aquatic organisms, the PNEC is compared to the PEC.

A PNEC of 830 µg/l was obtained for the aquatic species exposed to dichloromethane.

In coastal waters and estuaries, dichloromethane is observed up to 1 µg/l (worst case) but the concentrations levels in waters support a typical water concentration of less than 0.2 µg/l.

In non-industrialized areas, a typical river water concentration below 0.1 µg/l was derived from the measured levels; a worst case was also identified in industrialized zone with measured levels up to 13.6 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 dichloromethane

Type of water	PEC level	PEC/PNEC
Coastal waters/Estuaries		
• worst case	1 µg/l	0.0012
• typical case	< 0.1 µg/l	< 0.00012
River waters		
• worst case	13.6 µg/l	0.016
• typical case	< 0.1 µg/l	< 0.00012

These calculated ratios, **which do not take into account any dilution factor within the sea,** correspond to a safety margin of 60 to 4000 between the aquatic effect and the exposure concentration so that the present use of dichloromethane should not represent a risk to the aquatic environment.

10. REFERENCES

10.1. General references

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10.2. References for ecotoxicity data : see *Appendix 6*

These references are used in *Appendix 3*.

10.3. References for monitoring data : see *Appendix 7*

These 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 summarised in the following table according to criteria defined in IUCLID system).

Table: Quality criteria for acceptance of ecotoxicity data

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

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

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

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

APPENDIX 2

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

Fugacity Level I calculation

Chemical: dichloromethane

Temperature (C)	20
Molecular weight (g/mol)	84.90
Vapor pressure (Pa)	47500
Solubility (g/m3)	13700
Solubility (mol/m3)	161.37
Henry's law constant (PA.m3/mol)	294.36
Log octanol water part. coefficient	1.30
Octanol water part. coefficient	19.95
Organic C-water part. coefficient	8.18
Air-water partition coefficient	0.12
Soil-water partition coefficient	0.25
Sediment-water partition coefficient	0.49
Amount of chemical (moles)	1
Fugacity (Pa)	.40231011E-6
Total VZ products	2485644.70

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	.33971855E-2	.83372798E-3	.16674559E-2
VZ mol/Pa	.24617918E+7	.23780298E+5	.37517759E+2	.35016575E+2
Fugacity	.40231011E-6	.40231011E-6	.40231011E-6	.40231011E-6
Conc mol/m3	.16506729E-9	.13667221E-8	.33541720E-9	.67083440E-9
Conc g/m3	.14014213E-7	.11603470E-6	.28476920E-7	.56953840E-7
Conc ug/g	.11623957E-5	.11603470E-6	.18984613E-7	.37969227E-7
Amount mol	.99040376E+0	.95670547E-2	.15093774E-4	.14087522E-4
Amount %	99.04	0.96	.15093774E-2	.14087522E-2

APPENDIX 3

SUMMARY TABLE OF ECOTOXICITY DATA ON DICHLOROMETHANE

1. FISH

Species	Duration h(hours)/d(days)	Type of Study	Criterion (LC50/EC50 NOEC)	Concentration (mg/l)	Validity	Comments	Reference
ACUTE STUDIES							
1. Freshwater							
Pimephales promelas	96h	A,F-T	LC50	193	1	Flow-through, compared with static (below)	Alexander *et al*., 1978 US EPA, 1978
Pimephales promelas	96h	A,F-T,C	LC50	330	1		Geiger *et al*., 1986 Jaworska & Schultz, 1994
Pimephales promelas	96h	A,F-T	LC50	502	1	Method ASTM E729-80.	Dill *et al.*, 1987
Pimephales promelas	192h	A F-T	LC50	471	1	Method ASTM E729-80.	Dill *et al.*, 1987
Pimephales promelas	96h	N,S,C	LC50	310	3	Static, compared with flow-through (above). Vessels covered with plastic wrap for first 24h only.	Alexander *et al*., 1978 Daniels *et al*., 1985 Alexander *et al*., 1978
Lepomis macrochirus	96h	N,S,C	LC50	220	2	Closed system but no analysis.	Buccafusco *et al.*, 1981 LeBlanc, 1984 US EPA, 1978
Leuciscus idus	48h	N,S	LC50	528	3		Juhnke & Luedemann, 1978 Solari & Dierickx, 1994
Leuciscus idus	48h	N,S	LC50	521	3		Juhnke & Luedemann, 1978 Solari & Dierickx, 1994
Oryzias latipes	48h	N,S,O	LC50	331	3		MITI, 1992
Oryzias latipes	48h	N,S	LC50	1100	3	At 10 and 20ºC. IUCLID records 110 mg/l.	Tsuji *et al*., 1986
Oryzias latipes	48h	N,S	LC50	840	3	At 30ºC	Tsuji *et al*., 1986
Carassius auratus	24h	N,S,O	LC50	420	3		Jensen, 1978
2. Saltwater							
Fundulus heteroclitus	48h	A,S	LC50	97	1	Salinity 10‰	Burton & Fisher, 1990

