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

Monochloromethane

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Euro Chlor
representing the chlor-alkali industry

EURO CHLOR RISK ASSESSMENT FOR THE MARINE ENVIRONMENT

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1.   INTRODUCTION

Euro Chlor, the federation representing 97% of the chlor-alkali production capacity in the enlarged European Community, voluntarily initiated a sustainable development programme within the industry. It was one of the first sectors of the European chemical industry to do so. In this context, several stepwise actions have been taken. In January 2002, the Euro Chlor members (40 companies producing more than 20 million tonnes a year of chlorine, caustic soda and hydrogen) published six commitments to sustainable development (Euro Chlor, 2003). These were turned into 14 measurable goals on environmental protection, safety and socio-economic contribution. The environmental protection goals focus on reduction targets set for 2010 and on 'product knowledge'. A first progress report was published in early 2004 (Euro Chlor, 2004).

Aiming to extend product knowledge, Euro Chlor has committed to contribute to:
- the HPV initiative (Collecting environmental and human health data on high production volume chemicals),
- the EU existing chemicals risk assessments for prioritised substances and
- targeted risk assessments for the marine environment focussing on the OSPAR region (Calow, 1998; 2004). These marine risk assessments are carried out for substances that are on lists of concern of European nations participating in the North Sea Conference.

Environmental risk assessment refers to the likelihood of harm being done to ecological targets as a result of the production, use and disposal of a chemical. In principle, it involves comparing likely exposure concentrations with sensitivity distributions of targets (van Leeuwen and Hermens, 1995). However, in practice there is rarely sufficient information to apply this in a rigorous and detailed manner. As a pragmatic solution, risk quotient analysis is applied in which predicted environmental concentrations (PECs), indices of exposure, are compared with predicted no effect concentrations for the targets (PNECs), indices of effect. PNECs are derived by using application (uncertainty) factors to ecotoxicological endpoints. This analysis gives a quotient (PEC/PNEC = RQ). Clearly an RQ of one or more triggers further actions or indicates the likelihood of an adverse effect and gives cause for concern. An RQ of less than one suggests a low to zero likelihood of harm and is usually taken to be acceptable, without the need for further action.

This risk assessment uses the quotient analysis approach and basically follows guidance associated with EU chemicals regulation as laid down in Technical Guidance Document (TGD, 2003). The assessment has focused on regional conditions, using concentrations that reflect this rather than concentrations for local circumstances. Local discharges are covered by local authorities and comply with local permits.

This paper describes a risk assessment of monochloromethane in the marine environment paying particular attention to the North Sea. The organisation of the paper reflects the makeup of the risk assessment. It begins with a general description of the substance in terms of its physical and chemical characteristics and hence its potential to be released into, distribute between and to persist within environmental compartments. In turn, there are then accounts of exposure and effects, followed by a risk assessment carried out as described above. The report closes with some general conclusions.

2.   METHODOLOGY AND DATA SOURCES

The risk assessment was performed based on existing data on effect and exposure. Data on exposure was obtained by a literature search and from monitoring databases (see section 5.1 for details). Data on effects were also collected from a search of the literature, including a search of the US-EPA's ECOTOX database. Additionally, ecotoxicity was calculated using Quantitative Structure Activity Relationship (QSAR, see section 6.2 for details). An important general data source was the OECD Substance Initial Assessment Report (SIAR) and the underlying data set (OECD 2003).

3.   PHYSICO-CHEMICAL PROPERTIES AND ENVIRONMENTAL FATE

3.1   Compound description

The identity and physico-chemical properties of monochloromethane are summarised in Table 1. The predominant environmental compartment for monochloromethane is the atmosphere. Fugacity modelling according to MacKay and Patterson (1990) with a level I model indicates that more than 99% of the total, steady state mass will reside in the air compartment and about 0.4% in each of the soil and water compartments.

Table 1. Physico-chemical properties and degradation rates for monochloromethane

CAS name	Monochloromethane
Synonyms	Monochloromethane, methyl chloride, artic
Structural formula	CH_3Cl
CAS number	74-87-3
EINECS number	200-817-4
Physical state	Gas
Appearance	Colourless, faint sweet smell
Molecular weight	50.5 g/mol
Melting point	-97°C
Boiling point	-24.2°C
Aqueous solubility	4.8-5.3 g/L (25°C)
Log K_{ow}	0.91-1.09 (calculated)
Vapour pressure	4800 hPa (20 °C)
Henry's Law Constant	$8.82 \cdot 10^{-3}$ atm m^3/mol (25 °C)
Labelling	Harmful R40, EU carcinogenicity class 3 (lowest category)

Reference: OECD (2003)

3.2   Persistence

Monochloromethane's atmospheric residence time is estimated to be about 1 year. The major process for the removal of monochloromethane from air is the reaction with hydroxyl radicals with an estimated half-life of approximately one year . Natural environmental levels are about 700 parts per trillion in ambient air. The stratospheric steady-state ozone depletion potential (ODP) of monochloromethane has been determined to be 0.02 relative to CFC 11 (ODP=1). Hydrolysis of monochloromethane in water is relatively slow with a half-life of about 1.1 years at pH 7 and 25°C.

