

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

## Pentachlorophenol



#### EURO CHLOR RISK ASSESSMENT FOR THE MARINE ENVIRONMENT

#### **PENTACHLOROPHENOL**

## **OSPARCOM Region - North Sea**

#### **EXECUTIVE SUMMARY**

Euro Chlor has voluntarily agreed to carry out risk assessment of 25 chemicals related to the chlorine industry, for the marine environment especially for the North Sea, 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 assessment consists of the collection and evaluation of data on adverse effects and environmental concentrations. Basically, the adverse effects data are derived from laboratory toxicity tests and the 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) based on long-term chronic toxicity endpoints, expressed as a hazard quotient for the marine aquatic environment. If the PEC is less than the PNEC (i.e., a ratio less than one), then the prediction is that the risks are very low. If the PEC exceeds the PNEC, then further refinement of the risk assessment may be necessary as may be eventual risk reduction programmes.

To determine the PNEC value, three different trophic levels are considered: aquatic plants, invertebrates and fish. In the case of pentachlorophenol, there are numerous acute and chronic toxicity test results available for the assessment. Forty one (41) chronic aquatic toxicity test results, including 20 for fish, 14 for invertebrates, and 7 for plants, were identified as being of the highest reliability (Reliability Level 1) according to the quality criteria recommended by the EU guidelines. Because this is an assessment for the marine environment and because there are considerable Reliability Level 1 marine toxicity data available, the results of chronic toxicity studies with marine organisms were used, along with the appropriate assessment factors, to derive a final PNEC value of  $1\mu g/l$ .

Monitoring data were available for North Sea coastal and estuary waters, and for rivers which discharge to the North Sea. Recent data (1983 - 1997) were used to calculate PEC values for the marine environment under different scenarios. The typical PEC for pentachlorophenol in both estuarine/marine and river waters was 0.07  $\mu g/l$  during this time period. Based on monitoring data from 1992 - 1997, which is after the EU and individual countries imposed restrictions on the production and use of pentachlorophenol, the typical PEC in estuarine/marine waters was 0.01  $\mu g/l$ . The highest average, or worst case, PECs were 0.24  $\mu g/l$  (in the general vicinity of sources) and 0.79  $\mu g/l$  (immediately adjacent to industrial outfalls) for coastal/estuarine waters and 0.76  $\mu g/l$  for river waters during the period 1983 - 1991. The worst case PECs during the period

1993 - 1997 are 0.11  $\mu$ g/l and 0.15  $\mu$ g/l, respectively, for coastal/estuarine waters and river waters.

The calculated PEC/PNEC ratios for the marine waters are all less than one. When the predicted exposure concentrations (PECs) are below the predicted no effect concentrations for aquatic species (PNECs), the prediction is that the risks are very low. Based on the most recent monitoring data (1992 - 1997), which would reflect the production and use restrictions that are in place for pentachlorophenol, the ratio based on typical coastal and estuarine water concentrations provide a safety margin of 100 and the ratio based on worst case concentrations provide a safety margin of 9. Lower safety margins are found based on the most recent monitoring data in river waters. However, these ratios do not take into account the considerable dilution of pentachlorophenol as the rivers enter the North Sea estuaries and coastal waters.

For sediments, the calculated PEC/PNEC ratios are also less than one based on the most recent data (1995 - 1997) for both coastal/estuarine and river systems. As was seen for surface waters, the ratios were larger (some exceeding one) at earlier time periods. This indicates that pentachlorophenol sediment concentrations have been decreasing over time and are currently at levels at which no adverse effects to aquatic receptors are anticipated, under typical conditions in the North Sea.

In conclusion, present levels of pentachlorophenol in surface waters and sediments should not represent a risk to the marine environment in the North Sea region. As indicated in the assessment, the surface waters and sediments are showing a decreasing trend in pentachlorophenol concentrations with time. And finally, it is known that pentachlorophenol is not persistent (this is confirmed by the dropping levels in surface waters and sediments) and it is not expected to accumulate significantly in aquatic biota.

# 1. <u>INTRODUCTION: PRINCIPLES AND PURPOSES OF EURO CHLOR RISK ASSESSMENT</u>

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 prioritized 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 <u>Appendix 1</u>. 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 adverse effects and environmental concentrations. Basically, the effect data are derived from laboratory toxicity tests and exposure data from analytical monitoring programmes. Where necessary, the exposure data are backed up with calculated concentrations based on emission models. Finally, in the absence of secondary poisoning, the risk is indicated by comparing the "predicted environmental concentrations" (PEC) with the "predicted no effect concentrations" (PNEC) for long-term or chronic toxicity endpoints, expressed as a hazard quotient for the marine aquatic environment. If the PEC is less than the PNEC, then the prediction is that the risks are very low. If the PEC exceeds the PNEC, then further refinement of the risk assessment may be necessary as may be eventual risk reduction programmes.

## 2. DATA SOURCES

The data used in this risk assessment are primarily derived from the published literature (for effects data) and from country-specific chemical monitoring programs (for exposure data). References are provided in Section 10 for all data used in this risk assessment. The pentachlorophenol data are not in HEDSET.

## 3. <u>COMPOUND IDENTIFICATION</u>

## 3.1 <u>Description</u>

CAS number : 87-86-5
EINECS number : 201-778-6
EEC number : 604-002-00-8
IUPAC name : Pentachlorophenol

Pentachlorophenol is sometimes abbreviated to penta or to PCP.

Pentachlorophenol has the following formula: C<sub>6</sub>Cl<sub>5</sub>OH

and structure:

## 3.2 **EU labelling**

According to Annex I of Directive 93/72/EEC (1.9.93 - 19th TPA), pentachlorophenol is classified as carcinogenic, category 3: R40 (possible risks of irreversible effects); T+ (very toxic): R26 (very toxic by inhalation); T (toxic): R24/25 (toxic in contact with skin and if swallowed); and Xi (irritant): R36/37/38 (irritating to eyes, respiratory system, and skin). This classification is applicable to both pentachlorophenol and its salts.

Environmental labeling was discussed at the EU Working Group; the proposition that pentachlorophenol should be classified as "dangerous for the environment" (symbol N) according to the EU criteria was adopted. Accordingly, pentachlorophenol (and its salts) are labeled N (dangerous for the environment): R50/53 (very 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 pentachlorophenol which were adopted for the purpose of this risk assessment.

Table 1: Physical and chemical properties of pentachlorophenol

Property	Value
Molecular weight	266.34 g
Melting point	174°C
Boiling point	309°C
Density	1.978
Vapour pressure	0.00415 Pa (20°C)
Log octanol-water partition coefficient	3.32 at pH 7 (4.5 at pH 4, 1.3 at pH
	10)
Koc partition coefficient (measured)	706 – 3420 (four soil types)
Water solubility	14 mg/l (20°C)
	330 g/l for sodium salt
	(pentachlorophenate)
Dissociation constant	4.92

## 4.1 **Speciation**

The form of pentachlorophenol is dependent upon the environmental pH. At its  $pK_a$  of 4.7, one-half of the PCP is present as the parent compound and one-half as the more soluble pentachlorophenate anion. In the range of typical environmental pH (6-9), and including the relatively stable pH 8.2 of seawater, ninety percent or more of PCP is in the more soluble form (RIVM 1991).

## 5. COMPARTMENT OF CONCERN BY MACKAY LEVEL I MODEL

The risk assessment presented here focuses on the marine environment, with special attention for the North Sea conditions where appropriate. Although this risk assessment focuses on the water 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 through a Mackay level I calculation obtained using software included in Mackay *et al.* (1992). This model describes the ultimate distribution of the compound in various environmental compartments.

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 a Mackay level I calculation for pentachlorophenol are shown in Table 2.

Table 2: Partition of pentachlorophenol into different environmental compartments according to Mackay level I calculation (Mackay *et al.*, 1992)

Compartment	0/0
Water	74.2
Soil	12.3
Sediment	11.5
Air	2.1

See <u>Appendix 2</u> for details of the calculations.

### 6. **USE AND APPLICATIONS**

#### 6.1 Main uses

The uses of pentachlorophenol and its principal derivatives sodium pentachlorophenate (NaPCP) and pentachlorophenyl laurate (PCPL) in the European Union (EU) have been limited since the Member States adopted Council Directive 91/173/EEC (23 July 1987). In 1991, the Ninth Amendment of Council Directive 76/769/EEC was adopted through Council Directive 91/173/EEC which severely restricted the use of pentachlorophenol-containing products in the EU (ERM 1997).

There are currently three principal areas of use for pentachlorophenol-containing chemicals in the EU: (1) as anti-sapstain agents in green timber; (2) as a fungicide in the treatment of timber and masonry; and (3) as a preservative against fungal and bacterial attack in heavy-duty textiles (ERM 1997). The predominant use is in the timber processing industry where NaPCP is the primary agent used in the control of sapstain and surface staining of timber. PCPL is the principal derivative used in the preservation of textiles (ERM 1997).

