NEW POPs:
PENTACHLOROPHENOL, CHLORINATED NAPHTHALENES, HEXACHLOROBUTADIENE

Toxics Link
for a toxics-free world

NEW POPS IN STOCKHOLM CONVENTION

STOCKHOLM CONVENTION

The Stockholm Convention is a global treaty to protect human health and the environment from persistent organic pollutants (POPs). It was adopted in 2001 and entered into force in 2004.

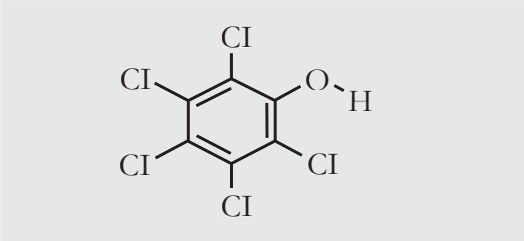
The Persistent Organic Pollutants Review Committee (POPRC) is a subsidiary body to the Stockholm Convention established for reviewing chemicals proposed for listing in Annex A, Annex B, and/or Annex C. Article 8 of the Stockholm Convention entails the reviewing process of new chemicals and Annex D, Annex E and Annex F specifies the information required for the review.

At its 7th meeting, the POPRC has proposed chlorinated naphthalenes and hexachlorobutadiene for listing under the convention and to prepare draft risk profiles for these chemicals. The Committee was also agreed to evaluate pentachlorophenol and its salts and esters.

In the seventh meeting of the Conference of the Parties (SC COP7), convened from 4-15th May in Geneva, three new chemicals have been listed as POPs: Pentachloro phenol (PCP), Chlorinated naphthalenes (CN or PCN) and Hexachlorobutadiene (HCBD).

PENTACHLOROPHENOL AND ITS SALTS & ESTERS

Pentachlorophenol (PCP) is an organochlorine compound belongs to the chlorophenol family. Among



the chlorophenols, pentachlorophenol (PCP) is quite persistent in the environment which causes serious pollution problem to the surface and subsurface environment.[i]

PCP, commonly known as "Penta", is used as pesticide and disinfectant. PCP was first produced in 1930s[ii] and is available as pure PCP, or as the sodium salts & esters.

USAGES OF PCP AND ITS SALTS & ESTERS

PCP has been used as a fungicide, molluscicide, insecticide, herbicide, algaecide, disinfectant, wood preservative and as an ingredient in antifouling paint. The use of PCP has been prohibited in agricultural and dometsic use however PCP is coninued to use for industrial purposes. The major usages of PCP are for masonry, wood preservation, cooling tower water, rope, and paper mills. During the manufacturing of PCP and its salts & esters, dioxins & furans are released as by-products.

PCPS AND ITS SALTS & ESTERS IN THE ENVIRONMENT

Pentachlorophenol has the tendency to adsorb to soil and sediment. It is moderately persistent in the soil environment, having half-life of 45[iii] days or less than 10 weeks[vii] in field. PCP degrades rapidly at higher temperatures in flooded or anaerobic (airless) soil, and in the presence of organic matter in soil[iii,vi]. The half-life for bacterial degradation of PCP ranges from 15 to 48 days.

PCP is strongly toxic to plants because of its defoliant and desiccant properties.[v] The chemical is also accumulated by aquatic organisms

through uptake from the surrounding water or along the food-chain (WHO, 1987)[vi].

HEALTH IMPACTS OF PCP AND ITS SALTS & ESTERS

There are research studies which show that PCP can cause health impacts on human being and animals. In human being, PCP is rapidly absorbed through the gastrointestinal tract following ingestion and accumulates in the liver, kidneys, plasma protein, brain, spleen, and fat.

There are evidences that PCP may have the potential to cause cancer. EPA has classified pentachlorophenol as a Group B2, probable human carcinogen.[vii]

STATUS OF PCP AND ITS SALTS & ESTERS IN DIFFERENT COUNTRIES

All EU Member States restricted the use of PCP in 1991 by Council Directive 91/173/EEC and all uses including wood preservation officially terminated at the end of 2008[xi]. In Sri Lanka all uses of PCP have been prohibited since 1994. Use of PCP as an agricultural chemical is banned in Japan. New Zealand has banned use of PCP in all forms since 1991. In Thailand, PCP has been banned for agricultural use since 1995, public health uses since 2000 and industrial use since 2001. In 1997, China restricted the production however, Na-PCP is still being used as the wood preservative.

