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Stockholm Convention on Persistent Organic Pollutants

Persistent Organic Pollutants Review Committee
Seventh meeting
Geneva, 10–14 October 2011
Item 6 (c) of the provisional agenda*

Consideration of chemicals newly proposed for inclusion in Annexes A, B and/or C to the Convention: pentachlorophenol and its salts and esters

Proposal to list pentachlorophenol and its salts and esters in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants**

Note by the Secretariat

1. The annex to the present note sets out a proposal submitted by the European Union and its member States that are parties to the Stockholm Convention on Persistent Organic Pollutants to list pentachlorophenol and its salts and esters in Annexes A, B and/or C to the Convention pursuant to paragraph 1 of Article 8 of the Convention. The proposal is being circulated as submitted and has not been formally edited. A detailed dossier prepared in support of the proposal is set out in documents UNEP/POPS/POPRC.7/INF/5, UNEP/POPS/POPRC.7/INF/5/Add.1 and UNEP/POPS/POPRC.7/INF/6. The Secretariat's verification of whether the proposal contains the information specified in Annex D is discussed in document UNEP/POPS/POPRC.7/INF/8.

Possible action by the Committee

2. The Committee may wish:

(a) To consider the information provided in the present note and in documents UNEP/POPS/POPRC.7/INF/5, UNEP/POPS/POPRC.7/INF/5/Add.1 and UNEP/POPS/POPRC.7/INF/6;

(b) To decide whether it is satisfied that the proposal fulfils the requirements of Article 8 of and Annex D to the Convention;

(c) To develop and agree on, if it decides that the proposal fulfils the requirements referred to in paragraph 2 (b) above, a workplan for preparing a draft risk profile pursuant to paragraph 6 of Article 8.

* UNEP/POPS/POPRC.7/1.

** Stockholm Convention on Persistent Organic Pollutants, Article 8, paragraph 1.

Annex

Proposal to list pentachlorophenol and its salts and esters in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants

Introduction

Pentachlorophenol (PCP) is an aromatic hydrocarbon of the chlorophenol family. PCP was first introduced for use as wood preservative in the 1930's. Since its introduction PCP has had a variety of other applications (biocide, pesticide, disinfectant, defoliant, anti-sapstain agent, anti-microbial agent, wood preservative and on the production of pentachlorophenyl laurate). The salt sodium pentachlorophenate (Na-PCP) was used for similar purposes as PCP and readily degrades to PCP. The ester pentachlorophenyl laurate (PCPL) is used in textiles. The environmental toxicity, fate and behaviour profile of PCP, Na-PCP and PCPL are quite similar. To provide a complete picture of the POP characteristics of PCP, its main metabolite pentachloroanisole (PCA) as well as the impurities in PCP and in PCPL (e.g. dioxins, furans and hexachlorobenzene) should be considered. In addition, formation of dioxins and furans during incineration of wastes is known in the presence of corresponding chlorinated precursors like PCP compounds.

Pentachlorophenol and its salts and esters are listed in Annex III to the Rotterdam Convention.

This dossier focuses solely on the information required under paragraphs 1 and 2 of Annex D of the Stockholm Convention and it is mainly based on the following documents:

(a) Pentachlorophenol, Dossier prepared in support of a proposal of pentachlorophenol to be considered as a candidate for inclusion in the Annex I to the Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants (LRTAP Protocol on POPs)[1].

(b) Addendum for PCP[2].

(c) Rotterdam Convention, Decision Guidance Documents, Pentachlorophenol and its salts and esters[3]

These review reports also serve as a source of further information referred to in paragraph 3 of Annex D of the Stockholm Convention on this candidate POP chemical.

1. Identification of the chemicals

1.1 Names and registry numbers

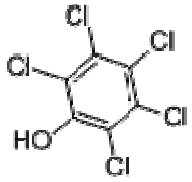
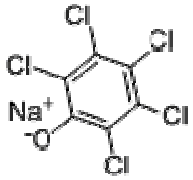
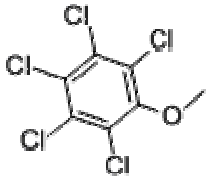
Pentachlorophenol: CAS RN: 87-86-5
Sodium Pentachlorophenate: CAS RN: 131-52-2
Sodium Pentachlorophenate monohydrate: CAS RN: 27735-64-4
Pentachloroanisole: CAS RN: 1825-21-4
Pentachlorophenyl laurate: CAS RN: 3772-94-9

1 http://www.unece.org/env/lrtap/TaskForce/popsxg/2008/Pentachlorophenol_RA%20dossier_proposal%20for%20submission%20to%20UNECE%20POP%20protocol.pdf