Of the three categories of use (Industrial, Professional, and Amateur) in the EU, the Directive restricted the use of pentachlorophenol for timber treatment to industrial facilities, with the added restriction that treated wood may not be used inside buildings or for the manufacture of materials (e.g., packaging) which might come in contact with foodstuffs consumed by man or domesticated animals. Certain exceptions are allowed relating to the continued sale and Industrial/Professional use of some pentachlorophenol formulations, on a case by case basis, for: (1) remedial timber treatment; (2) use as surface biocides; (3) the treatment of fibers and heavy-duty textiles not intended for use in clothing or decorative furnishings; and (4) use as a synthesizing and/or processing agent in

industrial processes. As of 1 July 1992, all Amateur uses of pentachlorophenol-based formulations were revoked and these chemicals are no longer marketed in the EU for direct use by the consumer (ERM 1997).

Council Directive 91/173/EEC, in 1987, also imposed a 4 ppm limit on the concentration of dioxin (HxCDD) in pentachlorophenol. There has been a reduction in the level of these and other microcontaminants in pentachlorophenol formulations since 1987. For example, current batches of PCP and its derivatives contain an average of 1.7 ppm of HxCDD (ERM 1997).

While the open burning of penta-treated wood may result in dioxin emissions, there is no evidence that such open burning is practiced in Europe. The practice is, in fact, banned in the United States and Canada. When penta-treated wood is burned under controlled conditions (i.e. in incinerators, boilers and other combustion units) there is no resulting significant contribution of dioxins to the atmosphere. For example, trial burns submitted in support of regulatory permits to allow the combustion of penta-treated wood show that the burning of such wood results in dioxin/furan emissions that are comparable to that from the burning of ordinary particle board and plywood (Viking Energy, 1995).

#### 6.2 Production and sales

As of 1991, the pentachlorophenol sold and used in Europe has originated from production facilities outside of Europe since the production of pentachlorophenol ceased in the EU with the passage of the Ninth Amendment of Council Directive 76/769/EEC. Pentachlorophenol is currently imported for sale and use in three forms (PCP, NaPCP, and PCPL) in the EU. Total usage levels of pentachlorophenol have been on the decline since the early 1980s. Usage levels of PCP dropped to about 100 metric tons in 1996. Usage levels of NaPCP have been relatively stable since about 1987 and were about 1,000 metric tons in 1996. Usage levels of PCPL are approximately 20-30 metric tons per year in the EU (ERM 1997). In Europe, pentachlorophenol is currently imported and used in France, Spain, Portugal, Italy, and the United Kingdom. Other EU Member States, and the remaining countries which border the North and Baltic Seas, have generally banned the use of pentachlorophenol-containing products (see Section 6.3).

## 6.3 **Applicable regulations**

As discussed in Section 6.1, the use of pentachlorophenol-containing products in the EU has been limited since the Member States adopted Counsel Directive 91/173/EEC in 1987 and has been severely restricted since 1991, when the Ninth Amendment of Council Directive 76/769/EEC was adopted through Council Directive 91/173/EEC. In concert with the Ninth Amendment, EU Member States have introduced national codes of practice governing the storage, handling, and processing of PCP and its derivatives (ERM 1997). In addition, many European countries have placed even tighter restrictions, or have instituted national bans, on the use of pentachlorophenol and pentachlorophenol-containing

products. These countries include Austria, Denmark, Finland, Germany, the Netherlands, Sweden and Switzerland.

#### 7. EFFECT ASSESSMENT

This section of the assessment considers the following three trophic levels: algae and aquatic macrophytes, invertebrates, and fish.

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

Data from all available sources, including data from the open literature, data identified from commercial on-line data base searches (subsequently traced to the original published reference), and from GLP-studies conducted for ongoing regulatory re-registration of pentachlorophenol in Europe, Canada, and the United States, were collected and evaluated against the quality criteria.

#### 7.1 Toxicity Data Summary

Considerable acute and chronic aquatic toxicity data for both marine and freshwater situations are available for pentachlorophenol. The database includes tests with both PCP and NaPCP forms of pentachlorophenol as well as with several formulations including "pure" PCP and several industrial and commercial sources. These differences in the test materials account, at least in part, for the orders of magnitude range in the toxicity values in the database. The toxicity data are described below.

#### **Acute Toxicity**

There is a large amount of acute toxicity data available for pentachlorophenol on a wide range of fish and invertebrate species. The *Scientific Criteria Document for Standard Development No. 2-84, Chlorinated Phenols in the Aquatic Environment* (Ontario Ministry of Environment 1984) provides a review of the available data, primarily for freshwater organisms, that are designated as "primary data" for the acute aquatic toxicity of pentachlorophenol.

Acute LC50 values for warmwater fish species, such as fathead minnows, bluegill, channel catfish, and goldfish ranged from 20  $\mu g/l$  to 600  $\mu g/l$  pentachlorophenol. Coldwater gamefish such as rainbow trout, various species of salmon, and brook trout had acute LC50 levels ranging from 34  $\mu g/l$  to 220  $\mu g/l$  pentachlorophenol.

Acute LC50 values for sensitive invertebrates including species of *Daphnia*, lymnaeid snails, and oligochaetes ranged from 240  $\mu$ g/l to 2,000  $\mu$ g/l. These data suggest that fish are somewhat more sensitive than invertebrates to pentachlorophenol. Acute (96-hour) EC50 values for aquatic plants ranged from 80  $\mu$ g/l to 7,000  $\mu$ g/l.

Pentachlorophenol toxicity is influenced by the pH of the water, being more toxic under acidic conditions. The LC50 values presented above cover a range of pH test conditions. This accounts, at least in part, for the order of magnitude range in LC50 values within each trophic level of organisms.

The Ambient Water Quality Criteria for Chlorophenol document issued by the British Columbia Ministry of Environment, Lands, and Parks (BC Environment 1993) provides a review of available acute toxicity data for marine aquatic organisms. The acute LC50 values for fish ranged from  $38 \mu g/l$  to  $440 \mu g/l$  and for invertebrates ranged from  $84 \mu g/l$  to over  $10,000 \mu g/l$ . The wide range in LC50 values for marine fish and invertebrates reflect differences among test conditions, species, and life stages. For marine aquatic plants, short-term EC50 values ranged from  $280 \mu g/l$  to  $300 \mu g/l$  pentachlorophenol.

#### **Chronic Toxicity**

The chronic toxicity data for pentachlorophenol are also numerous. Because chronic toxicity data are preferable to acute toxicity data in the derivation of the PNEC value (predicted no effect concentration) as specified in the EU methodology, these data are presented here in considerable detail.

Applying the quality criteria specified in the EU methodology (<u>Appendix 1</u>) to the entire data set, there are a total of forty-one (41) study results designated "Reliability Level 1". The additional pentachlorophenol chronic aquatic toxicity study results would be classified as Reliability Level 2-4; these study results are not necessary, or as applicable, to complete the PNEC derivation for the pentachlorophenol risk assessment.

The forty-one Reliability Level 1 chronic toxicity study results are detailed in <u>Appendix 3</u> for fish, invertebrates, and plants in both freshwater and saltwater exposure conditions. References for these forty-one study results are listed in (<u>Appendix 6</u>). References for the additional chronic toxicity studies, other than Reliability Level 1, are listed in <u>Appendix 6</u>.

The thirty-four (34) Reliability Level 1 chronic <u>freshwater</u> toxicity study results were established over a range of pH values. As described above for acute aquatic toxicity, the chronic toxicity of pentachlorophenol is influenced by the pH of the test medium, becoming more toxic as the pH is lowered. In order to directly compare these freshwater study results, the reported NOEC values were adjusted to a pH of 7.0 and are identified in this assessment as "pH-adjusted NOECs". The pH adjustment was done using the following conversion:

pH-adjusted NOEC concentration at desired  $pH = e^{Y}$ 

where:  $Y = \ln(NOEC \text{ concentration at study pH}) - 1.005(\text{study pH} - \text{desired pH})$ 

The pH slope factor (1.005) is the average from five pentachlorophenol studies as calculated by USEPA (1986) as part of the establishment of the ambient water quality criteria for pentachlorophenol in the United States.

The seven (7) Reliability Level 1 <u>marine</u> toxicity tests were conducted in saltwater which has a fairly constant pH of approximately 8.2; there is therefore no need to adjust the NOEC values for the marine tests.

The reported NOEC values for saltwater studies and the pH-adjusted NOEC values for freshwater are included in <u>Appendix 3</u>. The risk assessment is based on the lowest NOEC values in order to be protective of the most sensitive species. The lowest chronic toxicity NOEC values for fish, invertebrates, and plants representing both marine and freshwater situations are shown in Table 3.

Trophic Level (environment)	Number of Studies	Most Sensitive Species (endpoint)	Lowest NOEC (µg/l)
Fish (freshwater)	18	sockeye salmon (growth)	2
Fish (marine)	2	plaice (egg & larval mortality, growth & development)	10 <sup>a</sup>
Invertebrates (freshwater)	10	snail (survival, repro., growth)	<15
Invertebrates (marine)	4	worm (reproduction)	10
Plants (freshwater)	6	blue-green alga (growth inhibition)	5
Plants (marine)	1	diatom (growth inhibition)	11

Table 3: Lowest chronic toxicity NOEC values for pentachlorophenol

(a) This lowest NOEC, derived from tests with two marine fish species, is further supported by studies of three fish species (one salmon and two trout) that can inhabit both freshwater and saltwater and that were tested in freshwater. The pH-adjusted NOEC values (going from the freshwater test pH to a marine pH of 8.2) for these three species are in the same range as the NOECs for the two marine fish species.