PCP is banned partially or totally in many other countries as Austria, Denmark, Egypt, Germany, India, Indonesia, Italy, Jamaica, Korea, Malaysia, Netherlands, Panama, Sweden, Taiwan etc.

PCP AND ITS SALTS & ESTERS AS A NEW POP

PCP has been nominated as a candidate POP in the 7th meeting of POPRC of Stockholm Convention. The European Union and its Member States submitted a proposal to list pentachlorophenol and its salts & esters in Annex A, B and/or C of the Convention in the POPRC meeting held on October 10-14, 2011 in Geneva (UNEP/POPS/POPRC.7-4).

In 8th POPRC meeting, held in Oct 2012 at Geneva, the literature review and preliminary results from

ACUTE EXPOSURE

- Cardiovascular system
- Blood,
- Liver (jaundice),
- Eyes (visual damage and irritation)
- Neurological system

CHRONIC EXPOSURE

- Inflammation of the upper respiratory tract and bronchitis,
- Blood effects such as aplastic anemia,
- Effects on the kidney and liver,
- Reproductive effects
- Immunological effects, and
- Irritation of the eyes, nose, and skin

COUNTRY	LOCATION	YEAR	N[c]	AGE (YEARS)	MEDIAN	95TH	MAXIMUM	REFERENCE
Germany	National (GerES II)	1990-1992	695	6-14	4.6	14.9	26.5	Seifert *et al.*
Germany	National (GerES IV)	2003-2006	462	6-14	<0.6	1.6	___	Schulz *et al.*
USA	National (NHANES)[d]	2003-2004	290	6-11	<0.5	5.7	___	CDC
USA	AK. USA	1980' s[e]	197	2-6	14	110	240	Hill *et al.*
USA	NC. USA	1997	9	2-5	0.3[f]	___	0.7	Wilson *et al.*
USA	NC.USA	2000-2001	128	2-5	0.4	1.9	3.5	Wilson *et al.*
USA	OH. USA	2001	115	2-5	0.8	3.3	23.8	Curent study [g]

Note:
a,b All of these studies measured for total PCP in urine[viii,ix]; **c** Number of children; **d** The 1999–2002 NHANES data are not provided as they were withdrawn by the CDC because of "unacceptable calibration bias"[x] ; **e** Estimated date; **f** Mean value (no median value provided); **g** Values were calculated using data for 115 out of 128 children from Wilson et al.

Source:
Int. J. Environ. Res. Public Health

Figure 1: Urinary PCP levels (ng/ml) in young children from published studies worldwide [a,b].

the laboratory studies conducted by Japan were presented to the Committee. The Committee decided that, while the PCP and its salts & esters molecule do not meet all the screening criteria of POPs specified in Annex D, however their transformation product PentachloroAnisole (PCA) meets the criteria of being a POP.

In the tenth meeting of the Persistent Organic Pollutants Review Committee (POPRC-10), held at Geneva 27 to 30 October 2014, it was decided to adopt the risk management evaluation for PCP and its salts & esters.

In the 7th meeting of the conference of the parties of the Stockholm Convention was held in Geneva on 4-15, May 2015 adopted PCP and its salt & esters were included as POPs though India objected to the inclusion as a POPs. However for the first time in the history of Stockholm Convention voting took place and ninety-four countries voted in favor of global prohibition of pentachlorophenol and India opposed the voting.

STATUS OF PCP IN INDIA

In India, production, import and use of Penta or PCP is banned for agriculture, and leather industry. Its use as Na-PCP is allowed mainly as a wood preservative purpose on impregnated wood/ particle boards and also for the preservation of water-based 'distemper paints' while in storage. In India 1,800

International Regulations of PCP

PCP and its salts & esters are subject to a number of agreements, regulations and action plans:

(a) Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade;
(b) OSPAR List of Chemicals for Priority Action (1998) of the Convention for the Protection of the Marine Environment of the North-East Atlantic;
(c) Annex 1A (List of Priority Hazardous Substances) in the Third North Sea Conference;
(d) In addition, PCP has been nominated as a candidate for inclusion in Annex I of Long-range Transboundary Air Pollution (LRTAP) Protocol on POPs of the United Nations Economic Commission for Europe.