APPENDIX 3

SUMMARY TABLE OF ECOTOXICITY DATA ON DICHLOROMETHANE

1. FISH

Species	Duration h(hours)/d(days)	Type of Study	Criterion (LC50/EC50 NOEC)	Concentration (mg/l)	Validity	Comments	Reference
Cyprinodon variegatus	96h	NS	LC50	330	3		Heitmueller *et al*., 1981 LeBlanc, 1984 US EPA, 1978
CHRONIC STUDIES							
1. Freshwater							
Pimephales promelas	28d	A,F-T	NOEC	83	1	Embryo-larval study, parameter: growth.	Dill *et al.*, 1987
Pimephales promelas	28d	A,F-T	NOEC	142	1	Embryo-larval study, parameter: survival.	Dill *et al.*, 1987
Pimephales promelas	5d	A,F-T,C	LC50	>34	3	Duration= average hatching time	Black *et al*., 1982
Pimephales promelas	9d	A,F-T,C	LC50	~34	3	Duration= average hatching time + 4d.	Black *et al*., 1982
Onchorhynchus mykiss	23d	A,F-T,C	LC50	13.51	3	Duration= average hatching time.	Black *et al*., 1982
Onchorhynchus mykiss	27d	A,F-T,C	LC50	13.16	3	Duration= average hatching time + 4d.	Black *et al*., 1982
Poecilia reticulata	14d	N,SS,C	LC50	294	3	Closed system with air gap.	Koenemann, 1981 Verhaar *et al*., 1991
Oryzias latipes	21d	SS	LC50	106	4	Paper not obtained. Data abstracted from IUCLID.	RIVM, 1986
Oryzias latipes	21d	SS	NOEC	75	4	Paper not obtained. Data abstracted from IUCLID.	RIVM, 1986
2. Saltwater							
No data available							

APPENDIX 3

SUMMARY TABLE OF ECOTOXICITY DATA ON DICHLOROMETHANE

2. INVERTEBRATES

Species	Duration h(hours)/d(days)	Type of Study	Criterion (LC50/EC50 NOEC)	Concentration (mg/l)	Validity	Comments	Reference
ACUTE STUDIES							
1. Freshwater							
Daphnia magna	48h	N,S,C	LC50	220	2	Secondary sources quote 224 mg/l	LeBlanc, 1980 LeBlanc, 1984 Jaworska & Schultz, 1994 US EPA, 1978
Daphnia magna	48h	N,S,C	EC50	1682	2	DIN 38412 part I.I	Kuhn *et al.*, 1989
Daphnia magna	24h	N,S,C	EC50	1941	2	OECD method modified.	Lilius *et al.*, 1994
Daphnia magna	24h	N,S	LC50	2270	3	Paper in German - validated based upon IUCLID information.	Bringmann & Kuhn, 1977
Daphnia magna	48h	N,S,C	LC50	135.8	3	*Daphnia* 4-6 days old. Distilled water as diluent. Concn estimated from solubility. High temp (23ºC).	Abernethy *et al.*, 1986
Daphnia magna	24h	N,S,O	EC50	2100	3		Bringmann & Kuhn, 1982
Aedes aegyptus	4h	N,S,O	LC50	6890	3	In distilled water. Larva 2nd/3rd instar tested. Given as 0.52% v/v	Kramer *et al*, 1983
Daphnia magna	24h	?	EC50	909	3	OECD 202 (no method details)	Calleja *et al.*, 1994
Daphnia magna	48h	?	LC50	27	4	Secondary source. No citation given.	Daniels *et al.*, 1985
Daphnia magna	24h	N,S	EC50	12.5	3		Knie, 1988
Daphnia magna	48h	N	EC50	(190)	3	Calculated from QSAR.	Hermens *et al.*, 1984
Brachionus calyciflorus	24h	?	LC50	2021	3	Rotoxkit F system used (no method details).	Calleja *et al.*, 1994
2. Saltwater							
Palaemonetes pugio	48h	A,S	LC50	109	1	Salinity 10‰	Burton & Fisher, 1990
Artemia salina	24h	S,N	EC50-24h stage EC50-48h stage EC50 - 72h stage	122 99 87.5	2 (3) (3)	Lack of reported control data	Sanchez-Fortun *et al.*, 1997