## 7.2 **PNEC for Marine Environment**

As noted in the Introduction, this risk assessment is for the marine environment, specifically for the North Sea. As such, and because there are sufficient, high reliability, marine chronic toxicity data for pentachlorophenol, the PNEC for the marine environment is derived, following the EU methodology, from the marine toxicity database and using an assessment factor that is appropriate for the type and amount of available data. Because there are marine chronic toxicity data for all three trophic levels (fish, invertebrates, and plants), the assessment factor that is needed is relatively small; that is, there is a high degree of certainty in deriving the PNEC value from the available toxicity data.

The EU methodology specifies an assessment factor of 10 be applied to the lowest NOEC value from the long-term chronic toxicity tests when there are test results for fish, invertebrates, and algae (Table 4). The marine NOEC values are comparable for the three tropic levels; the lowest NOEC being 10  $\mu$ g/l. Applying the assessment factor of 10 to this NOEC, the PNEC for the marine environment is 1  $\mu$ g/l pentachlorophenol.

While there is considerable overlap between the pentachlorophenol NOEC values for the marine and freshwater species, as a group, the marine species have to be considered separately (see Figure 1). The mean and median NOEC values are about the same for freshwater species (NOECs adjusted to pH 7) and marine species (as indicated in the top and middle rows of data points in Figure 1). The difference in sensitivity can be seen, however, after normalizing the NOECs of all 41 chronic toxicity values to account for the known effect of pH on pentachlorophenol toxicity. The mean and median NOEC values for marine species are considerably lower when compared to the NOECs for freshwater species that have been normalized to a saltwater pH of 8.2 (as indicated in the middle and bottom rows of data points in Figure 1). Because of the known effect of pH on pentachlorophenol toxicity, it would be inappropriate to use the NOECs from studies conducted in freshwater (pH  $\sim$  7) to derive a PNEC for pentachlorophenol in the marine environment including this assessment for the North Sea.

For that reason, a PNEC is calculated separately for freshwater species. Considering the most sensitive species among the three trophic level (NOEC = 2  $\mu$ g/l, fish) and an assessment factor of 10, a PNEC of 0.2  $\mu$ g/l is derived. However, a field study including various trophic levels (including fish) showed some minor effects at 40  $\mu$ g/l (LOEC). Using an assessment factor of 2 to derive the NOEC and an additional assessment factor of 10 leads to a more realistic PNEC of 2  $\mu$ g/l. It has to be reminded that a European expert panel (CSTE, 1994) has agreed for a recommended Water Quality Objective of 1  $\mu$ g/l in 1982 although no detailed argumentation is available for this value.

Figure 1

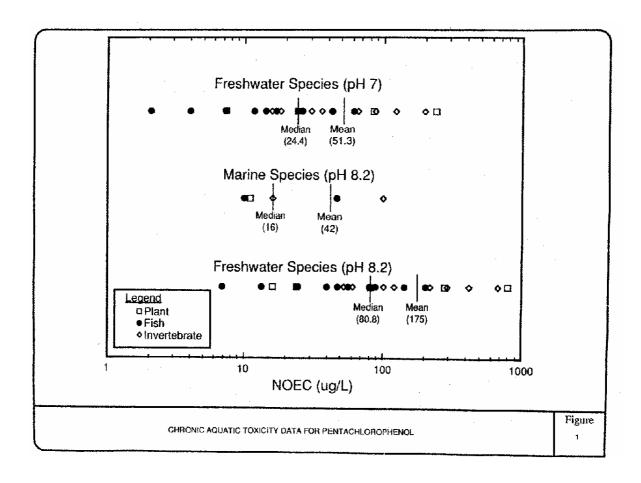


Table 4 : Summary of ecotoxicity data selected for the PNEC derivation, with the appropriate assessment factors for pentachlorophenol

Data set	Assigned Assessment Factor	Lowest Toxicity Values
At least 1 short-term	1000	Freshwater
LC50 from each trophic	1000	20 - 600 μg/l (fish LC50s); Ontario Ministry
level (fish, invertebrate,		of Environment (1984)
algae)		240 - 2,000 μg/l (invertebrate LC50s);
3)		Ontario Ministry of Environment (1984)
		80 - 7,000 μg/l (algae EC50s); Ontario
	$PNEC = 0.02  \mu g/l$	Ministry of Environment (1984)
	1000	Marine
		38 - 440 μg/l (fish LC50s); BC Environment
		(1993)
		84 - >10,000 μg/l (invertebrate LC50s); BC
		Environment (1993)
		280 - 300 μg/l (algae EC50s); BC
	$PNEC = 0.038 \mu g/l$	Environment (1993)
Long-term NOEC from	10	Freshwater $(pH = 7)$
at least 3 species		Oncorhynchus nerka: 56 d NOEC: 2 µg/l;
representing three		Webb & Brett, 1973
trophic levels (fish,	$PNEC = 0.2 \mu g/l$	Physa gyrina: 36 d NOEC: <15 μg/l; Hedtke
invertebrates, algae)		et al., 1986
		Anabaena flos-aquae: 5 d NOEC: 5 µg/l;
		Hoberg, 1993a
	10	Marine
		Pleuronectes platessa: 56 d NOEC: 10 µg/l;
		Adema & Vink, 1981
	$PNEC = 1.0  \mu g/l$	Ophryotrocha diadema: 30 d NOEC: 10 µg/l;
		Adema & Vink, 1981
		Skeletonema costatum: 5 d NOEC: 11 µg/l;
		Hoberg, 1993e
Field studies	Selected = 20	40 μg/l (LOEC; 84-day freshwater
	based on LOEC	experimental stream study which included
		bacteria, zooplankton, invertebrates, fish,
		phytoplankton, and periphyton); Hedtke and
	$PNEC = 2.0  \mu g/l$	Arthur, 1985

## 7.3 **PNEC for Sediments**

PNECs for pentachlorophenol in freshwater and marine sediments can be estimated using the surface water PNEC values from Section 7.2 and the equilibrium-partitioning

approach. The equilibrium-partitioning approach (U.S. EPA 1993) is widely used for determining PNEC values for non-ionic organic chemicals in sediments, as follows:

 $PNEC_{sed} (\mu g/kg) = (Koc) (PNEC_{water}) (TOC)$ 

where: Koc = adsorption coefficient (unitless)

 $PNEC_{water} = PNEC$  value for surface water (µg/l)

TOC = total organic carbon content of sediment (percent, as a fraction)

Using the midpoint of the measured Koc values (2063 from Table 1), a marine PNEC water of 1.0  $\mu$ g/l (from Table 4), and a standard default TOC value of three percent (0.03), the marine PNEC<sub>sed</sub> is 62  $\mu$ g PCP per kg of sediment [PNEC<sub>sed</sub> = (2063)(1)(.03)]. For freshwater sediments, the PNEC<sub>sed</sub> would be 12.4  $\mu$ g/kg based on the same Koc and TOC values used to derive the marine sediment PNEC and the worst case freshwater PNEC<sub>water</sub> of 0.2  $\mu$ g/l from Table 4 (PNEC<sub>sed</sub> = (2063)(.2)(.03). A more realistic PNEC sediment for freshwater would be 124  $\mu$ g/kg (based on PNEC<sub>water</sub> of 2  $\mu$ g/l). Since pentachlorophenol dissociates in water at environmental pHs and therefore is not a non-ionic compound, the PNEC<sub>sed</sub> values derived using the equilibrium-partitioning approach can only be considered estimates. The effects of dissociation would however have been factored into the Koc and toxicity measurements from studies conducted under environmental pH conditions.

## 7.4 Bioaccumulation

Significant bioaccumulation of pentachlorophenol in aquatic species is unlikely in view of its properties. The octanol-water partition coefficient (Kow) of pentachlorophenol is highly dependent and inversely related to pH. Measured log Kow values range from about 2.7 to 3.7 across the environmentally relevant pH range of 6 to 9 (Montgomery 1996). Chemicals with log Kow values in this range are not expected to have significant bioaccumulation. Log Kow values as high as 5.0 (measured at pH 1-2) have been reported but are inappropriate in environmental assessments considering the speciation of pentachlorophenol under environmental pH conditions (described in Section 4.1).

"In aquatic organisms PCP is cumulated to a limited extent. Bioconcentration factors (BCFs) for algae, invertebrates and fishes calculated on the basis of laboratory and field observations are generally in the order of 100 to 1000" (RIVM 1991). Recent UK and Dutch hazard assessments for PCP include BCF data; for example, the reported BCF for *Daphnia magna* is 400 (Hobbs *et al..*, 1993). In addition, "biomagnification of PCP (cumulated within food chains) does not play a significant role in the aquatic environment" (RIVM 1991).

