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Report of the Persistent Organic Pollutants Review Committee on the work of its third meeting

Addendum

Risk profile on pentachlorobenzene

At its third meeting, the Persistent Organic Pollutants Review Committee adopted the risk profile on pentachlorobenzene, on the basis of the draft contained in document UNEP/POPS/POPRC.3/15. The text of the risk profile, as amended, is set out below. It has not been formally edited.

PENTACHLOROBENZENE

RISK PROFILE

Adopted by the Persistent Organic Pollutants Review Committee
at its third meeting

November 2007

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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 PeCB 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 quinterozone. Major U.S. and European manufacturers of quinterozone 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 PeCB is of no commercial significance. No trade or stockpiles have been reported.

Nowadays PeCB enters the environment through various sources of which PeCB as a byproduct of incomplete combustion is the largest current source. 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 PeCB has a high bioaccumulation potential. Log Kow 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 ≤ 1 mg/L). Limited data are available on terrestrial ecotoxicity and data for toxicity to birds are lacking.

Physical and 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 and 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. Measured 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, PeCB 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 PeCB 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

PeCB 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. PeCB 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

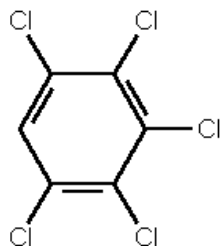
CAS Registry Number: 608-93-5

EINECS Number: 210-172-0

Trade names: -

1.1.2 Structure

1,2,3,4,5-Pentachlorobenzene



1.1.3 Physico-chemical properties

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 Kow 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. A full listing of the physical and chemical properties of PeCB is listed in Annex II, Table 1.1 in UNEP/POPS/POPRC.3/INF/21.

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

At its second meeting on 6-10 November 2006, the POP Review Committee applied the screening criteria specified in Annex D to the Stockholm Convention, and concluded, in accordance with paragraph 4 (a) of Article 8 of the Convention, that it was satisfied that the screening criteria were fulfilled for PeCB. 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

Information on the data sources (references and other literature) has been provided in UNEP/POPS/POPRC.3/INF/21 Annex I and III. 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).

1.4 Status of the chemical under international conventions

PeCB is not included in any international convention. The European Commission has submitted a proposal to include PeCB 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 objective of the LRTAP POPs protocol is to control, reduce or eliminate discharges, emissions and losses of persistent organic pollutants. The UNECE Task Force on POPs identified the following options for possible inclusion of PeCB into the Protocol:

- (a) Listing of PeCB in annex I to the Protocol in order to prevent production and use;
- (b) Listing of PeCB in annex I and annex III to the Protocol. [ECE/EB.AIR/WG.5/2007/14]

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 PeCB 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, 2003), the proposed risk management strategy for PeCB 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 (Canada, Czech Republic, Germany, Lithuania, Mauritius, Turkey, and USA). No intentional production was mentioned in the document submitted by the ICCA/WCC and according to Ullmann's Encyclopedia of Industrial Chemistry PeCB 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 PeCB 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), but new regulations prohibiting new uses of PCB-containing dielectric fluids resulted in a decline of the use of PeCB after 1980. 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 PeCB as impurities in chlorothalonil, PCNB, picloram, and several other pesticides. PeCB 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. 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 PeCB 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 PeCB 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 (2003). 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 PeCB 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 barrel burning of house-hold waste, wood treatment plants and in service utility poles, pesticide use, dielectric fluid spill and cleanup, municipal solid waste incineration, hazardous waste incineration, magnesium production, solvent use and long range transport. As potential sources of release are mentioned: magnesium production (less than 2% of total annual releases), chlorinated solvents (negligible), secondary copper and aluminium processing (no data), chemical manufacturing (unlikely), iron and steel mills (scarcity of data), petroleum refineries (unlikely), wastewater treatment plants

(unlikely), textile mills (unlikely), long range transport (amount not known, expected to decrease) (Table 2.1, Annex II, UNEP/POPS/POPRC.3/INF/21).