The OECD SIDS dossier concludes that the substance cannot be considered to be readily biodegradable, but may be degraded by adapted bacteria under aerobic or anaerobic conditions (OECD, 2003). Harper (2000) describes the global monochloromethane cycle and included an extensive review of degradation pathways. A number of micro-organisms capable of growing on CH_3Cl have been isolated. For two bacteria, the mechanism of dehalogenation has been studied in detail. An adapted bacteria strain, isolated from industrial sewage, was found to be very effective at degrading monochloromethane with release of chloride ions (Hartmans *et al.*, 1986). Once taken up by an organism, monochloromethane is also metabolised as has been shown in a variety of other *in vitro* assays, including liver detoxification (Kornbrust and Bus, 1983), bio-oxidation (Stirling and Dalton, 1979; Patel, *et al.*, 1982), and enzyme catalysed hydrolysis (Keuning, *et al.*, 1985).

It can be concluded that monochloromethane is susceptible to microbial degradation. This is not surprising, since it is a naturally occurring organochlorine produced in very large quantities. It is degraded in aerobic and anaerobic environment and in sewage treatment plants. It can also be metabolised in higher organisms.

3.3   Bioaccumulation

The calculated log K_{ow} for monochloromethane is 0.91-1.09, depending on method of calculation and assumptions, indicating that monochloromethane has a low potential for bioconcentration and therefore is not expected to accumulate to significant levels in aquatic organisms. It appears that bioconcentration in aquatic organisms has not been measured. The calculated bioconcentration factor for monochloromethane, based on a log K_{ow} of 0.91 ranges from 2.98 (NTIS, 1990) to 3.16 (USEPA, 2000). The minor difference occurs due to the slightly different equations used in the methods cited.

4.   PRODUCTION, USE AND EMISSIONS

Chloromethane enters the environment from natural and anthropogenic sources. For the industrial production of monochloromethane, there are basically two different reaction routes: thermal chlorination of methane and the reaction of methanol with hydrogen chloride. The production of monochloromethane for the year 2000 was estimated to be 158 ktonne for Europe and 497.7 ktonne/yr globally (ECSA, 2004). The sole use of monochloromethane is as a feedstock for the production of other chemicals (i.e. as an intermediate). Apart from the production of other higher chlorinated monochloromethanes (dichloromethane, chloroform and carbon tetrachloride), the main downstream products are methyl chlorosilanes. Approximately 90% is used in the production of methyl chlorosilanes, which are intermediates in the production of silicone fluids, elastomers and resins (data for 2000; ECSA, 2004). Monochloromethane is also used in the production of methyl cellulose, quaternary ammonium compounds, agricultural chemicals, butyl rubber and tetramethyl lead.

Harper (2000) states that monochloromethane is the most important organochlorine in the atmosphere. The volumes produced naturally exceed the industrial production by far. Natural production is estimated to be 4,000 ktonne/yr (Harper, 2000). This is about a factor of eight times higher than the total global anthropogenic production.

As monochloromethane is used as an intermediate with very limited emissions, the levels found in the environment are almost entirely governed by the natural sources.

5. EXPOSURE ASSESSMENT

5.1 Collection of measured data

Information on environmental concentrations of monochloromethane was obtained from an on-line literature search and from databases. The literature search was performed using the Web of Science database, which contains references from on-line peer-reviewed scientific journals dating back to 1988. The substance name and several synonyms were combined with matrix names, i.e. environmental compartments. Most articles retrieved from this search report on fluxes to, or levels in, the air. However, no reports on concentrations in fresh water (the SIAR gives concentrations in marine water only), sediment or biota were found.

5.2 Evaluation of measured data

Although most measured data available for CH_3Cl are atmospheric, an important source of this compound is considered to be the oceans, and perhaps also salt marshes and coastal zones (Rhew et al., 2000; Yokouchi *et al.*, 2000). CH_3Cl measured in ocean water is generally reported as a flux to the atmosphere (e.g. mol/m^2/day**.** These measurements are not suitable for establishing exposure concentrations for risk assessment purposes. Moore *et al.* (1996) reported that in the NW Atlantic, ocean water samples were at or below CH_3Cl saturation, while in warmer waters South of the Gulf Stream and in the Pacific Ocean, all samples were supersaturated. Concentrations ranged from 3 to 5 ng/l.