The limited bioaccumulation has been confirmed in a number of laboratory studies. At least six Reliability Level 1 fish bioconcentration tests have been reported. Test species have included fathead minnow, bluegill, rainbow trout, killifish, and flagfish. The whole body fish bioconcentration factors (BCFs) range from 64 for the saltwater killifish (study

conducted at pH 8.3) to 770 for the fathead minnow (pH 7.5) and 771 for the rainbow trout (dechlorinated tap water). The most recent study is a 1993 test with bluegill conducted as part of the pentachlorophenol chemical re-registration under USEPA protocols. The whole body BCF was 490 at a pH of 6.9-7.2. These studies also demonstrated rapid depuration which is accounted for by pentachlorophenol's rapid metabolism in the fish.

The six Reliability Level 1 fish bioconcentration tests are as follows:

Test Species	Whole Body BCF	<u>Reference</u>
fathead minnow	770	Veith <i>et al.</i> (1979)
fathead minnow	174 - 284	Huckins and Petty (1983)
bluegill	490	Dionne (1993)
rainbow trout	91 - 771	Niimi and McFadden (1982)
killifish (saltwater)	64	Trujillo <i>et al.</i> (1982)
flagfish	216	Smith et al. (1990)

#### 7.5 Persistence

The Mackay level I prediction of environmental partitioning of pentachlorophenol (see Section 5) indicates that under typical environmental pH conditions, a very small fraction is in the air, with the majority of PCP partitioning to water and considerably less to soils and sediments. The available published data on the persistence of pentachlorophenol is summarized in Howard *et al.* (1991). PCP does not hydrolyze, however, reported photolysis half-lives in water range from hours (1) to several days (4.6). Howard reports aqueous biodegradation half-lives range from 23 to 178 days under aerobic conditions, and half-lives from 42 days to more than a year under anaerobic conditions.

There are also recent biodegradation studies conducted as part of the pentachlorophenol chemical re-registration under USEPA protocol (Schmidt 1991, 1992a, 1992b, 1992c). The test substance for all four tests was uniform ring labeled <sup>14</sup>C-pentachlorophenol of 98% purity. The results of these studies are as follows:

Test type	<u>Duration</u>	Substrate	<u>Half-life</u>	PCP Residue
aerobic aquatic (including sediment)	30 days	sandy loam soil flooded with water	4.9 days	1%
anaerobic aquatic (includes sediment under nitrogen air)	365 days	sandy loam soil flooded with water	33.8 days	<1%
aerobic soil	365 days	sandy loam soil	63 days	1.4%

anaerobic soil	60 days	sandy loam soil	13.9 days aerobic;	38.6%
(under nitrogen air)	(after 19	(then flooded)	no degradation	
	days		under anaerobic	
	aerobic)		conditions for 60 day	'S

#### 7.6. Conclusion

Although pentachlorophenol is toxic to aquatic organisms, it can be deduced from the above information that pentachlorophenol is not a "persistent, toxic 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 for pentachlorophenol is based on data from analytical monitoring programs in the North Sea, adjacent coastal waters, and river systems discharging into the North Sea. The reported PCP concentrations in these surface waters have been measured at a number of locations and are detailed in <u>Appendix 4</u>. References for the available monitoring data can be found in <u>Appendix 7</u>. Since no HEDSET monograph could be located for pentachlorophenol, other data sources were consulted.

Since the data sources did not usually indicate if the sampling locations were close to an emission source (e.g., production or processing), it is generally assumed, for the purposes of the exposure assessment, that the lower levels (for the same time period) correspond to "regional" background concentrations and that the higher levels correspond "local" emission sources, with the highest reported levels being considered "a worst case". Recall from Section 6 that the 1991 EU Directive 91/173/EEC severely restricted the use of pentachlorophenol-containing products in the EU and that individual countries, many of which border the North Sea, have placed even tighter restrictions or have instituted national bans on the use of pentachlorophenol and PCP-containing products. The monitoring data available for this risk assessment, which are described below, include time periods before and after the action taken by the EU and individual countries. There are insufficient monitoring data to provide a compete "before" and "after" evaluation for each of the monitoring locations, however, the general trend has clearly been decreasing surface water concentrations with time in all surface waters.

#### 8.1 Marine waters and estuaries

In North Sea, coastal waters and estuaries, the concentrations are reported as either average (mean) or median PCP concentrations. Data are available for Germany, the Netherlands and Great-Britain (see <u>Appendix 4</u>). All are below 1  $\mu$ g/l, with a range of average/median concentrations from non detect to 0.79  $\mu$ g/l. The highest reported average/median concentrations are associated with industrial outfalls (e.g. papermill outfalls) and developed harbours. Monitoring data for PCP in North Sea waters, are illustrated on the <u>Appendix 5</u> map.

The summary statistic (average or median) used depended on what was reported in the particular study or reference. In some cases, only ranges or maximum values were reported and are labelled as such in this report. Where the actual data were reported, averages were calculated.

In estuary waters, average or median PCP concentrations have generally shown a decreasing trend with time during the period from 1983 to 1997 (see <u>Appendix 4</u>). This decreasing trend reflects the better environmental management and the restrictions and bans imposed by various European countries (beginning with Sweden in 1978) and the EU (in 1987 and 1991) on the use of PCP and its derivatives.

Hobbs *et al.* (1993) also report background concentrations (referred to in this report as "typical" concentrations) for PCP in various media. These values are based on samples taken two or more kilometers from known discharge sources in Great Britain. For surface water (fresh and coastal), background levels range from 0.00085 to 0.2  $\mu$ g/l, with a mean of 0.074  $\mu$ g/l. This mean value occurs at about the midpoint of the reported ranges for North Sea/coastal waters (0.009 to 0.24  $\mu$ g/l) and estuarine waters (0.010 to 0.20  $\mu$ g/l) given above when sites adjacent to industrial outfall discharges are eliminated.

Thus, considering all of the available monitoring data (covering the time period 1983 to 1997) the typical (or background) concentrations for coastal and marine waters are estimated to be  $0.07~\mu g/l$ . The highest (or worst case) concentrations range from  $0.24~\mu g/l$  (outside the immediate vicinity of industrial outfalls) to  $0.79~\mu g/l$  (in the immediate vicinity of outfalls). When only those data from the most recent period are considered (i.e., ~1993 forward), the North Sea and estuary water concentrations are considerably lower, in the range of <0.01 to  $0.02~\mu g/l$ , with a maximum of  $0.11~\mu g/l$ .

#### 8.2 River waters

The average or median PCP concentrations in river waters have generally shown a decreasing trend with time during the period from 1976 to 1997 in highly industrialized rivers such as the Rhine and Meuse (see <u>Appendix 4</u>). This decreasing trend reflects the better environmental management and the restrictions and bans imposed by various European countries (beginning with Sweden in 1978) and the EU (in 1987 and 1991) on the use of PCP and its derivatives. Based on the most recently collected data that was available for each river in the region (i.e., 1992 forward), average or median PCP

concentrations range from 0.01  $\mu$ g/l to 0.34  $\mu$ g/l, with about 20 of these 30 data points being  $\leq 0.1~\mu$ g/l. Average or median PCP concentrations are generally lower on the eastern side of the North Sea (Netherlands and Germany) than on the western side (Great Britain). This trend reflects general usage patterns and national regulations; the use of pentachlorophenol is essentially banned in the Netherlands and Germany but is still used for some purposes in the United Kingdom (see Section 6.3). Recent data (1994-1997) from numerous locations in Great Britain show concentrations at or below 0.1  $\mu$ g/l on average.

If the available studies are sorted by concentration (using the most recent data for each river), the study at the 50th percentile reports an average/median concentration of 0.07  $\mu$ g/l. This is the same value Hobbs *et al.* (1993) report as a mean background concentrations for PCP in surface water (based on samples taken two or more kilometers from known discharge sources in Great Britain). Thus, 0.07  $\mu$ g/l is considered a typical value for river water. The highest average or median concentration from the available studies (0.34  $\mu$ g/l in 1992) is considered the worst case for river water. The more recent data (1994-1997) from the same North East region of Great Britain show the highest average concentration at 0.15  $\mu$ g/l. Note also that there would be considerable dilution of the PCP in the rivers as they enter the North Sea estuaries and coastal waters.

## 8.3 Other monitoring data

Some data are available on PCP levels in estuarine and riverine sediments (<u>Appendix 4</u>). In coastal and estuarine waters the highest average PCP sediment concentration based on 77 samples analyzed from 1991-1994 was 26.5  $\mu$ g/kg. All 33 samples analyzed from the same locations in 1995-1997 were below the limit of detection (<10  $\mu$ g/kg).

In rivers, the highest average PCP sediment concentrations based on 244 samples analyzed from 1985-1994 was 29.7  $\mu$ g/kg. Most of the 40 samples analyzed from the same locations in 1995-1997 were below the limit of detection (<10  $\mu$ g/kg). The highest average concentration was 11.25  $\mu$ g/kg in samples where PCP was detected.

No recent data were found on PCP levels in aquatic organisms in the region.

#### 9. RISK ASSESSMENT CONCLUSIONS

#### **Surface Water**

In the risk characterization of pentachlorophenol for the aquatic organisms, the PNEC is compared to the PEC.

A PNEC of 1  $\mu$ g/l was derived for the marine species exposed to pentachlorophenol in marine surface waters.

