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

# Monochlorobenzene

February 1999

# EURO CHLOR RISK ASSESSMENT FOR THE MARINE ENVIRONMENT

## MONOCHLOROBENZENE

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## 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 programs. Finally the risk is indicated by comparing the „predicted environmental concentrations" (PEC) with the „predicted no effect concentrations" (PNEC), expressed as a hazard quotient for the marine aquatic environment.
To determine the PNEC value, three different trophic levels are considered: aquatic plants, invertebrates and fish.
In the case of monochlorobenzene 27 data for fish, 24 data for invertebrates and 13 data for algae have been evaluated according to the environmental quality criteria recommended by the European authorities. Both acute and chronic toxicity studies have been taken into account and the appropriate assessment factors have been used to define a final PNEC value of 32 µg/l.

The recent monitoring data available indicate that the concentration of monochlorobenzene in surface waters is below the determination limit of 0.1, 0.2, 0.5 µg/l used in the monitoring programs e.g. in the river Rhine. Using half of the lowest determination (0.1 µg/l) as a typical case assumption a PEC of 0.05 µg/l was derived. A worst case of 0.5 µg/l is assumed. Using that assumption the calculated PEC/PNEC ratio gives a safety factor of 60 to more than 500 between the predicted no effect concentration and the exposure concentration, without taking into account any further dilution within the sea.

Moreover, as the available data on persistence of monochlorobenzene indicate a half-life in water of a few hours or days, a significant biodegradation potential and no significant bioaccumulation potential in marine organisms, it can be concluded that the present use of monochlorobenzene 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 environmental concentrations. Basically, the effect data are derived from laboratory toxicity tests and exposure data from analytical monitoring programs.
Where necessary the exposure data are backed up with calculated concentrations based on emission models.

Finally 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

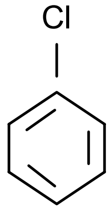
The data used in this risk assessment activity are primarily derived from the data given in the IUCLID data sheet (June 1995) and the BUA Report (1990) for this compound. Where necessary additional sources have been used.

# 3. COMPOUND IDENTIFICATION

## 3.1. Description

| | | |
|---|---|---|
| CAS number. | : | 108-90-7 |
| EINECS number. | : | 203-62-85 |
| EEC number | : | 602-033-00-1 |
| IUPAC name | : | Monochlorobenzene |
| Common name | : | Chlorobenzene |

Structural formula :



The purity of the technical product is > 99.8 %.
Impurities are:

| | | |
|---|---|---|
| Dichlorobenzenes | < | 0.06 % |
| Benzene | < | 0.08 % |

## 3.2 EU labelling

According to Annex I of the Directive 67/548/EEC monochlorobenzene is labelled and classified: Harmful (Xn) by inhalation (R20) and flammable (R10). Additional classification as dangerous for the environment should be added with the symbol N and risk phrases R51/53
(toxic to aquatic organisms / may cause long-term adverse effects in the aquatic environment).

# 4. PHYSICO-CHEMICAL PROPERTIES

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

Table 1: Physical and chemical properties of monochlorobenzene

| **Property** | **Value** |
|---|---|
| Molecular weight (g/mol): | 112,56 |
| Aspect | clear, colourless liquid with a characteristic, aromatic odour |
| Freezing point: | - 45.2 °C |
| Boiling point: | 132.2 °C at 1013 hPa |
| Density: | 1.106 g/cm³ at 20 °C |
| Vapour pressure: | 11.7 hPa at 20 °C |
| Water solubility | 0.207 g/l at 20 °C |
| log octanol-water partition coefficient, log $P_{ow}$ | 2.84 (measured) |
| log Koc | 2.25 (estimated) |
| Henry's Law constant: | 367 Pa.m³/mol |

## 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 monochlorobenzene are given in Table 2.

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

| **Compartment** | **%** |
|---|---|
| Air | 99.5 |
| Water | 0.44 |
| Soil | 0.02 |
| Sediment | 0.02 |

(see *Appendix 2* for details of calculation)

The Henry constant has a value of 367 Pa/$m^3$·mol. Chlorobenzene is thus regarded as readily volatile from aqueous solutions. Its evaporation from the hydrosphere into the atmosphere is a significant environmental transport mechanism.

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

# 6. PRODUCTION, USES, EMISSIONS

## 6.1. Production

Approx. 70,000 t of chlorobenzene were produced in Western Europe in 1993 and 10,000 t imported. Total consumption was 80,000 t.

Chlorobenzene is manufactured in Western Europe by Bayer AG (Germany), Elf Atochem, Rhodia (France) and EniChem (Italy).

Worldwide chlorobenzene production in 1993 was approx. 365,000 t (Bayer, 1995)

## 6.2 Uses

The breakdown of the 97,000 t of chlorobenzene used in Western Europe in 1987 is as follows (Srour, 1989):

| | | |
|---|---|---|
| Manufacture of Nitrochlorobenzenes | 75,000 t | 77 % |
| Other chemical transformations | 15,000 t | 16 % |
| Process solvents | 5,000 t | 5 % |
| Solvents in general (e.g. crop protection) | 2,000 t | 2 % |

Important quantitative chemical conversions other than the production of nitrochlorobenzenes are the production of diphenyl oxide and diphenyldichlorosilane.

Chlorobenzene is used as a process solvent in the production of isocyanates such as MDI and TDI and as a solvent in various crop protection formulations. It is further used as a solvent in condensation reactions in the dyes industry.

Chlorobenzene is a basic substance used in chemical syntheses with 95% of the quantity used converted in closed systems to intermediate and final products.

## 6.3. Emissions

The main routes by which it enters the environment during manufacture, processing and usage are the hydrosphere and atmosphere.

Emissions from about 78 sites from the European industry producing or using monochlorobenzene are estimated to be 6.6 t/y to water and 45.8 t/y to air in 1995 (Euro Chlor, 1996). These values represent a 70% to 85% reduction as compared to releases from 1985.

Chlorobenzene primarily enters the soil from the use of crop protection agents, in which it is used as an aid to formulation. The quantities used for this purpose have been decreased during the last years. It subsequently enters the hydrosphere and atmosphere through evaporation and leaching. The final distribution of the compound in the individual environment compartments cannot be quantified precisely. As a first approximation, we are using the results of table 2 as an equilibrium pattern.

Indirect, non-quantifiable amounts of chlorobenzene can enter the environment during incineration of household waste and special waste and through the biotic and abiotic degradation of more highly chlorinated benzenes.

# 7. EFFECT ASSESSMENT

As a first approach, only the following three trophic levels are considered: aquatic plants, invertebrates and fish.

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

A summary of all data is given in *Appendix 3.* Tests were conducted with a large number of aquatic organisms. In total 27 data for fish, 24 data for invertebrates and 13 data for algae including marine diatom have been evaluated. Respectively 6, 2 and 1 data were considered valid for risk assessment purposes. For the respective taxonomic group 12, 17 and 8 should be considered with care and 9, 5 and 4 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)..

As only a few data refers to marine species, and that it shows no significant difference in sensitivity with respect to fresh water species, we will consider that the PNEC derived from the present set of data is valid for marine as well as for fresh water ecosystems. Due to its low solubility and high vapour pressure, monochlorobenzene should be tested under closed conditions to avoid losses by volatilisation.

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

## 7.1 Marine fish

There is only one study on marine fish available which showed an 96 h-EC 50 values of 10 mg/l (*Cyprinodon variegatus*) (Heitmuller *et al.*, 1981). Although this study should be handled with care, the results can be used for risk assessment purpose.