CHEMICAL ALTERNATIVES FOR WOOD PRESERVATION

	CREOSOTE AND OIL BORNE PRESERVATIVES				WATERBORNE PRESERVATIVES						
Product/application	Creosote	Creosote-petroleum	Creosote Solution	PentaChloroPhenol	Copper Naphthenate [d]	Chromated Copper Arsenate [e]	Ammonium Copper Quaternary (ACQ) – type C and type D	Ammonium Copper Quaternary ACQ – type B	Copper Azole type B	Copper Azole *type A*	Ammonical Copper Zinc Arsenate *(ACZA)*
Lumber, timbers and plywood											
C2-lumber, timber, bridge ties and mines ties	+	+ [a]	+	+ [a]	+ [a]	+	+ [a]	NA	+ [a]	+ [a]	+
C9-Plywood	+	+	+	+	NA	+	+	NA	+	+	+
C22-Permanent Wood Foundations	NR	NR	NR	NR	NA	+	+	+	+	+	+
C28-Glued laminate members	+	NA	NA	+	+	+	+	NA	NA	NA	+
Piles											
C3-Piles	+	+	+	+	+ [b]	+	+	NR	NR	NR	+
C18-Marine construction	+	NR	+	NR	NA	+	NR	NR	NR	NR	+
C21-Marine lumbers and timbers	+	NA	NA	+	+	+	+	NA	+	+	+
C24-Sawn timber used to support residential & commercial structures	+	NA	NA	+	NA	+	+	NA	NA	NA	+
Poles											
C4-Poles	+	NR	+	+	NA	+	NR	+	NR	NR	+
C23-Round poles and posts used in building construction	+	NR	+	+	NA	+	NR	NR	NR	NR	+
Posts											
C5-Fence posts	+	+	+	+	+	+	+	+	+	+	+
C14 – Wood for highway	+	+	+	+	+	+	+	+ [f]	+ [c]	+ [c]	+
C15 – Wood for commercial residential construction	+	+	+	+	+	+	+	NA	+	+	+
C16 – Wood used on farms	+	+	+	+	NA	+	+	NA	+	+	+
Cross-ties and Switch ties											
C6-Cross-ties and Switch ties	+	+	+	+	NR	NR	NR	NR	NR	NR	NR

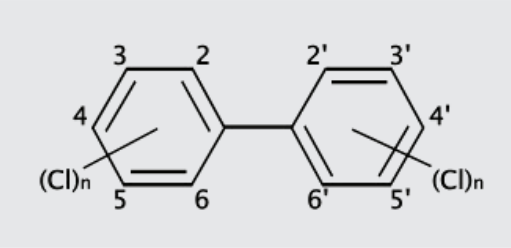
NA: Not available, NR: Not recommended

a) Not for saltwater use
b) Land and freshwater use; not for foundations
c) Posts sawn four sides only
d) Copper Naphthenate is also approved by AWPA as a waterborne preservative for some uses.
e) Chromated Copper Arsenate is available for industrial applications only
f) Round, half-round, and quarter-round only

Figure 2 Approved uses for preservatives in wood treatment (UNECE, 2010)

tons per year of Na-PCP is being produced in the state of Maharashtra and West Bengal[xii,xiii]. India is leading exporter of Na-PCB globally. Indian Chemical Council has opposed the listing of PCP as a wood preservative in Stockholm Convention. India has lodged protest in the UNEP secretariat against the inclusion of PCPs and its Salts and Easters as POP.

POLYCHLORINATED NAPHTHALENE



Polychlorinated Naphthalenes (PCNs) are halogenated organic compounds made from chlorine and naphthalene. The generic chemical formula is $C_{10}H_{8-n}Cl_n$. There are 75 possible chlorinated naphthalenes in eight homologue groups, based on the number of chlorine atoms in the molecule[xiv]. While PCNs are considered as a class, physical-chemical and toxicological properties vary by congener and homolog group[xv].

PCNs are structurally similar to the Polychlorinated Biphenyls (PCBs) and have dioxin-like activity. Due to their harmful POP properties and risks related to their possible releases to the environment, international action is necessary to control this pollution.

