

Stockholm Convention on Persistent Organic Pollutants

**Persistent Organic Pollutants Review Committee  
(POPRC)**

**DRAFT RISK PROFILE**

**For**

**Pentachlorobenzene**

Draft prepared by:

The ad hoc working group on pentachlorobenzene

**May, 2007**

## Draft Risk Profile for Pentachlorobenzene

### **Note:**

In accordance with the procedure laid down in Article 8 of the Stockholm Convention, this draft was prepared by the Persistent Organic Pollutants Review Committee (POPRC) during its inter-sessional work. Parties and observers to the Stockholm Convention are invited to provide technical and substantive comments on this draft. Comments received will be considered by the ad hoc working group and the revised draft will be made available for the third meeting of the POPRC (19-23 November in Geneva). Please submit your comments to the Secretariat of the Stockholm Convention preferably by e-mail before **July 1, 2007** to:

Secretariat of the Stockholm Convention  
POPs Review Committee  
11-13 chemin des Anémones  
CH-1219, Châtelaine, Geneva, Switzerland  
Fax: (+41 22) 917 80 98  
**E-mail: [ssc@pops.int](mailto:ssc@pops.int)**

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### Ad hoc working group on pentachlorobenzene

Chair: Mr. Dario Sabularse (Philippines)

Drafter: Mr. Martinus Petrus Mattheus Jenssen (The Netherlands)

Members: Mr. Ian Rae (Australia), Mr. Robert Chénier (Canada), Ms. Hala Sultan Al-Easa (Qatar), Mr. Thomas Yormah (Sierra Leone), Ms. Evlin Fabjan (Slovenia), Ms. Leena Ylä-Mononen (designated by the United Kingdom)

Observers: Mr. Lee Eeles (Australia), Mr. Lars Juergensen (Canada), Mr. Timo Seppälä (Finland), Ms. Indrani Chandrasekharan (India), Mr. Dzierzanouski (Poland), Ms. Bettina Hitzfeld (Switzerland), Ms. Sekai Ngarize (United Kingdom), Mr. Chris Blunck (USA), Mr. Alan Rush (USA), Mr. Sylvain Bintein (EC), Mr. Masayoshi Shibatsuji (WHO), Ms. Mariann Lloyd-Smith (IPEN), Mr. Joseph DiGangi (EHF), Mr. Mark Trehwitt (CropLife Int.), Mr. Robert Simon (ICCA/WCC), Mr. Allan Jones (WCC), Mr. Dolf Van Wijik (WCC)

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This draft risk profile is based on the draft prepared by RIVM  
for the European Commission, DG Environment

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## **EXECUTIVE SUMMARY**

The European Community and its Member States being Parties to the Stockholm Convention have proposed pentachlorobenzene (PeCB) to be listed to the Convention. The Persistent Organic Pollutants Review Committee concluded that pentachlorobenzene fulfilled the screening criteria set and decided to establish an ad hoc working group to review the proposal further.

Most of the countries who submitted information to the UNEP secretariat reported no production or use of PeCB (Czech Republic, Germany, Lithuania, Mauritius, Turkey, Canada), which is in agreement with the information in the dossier submitted. Past uses of PeCB are PeCB as a component in PCB products, in dyestuff carriers, as a fungicide and a flame retardant and as a chemical intermediate e.g. for the production of quintozene. Major U.S. and European manufacturers of quintozene have changed their manufacturing process to eliminate this use of PeCB. PeCB is also present at low levels as an impurity in several herbicides, pesticides and fungicides. In the United States, some pesticide manufacturers have changed their manufacturing processes to reduce the concentration of HCB impurities in their products, and these changes may have reduced concentrations of PeCB contaminants also, PeCB is also a low level degradation product of some pesticides. Literature sources show that pentachlorobenzene is of no economic significance. No trade or stockpiles have been reported.

Nowadays pentachlorobenzene enters the environment through various sources of which PeCB as a byproduct of incomplete combustion is the most important. However, there is considerable uncertainty on the release of PeCB by various sources and available data are limited to the United States and Canada. The limited data available makes it difficult to provide a proper global estimate on amounts and trends. Total estimated annual global emissions of PeCBs based on the US-TRI database were 85.000 kg/yr.

PeCB should be considered as persistent given the estimated and experimental half lives in atmosphere, soils, sediments, and water. According to the available data pentachlorobenzene has a high bioaccumulation potential. Log  $K_{ow}$  values vary between 4.88 and 6.12, with recommended values of 5.17-5.18. BCF values range from 1085 - 23000 L/kg for fish, 833 - 4300 L/kg for mollusca, and 577 - 2258 L/kg for crustacea. Due to the fact that biotransformation of PeCB will be insignificant and the substance is very hydrophobic, the compound may also have a high biomagnification potential.

PeCB is moderately toxic to humans and is not classified as a carcinogen. Within the European Union PeCB is classified as a substance which is very toxic to aquatic organisms (LC50 for fish, daphnia or algae  $\leq 1$  mg/L). Limited data are available on terrestrial ecotoxicity and data for toxicity to birds are lacking.

Physical-chemical characteristics, such as water solubility, vapour pressure and Henry's Law Constant, are within the range of the other POPs. PeCB can be photo-oxidized in the atmosphere, largely through reactions with hydroxyl (OH) radicals. However, estimated half-lives of PeCB in air of 45 to 467 days were reported. Considering its physical-chemical characteristics and persistence in air, PeCB has a potential for long range transport through the atmosphere. This is supported by the presence of PeCB in environmental compartments, including biota, from remote regions.

PeCB is spread widely in the environment on a global scale. Levels of PeCB in abiotic and biotic media in remote regions such as the (ant) arctic environment are

available, as well as monitoring data on PeCB in abiotic and biotic media of temperate zones. In general, data from developed countries indicates that concentrations of PeCB in the temperate zones of the world seem to decrease. For the (ant)arctic area, only recent data are available which do not allow to derive a trend.

Based on the available evidence, pentachlorobenzene is likely, as result of its long range environmental transport, to lead to significant adverse human health and/or environmental effects, such that global action is warranted.

## **1 INTRODUCTION**

The European Community and its Member States being Parties to the Stockholm Convention have proposed pentachlorobenzene to be listed in Annex A, B and/or C to the Convention pursuant to paragraph 1 of Article 8 of the Convention. The complete original proposal is contained in document UNEP/POPS/POPRC.2/INF/5. A summary of the proposal prepared by the Secretariat was provided in document UNEP/POPS/POPRC.2/13.

The acceptance of the original proposal for further consideration by the Persistent Organic Pollutants Review Committee implies that the properties of the substance fulfilled the screening criteria set out in Annex D of the Convention. The next step is to prepare a risk profile for the substance as described in Annex E. This draft risk profile has been prepared following the decision of the Committee, at its second meeting in November 2006, to establish an ad hoc working group to review the proposal further in accordance with the provisions of the Convention (Decision POPRC-2/7).

All data in this document are presented according to the International System of Units (SI) and, therefore, many have been recalculated from other units in the data sources. Furthermore, all concentrations are presented based on kg or L (e.g. µg/kg or mL/L).

### **1.1 Chemical Identity of the proposed substance**

#### **1.1.1 Names and registry numbers**

Pentachlorobenzene belongs to the group of chlorobenzenes, which are characterised by a benzene ring in which the hydrogen atoms are substituted by one or more chlorines. The chlorobenzenes are neutral, thermally stable compounds with increasing stability and higher melting and boiling points with increasing chlorine substitution. Pentachlorobenzene has a very low solubility in water (Rossberg et al., 2006).

*IUPAC Name:* benzene, pentachloro-

*CAS Chemical Name:*

*Synonyms:* 1,2,3,4,5-pentachlorobenzene; Pentachlorobenzene; PCB; PeCB; QCB; quintochlorobenzene

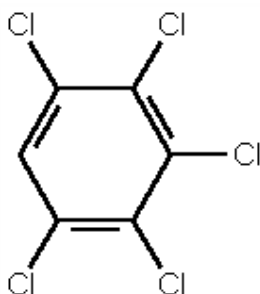
CAS Registry Number: 608-93-5

EINECS Number: 210-172-0

Trade names: -

### 1.1.2 Structure

1,2,3,4,5-Pentachlorobenzene



### 1.1.3 Physical chemical properties

The physical and chemical properties of pentachlorobenzene are listed in Table 1.1. Vapour pressure increases with temperature. Mackay et al (2006) provided a recommended value of 0.11 Pa at 20 °C. Water solubility at 25 °C varied between 0.135 and 3.46 mg/L, whereas the recommended value in various sources was around 0.55 mg/L. The log  $K_{ow}$  values in Mackay et al (2006) varied between 4.88 and 6.12. This source and the PHYSPROP and CHEMFATE databases recommend values of 5.17-5.18 as most reliable.

**Table 1.1 Physical and chemical properties of pentachlorobenzene**

Property	Unit	Value	Reference
Molecular formula		$C_6HCl_5$	
Molecular weight	g/mol	250.34	US NIST 2005, Rossberg et al., 2006
Appearance at normal temperature and pressure		colorless needles white crystalline solid	Rossberg et al., 2006 Government of Canada, 1993
Vapour pressure <sup>1</sup>	Pa	133 (at 98.6 °C) 0.212 (at 25°C) 0.11 (at 20 °C) 0.22 Pa at 25°C (est.)	Stull, 1947 in Mackay et al., 2006 Polednicek et al., 1996 in Mackay et al., 2006 Rohac et al., 1999 in Mackay et al., 2006, recommended Weast, 1972 -1973 in Government of Canada, 1993

<sup>1</sup> Relationship between vapour pressure and temperature provided in Mackay et al., 2006

Water solubility (at 25°C)	mg/L	0.551 mg/L  0.562 mg/L  0.552 mg/L	Yalkowsky et al., 1979 in IUPAC-NIST solubility database recommended value Horvath, 1982 in Mackay et al., 2006 recommended value Horvath & Getzen, 1985 in Mackay et al., 2006 recommended value
Melting point	°C	86  86	Mackay & Shiu, 1981 in Government of Canada, 1993 Weast et al., 1985 in SRC Chemfate database
Boiling point	°C	277  277	SRC PhysProp database Weast et al., 1985 in SRC Chemfate database
Log K <sub>ow</sub>		5.17  5.18  5.17 (exp.)  5.17	Sangster, 1993 in Mackay et al., 2006 recommended value Hansch et al., 1995 in Mackay et al., 2006 recommended value Hansch et al., 1995 in SRC PhysProp database Hansch & Leo, 1985 in SRC Chemfate database, recommended value
Log K <sub>oc</sub>		4.77  4.24 (calculated)  4.51 (measured)	Karickhoff et al., 1979 in WHO-IPCS, 1991 <sup>1)</sup> US EPA superfund (n.d.) US EPA superfund (n.d.)
Henry's Law constant	Pa m <sup>3</sup> /mol	59.0 at 20 °C <sup>2)</sup> (measured range 14.8-50.5 °C) 52.6 at 20 °C  71.9 at 25 °C  71.23 at 25°C (exp.)	Ten Hulscher et al., 1992 in Mackay et al., 2006 Staudinger & Roberts, 1996, 2001 in Mackay et al., 2006 Oliver, 1985 in Mackay et al., 2006 Ten Hulscher et al., 1992 in SRC PhysProp databas

1) WHO-IPCS mentions abusively Karlokoff et al., 1979

2) Mackay et al. (2006) provide a value of 59.0 at 25 °C, but from the data at the end of the chapter on PeCB it appears that this refers to the measured value at 20 °C.

n.d. = no date

## 1.2 Conclusion of the Persistent Organic Pollutants Review Committee on the Annex D information on Pentachlorobenzene

The POP Review Committee applied at its second meeting on 6-10 November 2006 the screening criteria specified in Annex D to the Stockholm Convention, and decided, in accordance with paragraph 4 (a) of Article 8 of the Convention, that it was satisfied that the screening criteria were fulfilled for pentachlorobenzene. The Committee decided furthermore, in accordance with paragraph 6 of Article 8 of the Convention and paragraph 29 of decision SC-1/7 of the Conference of the Parties to the Stockholm Convention, to establish an ad hoc working group to review the proposal further and to prepare a draft risk profile in accordance with Annex E to the Convention. It invited, in accordance with paragraph 4 (a) of Article 8 of the Convention, Parties and observers to submit to the Secretariat the information specified in Annex E of the Convention before 2 February 2007.