## 7.2 Freshwater fish

From the acute studies, for which LC50's vary between 4.1 and 45 mg/l, valid studies are available from *Lepomis macrochirus, Salmo gairdneri* and *Pimephales promelas*. The rainbow trout *Salmo gairdneri* was found to be the most sensitive (LC50-96h = 4.7 mg/l) to chlorobenzene in a flow-through test (Dalich *et al.*, 1982).

In a few chronic studies the toxicity of chlorobenzene to larvae from *Carassius auratus, Micropterus salmoides* and *Salmo gairdneri* was determined. The duration of the test was between 3.5 and 27 days. No data are given for the hatching frequency of controls so that NOEC (LC 1) cannot be calculated exactly and the results should be interpreted with care (Birge *et al.*, 1979, Black *et al.*, 1982). One study done under semi-static condition in a closed system in *Brachydanio rerio* found a NOEC of 5.6 mg/l. Although the results were presented as the nominal value, analytical measurements done during the study showed an actual value corresponding to 85% of the nominal data. Due to the extensive details available in this study, a lowest NOEC of 4.8 mg/l (85% of 5.6 mg/l) can be used.

## 7.3 Marine invertebrates

The toxicity of chlorobenzene to larvae of *Artemia salina* and embryos of *Paracentrotus lividus* was studied. Also a study with *Mysidopsis bahia* was reported. Concerning the validity, the methods or the endpoints of the *Paracentratus lividus* study are not considered to be relevant in the context of the risk assessment process. For the *Mysidopsis bahia* test, the original reference cannot be checked. These studies are focusing on embryo-larval stages and the method used not clearly described. The *Artemia salina* study (Abernethy et al., 1988) should be handled with care as this occurred under closed system but in static conditions. This latter study gives a 24h-LC50 of 40.6 mg/l.

No chronic data are available although a 48 h-NOEC of 1.1 mg/l has been found in *Paracentrotus lividus* embryos (Pagano *et al.*, 1988). The validity of this study is questionable due to lack of details concerning the methodology used.

## 7.4 Freshwater invertebrates

Studies on acute invertebrate toxicity are available with EC 50 values which range between 4.3 and 195 mg/l. Two of these studies are valid without restriction both performed with *Daphnia magna* using the AFNOR test under closed system. The EC50 from these studies are 4.3 (Calamari *et al.*, 1983) and 16 mg/l (Bazin *et al.*, 1987).

Concerning the chronic studies a 16d-NOEC of 0.32 mg/l from a test with restricted validity on *Daphnia magna* is available (Hermens *et al.*, 1984).

## 7.5 Marine algae

There are some studies on the marine diatom *Skeletonema costatum* which seems to be rather insensitive to chlorobenzene. In a study with restricted validity lasting 5 days a EC50 of 203 mg/l and a NOEC of 100 mg/l were determined (Cowgill *et al.*, 1989).

## 7.6 Freshwater algae

Algae seem to be less sensitive than fish and invertebrates with EC50 ranging from 12.5 to 280 mg/l. One valid study was found which resulted in a 96h-EC50 of 12.5 mg/l (Calamari *et al.*, 1983). Although a 3h-NOEC of 2 mg/l was found in an unstandardized test, a valid NOEC of 6.8 mg/l was reported in *Selenastrum capricornutum* (Calamari *et al.*, 1983).

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

| Available valid data | Assigned assessment factor | Lowest toxicity values |
|---|---|---|
| At least 1 short-term LC5O from each trophic level (fish, daphnia, algae) | 1000<br>**PNEC = 4.3 µg/l** | - *Salmo gairdneri* 96 h-LC50 = 4.7 mg/l (Calamari *et al.*, 1982) mg/l (Calamari *et al.*, 1983)<br>- *Daphnia magna* 48 h-EC50 = 43 mg/l (Calamari *et al.*, 1983)<br>- *Selenastrum capricornutum* 96 h-EC50 = 12.5 mg/l (Calamari *et al.*, 1983) |
| Long-term NOEC from at least 3 species representing three trophic levels (fish., daphnia, algae) | 10<br>**PNEC = 32 µg/l** | - *Brachydanio rerio* 28 d NOEC = 4.8 mg/l (Adema & de Ruiter, 1987)<br>- *Daphnia magna* 16 d NOEC = 0.32 mg/l (Hermens *et al.*, 1984)<br>- *Selenastrum capricornutum* 96 h NOEC = 6.8 mg/l (Calamari *et al.*, 1983) |

## 7.7 PNEC for marine environment

If the lowest effect data are used the PNEC (predicted no-effect concentration) for the marine environment has to be derived from the freshwater data.

A summary of the valid data for acute studies selected for the derivation of PNEC values at different levels is given in Table 3. This table summarises the lowest PNEC values derived from acute studies. Using the lowest acute toxicity value from valid data (*Daphnia magna* 48 h-EC50 of 4.3 mg/l) and applying an assessment factor of 1000 the PNEC is determined to be 4.3 µg/l.

For chronic studies, valid data are only available for fish and algae. For daphnia data with restricted validity are available. Based on the lowest NOEC in daphnia of 0.32 mg/l, a PNEC of 32 µg/l can be assumed using an assessment factor of 10.

**The final PNEC which is calculated for this risk assessment is 32 µg/l.**

The draft for surface waters quality objectives of the European Union for substances of List I of Directive 76/464 indicates a value of 1 µg/l (CSTE, 1994) for chlorobenzene.

## 7.8 Bioaccumulation

Bioaccumulation is likely to be low on the basis of the log $P_{OW}$ value of 2.84. Chlorobenzene is classified as having no or low bioaccumulation in the MITI list for 1987.

Table 4: Experimental bioconcentration factors

| Species | BCF | Exposure |
|---|---|---|
| Algae (*Chlorella fusca*)* | 50 | 24 h / 0.05 mg/l |
| *Leuciscus idus** | 75 | 72 h / 0.05 mg/l |

(*) radioactive labelled compounds

A log BCF of 2.65 has been reported for fathead minnows (Veith *et al.,* 1979). Another test was conducted by the MITI with the carp, *Cyprinus carpio* (MITI, 1992). The organisms were exposed during 8 weeks to monochlorobenzene at two concentration levels (0.15 mg/l and 0.015 mg/l). A BCF of 4.3 to 40 was determined at the higher concentration and a BCF of 3.9 to 23 at the lower concentration. A level I EQC modelling exercise (Mackay *et al.*,1996) gives a result of BCF 32 for fish, which is comparable to experimental data.

## 7.9. Persistence in water

The Henry constant has a value of 367 $Pa \cdot m^3 \cdot mol^{-1}$. Chlorobenzene is thus regarded as readily volatile from aqueous solutions. Its evaporation from the hydrosphere into the atmosphere is a significant environmental transport mechanism. The rate of evaporation will depend on the windspeed and water movement. The half-life for evaporation is estimated between 1 and 12 hours in a rapidly flowing stream (Cadena *et al.,* 1984). Simulation from the aquatic half-life in a river system by the SRC's EPIWIN software gives a value of 3.2 hours (1 m deep, 1 m/sec water current and 3 m/sec wind velocity) and 102 hrs in a lake system (1 m deep, 0.05 m/sec water current and 0.5 m/sec wind velocity). In a marine model ecosystem, a half-life between 4.6 and 21 days was found (Wakeham *et al.,* 1983).