APPENDIX 3

SUMMARY TABLE OF ECOTOXICITY DATA ON DICHLOROMETHANE

2. INVERTEBRATES

Species	Duration H(ours)/D(ays)	Type of Study	Criterium (LC50/EC50 NOEC)	Concentration (mg/l)	Validity	Comments	Reference
Artemia salina	24h	S,N,C	LC50	510	2	Partial volatility control	Abernethy *et al*., 1988
Artemia salina	24h	?	LC50	1045	3	Artoxkit (no method details).	Calleja *et al*., 1994
Mysidopsis bahia	96h	N,S	LC50	256	4	Secondary data sources	LeBlanc, 1984 US EPA, 1978
CHRONIC STUDIES							
1. Freshwater							
No data available							
2. Saltwater							
No data available							

APPENDIX 3

SUMMARY TABLE OF ECOTOXICITY DATA ON DICHLOROMETHANE

3. AQUATIC PLANTS

Species	Duration h(hours)/d(days)	Type of Study	Criterion (LC50/EC50 NOEC)	Concentration mg/l	Validity	Comments	Reference
1. Freshwater							
Chlamydomonas angulosa	3h	N,S,C	EC50	1478	3	Flasks closed with cotton wool.	Kuhn *et al.*, 1989
Chlorella vulgaris	3h	N,S,C	EC50	2293	3	Flasks closed with cotton wool.	Kuhn *et al.*, 1989
Selenastrum capricornutum	96h	?	LC50	>662	4	Cell multiplication inhibition test. US EPA 1975 protocol. No experimental details.	Bayard *et al.*, 1985 LeBlanc, 1984 US EPA, 1978
Microcystis aeruginosa	8d	N,S,C	toxicity threshold	550	3	Cell multiplication inhibition test.	Bringmann, 1978a,b
Scenedesmus quadricauda	8d	N,S,C	toxicity threshold	1450	3	Cell multiplication inhibition test.	Bringmann, 1978a,b Bringmann, 1977
2. Saltwater							
Skeletonema costatum	96h	?	LC50	>662	4	US EPA 1975 protocol. No experimental details. Cell multiplication inhibition test. Not on IUCLID.	LeBlanc, 1984 Bayard *et al.*, 1985 US EPA, 1978

APPENDIX 3

ABBREVIATIONS

A	=	analysiss
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 dichloromethane in natural surface water

1. Coastal waters and estuaries

Location	Year of measurement	Mean concentration (µg/l)	Reference
- North sea (German coast)	1983	0.06 - 0.20	Hellmann, 1984
- Great-Britain, Solent estuary	1990	0.015 - 1.000	BIANCHI *ET AL*, 1991
- Great-Britain, Tees estuary	1995	< 0.11	UK Environmental Agency, 1996

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

Environmental Monitoring levels of dichloromethane in natural surface water

2. River waters

Location	Year of measurement	Mean concentration (µg/l)	Reference
Belgium, Meuse, Tailfer	1992-94	< 0.1	RIWA, 1994, 1995, 1996a
Netherlands / Belgium			
- borderline, Meuse	1979	1.7	Dequinze *et al*, 1984
Netherlands :			
- Maas, Eijsden	1992 1993 1995	< 0.1 0.1 0.03 (median)	RIWA, 1994 RIWA, 1995 RIWA, 1996b
- Maas, Keizersveer	1992-95	< 0.5	RIWA, 1994, 1995, 1996, 1996b
- Ijsselmeer, Andijk	1980 1990	5 < 2	Zoeteman *et al*, 1980 RIWA, 1993
Germany, various rivers :			
- Mosel (Lux/G borderline)	1983	1.5 - 2.0	Hellmann, 1984
- Neckar	1983	0.6 - 1.0	Hellmann, 1984
- Elbe	1983 1988	0.7 - 2.1 max. 11	Hellmann, 1984 LWA, 1990
- Weser	1982-83 1988	< 0.5 max. 6	Hellmann, 1984 LWA, 1990

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

APPENDIX 4

Environmental Monitoring levels of dichloromethane in surface freshwaters

Location	Year of measurement	Mean concentration (µg/l)	Reference
Germany, Rhine at various sites			
- Various sites	1981-83	< 1	LWA, 1981, 1982, 1983
	1988	max. 3.3	LWA, 1989
	1989	max. 1.0	LWA, 1990
	1990	1.1 - 3.9 (90th percentile)	LWA, 1991
	1991	max. < 0.1	LWA, 1992
- Koblenz	1983	5.35 - 171 (monthly mean)	Hellmann, 1984
- Wesel	1983	< 2.0	Hellmann, 1984
- Basel	1981	0.4	Bolzer, 1981
- Köln	1981	7.7	Bolzer, 1981
- Duisburg	1981	0.1	Bolzer, 1981
	1984	max. 1.5	LWA, 1984
Germany, Rhine tributaries:			
- Main at Frankfurt - Hoechst	1986	0.1	Hoechst, 1985
- Main	1985	ca. 0.2	Van de Graaff, 1988
- Emscher	1988	max. 8.5	LWA, 1989
	1989	max. 2.5	LWA, 1990
	1990	max. 3.9	LWA, 1991