## 1.3 Data sources

This Draft Risk Profile for Pentachlorobenzene is mainly based on information from the following review reports:

- Mackay et al. (2006). Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals.
- CHEMFATE Database; Environmental Fate Data Base (EFDB) at Syracuse Research Centre. Available at: <http://www.syrres.com/esc/efdb.htm>
- WHO-IPCS International Programme on Chemical Safety. (1991). Environmental Health Criteria (EHC) 128: Chlorobenzenes other than Hexachlorobenzene. United Nations Environment Programme. International Labour Organisation. World Health Organization. Geneva. Available at: <http://www.inchem.org/documents/ehc/ehc/ehc128.htm>
- Government of Canada. (1993). Pentachlorobenzene. (Priority substances list assessment report). Available at: [http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl1-lspl/pentachlorobenzene/index\\_e.html](http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl1-lspl/pentachlorobenzene/index_e.html)
- Government of Canada (2003). Follow-up Report on Five PSL1 Substances for Which There Was Insufficient Information to Conclude Whether the Substances Constitute a Danger to the Environment 1,2-Dichlorobenzene, 1,4-Dichlorobenzene, Trichlorobenzenes, Tetrachlorobenzenes, Pentachlorobenzene. Available at: [http://www.ec.gc.ca/substances/ese/eng/psap/assessment/PSL1\\_chlorobenzenes\\_followup.pdf](http://www.ec.gc.ca/substances/ese/eng/psap/assessment/PSL1_chlorobenzenes_followup.pdf)
- Environment Canada 2005. Risk management strategy for Pentachlorobenzene (QCB) and tetrachlorobenzenes (TeCBs). Available at: [http://www.ec.gc.ca/Toxics/docs/substances/certToxics/rms/en/CBz\\_RMS\\_E\\_05-01-05.pdf](http://www.ec.gc.ca/Toxics/docs/substances/certToxics/rms/en/CBz_RMS_E_05-01-05.pdf)
- ICCA/WCC, International Council of Chemical Associations/World Chlorine Council (2007). ICCA-WCC Submission for PeCB & All Risk Profiles for the POPs Review Committee of the Stockholm Convention including annexes.

Where the reviews mentioned above have been cited, the text quoted (or quoted with modifications) includes the references cited in the original review. These references

are not shown individually in the reference list. The following parties and observers have answered the request for information specified in Annex E of the Convention: Canada, Czech Republic, Germany, Japan, Lithuania, Mauritius, Switzerland, Turkey, United States of America, International POPs Elimination Network (IPEN), and the International Council of Chemical Associations/World Chlorine Council (ICCA-WCC).

Additional information was retrieved through a search using Current Contents and through a search on the Internet using various public databases. Search terms used were pentachlorobenzene, PeCB, 608-93-5, bioaccumulat\*, bioconc\*, biomagnificat\*, BSAF\*, BCF\*, BMF\*, BAF\*, elimination, uptake, persist\*, degradation, resistance, half-life, toxic\*, release and inventory. The databases used included the United States Environmental Protection Agency Toxics Release Inventory (TRI) Program <http://www.epa.gov/tri/tridata/index.htm#pdr>, the EMEP activity data and emission database of the Convention of long-range transboundary air pollution at <http://webdab.emep.int/>, the European Pollutant and Transfer Register (E-PRTR) at [http://www.bipro.de/\\_prtr/sub/purpose\\_scope.htm](http://www.bipro.de/_prtr/sub/purpose_scope.htm), the Aquire ecotox database of US EPA at <http://www.epa.gov/ecotox/>, the HSDB Hazardous Substances Data Bank of the U.S. National Library of Medicine. Information on pentachlorobenzene. <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/r?dbs+hsdb:@term+@rn+@rel+608-93-5>, the database on biodegradation and bioconcentration of NITE (Japan, National Institute of Technology and Evaluation) at <http://www.safe.nite.go.jp/english/db.html>, the European chemical Substances Information System (ESIS) at <http://ecb.jrc.it/esis/index.php?PGM=ein>, BUA Reports at <http://www.gdch.de/taetigkeiten/bua/berichte.htm> the US-ATSDR <http://www.atsdr.cdc.gov/toxpro2.html#bookmark05> and OECD-SIDS <http://www.inchem.org/pages/sids.html>. No information on PeCB was found in The EMEP and E-PRTR databases and the latter three sources.

#### **1.4 Status of the chemical under international conventions**

Pentachlorobenzene is not included in any international convention. The European Commission has submitted a proposal to include pentachlorobenzene to the Protocol to the 1979 Convention on Long Range Transboundary Air Pollution (LRTAP) on Persistent Organic Pollutants to the Executive Secretariat of the United Nations Economic Commission for Europe in 2006 (European Commission, 2007). The provisions of the Protocol oblige Parties to phase out all production and uses of pentachlorobenzene.

PeCB is identified as a priority substance within the European Water Framework Directive (2000/60/EC). Within the list of these priority substances so-called priority hazardous substances are identified which are of particular concern for the freshwater, coastal and marine environment. These substances will be subject to cessation or phasing out of discharges, emissions and losses within 20 years after adoption of the Directive. The European Commission has proposed to include pentachlorobenzene as a priority hazardous substance. [COM(2006) 397 final]. PeCB is listed on the OSPAR 1998 List of Candidate Substances (OSPAR, 1998).

## **2 SUMMARY INFORMATION RELEVANT FOR THE RISK PROFILE**

### **2.1 Sources**

Production, use and sources of release have been described extensively in the two documents submitted by Canada (Government of Canada, 1993, 2002), the proposed risk management strategy for Pentachlorobenzene by Canada (Environment Canada, 2005) and the document submitted by the ICCA/WCC (2007). Additional information was retrieved from the documents submitted by other Parties and Observers and from the open literature.

#### **2.1.1. Production, trade, stockpiles**

The submission document for PeCB reported that PeCB was not produced anymore within Europe and North America (Van de Plassche et al., 2002). PeCB has not been reported by EU Industry as an HPVC or LPVC (<http://ecb.jrc.it/esis/>). Most of the countries who submitted information to the UNEP secretariat reported no production (Czech Republic, Germany, Lithuania, Mauritius, Turkey, and Canada). WHO-IPCS (1991) reported no manufacturing within the USA in 1985. The USA reported that PeCB is subject to a Toxic Substances Control Act (TSCA) Significant New Use Rule requiring notification to EPA prior to manufacture, import or processing of 10,000 pounds (4,536 kg) or more of PeCB per year per facility for any use. No such notification has been received. No intentional production was mentioned in the document submitted by the ICCA/WCC and according to Ullmann's Encyclopedia of Industrial Chemistry pentachlorobenzene is of no economic significance (Rossberg et al., 2006). No trade or stockpiles have been reported.

#### **2.1.2. Uses**

Canada and the USA reported that there is no current domestic commercial demand for pentachlorobenzene and that PeCB is not used as an end product. Ullmann's Encyclopedia of Industrial Chemistry does not mention any present use of PeCB (Rossberg et al., 2006). However, various past uses or unintentional uses of PeCB are mentioned in the literature:

1. PeCB was a component of a chlorobenzenes mixture used to reduce the viscosity of PCB products employed for heat transfer (Environment Canada, 2005). However, after regulations prohibiting new uses of PCB-containing dielectric fluids were introduced in 1980, the amount of pentachlorobenzene used for this purpose declined considerably in Canada. Based on the results of a survey small amounts of pentachlorobenzene (40 kg during the first 6 months of 1992) were still imported into Canada in dielectric fluids for use in the maintenance of transformers (Government of Canada, 1993). PCBs are still in use in some old electrical equipment in North America and Europe so that there is a small potential for release of PeCB from this source (Environment Canada, 2005).

It can be presumed that some PCBs are also still in use elsewhere in the world and some fraction of them contain PeCB. PCBs are being taken out of service in many countries of the world so that any related PeCB emissions are expected to decrease with time.

2. Formerly, PeCB and TeCB could be found in dyestuff carriers. The applications in dye carriers have been discontinued (Environment Canada, 2005). It is not clear from the Canadian document if PeCB, TeCB or both have been used in dyestuff carriers.

3. PeCB can be found as an impurity in several herbicides, pesticides and fungicides currently in use in Canada (Environment Canada, 2005). The US EPA carried out a study to assess the dietary cancer risk of hexachlorobenzene and pentachlorobenzene as impurities in chlorothalonil, PCNB, picloram, and several other pesticides. Pentachlorobenzene was identified in pentachloronitrobenzene (quintozene), endosulfan, chlorpyrifos-methyl, atrazine, and clopyrilid, but not in simazine, chlorothalonil, picloram and dacthal (US EPA, 1998). Technical grade hexachlorobenzene (HCB) contains about 98 % HCB, 1.8 % pentachlorobenzene and 0.2 % 1,2,4,5-tetrachlorobenzene (WHO-IPCS, 1997). HCB is already listed in annex A and C of the Stockholm convention and it may thus be expected that HCB is of minor importance as a source for PeCB. The present situation for the other pesticides is unknown.

4. The use of PeCB as chemical intermediate is mentioned in WHO-IPCS (1991). So far, only the use as an intermediate in the manufacture of pentachloronitrobenzene (quintozene) has been found in the literature. PeCB is present as an impurity in this fungicide. Quintozene has been commercially produced since the 1930s (US EPA TRI 2001). In 2000 there were at least two producers of quintozene in the EU and several more suppliers. Quintozene was only authorized for use in the UK, Ireland, France, Spain and Greece (RPA, 2000). In 2000 authorisations for plant protection products in the EU containing quintozene were withdrawn (European Commission, 2000). Quintozene is currently used, but not produced, in Canada (Environment Canada, 2005). HSDB mentions one manufacturer in the US citing a reference from 1989. Production in the US in 1979 was at least  $4.54 \times 10^5$  kg (HSDB, 2003). Van de Plassche et al. (2002) report on the production and use of quintozene in various countries and indicated that the use outside the UNECE region is unknown. Van de Plassche et al. (2002) stated: 'Nowadays, quintozene is manufactured using another production process without PeCB. Amvac does not know of any current quintozene producer using PeCB as feedstock. They conclude that it is unlikely that there are any stockpiles of quintozene containing appreciable quantities of PeCB.' Feiler (2001) in ICCA/WCC (2007) reported that quintozene is now being made by chlorination of nitrobenzene instead of using PeCB as an intermediate. The available data suggest a decrease in pentachlorobenzene use for the preparation of quintozene. However, this conclusion is based on data for Europe and North America only.

5. PeCB may have been used in the past as a fungicide and as a flame retardant (Van de Plassche et al., 2002). WHO-IPCS (1991) mentions that PeCB was formerly used in a pesticide to combat oyster drills. No further sources of these applications have been found.

6. Less than 0.1 kg per year of pure pentachlorobenzene was imported into Canada from the United States for use as a laboratory reagent (Government of Canada, 1993). The use as laboratory reagent, based on data applicable to 1995, is also mentioned in Government of Canada (2002). The present situation is unknown.

From the data submitted and data in the literature it is obvious that production and use of PeCB in Europe and North America are negligible. The situation in other parts of the world is less clear.

### 2.1.3. Releases to the environment

The proposed risk management strategy for pentachlorobenzene prepared by Environment Canada in 2005 mentions various routes through which PeCB can be released into the Canadian environment (Environment Canada, 2005). The main sources of release in Canada are given in Table 2.1.