Chlorobenzene is not hydrolysed at environmental temperatures and pH values. Chlorobenzene absorbs light in the 290-310 nm region (Uyetta *et al.,* 1976). Based on experimental data, the half-life for direct photolysis in surface water at 40° latitude during the summer season has been estimated to be 170 years (Atkinson, 1987). Photodegradation in water can be accelerated through indirect photodegradation mechanisms (effect of humic acids, nitrates etc. in natural waters) (BUA, 1990)

## 7.10. Persistence in air

The most important degradation reaction of chlorobenzene under tropospheric conditions is the reaction with OH radicals. With a rate constant of $7.710^{-13}$ $cm^3$/mol.sec (Atkinson, 1989) and assuming the OH concentration in the troposphere to be $5 \times 10^6$ molecules/$cm^3$, the reaction half-life of chlorobenzene is 10 days. Half-life simulation with the SRC's EPIWIN software gives a value of 7.8 days in the atmosphere.

## 7.11. Degradation in biological systems

A modified MITI test was conducted during 4 weeks at a chlorobenzene concentration of 30 mg/l; no biodegradation was observed (MITI, 1992).

In a closed-bottle test (OECD Guideline 301D) with non-adapted micro-organisms from the run-off from a test treatment plant primarily handling communal waste water, a 55% degradation of a monochlorobenzene concentration of 2.4 mg/l was observed after 28 days (unpublished data in BUA, 1990). This means that the compound can be considered as inherently biodegradable. Biodegradation is markedly improved with adapted microorganisms and higher temperatures. For example with pseudomonas species micro-organisms a 100% cleavage of the ring structure of chlorobenzene was seen after 58 hours at a concentration of 200 mg/l and an incubation temperature of 30 °C. Degradation rates were determined in a closed system through oxygen consumption established using a pressure gauge (Worne, 1972).

Studies conducted in 1989 in a large-scale treatment plant in the Chicago, USA region - handling both communal waste water and a high percentage of industrial effluent - showed that chlorobenzene was 95.1% biodegraded, with 2.3% evaporation and 0.1% adsorption. Total elimination of chlorobenzene was assessed at 97.5% (Namkung & Rittmann, 1987).

Measurements of the chlorobenzene concentration in effluent from the Bayer AG plant in Leverkusen before and after treatment in a sewage plant showed an elimination rate of ≥98.6% (Bayer, unpublished data).

Biodegradation will occur during the warmer season when the microbial activity is increased and will proceed more rapidly in fresh water than in estuarine and marine systems (Bartholomew & Pfaender, 1983; Pfaender & Bartholomew, 1982). A half-life of 75 days was reported for an estuarine river with near natural conditions (Lee & Ryan, 1979).

Degradation under anaerobic conditions could not be unequivocally demonstrated.

## 7.12. Conclusions

Although monochlorobenzene is toxic to aquatic organisms, it has a low bioaccumulation potential and a low persistance due to its volatility. It can be deduced from the above information that Monochlorobenzene 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 programs. Monochlorobenzene 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 IUCLID Data Sheet for Monochlorobenzene (updated version of 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 background "regional" concentrations and the higher to contamined areas, or "local" concentrations, considered as worst cases.

## 8.1 Marine waters and estuaries

Measurement data on the presence of chlorobenzene in the North Sea or coastal areas is not available.

Within the scope of the research report „Organische Umweltchemikalien in deutschen Ästuarien und Küstengewässern“ (Organic environmental chemicals in German estuaries and coastal waters) (Ernst *et al.*, 1986) chlorobenzene level in water, sediment or organisms in the estuaries of the Elbe, Weser or Ems, or in coastal waters was always under the detection limit of 0.1 µg/l. Levels from < 0.01 to 0.12 µg/l were found in the Solent estuary (UK, Bianchi *et al.*, 1991)

The typical case for the coastal region could be adequately described using a half of the chlorobenzene determination limit (0.1 µg/l). This results in an estimation of the chlorobenzene concentration in water of 0.05 µg/l.

$$PEC_{est} = 0.05\ \mu g/l$$

Measurements of the 1,2-dichlorobenzene concentration in the Rhine and North Sea show that there is a tenfold dilution in the coastal region and a 100-fold dilution at a distance of 70 - 80 km from the coast. The dilution is attributable to strong Atlantic currents.

## 8.2 River Waters

Typical recent monitoring data for monochlorobenzene in river waters from Germany, the Netherlands, France and United Kingdom which are part of the OSPARCOM region are given hereafter and illustrated on the North Sea map in *Appendix 5*. The measured levels of chlorobenzene in the environment are given in *Appendix 4*.

A number of studies to establish the presence of chloroorganic compounds in the aquatic environment failed to reveal any chlorobenzene above the detection limit.

The presence of chlorobenzene cannot be demonstrated in Rhine water treated to yield drinking water (Kühn & Brauch, 1988).

Chlorobenzene is not specified in the more recent Water Authority publications. It is assumed that the concentrations were below the limits of detection (Gewässergütebericht ’91, 1992; Rheingüterbericht NRW ’92, 1993).

Chlorobenzene is no longer listed in the RIWA annual report for 1992, nor in the water quality data for the Elbe in 1993 (RIWA, 1992; Wassergütedaten der Elbe, 1994).

The monochlorobenzene has been removed from most of the monitoring programmes due to the fact that the measured values are systematically under the detection limit.

## 9. RISK ASSESSMENT CONCLUSION

In the risk assessment of monochlorobenzene for the aquatic organisms, the PNEC is compared to the PEC. A PNEC of 32 µg/l was obtained for the aquatic species exposed to monochlorobenzene.

Based on estimation, the concentrations in estuaries of big rivers coming into the North Sea could be 0.05 µg/l (half of the determination limit).

For big rivers coming into the North Sea, a worst case concentration of $< 0.5$ µg/l (detection limit) is suggested with typical values around 0.05 µg/l (half the determination limit).

These monitoring or estimated values allow calculation of the PEC/PNEC ratio as in table 5:

Table 5 : Calculation of PEC/PNEC ratios for monochlorobenzene

| Type of water | PEC level | PEC/PNEC |
|---|---|---|
| <u>Coastal waters/estuaries</u> | | |
| • typical (estimated) | < 0.05 µg/l | < 0.002 |
| <u>River waters</u> | | |
| • worst case | < 0.5 µg/l | < 0.015 |
| • typical (estimated) | 0.05 µg/l | 0.002 |

These calculated ratios, **which do not take into account any dilution factor within the sea**, correspond to a <u>safety margin of 60 to more than 500</u> between the aquatic effect and the exposure concentration so that the present use of monochlorobenzene should not represent a risk to the aquatic environment. Additionally, monochlorobenzene has a low bioaccumulation potential and is inherently biodegradable.

# 10. REFERENCES

## 10.1 General References

Atkinson, R. (1987); Inter. J. Chem. Kinet., 19: 799-828

Bartholomew, G.W., Pfaender, F.K. (1983): Influence of spatial and temporal variations on organic pollutant biodegradation rates in an estuarine environment. Appl. Environ. Microbiol.. 45, 103-109

Bayer AG (1995): internal details on manufacture, export, import, uses and quantities

BUA-Stoffbericht 54: Chlorbenzol (November 1990)

Cadena, F. *et al.* (1984); Journal Water Pollution Control Fed, 460-463

CSTE (1994): EEC water quality objectives for chemicals dangerous to aquatic environment (List 1); The views of the Scientific Advisory Committee on Toxicity and Ecotoxicity of Chemicals, DGXI; Environmental Contamination and Toxicology, 137, 83-110

Euro Chlor (1996): Personal communication from the COCEM group

Kühn, W.; Brauch, H.-J. (1988): Organische Spurenstoffe im Rhein und bei der Trinkwasser aufbereitung, gwf Wasser und Abwasser, 129

