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

Monochlorophenols

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EURO CHLOR RISK ASSESSMENT FOR THE MARINE ENVIRONMENT

MONOCHLOROPHENOLS

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 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 chlorophenols (2 chlorophenol, 3 chlorophenol, 4 chlorophenol) 34 data for fish, 30 data for invertebrates and 15 data for algae have been evaluated according to the quality criteria recommended by the European authorities. As toxicity results on aquatic organisms seem to be comparable for the three isomers considered, data were pooled for the final PNEC calculation. Both acute and chronic toxicity studies have been taken into account and the appropriate assessment factors have been used to define a final $PNEC_{water}$ value of 30 µg/l, and a $PNEC_{sed}$ value of 258 µg/kg.

The available monitoring data, applied to various surface waters and sediments, were used to calculate PECs. As for ecotoxicological data, the three isomers were considered equivalent as regarded to their environmental concentrations. The review of the available data permitted us to distinguish two situations, a typical case and a worst case, in which values of PECs retained were, for water <0.1 and 0.5 µg/l respectively, and for sediments 50 and 125 µg/kg respectively. The calculated PEC/PNEC ratios give safety margins of 50 to 333 for water, and 2 to 5 for sediments. Dilution within the sea would of course increase these safety margins.

Moreover, all the data concerning biodegradation and bioaccumulation of monochlorophenols agreed to state that these substances are neither persistent nor bioaccumulable. Thus it can be concluded that the present use of monochlorophenols does not represent a risk to the aquatic environment.

1. INTRODUCTION : PRINCIPLES AND PURPOSES OF EUROCHLOR 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 co-operating 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 in the collection and evaluation of data on effects and environmental concentrations. Basically, the effect data are derived from laboratory toxicity tests and exposure data from analytical monitoring programs. 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 published literature and data from IUCLID (2000).

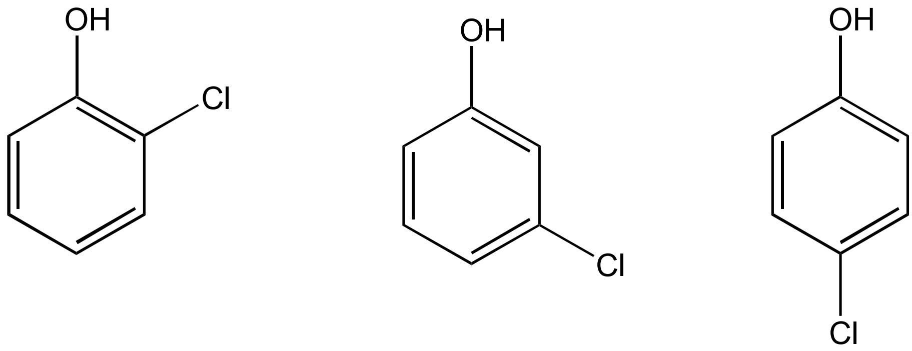
3. COMPOUND IDENTIFICATION

3.1. Description

IUPAC name	2-chlorophenol	3-chlorophenol	4-chlorophenol
CAS number	95-57-8	108-43-0	106-48-9
EINECS number	202-433-2	203-582-6	203-402-6
Annex I entry	604-008-00-0	604-008-00-0	604-008-00-0

Monochlorophenols have the following formula: C_6H_5OCl

and structure:



2-chlorophenol 3-chlorophenol 4-chlorophenol

Fig. 1 Structure of the monochlorophenols.

3.2. EU labelling

According to Annex I of Directive 93/72/EEC (16.11.98 - 24th TPA), the monochlorophenols are classified as Xn, R20/21/22 (harmful by inhalation, in contact with skin, and if swallowed) and N, 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 compounds which were adopted for the purpose of this risk assessment. The molecular weight of chlorophenols is 128.6 g/mol.

Table 1
Physico-chemical properties of monochlorophenols

IUPAC name	2-chlorophenol	3-chlorophenol	4-chlorophenol
Melting point	9.3 °C	33.5 °C	43 °C
Boiling point	175 °C	214 °C	217 °C
Relative density	1.257 at 25 °C	1.268 at 25°C	1.306 at 20 °C
Vapour pressure	1.39 hPa at 25 °C	1.25 hPa at 25 °C	0.51 hPa at 25 °C
Water solubility	28500 mg/l at 20 °C	26000 mg/l at 20 °C	27100 mg/l at 20 °C
PKa	8.48 at 25 °C	9.12 at 25°C	9.38 at 25 °C
Partition coefficient	Log Kow = 2.15	Log Kow = 2.50	Log Kow = 2.39
Henry's Law Constant	0.63 Pa.m^3/mol	0.62 Pa.m^3/mol	0.24 Pa.m^3/mol

5. COMPARTMENT OF CONCERN BY MACKAY LEVEL I MODEL

The risk assessment presented here focuses on the aquatic marine environment, with special attention to 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 data used for the calculation and calculation details are given in *Appendix 2* and the results are summarised in Table 2.

Table 2 : Partition of chlorophenols into different environmental compartments according to Mackay level I

Compartment	%		
	2-chlorophenol	3-chlorophenol	4-chlorophenol
Air	17.7	17.2	7.6
Water	80.6	79.0	89.1
Soil	0.9	2.0	1.7
Sediment	0.8	1.8	1.6

6. USE AND APPLICATIONS

6.1. Production and sales

2-chlorophenol:
About 2000 to 3000 tonnes per year are produced at two sites, where effluents are partly released to a river flowing to the Mediterranean Sea. However, the production is for nearly 100 % used as an intermediate for further synthesis in the North Sea area..

3-chlorophenol:
No IUCLID file is available for this compound which is produced at less than 1000 tonnes per year by producers in Europe.

4-chlorophenol:
About 2000 to 3000 tonnes per year are produced at two sites where effluents are partly released to a river flowing to the Mediterranean Sea. However, the production is for nearly 70 % used as an intermediate for further synthesis in the North Sea area at three sites using 50%, 15% and 5%, respectively. The remaining 30 % of the production are exported outside Europe.

6.2. Main uses

The only use categories are industrial chemicals, chemicals used in synthesis and intermediates.

6.3. Emissions

Emissions from the production of 2-chlorophenol were inventarised in a survey by Euro Chlor, 1976, covering almost the entire chlor-alkali production in Western Europe. The emissions in 1985 were 3200 kg and 150 kg to air and water, respectively. For 1997 these amounts fell to 0 and 70 kg to air and water, respectively. 4-chlorophenol was only emitted to water, with an amount of 2000 kg in 1985 and 70 kg in 1997.(Euro Chlor, COCEM, 2002).

6.4. Natural occurrence and other sources

Many chlorinated phenols are produced by nature (Euro Chlor, 1995). 2,4-dichlorophenol has been shown to be naturally produced by a soil fungus (*Penicillium* sp.) (Gribble, 1994). Experiments by Baker & Mayfield (1980) in surface water and sediment without microflora adaptation have shown that the primary degradation of 2,4-DCP was 74 % after 10 days in water and 73 % after 15 to 30 days in sediment, giving 4-chlorophenol in the first step. Therefore, it can reasonably be assumed that at least also 4-chlorophenol is naturally produced.

7. EFFECT ASSESSMENT

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

The evaluation of 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*.

Data from all available sources, including company data and data from the open literature, were collected and incorporated into the HEDSET for chlorophenols, including their references (updated version of 1/96).

It is necessary to distinguish the acute studies (LC_{50}/EC_{50}) from chronic studies (NOEC/LOEC) 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 in EU risk assessments (TGD, 1996).

7.1. 2-chlorophenol

In total, 18 different data for fish, 11 data for aquatic invertebrates and 4 different data for algae have been evaluated. For each of the taxonomic groups considered, respectively 7, 4 and 2 were considered valid, 9, 4 and 2 were judged valid but considered with care and 2, 3 and 0 were not valid for risk assessment.

7.1.1. Marine fish

Three short-term studies were reported for 2 species. The LC_{50} values were very close to each other, between 6.3 and 7.0 mg/l. The lowest 96 h-LC_{50} is 6.29 mg/l for *Platichthys flesus* (validity 2, nominal concentrations, closed semi-static test systems, Smith *et al.*, 1994).

7.1.2. Freshwater fish

Ten valid short term toxicity studies were reported for 5 species with survival as determining criterion. The lowest 96 h-LC_{50} was 2.6 mg/l for *Oncorhynchus mykiss* (but this paper has been cited in Krijgsheld and Van der Gen (1986), so could not be checked: validity 4, Sletten, 1972). The following lowest 96h-LC_{50} was 6.6 mg/l (*Lepomis macrochirus*, validity 2, Buccafusco *et al.*, 1981). All other values range between 8.3 and 20.2 mg/l (Pickering & Hendersen, 1966; Dietz *et al.*, 1978; Phipps *et al.*, 1981; Saarikoski & Viluksela, 1981; Brook *et al.*, 1985). Two experiments with longer exposure times did not yield lower LC_{50} values (6.3 and 11.2 mg/l for 7-8 days exposure, Phipps *et al.*, 1981 and Könemann & Musch, 1981, respectively). The freshwater data are well in line with the data for the marine species.