Table 2.1. Estimate of releases of pentachlorobenzene to the environment in Canada in kg/yr (Environment Canada, 2005)

Sources	Releases in kg/yr			
	Air	Water	Soil	Total
Barrel burning of house-hold waste	1.814		20.116	21.93
Wood treatment plants and in service utility poles	2.24		0.1	2.34
Pesticide use			6.2	6.2
Dielectric fluid spill and cleanup	0.004	4.171	1.451	5.63
Municipal solid waste incineration	0.364		2	2.36
Hazardous waste incineration	1.835			1.84
Magnesium production	1.449	0.079		1.53
Solvent use	0.037			0.04
Long-range transport				n.a.
<b>Total</b>				<b>41.9</b>

As potential sources of release are mentioned:

1. Magnesium production (less than 2% of total annual releases)
2. Chlorinated solvents (negligible)
3. Secondary copper and aluminium processing (no data)
4. Chemical manufacturing (unlikely)
5. Iron and steel mills (scarcity of data)
6. Petroleum Refineries (unlikely)
7. Wastewater treatment plants (unlikely)
8. Textile mills (unlikely)
9. Long range transport (amount not known, expected to decrease)

The sources of release and potential sources are described more extensively in Environment Canada (2005).

The total release provided by Environment Canada in the risk management strategy of PeCB (Environment Canada, 2005), 41.8 kg/yr, is a factor of 10 lower than the release of >580 kg/yr provided in the Priority substances list assessment report for pentachlorobenzene (Government of Canada, 1993), submitted by Canada for the drafting of this Risk profile. Main differences can be related to the phasing out of

pentachlorobenzene in dielectric fluids which changed the release from 180 kg/yr to 5.6 kg/yr, PeCB in pesticides, which changed from 17 to 6.2 kg/yr, PeCB release through solvent use, which decreased from 4 to 0.04 kg/yr and long range transport and deposition which accounted for 286 kg/yr in the 1993 report and which was reported as n.a. in 2005. The 2005 document indicates that the amount of 286 kg/yr should be regarded as an overestimation, and that the other emissions are expected to be reduced through a combination of different national and international measures (Environment Canada, 2005). The most important sources in the Canadian risk management report (Environment Canada, 2005), barrel burning of household waste (21,93 kg/yr), municipal solid waste incineration (2.36 kg/yr), hazardous waste incineration (1.84 kg/yr) and magnesium production (1.53 kg/yr), were not identified as sources in 1993.

Data on releases of PeCB in the USA can be found in the U. S. EPA Toxics Release Inventory (TRI). The TRI contain release data for 2000 – 2004, which are summarized in Table 2.2 (US EPA 2007a, <http://www.epa.gov/tri/tridata/index.htm#pdr>).

Pentachlorobenzene was not included in the decision of the European Commission on the implementation of a European Pollutant Emission Register (EPER) (2000/479/EC), but it is in the regulation concerning the establishment of a European Pollutant Release and Transfer Register (E-PRTR) (EC/166/2006). No data on PeCB are available yet.

Table 2.2. Releases inventory for PeCB in the U.S between 2000 and 2004 in kg/year.

year	On-site releases				Off-site releases	Total releases on- and off-site
	Air emissions	Surface water discharges	Underground injection	On-site releases to land	Transfers off-site to disposal	
	kg	kg	kg	kg	kg	kg
2000	74	79	5	1192	161	1512
2001	34	60	0	1069	105	1270
2002	37	61	1	875	391	1365
2003	40	5	0	606	111	763
2004	100	8	0	1006	38	1151

The ICCA/WCC provided a document with an estimation of the annual global emissions of PeCB based on the U. S. Toxics Release Inventory (TRI) (ICCA/WCC, 2007). A total of 20 industrial facilities are listed as emitting or transferring 2533 pounds (1151 kg) of PeCB in 2004. The industries represented are chemical, waste treatment, and coal burning electric power. Total reported air emissions were 220 pounds (100 kg) and water emissions of 17 pounds (7.8 kg). In industrial chlorination reactions it is possible to produce PeCB as a byproduct and it probably accounts for some of the emissions reported in the TRI. PeCB formation has been observed during combustion of PVC, a common component of municipal solid waste (Kim et al., 2004; Aracil et al., 2005; Muller et al., 1997). There are other processes which produce a variety of chlorinated aromatics that may contribute to PeCB even if PeCB has not been explicitly detected and reported yet. TRI includes only industrial facilities handling relatively large amounts of chemicals so that additional emissions are expected.

Total estimated annual global emissions of PeCBs by ICCA/WCC (2007) were 85.000 kg/yr, about 2000 times the amount estimated for Canada and 850 times the total release of the United States. Most of the emission sources are similar with those provided in the Canadian risk management document (Environment Canada, 2005), but some are different. Hazardous waste incineration and wood treatment plants are lacking in the ICCA/WCC study, whereas combustion of coal and combustion of biomass, which amounts half of the total global emissions, are lacking in the Canadian study. Although chemical manufacturing was thought to be unlikely as a source, the highest reported chlorobenzene concentrations in Canadian sediment have been observed near industrial sites (Government of Canada, 2003).

In conclusion, pentachlorobenzene can enter the environment through various sources of which PeCB as a byproduct of incomplete combustion is the most important. Nearly all fuels contain some chlorine, especially biomass and waste. In industrial chlorination reactions it is possible that PeCB is produced as a byproduct and it probably accounts for some of the emissions reported. For a number of potential sources, such as copper and aluminium processing plants and steel mills no or limited data are available. From the data provided in the various documents one may expect a decrease of releases through past intentional use, due to phasing out of PeCB. In the case of unintentional releases a decrease can be expected in those cases where measures were taken to reduce the releases of other compounds or materials. The global estimate should be considered taking into account these uncertainties and the variation in industrial and waste handling processes among the various countries.

## **2.2 Environmental fate**

### **2.2.1 Persistence**

Pentachlorobenzene (PeCB) can be photo-oxidized in the atmosphere, largely through reactions with hydroxyl (OH) radicals (CEPA, 1993). There are no experimental data on atmospheric degradation, but the estimated half-life of PeCB is 45 to 467 days. For PeCB, the calculated half-life in air based on reaction with OH-radicals is 277 days (EPISUITE, US EPA, 2007b). Vulykh et al. (2005) estimate a half-life in air of 65 days based on modelling data. This estimate is the result of degradation as well as dry and wet deposition and gaseous exchange with various surfaces. The atmospheric half-life of PeCB due to the degradation process only is estimated to be 155 days.

In the OECD TG 301C test PeCB was non-biodegradable (NITE, 2007). Photodegradation of PeCB is fast in surface water under sunlight irradiation: 41% loss after 24 hours (HSDB, February 2000). The half-life of PeCB in surface water was estimated to range from 194 to 1250 days, the estimated half-life for the anaerobic biodegradation in deeper water ranged from 776 to 1380 days (CEPA, 1993).

Wang et al. (1994) studied PeCB in spiked (4.5 µg/kg) and sewage sludge-amended soil (3 µg/kg) at 20-30 °C. Half of the dosage of PeCB is rapid loss by volatilization, followed by degradation with half-lives of 187 days (spiked soil; 1.4 o.m.) to 1550 days (amended soil, 4.5% o.m.). Formation of bound residues is a relatively minor

route of dissipation on soil. Scheunert et al. (1985) recovered 1% of a 2 mg/kg dosage as bound residue after 126 days. Under aerobic conditions PeCB is persistent in soil. Beck and Hansen (1974) found disappearance half-lives based on duplicate samples, of 194 – 345 days in an aerobic loamy sand soil (1.9% o.m.); 18-20°C) treated at 7 mg/kg. Standard deviations were 20 to 25%. The 95% confidence limits are thus 112-726 and 289-3176 days. Since the values were based on duplicates, the total range of 112-3176 days represents the experimental results. Soils were kept in 10L buckets covered with two plastic sheets. During the experiment that lasted 600 days, water losses were compensated; apparently the total water content of the soil evaporated from the soils every 100 days (Bro-Rasmussen et al., 1970). The reported disappearance values are based on  $\log(2)/k$ ; instead of  $\ln(2)/k$ . Correct half lives thus span the range of 260 – 7300 days. The contribution of volatilization of PeCB to these half lives is unknown.

Susarla et al. (1997) investigated the degradation of HCB in a methanogenic slurry of sandy sediment (<1% o.m.) with lake water (1:3 v/v), spiked at 1.14 mg/L. After 75% of the HCB had degraded after 150 days, the degradation of the primary metabolite PeCB followed first order kinetics with a half life of approximately 50 days at 25 °C. Masunaga et al. (1996) investigated the degradation of PeCB in sulfidogenic estuarine sediments that had been pre-exposed to various chemicals from local industries. Sediment slurries contained 272 g/kg solids; of which 12% can be lost by ignition, and were kept at 25°C. PeCB half-life was 18 days. In autoclaved samples the half-life was 990 days.

In sediment cores of Ketelmeer in The Netherlands, that had been selectively enriched with HCB to get a dechlorinating anaerobic community, PeCB is not persistent: the adapted anaerobic microflora gives half-lives of about 6 days at 25 °C when spiked at 50 µg/L (Beurskens et al., 1994). A mixture of clay loam soil (5.38% o.m.) and a sterile medium (50 g soil and 70 ml medium) was incubated anaerobically at room temperature after inoculation with a 10% slurry of an adapted microbial culture. The soil was spiked with 14.2 mg/L HCB, 25 mg/L PeCB, and 254.1 mg/L 1,2,4-TCB. Concentrations PeCB decreased with a half-life of approximately 23 days. Chlorobenzene accumulated as the major metabolite after 80 and 142 days to 1 mmol/L (Ramanand et al., 1993). So far, only one bacterial strain which reductively dechlorinates chlorobenzenes has been isolated (Adrian and Görisch, 2002).

Comparison of PeCB concentrations in Ketelmeer sediment (The Netherlands) sampled and measured in 1972 to concentrations in samples taken in 1988 from sediment layers deposited around 1970, showed a small but statistically significant decline of 35%. HCB had decreased by 80%. Lower chlorinated benzenes like di and tetrachlorinated benzenes had increased up to 80% (Beurskens et al., 1993). Lake Ketelmeer sediment contains 9-13% o.m. (Aarnoutse et al., 1996; Cornelissen and Gustafsson, 2004). In a UK soil (Woburn) that had received 25 separate sewage sludge applications in 20 years time (until 1961), approximately 21% of the added PeCB was still in the soil 30 years after application had stopped (Wang et al., 1995). This soil received about 25% of its dry weight in sludge. Assuming that sludge contained 80% organic matter and a 2% organic matter breakdown per year, the mean o.m. content was 15%. Input of HCB during these years was about 4 times higher than the PeCB input; and HCB residues also declined to 22% in these 30 years.

Experimental data on degradation of PeCB in water are lacking. PeCB is expected to dissipate from the water phase to the sediment or into the air. PeCB is persistent in

soils and sediments under aerobic conditions. In anaerobic sediment-water slurries PeCB is considered persistent, except at temperatures above 10°C in combination with low organic matter contents. Higher organic matter contents seem to drastically increase the persistency. Actual field measurements of PeCB may overestimate persistency as a result of formation of PeCB from HCB. The true field half life of PeCB is estimated around 6 years in organic soil and sediment in the temperate zone.

PeCB should be considered as persistent given the magnitude of estimated and experimental half-lives in atmosphere, soils, sediments, and water. Persistence in the environment depends on the rate of photo-oxidation, the presence of oxygen and organic matter.

## 2.2.2 Bioaccumulation

Pentachlorobenzene is highly hydrophobic. Mackay et al. (2006) report log  $K_{ow}$  values between 4.88 and 6.12, with recommended values of 5.17-5.18. Therefore, it can be assumed that the compound has a high bioaccumulation potential. This is confirmed by the data shown in Table 2.3. In this table, BCFs are summarized which were evaluated and which were considered reliable according to the Klimisch criteria (Klimisch, 1997).

The results in Table 2.3 show that BCFs range from 1085 - 23000 L/kg for fish; 833 – 4300 L/kg for mollusca, and 577 – 2258 L/kg for crustacea. It should be noted that for the lowest BCF data for fish it is not explicitly clear if exposure concentrations have been measured (Schuler et al., 2007). If these BCFs are based on nominal instead of measured exposure concentrations, then they are probably lower than the ‘real’ BCFs based on measured concentrations.