USAGES OF PCN

PCNs started to be produced for high-volume uses around 1910 in both Europe and the United States. PCNs have been used mainly in the electrical industry as separators in storage batteries, capacitor impregnates, as binders for electrical grade ceramics and sintered metals, and in cable covering compositions.

PCNs have also been used for impregnation of wood, paper and textiles to attain water-proof ness, flame resistance and protection against insects, molds and fungi.

Uses include:[xvi]

- Cable insulation
- Wood preservation
- Engine oil additives
- Other lubricant uses
- Electroplating masking compounds
- Dye carriers
- Capacitor fluids refractive index testing oils
- Flame proofing
- Preservatives
- Moisture proofing sealant
- Temporary binders for ceramic component manufacture
- Casting material for alloys

PCNs are also formed in various incineration processes[xvii] and industrial processes such as production of magnesium, copper and chloroalkali[xviii].

PCN IN THE ENVIRONMENT

PCNs are generally found in all types of biological samples, even from the remote areas. PCNs have been detected in air, sediment, soil, water, biota (freshwater and marine organisms as well as birds and otters) and human beings[xix].

Besides the industrial production of PCNs, there is also a release of PCNs to the environment via polychlorinated biphenyl (PCB) commercial products, in which PCNs are present as minor contaminants[xx].

HEALTH IMPACTS OF PCN

PCNs can be absorbed via all routes of exposure: ingestion, inhalation & dermal absorption. PCNs have been concluded to be potent foetotoxic and teratogenic agents producing effects similar to those for other toxic dioxin-like compounds. In addition, a potential for endocrine disruption is suggested at very low exposure concentrations.

STATUS OF PCN IN DIFFERENT COUNTRIES

At present, there is no intentional production and use of PCNs within the UNECE region [UNECE

2009]. Only unintentional emissions of PCNs in UNECE regions originating from thermal processes have been reported[xxi]. In Japan, PCNs are prohibited entirely since 1979[xxii]. The production of CN is ceased in United States & Europe since 1980s[xxiii]. There is no information available about the production of technical CN formulations in China[xxiv]. In Australia commercial production is ceased however PCN-1 and PCN-2 (1-chloronaphthalene and 2-chloronaphthalene) are still used in small amounts for scientific research[xxv].

PCN AS A NEW POP

European Union and its Member States submitted a proposal to list chlorinated naphthalene under Annex A, B and/or C to the Convention in the 7th POPRC meeting held, October 10-14, 2011 in Geneva (UNEP/POPS/POPRC.7-4) together with a detailed dossier to support the proposal (UNEP/POPS/POPRC.7/INF/3).

In ninth POPRC meeting, held on 14 to 18 October 2013 at Geneva, the POPRC Committee recommended to consider listing and specifying the related control measures for PCN in Annexes A and C.

Status of the PCN under International Conventions

Chlorinated Naphthalenes are subject to a number of international treaties and conventions:

(a) In December 2009, PCN were proposed for inclusion in Annex I (prohibition of production and use) to the Aarhus Protocol on Persistent Organic Pollutants under the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP), according to Decision 2009/2. The amendment will come into force when two thirds of the Parties have adopted the amendment.

(b) The OSPAR Commission has included PCN in the List of Chemicals for Priority Action. http://www.ospar.org/.

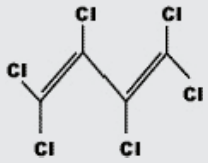
(c) Waste containing PCN is characterized as hazardous waste under Annex VIII of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal.

7th Ex-COP meeting was held on 4-15 May 2015 at Geneva. In the meeting, Committee has accepted and listed Polychlorinated Naphthalene as POPs in Annex A & C to the Convention. However the specific exemptions were granted for PCNs in the production of polyfluorinated naphthalenes, including octafluoronaphthalene and polyfluorinated naphthalenes, including octafluoronaphthalene. Russia is the only country which opposed the inclusion of PCN.

STATUS OF PCN IN INDIA

In India, details of use and production of PCNs are not available; however, it is banned in printing ink for food packaging under BIS standard IS 15495:2004.

