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Consideration of chemicals newly proposed for inclusion in Annexes A, B or C of the Convention: pentachlorobenzene

Pentachlorobenzene proposal**

Note by the Secretariat

The annex to the present note contains a proposal by the European Union and its member States that are Parties to the Stockholm Convention on Persistent Organic Pollutants for listing pentachlorobenzene in Annexes A, B or C of the Stockholm Convention pursuant to paragraph 1 of Article 8 of the Convention. The annex is being circulated as submitted and has not been formally edited by the Secretariat.

* UNEP/POPS/POPRC.2/1.

** Stockholm Convention, Article 8, paragraph 1.

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Proposal for listing

Pentachlorobenzene

in the Stockholm Convention

on Persistent Organic Pollutants

Introduction

Pentachlorobenzene belongs to the group of chlorobenzenes. This substance has been used in the past as a pesticide, flame retardant, and in combination with PCBs in dielectric fluids. It is not clear whether it is still used as a pesticide or flame retardant on its own, but it can also appear as an impurity of pentachloronitrobenzene (quintozene) and other pesticides such as clopyralid, atrazine, chlorothalonil, dacthal, lindane, pentachlorophenols, picloram and simazine. It may be emitted to the environment indirectly because of waste incineration, barrel burning of household waste, in waste streams from pulp and paper mills, iron and steel mills, petroleum refineries and activated sludge waste water treatment. Apparently, it is not produced as such in the UNECE Europe any more (Belfroid et al. 2005).

This dossier provides the information required under paragraphs 1 and 2 of Annex D of the Stockholm Convention and it is mainly based on the Dutch dossier by Van de Plassche et al. (2002) presented for the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP), Protocol on Persistent Organic Pollutants (publicly available in the web of the Convention, at http://www.unece.org/env/popsxg/docs/2005/EU%20pentachloorbenzeen.pdf) and the addendum to that dossier (Belfroid et al 2005, also available at http://www.unece.org/env/popsxg/docs/2005/PeCB%20_def__NL.pdf).

1 Chemical identity

1.1 Names and registry numbers

IUPAC Name: Pentachlorobenzene

Synonyms: 1,2,3,4,5-pentachlorobenzene; benzene, pentachloro-; quintochlorobenzene; PeCB

CAS Number: 608-93-5

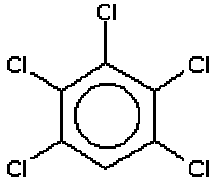
EINECS Number: 210-172-0

1.2 Structure

Molecular formula: C_6HCl_5

Molecular weight: 250.32 g/mol

Chemical structure:



2 Persistence

According to CEPA (1993) pentachlorobenzene (PeCB) can be photo-oxidized in the atmosphere, largely through reactions with hydroxyl (OH) radicals. There are no experimental data on atmospherical degradation, but the estimated half-life of PeCB is 45 to 467 days. Vulykh *et al*. (2005) estimate a half life in air of 65 days based on modelling data.

Although photodegradation in surface water is fast under sunlight irradiation (41% loss after 24 h), under field conditions the strong adsorption to solids may counteract this process (HSDB, February 2000). The half-life of PeCB in surface water was estimated to range from 194 to 1 250 days, the estimated half-life for the anaerobic biodegradation in deeper water ranged from 776 to 1 380 days (CEPA, 1993).

Although anaerobic degradation occurs, half-lives for anaerobic degradation are still high. In sediment cores at Ketelmeer (the Netherlands), PeCB is apparently persistent: the native anaerobic microflora gives half-lives of several years. A special mixed culture of anaerobic species showed a half-life of several days (J.E.M. Beurskens et al., 1994). Beck and Hansen (1974) observed a half-life of 194-345 days in soils.

In sediments and soils oxygen is generally scarce which favours reductive dechlorination. Information on PeCB's degradation pathways is scarce. Most work for the higher chlorinated benzenes has been done on hexachlorobenzene, for which the first step in the proposed pathway is dechlorination to PeCB. Further dechlorination leads to monochlorobenzene (Van Agteren et al., 1998).

Min-Jian Wang et al. (1994, 1995) have done research on behaviour and fate of chlorobenzenes (CB) in spiked and sewage sludge-amended soil from a longterm (from 1942 to 1961) agricultural experiment. Their conclusion is that about 10% of the applied total CBs became recalcitrant and that the main loss of CBs is by volatilisation. Half-lives of 219 and 103 days were reported for PeCB. It is expected that if PeCB is released to soil, it will absorb strongly to the soil and will not leach to the groundwater. It will not be expected to be subject to significant hydrolysis or biodegradation.