Based on all the available monitoring data from as early as 1983 (before restrictions were in place) the "worst case" concentrations of PCP in North Sea coastal waters and estuaries are up to  $0.24~\mu g/l$  outside the immediate vicinity of industrial outfalls, and  $0.79~\mu g/l$  in the immediate vicinity of outfalls. A typical marine water concentration during this period is  $0.07~\mu g/l$ . Based on the data from 1993 to the present, all of the data are in the range of  $0.01~\mu g/l$ . There is a  $0.12~\mu g/l$  concentration reported in a Great Britain harbour in 1992 and a  $0.11~\mu g/l$  in the North East region in 1994 and 1995.which could represent a "worst case" in more recent times.

A PNEC of 0.2-2  $\mu$ g/l was derived for freshwater species exposed to pentachlorophenol. A typical (average) river water concentration of 0.07  $\mu$ g/l was derived from the available data; a worst case (highest reported) river water concentration of 0.15  $\mu$ g/l in 1996 was also identified. These values are representative of most recent times.

Table 5 : Calculation of PEC/PNEC ratios for surface waters – Pentachlorophenol

Type of water	PEC level	PEC/PNEC
Coastal waters/estuaries:		
<u> 1983 – 1991</u>		
• typical water	0.07 μg/l	0.07
• worst case	0.24 μg/l	0.24
• worst case (at outfall)	0.79 μg/l	0.79
<u> 1992 – 1997</u>		
• typical water	0.01 μg/l	0.01
• worst case	0.11 μg/l	0.11
River waters:		
<u> 1993 – 1997</u>		
typical water	0.07 μg/l	0.35-0.035
• worst case	0.15 μg/l	0.75-0.075

The calculated PEC/PNEC ratios are all less than one for the marine environment as shown in Table 5. When the exposure concentrations (PECs) are below the predicted no effect concentrations (PNECs), the prediction is that the risks are low. Based on the most recent monitoring data, which would reflect the production and use restrictions that are in place for pentachlorophenol, the ratio based on typical coastal and estuarine water concentrations provide a safety margin of 100 and the ratio based on worst case concentrations provide a safety margin of 8. The PEC/PNEC ratios are generally less than one for the river environment indicating acceptable safety margins. An exception is for the combination of the worst case river concentration and the lowest end of the PNEC range. In this case the ratio marginally exceeds one suggesting a potential risk under specific local circumstances. These ratios do not take into account the considerable dilution of the PCP as the rivers enter the North Sea coastal waters and estuaries.

#### **Sediment**

PNECs of 62 and 12.4 to 124  $\mu$ g/kg were estimated for the marine and freshwater species, respectively, exposed to pentachlorophenol in sediments. These PNEC values, and the sediment monitoring values described in Section 8.3, are used to calculate the PEC/PNEC ratios, which are summarized in Table 6.

Table 6 : Calculation of PEC/PNEC ratios for sediments – Pentachlorophenol

Type of water	PEC level	PEC/PNEC
Coastal		
waters/estuaries:		
<u>1991 – 1994</u>	26.5 μg/kg	0.43
<ul> <li>highest average</li> </ul>		
1005 1007	ND (<10 u a/l-a)	< 0.16
1995 – 1997 • highest average	ND (<10 μg/kg)	<0.16
Ilighest average		
Rivers:		
rety of S.		
<u> 1985 – 1994</u>		
• highest average	29.7 μg/kg	2.40-0.24
<u> 1995 – 1997</u>		
<ul> <li>highest average</li> </ul>	11.25 μg/kg	0.91-0.09

The calculated ratios are less than one based on the most recent data (1995 - 1997) for both coastal waters/estuaries and rivers. As was seen for surface waters, the more recent ratios are smaller than at earlier time periods. This indicates that PCP sediment concentrations have been decreasing over time and are currently at levels at which no adverse effects to aquatic receptors are anticipated under typical conditions in the North Sea.

## **Conclusion**

In conclusion, present levels of pentachlorophenol in surface waters and sediments should not represent a risk to the marine environment in the North Sea region. As indicated in the assessment, the surface waters and sediments are showing a decreasing trend in PCP concentrations with time. And finally, it is known that pentachlorophenol is not persistent (this is confirmed by the dropping levels in surface waters and sediments) and that it has a relatively low bioaccumulation potential so it is not expected to accumulate significantly in aquatic biota.

#### 10. REFERENCES

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#### **Environmental Quality Criteria for Assessment of Ecotoxicity Data**

The principal quality criteria for acceptance of data in the derivation of a predicted no [chronic] effect concentration (PNEC) are that the test procedure should be well described as regards test organism, duration, exposure conditions, influential water quality parameters and toxicological endpoints (with reference to official guideline or established methodology) and that the chemical concentrations must be measured with an adequate analytical method.

The following four cases are distinguished according to criteria defined in IUCLID system:

## **Quality Criteria for Acceptance of Ecotoxicity Data**

Case	Detailed description of the test	Accordance with scientific guidelines	Measured concentration	Conclusion: Reliability Level
I	+	+	+	[1] : valid without restriction
II	±	±	±	[2]: valid with restrictions; to be considered with care
III	insufficient (-)	-	-	[3] : invalid
IV	the information to available	[4] : not assignable		

The selected validated data LC50, EC50 or NOEC are divided by an assessment factor to determine a PNEC 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, etc. Assessment factors will decrease in magnitude as the available data are more relevant and account for the various trophic levels.

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

```
Fugacity Level I calculation
  Chemical: pentachlorophenol
                                                       20
  Temperature (C)
                                                      266.34
  Molecular weight (g/mol)
                                                .41500000E-2
  Vapor pressure (Pa)
Solubility (g/m3)
                                                       14
                                                        0.05
  Solubility (mol/m3)
                                                        0.08
  Henry's law constant (PA.m3/mol)
  Log octanol water part. coefficient
                                                        3.32
                                                     2089.30
  Octanol water part. coefficient
  Organic C-water part. coefficient
Air-water partition coefficient
                                                     856.61
                                               .32393400E-4
                                                       25.70
  Soil-water partition coefficient
  Sediment-water partition coefficient
                                                       51.40
                                                        1
  Amount of chemical (moles)
                                               .83721964E-8
  Fugacity (Pa)
                                               119442968.25
  Total VZ products
  Phase properties and compositions:
                                                     Soil
                                                                      Sediment
                : Air
                                   Water
  Phase
                                                    .45000E+5
                                    .70000E+7
                                                                       .21000E+5
  Volume (m3) : .6000E+10
                                    .10000E+4 .15000E+4
                                                                       .15000E+4
  Density(kgm3): .12056317E+2
                                                                      .4000000E-1
                                                     .2000000E-1
  Frn org carb.: .00000E+0
Z mol/m3.Pa : .41029864E-3
                                    .00000E+0
                                                                      .65099649E+3
                                    .12666118E+2
                                                     .32549824E+3
  Z mol/m3.Pa :
                                                     .14647421E+8
                                                                      .13670926E+8
  VZ mol/Pa : .24617918E+7
Fugacity : .83721964E-8
Conc mol/m3 : .3435100E-11
                                    .88662828E+8
                                                                      .83721964E-8
                                    .83721964E-8
                                                      .83721964E-8
                                    .10604323E-6
                                                      .27251352E-5
                                                                      .54502705E-5
                                                    .72581253E-3
                                                                       .14516250E-2
  Conc g/m3 : .91490476E-9
                                    .28243554E-4
                                                                       .96775004E-3
                   .75885918E-7
.20610605E-1
                                     .28243554E-4
                                                      .48387502E-3
  Conc ug/g
                :
                                     .74230262E+0
                                                      .12263108E+0
                                                                      .11445568E+0
  Amount mol
                                                              12.26
                                                                              11.45
                             2.06
                                            74.23
  Amount %
```

**APPENDIX 3** 

Species	Test Substance	Duration (days)	NOEC (mg/L)	pН	pH - adjusted NOEC <sup>1</sup>	Reliability Level	Toxicity Endpoints	Reference
1. Fishes (Freshwater)								
Jordanella floridae	PCP	28	0.055	6.9	0.061	1	larval and fry survival	Smith <i>et al.</i> 1991
Lepomis machrochirus	NaPCP	22	< 0.048	7.2	< 0.039	13	growth rate	Samis <i>et al.</i> 1991
Lepomis machrochirus	NaPCP	96	< 0.048	8.1	< 0.017	13	Growth	Zischke et al. 1985
Oncorhynchus mykiss	PCP	28	0.011	8.0	0.004	1	biomass and mortality of eggs, alevins, fry	Hodson & Blunt 1981
Oncorhynchus nerka	NaPCP	56	0.0017	6.8	0.0021	1	growth rate and food conversion efficiency	Webb and Brett 1973
Pimephales promelas	PCP	90	>0.130	9.4	>0.012	14	survival and growth	Hamilton et al. 1986
Pimephales promelas	NaPCP	32	0.118	8.0	0.043	1	hatch, survival, growth	Hedtke et al. 1986
Pimephales promelas	PCP	32	0.045	7.6	0.025	1	hatch, survival, growth	Holcombe et al. 1982
Pimephales promelas	PCP	32	0.016	6.5	0.026	1	hatch, survival, growth	Spehar et al. 1985
Pimephales promelas	PCP	32	0.028	7.5	0.017	1	hatch, survival, growth	Spehar et al. 1985
Pimephales promelas	PCP	32	0.032	8.0	0.012	1	hatch, survival, growth	Spehar et al. 1985
Pimephales promelas	PCP	32	0.064	8.5	0.014	1	hatch, survival, growth	Spehar et al. 1985
Pimephales promelas	NaPCP	96	< 0.048	8.1	< 0.017	13	Growth	Zischke et al. 1985
Pimephales promelas	PCP (industrial composite)	90	0.006	7.4	0.004	1	survival and growth	Cleveland et al. 1982
Pimephales promelas	PCP (purified)	90	0.036	7.4	0.024	1	survival and growth	Cleveland et al. 1982
Pimephales promelas	PCP (Dowicide)	90	>0.139	7.4	>0.093	14	survival and growth	Cleveland et al. 1982
Salmo gairdneri	NaPCP	72	0.011	7.4	0.007	1	survival and growth	Dominguez and Chapman 1984
Salmo gairdneri	PCP	18	0.012	7.5	0.007	1	number of viable oocytes	Nagler et al. 1986