Table 2.3. BCF values for pentachlorobenzene

Species	Exp. time	Exp. concn. [mg/L]	BCF [L/kg <sub>ww</sub> ]	Reference
<b>Algae</b>				
<i>Chlorella fusca</i>	24h	0.05	4000	Geyer et al., 1984
<b>Macrophytes</b>				
<i>Myriophyllum spicatum</i>	25d	0.0059	1375	Gobas et al., 1991
<b>Crustacea</b>				
<i>Hyalella azteca</i>	28d	0.0048	1913	Landrum et al., 2004
<i>Hyalella azteca</i>	28d	0.009	1452	Landrum et al., 2004
<i>Hyalella azteca</i>	28d	0.02	1874	Landrum et al., 2004
<i>Hyalella azteca</i>	28d	0.03	2164	Landrum et al., 2004
<i>Hyalella azteca</i>	28d	0.05	2258	Landrum et al., 2004
<i>Hyalella azteca</i>	28d	0.08	1139	Landrum et al., 2004
<i>Hyalella azteca</i>	28d	0.105	2143	Landrum et al., 2004
<i>Hyalella azteca</i>	28d	0.118	871	Landrum et al., 2004
<i>Hyalella azteca</i>	28d	0.14	666	Landrum et al., 2004
<i>Hyalella azteca</i>	28d	0.14	780	Landrum et al., 2004
<i>Hyalella azteca</i>	28d	0.2	577	Landrum et al., 2004
<i>Portunus pelagicus</i>	24h	0.025; 0.05	678	Mortimer and Connell, 1993
<b>Molluscs</b>				
<i>Lymnaea stagnalis</i>	10d	0.012	833	Legierse et al., 1998

Species	Exp. time	Exp. concn. [mg/L]	BCF [L/kg <sub>ww</sub> ]	Reference
<i>Lymnaea stagnalis</i>	10d	0.008	1563	Legierse et al., 1998
<i>Mytilus edulis</i>	21d	0.001	4300	Renberg et al., 1985
<b>Fish</b>				
<i>Cyprinus carpio</i>	56d	0.0003	5656	Yakata et al., 2006
<i>Gambusia affinis</i>	96h	0.0157; 0.0062; 0.0033	4000	Chaisuksant et al., 1997
<i>Lepomis macrochirus</i>	48h		5100	Banerjee et al., 1984
<i>Lepomis macrochirus</i>	28d	0.0052	3400	Barrows et al., 1980
<i>Oncorhynchus mykiss</i>	48h		7100	Banerjee et al., 1984
<i>Oncorhynchus mykiss</i>	48h	0.0006	4000	Banerjee et al., 1984
<i>Oncorhynchus mykiss</i>	48h	0.0076	4300	Banerjee et al., 1984
<i>Oncorhynchus mykiss</i>	48h	0.0328	6900	Banerjee et al., 1984
<i>Oncorhynchus mykiss</i>	48h	0.0708	5800	Banerjee et al., 1984
<i>Oncorhynchus mykiss</i>	48h	0.106	5500	Banerjee et al., 1984
<i>Oncorhynchus mykiss</i>	119d	3E-07	14000	Oliver and Niimi, 1983
<i>Oncorhynchus mykiss</i>	105d	9E-06	23000	Oliver and Niimi, 1983
<i>Pimephales promelas</i>	31d	0.028	9600	Carlson and Kosian, 1987
<i>Pimephales promelas</i>	31d	0.055	6900	Carlson and Kosian, 1987
<i>Pimephales promelas</i>	10d	0.1	1582	Schuler et al., 2007
<i>Pimephales promelas</i>	10d	0.15	1346	Schuler et al., 2007
<i>Pimephales promelas</i>	10d	0.2	1300	Schuler et al., 2007
<i>Pimephales promelas</i>	10d	0.25	1773	Schuler et al., 2007
<i>Pimephales promelas</i>	10d	0.3	1085	Schuler et al., 2007
<i>Poecilia reticulata</i>	5d	0.1 x the 96h LC50, which is probably ±0.54 µmol/L	4700	Van Hoogen and Opperhuizen, 1988
<i>Poecilia reticulata</i>	48h		7300	Banerjee et al., 1984

In conclusion, these values show that pentachlorobenzene can be considered to have a high bioaccumulation potential. Due to the high logK<sub>ow</sub> and the fact that biotransformation may be insignificant (Schuler et al., 2006, 2007), the compound may also have a biomagnification potential. However, data on the biomagnification of pentachlorobenzene are lacking.

### 2.2.3 Potential for Long range environmental transport

The potential for long-range environmental transport can be estimated from monitoring data in remote regions, through physical-chemical properties of the molecule which are promoting such transport and/or through model results. The most well known mechanism of long-range transport is atmospheric transport of substances in the vapour phase. A prerequisite for long-range atmospheric transport is its persistence to degradation.

Overall persistence and long-range transport potential were estimated for five new POP candidates (including PeCB) with the OECD Pov & LRTP Screening Tool using the input properties in the POPRC proposal documents (Wegmann et al, 2007). The tool does not provide absolute levels in the environment, but facilitates comparison

with earlier identified POP substances. The authors conclude that, although there are considerable uncertainties in the chemical characteristics of the five chemicals investigated, the POP candidates (including PeCB) have Pov and LRTP properties similar to those of several earlier identified POPs.

There is also evidence based on calculations of the transport distance of PeCB through the atmosphere. Mantseva et al. (2004) developed a multi-compartment transport model for the evaluation of long-range atmospheric transport and deposition of POPs. Based on this model assessment a transport distance in Europe of over 8 000 km is calculated for PeCB. The model is described in detail by Vulykh et al. (2005) who assessed a transport distance of 8 256 km. Based on measured concentrations in air samples of North America an empirical estimation of 13 338 km was made for the long range transport of PeCB through air (Shen et al., 2005). This distance is larger than that of the other organochlorine pesticides that were part of this study including the currently listed POPs dieldrin, DDT and heptachlor.

Monitoring data also indicate that PeCB is subject to long range transport. PeCB was detected in air and precipitation at various locations in the world, many of those far from its sources.

In a survey of ambient air at Windsor and Walpole Island, Ontario, mean concentrations in samples taken between August 1988 and October 1989 were 0.12 ng/m<sup>3</sup> in Windsor (detected in 31 of 32 samples) and 0.07 ng/m<sup>3</sup> for Walpole Island (detected in 27 of 30 samples), respectively. Maximum concentrations at the 2 sites were 0.28 and 0.22 ng/m<sup>3</sup> at Windsor and Walpole Island, respectively (Government of Canada, 1993). These concentrations are in the same range, notwithstanding the fact that Windsor is located 6 km from a municipal waste incinerator plant in Detroit, Michigan, while Walpole Island is a rural location located 55 km from the same plant. According to the Integrated Atmospheric Deposition Network (IADN), the average atmospheric concentration of PeCB measured above the North American Great Lakes in 2000 is about 0.072 ng/m<sup>3</sup> (ICCA/WCC 2007 citing Buehler et al., 2004).

In all air samples collected in 2000-2001 at the 40 sampling stations in North America (including 5 arctic stations), PeCB was detected. The measured concentrations were relatively constant across the continent, averaging 0.045 ng/m<sup>3</sup> with a range of 0.017 to 0.136 ng/m<sup>3</sup> (Shen et al., 2005). According to the authors, the small spatial variability across the Northern Hemisphere indicates that PeCB has a very long atmospheric residence time, which allows it to become widely distributed in the global hemisphere.

At the European arctic locations Bear Island, Lillestroem and Spitzbergen PeCB concentrations in air collected in the period 1980/1981 ranged from 0.0033 to 0.078 ng/m<sup>3</sup> (Vulykh, 2005 citing Oeme and Manø, 1984). At the arctic station Alert (Northwest Territories, Canada) PeCB concentrations in air collected between February and April 1988 ranged from 0.0031 to 0.135 ng/m<sup>3</sup> (Government of Canada, 1993).

The presence of PeCB has been reported in several abiotic (air, rainwater, water, sediment and soil) and biotic (fishes, birds, mammals) matrices at remote regions including the arctic region and Antarctica. These are described in detail in the section Exposure.

In conclusion, modeling, monitoring data of PeCB in air, as well as PeCB's chemical properties indicate that this substance has a considerable potential for long range environmental transport. The presence of PeCB in matrices from remote regions,

some that can only have received PeCB after transport via air, supports the conclusion that PeCB is subject to long range transport.

## 2.3 Exposure

PeCB is spread widely in the global environment. The first two sections will focus on the levels of PeCB in abiotic and biotic media in remote regions such as the (ant)arctic environment. The third section will focus on monitoring data on PeCB in abiotic and biotic media of temperate zones, as well as observed trends. The last section discusses human exposure.

### 2.3.1 Levels in abiotic environmental matrices of remote regions

Atmospheric concentrations of PeCB have been measured at various locations around the world. Concentrations in air collected at Alert (Northwest Territories, Canada) ranged from 0.0031 to 0.135 ng/m<sup>3</sup> (Government of Canada, 1993). PeCB was also detected in all air samples collected in 2000-2001 at the 40 sampling stations in North America (including 5 arctic stations). The measured concentrations were relatively constant across the continent, averaging 0.045 ng/m<sup>3</sup> with a range of 0.017 to 0.136 ng/m<sup>3</sup> (Shen et al., 2005). Shen et al., 2005, also observed that atmospheric levels of organochlorine compounds including PeCB increased with increasing elevation in the Canadian Rocky Mountains. This proposed cold-trapping of PeCB is also reflected by increasing concentrations of PeCB in mosses in the Andean mountains and the occurrence of PeCB in the arctic and Antarctic regions in several biotic and abiotic matrices.

A study of the influence of emission sources on atmospheric PeCB concentrations in Germany showed that concentrations were higher at industrial or urban locations (ranging from 0.057 to 0.286 ng/m<sup>3</sup>) than at a rural reference site (0.031 ng/m<sup>3</sup>) (ICCA/WCC 2007 citing Wenzel et al., 2006). Concentrations at the rural site are comparable to the average atmospheric concentration measured by the Integrated Atmospheric Deposition Network (IADN) above the North American Great Lakes in 2000, i.e., about 0.072 ng/m<sup>3</sup> (ICCA/WCC 2007 citing Buehler et al., 2004)

Samples of rain collected in Canada from 1987 to 1991 on average contained 0.02 ng/L PeCB, with a range of <0.01 to 0.09 ng/L (Government of Canada, 1993 citing Muir, 1993 and Strachan, 1993). A study from the river Ob region in the Russian arctic reported traces of PeCB in snow and ice (Melnikov et al., 2003). This was not further quantified.

PeCB was found in all water samples collected during a study of the distribution of chlorinated organics in the North Pacific Ocean, the Bering and Chukchi streets (ICCA/WCC 2007 citing Strachan et al., 2001). Concentrations of PeCB in the dissolved phase averaged 0.016 ng/L, while suspended solids represented only a small fraction of the total amount of PeCB. Bottom sediment samples taken from harbours in northern Norway and the Kola Peninsula in the arctic contained PeCB in concentrations ranging from 2 to 5 µg/kg dry weight. PeCB concentrations in four

Alaskan arctic lakes sampled from 1991 to 1993 averaged  $0.10 \pm 0.10$   $\mu\text{g}/\text{kg}$  dry weight (ICCA/WCC, 2007 citing Allen-Gil et al., 1997). Concentrations in soil samples from the coastal areas of Victoria Land (Antarctica) varied between 0.4 and 1.3  $\mu\text{g}/\text{kg}$  dry weight (Borghini et al., 2005). In these soil samples PeCB was the dominant organic compound. Muir et al. (1995 as cited by ICCA/WCC, 2007) reported PeCB in sediment of a series of remote lakes in northern Canada. Sediment surface layer concentrations (representing a period of time estimated between 1979-1988) of PeCB in these northern lake ranged from less than 0.01 to 0.73  $\mu\text{g}/\text{kg}$  sediment.