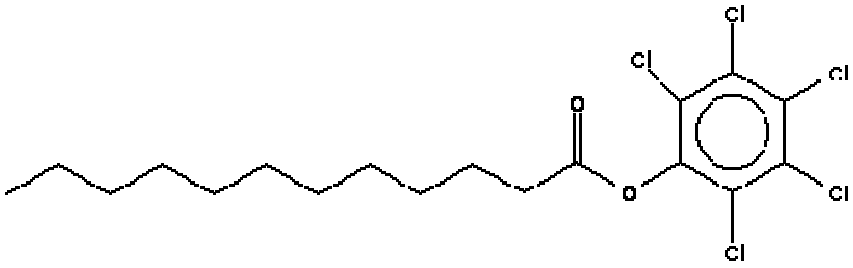
2 http://www.unece.org/env/lrtap/TaskForce/popsxg/2010/Updated%20documetns_June2010/Addendum%20PCP_100520%20final.pdf

3 http://www.pic.int/en/DGDs/PentachlophEN.doc

1.2 Structures

	Pentachlorophenol :	Sodium Pentachlorophenate	Pentachloroanisole
			
Formula	C_6Cl_5OH	C_6Cl_5ONa, $C_6Cl_5ONa \times H_2O$ (monohydrate)	$C_7H_3Cl_5O$
Molecular Weight	266.34	288.32	280.36

Pentachlorophenyl laurate



Formula C18H23Cl5O2
Molecular Weight 448.64

2 Persistence

Photolysis is the fastest known mechanism of PCP degradation and can lead to total mineralization of PCP in water within hours of its release. In air and clean water this is the relevant mechanism. In waters where turbidity and depth prevent exposure to light, in sediment and in soil, biodegradation is the relevant process.

Under normal environmental conditions the microflora will adapt and biodegrade PCP in water with half-lives less than 4 weeks, in the sediment less than 20 weeks and in soil less than 10 weeks. Many studies discuss the degradation of PCP in terms of mineralization, with some of them showing a slow rate of mineralization.
Under environmental conditions PCP is metabolised to PCA and vice versa. PCA is also considered as a substance of very high concern.

It has to be noted that only few data is available which makes it difficult to make a clear statement on persistency of PCA based on scientific facts. Studies pointing at disappearance of PCA from media such as soil and water are mainly driven by dissipation due to advective transport, governed by the volatilization to air. For overall environmental persistence the degradation rates are important and not the dissipation. It should be noted that under anaerobic conditions PCA is known to be demethylated to PCP. PCA were measured in the soil at a sawmill that was abandoned 28 years ago at concentrations from 0.06-1 µg/g dry soil. In addition, the presence and widely distribution of PCA in the environment, including remote area, demonstrated its persistence in the environment. This is also confirmed by the QSAR estimates of EPIWIN, which unanimously predict PCA to be persistent. So, PCA in itself is likely to be persistent

PCPL is used as a preservative treatment for textiles and leathers which will be subjected during use to microbiological attack by fungi and bacteria. The compound is very water insoluble but it slowly de-esterifies to produce PCP. It is believed that it takes 10 years for the PCPL concentration of treated materials to drop from 2% to <1% (Alcock and Jones 1997)[4]. When textile-finishing operations include a highly alkaline wash the pH of the wastewater is high and when wastewater-containing

4 Alcock, R. E. and K. C. Jones (1997). "Pentachlorophenol (PCP) and chloranil as PCDD/F sources to sewage sludge and sludge amended soils in the UK." Chemosphere 35(10): 2317-2330.

PCPL is mixed with this water, PCPL is likely to undergo chemical hydrolysis, producing PCP in its ionic form. When treated tents and tarpaulins are exposed to the weather, PCPL may undergo photodegradation but no studies on this release have been reported.

The presence of PCA in remote areas, the overall persistence of PCP and PCA, as well as quantitative structure-activity relationship estimates provide solid evidence of the persistency of these compounds.

3 Bioaccumulation

Log Kow of PCP varies between 1.3 and 5.86 with recommended values of 5.12 and 5.18. However, in this particular case, log Kow is not a good indicator of bioconcentration as PCP is subject to biotransformation. Furthermore logKow is strongly pH dependent.
The BCF in *crustacea*, bivalves, aquatic and terrestrial worms and in fish varies between 0.9 – 4900.

PCA is highly hydrophobic. The estimated log Kow is 5.30 and the experimentally log Kow value is 5.45.
For fish BCFs range from approximately 11000 - 24000 L/kg. In two studies on the bioaccumulation of organochlorine compounds in earthworms, concentrations of PCA in the soil and earthworms were measured at a sawmill that was abandoned 28 years ago. PCA concentrations in earthworms varied from 0.09 – 8 µg/g fat. Estimated BCF's from these studies range from 5-40 kg fat/kg dry soil.
PCA has been detected in several biotic matrices confirming the suggestion of a high bioaccumulation potential.

4 Potential for long-range environmental transport

PCP has been detected associated with particulate matter in air. This PCP will be lost by gravitational settling. Vapour phase PCP will be lost by photolysis and to a lesser extent, reaction with photochemically produced hydroxyl radicals. The loss from these processes in noon-day summer sunshine is 6.2 and 1.5 hr, respectively.
Pilot calculations of PCP transport from Hungarian and United Kingdom emission sources demonstrated that PCP is capable of being transported over considerable distances. Other model estimations resulted in transport distances of 1500-3000 km and an average half-life time in the environment equal to about 1.5 months.
The first peer-reviewed scientific studies of PCP in sub-arctic wildlife came out in 2004 and showed contamination of the eggs of 4 Norwegian bird-of-prey species – golden eagles, ospreys, peregrine falcons, and white-tailed sea eagles. PCA has been found in Canadian arctic snow and lake sediments indicating likely long-range transport of PCP to remote regions.