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

APPENDIX 4

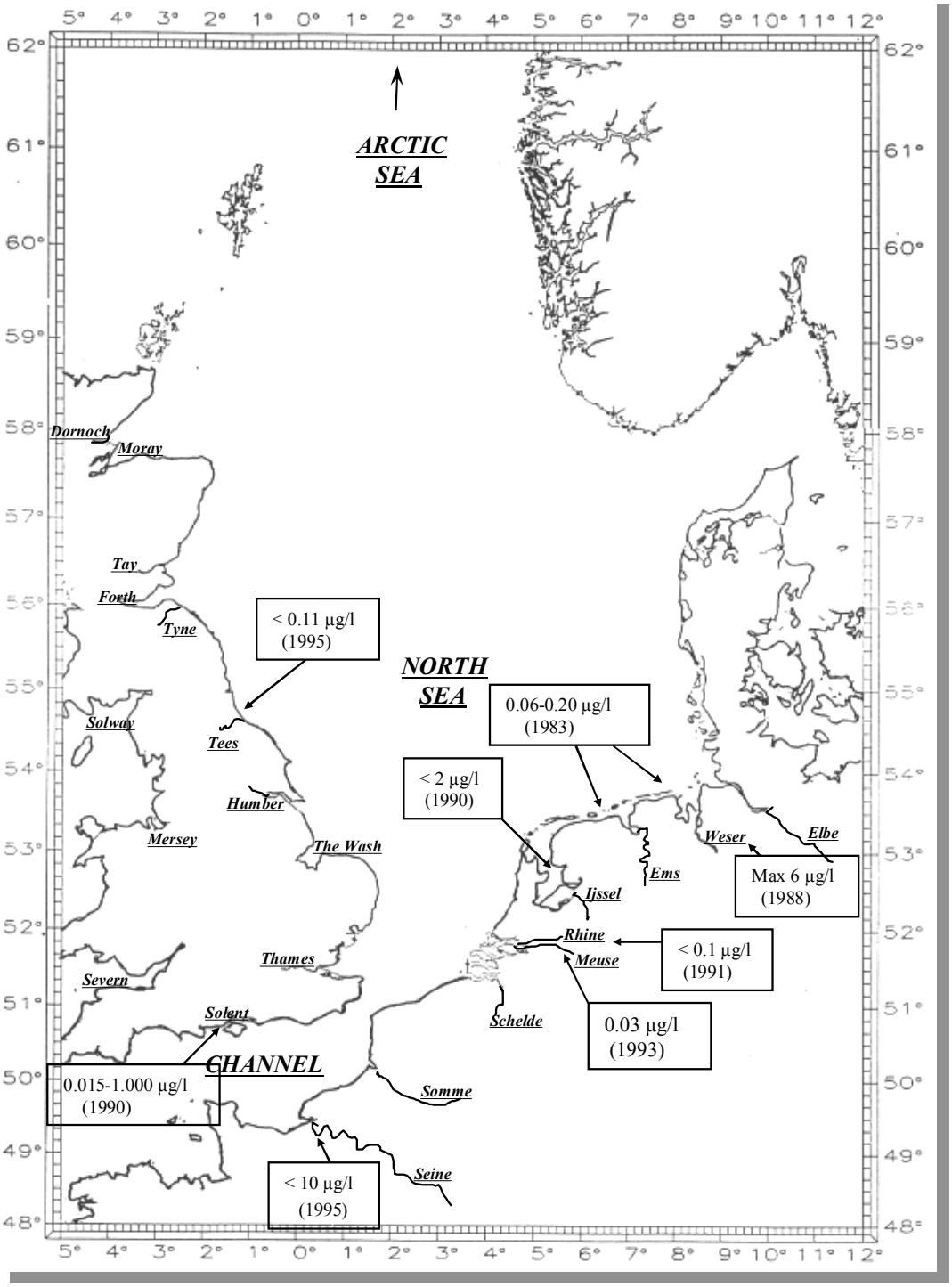
Environmental Monitoring levels of dichloromethane in surface freshwaters

Location	Year of measurement	Mean concentration (µg/l)	Reference
- Emscher	1991	max. < 0.1	LWA, 1992
- Lippe	1988	max. 5.5	LWA, 1989
	1989	max. <1	LWA, 1990
	1990	2.4 (90th percentile)	LWA, 1991
	1991	max. < 0.1	LWA, 1992
- Wupper	1988	max. 2.3 (max)	LWA, 1989
	1989	13.6 (90th percentile)	LWA, 1990
	1990	3.0 (90th percentile)	LWA, 1991
France			
- Seine (Honfleur)	1995	< 10	Agence de Bassin, Seine Normandie (1996)

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

APPENDIX 5

NORTH SEA MONITORING DATA ON DICHLOROMETHANE



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