### 2.3.2. Levels in biota of remote regions

Contamination of the environment and biota in remote regions can be a threat to vulnerable species and ecosystems. PeCB is detected in mosses, fish, penguin eggs, seals and predatory mammals in the arctic and antarctic regions.

PeCB concentrations in mosses from coastal areas of Victoria Land (Antarctica) varied between 1 and 2.4  $\mu\text{g}/\text{kg}$  dry weight (Borghini et al., 2005). The mosses do not have a root system and their supply is largely dependent on atmospheric deposition. Also Antarctic soil has received PeCB through contact with the atmosphere. The measured PeCB concentrations in both mosses and soils were higher than those of the currently listed POPs HCB and DDT that were also included in this study. PeCB concentrations in mosses growing in the Andean Mountains at elevations between 700-4500 m ranged from 0.2 – 2.4  $\mu\text{g}/\text{kg}$  dw (Grimalt et al., 2004). This study shows that PeCB is likely subject to cold-trapping. An inverse relationship was established with higher PeCB concentrations at lower temperatures. A similar relationship was established for mountain soils in Tenerife (Ribes et al., 2002).

Concentrations ( $\mu\text{g}/\text{kg}$  wet weight) of PeCB in fish from four Alaskan lakes averaged at  $1.42 \pm 1.82$  in grayling liver,  $0.06 \pm 0.08$  in grayling muscle,  $0.48 \pm 0.35$  in lake trout liver and  $1.21 \pm 3.66$  in lake trout muscle (ICCA/WCC, 2007 citing Allen-Gil et al., 1997). Navaga fish from the White Sea in Northwestern Russia contained 5.06  $\mu\text{g}/\text{kg}$  wet weight PeCB (ICCA/WCC, 2007 citing Muir et al., 2003). Fish liver samples from near Adak Island (Alaska) contained 0.8 and 1.4  $\mu\text{g}/\text{kg}$  of PeCB in cod and 1.4  $\mu\text{g}/\text{kg}$  of PeCB in halibut (ICCA/WCC, 2007 citing Arend et al., 2001). Furthermore PeCB has been found in other arctic biota, such as krill (0.05  $\mu\text{g}/\text{kg}$  ww), emerald rock cod muscle (0.08  $\mu\text{g}/\text{kg}$  ww), emerald rock cod whole body (0.09  $\mu\text{g}/\text{kg}$  ww) and Greenland arctic char (0.07  $\mu\text{g}/\text{kg}$  ww which is equivalent to 3.9  $\mu\text{g}/\text{kg}$  lipid weight) (Vorkamp et al., 2004; Corsolini et al., 2006).

In Greenland PeCB was observed at levels of 23  $\mu\text{g}/\text{kg}$  lipid weight in ptarmigan liver (1.5  $\mu\text{g}/\text{kg}$  wet weight) and 8  $\mu\text{g}/\text{kg}$  lipid weight in kittiwake muscle (1.1  $\mu\text{g}/\text{kg}$  wet weight) (Vorkamp et al., 2004). Adelie penguin eggs (Antarctic) contained 0.68  $\mu\text{g}/\text{kg}$  ww PeCB (Corsolini et al., 2006).

Inuit hunter collected tissue samples of ringed seals from the east and west sides of the Northwater Polnya between Canada and Greenland during the spring of 1998 (ICCA/WCC, 2007 citing Fisk et al., 2002). The concentration (wet weight) of PeCB in these sampled ranged from  $7.3 \pm 1.9$   $\mu\text{g}/\text{kg}$  in male ringed seals to  $8.4 \pm 1.1$   $\mu\text{g}/\text{kg}$  in females from the west side. Seals from the east side (Quebec) contained  $5.0 \pm 0.5$

$\mu\text{g}/\text{kg}$  (males) and  $7.0 \pm 1.5 \mu\text{g}/\text{kg}$  (females). Seals from the White Sea in Northwestern Russia collected in the period 1992-1998 contained PeCB at concentrations ranging from 0.9 (bearded seal) to  $12.0 \mu\text{g}/\text{kg}$  lipid weight (harp seal) in their blubber (ICCA/WCC, 2007 citing Muir et al., 2003). The mean concentration ( $\pm$  standard deviation of the 10 samples) of PeCB in 1992 was  $11 \pm 2.0 \text{ ng}/\text{g}$  lipid weight whereas the concentration of PeCB in 1998 was  $5.0 \pm 1.8 \text{ ng}/\text{g}$  lipid weight. PeCB concentrations in bowhead whales collected between 1994 and 1998 averaged at  $0.3 \pm 0.1$  and  $0.8 \pm 0.1 \mu\text{g}/\text{kg}$  wet weight in liver and blubber, respectively (ICCA/WCC, 2007 citing Hoekstra et al., 2002). St. Lawrence Bay (Canada) Beluga Whale blubber was found to contain 24.5 (1.56 – 1510)  $\mu\text{g}/\text{kg}$  (lipid weight) PeCB for females and 144.5 (1.5 - 1500)  $\mu\text{g}/\text{kg}$  for males (ICCA/WCC, 2007 citing Hobbs et al., 2003). In Greenland, blubber of musk ox (captured between 1998 and 2001) was reported to contain  $0.32 \mu\text{g}/\text{kg}$  lipid weight PeCB (equivalent to  $0.29 \mu\text{g}/\text{kg}$  ww) (Vorkamp et al., 2004).

PeCB has also been detected in polar bears. The compound was present in all 15 fat and plasma samples taken from polar bears from the arctic Svalbard islands (Gabrielsen et al., 2004) at an average concentration of 7.9 and a maximum of  $13.9 \mu\text{g}/\text{kg}$  (wet weight). Similar concentrations are observed in polar bears from Alaska, Canada and East-Greenland, according to the authors. Concentrations and body burdens of chlorobenzenes (including PeCB) in polar bears of different ages have been studied before and after their seasonal fasts (ICCA/WCC, 2007 citing Polischuk et al., 2002). The authors conclude that no PeCB is metabolized or excreted during the fast, leading to increasing concentrations of the compound in fat tissue. Amounts of PeCB in cubs is reported to be greater than in adults due to the fact that nursing bear cubs receive an increased amount of PeCB.

The accumulation of PeCB has also been measured in the arctic fox during 1999-2001 (ICCA/WCC 2007, citing Hoekstra et al., 2003). The animals were collected some distance from human habitation to minimize effects of garbage scavenging. About 20 animals were collected at each site. PeCB concentrations ( $\mu\text{g}/\text{kg}$ ) found in arctic foxes were  $0.61 \pm 0.12$  in muscle (Arivat),  $0.29 \pm 0.06$  in muscle (Holman),  $0.57 \pm 0.11$  in liver (Holman),  $0.55 \pm 0.20$  in muscle (Barrow) and  $0.73 \pm 0.17$  in liver (Barrow).

King et al (2003) studied the chlorobenzenes spilled after an accident in the Gulf of St Lawrence. There was a rapid decline in tri- to peCB concentrations in snow crabs from sampling location 1 [near the spill] between 1996 and 1998. From 1998 to 2000 the chlorobenzenes concentrations in snow crabs persisted at low levels. In 1996, chlorobenzenes concentrations at locations 2 to 11 were much lower than at location 1, but showed no consistent decrease with time.

### **2.3.3. Levels at temperate regions including trends**

A large quantity of monitoring data exists on PeCB detected in abiotic matrices as well as in biota in temperate zones, mainly originating from developed countries. In general, concentrations of PeCB in the temperate zones of the world seem to decrease. This pattern is representative for that of most POPs. For the (ant)arctic area, only recent data are available which do not allow to derive a trend.

A clear trend of the presence of PeCB in the environment can be derived from its presence in sediment cores. Sediment cores from the industrially impacted area from Lake Ontario near the mouth of the Niagara River (Canada) show an increase in PeCB concentration from early 1900 until the period 1960-1970 (peak concentration of over 100 µg/kg) after which concentrations declined to about 10% of the peak concentration by 1980 (ICCA/WCC, 2007 citing Durham and Oliver, 1983 and NYDEC, 1998). Also PeCB concentrations in the Niagara river water dropped from 0.351 to 0.093 ng/L during the period 1987-1997 (ICCA/WCC 2007, citing Williams et al., 2000). However, data in the mussel watch programme for the Niagara river do not show a decrease in PeCB concentrations between 1997 and 2000 on several locations (Ministry of the Environment Ontario, 1999, 2003 ). Concentrations of PeCB in sediment of the Ketelmeer in The Netherlands dropped by 37% in the period 1972-1988 (Beurskens et al., 1993). PeCB concentrations in Herring gull eggs from Muggs Island / Leslie spit (Canada) have dropped from 50 µg/kg in 1970 to non-detected at 1 µg/kg in the mid 1990s (ICCA/WCC 2007, citing Bishop et al., 1992; Petit et al., 1994; Pekarik et al., 1998; Jermyn-Gee et al., 2005; Havelka, 2006). Calambokis et al (1999) studied persistent pollutants in Harbor seals (*Phoca vitulina*) in Puget harbor(US) during the period 1984-1997. They concluded that total TEQ showed a near significant decline by year (p=0.07) and that other pesticides also showed general declining trends. Only for HCB, total chlorobenzenes, and chlordanes was the decline statistically significant.

Because concentrations of PeCB have decreased, only recent data (last 15 years) are summarized in Table 2.5 for abiotic and Table 2.6 for biota matrices.

Table 2.5 Concentrations of pentachlorobenzene in abiotic matrices from temperate regions. Data of the last 15 years.

Year	Location	Compartment	Concentration	Reference
2004	Sweden	Air	0.033 ng/m <sup>3</sup>	Kaj and Dusan, 2004
2004	Sweden	Atmospheric deposition	0.16 ng/m <sup>2</sup> .day	Kaj and Dusan, 2004
1997-1998	Lake Malawi, Africa	Precipitation	0.01 ± 0.014 ng/L	Karlsson et al., 2000*
2002	Sweden	Sediment, lakes	<6 µg/kg dry weight	Sternbeck et al., 2003
2002	Sweden	Sediment, C. Stockholm	<4 µg/kg dry weight	Sternbeck et al., 2003
1996-1997	Niagara river, US	Water	0.093 ng/L	Williams et al., 2000*
2002	Danube, Central Europe	Sediment	0.0001 – 3.5 mg/kg	Slobodník, & Dogterom, 2003
1998	Yangtse river, China	Water; sediment	0.4 ng/l; 3 µg/kg	Jiang et al., 2000*
?	Elbe river, Germany	Sediment	<1 - 71 µg/kg	Witter et al., 1998*
1993-1994	Spree river; Havel river, Germany	Sediment	<10 - 17; <10 - 76 µg/kg	Schwarzbauer et al., 2001*
1999-2001	Lippe river, Germany	Sediment	1 - 6 µg/kg	Kronimus et al., 2004*
2003	Ebro river, Spain	Sediment	1.17 µg/kg	Lacorte et al., 2006*
2004	Sweden	Sediment	1 µg/kg	Kaj and Dusan, 2004
?	Mulde reservoir, Germany	Sediment	0.4 ug/kg	Zoumis et al., 2001*
1996	Taiwan	Sediment	Up to 15.7 µg/kg	Lee et al., 2000*

?	Kishon river, Israel	Sediment	0.01- 0.06 µg/kg	Oren et al., 2006*
1997	Masan bay, Korea	Sediment	Up to 0.28 µg/kg	Hong et al., 2003*

\*Data cited by ICCA/WCC (2007)

? = Year of sampling unknown.

Table 2.6 concentrations of pentachlorobenzene in biotic matrices from temperate regions. Data of the last 15 years.