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), 41.9 kg/yr, is a factor of 10 lower than the release of >580 kg/yr provided in the Priority substances list assessment report for PeCB (Government of Canada, 1993), submitted by Canada for the drafting of this Risk profile. The most significant 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) (US EPA 2007a, <http://www.epa.gov/tri/tridata/index.htm#pdr>). The TRI contain release data for 2000 – 2004. Total releases vary between 1512 and 763 kg PeCB/yr and include air emissions, surface water discharges, underground injection, on site releases to land and transfers off-site to disposal. Air emissions between 2000 and 2004 were 74, 34, 37, 40 and 100 kg/yr respectively. Water emissions are in the same order of magnitude (See Table 2.2, Annex II, UNEP/POPS/POPRC.3/INF/21). The US also indicated in their comments that the data provided by TRI on “on-and-off-site releases” include amounts that would not be released to the environment because they were subject to treatment or other management activities. The TRI data does not cover all the industry sectors, which implies that total releases in the US can be much higher than those provided. Release data from other countries are not yet available.

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). PeCB formation has been observed during combustion of municipal solid waste. The reported emission factors varied primarily due to differences in combustion conditions rather than fuel composition or waste content. The combustion of PVC may be a source of PeCB formation (Kim et al., 2004; Aracil et al., 2005; Muller et al., 1997), but the relative importance of this source is debated. 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. 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. Other PeCB sources could include quitozene degradation, titanium dioxide production, and ore treatment for the production of metals including magnesium, copper, niobium, and tantalum (ICCA/WCC 2007 citing Beck and Hansen, 1974; Knutzen and Oehme, 1989; Doering et al., 1992, and Vogelgesang 1986). No quantitative estimates are provided, because there is no quantitative information on which to base them. 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, PeCB can enter the environment through various sources of which PeCB as a byproduct of incomplete combustion is the most significant current source. Nearly all fuels contain some chloride, 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 aluminum 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 as a byproduct of combustion a decrease can be expected in those cases where measures were taken to reduce the releases of other byproducts/emissions. 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 lost rapidly 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 of 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

PeCB 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, Annex II, UNEP/POPS/POPRC.3/INF/21 which summarizes values considered reliable according to the Klimisch criteria (Klimisch, 1997).

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.

In conclusion, these values show that PeCB can be considered to have a high bioaccumulation potential. Due to the high log K_{ow} 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 PeCB are lacking.

2.2.3 Potential for Long range environmental transport

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 for long range transport of PeCB 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 rang 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 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/m³ with a range of 0.017 to 0.136 ng/m³ (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 atmosphere. 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/m³ (Government of Canada, 1993). Measured concentrations across North America averaged 0.045 ng/m³ with a range of 0.017 to 0.136 ng/m³ (Shen et al., 2005). They also observed that atmospheric levels of organochlorine compounds including PeCB increased with increasing elevation in the Canadian Rocky Mountains.

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 ± 0.10 µg/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 µg/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 µg/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 µg/kg dry weight (Borghini et al., 2005). The mosses do not have a root system and their supply is largely dependent on atmospheric deposition. The measured PeCB concentrations in both mosses 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 µg/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 (µg/kg wet weight) of PeCB in organs from fish from Alaska and Northwestern Russia and other arctic locations varied between 0.06 ± 0.08 and 5.06 µg/kg wet weight PeCB (ICCA/WCC, 2007 citing Allen-Gil et al., 1997, citing Muir et al., 2003, citing Arend et al., 2001, Vorkamp et al., 2004; Corsolini et al., 2006).

In Greenland PeCB was observed at levels of 23 µg/kg lipid weight in ptarmigan liver (1.5 µg/kg wet weight) and 8 µg/kg lipid weight in kittiwake muscle (1.1 µg/kg wet weight) (Vorkamp et al., 2004). Adelie penguin eggs (Antarctic) contained 0.68 µg/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 ± 1.9 µg/kg in male ringed seals to 8.4 ± 1.1 µg/kg in females from the west side. Seals from the east side (Quebec) contained 5.0 ± 0.5 µg/kg (males) and 7.0 ± 1.5 µg/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 µg/kg lipid weight (harp seal) in their blubber (ICCA/WCC, 2007 citing Muir et al., 2003). The mean concentration (± standard deviation of the 10 samples) of PeCB in 1992 was 11 ± 2.0 ng/g lipid weight whereas the concentration of PeCB in 1998 was 5.0 ± 1.8 ng/g lipid weight. PeCB concentrations in bowhead whales collected between 1994 and 1998 averaged at 0.3 ± 0.1 and 0.8 ± 0.1 µg/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) µg/kg (lipid weight) PeCB for females and 144.5 (1.5 - 1500) µg/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 µg/kg lipid weight PeCB (equivalent to 0.29 µg/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 µg/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 (µg/kg) found in arctic foxes were 0.61 ± 0.12 in muscle (Arivat), 0.29 ± 0.06 in muscle (Holman), 0.57 ± 0.11 in liver (Holman), 0.55 ± 0.20 in muscle (Barrow) and 0.73 ± 0.17 in liver (Barrow). Hoydal and Dam (2003) measured concentrations of $<0.1 - 37$ ng/g wet weight in biota captured in the environment of the Faroe Islands.