Lee, R.F., Ryan, C.C. (1986):Microbial degradation of pollutants in marine environments; USEPA-600/9-79-012, p. 443-450

Mackay, D., Patterson, S. (1990): Fugacity models, in: Karcher, W. Bevillers, J. (Eds); Practical applications of quantitative activity relations in environmental chemistry and toxicology. 433-460

Mackay, D., Di Guardo, A., Paterson, S., Kicsi, G., Cowan, C. and Kane, D. (1996): Assessment of chemical fate in the environment using evaluative, regional and local-scale models: Illustrative application to chlorobenzene and linear alkylbenzene sulfonates, Environmental Toxicology and Chemistry, 15:9, 1638-1648

MITI-LIST (Ministry of International Trade and Industry) (1987). The list of existing chemical substances tested on biodegradability by microorganisms or bioaccumulation in fish body by Chemicals Inspection & Testing Institute. Japan, 1 14, 16, 18, 31

MITI (1992): Biodegradation and bioaccumulation data of existing chemicals based on the CSCL Japan

Namkung, E., Rittmann, B.E. (1987): Estimating volatile organic compound emissions from publicly owned treatment works. Journal WPCF 59, 670-678

Pedersen, F., Tyle, H., Niemelä, J.R., Guttmann, B., Lander, L., Wedebrand, A. (1994): Environmental Hazard Classification – Data collection and interpretation guide; TemNord 1994:589

Pfaender, F.K., Bartholomew, G.W. (1982): Measurement of aquatic biodegradation rates by determining heterotrophic uptake of radiolabeled pollutants; Appl. Environ. Microbiol., 44: 159-164

Srour, R. (French Consultant, 10, Rue Riquet 75019 Paris): Aromatic Intermediates and Derivatives (June 1989)

TGD (1996) – Technical Guidance Documents in support of the Commission Directive 93/67/EEC on Risk Assessment for new notified substances and the Commission Regulation (EC) 94/1488/EEC on risk assessment for existing substances (Parts I, II, III and IV) EC Catalogue numbers CR-48-96-001-EN-C, CR-48-96-002-EN-C, CR-48-96-003-EN-C, CR-48-96-004-EN-C

Uyetta, M. *et al.* (1976); Nature, 264: 583-584

Veith, G.D., Defoe, D.L., Bergstedt, B.V. (1979), Measuring and estimating the bioconcentration factors in fish, J. Fish. Res. Board Can 26, 1040-1048

Wakeham, S.G., Davis, A.C., Karas, J.L.: Mesocosm experiments to determine the fate and persistence of volatile organic compounds in coastal seawater. Environ. Sci. Technol. 17, 611-617 (1983)

Worne, H.E. (1972):The activity of mutant microorganisms in the biological treatment of industrial wastes. Tijdschrift van het BECEWA (Belgisches Zentrum für Wasseruntersuchung), Liège, Belgium 22, 61-71

## 10.2 References for ecotoxicity data: see *Appendix6*

Those references are used in *Appendix 3*

## 10.3 References for exposure 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 EUCLID 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]:**<br>valid without restriction |
| II | ± | ± | ± | **[2]:**<br>valid with restrictions;<br>to be considered with care |
| III | insufficient or<br>- | - | - | **[3]:**<br>invalid |
| IV | the information to give an adequate opinion is not available | | | **[4]:**<br>not assignable |

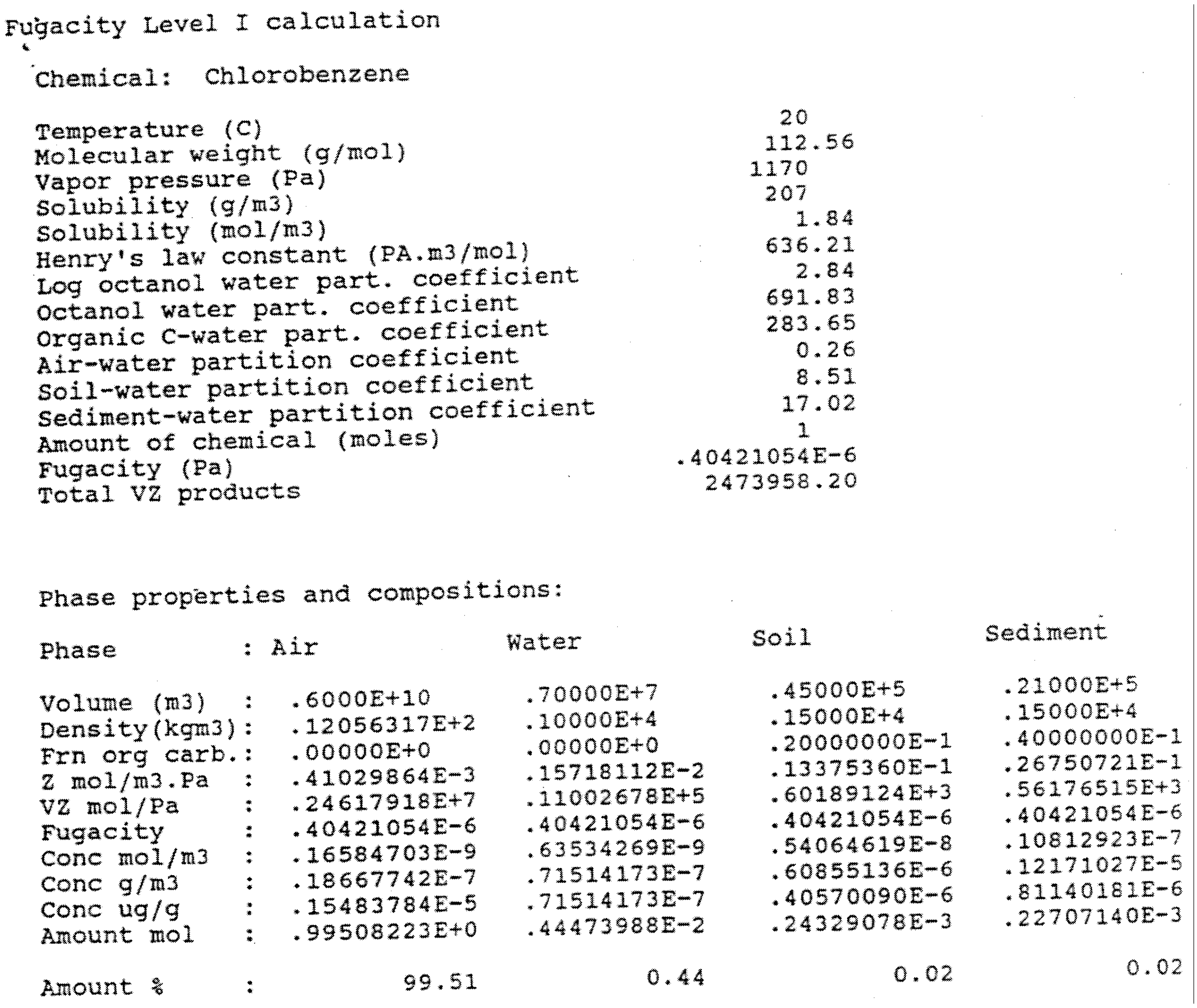
The selected validated data LC5O EC5O or NOEC are divided by an assessment factor to determine a PNEC (Predicted No Effect Concentration) for the aquatic environment.