Year	Location	Species	Tissue	Concentration (ng/kg)	Reference
1996	The Netherlands	Flounder (Platichthys flesus)	Liver	Reference site: 3 (0.64); polluted site: 1100000 (280000), lipid weight (wet weight)	De Boer et al., 2001
2002	Sweden	Herring (Clupea harengus); Perch (Perca fluviatilis)	Muscle	2.2; 16 (lipid weight)	Kaj and Dusan, 2004
1993	Detroit River, US	Brown bullhead fish (Ameiurus nebulosus)	Whole body	13000 (Amherstburg Channel); 29400 (Trenton Channel); 16100 (Peche Island), wet weight	Leadley et al., 1998*
1994	Rhine; Meuse; Hollandsch Diep, The Netherlands	Eel (Anguilla anguilla)	Whole body	15000; 2900; 7700 (wet weight)	Hendriks et al., 1998*
2003	The Netherlands	Eel (Anguilla anguilla); Pike perch (Sander lucioperca)	Whole body	1 -10 (wet weight)	Van Leeuwen et al., 2004
2006	Ebro river, Spain	Fish	Whole body	1100 (320 - 3310)	Lacorte et al., 2006*
1994	Rhine; Meuse; Ysselmeer, The Netherlands	Zebra Mussel (Dreissena polymorpha)	Whole body	490; 270; 500 (wet weight)	Hendriks et al., 1998*

\*Data cited by ICCA/WCC (2007)

During a survey within the Danube Regional Project for the European Water Framework Directive pentachlorobenzene was detected in almost all sediment samples at concentration levels of 0.0001 – 3.5 mg/kg and in most of the suspended solid samples at concentration levels of 0.001 – 0.028 mg/kg (Slobodnik and Dogterom, 2003).

The ATSDR database from the US Government contains 41 records of polluted sites with pentachlorobenzene. Maximum concentrations of pentachlorobenzenes at these sites vary between 147 and 5100 mg/kg in sediments and between 0.43 and 2040 mg/kg in soil. Concentrations in fish vary between 0.00019 and 2.4 µg/g. The data does not mention if these concentrations are based on wet or dry weight basis (ATSDR, 2007).

### 2.3.4. Human exposure

PeCB has been detected in breast milk and found to accumulate in human placenta (Shen et al., 2007). The mean concentration of PeCB in the breast milk of Canadian women taken 3 to 4 weeks after parturition was < 1 µg/kg (trace) with a maximum value of 1 µg/kg. In this survey, the compound was detected in 97% of the 210 samples analyzed (detection limit and sampling period unspecified) (Government of Canada, 1993 citing Mes *et al.*, 1986). In the breast milk of women of Canadian

indigenous population, "trace" ( $< 1 \mu\text{g}/\text{kg}$ ) amounts of PeCB were observed in 17% of the 18 samples (detection limit not specified) (Government of Canada, 1993 citing Davies and Mes, 1987). Two other studies investigating PeCB in human milk reported concentrations in the range of 1 to 5  $\mu\text{g}/\text{kg}$  (WHO-IPCS, 1991).

PeCB has also been measured in abdominal, mammary, and perirenal fat tissue from 27 adult Finnish males and females (Smeds and Saukko, 2001). Workers with occupational exposure to PeCB were found to have higher levels of the substance in blood than control groups (Lunde and Bjorseth, 1977).

### **2.3.5. Bioavailability**

The Environmental Health Criteria on chlorobenzenes (WHO/IPCS, 1991) concluded that limited evidence was available showing that sediment-bound residues of chlorobenzenes are bioavailable to organisms; i.e., aquatic invertebrates can take up residues from sediment, and plants, from soil. Since then, more information on the bioavailability of hydrophobic substances became available.

Bioavailability of chlorobenzenes is inversely proportional to the organic carbon content of the soil or sediment (Government of Canada (2003) citing e.g. van Gestel and Ma, 1988; Hulzebos et al., 1993). It was furthermore stated in the Canadian Follow-up Report that persistent substances can remain bioavailable for long periods of time, thereby increasing the probability and duration of potential exposure relative to compounds that do not persist in the environment.

It is generally accepted that not all fractions of organic pollutants bound on sediments or soils are equally toxic due to their various resistances to desorption. The resistant and sequestered fractions of pentachlorobenzene are environmentally less harmful than the more readily desorbing, labile, or available fractions. The large fraction of water soluble organic matter in the sediments is potentially highly mobile and could be easily resuspended or leached to the overlying water column. If the soluble organic matter carries the major amount of pentachlorobenzenes as expected, continuous contamination of the water body from the sediments is very likely. Qiao & Farrell (1996) carried out experiments with PeCB in rainbow trout and concluded that mass balance analysis suggests that the appearance of HCBP and PeCB in the fish after 6 days could not be accounted for solely by the amount of chemical dissolved in the water at the time when the fish were introduced. The chemical uptake in fish with the pharynx plugged, to eliminate the gut uptake route, was similar to that in control fish. Because direct access to bottom sediments did not alter chemical uptake, they concluded that hydrophobic chemicals such as PeCB and HCBP associated with suspended sediments from the Fraser River can readily desorb and be taken up across the gill. Åkerblom (2007) concluded that pesticide sorption to organic particles in standardized toxicity tests is fast and efficient and that substances bound to the sediment may act as a reservoir, continuously supplying the pore water with low pesticide concentrations.

As sediment or organic matter bound organic pollutants may still become available, an evaluation should focus on sorption and desorption kinetics of pentachlorobenzene and modifying circumstances rather than on statements on bioavailability. Such data are however scarce.

## 2.4 Hazard assessment for endpoints of concern

### 2.4.1. Toxicity

#### Toxicokinetics

Toxicokinetic studies with rats show that after an oral dose, the substance is distributed to the blood and tissues (Umegaki et al., 1993; WCC, 2007 citing Thomas and coauthors). Linder et al., (1980) observed that rats fed with PeCB accumulated approximately 1.5 – 2.2 times the dietary concentration in their adipose tissues. Umegaki et al., (1993) studied the kinetics of PeCB in blood and tissues of rats given a single oral dose by gavage of either 15 mg or 20 mg. PeCB was observed in the blood, liver, kidney, brain, and fat tissue as well as in the feces (4.8% of the dose). In the blood, also the major metabolite pentachlorophenol was observed.

Using the blood concentrations after a single gavage of 15 mg PeCB (results of the study of Umegaki et al., 1993), WCC (2007) calculated that after exposure to repeated oral daily doses of 15 mg (or 77 mg/kg) the steady-state blood concentration of PeCB would be 2.6 µg/ml in rats. Assuming linear kinetics in this dose range, WCC (2007) extrapolated this value from the 77 mg/kg-day exposure to the lowest observed adverse effect level (LOAEL) for PeCB of 8.3 mg/kg-day (value derived from the study of Linder et al., (1980), see section Subchronic Toxicity). According to the calculations of WCC, this resulted in a predicted steady-state blood concentration of PeCB of 0.28 µg/ml. Since PeCB partitions predominantly in the lipid portion of blood and adipose tissue, the concentration of PeCB in blood lipid fraction would be predicted to be approximately 46 µg/g lipid.

Den Besten et al (1994) studied the urinary metabolite profile of PeCB in the rat after dietary exposure for 13 weeks. PeCB was metabolized to the major metabolites pentachlorophenol (PCP), 2,3,4,5-tetrachlorophenol (TCP), mercaptotetrachlorophenol (MTCP), the glucuronide derivative of pentachlorothiophenol (PCTP), and the minor metabolites tetrachlorohydroquinone (TCHQ), methylthiotetrachlorophenol (MeTTCP), hydroxytetrachlorophenyl sulphoxide (HTCPS), and bis(methylthio)-trichlorophenol (bis-MeTTriCP). The study also revealed that oxidation of PeCB to 2,3,4,5-TCP was not mediated by cytochrome P450III<sub>A</sub>. In the urine of rabbits exposed to a single oral dose of PeCB, also pentachlorophenol and 2,3,4,5-tetrachlorophenol was observed (Slooff et al., 1991, citing Kohli et al., 1976).

A study with coyotes showed that PeCB is secreted in the faeces (Johnston et al., 1997). Coyotes were dosed with PeCB (single dose of 130, 260 or 520 mg). In both studied matrices, faeces and adipose tissue, residues of PeCB were determined. PeCB was detectable in faeces for six months post-dosing. In the faeces, also the metabolites pentachlorophenol and 2,3,4,5-tetrachlorophenol were detected.

#### Acute toxicity

Pentachlorobenzene has been tested on rats and mice. Results of acute toxicity tests are available for oral and dermal exposure, see Table 2.7.

LD<sub>50</sub>s for PeCB (by gavage in peanut oil) are 940 to 1125 mg/kg bw in adult and weanling rats and 1175 and 1370 mg/kg bw in Swiss Webster mice (Linder et al., 1980 cited in Government of Canada, 1993). Decreased activity and tremors were observed in both species at sublethal doses; the kidneys, liver and adrenal glands of rats were also enlarged. In some rats, the gastric mucosa was hyperaemic, and a slight

reddish fluorescence of the gastrointestinal tract was observed in both rats and mice under ultraviolet light, suggesting porphyria (Government of Canada, 1993). In the study of Allen et al., (1979, cited in Slooff, 1991), a LD50 of 250 mg/kg bw was observed in rats.

Ariyoshi et al., (1975, cited in Slooff, 1991) observed an increase of cytochrome P450 content in rats as well as an increase in the activity of two hepatic enzymes after oral administration of 250 mg/kg bw once daily during 3 days.

To determine a dermal LD50 one concentration (i.e., 2500 mg/kg bw) was tested on rats, but no toxic effects were seen at this dose (Linder et al., 1980 cited in Slooff, 1991). Based on this study, a NOEC of > 2500 mg/kg bw can be established for dermal exposure.

### **(Sub)chronic toxicity**

In female Sherman rats ingesting diets containing 500 ppm (mg/kg) and greater (> 37.5 mg/kg bw/day) PeCB for 100 days, there was an increase in liver weight and hypertrophy of hepatic cells (Linder et al., 1980). There was also an increase in kidney weights and renal hyaline droplet formation in males at exposure levels  $\geq 125$  ppm (mg/kg) (equivalent to  $\geq 8.3$  mg/kg bw/day). In addition, at 1 000 ppm (equivalent to 81.1 mg/kg bw/day for males and 78.7 mg/kg bw/day for females), the effects observed were: an increase in adrenal weight and focal areas of renal tubular atrophy and interstitial lymphocytic infiltration in males; an increase in kidney weight in females; a decrease in haemoglobin and an increase in white blood cells in both sexes; and decreases in red blood cells and haematocrit in males. The no-observed-effect-level (NOEL) in female rats, derived on the basis of the results of this study, was 250 ppm (equivalent to 18.2 mg/kg bw/day); the lowest-observed-effect-level (LOEL) in males was 125 ppm (equivalent to 8.3 mg/kg bw/day) (calculations by Government of Canada, 1993).

In a study of NTP (1991) rats and mice were exposed to PeCB through their diet. Observed effects were among others: decreases in the mean body weights of male rats at exposure levels  $\geq 1 000$  ppm (mg/kg diet) and in females at all concentrations ( $\geq 33$  ppm), increase in absolute and relative liver weights (33 ppm in males), centrilobular hepatocellular hypertrophy (as low as 330 ppm for males), increases in kidney weights and renal histopathological effects at concentrations as low as 100 ppm, nephrotoxic effects in females ( $\geq 1 000$  ppm), increase of the concentration of protein in the urine in male and female rats at  $\geq 1 000$  ppm, decrease of free thyroxin and total thyroxin concentrations in male and female rats indicating moderate hypothyroxinemia and abnormalities were observed at concentrations of  $\geq 330$  ppm in females and  $\geq 1 000$  ppm in males. The incidence of abnormal sperm in males was also increased at both dietary concentrations at which it was examined (330 and 2 000 ppm). On the basis of histopathological lesions, the authors considered the NOELs to be 33 ppm in male rats and 330 ppm in females (approximately 2.4 and 24 mg/kg bw/day, respectively) (calculations by Government of Canada, 1993).