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 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/m³) than at a rural reference site (0.031 ng/m³) (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/m³ (ICCA/WCC 2007 citing Buehler et al., 2004)

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). Calambokidis 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. Only recent data (last 15 years) are summarized in Table 2.4 for abiotic and Table 2.5 for biota matrices in Annex II, UNEP/POPS/POPRC.3/INF/21.

During a survey within the Danube Regional Project for the European Water Framework Directive, PeCB 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 PeCB. Maximum concentrations of PeCBs 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 (ATSDR, 2007). Neither references mention if these concentrations are based on wet or dry weight basis.

2.3.4. Human exposure

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 quintozone 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).

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 µg/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 µg/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 PeCB 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 PeCBs 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 organic pollutants bound to sediment or organic matter may still become available, an evaluation should focus on sorption and desorption kinetics of PeCB 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; ICCA/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.

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), mercaptotetrachloro-phenol (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_A. 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 excreted 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.

Data on other than the oral exposure route are limited available. WHO-ICPS (1991) indicates that the chlorobenzenes are less readily absorbed through the skin, but that levels of the same isomer of the chlorobenzenes in various tissues appear to be similar, regardless of the route of administration. The ingestion of a lethal dose leads to respiratory paralysis, while the inhalation of high doses causes local irritation and depression of the central nervous system WHO-ICPS (1991).

Acute toxicity

PeCB has been tested on rats and mice. Results of acute toxicity tests are available for oral and dermal exposure (see Table 2.6, Annex II, UNEP/POPS/POPRC.3/INF/21). LD₅₀s 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.

PeCB is classified in the European ESIS database as R22, harmful if swallowed (European Chemicals Bureau, 2007). WHO-IPCS (1991) reported that data on skin and eye irritation potential and on sensitization potential were mainly restricted to 1,2,4-trichlorobenzene. No data were available for PeCB.

Subchronic toxicity

PeCB has been tested on rats and mice. Results of (sub)chronic toxicity tests are available for dietary exposure, see Table 2.6, Annex II, UNEP/POPS/POPRC.3/INF/21. In female Sherman rats ingesting diets containing 500 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 ≥ 125 mg/kg (equivalent to ≥ 8.3 mg/kg bw/day). In addition, at 1 000 mg/kg (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 mg/kg (equivalent to 18.2 mg/kg bw/day); the lowest-observed-effect-level (LOEL) in males was 125 mg/kg (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 ≥ 1 000 mg/kg diet and in females at all concentrations (≥ 33 mg/kg), increase in absolute and relative liver weights (33 mg/kg in males), centrilobular hepatocellular hypertrophy (as low as 330 mg/kg for males), increases in kidney weights and renal histopathological effects at concentrations as low as 100 mg/kg, nephrotoxic effects in females (≥ 1 000 mg/kg), increase of the concentration of protein in the urine in male and female rats at ≥ 1 000 mg/kg, decrease of free thyroxin and total thyroxin concentrations in male and female rats indicating moderate hypothyroxinemia and abnormalities were observed at concentrations of ≥ 330 mg/kg in females and ≥ 1 000 mg/kg 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 mg/kg). On the basis of histopathological lesions, the authors considered the NOELs to be 33 mg/kg in male rats and 330 mg/kg 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 mg/kg), increase of kidney weights (≥ 330 mg/kg in males), functional effects on the thyroid at all concentrations in both sexes (≥ 33 mg/kg), increase in liver weights (at 100 mg/kg 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 ≥ 330 mg/kg (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 mg/kg (approximately 22 mg/kg bw/day). No NOEL for males could be established (LOEL = 33 mg/kg or approximately 5.2 mg/kg bw/day) (calculations by Government of Canada, 1993).