One long term toxicity study was reported for fish. In an ELS test the 4 week-NOEC was 4 mg/l for *Pimephales promelas* (validity 1, hatchability, survival and growth, flow-through systems, measured concentrations, LeBlanc, 1984b).

7.1.3. Marine invertebrates

Crustaceans
One study on marine species was found. The 96 h lethal threshold, the lowest tested concentration where lethality is observed, i.e. LOEC, or LCx, where x is generally below 50 %) was 5.2 mg/l for *Crangon septemspinosa* (val. 1, measured concentrations, semi-static system, McLeese *et al.*, 1979).

Other invertebrates
Short or long term toxicity studies on other marine invertebrates have not been found.

7.1.4. Freshwater invertebrates

Crustaceans
Six valid studies report acute toxicity for *Daphnia*. The lowest 48 h-LC_{50} was 2.6 mg/l (validity 2, static system, nominal concentrations, LeBlanc, 1980). All other LC_{50} values range between 6.2 and 18 mg/l (Kopperman *et al.*, 1974;Trabalka & Burch, 1978; Randall & Knopp, 1980; Devillers & Chambon, 1986; Kühn *et al.*, 1989b). Two more studies on acute toxicity to *D. magna* report LC_{50} values in the same range (Carlson, 1975; Knie *et al.*, 1983). However, since the original publications have not been checked, they were classified with validity 4. The 96h-LT found for a marine crustacean is well in line with these results.

Two studies report on the long-term toxicity for *D. magna*. The 3 week-NOEC was 0.5 mg/l (validity 1, reproduction and survival, semi-static closed system, measured concentrations, Kühn *et al.*, 1989b). A lower value was found, viz. a 14 days NOEC of 0.1mg/l (Shigeoka *et al.*, 1988b, reproduction, measured concentrations, protocol similar to OECD 202). However the tested concentration range was made with a geometric progression with a factor of 5. The OECD guideline 211 recommends a progression factor below and at maximum equal to 3.2. So the NOEC cannot be retained as a validated one. One possibility could be to take the LOEC and divide it by 2, according to the TGD, which is acceptable when the effect observed at LOEC is not greater than 20 %. As no raw data are given in the original paper, this could not be achieved and the study was attributed validity 3.

Other freshwater invertebrates
No studies were available on the short or long term toxicity for other invertebrates.

7.1.5. Algae

Four studies report on the toxicity to four algae species (Huang & Gloyna, 1968; Shigeoka *et al.*, 1988a; Kühn & Pattard, 1990). The lowest EC_{50} was 50 mg/l for *Scenedesmus subspicatus* (validity 2, cell multiplication, nominal concentrations, static closed system, Kühn& Pattard, 1990). The same study reports a 48 h-EC_{10} on multiplication of 24 mg/l, which may be interpreted as a NOEC. The highest EC_{50} value is 170 mg/l (*Chlorella vulgaris*, Shigeoka *et al.*, 1988a).
No studies on marine species have been reported.

7.1.6. PNEC for aquatic organisms

Toxicity data are available for freshwater as well as for a few marine organisms. The results of the marine studies are always within the range of similar freshwater studies, therefore the data may be pooled for the derivation of $PNEC_{water}$.

In table 3 the lowest data for the major taxonomic groups are presented. There are EC/LC_{50} -values for the three trophic levels of the base-set, fish, *Daphnia* and algae. On the basis of acute data only, the PNEC could be derived from the lowest of these EC/LC_{50}-values with an assessment factor of 1000 .
However, prolonged toxicity studies were also found for fish, *Daphnia* and algae, leading to an assessment factor of 10 to the lowest NOEC.

Table 3: Summary of aquatic ecotoxicity data selected for the $PNEC_{water}$ derivation, with the appropriate assessment factors for 2-chlorophenol

Data Set	Assigned Assessment Factor	Lowest Toxicity Values
At least 1 short-term LC_{50} from each trophic level (fish, daphnia , algae)	1000	- *P. flesus,* 96h LC_{50} 6.29 mg/l (val. 2, Smith *et al.*, 1994) - *Daphnia magna,* 48h LC_{50} 2.6 mg/l (val. 2, LeBlanc, 1980) - *Scenedesmus subspicatus*, 48h EC_{50} 50 mg/l (val. 2, Kühn & Pattard, 1990)
Long-term NOEC from at least 3 species representing three trophic levels (fish, daphnia, algae)	10	- *P. promelas*, > 4w NOEC mortality, growth 4 mg/l (e.l.s., val. 1, LeBlanc, 1984b) - *D. magna*, 3w NOEC mortality, reproduction 0.5 mg/l (val. 1, Kühn *et al.*, 1989b) - *S. subspicatus* 48h NOEC 24 mg/l (val 2, Kühn & Pattard 1990)

Application of an assessment factor of 1000 to the short term tests would result in a $PNEC_{water}$ of 0.003 mg/l, whereas with an assessment factor of 10 to the lowest of the long term NOEC values, $PNEC_{water}$ would be 0.05 mg/l.

7.2. <u>3-chlorophenol</u>

In total, 5 different data for fish, 2 data for aquatic invertebrates and 2 different data for algae have been evaluated. For each of the taxonomic groups considered respectively 1, 0 and 0 were considered valid, 2, 2 and 2 were judged valid but considered with care and 2, 0 and 0 were not valid for risk assessment.

7.2.1. Marine fish

One short term toxicity study was reported. The 96 h-LC_{50} for *Platichthys flesus* was 3.99 mg/l (validity 2, nominal concentrations, closed semi-static test systems, Smith *et al.*, 1994).

No long term toxicity studies were reported for marine fish species.

7.2.2. Freshwater fish

Three short term toxicity studies were reported for 3 species. The lowest 48 h-LC_{50} was 3 mg/l for *Leuciscus idus melanotus* (validity 2, static system, measured concentrations, Dietz *et al.*, 1978). The two other studies reported LC_{50} values between 3.5 and 10 mg/l (validity 4, Benoit-Guyod *et al.*, 1984 and Shumway & Palensky, 1973, respectively). In a longer term study the ≥7d-LC_{50} ranged from 6.4 to 7.8 mg/l, depending on pH (Könemann & Musch, 1981). This indicates that longer exposure does not lower the LC_{50}. The LC_{50} value reported for the marine species falls well within this range.

No true longer term studies were reported for freshwater fish species.

7.2.3. Marine invertebrates

Toxicity studies on marine invertebrates have not been found.

7.2.4. Freshwater invertebrates

Crustaceans
Two short term studies are reported for *Daphnia*. The lowest 96 h-LC_{50} was 5.6 mg/l for *D. pulex* (validity 2, nominal concentrations, renewal 2 times a week, Trabalka & Burch, 1978). The other study reports a 24 h-EC_{50} of 15.8 mg/l for *D. magna* (validity 2, mobility, static closed systems, nominal concentrations, Devillers & Chambon, 1986). No studies were available on the longer term toxicity to crustaceans.

Other freshwater invertebrates
No studies were reported for other invertebrates.

7.2.5. Algae

For two algae species toxicity studies were reported. The lowest 96 h-EC_{50} was 29 mg/l for *Selenastrum capricornutum* (validity 2, static closed system, nominal concentrations, Shigeoka *et al.*, 1988a). The other 72 h-EC_{50} was 40 mg/l (Huang & Gloyna, 1968).

For marine species no studies have been found.

7.2.6. PNEC for aquatic organisms

Toxicity data are available mainly for freshwater organisms. Therefore the $PNEC_{water}$ will have to be derived on the basis of data for freshwater organisms.
In table 4 the lowest data for the major taxonomic groups are presented. There are EC/LC_{50} -values for the three trophic levels of the base-set: fish, *Daphnia* and algae, implying an assessment factor of 1000 to the lowest EC/LC_{50} . No prolonged or long term toxicity studies were found.

Table 4: Summary of ecotoxicity data selected for the PNEC derivation, with the appropriate assessment factors for 3-chlorophenol

Data Set	Assigned Assessment Factor	Lowest Toxicity Values
At least 1 short-term LC_{50} from each trophic level (fish, daphnia, algae)	1000	- *L. melanotus,* 48h LC50 3 mg/l (val. 1, Dietz *et al.*, 1978) *D. pulex,* 96h LC_{50} 5.6 mg/l (val. 2, Trabalka & Burch, 1978) - *S. capricornutum*, 96h EC_{50} 29 mg/l (val. 2, Shigeoka *et al.*, 1988a)

Application of an assessment factor of 1000 to the short term tests would result in a $PNEC_{water}$ of 0.003 mg/l.