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:  Chlorobenzene

 Temperature (C)                                20
 Molecular weight (g/mol)                      112.56
 Vapor pressure (Pa)                          1170
 Solubility (g/m3)                             207
 Solubility (mol/m3)                             1.84
 Henry's law constant (PA.m3/mol)              636.21
 Log octanol water part. coefficient             2.84
 Octanol water part. coefficient               691.83
 Organic C-water part. coefficient             283.65
 Air-water partition coefficient                 0.26
 Soil-water partition coefficient                8.51
 Sediment-water partition coefficient           17.02
 Amount of chemical (moles)                      1
 Fugacity (Pa)                            .40421054E-6
 Total VZ products                          2473958.20


 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    .15718112E-2    .13375360E-1     .26750721E-1
 VZ mol/Pa     :  .24617918E+7    .11002678E+5    .60189124E+3     .56176515E+3
 Fugacity      :  .40421054E-6    .40421054E-6    .40421054E-6     .40421054E-6
 Conc mol/m3   :  .16584703E-9    .63534269E-9    .54064619E-8     .10812923E-7
 Conc g/m3     :  .18667742E-7    .71514173E-7    .60855136E-6     .12171027E-5
 Conc ug/g     :  .15483784E-5    .71514173E-7    .40570090E-6     .81140181E-6
 Amount mol    :  .99508223E+0    .44473988E-2    .24329078E-3     .22707140E-3