Given the considerable estimated and experimental half lives in soils, water and the atmosphere, PeCB should be considered as persistent Thus it can be concluded that PeCB meets the screening criteria for persistency laid down in Annex D of the Stockholm Convention.

3 Bioaccumulation

Measured and calculated log Kow values for PeCB vary between 4.8 and 5.18. The measured BCF values based on whole body wet weight vary between 3 400 and 13 000. In many cases the BCF value exceeds the limit of 5 000, indicating a high potential for accumulation. Van de Plassche (1994) reviewed the information on bioconcentration in fish and molluscs for PeCB and derived a geometric mean BCF for fish of 5 300 L/kg. The Canadian Environmental Protection Agency (2002) reports BAFs of 810 in mussel (*Mytilus edulis*), 20 000 in rainbow trout (*Oncorynchus mykiss*) and 401 000 for earthworms (*Eisenia andrei*).

As the reported bioaccumulation factors are high, in can be concluded that PeCB meets the screening criteria for bioaccumulation laid down in Annex D of the Stockholm Convention.

4 Potential for long-range environmental transport

The vapour pressure of PeCB is 2.2 Pa at 25 °C, and the calculated half-life in air is 277 days, ranging from 45 to 467 days (Van de Plassche et al. 2002). These two properties seem to indicate the PeCB is very likely to undergo long range environmental transport (LRET). In table 1 the values for water solubility, vapour pressure and Henry's law constant for PeCB, can be compared with the maximum and the minimum for currently listed POPs. Henry's law constant, a key property to determine if there is risk of long range environmental transport for a substance, is well inside the range set by the other POPs, which also supports the potential of LRET for PeCB.

Table 1: Water solubility (WS), vapour pressure (VP) and Henry's Law Constant (HLC) for pentachlorobenzene and currently listed POPs.

Substance	WS mg/L	VP Pa	HLC Pa m^3/mol
PeCB	0.56 *	2.2 *	983.4 **
POP-min	0.0012 (DDT)	2.5×10^{-5} (DDT)	0.04 (endrin)
POP-max	3.0 (toxaphene)	27 (toxaphene)	3 726 (toxaphene)
POP-2nd max	0.5 (dieldrin)	0.04 (heptachlor)	267 (heptachlor)

* Van de Plassche et al. 2002
** Calculated from VP and WS

There is also evidence based on modelling data. 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 modelling performed by Vulykh *et al*. (2005) gives a similar value: 8 256 km.

PeCB was also actually detected in air samples collected in 2000 at the 40 sampling stations in North America (Canada, USA, Mexico, Belize and Costa Rica), including 5 Arctic stations (Shen et al 2005). The air concentrations were almost uniform across North America with an average concentration of 0.045 ng/m^3 and a range 0.017 – 0.138 ng/m3. According to the authors, this 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.

In Sweden PeCB was also detected in all 8 analyzed air samples (median 0.033 ng/m^3) and in two atmospheric deposition samples (max 0.16 ng/m2.day) collected in the Stockholm area (Kaj and Palm 2004).

In all bottom sediments from harbours of northern Norway and the Kola Peninsula in the Arctic, PeCB ranged from 2 - 5 µg/kg dry weight (n= 6, AMAP 2004). These concentrations are similar as detected in less remote areas in Sweden: PeCB was detected in 3 of the 20 freshwater sediment samples collected in 2002 in the Stockholm area (Sternbeck et al 2003). The maximum concentration was 6 µg/kg dry weight. Also in another study, PeCB was detected in Swedish sediment samples (4 out of 6 samples, median 1 µg/kg dry weight) (Kaj and Palm 2004).

PeCB was detected in fish muscle collected in 2002 at Swedish marine and freshwater sites regarded as uncontaminated. Kaj and Dusan (2004) measured 2.2 ng PeCB/g lipid weight in herring from one location and maximum 16 ng PeCB/g lipid weight in perch from two different locations.

In the Netherlands, PeCB was detected in all 10 flounder liver samples collected in 1996, including from 2 relatively unpolluted reference locations (De Boer et al 2001). The highest concentration was 1100 μg/kg lw (280 μg/kg ww), and at the reference location 3 ng/g lw (0.64 ng/g ww). Also in 2003, PeCB was detected in 50% of the freshwater fish samples (eel and pike perch) in concentrations ranging between 1 – 10 ng/g ww (Van Leeuwen et al 2004).