7.3. 4-chlorophenol

In total, 11 different data for fish, 17 data for aquatic invertebrates and 9 different data for algae have been evaluated. For each of the taxonomic groups considered respectively 4, 6 and 2 were considered valid, 4, 8 and 5 were judged valid with care and 3, 3 and 2 were not valid for risk assessment.

7.3.1. Marine fish

Two short term studies were reported for 2 species. The lowest 96 h-LC_{50} is 5 mg/l for *P. flesus* (validity 2, nominal concentrations, closed semi-static test systems, Smith *et al.*, 1994). The other 96 h-LC_{50} was 5.4 mg/l (Heitmuller *et al.*, 1981).

There are no long-term toxicity studies available for marine fish

7.3.2. Freshwater fish

Six valid short-term toxicity studies were reported for the same number of species. The lowest 96 h-LC_{50} was 1.9 mg/l for *Oncorhynchus mykiss* (Hodson *et al.*, 1984). The validity of this study was classified as validity 1 (flow-through system, measured concentrations). The next higher valid LC_{50} value was 3 mg/l for *L. melanotus* in 48h (validity 2, static system, measured concentrations, Dietz *et al.*, 1978). All other studies report LC_{50} values ranging between 3.8 and 8.49 mg/l (Buccafusco *et al.*, 1981; Kuiper, 1982; Saarikoski & Viluksela, 1982; Mayes *et al.*, 1983).
The results of the tests with marine organisms match this range rather well.
There were no chronic studies available for freshwater fish.

7.3.3. Marine invertebrates

Crustaceans
One valid study on marine pelagic species was found. The 24h-LC_{50} was 21 mg/l in *Tisbe battagliai* (validity 2, nominal concentrations, aerated seawater, Smith *et al.* 1994).
Two other valid studies on marine benthic species were found. The lowest 96h- LC_{50} was 4.1 mg/l for *Chaetogammarus marinus* (validity 1, measured concentrations, Kuiper, 1982). A lethal threshold (LCx) was 4.6 mg/l in *C. septemspinosa* (validity 1, measured concentrations, semi-static system, McLeese *et al.* 1979).
Chronic toxicity studies on marine invertebrates have not been found.

7.3.4. Freshwater invertebrates

Crustaceans
Eight valid studies report on the short-term toxicity for *Daphnia*. The lowest 48 h-EC_{50} was 2.5 mg/l (validity 2, static closed system, nominal concentrations, Kühn *et al.*, 1989a). All other EC_{50} values range between 3.5 and 8.9 mg/l (Kopperman *et al.*, 1974; Trabalka & Burch, 1978; LeBlanc, 1980; Kuiper, 1982; Devillers & Chambon, 1986; Steinberg *et al.*, 1992).
One more study on the toxicity to *D. magna* reports EC_{50} value in the same range (USEPA, 1978). However, since this study could not be checked, it was classified with validity 4.
The short term toxicity data for marine organisms fall in the same range.

Two studies report on the long-term toxicity for *D. magna*. The lowest 3 week-NOEC on the reproduction and survival of *D. magna* was 0.63 mg/l (validity 1, semi-static closed system, measured concentrations, Kühn *et al.*, 1989b), whereas, on a 14 days exposure, the NOEC was 1 mg/l (Kuiper, 1982).

The freshwater crustaceans sensitivity to 4-chlorophenol is in the same range as for marine crustaceans.

Other freshwater invertebrates
McLeese *et al.* (1979) have found a 96h LCx (lethal threshold) of 37 mg/l in the clam : *Mya arenaria* (validity 1).

Another publication could not be checked and was attributed validity 4 : Oksama and Kristoffersson (1979) have found a 96 hours EC_{50} of 40 mg/l in *Mesidotea entomon* (aquatic arthropod), and an EC_5 96h of 27.5 mg/l, which confirms the above LOEC. Freshwater bivalves and arthropods seem to be less sensitive than crustaceans.

7.3.5. Marine algae

Two studies report EC_{50} values for marine algae ranging from 3.27 to 9.6 mg/l. The lowest one could not be checked (USEPA, 1978, cited in Krijgsheld and van der Gen,1986), (validity 4). However, the 96h EC_{50} in *Phaeodactylum tricornutum* of 9.6 mg/l was given a validity 1 (Kuiper, 1982). The values are in line with the results of tests with freshwater algae. The study in *P. tricornutum* gave a relatively low NOEC of 0.32 mg/l (validity 1, Kuiper, 1982).

7.3.6. Freshwater algae

Five valid studies report toxicity to freshwater algae. The lowest EC_{50} value of 4.79 mg/l was reported for a study on *S. capricornutum* which could not be checked (val. 4, static closed system, nominal concentrations, US-EPA, 1978). The next lowest 72h-EC_{50} was 8.3 mg/l for *S. subspicatus* (validity 2, nominal concentrations, static closed system, Kühn.& Pattard, 1990). The same study reports a 72h-EC_{10} of 1.9 mg/l for *S. subspicatus* (validity 2, nominal concentrations, cell multiplication, static closed system, Kühn & Pattard, 1990). This value could be used as a NOEC. The EC_{50} values ranged up to 50 mg/l (Huang & Gloyna, 1968; Shigeoka *et al.*, 1988a).

7.3.7. PNEC for aquatic organisms

Toxicity data are available for freshwater as well as marine organisms. The results of the marine and freshwater studies are always in the same range and therefore $PNEC_{water}$ was derived on the basis of data for both freshwater and marine organisms. Table 5 presents the lowest data for the main taxonomic groups. EC/LC_{50} -values are available for the three trophic levels of the base-set, fish, *Daphnia*, and algae.

One prolonged study was found for *Daphnia* and one EC_{10} for algae, which can be considered as a NOEC according to TGD recommendations. Chronic data for fish are lacking, but *Daphnia* and fish show similar acute toxicity values, $E(L)C_{50}$ fish 1.9 to 3 mg/l, and *Daphnia* 2.5 mg/l). It can be concluded that the two taxa have the same sensitivity and that the long term NOEC in *Daphnia* represents one of the most sensitive species. Therefore it is justified to apply an assessment factor of 50 to the lowest NOEC.

Application of an assessment factor of 1000 to the short term tests would result in a $PNEC_{water}$ of 0.002 mg/l, whereas with an assessment factor of 50 to the lowest of the long term NOEC values the $PNEC_{water}$ would be 0.013 mg/l.

Table 5: Summary of ecotoxicity data selected for the PNEC derivation, with the appropriate assessment factors for 4-chlorophenol

Data Set	Assigned Assessment Factor	Lowest Toxicity Values
At least 1 short-term LC_{50} from each trophic level (fish, daphnia , algae)	1000	- *O.s mykiss,* 96h LC_{50} 1.9 mg/l (val. 1, Hodson *et al.*, 1984) - *D. magna,* 48h LC_{50} 2.5 mg/l (val. 2, Kühn *et al.*, 1989a) - *S. subspicatus* 72 h EC_{50} 8.3 mg/l (val. 2, Kühn .& Pattard, 1990)
Long-term NOEC from at least 2 species representing three trophic levels (fish, daphnia, algae)	50	- *D. magna*, 3w NOEC mortality, reproduction 0.63 mg/l (val. 2, Kühn *et al.*, 1989b) - *P. tricornutum,* 96h NOEC 0.32 mg/l (val 1, Kuiper, 1982)

7.4. <u>Comparison of toxicity data for the chlorophenol isomers</u>

In table 6, the lowest validated $E(L)C_{50}$ and NOEC are shown. The acute/chronic (A/C) ratios have been calculated for each species where a NOEC was available, dividing the mean of all validated available $E(L)C_{50}$ values in this species by the NOEC in this species.
From comparison of the toxicity data for the different isomers, it can be concluded that all three isomers have comparable toxicity. The few toxicity data for marine organisms available indicate that the sensitivity is similar to freshwater organisms. Algae seem to be less sensitive than fish and invertebrates. However, they were found to be more sensitive to 4-chlorophenol, than to 2- and 3- chlorophenol.