Species	Test Substance	Duration (days)	NOEC (mg/L)	pН	pH - adjusted NOEC <sup>1</sup>	Reliability Level	Toxicity Endpoints	Reference
2. Fishes (Saltwater)								
Cyprinodon variegatus	PCP	life cycle	0.047	8.2	0.047	1	survival and growth	Parrish et al. 1978
Pleuronectes platessa	PCP	56	0.010	8.2	0.010	1	egg and larvae mortality, growth, development	Adema & Vink 1981
3. Invertebrates (Fresh	water)							
Ceriodaphnia affinis	NaPCP	7	0.075	7.9	0.030	1	survival and repro.	Hedtke et al. 1986
Ceriodaphnia dubia	NaPCP	7	0.200	NR <sup>2</sup>	0.200	1	survival and repro.	Winner 1988
Daphnia magna	СР	21	0.180	8.0	0.066	1	survival and repro.	Adema 1978
Daphnia magna	PCP	21	0.340	8.0	0.124	1	Reproduction	Adema and Vink 1981
Daphnia magna	PCP	life cycle	0.100	8.0	0.037	1	Reproduction	Stephenson 1991
Daphnia magna	NaPCP	7	0.200	NR <sup>2</sup>	0.200	1	survival and repro.	Winner 1988
Lymnaea stagnalis	PCP	16	0.050	8.0	0.018	1	Reproduction (viable eggs per young)	Adema & Vink 1981
Physa gyrina	NaPCP	36	< 0.026	7.6	< 0.015	13	survival, repro., growth	Hedtke et al. 1986
Physa gyrina	NaPCP	96	0.048	8.1	0.016	1	egg number and survival	Zischke et al. 1985
Simocephalus vetulus	NaPCP	14	0.119	7.3	0.088	1	survival and repro.	Hedtke et al. 1986
4. Invertebrates (Saltwa	ater)							
Chaetogammarus marinus	PCP	56	0.100	8.2	0.100	1	Growth	Adema & Vink 1981
meiobenthic nematode	PCP	91	0.016	8.2	0.016	1	biomass and density	Cantelmo & Rao 1978
Ophryotrocha diadema	PCP	30	0.010	8.2	0.010	1	Reproduction	Adema & Vink 1981

Species	Test Substance	Duration (days)	NOEC (mg/L)	рН	pH - adjusted NOEC <sup>1</sup>	Reliability Level	Toxicity Endpoints	Reference
Paleamonetes pugio	NaPCP	66	0.100	8.2	0.100	1	Mortality	Conklin & Rao 1978
5. Plants (Freshwater)								
Anabaena flos-aquae	PCP	5	0.008	7.5	0.005	1	cell growth inhibition	Hoberg 1993a
Navicula pelliculosa	PCP	5	0.040	7.5	0.024	1	cell growth inhibition	Hoberg 1993b
Selenastrum capricornutum	PCP	5	0.012	7.5	0.007	1	cell growth inhibition	Hoberg 1993c
Elodea canadensis	PCP	21	0.230	8.0	0.084	1	growth/biomass reduction	Hedtke et al. 1986
Lemna gibba	PCP	14	0.032	5.0	0.239	1	frond density/biomass	Hoberg 1993d
Lemna gibba	NaPCP	21	>1440	7.5	>916	14	frond production and chlorosis	Hedtke et al. 1986
6. Plants (Saltwater)								
Skeletonema costatum	PCP	5	0.011	8.2	0.011	1	cell growth inhibition	Hoberg 1993e

Species	Test Substance	Duration (days)	NOEC (mg/L)	pН	pH - adjusted NOEC <sup>1</sup>	Reliability Level	Toxicity Endpoints	Reference
7. Field study – Stream	Mesocosm							
Bacteria, zooplankton, invertebrates (macrobenthos and insects), fish (bluegill and fathead minnows), phytoplankton, periphyton	PCP (Dowicide)	84	<0.040	7.5 - 8.2	<0.015 (at pH 8)	13	Survival, growth and fecundity of fish; taxa and numbers of invertebrates, snail reproduction and insect emergence; species and biomass of plankton, periphyton and bacteria; plant ATP and chlorophyllA  10 -15 percent weight reduction of fathead minnows was the most sensitive endpoint	Hedtke & Arthur, 1985

<sup>1.</sup> pH-adjusted NOECs are based on pH = 7.0 for freshwater tests as described in Section 7.1. No adjustment needed for saltwater tests which were all conducted at ambient pH  $\sim 8.2$ .

<sup>2.</sup> NR = not reported; however author reported using laboratory reconstituted water that is assumed to have an approximately neutral pH.

<sup>3.</sup> Some effects were observed at the lowest test concentration, therefore the NOEC value is indicated as less than (<).

<sup>4.</sup> No effect was observed at the highest test concentration, therefore the NOEC value is indicated as greater than (>).

Area	Year of Measurement	Sample Size <sup>a</sup>	Average (A) or Median (M) Concentration (μg/L) <sup>b</sup>	Reference
1. Coastal Waters and Estuaries				
Netherlands:				
• North Sea coast, 2 sites	1983-1985	12	A = 0.009  (max  0.034)	NICMM 1997
North Sea coast, 1 site	1983-1985	10		
			A = 0.019  (max  0.103)	NICMM 1997
North Sea coast, 6 sites	1993	15 (0)	ND (0.010)	Phernambucq et al. 1996
North Sea coast, 9 sites	1993	28 (3)	A = 0.012  (max  0.050)	Phernambucq et al. 1996
Ems Estuary, 3 sites	1983-1985	38	A = 0.018  (max  0.103)	NICMM 1997
5 sites	1993	16 (2)	A = 0.010  (max  0.010)	Phernambucq et al. 1996
• Ijsselmeer (Outer Harbor), 7 sites	1982-1985	29	A = 0.028  (max  0.206)	NICMM 1997
, , , , , , , , , , , , , , , , , , , ,	1986-1988	25	A = 0.008  (max  0.045)	
	1989-1991	28	A = 0.015  (max  0.070)	
	1992-1994	74	A = 0.012  (max  0.090)	
	1995-1997	16	A = 0.010  (max  0.010)	
• Ijsselmeer (Inner Harbor), 10 sites	1985	10	A = 0.011  (max  0.041)	NICMM 1997
	1988	7	A = 0.011  (max  0.070)	
	1989	7	A = 0.017  (max  0.060)	
	1992-1994	91	A = 0.010  (max  0.010)	
	1995-1997	13	A = 0.010  (max  0.010)	
• Ijsselmeer (Channel), 10 sites	1985	13	A = 0.047  (max  0.299)	NICMM 1997
	1988	17	A = 0.030  (max  0.100)	
	1993-1994	114	A = 0.012  (max  0.100)	
	1995-1997	43	A = 0.010  (max  0.010)	
• Four Southern Estuaries, 17 sites	1982-1985	109	A = 0.051  (max  0.230)	NICMM 1997
	1986-1988	109	A = 0.029  (max  0.250)	
	1989-1991	79	A = 0.023  (max  0.180)	
	1992-1994	128	A = 0.017  (max  0.140)	
	1995-1997	106	A = 0.011  (max  0.030)	D1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
Four Southern Estuaries, 9 sites	1993	31 (0)	ND (0.010)	Phernambucq et al. 1996
• Scheldt River Estuary	1987-1989	NR <sup>c</sup>	0.020	Hobbs et al. 1993