Harper (2000) reported air concentration measurements of 600 ppt (vol.) (570-620) above oceans and 550-950 pptv was estimated for air above terrestrial areas. He reported measured concentrations in seawater of 4-6 ng/l.

6. EFFECT ASSESSMENT

Documented data from all available sources were collected for monochloromethane. A literature search was carried out, starting with the year 1998. This year was chosen, because a review on monochloromethane was published by WHO in 2000 (WHO, 2000).

Few ecotoxicological data on monochloromethane were found for aquatic organisms. To complement the few measured data, the toxicity was also assessed using Quantitative

Structure-Activity Relationships (QSARs), as recommended in the EU Technical Guidance Document (TGD, 2003).

6.1   Evaluation of ecotoxicological data

Data on aquatic plants, invertebrates and fish (Blum and Speece, 1991; Tang *et al.*, 1992; Bringmann and Kühn, 1976; 1980) were reviewed according to the quality criteria used in the EU (TGD, 2003). These data are presented in Table 2.

As monochloromethane is a volatile substance, closed systems are required to maintain stable test concentrations. Alternatively, exposure concentrations can be verified using analytical measurements. It is unclear from the description of the studies presented in Table 2 if vessels were closed or not. Because all results are based on nominal concentrations, a validity score of 3 is assigned (not valid).

One acute study is available for a freshwater and a marine fish (Dawson *et al.*, 1977). In the study with bluegill sunfish (*Lepomis macrochirus*) it is unclear if aeration actually occurred, as it is stated by the authors that "If dissolved oxygen was being depleted rapidly ... aeration was initiated". In the test with tidewater silversides (*Menidia beryllina*) vessels were aerated.

No toxicity studies are reported for marine algae. Two studies are available for freshwater algae (Bringmann and Kühn, 1976; 1980). The results suggest that freshwater algae and fish are equally sensitive to monochloromethane.

6.2   QSARs

Monomonochloromethane can be considered as a chemical which acts by baseline toxicity (narcosis), based on the classification system developed and validated by Verhaar *et al.* (1992; 2000). It is a chemical containing carbon, hydrogen and a halogen. It is acyclic without halogens at β-positions from unsaturations. This implies that the effects in the aquatic environment of monochloromethane can be well described by QSARs for so-called Narcosis Class I type compounds (Verhaar *et al*, 1992). This QSAR uses the octanol-water partitioning constant K_{ow} as a descriptor to assess the toxicity. For monochloromethane, calculated log K_{ow} values of 0.9-1.09 have been published and the upper value was used as conservative input for assessing the toxicity. Calculations were carried out using log K_{ow} of 1.09 for monochloromethane giving the highest estimated toxicity. This value was estimated using the EPIWIN software program from Syracuse (Howard *et al.*, 2004). The results of the calculations are presented in Table 3.

6.3   Derivation of PNEC for the marine environment

Only a few ecotoxicological data are available for monochloromethane and all are classified as 'not valid' for risk assessment purposes (validity 3). However, all data - experimental as well as QSAR estimates - give comparable results for fish and aquatic plants. They indicate a relatively low toxicity. It therefore seems justified to derive a PNEC based on the combined data set of measured and calculated ecotoxicity data.

The PNEC is derived applying the method described in the second edition of the EU Technical Guidance Document (TGD, 2003). Two long term NOECs (based on QSARs) are available for fish and daphnids, leading to the use of an assessment factor of 50 on the QSAR estimate for fish (TGD, 2003). Applying this to the lowest NOEC for fish of 26 mg/L gives a PNEC of 0.52 mg/L. According to the TGD (2003), an additional assessment factor of 10 should be used to allow for the increased biodiversity in marine as compared to freshwater ecosystems, although this is scientifically disputed (see section 8). This would result in a PNEC of 0.052 mg/L (52 µg/L).

7.   RISK ASSESSMENT CONCLUSION

Two ranges of (marine) aquatic exposure concentrations are given in the literature. These are in good agreement. The ranges are 3 to 5 ng/L for ocean water samples (Moore *et al.*, 1996) and concentrations in sea water reported by Harper (2000) were 5 ng/L, with a range of 4-6 ng/L. For the exposure in the risk calculations 5 ng/L (0.005 µg/L) was used as a PEC.

The effect assessment used QSAR estimations as the most reliable basis to derive a PNEC of 52 µg/L based on safety factor guidelines by the TGD, revision 2003.