Table 6 : Lowest E(L)C50 and NOEC values for monochlorophenols and their acute: chronic ratios

Isomer	Lowest E(L)C50	Organism	Lowest NOEC	Organism	A/C ratio
2-chlorophenol	6.6 mg/l **2.6 mg/l** 50 mg/l *(24)*	*L. macrochirus* ***D. magna*** Freshwater algae	4 mg/l **0.5 mg/l** 24 mg/l (EC 10) *(4)*	*P. promelas* ***D. magna*** Freshwater algae	1.65 5.2 2.1
3-chlorophenol	**3 mg/l** 5.6 mg/l 29 mg/l *(7)*	***L. idus*** (48 h) *D. pulex* (96 h) Freshwater algae	n.a.		
4-chlorophenol	**1.9 mg/l** 2.5 mg/l 8.3 mg/l 9.6 *(26)*	***O. mykiss*** *D. magna* Freshwater algae Marine algae	n.a. 0.63 mg/l 1.9 mg/l (EC10) **0.32 mg/l** *(3)*	 *D. magna* Freshwater algae **Marine algae**	- 4 4.4 30

(Numbers in brackets) : number of valid studies compared

7.4.1. Acute toxicity

The lowest EC_{50} values in fish and *Daphnia* for the three chlorophenol isomers lie within a factor 3.5 for all data in both species (due to fish values) and even 2.2 for *Daphnia*. They are based on data sets sufficiently abundant to be reliable. The most toxic isomer appears to be 4-chlorophenol with the overall $E(L)C_{50}$ is for fish, *Daphnia* and algae, which is more often observed for para isomers. Nevertheless, the differences are small with all isomers having very similar toxicity levels.

7.4.2. Chronic toxicity

Chronic values are only available for 2- and 4-chlorophenol. However, as the acute values for fish and *Daphnia* are within a narrow range for all 3 monochlorophenols, it is relevant to consider all chronic data to select the lowest one. Of all 3 substances 0.5 mg/l is the lowest daphnia NOEC, with an acute/chronic ratio of 5.2. If this ratio was applied to the lowest $E(L)C_{50}$ value in fish of 1.9 mg/l in *O. mykiss* this would give a NOEC value of 0.36 mg/l.The lowest NOEC value in algae for the most toxic 4-chlorophenol is 0.32 mg/l in *P. tricornutum* (marine algae), with a high acute/chronic ratio of 30 (EC_{50} in *P. tricornutum* = 9.6 mg/l). In fact, this exceptionally high acute/chronic ratio leads to the lowest NOEC value for the 3 trophic levels in the least sensitive group at acute level. The ratio observed for the other algae species where EC_{50} and EC_{10} data were available were only 2.1and 4.4.

7.4.3. $PNEC_{water}$ derivation

Taking into account the exceptional value for the marine algae and the calculation made for a possible NOEC in the most sensitive fish lead to the proposed worst-case lowest NOEC = 0. 3 mg/l. Pooling of all chronic data of the 3 isomers authorises to derive a

PNEC with an assessment factor of 10, applied to the overall lowest NOEC. This results in a worst-case **PNEC = 0.03 mg/l.**

7.4.4. $PNEC_{sediment}$ derivation

The $PNEC_{sed}$ can be derived by a calculation using the $PNEC_{water}$ and the log K_{ow} (TGD, 1996). The log K_{ow} values of the chlorophenols are quite similar, with a range of 2.15 to 2.50 and a mean value of 2.3. It must be born in mind that these values refer to the molecular form. Monochlorophenols can dissociate at high pH, but under environmental pH conditions the molecular form is the most relevant one.
A common $PNEC_{water}$ of 0.03 mg/l was derived for all three compounds, and their log K_{ow} values are rather similar with a mean of 2.3. Therefore, it is considered appropriate to derive a $PNEC_{sed}$ value for the three monochlorophenols of: **$PNEC_{sed}$ = 0.258 mg/kg (ww) or 258 µg/kg**

This value has been determined by applying the formula based on the equilibrium partitioning according to the TGD (1996):

$$PNEC_{sed} = K_{sed\text{-}water} / RHO_{sed} * PNEC_{water} * 1000$$

With :
$\text{Log } K_{oc} = 0.63 \text{ Log}K_{ow} + 0.90$
$K_{sed\text{-}water} = Foc_{sed} * K_{oc}$
$Foc_{sed} = 0.05$ kg/kg
$RHO_{sed} = 1300$ kg/m^3

7.5. <u>Bioaccumulation</u>

The log octanol-water partition coefficients ($\text{Log}K_{ow}$) found for these substances were 2.15 for 2-chlorophenol, 2.50 for 3-chlorophenol and 2.39 for 4-chlorophenol. Calculations from the log K_{ow} lead to bioconcentration factors (BCFs) of 13, 26 and 21 for the three isomers, respectively. These values do not indicate a potential for bioaccumulation.
In addition to the low BCF based on the Log K_{ow}, the fact that only sulfate and glucuronide conjugates of chlorophenols are detected in exposed fish shows that conjugation occurs which supports that bioaccumulation does not occur (Krijgsheld & van der Gen, 1986). The same authors have reported BCFs for 2- and 4-chlorophenol, but these were not reliable since they were determined after exposure periods of 12 to 42-hours, which is insufficient to reach equilibrium.
For tests of six weeks at 0.04 mg/l the Japanese Chemicals Inspection and Testing Institute reported BCF values of 14-24, 5-10 and 6-18 for 2-, 3- and 4-chlorophenol, respectively (CITI, 1992). For similar tests at 0.004 mg/l the respective values were 16-29, 7-16 and 11-52. These results clearly confirm the prediction from octanol/water partition coefficients that the monochlorophenols do not bioaccumulate.

7.6. Persistence

7.6.1. Abiotic degradation

Only data on photodegradation in water are available (Boule *et al.*, 1982). The first step of photochemical degradation of monochlorophenols in water is a C-Cl bond scission, which is not influenced by oxygen (the same products were obtained in aerated and degassed solutions). Chlorine is converted into hydrochloric acid. The position of the chlorine on the ring strongly influences the tranformation. In the molecular form 2-chlorophenol is converted into catechol. In the anionic form, however, it is reduced into a cyclopentadienic acid which dimerises according to a Diels-Alder reaction. The irradiation of 3-chlorophenol leads to resorcinol at any pH. This would appear to suggest a photohydrolysis mechanism. With 4-chlorophenol, the photochemical conversion is not so specific. Hydroquinone is formed (mainly in aerated solution) along with polyphenolic oligomers. A radical mechanism is probably involved.

7.6.2. Biodegradation

Most of the available studies demonstrate primary biodegradation, measured as decay of parent substance using specific analytical methods.
Activated sludge of secondary treatment plants treating combined domestic and industrial discharges achieved 97% biodegradation for a 10 mg/l 2-chlorophenol solution and 80 % for 10 mg/l of 4-chlorophenol after 6 hours. 100 % biodegradation was found for both chlorophenols at 1 mg/l. At 100 mg/l only 20 % for 2-chlorophenol and 16 % for 4-chlorophenol were found (Baird *et al.*, 1974). The EC_{50} values of phenol biodegradaton inhibition by 2-chlorophenol and 4-chlorophenol in an activated sludge flow through system were 104 and 71 mg/l respectively (Beltrame *et al.*, 1984) Which supports the observed biodegradation results.
Micro-organisms collected from a depth of 0.5 m above a river sediment achieved 68 % primary biodegradation of a 40 mg/l solution of 2-chlorophenol after 40 days, but 17 % only for 4-chlorophenol (Baker & Mayfield, 1980). This result reflects both phenomena of toxicity at this concentration and adaptation of the natural inoculum collected, as mineralisation could at last be achieved. However, with a sediment sample collected in the same place, the biodegradation was 100 % after 10-15 days, and more than 70 % of 3-chlorophenol disappeared within 80 days.
Inoculation of a 50 mg/l solution with soil showed an even better result of 100 % primary biodegradation after 14 days for 2-chlorophenol and 3 days for 4-chlorophenol (Alexander & Aleem, 1961).
Isolates from a petroleum waste lagoon, which was likely to contain adapted organisms, degraded 95 % of a 300 mg/l 4-chlorophenol solution after 6 days and 95 % of a 150 mg/l 3-chlorophenol solution in 3 days (Tabak *et al.*, 1964).

A study with results of ultimate aerobic biodegradation was reported by Ingols *et al.* (1966). After adaptation, activated sludge showed a removal of 100 % of parent substance from a 100 mg/l solution after 4, 2 and 3 days for 2-, 3- and 4-chlorophenol, respectively. The aromatic ring degradation was 100 % after 3 days, as well as chloride ion evolution. Based on the available data, the monochlorophenols should be classified as inherently biodegradable, but the results also show that the biodegradation potential is quite high.