Area	Year of Measurement	Sample Size <sup>a</sup>	Average (A) or Median (M) Concentration (µg/L) <sup>b</sup>	Reference
Scheldt River Estuary				
- Hoboken	1987-1989	3	M = 0.100  (max  1.100)	van Zoest & van Eck 1991
- Buoy 87	1987-1989	3	M = 0.180  (max  0.350)	
- Hansweert	1987-1989	3	M = 0.020  (max  0.150)	
- Vlissingen	1987-1989	3	M = 0.020  (max  0.070)	
Great Britain:				
• North Sea, 9 sites	1991	102 (27)	M = 0.13  (max  2.00)	A CD 1004 (D 11' t)
				ACP 1994 (Redlist)
North Sea outfalls	1001	11 (10)	16 0 70 / 10 10	
- Papermill	1991	11 (10)	M = 0.79  (max  1.94)	
- Papermill	1991	11 (11)	M = 0.76  (max 5.80)	ACP 1994 (Redlist)
• North Sea/English Channel (offshore), 22 sites	1991-1992	NR	All < 1.00	ACP 1994
North Sea Coast	1991	49 (15)	M = 0.24  (max 1.10)	
- Brans Sands, 6 sites	1992	24 (17)	M = 0.12  (max  0.53)	
,	1991	20 (5)	M = 0.06  (max 3.90)	ACP 1994
- North Gare, 4 sites	1992	7 (4)	M = 0.05  (max  0.05)	
,	1991	36 (3)	M = 0.06  (max  0.18)	
- Seal Sands, 6 sites	1992	25 (23)	M = 0.11  (max  1.53)	
• Greatham Harbor, 2 sites	1991	13 (3)	M = 0.04  (max  0.05)	
Greatham Haroot, 2 sites	1992	5 (4)	M = 0.12  (max 0.34)	ACP 1994
• Six River Estuaries	1984	20 (6)	A = 0.20  (max 0.47)	1101 1991
SIX RIVEL Estudies	1704	20 (0)	14 0.20 (max 0.47)	Hobbs <i>et al.</i> 1993
North Sea				
- Anglian Region	1994	93 (11)	A = 0.019  (max  0.15)	National centre for
	1995	74 (0)	ND (0.1)	Environmental Data and
	1996	72 (0)	ND(0.1)	Surveillance,
	1997	72 (0)	ND(0.1)	Environmental Agency,
		` ′	, ,	Bath, UK. March 1999
North East Region	1994	237 (8)	A = 0.11  (max  0.7)	National centre for
	1995	326 (3)	A = 0.11  (max 2.2)	Environmental Data and
	1996	370 (0)	ND (0.1)	Surveillance,
	1997	359 (0)	ND (0.1)	Environmental Agency,
			,	Bath, UK. March 1999

Area	Year of Measurement	Sample Size <sup>a</sup>	Average (A) or Median (M) Concentration (µg/L) <sup>b</sup>	Reference
Southern Region	1994	51 (6)	A = 0.013  (max  0.052)	National centre for
Southern Region	1995	77 (0)	ND (0.05)	Environmental Data and
	1996	69 (0)	ND (0.03)	Surveillance,
	1997	90 (1)	A = 0.067  (max 1.6)	Environmental Agency,
	1997	) (1)	11 0.007 (11411 1.0)	Bath, UK. March 1999
Thames Region	1994	63 (10)	A = 0.016  (max  0.072)	National centre for
	1995	57 (0)	ND (0.1)	Environmental Data and
	1996	66 (0)	ND(0.1)	Surveillance,
	1997	91 (0)	ND(0.1)	Environmental Agency,
		` '	,	Bath, UK. March 1999
Germany:				
• Elbe Estuary	1983	NR	range = $0.02$ to $0.10$	Ernst 1985
	1983-1985	NR	range = $0.01$ to $0.02$	Hobbs <i>et al.</i> 1993
Weser Estuary	1983	NR	range = $0.02$ to $0.10$	Ernst 1985
	1983-1985	NR	range = $0.006$ to $0.10$	Hobbs <i>et al</i> . 1993
• Ems Estuary	1983	NR	range = $0.02$ to $0.10$	Ernst 1985
North Sea coast	1983-1985	NR	range = $0.0003$ to $0.05$	Hobbs <i>et al.</i> 1993
2. River Waters				
Belgium: • Schelde, 8 sites	1991-1994	45 (38)	A = 0.169  (max  1.500)	Ministerie van Sociale Zaken 1996
Maas/Meuse, 4 sites	1991-1992	20 (12)	A = 0.112  (max  0.500)	Ministerie van Sociale Zaken 1996
France • Seine (Caudebec - 30 km from Sea), 1 site	1995	NR	A = 0.027	Agence de Bassin Seine- Normandie 1995
Netherlands:				
• Ijssel Canal, 3 sites	1985	5	A = 0.017  (max  0.026)	
	1988	6	A = 0.047  (max  0.120)	NICMM 1997
	1990-1991	20	A = 0.065  (max  0.230)	

**APPENDIX 4** 

			Average (A) or Median (M)	Reference
Area	Year of Measurement	Sample Size <sup>a</sup>	Concentration (µg/L) <sup>b</sup>	
	1992-1994	31	A = 0.014  (max  0.040)	
	1995-1996	12	A = 0.011  (max  0.020)	
Canal (Rhine/Waal River to North	1982-1985	51	A = 0.026  (max  0.113)	NICMM 1997
Sea), 7 sites	1986-1988	38	A = 0.023  (max  0.107)	
,,	1989-1991	80	A = 0.026  (max  0.530)	
	1992-1994	56	A = 0.016  (max  0.110)	
	1995-1997	46	A = 0.010  (max  0.020)	
• Schelde Canal, 2 sites	1983-1985	13	A = 0.472  (max  1.780)	NICMM 1997
,	1986-1988	15	A = 0.205  (max  0.593)	
	1989-1991	19	A = 0.197 (max 0.530)	
	1992-1994	19	A = 0.112  (max  0.530)	
	1995-1997	14	A = 0.080  (max  0.210)	
Meuse/Maas River, 7 sites	1976-1982	85	A = 0.449  (max  8.900)	NICMM 1997
,	1983-1985	53	A = 0.052  (max  0.214)	
	1986-1988	51	A = 0.020  (max  0.145)	
	1989-1991	86	A = 0.022  (max  0.140)	
	1992-1994	153	A = 0.018  (max  0.200)	
	1995-1997	130	A = 0.010  (max  0.020)	
Rhine/Waal River, 6 sites	1980-1982	72	A = 0.205  (max  0.820)	NICMM 1997
,	1983-1985	86	A = 0.050  (max  0.145)	
	1986-1988	91	A = 0.023  (max  0.093)	
	1989-1991	92	A = 0.017 (max 0.070)	
	1992-1994	162	A = 0.013  (max  0.120)	
	1995-1997	117	A = 0.011  (max  0.030)	
Rhine, at Netherlands/Germany border	1978	NR	A = 0.64	Slooff et al. 1991
(Lobith)	1979	NR	A = 0.45	
	1980	NR	A = 0.39  (max  0.82)	
	1981	NR	A = 0.13  (max  0.38)	
	1982	NR	A = 0.08  (max  0.20)	
	1983	NR	A = 0.07  (max  0.15)	
	1984	NR	A = 0.05  (max  0.13)	
	1985	NR	A = 0.03  (max  0.06)	
	1986	NR	A = 0.03  (max  0.07)	
	1987	NR	A = 0.02  (max  0.09)	

**APPENDIX 4** 

Area	Year of Measurement	Sample Size <sup>a</sup>	Average (A) or Median (M) Concentration (µg/L) <sup>b</sup>	Reference
	1988	NR	A = 0.03  (max  0.04)	
	1990	4 (4)	A = 0.022  (max  0.047)	ICPR 1991
	1991	2(2)	A = 0.047  (max  0.047)	
Great Britain:				
Thames, 10 sites	1991	83 (42)	M = 0.16  (max  1.01)	ACP 1994 (Redlist)
1 site	1993		M = 0.20	WRc, 1998
Humber, 7 sites	1991	65 (55)	M = 0.15  (max  11.8)	ACP 1994 (Redlist)
2 sites	1991	14 (11)	M = 0.03  (max  0.06)	ACP 1994
Welland	1991	17 (8)	M = 0.02  (max  0.22)	ACP 1994 (Redlist)
Witham	1991	11 (7)	M = 0.04  (max  0.34)	ACP 1994 (Redlist)
	1991	11 (7)	M = 0.03  (max  0.06)	ACP 1994
Yare	1991	15 (11)	M = 0.09  (max  4.07)	ACP 1994 (Redlist)
Nene	1991	28 (22)	M = 0.07  (max  0.17)	
		- ( )	()	ACP 1994 (Redlist)
Ouse, 1 site	1991	12 (11)	M = 0.02  (max  0.03)	
6 sites	1991	21 (12)	M = 0.02  (max  0.08)	ACP 1994 (Redlist)
			,	ACP 1994
Stour	1991	12 (4)	M = 0.05  (max  0.07)	
			,	ACP 1994 (Redlist)
	1001	21 (11)		4 GD 4004 (D 41)
Blackwater	1991	21 (11)	M = 0.11  (max  1.24)	ACP 1994 (Redlist)
	1991	7 (3)	M = 0.10  (max  0.20)	ACP 1994
	1992	1 (0)		
Tyne-Team	1991	10 (4)	M = 0.10  (max  2.10)	
				ACP 1994 (Redlist)
Tyne, 6 sites	1990	15 (4)	M = 0.03  (max  0.04)	ACP 1994
	1991	33 (8)	M = 0.50  (max 1.15)	
	1992	31 (8)	M = 0.05  (max  0.17)	
North Tyne	1990	4(2)	NR	ACP 1994
-	1991	6(2)	M = 0.20  (max  0.33)	
	1992	5 (1)	M = 0.04  (max  0.04)	