In contrast to ingestion, WHO-ICPS (1991) does not provide data on dermal exposure and inhalation of PeCB, which indicates that such data are limited. The lowest NOELs reported for the ingestion of PeCB were between 2.4 and 24 mg/kg per day. Ingestion of high doses by rats and mice resulted in hepatic and renal toxicity.

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 (see Table 2.6, Annex II, UNEP/POPS/POPRC.3/INF/21). 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.

Both Health Canada and U.S. EPA have reviewed the cancer toxicity data of PeCB. The cancer weight-of-evidence classification is based on all routes of exposure. Neither group derived a risk value. Both groups concluded that the substance is unclassifiable with respect to its carcinogenicity in humans due to the lack of data. PeCB is not classified as a carcinogen by IARC or by the EU (European ESIS database).

Reproductive and developmental toxicity

Available studies concerning the embryotoxicity, foetotoxicity and teratogenicity of PeCB include one study in rats (and one in mice (Villeneuve and Khera, 1975 and Courtney et al., 1977, cited in Government of Canada, 1993) (see Table 2.6, Annex II, UNEP/POPS/POPRC.3/INF/21). Results of the study of Villeneuve and Khera (1975) 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). In the only identified study on reproductive toxicity of PeCB, Linder et al. (1980) reported that suckling pups of PeCB treated mothers fed ≥ 250 mg/kg developed tremors (LOAEL = 18.2 mg/kg/day). At 1000 mg/kg, most sucklings died before weaning.

The studies above are also cited in WHO-ICPS (1991) who conclude that there is some evidence that the higher chlorinated benzenes (TCBs, TeCBs, PeCB) are embryotoxic or fetotoxic at dose levels that are not maternally toxic. WHO-ICPS (1991) also remark that the available data are not consistent and that the toxicities of the various isomers of the TCBs and TeCBs for the mother and fetus vary considerably. Most reported effect (NOAEL, NOEL) and no effect levels (LOAEL, LOEL) vary between 17 and 200 mg/kg PeCB per day.

PeCB showed high oral toxicity with LD50 doses as low as 250 mg/kg bw in rats. From the limited data available, dermal LD50s are higher. Data on skin and eye irritation potential and on sensitization potential are limited. In contrast to ingestion, WHO-ICPS (1991) does not provide data on dermal exposure and inhalation of PeCB, which indicates that such data are limited. The lowest NOELs reported for the ingestion of PeCB were between 2.4 and 24 mg/kg bw per day. Ingestion of high doses by rats and mice resulted in hepatic and renal toxicity.

PeCB showed no genotoxicity in a small number of *in vitro* and *in vivo* studies of a limited range of investigated genetic endpoints. Data on mutagenity and carcinogenity are limited. Both Health Canada and US-EPA concluded that the PeCB is unclassifiable with respect to its carcinogenity in humans due to the lack of data. PeCB is not classified as a carcinogen by IARC, nor by the EU (European ESIS database). There is some evidence that PeCB is embryotoxic or fetotoxic at dose levels that are not maternally toxic.

2.4.2. Ecotoxicity

Aquatic toxicity

Acute and chronic toxicity data are available for both freshwater (see Table 2.7, Annex II, UNEP/POPS/POPRC.3/INF/21) and marine organisms (see Table 2.8, Annex II, UNEP/POPS/POPRC.3/INF/21). The lowest acute toxicity values are 100 $\mu\text{g/L}$ for freshwater fish species (EC50) and 87 $\mu\text{g/L}$ for a marine crustacean (LC50). The lowest chronic values (NOECs) are 2 $\mu\text{g/L}$ for a freshwater fish and 14 $\mu\text{g/L}$ 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 ($\text{LC}_{50} \leq 1$ 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 $\mu\text{g/L}$. 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 PeCB in plants was identified. Duplicate tests were carried out in which *Lactuca sativa* seedlings were grown on OECD soil contaminated with PeCB. 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 2.9, Annex II, UNEP/POPS/POPRC.3/INF/21.

Toxicity to birds

No toxicity data on birds are available for PeCB.