In PeCB exposed mice in the same study NTP (1991), observed effects were among others: ventral swelling and ruffled fur (2 000 ppm [mg/kg]), increase of kidney weights ( $\geq 330$  ppm in males), functional effects on the thyroid at all concentrations in both sexes ( $\geq 33$  ppm), increase in liver weights (at 100 ppm in males). The only exposure-related histological lesion in mice of either sex was centrilobular hepatocellular hypertrophy and minimal necrosis, observed at all concentrations in males and at  $\geq 330$  ppm (equivalent to 68 mg/kg bw/day) in females. On the basis of the histopathological lesions, the authors considered the NOEL in female mice to be

100 ppm (approximately 22 mg/kg bw/day). No NOEL for males could be established (LOEL = 33 ppm or approximately 5.2 mg/kg bw/day) (calculations by Government of Canada, 1993).

### **Mutagenicity and carcinogenicity**

Epidemiological studies of exposed populations are not available and information on carcinogenicity in experimental animals has not been identified. PeCB showed no genotoxicity in a small number of *in vitro* and *in vivo* studies of a limited range of investigated genetic endpoints.

PeCB has been tested negative in the Ames test (Table 2.7). Based on limited available data, mutagenicity in *S. typhimurium* with and without metabolic activation, effects on chromosomes in Chinese Hamster ovary cells *in vitro*, and micronuclei in peripheral blood smears in animals from the NTP sub-chronic study, PeCB has been assessed as not genotoxic (Haworth et al., 1983 and NTP, 1991 cited in Government of Canada, 1993).

Several studies (Thomas et al., 1998 and Gustafson et al., 2000; Ying et al., 2001) investigated the tumor-promoting activity in medium term carcinogenicity assays of various chlorobenzene isomers including PeCB. The results suggest that PeCB promotes glutathione *S*-transferase (GSTP1-1) positive preneoplastic foci formation in rat liver, following diethylnitrosamine (DEN) initiation.

Pentachlorobenzene has been classified, therefore, in Group V (inadequate data for evaluation) of the classification scheme for carcinogenicity developed for use in the derivation of the *Guidelines for Canadian Drinking Water Quality* (Environmental Health Directorate, 1989 cited in Government of Canada, 1993).

The only risk phrase for pentachlorobenzene in the European ESIS database is R22, harmful if swallowed (European Chemicals Bureau, 2007). According to HSDB (2003) pentachlorobenzene is not classifiable as to human carcinogenicity because there are no human data and no animal data available. WHO-ICPS (1991) concludes: 'Available data are inadequate for the assessment of the carcinogenicity of the higher chlorinated benzenes (tri- to penta-).' On mutagenity WHO-ICPS (1991) concludes that although the available data from *in vitro* and *in vivo* assays for isomers other than 1,4-DCB are limited, chlorobenzenes do not appear to be mutagenic.

### **Reproductive and developmental toxicity**

Available studies concerning the embryotoxicity, foetotoxicity and teratogenicity of PeCB include one study in rats (Villeneuve and Khera, 1975, cited in Government of Canada, 1993) and one in mice (Courtney et al., 1977, cited in Government of Canada, 1993). Results of the study of Villeneuve and Khera (1975, cited in Government of Canada, 1993) indicated that PeCB is foetotoxic (an increased incidence of extra ribs and sternal defects was observed in the offspring) at maternal exposure doses of 50 mg/kg bw/day. The exposure concentration was below the concentration that induced toxic effects in the mothers. In mice, no embryotoxic, foetotoxic or teratogenic effects were observed in the offspring at doses which were maternally toxic (50 mg/kg bw/day and above)(Courtney et al., 1977, cited in Government of Canada, 1993). In the only identified study on reproductive toxicity of PeCB, Linder et al. (1980) reported that suckling pups of PeCB treated mothers fed  $\geq$  250 ppm developed tremors (LOAEL = 18.2 mg/kg/day). At 1000 ppm, most sucklings died before weaning.

**Table 2.7: Toxicity of PeCB**

	Test result	Test details			Remarks	Reference
		Exposure period	Observation period	Dose		
<b>Acute oral toxicity</b>						
Rat	LD <sub>50</sub> = 250 mg/kg bw					Allen et al 1979 cited in Slooff (1991).
Mouse, Swiss Webster	LD <sub>50</sub> = 1,175 - 1,370 mg/kg bw				Decreased activity and tremors; a slight reddish fluorescence of the gastrointestinal tract was observed under ultraviolet light, suggesting porphyria	Linder et al 1980, cited in CEPA (1993)
Rat, adult and weanling	LD50 = 940 - 1,125 mg/kg bw				Decreased activity and tremors; kidneys, liver and adrenal glands enlarged. In some rats, hyperaemic gastric mucosa and indications for porphyria	Linder et al 1980, cited in Government of Canada (1993)
Rat		3 days		250 mg/kg bw/day	Content of Cyt P-450 and enzymatic activities in liver increased	Ariyoshi et al 1975 cited in Slooff (1991).
<b>Acute dermal toxicity</b>						
Rat	LD50 > 2,500 mg/kg bw				No mortality, no toxic effects observed	Linder et al 1980 cited in Slooff (1991).
<b>(sub)Chronic oral toxicity</b>						
Rat, female Sherman	NOEL = 250 mg/kg diet Equiv. to a NOEC of 18.2 mg/kg bw	100 days		0 – 1000 ppm	Increase in liver weights and hypertrophy of hepatic cells	Linder et al. 1980 cited in Government of Canada 1993
Rat, male	LOEL = 125 mg/kg diet Equiv. to a NOEC 8.3 mg/kg bw	100 days		0 – 1000 ppm	Increase in liver and kidney weights, hypertrophy of hepatic cells and renal hyaline droplet formation	Linder et al. 1980 cited in Government of Canada 1993
Rat F344/N, male	NOEL = 33 mg/kg diet Equiv. to a NOEL 2.4 mg/kg bw	91 days		0-2000 ppm	Histopathological lesions	NTP 1991
Rat F344/N, female	NOEL = 330 mg/kg diet Equiv. to a NOEL mg/kg bw	91 days		0-2000 ppm	Histopathological lesions	NTP 1991
Mouse B6C3F1, female	NOEL = 100 mg/kg diet Equiv. to a NOEL 22 mg/kg bw	91 days		0-2000 ppm	Histopathological lesions	NTP 1991
Mouse, male	LOEL = 33 mg/kg diet Equiv. to a LOEL 5.2 mg/kg bw	91 days		0-2000 ppm	Histopathological lesions	NTP 1991
<b>Genetic toxicity</b>						
Salmonella typhimurium TA98, 1537, 1538	Negative				Gene mutation	Lawlor et al 1979 cited in Slooff (1991)
Salmonella typhimurium	Negative			0-1000	Gene mutation	Haworth et al 1983, cited in Slooff

	Test result	Test details			Remarks	Reference
		Exposure period	Observation period	Dose		
TA98, 100, 1535, 1537				µg/plate		(1991)
<b>Developmental toxicity – oral</b>						
Rat	NOAEL (developmental) = 6.3 mg/kg bw (Maternal dose) LOAEL (developmental) = 18.2 mg/kg bw LOAEL (maternal toxicity) = 37.5 mg/kg bw/day	180 days			tremors in offspring	Linder et al 1980, also cited in Slooff 1991
Mouse	NOEL (developmental) = 50 mg/kg bw/day Maternal toxicity ≥ 50 mg/kg bw/day				No effects observed	Courtney et al 1977, cited in Government of Canada 1993
Rat	LOAL = 50 mg/kg bw/day Maternal toxicity > 50 mg/kg bw/day				increased incidence of extra ribs and sternal defects in the offspring	Villeneuve and Khera 1975, cited in Government of Canada 1993

### **Human studies**

Occupational exposure to PeCB may be through inhalation and dermal contact with this compound at workplaces where PeCB is produced or used. Examples are wood treatment plants, dielectric fluid spill and cleanup, municipal solid waste incinerators, hazardous waste incinerators, and magnesium production plants. Exposure may also arise in occupational settings where the pesticide quintozene is produced and used. The general population may be exposed to PeCB via inhalation of ambient air, ingestion of food and drinking water. Case reports of adverse effects in individuals, or epidemiological studies of populations exposed to PeCB have not been identified (Government of Canada, 1993).

## **2.4.2. Ecotoxicity**

### **Aquatic toxicity**

Acute and chronic toxicity data are available for both freshwater (Table 2.8) and marine organisms (Table 2.9).

The lowest acute toxicity values are 100 µg/L for freshwater fish species (EC50) and 87 µg/L for a marine crustacean (LC50). The lowest chronic values (NOECs) are 2 µg/L for a freshwater fish and 14 µg/L for a marine crustacean. According to these findings, species sensitive to PeCB can be found in both the freshwater and the marine environment.

Within the European Union PeCB is classified as a substance which is very toxic to aquatic organisms and which may cause long-term adverse effects in the aquatic environment (Risk phrases N; R50 and R53) (European Chemicals Bureau, 2007). This classification is based on the fact that the substance is very toxic to fish, daphnia or algae (LC50 ≤1 mg/L) and the substance is not readily degradable or bioaccumulative.

### **Soil and sediment toxicity**

Limited data are available for soil and sediment. Tests with various chlorobenzenes were carried out by Van Gestel et al (1991). Two earthworm species were raised on a natural sandy soil (KOBG) and an artificial OECD standard soil. Average LC50 values varied between 115 and 238 mg/kg dry weight, whereas LC50 values in pore water varied between 55.1- 117.7 µg/L. Van Gestel et al (1991) concluded that based on pore water concentrations earthworms are more sensitive to PeCB than fish, but that this may be due to differences in test design.

Only one study on the toxicity of pentachlorobenzene in plants was identified. Duplicate tests were carried out in which *Lactuca sativa* seedlings were grown on OECD soil contaminated with pentachlorobenzene. The seedlings were harvested after 7 and 14 days. EC50 values varied between 56 and 862 mg/kg dw (Hulzebos et al. 1993). Experiments in solution resulted in an EC50 value of ±1.0 mg/L. Details of the tests are provided in Table 2.10.

### **Toxicity to birds**

No toxicity data on birds are available for PeCB.

Table 2.8. Freshwater species: selection of acute and chronic aquatic toxicity data.

Species	Exp. time	Criterion	Test endpoint	Value (mg/L)	Reference
<b>Algae</b>					
<i>Ankistrodemus falcatus (acicularis)</i>	4 h	Primary production ( <sup>14</sup> C uptake)	EC50	1.25 <sup>a</sup>	Wong et al, 1984 in Hesse et al., 1991
<i>Selenastrum capricornutum</i>	96 h	Growth	EC50	6.63 <sup>a</sup>	EPA, 1978 in Priority Substance No. 26. Pentachlorobenzene. Substance Data Sheet., 2005
<b>Crustacea</b>					
<i>Daphnia magna</i>	48 h	Mortality	LC50	0.300, 1.25 <sup>a</sup> , 5.3 <sup>a</sup>	Abernethy <i>et al.</i> , 1986; Bobra <i>et al.</i> , 1983; Leblanc, 1980 in Hesse <i>et al.</i> , 1991
<i>Ceriodaphnia dubia</i>	7 d	Reproduction	IC50	0.520 <sup>a</sup>	Oris <i>et al.</i> , 1991 in Priority Substance No. 26. Pentachlorobenzene. Substance Data Sheet., 2005
<i>Daphnia magna</i>	16 - 21 d	Reproduction	NOEC	0.010, 0.031, 0.100	Hermens <i>et al.</i> , 1984, De Wolf <i>et al.</i> , 1988, Van Leeuwen 1987 in Hesse <i>et al.</i> , 1991
<b>Insects</b>					
<i>Chironomus thummi</i>	48 h	Mortality	LC50	0.230	Roghair <i>et al.</i> , 1994 in Priority Substance No. 26. Pentachlorobenzene. Substance Data Sheet., 2005
<i>Chironomus tentans</i>	2 h	Mortality	LC50	168 (10 °C)	Lydy <i>et al.</i> , 1999
<i>Chironomus tentans</i>	2 h	Mortality	LC50	150 (20 °C)	Lydy <i>et al.</i> , 1999
<i>Chironomus tentans</i>	2 h	Mortality	LC50	137 (30 °C)	Lydy <i>et al.</i> , 1999
<b>Fish</b>					
<i>Oncorhynchus mykiss</i>	48 h	Behaviour	EC50	0.100	Ahamd <i>et al.</i> , 1984 in Priority Substance No. 26. Pentachlorobenzene. Substance Data Sheet., 2005
<i>Lepomis macrochirus</i>	96 h	Mortality	LC50	0.250	Buccafusco <i>et al.</i> , 1981 in Hesse <i>et al.</i> , 1991
<i>Poecilia reticulata</i>	8 - 14 d	Mortality	LC50	0.100, 0.180	Van Hoogen & Opperhuizen, 1988 in Priority Substance No. 26. Pentachlorobenzene. Substance Data Sheet., 2005, Könemann, 1979 in Hesse <i>et al.</i> , 1991
<i>Brachydanio rerio</i>	28 d	Reproduction	NOEC	0.034	Van Leeuwen <i>et al.</i> , 1990 in Priority Substance No. 26. Pentachlorobenzene. Substance Data Sheet., 2005
<i>Gambusia affinis</i>	96 h	Mortality	LC50	3.2	Chaisuksant <i>et al.</i> , 1998
<i>Gambusia affinis</i>	42 d	Growth rate	EC50	0.15	Chaisuksant <i>et al.</i> , 1998
<i>Gambusia affinis</i>	42 d	Growth rate	EC10	0.002	Chaisuksant <i>et al.</i> , 1998

<sup>a</sup> Value above water solubility (0.56 mg/L at 25 °C).