The calculated vapour pressure of PCA is very low (0.05 Pa). The calculated atmospheric half-live of PCA is at least 9.8 days.
PCA has been detected in remote areas far from point sources e.g. in the northern and southern hemisphere, in arctic snow and in fish in a remote lake. The physical-chemical properties of PCA suggest that it could be transported directly, but as PCA is a biodegradation product of PCP, its formation after transport of PCP cannot be excluded.

5 Adverse effects

PCP is highly toxic to mammals and birds. It is the most acutely toxic of the chlorophenols tested. Some of the acute effects of exposure to commercial PCP are attributable to microcontaminants present in the technical preparation. Numerous studies have described the developmental effects of pentachlorophenol and its dioxin and hexachlorobenzene contaminants. Depending on if certain manufacturing methods of PCP are still in use, contaminants may add considerably to the adverse effects of producing and using PCP. PCP is foetotoxic and teratogenic when administered during early gestation. There is a general agreement that PCP is a foetotoxic agent; however, it does not appear to be teratogenic. The data available on the carcinogenic properties of PCP were reviewed and it was concluded that no carcinogenic effects were evident in either species. The IARC therefore concluded that there is inadequate evidence for carcinogenicity to animals. A review of data by the Carcinogenic Assessment Group of the US EPA concluded that PCP was negative with respect to oncogenic effects. PCP probably does not cause mutations. The data available are insufficient to fully assess the mutagenicity of PCP. PCP has proved to be immunotoxic for mice, rats, chicken and cattle. Neurotoxic effects have also been reported.

Most of the available information regarding effects of pentachlorophenol in humans comes from cases of acute over-exposure following the home use of PCP in wood preservation and herbicides and occupational exposure in agriculture and the wood treatment industry. The few available industrial surveys and epidemiological studies are limited in their usefulness because of small sample size, short follow-up periods and brief exposure periods. Nevertheless, these studies suggest that PCP can adversely affect the liver, kidney, skin, blood, lungs and central nervous system.

PCP is highly toxic to aquatic organisms. Acute LC50 values for fish species ranged from 20 µg/l to 600 µg/l. Acute LC50 values for sensitive invertebrates including species of Daphnia, lymnaeid snails, and oligochaetes ranged from 240 µg/l to 2,000 µg/l. These data suggest that fish are somewhat more sensitive than invertebrates to PCP. Acute (96-hour) EC50 values for aquatic plants ranged from 80 µg/l to 7,000 µg/l. Lowest chronic NOECs varied between 2 µg/l and < 15 µg/l PCP with freshwater fish showing the lowest value.

PCA is not industrially produced and therefore not well studied and there is only limited data available dealing with its toxicity.
PCA was evaluated for its mutagenic potential. Based on the results, it can be concluded that PCA has to be considered as having mutagenic properties.
Toxicology and Carcinogenesis Studies of PCA were performed in the scope of the National Toxicology Program. The results show that PCA should be considered as a potential carcinogen. However, the present knowledge is not sufficient for a definite assessment. Nevertheless, it can be concluded that there is some evidence that PCA possesses carcinogenic properties.

Male and female rats were exposed to dietary levels of PCA for 181 days, through mating and pregnancy. The highest daily intake of PCA was associated with a decrease in the number of corpora lutea and increase in embryolethality. PCA exposure also resulted in reductions in fetal body weight and crown-rump lengths of males. Female foetuses were unaffected. The results indicate that PCP might be toxic to reproduction.
PCA should be considered as very toxic for aquatic organisms (lowest L(E)C50 is 27 µg/l).

However, even if PCA might not be as toxic as PCP the increased hydrophobicity resulting in longer body half-lives and higher potential to bioaccumulate should be considered when evaluating potential risks to environmental and human health. In addition, when assessing the toxicological potential of PCA it should be considered that PCA is demethylated back to PCP in living organisms.

6 Statement of the reasons for concern

According to the available data, PCP and its related compounds are persistent in the environment and are frequently found in environmental compartments in remote area. Some of the related compounds are precursors to PCP. They have a great potential for bioaccumulation. On the basis of their physical and chemical properties, atmospheric half-life, modelling data and findings in environmental samples, it has been proved that they are transported long distances, far from its sources. PCP and its related compounds are very toxic chemical for wildlife species and humans. In addition, technical PCP and PCP products contain POP contaminants (e.g., dioxin, PCBs, hexachlorobenzene) depending on the manufacturing method.

Placing on the market and use of PCP and its related compounds has been prohibited or restricted in several countries representing different regions of the world. However, it is still produced in some countries (Worldwide production estimated at 10,000 metric tonnes.) and it continues to be used in many countries. As these substances can move far from their sources, single countries or groups of countries alone cannot abate the pollution caused by them. Due to the harmful POP properties and risks related to their production and use, international action is warranted to control this pollution.