Boyd & Shelton (1984) reported anaerobic biodegradability. A non adapted anaerobic sludge degraded a 50 mg/l 2-chlorophenol solution and a 45 mg/l 4-chlorophenol solution at 72 % after 21 days, and 60 % after 42 days respectively. An adapted anaerobic sludge however degraded the same solutions at 98 % after 4 days for 2-chlorophenol and after 3 days for 4-chlorophenol.

In the soils, the three isomers are rapidly degraded, as shown by a study by Baker & Mayfield (1980). 119 mg/kg soil of 2-chlorophenol were applied on a clayloam soil collected from the surface (15 cm) of an uncultivated grassland site in Waterloo County, Ontario, and chlorophenol decay was measured at a temperature range from 0 to 23 °C. The degradation observed was 91 % after 8 days at 0 °C, and 100 % after 1.5 days at 23 °C. The same experiments with 4-chlorophenol lead to the same degradation kinetics. This leads to the conclusion that monochlorophenols deposited on a soil will be rapidly degraded even at low temperatures (half-lives below one week at 0°C and in a one day order of magnitude at 23 °C).

All these results suggest that the monochlorophenols are inherently biodegradable. The 2-chlorophenol is more rapidly degraded by a non-adapted inoculum than the 4-chlorophenol, however, the 4-chlorophenol is more rapidly degraded by an adapted inoculum. 3-chlorophenol is less rapidly biodegraded than both other isomers (Alexander & Aleem, 1961).

The general conclusion is that parent compound would undergo rapid primary biodegradation in surface waters, sediments and soils, and subsequent mineralisation.

7.7. Conclusion

Although the compounds are toxic for aquatic organisms (1 mg/l < $E(L)C_{50}$ < 10 mg/l), it can be concluded from the above information that monochlorophenols are not «persistent, toxic and liable to bioaccumulate substances» according to the current criteria (e.g. OSPARCOM, UNECE, TDG).

8. EXPOSURE ASSESSMENT

The number of reported monitoring data is not very high. Levels in surface waters (river and marine waters) are detailed in Appendix 6.

8.1. 2-chlorophenol

Concentrations of 2-chlorophenol in various surface waters are given by Rippen (1998). The values reported cover the period 1974-1986 and vary from 0.050 to 2.3 µg/l .
Recent data from several sites in The Netherlands (including some marine sites) (RWS, 1997) and data from UK rivers show that in most locations the concentrations are under the detection limit of 0.1 µg/l and that 90% of the reported values are under 0.5

µg/l (EU COMMPS, 1998). The proposed worst-case PEC_{water} value used for all 3 monochlorophenols is set at 0.5 µg/l , which is also used for the final risk calculations. 0.1 µg/l is used as the typical value.

The only measured values of 2-chlorophenol concentrations in sediment are obtained in The Netherlands in 1995 (RWS, 1997). All values are under the detection limit of 0.1 mg/kg. The proposed $PEC_{sediment}$ for 2chlorophenolvalue of 50 µg/kg corresponds to half the detection limit.

8.2. 3-chlorophenol

Concentrations of 3-chlorophenol in various surface waters in The Netherlands and Germany are given by Rippen (1998). The values reported cover the period 1976-1986 and mainly vary from 0.050 to 2 µg/l.
More recent concentration values reported in the EU COMMPS database for freshwater and some estuarine/marine sites in The Netherlands in 1996-1997 are all under the detection limit of 0.1 µg/l (EU COMMPS, 1998).

Similarly, the concentrations measured in freshwater and marine sediments in The Netherlands in 1995-1997 are all under the detection limit of 0.1 mg/kg (RWS, 1997; EU COMMPS, 1998). The proposed $PEC_{sediment}$ value of 50 µg/kg for 3-chlorophenolcorresponds to half the detection limit.

8.3. 4-chlorophenol

Concentrations of 4-chlorophenol in various surface waters in The Netherlands and Germany are given by Rippen (1998). The values reported cover the period1974-1986 and vary from 0.050 to 2 µg/l.
More recent concentration values reported in the EU COMMPS database have been measured in UK rivers and in freshwater sites (including some marine sites) in The Netherlands over the period 1994-1997. Most of the values for 4-chlorophenol are under the detection limit of 0.1 µg/l(EU COMMPS, 1998).

In sediment, the only available values have been measured in The Netherlands (RWS, 1997; EU COMMPS, 1998). The mean value for the most recent data (1996-1997) is 68 µg/kg and the 90-percentile is 125 µg/kg (EU COMMPS, 1998). This value is proposed as $PEC_{sediment}$ and is used for all chlorophenols in the final risk calculations.

9. RISK ASSESSMENT CONCLUSION

The natural production of several chlorophenols has been well documented in scientific literature and for monochlorophenols there is evidence that at least 4-chlorophenol is naturally produced. However, in the quantification of the risks of monochlorophenols the natural production has not been included, which can be considered as a worst-case.

In the risk characterisation of chlorophenols, PNECs are compared with PEC. For the effect assessment, it is thought appropriate to consider all isomers similarly as no significant differences in test results were found. A PNEC of 30 µg/l was obtained for aquatic species and a PNEC of 258 µg/kg wet weight was calculated for sediments.

For monitoring data also, the various isomers can be considered equivalent. The monitoring data recorded in surface waters (mainly in rivers) showed typical mean concentrations lower than the detection level. As a worst case a PEC value of 0.5 µg/l corresponding to the 90 percentile of the concentration distribution, is used.

On the basis of these monitoring data, the PEC/PNEC ratios for the water compartment can be calculated, the results are summarised in Table 7.

Table 7: Calculation of PEC/PNEC ratios for chlorophenols
in the water compartment

Type of water	PEC level	PEC/PNEC
River waters		
• worst case	0.5 µg/l	0.02
• typical water	< 0.1 µg/l	< 0.003

The calculated ratios for the water compartment indicate that the present levels of 2-, 3- and 4-monochlorophenol do not represent a risk to aquatic organisms in the North Sea region. The calculated margins are 50 and more than 333 for the worst-case and typical monitoring data, respectively. Moreover, it must be emphasized that these data are based on concentrations measured in rivers and do not take into account any degradation or dilution of these concentrations before reaching the sea.
In addition, it is concluded that there is no risk of bioaccumulation for the monochlorophenols, based on both the intrinsic properties of the substances as well as on studies measuring BCFs.

Combining the monitoring data available for sediment showed levels ranging from 50 µg/kg, representing half the detection limit, to 125 µg/kg, representing the 90-percentile of data for 4-chlorophenol. When assessing the risks for the monochlorophenols it should be born in mind that the $PNEC_{sediment}$ does not take into account the potential for ionisation. At the same time it must be emphasised that the monitoring data include the natural production, which in particular has been established for 4-chlorophenol. This isomer shows the highest sediment concentrations which were used to derive the PEC for all isomers.

It can therefore be concluded that on the basis of these monitoring data and the calculated PNEC for sediment the risks can be evaluated adequately. The PEC/PNEC ratios for the sediment compartment are summarised in Table 8.

Table 8: Calculation of the PEC/PNEC ratios for chlorophenols in the sediments

	PEC level	PEC/PNEC
• worst case	125 µg/kg	0.48
• typical sediment	50 µg/kg	0.19

The calculated ratios for the sediment compartment indicate that the current levels of the three monochlorophenols do not represent a risk to organisms living in the sediment compartment in the North Sea region.

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APPENDIX 1

Environmental quality criteria for assessment of ecotoxicity data

The principal quality criteria for acceptance of data are that the test procedure should be well described (with reference to an official guideline) and that the toxicant concentrations must be measured with an adequate analytical method.

Four cases can be distinguished and are summarized in the following table (according to criteria defined in IUCLID system).