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

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 general knowledge on substances with a narcotic mode of action and the available data on PeCB, such as the *Hyalella* growth/mortality study and other information discussed, an estimation of 25 mg/kg PeCB/kg (0.1 mmol) was tentatively proposed by ICCA/WCC (2007) as a Critical Body Burden for chronic effects.

A very recent publication of Schuler et al (2007b) has reported critical whole body residues of pentachlorobenzene of 58 mg/kg and 5 mg/kg for *Hyalella azteca* and *Chironomus tentans* respectively. These residue levels are lower than the highest concentrations reported for temperate regions in Table 2.5 in the Annex POPRC3/INF21 and 150-1500 times higher than the highest values of <0.1 – 37 µg/kg wet weight in biota reported for the Faroe Islands by Hoydal and Dam (2003). Other concentrations reported from remote areas are of the same order of magnitude, e.g. Adelie penguin eggs (Antarctic) contained 0.68 µg/kg ww (Corsolini et al., 2006) and whole body concentrations from fish in the White Sea were up to 5 µg/kg ww (ICCA/WCC, 2007 citing Muir et al., 2003).

The World Chlorine Council (ICCA/WCC, 2007) has provided information related to two other approaches. The first approach focused on PeCB organic carbon concentrations in sediments from Canadian lakes and showed that in both rural and remote sites, PeCB organic carbon concentrations were 410-75000 times lower than Environment Canada’s “estimated no effect value” for freshwater benthic organisms. In the second approach, comparisons were made between exposure estimations for a piscivorous predator and for polar bear using assumptions considered by the WCC as “worst case assumptions”, and effect levels derived from human Reference Dose and Tolerable Daily Intakes from USA and Canada. These estimations of exposure were 13 and 20 times lower than the derived effect levels, respectively.

The available information has not been sufficient for confirming if the values given above represent real critical body burdens or just expressions of internal dose or whole body residues levels. Both concepts have fundamental differences related to the understanding of the mechanism of action of the chemical. Nevertheless, it should be noted that expressing the toxicological effects as internal dose or, whenever possible, critical body burdens, improves the effect assessment but only reduces partially its uncertainty. In addition, all the uncertainty related to the exposure assessment remains. While monitoring levels above critical body burdens or internal toxic doses clearly indicate a risk, the fact that current measured concentrations are below these triggers should in no case be interpreted as a confirmation of the absence of risk, particularly in the assessment of POPs and POPs candidates.

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 logK_{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 and chemical characteristics are within the range of the other POPs. Model estimations on the transport distance resulted in distances of 8 000 km, 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 be decreasing. This pattern is representative for most POPs. For the Arctic and Antarctic area, only recent data are available which do not enable a trend to be derived.

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. Repeat-dose mammalian toxicity tests result in evidence of hepatic, nephric, hematological, and developmental toxicity for this chemical. 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.

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 largest current source. However, this conclusion is based on data for Europe and North America only.

An important element in the assessment of the potential risk of PeCB is the assessment of the risk associated with intended and non-intended uses. This distinction is not possible with the current information but it should be very useful for the decision making process. Such an analysis would request precise information on the amounts released by intentional production and use in the past and the unintentional releases plus a correction for the degradation rate of the substance after release. Data on past production and use are currently lacking.

PeCB meets all screening criteria on long range transport, persistence, bioaccumulation and toxicity. Generally, environmental concentrations seem to be decreasing. 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 PeCB in the environment.

The available information does not allow the Committee to distinguish between the environmental burden caused by intentional use and the burden caused by the unintentional production and releases of PentaCB. Clarifying this distinction would help the Committee to prepare the risk management evaluation and to formulate its final conclusions. Hence, additional data on this issue should be sought.

4 Concluding statement

PeCB is persistent in the environment and is bioaccumulative. The small spatial variability in the ranges of air concentrations 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. 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.

As a result of the long range transport of PeCB, neither a single country nor a group of countries alone can abate the pollution caused by this substance. Unintentional release of PeCB, as a byproduct of incomplete combustion, appears to be the largest current 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, PeCB is likely, as a result of its long

range environmental transport, to lead to significant adverse human health and/or environmental effects, such that global action is warranted.

As the distinction between the environmental burden caused by intentional use and the burden caused by unintentional production and releases would support the preparation of the risk management evaluation and making the final recommendation, the Committee considers that an additional effort should be made to fill this gap.

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