 Amount %      :          99.51            0.44             0.02             0.02
```

**APPENDIX 3**

## SUMMARY OF ECOTOXICITY DATA ON MONOCHLOROBENZENE

### 1. FISH

| Species | Duration d (days) h (hours) | Type of study | Criterion (LC/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| **ACUTE STUDIES** | | | | | | | |
| **1. FRESHWATER** | | | | | | | |
| *Salmo gairdneri* | 96 h | F-T | LC50 | 4.7 | 1 | | Dalich *et al.* (1982) |
| *Salmo gairdneri* | 96 h | F-T, A | LC50 | 7.5 | 1 | | Hodson *et al.* (1984) |
| *Pimephales promelas* | 96 h | F-T, A | LC50 | 19.1 | 1 | | Hall *et al.* (1984) |
| *Lepomis macrochirus* | 96 h | S,A | LC50 | 4.5 | 1 | | Bailey *et al* (1985) |
| *Lepomis macrochirus* | 96 h | F-T, A | LC50 | 7.4 | 1 | | Bailey *et al* (1985) |
| *Brachydanio rerio* | 24 h | S,C,A | LC50 | 10.5 | 2 | | Calamari *et al.* (1983) |
| *Salmo gairdneri* | 24 h | S,C,A | LC50 | 4.1 | 2 | | Calamari *et al.* (1983) |
| *Lepomis macrochirus* | 96 h | S,N | LC50 | 20.0 | 2 | | Pickering *et al* (1966) |
| *Lepomis macrochirus* | 96 h | S,N | LC50 | 16.0 | 2 | | Buccafusco *et al.* (1981) |
| *Poecilia reticulata* | 24 h | S | LC50 | 5.6 | 2 | | Benoit-Guyod *et al.* (1984) |
| *Carassius auratus* | 96 h | S,N | LC50 | 45 | 2 | | Pickering *et al.* (1966) |
| *Pimephales promelas* | 96 h | S,N | LC50 | 29-35 | 2 | | Pickering *et al.* (1966) |
| *Poecilia reticulata* | 96 h | | LC50 | 23 | 4 | quotation | Dalich *et al.* (1982) |
| *Salmo sp.* | 96 h | S,N | LC50 | 10.4 | 4 | 0ECD 203 | Monsanto Report |
| *Pimephales promelas* | 96 h | S | LC50 | 22-35 | 4 | age dependence | Mayes *et al.* (1983) |
| *Pimephales promelas* | 96 h | | LC50 | 26 | 4 | | Cowgill *et al.* (1991) |
| *Oryzias latipes* | 48 h | S | LC50 | 17 | 4 | | MITI (1992) |
| *Lepomis macrochirus* | 96 h | S | LC50 | 19.9 | 4 | | Janard *et al.* (1984) |
| *Leuciscus idus* | 48 h | S | LC50 | 22 | 4 | | Juhnke & Lüdemann (1978) |
| *Poecilia reticulata* | 96 h | S,N | LC50 | 44 | 4 | | Pickering *et al.* (1966) |

## APPENDIX 3

# SUMMARY OF ECOTOXICITY DATA ON MONOCHLOROBENZENE

## 1. FISH

| Species | Duration d (days) h (hours) | Type of study | Criterion (LC/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| **ACUTE STUDIES** | | | | | | | |
| **2. SALTWATER** | | | | | | | |
| *Cyprinodon variegatus* | 96 h | S,N | LC50 | 10 | 2 | | Heitmuller *et al.* (1981) |
| **CHRONIC STUDIES** | | | | | | | |
| **1. FRESHWATER** | | | | | | | |
| *Brachydanio rerio* | 28 d | SS,C,A | NOEC<br>LC50 | 5.6 (N)<br>4.8 (A)<br>12.1 (N) | 1 | embryo-larval | Adema & de Ruiter (1987) |
| *Carassius auratus* | 4-8 d | FT, A | NOEC | 0.88-3.48 | 2 | larvae | Birge *et al.* (1979) |
| *Micropterus salmoides* | 3.5-7.5 d<br>3.5-4 d | F-T, A | NOEC<br>LC50 | 0.008<br>0.39-0.05 | 2 | $CaCO_3$, larvae | Birge *et al.* (1979) |
| *Poecilia reticulata* | 14 d | SS,N,C | LC50 | 19.1 | 2 | | Könemann (1981) |
| *Salmo gairdneri* | 16-27 d | F-T, A | NOEC | 0.013 | 2 | larvae | Black *et al.* (1982) |
| *Pimephales promelas* | | | NOEC | 2 | 4 | embryo-larval | US EPA (1978) |
| **2. SALTWATER** | | | | | | | |
| No data available | | | | | | | |

**APPENDIX 3**

## SUMMARY OF ECOTOXICITY DATA ON MONOCHLOROBENZENE

### 2. INVERTEBRATES

| Species | Duration d (days) h (hours) | Type of study | Criterion (LC/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| **ACUTE STUDIES** | | | | | | | |
| **1. FRESHWATER** | | | | | | | |
| *Daphnia magna* | 24 h | S, C, A | EC50 | 4.3 | 1 | | Calamari *et al.* (1983) |
| *Daphnia magna* | 24 h | S, C, A | EC50 | 16 | 1 | | Bazin *et al.* (1987) |
| *Daphnia magna* | 24 h | S, C | EC50 | 12 | 2 | | Devillers *et al.* (1987) |
| *Daphnia magna* | 48 h | S,A | EC50 | 26 | 2 | immobilization | Hermens *et al.* (1984) |
| *Daphnia magna* | 24 h | S,N | EC50 | 34 | 2 | | Kühn *et al.* (1989) |
| *Daphnia magna* | 24 h | S,C | EC50 | 140 | 2 | | Bazin *et al.* (1987) |
| *Daphnia magna* | 24 h | S | EC50 | 195 | 2 | | Bringmann & Kühn (1982) |
| *Daphnia magna* | 48 h | N,S,C | EC50 | 86 | 2 | | LeBlanc (1980) |
| *Daphnia magna* | 48 h | N,S | EC50 | 12.9 | 2 | | Gersich *et al.* (1986) |
| *Daphnia magna* | 48 h | N,S,C | EC50 | 13-20.6 | 2 | | Cowgill *et al.* (1985) |
| *Daphnia magna* | 48 h | S | EC50 | 31 | 2 | | Cowgill. (1991) |
| *Daphnia magna* | 48 h | N,S,C | EC50 | 5.8 | 2 | | Abernethy. *et al.* (1986) |
| *Ceriodaphnia dubia/ magna* | 48 h | N,S, C | EC50 | 7.9-11.0 | 2 | | Cowgill *et al.* (1985) |
| *Ceriodaphnia dubia* | 96 h | S | EC50 | 47 | 2 | | Cowgill *et al.* (1985) |
| *Daphnia magna* | 48 h | S,N | EC50<br>NOEC | 19.9<br>6.25 | 4 | OECD 202 | Monsanto Report |
| *Daphnia magna* | 48 h | S, C | EC50 | 5.0 | 4 | | Mackay *et al.* (1985) |

**APPENDIX 3**

## SUMMARY OF ECOTOXICITY DATA ON MONOCHLOROBENZENE

### 2. INVERTEBRATES

| Species | Duration d (days) h (hours) | Type of study | Criterion (LC/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| **ACUTE STUDIES** | | | | | | | |
| **2. SALTWATER** | | | | | | | |
| *Paracentrotus lividus* | 48 h | | EC<br>NOEC | 11.3<br>1.1 | 3 | embryos | Pagano *et al.* (1988) |
| *Artemia salina* | 24 h | S,C,N | EC50 | 40.6 | 2 | larva | Abernethy *et al*. (1988) |
| *Mysidopsis bahia* | 96 h | S | EC50 (mortality) | 16.4 | 4 | <24 h old stage | US EPA (1980) |
| **CHRONIC STUDIES** | | | | | | | |
| **1. FRESHWATER** | | | | | | | |
| *Daphnia magna* | 16 d | | NOEC | 1.0 | 2 | | De Wolf *et al.* (1988) |
| *Daphnia magna* | 16 d | SS | NOEC | 1.0 | 2 | mortality | Hermens *et al.* (1984) |
| *Daphnia magna* | 16 d | SS | NOEC<br>EC50 | 0.32<br>1.1 | 2 | reproduction | Hermens *et al.* (1984) |
| *Daphnia magna* | 14 d | S,C | EC50 | 2.5 | 2 | fertility | Calamari *et al.* (1983) |
| *Daphnia magna* | 21 d | N | NOEC | 2.5 | 3 | | Kühn *et al.* (1989) |
| **2. SALTWATER** | | | | | | | |
| No data available | | | | | | | |

**APPENDIX 3**

## SUMMARY OF ECOTOXICITY DATA ON MONOCHLOROBENZENE

## 3. ALGAE

| Species | Duration d (days) h (hours) | Type of study | Criterion (LC/EC50 NOEC) | Concentration (mg/l) | Validity | Comments | Reference |
|---|---|---|---|---|---|---|---|
| **1. FRESHWATER** | | | | | | | |
| *Selenastrum capricornutum* | 96 h | S, C, A | EC50<br>NOEC | 12.5<br>6.8 | 1 | Chlorophyll *a* /biomass | Galassi & Vighi (1981)<br>Calamari *et al.* (1983) |