Table 2.9. Marine species: selection of acute and chronic aquatic toxicity data.

Species	Exp. time	Criterion	Test endpoint	Value (mg/L)	Reference
<b>Algae</b>					
<i>Skeletonema costatum</i>	96 h	Chlorophyll	EC50	2.23 <sup>a</sup>	US-EPA 1978 in Priority Substance No. 26. Pentachlorobenzene. Substance Data Sheet., 2005
<b>Crustacea</b>					
<i>Mysidopsis bahia</i>	96 h	Mortality	LC50	0.160	US EPA 1978 in Priority Substance No. 26. Pentachlorobenzene. Substance Data Sheet., 2005
<i>Portunus pelagicus</i>	96 h	Mortality	LC50	0.087	Mortimer and Connell, 1995
<i>Portunus pelagicus</i>	40 d	Growth	EC50	0.041	Mortimer and Connell, 1995
<i>Portunus pelagicus</i>	40 d	Growth	EC10	0.014	Mortimer and Connell, 1995
<b>Fish</b>					
<i>Cyprinodon variegatus</i>	96 h	Mortality	LC50	0.8 <sup>a</sup> , 0.46	Heitmuller, 1981 in Hesse et al., 1991; Mayer, 1987 in Van der Plassche et al., 1993
<i>Cyprinodon variegatus</i>	28 d	Growth	NOEC	0.018	Hansen et al. 1991 in Priority Substance No. 26. Pentachlorobenzene. Substance Data Sheet., 2005

Table 2.10. Soil species: selection of acute and chronic aquatic toxicity data.

Species	Exp. time	Criterion	Test endpoint	Value (mg/kg dw)	Reference
<b>Macrophyta</b>					
<i>Lactuca sativa</i>	7 d	Growth	EC50	228	Hulzebos et al., 1993
<i>Lactuca sativa</i>	7 d	Growth	EC50	862	Hulzebos et al., 1993
<i>Lactuca sativa</i>	14 d	Growth	EC50	56	Hulzebos et al., 1993
<i>Lactuca sativa</i>	14 d	Growth	EC50	±320	Hulzebos et al., 1993
<b>Annelida</b>					
<i>Eisenia Andrei</i>	14 d	Mortality	LC50	134	Van Gestel et al, 1991
<i>Eisenia Andrei</i>	14 d	Mortality	LC50	238	Van Gestel et al, 1991
<i>Lumbricus rubellus</i>	14 d	Mortality	LC50	115	Van Gestel et al, 1991
<i>Lumbricus rubellus</i>	14 d	Mortality	LC50	201	Van Gestel et al, 1991

In conclusion, based on the fact that the lowest acute aquatic toxicity value (LC50) of PeCB is < 1 mg/L and the lowest NOEC is 10 µg/L, PeCB is considered very toxic to aquatic organisms.

### Multiple chemicals and toxicological interactions

Annex E request information on toxicological interactions involving multiple chemicals (Annex E, b). Limited information is available on this subject. Yoo et al (2003) report on their studies on the kinetics of PeCB: “The kinetics and toxicity of pentachlorobenzene were assessed using a freshwater (*Hyalella azteca*) and marine

amphipod (*Leptocheirus plumulosus*). The results of these studies demonstrated the additive toxicity of PeCB with other organic chemicals (pyrene).”

#### **Comparison of exposure and effect data**

ICCA/WCC (2007) followed several approaches for relating exposure to adverse effects of pentachlorobenzene, one of which is presented here. Environment Canada calculated an estimated no effect value (ENEV<sub>sed</sub>) for freshwater benthic organisms exposed to PeCB of 25 µg/g (25,000 ng/g) organic carbon (Environment Canada, 2003 cited by ICCA/WCC, 2007). This PeCB ng/g-OC concentration was exceeded in 1994 in Canada only at a location near a single site of industrial contamination, which has since undergone remediation activities. Rural and remote sites which have been studied for long range transport have PeCB ng/g-OC concentrations typically more than three orders of magnitude less than, or 1/1000, of the ENEV<sub>sed</sub>. For example, Muir et al. (1995) report sediment surface layer concentrations of PeCB in northern Canada lake sediments of less than 0.01 to 0.73 ng/g sediment between 1979 and 1988 (ICCA/WCC, 2007). The other two approaches also showed considerable difference between exposure and effect concentrations.

Several methods, exposure routes and species with very different feeding strategies were used by ICCA/WCC to determine the lethal and critical body burden of PeCB. Based on the estimations a Lethal Body Burden of 1 to 2.5 mmol/kg (250 to 626 mg PeCB/kg) would be expected. Based on the general knowledge on substances with a narcotic mode of action and the available data on PeCB, such as the *Hyaella* growth/mortality study and other information discussed, an estimation of 0.1 mmol PeCB/kg (25 mg/kg) was tentatively proposed by ICCA/WCC as a Critical Body Burden for chronic effects.

Hoydal and Dam (2003) measured concentrations of <0.1 – 37 ng/g wet weight in biota captured in the environment of the Faroe Islands. The highest amount is a factor of 5000-20000 lower than the critical tissue residues of 165-861 µg/g reported by ICCA/WCC (2007). The highest concentrations reported in chapter 2.3.3 are a factor of 50 lower than these critical tissue residue concentrations. We may conclude that in most cases environmental concentrations do not reach the estimated effect concentrations.

A very recent publication of Schuler et al (2007b) have reported critical whole body residues of pentachlorobenzene of 58 µg/g and 5 µg/g for *Hyaella azteca* and *Chironomus tentans* respectively. In contrast to most other studies chronic toxicity data was used to establish these critical whole body residues instead of acute toxicity data. These critical whole body residues values are 2-25 times higher than the highest concentrations reported in chapter 2.3.3 and 150-1500 times higher than the highest value reported for the Faroe Islands.

### **3 SYNTHESIS OF THE INFORMATION**

Pentachlorobenzene is a chlorinated organic compound. According to available data, pentachlorobenzene should be considered as persistent given the considerable number of estimated and experimental half-lives in atmosphere, soils, sediments, and water. Persistence in the environment depends on the rate of photo-oxidation, the presence of oxygen and organic matter. Pentachlorobenzene meets the criterion on bioaccumulation. BCF values for pentachlorobenzene range from 1085 – 23 000 L/kg for fish, 833 – 4 300 L/kg for mollusca, and 577 – 2258 L/kg for crustacean.

Biomagnification may be expected due to the high  $\log K_{ow}$  and the fact that biotransformation is insignificant. However, data on the biomagnification of pentachlorobenzene are lacking.

The available data support the potential for long range transport of pentachlorobenzene. The physical-chemical characteristics are within the range of the other POPs. Model estimations on the transport distance resulted in distances of 8 000, while estimates based on air measurements suggested 13 338 km. Monitoring data also indicate that PeCB is subject to long range transport. PeCB was detected in air and precipitation at various locations in the world, many of those far from its sources. The small spatial variability across the Northern Hemisphere observed in some studies also indicate that PeCB has a very long atmospheric residence time, which allows it to become widely distributed in the global hemisphere.

A large quantity of monitoring data exists on PeCB detected in abiotic matrices as well as in biota in temperate zones, mainly originating from developed countries. In general, concentrations of PeCB in the temperate zones of the world seem to decrease. This pattern is representative for most POPs. For the (ant)arctic area, only recent data are available which do not allow to derive a trend.

Case reports of adverse effects in individuals, or epidemiological studies of populations exposed to PeCB have not been identified. The only risk phrase for pentachlorobenzene in the European ESIS database is R22, harmful if swallowed. Lowest LD50 observed for acute exposure was 250 mg/kg bw. According to the American Hazardous Substances Data Bank pentachlorobenzene is not classifiable as to human carcinogenicity because there are no human data and no animal data available. PeCB is moderately toxic to humans. Pentachlorobenzene is very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. Data on soil and sediment organisms are limited or lacking. Bioavailability of pentachlorobenzene is inversely proportional to the organic carbon content of the soil or sediment. However, experiments suggest that hydrophobic chemicals bound to the sediment or suspended sediment may act as a reservoir and result in continuous uptake. There are limited quantitative data on this process for pentachlorobenzene.

Generally, the levels that are found in environmental compartments, including biota, are well below known and established critical effect levels based on acute toxicity data. Recently established critical body residues based on chronic toxicity data are 2-25 times higher than the highest concentrations reported in chapter 2.3.3 and 150-1500 times higher than the highest value reported for the Faroe Islands.

The data from Europe and North America show that production and use of pentachlorobenzene has ceased over the last decades, but it cannot be excluded that PeCB is produced or used elsewhere. Unintentional release of pentachlorobenzene as a byproduct of incomplete combustion appears to be the most important source. However, this conclusion is based on data for Europe and North America only.

PeCB meets all screening criteria on long range transport, persistence, bioaccumulation and toxicity. Data on biomagnification and bioavailability do not permit a conclusive statement on these topics as data are lacking, not quantitative or

controversial. Environmental concentrations in remote areas are well below the established critical effect levels, but approach these effect levels at highly polluted sites. Generally, environmental concentrations seem to decrease. Production and use have ceased in Europe and North America, but data from other parts of the world are limited. Unintentional release as a byproduct of incomplete combustion appears to be the most important source of pentachlorobenzene in the environment.

#### **4 CONCLUDING STATEMENT**

It has been demonstrated that pentachlorobenzene meets all the criteria laid down in Annex D of the Stockholm Convention. Its physical-chemical characteristics are within the range of the other POPs in the Convention.

The substance is persistent in the environment and is bioaccumulative. The small spatial variability across the Northern Hemisphere indicates that pentachlorobenzene has a very long atmospheric residence time, which allows it to become widely distributed in the global hemisphere. There are monitoring data from remote areas, backed up by modelling results that suggest that pentachlorobenzene can be transported over great distances. Pentachlorobenzene is moderately toxic to humans, but is very toxic to aquatic organisms. Present concentrations in remote areas are well below estimated critical body burdens.

Because of its long range transport, neither a single country nor a group of countries alone can abate the pollution caused by this substance. Unintentional release of pentachlorobenzene as a byproduct of incomplete combustion appears to be the most important source. Measures to reduce these releases can only be taken at a global scale. Although the production and use of pentachlorobenzene seems to have ceased in most countries, its reintroduction remains possible. This could lead to increased releases and levels in the environment. Based on the available evidence, it is thus likely that pentachlorobenzene can, as a result of long range environmental transport, cause significant adverse effects on human health and/or the environment, such that global action is warranted.

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