HEXACHLOROBUTADIENE (HCBD)



Hexachlorobutadiene (HCBD) is a halogenated aliphatic hydrocarbon mainly generated as a by-product in the manufacturing of chlorinated hydrocarbons like tri- and tetrachloroethene and tetrachloromethane. It has the empirical molecular formula C_4C_{16}.

HCBD has been used in several technical and agricultural applications e.g. as intermediate in the chemical industry or as a product.

USAGES OF HCBD

Hexachlorobutadiene is used mainly as[xxvi].

- solvent (for rubber and other polymers);
- scrubber to recover chlorine containing gas or to remove volatile organic components from gas;
- hydraulic, heat transfer or transformer fluid;
- in gyroscopes
- in production of aluminium and graphite rods
- an insecticide in vineyards (a pesticidal fumigant.)

HCBD is still unintentionally released by industry, including during waste management. Relevant sources are the production of chlorinated hydrocarbons, production of magnesium, and incineration processes.

HCBD IN THE ENVIRONMENT

HCBD is detected in abiotic and biotic media as surface waters, drinking water, and ambient air, aquatic and terrestrial organisms, even in remote areas such as the Arctic.

Estimated half-lives of HCBD in water range from 3 days to 12 months. Half-lives in soil estimated to be 4 to 26 weeks based on estimated aqueous aerobic biodegradation half-life[xxvii]. Half-life data for sediment are not available, although sediments are a sink for HCBD. HCBD can also leach from waste landfills[xxviii].

HEALTH IMPACTS OF HCBD

Hexachlorobutadiene has been observed to produce systemic toxicity following exposure via oral, inhalation, and dermal routes. Effects may include fatty liver degeneration, epithelial necrotizing nephritis, arterial hypotension, myocardial dystrophy, chest pains, upper respiratory tract changes, sleep disorders, hand trembling, nausea and disordered smell functions, central nervous system depression and cyanosis[xxix].

The carcinogenicity of HCBD has been classified by the United States Environmental Protection Agency as a group C Possible Human Carcinogen[xxx].

STATUS OF HCBD IN DIFFERENT COUNTRIES

Its use and production have ceased in the UN-ECE countries but information about ongoing application outside the UN-ECE is not currently available.

HCBD is strictly banned in Canada & Japan. It is no longer intentionally produced in the UN-ECE region including the USA (terminated around 1970) and Canada[xxxi]. Its intentional production in Europe ended in the late 1970s. However, data from China[xxxii] and Taiwan[xxxiii] suggest that production has continued till now.

HCBD AS A NEW POP

The European Union and its Member States submitted a proposal to list Hexachlorobutadiene (HCBD) in Annex A, B or C in the seventh meeting of the Stockholm Convention held on 10 May 2011.

In its ninth meeting, of POPRC committee from 14 to 18 October 2013, the Committee adopted a risk management evaluation for Hexachlorobutadiene and concluded that although HCBD is not known to be intentionally produced or used, it is important to prevent its re-introduction and manage the risks associated with its unintentional release. The Committee recommended the listing and specifying the related control measures for HCBD in Annexes A and C.

In SC COP7, convened from 4-15 May in Geneva, HCBD is listed as new POPs in Annex A & C. HCBD without any exemption to any country.

Status of HCBD under international conventions

HCBD is subject to a number of international treaties and regulations:

(a) Production and use of HCBD is banned under the Convention on Long-Range Transboundary Air Pollution (Dec 2009). The amendment will come into force when 2/3rd of the Parties have adopted the amendment.

(b) The UN-ECE (United Nations Economic Commission for Europe) has included HCBD in Annex II of the Protocol on Pollutant Release and Transfer Registers (PRTR) to the AARHUS Convention on access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters.

(c) HCBD is currently under a review process by the Chemical Review Committee (CRC) for inclusion under the Rotterdam Convention. (http://www.pic.int)

(d) Within the Great Lakes Bi-national Toxics Strategy, a U.S.-Canada agreement under the Great Lakes Water Quality Agreement, HCBD is identified as a Level II Substance (US EPA, 2012b)

(e) In the European Union, Decision No 2455/2001/EC on a first list of priority substances of the adopted EU Water Framework Directive 2000/60/EC listed HCBD in its Annex.

(f) HCBD is on the List of Substances of Possible Concern, Section B under the OSPAR Commission for the Protection of the Marine Environment of the Northeast Atlantic.

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