Table : Quality criteria for acceptance of ecotoxicity data

Case	Detailed description of the test	Accordance with scientific guidelines	Measured concentratio n	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: 2-chlorophenol

Temperature (c)	20
Molecular weight (g/mol)	128.56
Vapor pressure (Pa)	139
Solubility (g/m3)	28500
Solubility (mol/m3)	221.69
Henry's law constant (PA.m3/mol)	0.63
Log octanol water part. coefficient	2.15
Octanol water part. coefficient	141.25
Organic C-water part. coefficient	57.91
Air-water partition coefficient	.25726214E-3
Soil-water partition coefficient	1.74
Sediment-water partition coefficient	3.47
Amount of chemical (moles)	1
Fugacity (Pa)	.72114031E-7
Total VZ products	13866926.76

Phase properties and compositions:

Phase	:	Air	Water	Soil	Sediment
Volume (m3)	:	.600OE+10	.7000OE+7	.4500OE+5	.2100OE+5
Density(kgm3)	:	.12056317E+2	.1000OE+4	.1500OE+4	.1500OE+4
Frn org carb.	:	.00000E+0	.00000E+0	.2000000OE-1	.4000000OE-1
Z mol/m3.Pa	:	.41029864E-3	.15948659E+1	.27709539E+1	.55419078E+1
VZ mol/Pa	:	.24617918E+7	.11164061E+8	.12469292E+6	.11638006E+6
Fugacity	:	.72114031E-7	.72114031E-7	.72114031E-7	.72114031E-7
Cone mol/m3	:	.2958828E-10	.11501221E-6	.19982466E-6	.39964932E-6
Cone g/m3	:	.38038704E-8	.14785970E-4	.25689458E-4	.51378916E-4
Cone ug/g	:	.31550847E-6	.14785970E-4	.17126305E-4	.34252611E-4
Amount mol	:	.17752973E+0	.80508551E+0	.89921097E-2	.83926357E-2
Amount %	:	17.75	80.51	0.90	0.84

APPENDIX 2

Fugacity Level I calculation

Chemical: 3-chlorophenol

Temperature (C)	20
Molecular weight (g/mol)	128.56
Vapor pressure (Pa)	125
Solubility (g/M3)	26000
Solubility (mol/M3)	202.24
Henry's law constant (PA.m3/mol)	0.62
Log octanol water part. coefficient	2.50
Octanol water part. coefficient	316.23
Organic C-water part. coefficient	129.65
Air-water partition coefficient	.25359612E-3
Soil-water partition coefficient	3.89
Sediment-water partition coefficient	7.78
Amount of chemical (moles)	1
Fugacity (Pa)	.69760594E-7
Total VZ products	14334740.13

Phase properties and compositions:

Phase	: Air	Water	Soil	Sediment
Volume (m3)	: .600OE+10	.7000OE+7	.4500OE+5	.2100OE+5
Density(kgm3)	: .12056317E+2	.1000OE+4	.1500OE+4	.1500OE+4
Frn org carb.	: .00000E+0	.00000E+0	.20000000E-1	.4000000OE-1
Z mol/m3.Pa	: .41029864E-3	.16179215E+1	.62930702E+1	.1258614OE+2
VZ mol/Pa	: .24617918E+7	.11325451E+8	.28318816E+6	.26430895E+6
Fugacity	: .69760594E-7	.69760594E-7	.69760594E-7	.69760594E-7
Cone mol/m3	: .2862267E-10	.11286717E-6	.43900832E-6	.87801665E-6
Cone g/m3	: .36797314E-8	.14510203E-4	.5643891OE-4	.11287782E-3
Cone ug/g	: .30521187E-6	.14510203E-4	.37625940E-4	.7525188OE-4
Amount mol	: .17173606E+0	.79007021E+0	.19755374E-1	.18438349E-1
Amount %	: 17.17	79.01	1.98	1.84

APPENDIX 2

Fugacity Level I calculation

Chemical: 4-chlorophenol

Temperature (C)	20
Molecular weight (g/mol)	128.56
Vapor pressure (Pa)	51
Solubility (g/m3)	27100
Solubility (mol/M3)	210.80
Henry's law constant (PA.m3/mol)	0.24
Log octanol water part. coefficient	2.39
Octanol water part. coefficient	245.47
Organic C-water part. coefficient	100.64
Air-water partition coefficient	.99267441E-4
Soil-water partition coefficient	3.02
Sediment-water partition coefficient	6.04
Amount of chemical (moles)	1
Fugacity (Pa)	.3078783OE-7
Total VZ products	32480366.34

Phase properties and compositions:

Phase	: Air	Water	Soil	Sediment
Volume (m3)	: .6000E+10	.7000OE+7	.4500OE+5	.2100OE+5
Density(kgm3)	: .12056317E+2	.1000OE+4	.1500OE+4	.1500OE+4
Frn org carb.	: .00000E+0	.00000E+0	.20000000E-1	.4000000OE-1
Z mol/m3.Pa	: .41029864E-3	.4133265OE+1	.12479533E+2	.24959067E+2
VZ mol/Pa	: .24617918E+7	.2893285SE+8	.56157902E+6	.52414042E+6
Fugacity	: .3078783OE-7	.3078783OE-7	.3078783OE-7	.3078783OE-7
Cone mol/m3	: .1263220E-10	.12725426E-6	.38421776E-6	.76843553E-6
Cone g/m3	: .16239962E-8	.16359807E-4	.49395036E-4	.98790072E-4
Cone ug/g	: .13470084E-6	.16359807E-4	.32930024E-4	.65860048E-4
Amount mol	: .75793229E-1	.89077982E+0	.17289799E-1	.16137146E-1
Amount %	: 7.58	89.08		1.61

SUMMARY TABLE OF ECOTOXICITY DATA ON 2-CHLOROPHENOL

1 FISH

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	References
LC50/EC50 STUDIES							
1. FRESHWATER							
Pimephales promelas	8 d	A;F-T	LC50	6.3	1	life stage: 30-35 d; pH 7.5; lake water; hrdn 45 mg/l $CaCO_3$; temp 25°C	Phipps *et al.*, 1981
Pimephales promelas	96 h	A;F-T	EC50 LC50	9.22 9.41	1	respiration, loss of equilibrium; life stage: 28 day, weight 0.043 g; lake water; pH 7.8; temp 25.4 °C; hrdn 42.6 mg/l $CaCO_3$; DO 7.0 mg/l;	Brooke *et al.* 1985
Pimephales promelas	96 h	A;F-T	LC50	11	1	life stage: 30-35 d;lake water; pH 7.5; temp 25 °C; hrdn 45 mg/l $CaCO_3$	Phipps *et al.*, 1981
Poecilia reticulata	≥ 7 d	N;SS (1-d);C	LC50	11.2	1	life stage: 2-3 month; Alabaster and Abram water; pH 7.3; hrdn 25 mg/l $CaCO_3$; temp 22 °C; DO >5 mg/l	Könemann & Musch, 1981
Poecilia reticulata	96 h	A;SS(12h; 4/5)	LC50	14	1	weight: 40-60 mg; tap water; pH 7; temp26°C; hrdn 80-100 mg/l $CaCO_3$;	Saarikoski & Viluksela, 1982
Pimephales promelas	96 h	A;F-T	LC50	13.8	1	life stage: 34 day; temp 24.7 °C; pH 7.47; DO 8.2 mg/l; hrdn 44.9 mg/l $CaCO_3$; lake water	Brooke *et al.* 1985
Oncorhynchus mykiss	96 h		LC50	2.6	4	fingerlings; standard fish bioassay (1960)	Sletten, 1972
Lepomis macrochirus	96 h	N;S;C	LC50	6.6	2	weight: 0.32-1.3 g; pH 6.5-7.9, well water; hrdn 32-48 mg/l $CaCO_3$; temp 22 °C	Buccafusco *et al.*, 1981
Leuciscus idus melanotus	48 h	A;S	LC50	8.3	2	pH 7; hrdn 267 mg/l $CaCO_3$; temp 20 °C	Dietz et al.,, 1978

SUMMARY TABLE OF ECOTOXICITY DATA ON 2-CHLOROPHENOL

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	References
Lepomis macrochirus	96 h	N;S	LC50	10	2	life stage: 1-2 g; soft water; pH 7.5; DO 7.8 mg/l; temp 25 °C;	Pickering & Henderson, 1966
Lepomis macrochirus	48 h	SS	LC50	8.1	4	pH 7.6-8.4	Lammering, 1960
Carassius auratus	96 h	N;S	LC50	12.37	2	weight: 1-2 g; soft water; pH 7.5; temp 25°C; DO 7.8 mg/l;	Pickering & Henderson, 1966
Poecilia reticulata	96 h	N;S	LC50	20.17	2	weight: 0.1-0.2 g; pH 7.5; soft water; DO 7.8 mg/l; temp 25 °C	Pickering & Henderson, 1966
Pimephales promelas	96 h	N;S	LC50 LC50	11.6 14.5	2	life stage: 1-2 g; soft water; pH 7.5; DO 7.8 mg/l; temp 25 °C; hard water, pH 8.2 duplicate	Pickering & Henderson, 1966
2. Saltwater							
Platichthys flesus	96 h	N;SS(2d);C	LC50	6.29	2	weight: 56 g; temp 6 °C; pH 8; sal 5‰; pur 98-99+%	Smith *et al.* 1994
Solea solea	96 h	N;SS(2d);C	LC50	6.6	2	weight: 45 g; temp 6 °C; pH 8; sal 20‰; pur 98-99+%	Smith *et al.*, 1994
Platichthys flesus	96 h	N;SS(2d);C	LC50	6.99	2	weight: 56 g; temp 6 °C; pH 8; sal 5‰; pur 98-99+%	Smith *et al.*, 1994