| *Microcystis aeruginosa* | 8 d | S,C | NOEC | 120 | 2 | | Bringmann *et al.* (1975) |
| *Scenedesmus quadricauda* | 8 d | S | NOEC | ≥ 390 | 2 | | Bringmann & Kühn (1977) |
| *Selenastrum capricornutum* | 3 h | S, C | EC50<br>NOEC | 33<br>2 | 2 | photosynthesis | Calamari *et al.* (1983) |
| *Chlamydomonas angulosa* | 3 h | S, C | EC50 | 57 | 2 | $^{14}$C-CO$_2$ uptake | Hutchinson *et al.* (1980) |
| *Chlorella vulgaris* | 3 h | S, C | EC50<br>EC50 | 99<br>220 | 2 | $^{14}$C-CO$_2$ uptake<br>photosynthesis | Hutchinson *et al.* (1980) |
| *Ankistrodesmus falcatus* | 4 h | S | EC50 | 50 | 2 | $^{14}$C-CO$_2$ uptake | Wong *et al.* (1984) |
| *Selenastrum capricornutum* | 5 d | S | EC50 | 280 | 2 | cell count | Cowgill *et al.* (1991) |
| *Scenedesmus subspicatus* | 48 h | S | EC50<br>EC10<br>EC50<br>EC10 | 110<br>38<br>220<br>50 | 4 | biomass<br><br>growth rate | Kühn *et al.* (1989) |
| *Selenastrum capricornutum* | 96 h | S | EC50 | 224 | 4 | cell count | US EPA (1980) |
| *Selenastrum capricornutum* | 96 h | | EC50 | 232 | 4 | | US EPA (1978) |
| **2. SALTWATER** | | | | | | | |
| *Skeletonema costatum* | 5 d | S | EC50<br>NOEC | 203<br>100 | 2 | cell count | Cowgill *et al.* (1991)<br>Cowgill *et al.* (1989) |
| *Skeletonema costatum* | 96 h | S | EC50 | 341 | 4 | cell count | US EPA (1980) |

## LIST OF ABBREVIATIONS USED IN TABLES

A = Analysis

C = Closed system or controlled evaporation

h = hour(s)

d = day(s)

N = nominal concentration

S = static

SS = semistatic

FT = flowthrough

Validity column:
1 = valid without restriction
2 = valid with restrictions: to be considered with care
3 = invalid
4 = not assignable

**APPENDIX 4**

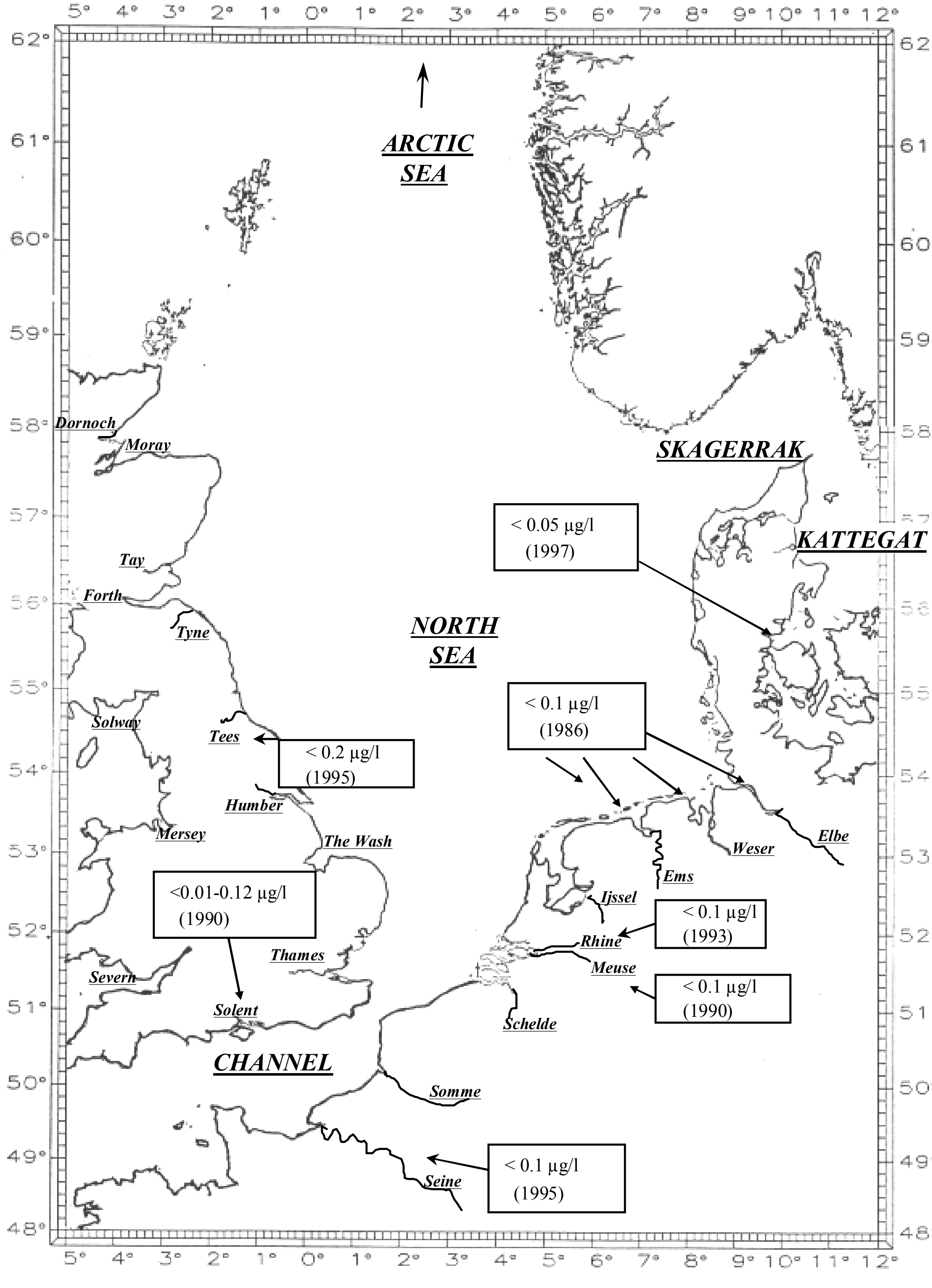
## ENVIRONMENTAL MONITORING LEVELS OF MONOCHLOROBENZENE IN NATURAL SURFACE WATER

| Area | Year of Measurement | Mean concentration (µg/l) | Reference |
|---|---|---|---|
| Germany | | | |
| Rhine - Leverkusen | 1987 | < 0.5 | BUA (1990) |
| - Düsseldorf | 1987 | < 0.5 | BUA(1990) |
| - Ruhr | 1987 | < 0.5 | BUA (1990) |
| - Nord Rhein | 1991 | < 0.5 | Gewässergütebericht 91 (1992) |
| Westfalen | 1992 | no more measurement needed | Gewässergütebericht 92 (1993) |
| Elbe, Weser, Ems estuaries and coastal waters | < 1986 | < 0.1 | Ernst, 1986 |
| Elbe (Rosenburg) | 1995 & 1996 | < 0.2 | EU COMMPS (1998) |
| Elbe estuary | | no more measured | EU COMMPS (1998) |
| Weser estuary | 1992 | no more measurement needed | Wesergütebericht (1993) |
| The Netherlands | | | |
| Various rivers | 1983-1986 | < 0.1 | Slooff *et al.* (1991) |
| Meuse – Eysden | 1990 | < 0.1 | RIZA (1991) |
| Rhine – Lobith | 1990 | < 0.1 | RIZA (1991) |
| Rhine Maasluis | 1993 | < 0.1 | RIZA (1995) |
| Rhine estuary | 1991 | no more measurement needed | CIPR (1993) |
| France | | | |
| Seine | 1995 | < 0.1 | Agence de Bassin (1995) |
| United Kingdom | | | |
| Tees (Redcar Jetty) | 1995 | < 0.2 | UK Environment Agency (1997) |
| Solent estuary | 1990 | < 0.01-0.12 | Bianchi *et al.* (1991) |
| Denmark | | | |
| Country of Aarhus Møddebro baek | 1997 | < 0.05 | EU COMMPS (1998) |

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

## APPENDIX 5

### NORTH SEA MONITORING DATA ON MONOCHLOROBENZENE



## APPENDIX 6

## REFERENCES LIST FOR ECOTOXICITY

Abernethy, S., Bobra, A.M., Shiu, W.Y., Wells, P.G., Mackay, D. (1986); Acute lethaltoxicity of hydrocarbons and chlorinated hydrocarbons to two planktonic crustaceans: The key role of organism-water partitioning; Aquat. Toxicol. 8, 163-174

Abernethy, S.G., Mackay, D., McCarty, L.S. (1988): Volume fraction: Correlation for narcosis in aquatic organisms: the key role of partitioning; Environmental Toxicology and Chemistry, 7, 469-481

Adema, D.M.M., A. de Ruiter (1987); De invloed van een aantal gechloreerde benzenen en gechloreerde anilines op de embryonale ontwikkeling van brachydanio rerio

Bailey, H.C., Liu, D.H.W., Javitz, H.A. (1985): ASTM Spec.Tech. Publ., 891 (Aquatic Toxicol. Hazard Assess.) 193-212

Bazin, C., Chambon, P., Bonnefille, M., Larbaigt, G. (1987): Comparaison des sensibilités du test de luminescence bactérienne (photobacterium phosphoreum) et du test Daphnie (Daphnia magna) pour 14 substances à risque toxique élevé; Sci. Eau 6, 403-413

Benoit-Guyod. J.L., Andre, C., Clavel, K.: J. (1984): Chlorophenols: Dégradation et toxicité; Fr. Hydrol. 15, 249-263

Birge, W.J., Black, J.A. Bruser, D.M. (1979): Toxicity of organic chemicals to embryo-larval stages of fish; Report EPA 560/11-79/007, U.S. EPA, Washington, D.C.

Black. J.A., Birge, W.J., McDonnell, W.E., Westerman, A.G., Ramey, B.A., Bruser, D.M. (1982): The Aquatic Toxicity of Organic Compounds to Embryo-Larval Stages of Fish and Amphibians. Kentucky, Water Resources Research Inst. PB82-224601, Lexington, Research Report No. 133

Bringmann, G., Kühn, R. (1975): Bestimmung der biologischen Schadwirkung wassergefährdender Stoffe aus der Hemmung der Zellvermehrung der Blaualge Microcystis; Gesundheits-Ingenieur 96, 238-241

Bringmann, G., Kühn, R. (1977): Grenzwerte der Schadwirkung wassergefährdender Stoffe gegen Bakterien (Pseudomonas putida) und Grünalgen (Scenedesmus quadricauda) im Zellvermehrungs- hemmtest; Z. f. Wasser und Abwasser-Forschung 10, 87-98

Bringmann, G., Kühn, R. (1982): Befunde der Schadwirkung wassergefährdender Stoffe gegen Daphnia magna.; Z. F. Wasser- und Abwasser-Forschung 15, 1-6

BUA Stoffbericht 54 (November 1990); Chlorobenzol

Buccafusco, R.J., Ells, S.J., LeBlanc, G.A. (1981): Acute toxicity of priority pollutants to bluegill (Lepomis macrochirus); Bull. Environ. Contam. Toxicol. 26, 446-452

## APPENDIX 6

Calamari, D., Galassi, S., Setti, F., Vighi, M. (1983): Toxicity of selected chlorobenzenes to aquatic organisms; Chemosphere 12, 253-262

Cowgill, U.M., Milazzo, D.P., Landenberger, B.D. (1989): Toxicity of nine benchmark chemicals to Skeletonema costatum, a marine diatom.; Environ. Toxicol. Chem. 8, 451-455

Cowgill, U.M., Milazzo, D.P., (1991); Arch. Environ. Contam. Toxicol. 20 , 211-217

Cowgill, U.M., Takahashi, I.T., Applegath, S.L. (1985): A comparison of the effect of four benchmark chemicals on Daphnia magna and Ceriodaphnia dubia affinis tested at two different temperatures; Environ. Toxicol. Chem. 4, 415-422

Dalich, G.M., Larson, R.E., Gingerich, W.H. (1982): Acute and chronic toxicity studies with monochlorobenzene in rainbow trout; Aquat. Toxicol. 2, 127-142