PeCB was detected in different arctic species. Vorkamp et al (2004) analysed PeCB in biota from Greenland and measured the following concentrations in lipid and wet weight:
• Ptarmigan liver approx 23 ng/g lw (1.5 ng/g ww);
• Kittiwake muscle approx 8 ng/g lw (1.1 ng/g ww);
• Musk ox blubber approx 0.32 ng/g lw (0.29 ng/g ww);
• Arctic char approx 3.9 ng/g lw (0.07 ng/g ww).

A study by Verreault et al. (2005) shows that PeCB was found in polar bears' adipose tissue in a variety of Arctic populations (Alaska, Canada, East Greenland and Svalbard Islands). PeCB was also detected in all 15 plasma and fat samples of polar bear from the arctic Svalbard Islands with an average concentration of 7.9 and a maximum of 13.3 ng/g ww (Gabrielsen et al 2004). PeCB was detected in soils and mosses from coastal areas of Victoria Land (Antarctica) (Borghini et al 2005). Concentrations in the six mosses samples varied between 1-2.4 ng/g dw and in the four soil samples between 0.4 and 1.3 ng/g dw.

To sum up, modelling and monitoring data, as well as PeCB's chemical properties, indicate that this substance has a considerable potential for long range environmental transport and that it thus meets the screening criterion for bioaccumulation laid down in Annex D of the Stockholm Convention.

5 Adverse effects

PeCB is classified within the EU as "Harmful if swallowed" and "Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment". A review of the different adverse effects of PeCB can be found in the dossier by Van de Plassche et al. (2002). PeCB has been tested on rats and mice. Acute toxicity tests were available after oral and dermal exposure. The lowest LD50-value after oral exposure was for rats, i.e. 250 mg/kg body weight. In a study in which the rats were orally exposed to 250 mg/kg bw/day during 3 days, some liver functions were increased. 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. In a subchronic toxicity study oral uptake of 25 mg/kg bw and more resulted in effects on the liver and kidneys (increased weight and histopathological changes). A concentration of 12.5 mg/kg bw has been determined as NOEC. In a 15 days study by McDonald for the National Toxicologic Program (1991) the no-observed effect levels (NOELs) for histologic lesions were 33 mg/kg for male rats and 330 mg/kg bw for female rats. The NOEL for histologic lesions in female mice was 100 mg/kg bw. A NOEL was not reached for male mice.

PeCB was classified in Group V (inadequate data for evaluation) of the classification scheme for carcinogenicity (CEPA, 1993). Regarding teratogenic effects, suckling pups from mothers fed a dose of 12.5 mg/kg bw developed tremors 4- 14 days after birth. At a (maternal) dose of 6.3 mg/kg bw this effect did not occur. In another study female rats were administered PeCB at levels of 50,

100 and 200 mg/kg bw daily on day 6 through 15 of gestation. The number of live foetuses was not affected. The mean foetal weight was decreased in the highest dose group (Sloof et al., 1991).

Acute toxicity data for freshwater organisms is available on algae, crustaceans and fish. Chronic toxicity data is only available on crustaceans and fish. For marine organisms, only acute toxicity data is available for fish. Based on the data available, marine and freshwater organisms do not seem to differ significantly in sensitivity to PeCB. The lowest LC50 value for fresh water organisms is 250 µg/l for fish. The lowest NOEC is 10 µg/l for crustaceans.

The acute and subchronic tests, as well as the effects found in aquatic species, show that PeCB is moderately toxic to humans and toxic to aquatic organisms, and therefore fulfils the criteria for adverse effects.

6 Statement of the reasons for concern

PeCB is persistent in soil, water and the atmosphere. It has been prove to bioconcentrate in different species and to be toxic to aquatic organisms. It is also widely found in humans and biota in the environment as a result of its potential for long range transport.

Although its production seems to have ceased in Europe and North America, it is still present as an impurity in commercial pesticides which are still used, and it is unclear whether it may be used as a pesticide or flame retardant in other parts of the world. As PeCB can move in the atmosphere far from its sources, single countries or groups of countries alone cannot abate the pollution caused by it. Due to its harmful POP properties and risks related to its possible continuing production, use and releases to the environment, international action is warranted to control this pollution.

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