SUMMARY TABLE OF ECOTOXICITY DATA ON 2-CHLOROPHENOL

Species	Dur.	Type of study	Criterion (LC50/EC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	References
LOEC/NOEC STUDIES							
1. FRESHWATER							
Pimephales promelas	> 4 w	A;F-T	NOEC	4	1	hatchability, survival, growth; life stage: eggs 4-w post hatching (els)	LeBlanc, 1984b
2. Saltwater							
No data available							

2 INVERTEBRATES

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	References
LC50/EC50 STUDIES							
1. FRESHWATER							
Daphnia magna	24 h	N;S;C	LC50	6.3	1	life stage: 6-24 h; pH 8; artificial water; hrdn 250 mg/l $CaCO_3$;temp 20 °C	Kühn *et al.*, 1989b
Daphnia magna	48 h	N;S:C	LC50	7.4	1	life stage ≤ 24 h; lake water; temp 18 °C	Kopperman *et al.*, 1974
Daphnia magna	24 h	N;S;C	EC50	17.95	2	life stage < 72 h; pH 7.0-8.2; artificial water; hrdn 200 mg/l $CaCO_3$; temp 20 °C	Devillers & Chambon, 1986
Daphnia magna	48 h	N;S	LC50	2.6	2	well water; pH 7.4-9.4; hrdn 173mg/l $CaCO_3$	LeBlanc, 1980
Daphnia magna	48 h	N;S	EC50	6.2	2	immobility; life stage: ≤ 24 h; pond water, hrdn 154.5; 22 °C; pH 7.7	Randall & Knopp, 1980

SUMMARY TABLE OF ECOTOXICITY DATA ON 2-CHLOROPHENOL

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	References
Daphnia pulex	96 h	N;SS(2* /wk)	LC50	6.9	2	life stage: 12 h; temp 20°C	Trabalka & Burch, 1978
Daphnia magna	48 h		LC50	7.43	4		Carlson, 1975
Daphnia magna	24 h		EC50	23	4	pH 8	Knie, 1983
2. Saltwater							
No data available							
3. Freshwater benthic org.							
No data available							
4. Marine benthic org.							
Crangon septemspinosa	96 h	A;SS (2d)	LT	5.2	1	lethal threshold (=LCx); length 3.8 cm, weight 0.6 g; aerated seawater; temp 10 °C; sal 30 ‰	McLeese *et al*., 1979
LOEC/NOEC STUDIES							
1. FRESHWATER							
Daphnia magna	3 w	A;SS;C	NOEC	0.5	1	survival, reproduction; life stage: 1-d old; standard water; pH 8; hrdn 250 mg/l $CaCO_3$	Kühn *et al*., 1989b
Daphnia magna	14 d		NOEC	0.1 (MATC)	3	survival, reproduction	Shigeoka *et al*., 1988b
2. Saltwater							
No data available							

SUMMARY TABLE OF ECOTOXICITY DATA ON 2-CHLOROPHENOL

3. AQUATIC PLANTS

Species	Duration d (days) h (hours)	Type of study	Criterion (EC50/LC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	Reference
EC50/LC50 and LOEC/NOEC STUDIES							
1. FRESHWATER							
ALGAE							
Scenedesmus subspicatus	48 h	N;S;C	EC50 EC10	50 24	2	cell multiplication; inoculum 10^5 cells/ml; artificial medium; pH 8; hrdn 55.6 mg/l $CaCO_3$;	Kühn & Pattard, 1990
Selenastrum capricornutum	96 h	N;S;C	EC50	70	1	growth; inoculum: $5x10^4$ cells/ml; artifial medium; pH 7.5; hrdn 11mg/l $CaCO_3$; temp 21 °C; contin. illumin. 4000 Lux	Shigeoka *et al.*, 1988a
Chlorella vulgaris	96 h	N;S;C	EC50	170	1	growth; inoculum: $5x10^4$ cells/ml; artifial medium; pH 7.5; hrdn 11mg/l $CaCO_3$; temp 21 °C; contin. illumin. 4000 Lux	Shigeoka *et al.*, 1988a
Chlorella pyrenoidosa	72 h	N;S	EC50	100	2	chlorophyll production; extrapolated from graph; temp 25°C; pH 7	Huang & Gloyna, 1968
2. Saltwater							
No data available							

SUMMARY TABLE OF ECOTOXICITY DATA ON 3-CHLOROPHENOL

1 FISH

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. FRESHWATER							
Leuciscus idus melanotus	48 h	A;S	LC50	3	2	pH 7; hrdn 267 mg/l $CaCO_3$; temp 20 °C	Dietz *et al.*, 1978
Poecilia reticulata	≥ 7 d	N;SS(1-d);C	LC50 LC50 LC50	6.4 6.4 7.8	1	pH 6.1; pH 7.3; pH 7.8; life stage: 2-3 month; Alabaster water; hrdn 25 mg/l $CaCO_3$; temp 22 °C; DO >5 mg/l	Könemann & Musch, 1981
Poecilia reticulata	24 h	N	LC50	3.47	4	Aquire: No review of study	Benoit-Guyod et al., 1984
Oncorhynchus mykiss	48 h		LC50	10	4		Shumway & Palensky, 1973
2. Saltwater							
Platichthys flesus	96 h	N;SS(2 d);C	LC50	3.99	2	weight: 56 g; pH 8; temp 6 °C; sal 5 ‰; pur 98-99+%	Smith et al., 1994
LOEC/NOEC STUDIES							
1. FRESHWATER							
No data available							
2. Saltwater							
No data available							

SUMMARY TABLE OF ECOTOXICITY DATA ON 3-CHLOROPHENOL

2 INVERTEBRATES

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. FRESHWATER							
Daphnia pulex	96 h	N;SS(2*/wk)	LC50	5.6	2	life stage: <24 h; temp 20°C	Trabalka & Burch, 1978
Daphnia magna	24 h	N;S;C	EC50	15.78	2	immobility; life stage < 72 h; pH 7.0-8.2; artificial water; hrdn 200 mg/l $CaCO_3$; temp 20 °C;	Devillers & Chambon, 1986

3 AQUATIC PLANTS

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	Reference
EC50/LC50 STUDIES							
1. FRESHWATER							
ALGAE							
Selenastrum capricornutum	96 h	N;S;C	EC50	29	2	growth; inoculum: $5x10^4$ cells/ml; artificial medium; pH 7.5; hrdn 11 mg/l $CaCO_3$; temp 21 °C; life contin. illumin. 4000 Lux	Shigeoka et al., 1988a
Chlorella pyrenoidosa	72 h	N;S	EC50	40	2	chlorophyll A production; extrapolated from graph; temp 25 °C; pH 7	Huang & Gloyna, 1968
2. Saltwater							
No data available							

SUMMARY TABLE OF ECOTOXICITY DATA ON 4-CHLOROPHENOL

1 FISH

Species	Duration d (days) h (hours)	Type of study	Criterion (EC50/LC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. FRESHWATER							
Leuciscus idus melanotus	48 h	S;A	LC50	3	2	pH 7; hrdn 267 mg/l $CaCO_3$; temp 20 ° C	Dietz et al., 1978
Pimephales promelas	96 h	N;S;C	LC50	3.8-5	1	LC50: juv. 3.8, fry 4, subadult 5mg/l lake water; pH 7.2-8.5; temp 22°C; hrdn 96-125 mg/l $CaCO_3$;	Mayes et al., 1983
Poecilia reticulata	96 h	A;SS(12h ;4/5)	LC50	8.49	1	weight: 40-60 mg; tap water; pH 7; hrdn 80-100 mg/l $CaCO_3$; temp 26 °C;	Saarikoski & Viluksela, 1982
Lepomis macrochirus	96 h	N;S	LC50	3.8	2	weight: 0.32-1.3 g; well water; pH 6.5-7.9, temp 22 °C; hrdn 32-48mg/l $CaCO_3$;	Buccafusco et al., 1981
Oncorhynchus mykiss	48 h		ETC	0.045	4		Shumway & Palensky, 1973
Oncorhynchus mykiss	96 h	A;F-T; not aerated	LC50	1.91	1	length: 4.6-6.4 cm; weight 1.2-3.8g; pH 7.6-8.2 measured concentrations	Hodson et al. 1984
Pimephales promelas	96 h		LC50	3.8	4		Lindstrom, 1980
Brachydanio rerio	96 h		LC50	5.6	1		Kuiper, 1982
Poecilia reticulata	96 h	N; SS	LC50	6.3	4	pH 5; Hrdn 80-100 mg/l $CaCO_3$	Saarikoski & Viluksela, 1981
2. Saltwater							
Platichthys flesus	96 h	N;SS;C	LC50	5	2	weight: 56 g; 6 °C; pH 8; sal 5‰; pur 98-99+%, nominal conc.	Smith et al., 1994
Cyprinodon variegatus	96 h	N;S	LC50	5.4	2	length: 8-15 mm; natural sea	Heitmuller et al.,