De Wolf, W., Canton, J.H., Deneer, J.W., Wegman, R.C.C., Hermens, J.L.M. (1988): Quantitative structure-activity relationships and mixture-toxicity studies of alcohols and chlorohydrocarbons: reproducibility of effects on growth and reproduction of Daphnia magna; Aquatic Toxicol. 12, 39-49

Devillers, J. Chambon, P. Zakarya, D. (1987): A predictive structure-toxicity model with Daphnia magna; Chemosphere 16, 1149-1163

Galassi, S., Vighi, M. (1981): Testing toxicity of volatile substances with algae; Chemosphere 10, 1123-1126

Gersich, F.M., Blanchard, F.A., Applegath, S.L.. Park, C.N. (1986): The precision of daphnid (Daphnia magna Straus, 1820) static acute toxicity tests; Arch. Environ. Contam. Toxicol. 15, 741-749

Hall, L.H., Kier, L.B., Phipps, G. (1984): Structure-activity relationship studies on the toxicities of benzene derivatives; Environ. Toxicol. Chem. 3, 355-365

Heitmuller, P.T., Hollister, T.A., Parrish, P.R. (1981): Acute toxicity of 54 industrial chemicals to sheepshead minnows (Cyprinodon variegatus); Bull. Environm. Contam. Toxicol. 27, 596-604

Hermens, J., Canton, H., Janssen, P., De Jong, R. (1984): Quantitative structure-activity relationships and toxicity studies of mixtures of chemicals with anaesthetic potency: Aquat. Toxicol. 5, 143-154

Hodson, P.V., Dixon, D.G., Kaiser. K.L.E. (1984): Measurement of median lethal dose as a rapid indication of contaminant toxicity to fish; Environ. Toxicol. Chem. 3, 243-254

Hutchinson, T.C., Hellebust, J.A., Tam, D., Mackay, D., Mascarenhas, R.A., Shiu, W.Y. (1980): The correlation of the toxicity to algae of hydrocarbons and halogenated hydrocarbons with their physical-chemical properties; Environ. Sci. Res. 16, 577-586

## APPENDIX 6

Janardan, S.K., Olson, C.S:, Schaeffer, D.J. (1984): Qunatitative comparison of acute toxicity of organic chemicals to rat and fish; Ecotoxicology and Environmental Safety 8, 531-539

Juhnke, I., Lüdemann, D. (1978): Ergebnisse der Untersuchung von 2300 chemischen Verbindungen auf akute Fischtoxizität mit dem Goldorgentest; Z. f. Wasser und Abwasser-Forschung 11, 161-164, annex: personal communication from Juhnke (see BUA Report)

Könemann, H. (1981): Quantitative structure-activity relationships in fish toxicity studies. Part 1: Relationship for 50 industrial pollutants; Toxicology 19, 209-221

Kühn, R., Patlard, M., Pernak, K.D., Winter, A. (1989): Results of the harmful effects of water pollutants to *Daphnia magna* in the 21 day reproduction test; Wat. Res. 23, 501-510

LeBlanc, G.A. (1980): Acute toxicity of priority pollutants to water flea (Daphnia magna); Bull. Environm. Contam. Toxicol. 24, 684-691

Mackay, D., Abernethy, S., Charles, C. (1985): Development of predictive organic contaminant structure-property-toxicity relationships for aquatic organisms; Proceedings , Technology Transfer Conference, Toronto, Ontario, December 1985, 7, 333-356

Mayes, M.A., Alexander, H.C., Dill, D.C (1983): A study to assess the influence of age on the response of fathead minnows in static acute toxicity tests; Bull. Environ. Contam. Toxicol. 31, 139-147

MITI (1992); Biodegradation and Bioaccumulation Data of Existing Chemicals Based in the CSCL Japan, Compiled under the Supervision of Chemical Products Safety Division, Basic Industries Bureau MITI, Ed. by CITI, October 1992. Published by Japan Chemical Industry Ecology-Toxicology & Information Center

Monsanto Report ES-83-SS-4: „Acute Toxicity of Monochlorobenzene to Daphnia magna“

Monsanto Report NC-89-510 : Investigation of the lethal effects of the test material Chlorobenzene to the Rainbow Trout (static test) according to OECD guideline 203”

Pagano, G., Cipollaro, M., Corsale, G., Esposito, A., Giordano, G.G., Ragucci, E., Trieff, N.M. (1988): Comparative toxicities of benzene, chlorobenzene and dichlorobenzenes to sea urchins embryos and sperm; Bull. Contam. Toxicol. 40, 481-488 (1988)

Pickering, Q.H., Henderson, C. (1966): Acute toxicity of some important petrochemicals to fish; J. Water Pollut. Control Fed. 38, 1419-1429

US EPA, Contract No. 68-01-4646 (1978)

US EPA (1980): Ambient water quality criteria for chlorinated benzenes, EPA 440/5-80-028, U.S. Environ. Prot. Agency, Washington D.C., C1-C22

Wong. P.T.S., Chau. Y.K., Rhamey. J.S., Docker, M. (1984): Relationship between water solubility of chlorobenzenes and their effects on a freshwater green alga; Chemosphere 13,

991-996

## APPENDIX 7

## REFERENCES FOR EXPOSURE DATA

Agence du Bassin Seine Normandie (1995) – Personal communication

Bianchi, A.P., Varney, M.S., Phillips, J. (1991); Analysis of voaltile organic compounds in estuarine sediments using dynamic headspace and gas chromatography-mass spectrometry; Journal of chromatography, 542: 413-450

BUA-Stoffbericht 54: Chlorbenzol (November 1990)

CIPR (1993) – Rapport sur l'Etat du Rhin – Analyses physico-chimiques et biologiques jusqu'en 1991 – Ed. "Commission Internationale pour la Protection du Rhin (CIPR), Sept. 1993

EU COMMPS Database, Fraunhofer Institute, Umweltchemie und Ökotoxicologie, Report 97/723/3040/DEB/EI prepared for the European Commission DGXI – Proposal for a list of priority substances in the context of the draft water framework directive COM(97)49FIN, 13 August 1998

Ernst, W. *et al.* (1986): Forschungsbericht M 86-001 des Bundesministerium für Forschung und Technologie, "Organische Umweltchemikalien in deutschen Ästuarien und Küstengewässern, Vorkommen, Biotransfer, Abbau"

EU COMMPS Database, Fraunhofer Institute, Umweltchemie und Ökotoxicologie, Report 97/723/3040/DEB/EI prepared for the European Commission DGXI – Proposal for a list of priority substances in the context of the draft water framework directive COM(97)49FIN, 13 August 1998

Gewässergütebericht '91 des LWA Nordrhein-Westfalen (1992)

Rheingütebericht NRW '92 des LWA Nordrhein-Westfalen (1993)

RIWA Jahresbericht, Teil A: Der Rhein (1992)

RIZA (1991) Rhein en Maas 1988-1990

RIZA (1995) – Resultaten van het Waterkwaliteitsonderzoek in de Rhijn in nederland 1974-1993 – Directoraat Generaal Rijkswaterstaat – RIZA – Nota Nr 95.010

Slooff, W. *et al.*: Basis Document "Chlorobenzenen". Rapport No. 710401005 Rijksinstitut voor Volksgezondheid en Milieuhygiene (RIVM), Bilthoven (1991)

UK Environment Agency (1997) – Personal communication

Wassergütedaten der Elbe, Zahlentafeln 1993 der Arbeitsgemeinschaft für die Reinhaltung der Elbe (1994)