			Average (A) or Median (M)	Reference
Area	Year of Measurement	Sample Size <sup>a</sup>	Concentration (µg/L) <sup>b</sup>	
• South Tyne, 2 sites	1990	3 (1)	M = 0.20  (max  0.20)	ACP 1994
•	1991	9(1)	M = 0.04  (max  0.04)	
	1992	13 (3)	M = 0.03  (max  0.26)	
• Team	1990	10 (5)	M = 0.13  (max  2.40)	ACP 1994
	1991	12 (4)	M = 0.10  (max  2.10)	
	1992	5 (4)	M = 0.34  (max  0.51)	
• Tees, 4 sites	1991	59 (23)	$M = 0.41 \text{ (max } 32.0)^d$	ACP 1994 (Redlist)
• Tees, 13 sites	1990	49 (11)	M = 0.08  (max  0.31)	ACP 1994
,	1991	114 (32)	M = 0.10  (max  0.34)	
	1992	126 (89)	M = 0.25  (max  45.5)	
• Derwent, 2 sites	1990	4(2)	M = 0.10  (max  0.15)	ACP 1994
•	1991	8 (3)	M = 0.03  (max  0.50)	
	1992	10 (4)	M = 0.11  (max  0.30)	
• Wear, 10 sites	1990	11 (0)		ACP 1994
•	1991	48 (18)	M = 0.50  (max  1.36)	
	1992	56 (31)	M = 0.13  (max  0.38)	
• Tweed, 2 sites	1990	7 (0)		ACP 1994
	1991	8 (2)	M = 0.05  (max  0.65)	
	1992	6(2)	M = 0.18  (max  0.24)	
• Coquet	1990	5 (0)	<del></del>	
•	1991	9(2)	M = 0.29  (max  0.54)	ACP 1994
	1992	10(3)	M = 0.07  (max  0.11)	
Wansbeck	1990	3 (0)		
	1991	8 (1)	M = 0.76  (max  0.76)	ACP 1994
	1992	5 (3)	M = 0.10  (max  0.18)	
Billingham Beck	1990	0(2)	M = 0.08  (max  0.08)	ACP 1994
-	1991	16(2)	M = 0.04  (max  0.47)	
	1992	6 (4)	M = 0.14  (max  0.33)	
• Greatham Creek, 6 sites	1991	1 (17)	M = 0.05  (max  4.80)	ACP 1994
,	1992	67 (46)	M = 0.22  (max  1.49)	
North Sea			,	
- Anglian Region	1994	279 (27)	A = 0.024  (max  0.22)	National centre for
	1995	294 (3)	A = 0.054  (max 1.2)	Environmental Data and
	1996	303 (2)	A = 0.056  (max  0.87)	Surveillance,

Area	Year of Measurement	Sample Size <sup>a</sup>	Average (A) or Median (M) Concentration (μg/L) <sup>b</sup>	Reference
	1997	308 (4)	A = 0.055  (max  0.64)	Environmental Agency,
			(	Bath, UK. March 1999
North East Region	1994	1,171 (81)	A = 0.12  (max  2.9)	National centre for
•	1995	1,175 (89)	A = 0.14  (max 3.2)	Environmental Data and
	1996	937 (80)	A = 0.15  (max 5.7)	Surveillance,
	1997	1,210 (60)	A = 0.067  (max 2.4)	Environmental Agency, Bath, UK. March 1999
Southern Region	1994	33 (9)	A = 0.026  (max  0.17)	National centre for
2	1995	25 (1)	A = 0.044  (max  0.1)	Environmental Data and
	1996	24 (0)	ND(0.1)	Surveillance,
	1997	88 (1)	A = 0.051  (max  0.1)	Environmental Agency,
		. ,	, , ,	Bath, UK. March 1999
• Thames Region	1994	315 (102)	A = 0.024  (max  0.97)	National centre for
-	1995	364 (2)	A = 0.052  (max  0.5)	Environmental Data and
	1996	388 (2)	A = 0.052  (max  0.45)	Surveillance,
	1997	366 (3)	A = 0.063  (max 3.7)	Environmental Agency,
				Bath, UK. March 1999
Scotland:				
<ul> <li>Tweed Region, 4 rivers</li> </ul>	1991-1992	NR	Max = 0.15 (Teviot River)	ACP 1994
Tay Region	1992	19	All < 0.02	ACP 1994
Germany:				
• Weser, 11 sites	1993	22 (6)	A = 0.008  (max  0.020)	Gutebericht 1993
• Elbe, 14 sites	1993	162 (41)	A = 0.019  (max  0.16)	IKSE 1993
13 sites	1994	193 (47)	A = 0.017  (max  0.41)	ARE 1996
• Rhine, 2 sites	1993	24 (6)	A = 0.013  (max  0.05)	DKRR 1995

a Total samples (number of detects).
b Unless otherwise indicated, average (mean) values include non-detect samples at the detection limit. Median values are calculated using only those samples with values exceeding the detection limit.
c Not reported.

d Maximum value occurred near a chemical plant outfall.

## **Environmental Monitoring Levels of Pentachlorophenol in Sediments**

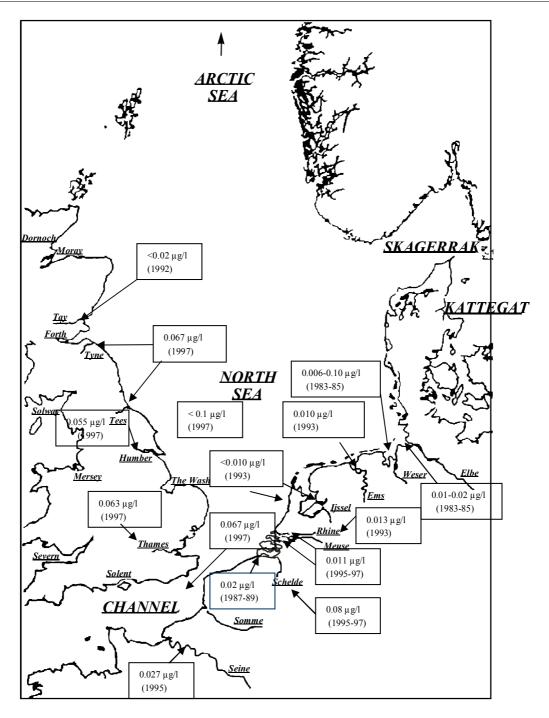
Area	Year of Measurement	Sample Size <sup>a</sup>	Average (A) or Median (M) Concentration (μg/kg) <sup>b</sup>	Reference
1. Coastal Waters and Estuaries				
Netherlands:	1991			
• Ijsselmeer (Outer Harbor), 7 sites	1992	3	ND (20.00) <sup>c</sup>	NICMM 1997
	1996	5	A = 25.40  (max  36.00)	
		1	ND (10.00)	
• Ijsselmeer (Inner Harbor), 10 sites	1992	4	ND (20.00)	NICMM 1997
	1996	1	ND (10.00)	
• Ijsselmeer (Channel), 10 sites	1996	3	ND (10.00)	NICMM 1997
• Four Southern Estuaries, 17 sites	1991	14	A = 26.50  (max  100.0)	NICMM 1997
	1992-1994	51	A = 24.02  (max  210.0)	
	1995-1997	28	ND (10.00)	
2. River Waters			I	
Netherlands: • Ijssel Canal, 3 sites	1991	8	A = 29.63  (max  90.00)	NICMM 1997
• Canal (Rhine/Waal River to North Sea),	1991	7	A = 29.03  (max  90.00) A = 25.71  (max  60.00)	NICMM 1997 NICMM 1997
7 sites	1991	2	ND (20.00)	NICIVIIVI 1997
/ Sites	1996	1	ND (10.00)	
• Rhine/Waal River, 6 sites	1991	23	A = 29.70  (max  200.0)	NICMM 1997
remie, waarrever, o sites	1992-1994	72	A = 22.42  (max  60.00)	Trienini 1997
	1995-1997	31	ND (10.00)	
• Meuse/Maas River, 7 sites	1991	13	A = 25.00  (max  55.00)	NICMM 1997
	1992-1994	19	A = 23.37  (max  60.00)	
	1995-1996	8	A = 11.25  (max  20.00)	
Germany:				
• Elbe, 8 sites	1994	92 (72)	$A = 4.48 \text{ (max } 15.0)^d$	ARE 1996
• Rhine, 8 sites	1985	8 (8)	= 13.5 (max 23.0)	Evers <i>et al.</i> 1988

#### **Environmental Monitoring Levels of Pentachlorophenol in Sediments**

Area	Year of Measurement	Sample Size <sup>a</sup>	Average (A) or Median (M) Concentration (µg/kg) <sup>b</sup>	Reference
			Concentration (µg/kg)	

Total samples (number of detects).
 Unless otherwise indicated, average (mean) values include non-detect samples at the detection limit. Median values are calculated using only those samples with values exceeding the detection limit.
 Not detected (detection limit).
 The frequency of detection (detection limit of 1 μg/kg) was 1 of 12 samples (maximum value = 3.0 μg/kg) at the entrance to the estuary.

#### NORTH SEA MONITORING DATA ON PENTACHLOROPHENOL



While there is not sufficient space on this Figure to fit all of the monitoring data cited in Appendix 4, the data points shown are representative of the sampling locations, time periods and pentachlorophenol concentrations cited in Appendix 4.

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