SUMMARY TABLE OF ECOTOXICITY DATA ON 4-CHLOROPHENOL

Species	Duration d (days) h (hours)	Type of study	Criterion (EC50/LC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	Reference
						water; sal 10-31 ‰; temp 25-31°C;	1981
LOEC/NOEC STUDIES							
1. FRESHWATER							
No data available							
2. Saltwater							
No data available							

2 INVERTEBRATES

Species	Duration d (days) h (hours)	Type of study	Criterion (EC50/LC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. FRESHWATER							
Daphnia magna	48 h	N;S;C	LC50	2.5	2	life stage: 6-24 h; artificial water; pH 8; hrdn 250 mg/l $CaCO_3$; 20°C; nominal concentrations	Kühn et al., 1989a
Daphnia pulex	96 h	N;SS(2*/ wk)	LC50	3.5	2	life stage: 12 h; temp 20°C	Trabalka & Burch 1978
Daphnia magna	48 h	N;S	LC50	4.1	2	well water; pH 7.4-9.4; hrdn 173mg/l $CaCO_3$	LeBlanc, 1980
Daphnia magna	48 h	N;S:C	LC50	4.82	2	life stage ≤ 24 h; lake water; temp 18°C;	Kopperman et al., 1974
Daphnia magna	48 h	N;S	EC50	6.8	2	motility; life stage: < 24 h, neonate; temp 20 °C; pur > 98%	Steinberg et al., 1992
Daphnia magna	24 h	N;S;C	EC50	8.07	2	life stage < 72 h; pH 7.0-8.2; artificial medium; hrdn 200 mg/l $CaCO_3$; temp 20 °C	Devillers & Chambon, 1986

SUMMARY TABLE OF ECOTOXICITY DATA ON 4-CHLOROPHENOL

Species	Duration d (days) h (hours)	Type of study	Criterion (EC50/LC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	Reference
Daphnia magna	48 h	N;S	EC50	8.78	2	motility; life stage: < 24 h, neonate; temp 20 °C; pur > 98%	Steinberg et al., 1992
Daphnia magna	48 h	N;S	EC50	4.42 (4.06?)	4		US EPA, 1978
Daphnia magna	48 h		LC50	8.9	1		Kuiper, 1982
2. Saltwater							
Tisbe battagliai	24 h	N;S	LC50	21	2	life stage: 6 day, copepodid stage; sea water; pH 8; temp 20 °C; sal 30 ‰; pur 98-99+%	Smith et al., 1994
Mysidopsis bahia	??		LC50	29.7	4		US EPA, 1978
3. Freshwater benthic org.							
Mya arenaria	96 h	A, SS	LT	37	1	lethal threshold(= LCx)	McLeese et al., 1979
Mesidotea entomon	96 h		EC50 EC5	40 27.5	4		Oksama and Kristoffersson, 1979
4. Marine benthic org.							
Crangon septemspinosa	96 h	A;SS(2-d)	LT	4.6	1	lethal threshold(= LCx); length: 3.8 cm, weight 0.6; aerated seawater; temp 10 °C; sal 30 ‰;	McLeese et al., 1979
Chaetogammarus marinus	96 h		LC50	4.1	1		Kuiper, 1982
LOEC/NOEC STUDIES							
1. FRESHWATER							
Daphnia magna	3 w	A;SS(2 d);C	NOEC	0.63	1	survival, reproduction; life stage: P 1-d old ® F (lc); pH 8; standard water; hrdn 250 mg/l $CaCO_3$	Kühn et al., 1989b
Daphnia magna	14 d		NOEC	1	1		Kuiper, 1982
2. Saltwater							
No data available							

3 AQUATIC PLANTS

Species	Duration d (days) h (hours)	Type of study	Criterion (EC50/LC50 NOEC/LOEC)	Concentration (mg/l)	Validity	Comments and remarks	Reference
LOEC/NOEC STUDIES							
1. FRESHWATER							
ALGAE							
Scenedesmus subspicatus	72 h	N;S;C	EC10 EC50	1.9 8.3	2	cell multiplication; inoculum 10^4 cells/ml; artificial medium; pH 8; hrdn 55.6 mg/l $CaCO_3$;	Kühn & Pattard, 1990
Chlorella vulgaris	96 h	N;S;C	EC50	29	2	growth; inoculum: $5x10^4$ cells/ml; artificial medium; pH 7.5; hrdn 11mg/l $CaCO_3$; temp 21 °C; contin. illumin. 4000 Lux	Shigeoka et al., 1988a
Selenastrum capricornutum	96 h	N;S;C	EC50	38	2	growth; inoculum: $5x10^4$ cells/ml; artificial medium; pH 7.5; hrdn 11mg/l $CaCO_3$; temp 21°C; contin. illumin. 4000 Lux	Shigeoka et al., 1988a
Chlorella pyrenoidosa	72 h	N;S	EC50	50	2	chlorophyll A production; extrapolated from graph; temp 25°C; pH 7	Huang & Gloyna, 1968
Selenastrum capricornutum	96 h	N;S;C	EC50	4.79	4	growth	US EPA, 1978
Scenedesmus pannonicus	96 h		EC50	10	1	growth; NOEC: 3.2 mg/l	Kuiper, 1982
PLANTS							
Lemna minor	48 h	N;S	EC50	280	2	chlorosis; pH 5.1; temp 25°C	Blackman, et al., 1955
2. Saltwater							
ALGAE							
Skeletonema costatum	??		EC50 EC50	3.27 3.56	4	chlorophyll A production; biomass	US EPA, 1978
Phaeodactylum tricornutum	96 h		EC50	9.6	1	growth; NOEC : 0.32 mg/l	Kuiper, 1982

SUMMARY TABLE OF ECOTOXICITY DATA ON 4-CHLOROPHENOL

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 6

Compilation of environmental monitoring data in surface waters and sediments for monochlorophenols

2-chlorophenol – Surface water			
Area	**Year of measurement**	**Concentration (µg/l)**	**Reference**
The Netherlands			
2 river sites	1976	< 2-2.3	Rippen, 1998
	1977	< 2	Rippen, 1998
24 mainly freshwater sites	1995	< 0.1	RWS, 1997
Germany			
9 river sites	1974-1986	< 0.05-2.3	Rippen, 1998
United Kingdom			
many freshwater sites	1994-1996	< 0.1 mostly, 90-percentile: 0.5	EU COMMPS, 1998
2-chlorophenol – Sediment			
Area	**Year of measurement**	**Concentration (mg/kg dw)**	**Reference**
The Netherlands			
2 freshwater sites	1995	< 0.1	RWS, 1997
3-chlorophenol – Surface water			
Area	**Year of measurement**	**Concentration (µg/l)**	**Reference**
The Netherlands			
2 river sites	1976	< 2-6	Rippen, 1998
	1977	< 2	Rippen, 1998
24 mainly freshwater sites	1995	< 0.1	RWS, 1997
7 sites, freshwater, some estuarine/ marine	1996-1997	< 0.1	EU COMMPS, 1998
Germany	1986	< 0.05	Rippen, 1998
9 river sites			
3-chlorophenol – Sediment			
Area	**Year of measurement**	**Concentration (mg/kg dw)**	**Reference**
The Netherlands			
2 freshwater sites	1996-1997	< 0.1	EU COMMPS, 1998
4 sites (including marine)	1995	< 0.1	RWS, 1997
4-chlorophenol – Surface water			
Area	**Year of measurement**	**Concentration (µg/l)**	**Reference**
The Netherlands			
2 river sites	1976	< 2-3.9	Rippen, 1998
	1977	< 2	Rippen, 1998
24 mainly freshwater sites	1995	< 0.1	RWS, 1997
many (mainly) freshwater sites	1994-1997	< 0.1 mostly 90-percentile: 0.05	EU COMMPS, 1998
Germany			
9 river sites	1974-1986	< 0.05-2	Rippen, 1998
United Kingdom			
many freshwater sites	1994-1997	< 0.2 mostly, 90-percentile: 0.1	EU COMMPS, 1998
4-chlorophenol – Sediment			
Area	**Year of measurement**	**Concentration (mg/kg dw)**	**Reference**
The Netherlands			
2 freshwater sites	1995	< 0.1	RWS, 1997
4 sites (including 1 marine)	1996-1997	mean 0.068, 90-percentile: 0.125	EU COMMPS, 1998

APPENDIX 7

NORTH SEA MONITORING DATA ON MONOCHLOROPHENOLS
(only recent data, see Appendix 6)