The risk can then be calculated expressed as the risk quotient of PEC/PNEC, giving $0.005/52 = 9.6 \times 10^{-5}$. The calculated PEC/PNEC ratio gives a safety margin of 10400 between actual exposure (PEC) and the level at which no effect on the environment would be expected (PNEC). This indicates that the current use of monochloromethane does not pose a risk to the marine environment.

8.   DISCUSSION

This risk assessment used the quotient analysis approach and followed the concept laid down in the revised Technical Guidance Document (TGD, 2003). The assessment has

focused on regional conditions, using concentrations that reflect this rather than concentrations for local circumstances. This assessment cannot rule out that the safe concentrations are exceeded locally. Second, the PNECs are derived on the basis of application factors specified in the TGD 2003 version. When updating the 2003 version from the 1996 version, extra application factors have been included in the marine assessments to allow for the increased biodiversity in marine as compared with freshwater ecosystems. Such an adjustment is not without contention since, taxa for taxa, there do not appear to be consistent differences in sensitivity between freshwater and marine organisms (ECETOC, 2001). Thus all will depend upon the relative sensitivity of taxa such as ctenophores, anemones and cephalopods, that are unique to the marine environment but for which there are few if any ecotoxicological data. Moreover, for chemicals which act by narcosis, as does monochloromethane, large differences in sensitivity or specific sensitivities between taxa are not expected. Studies on freshwater organisms have shown that the variation in species-sensitivity is low for narcotic chemicals. De Zwart (2002) reported that the standard deviation of log transformed NOECs across different taxa for 34 individual narcotic chemicals averaged 0.39. Moreover, the estimate of the standard deviation was relatively constant across the different narcotic chemicals. This supports the assumption that substances which act by a narcotic mode of action have a narrow species-sensitivity distribution. That means that the calculated risk quotients could well be a factor 10 too high which would mean that the actual risk quotient is 9.6×10^{-6}. This represents a safety margin of 104,000. Further research into the ecotoxicity of substances for the specific marine taxa mentioned above will be needed to demonstrate which approach is justified. However, whatever the outcome will be, this risk assessment has demonstrated that for both assumptions no environmental risks should be expected for monochloromethane.

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Table 2. Ecotoxicity data on monochloromethane

Species	Duration	Study type	Criterion	Concentration (mg/L)	Validity[a]	Comments	Reference
FISH							
Lepomis macrochirus	96 hours	Nominal Static	LC50	550	3		Dawson *et al.* (1977)
Menidia beryllina	96 hours	Nominal Static	LC50	270	3	Continuous aeration	
AQUATIC PLANTS							
Microcystis aeruginosa	8 days	Nominal Static	LOEC[b]	550	3	Growth, toxicity threshold	Bringmann and Kühn (1976)
Scenedesmus quadricauda	8 days	Nominal Static	LOEC[b]	1450	3	Growth, toxicity threshold	Bringmann and Kühn (1980)

[a] Validity:
(1) valid without restriction; (2) valid with restrictions; to be considered with care; (3) invalid; (4) not assignable
[b] in the test the "Toxische Grenzkonzentration" is determined which can be regarded as a LOEC.
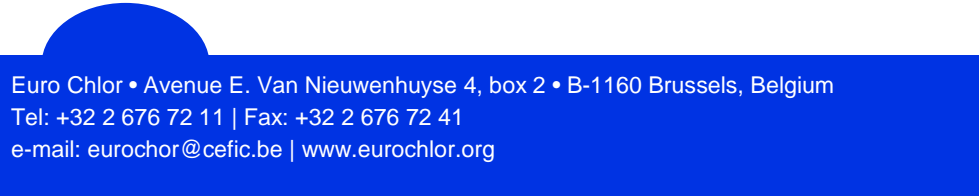
Table 3. QSAR estimates for monochloromethane

Species	Criterion	Concentration (mg/L)
FISH		
Pimephales promelas	96 hours LC50	240
Pimephales promelas	30 days ELS NOEC	26
INVERTEBRATES		
Daphnia magna	48 hours EC50	220
Daphnia magna	16 days NOEC reproduction	51
AQUATIC PLANTS		
Selenastrum capricornutum	72-96 hours EC50 growth	240

Euro Chlor

The voice of the European chlorine industry, Euro Chlor plays a key communication and representation role on behalf of its members, listening and responding to society's concerns about the sustainability of chlorine chemistry.

Euro Chlor helps members improve safety standards whilst conducting science, advocacy and communications programmes. The Brussels-based federation was founded in its current form in 1989 and has 118 members comprising 37 chlorine producers, 44 associates and 37 technical correspondents. Euro Chlor speaks on behalf of 98% of chlorine production in the EU and 2004 Accession countries.