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**Stockholm Convention on Persistent Organic Pollutants**

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

**Consideration of chemicals newly proposed for inclusion in Annexes A, B and/or C to the Convention: chlorinated naphthalenes**

# Proposal to list chlorinated naphthalenes 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 chlorinated naphthalenes 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 document UNEP/POPS/POPRC.7/INF/3 and 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 document UNEP/POPS/POPRC.7/INF/3;

(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 chlorinated naphthalenes in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants

### Introduction

Chlorinated naphthalenes (CNs) are a group of theoretically 75 possible chlorinated naphthalenes, containing one to eight chlorine atoms. They are structurally similar to the PCBs.
CNs - commercially produced as mixtures of several congeners e.g. Halowax, Nibren Waxes, Seekay Waxes and Cerifal Materials - became popular chemicals after 1910 but their production decreased in the late1970s. CNs were commercially produced as mixtures of several congeners with different product names. Until the 1970s CNs were high volume chemicals. The total global production of CNs was estimated at 150,000 metric tonnes until that period. Production ceased in the UNECE region in the 1980's. Most important uses of CNs were for wood preservation, as additive to paints and engine oils, and for cable insulation and in capacitors. Some uncertainties remain with regards current production and uses of CNs outside the UNECE region.

Besides these uses CNs are present in technical PCB formulations and can be formed in thermal processes, of which waste incineration is the most important.

Current emissions of CNs are probably mainly caused by unintentional releases from combustion processes to produce heat and power, from industrial processes, solvent use and waste incineration.

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 document: :

- Polychloronaphthalenes, Dossier prepared in support of a proposal of polychloronaphthalenes 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].

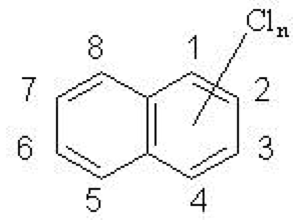
This extensive review report also serves as a source of further information referred to in paragraph 3 of Annex D of the Stockholm Convention on this candidate POP chemical.

#### 1. Identification of the chemical

The identity and chemical structure of chlorinated naphthalenes is shown below:

CAS number: All CNs and their mixtures have different CAS-numbers which can be found in Crookes and Howe (1993)[2];

Chemical formula: $C_{10}H_{8-n}Cl_n$
Synonyms / trade names: Halowax, Nibren Waxes, Seekay Waxes and Cerifal Materials, N-Oil;
Abbreviations: monochlorinated naphthalene: mono-CN; dichlorinated naphthalene: di-CN etc.




The technical formulations exhibit a wide range of patterns from nearly pure mono-CNs (Halowax 1031) to nearly pure octa-CNs (Halowax 1051).

1 http://www.unece.org/env/lrtap/TaskForce/popsxg/2000-2003/pcn.pdf

2 Crookes, M.J. and Howe, P.D. (1993). Environmental hazard assessment: halogenated naphthalenes. Department of the Environment, Directorate for Air, Climate and Toxic Substances, Toxic Substances Division.

## 2 Persistence

Limited information is available on biodegradation of CNs in water, sediment and soil. The biodegradability has been reported as poor. Only half-lives for 2-mono-CN are presented varying from 38 to 104 days (Crookes and Howe, 1993). As it is the case for PCBs, higher chlorinated congeners of CN should be even less biodegradable than the 2-mono-CN.

Indirect evidence for the persistence of CNs is based on the identical congener distribution of contaminated soil compared to Halowax 1013 after 10-15 years being covered by a Dutch landfill (Crookes and Howe, 1993).

A substantial amount of monitoring data is available for CNs, also in remote regions. CNs have been detected in air, sediment, soil, water, biota (freshwater and marine organisms as well as birds and otters) and human beings. Overviews are presented by Crookes and Howe (1993) and Falandysz (1998)[3]. In the past few years CNs have also been monitored in arctic air and in some other remote regions. Such monitoring data indirectly show that CNs are persistent substances.

Their chemical analogy with PCBs is an additional argument for concluding on the persistency of the CNs.

## 3 Bioaccumulation

The BCF of CNs increases with increasing degree of chlorination up to the penta-CNs with values as high as 33113 L/kg. No uptake occurs for hepta- and octachloro-CNs having molecular diameters higher than 0.95 nm. It is clear that the BCF for fish for CNs is higher than 5000 for several congeners. This is supported by the high log Kow values for CNs ranging from 3.9 and up to 8. Lower BCFs have been found in shrimps, algae and worms.

## 4 Potential for long-range environmental transport

The vapour pressure of CNs at 25 °C ranges from 1.3 $10^{-4}$ (octa-CN) to 2.1 (mono-CN). The estimated half-life in air ranges from 1 day (mono -CN) to 4.37 days (octa-CN).

Mantseva et al (2004)[4] developed a multicompartment 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 2000 km is calculated for CN-47 (tetra-CN).

The presence of CNs in air at remote locations, and locations receiving unpolluted air also indicates that CNs are subject to long range transport.

## 5 Adverse effects

CNs are structurally similar to the PCBs and some congeners may have a similar toxicity as some of the most toxic coplanar congeners of PCBs. CNs have dioxin-like activity. TEFs ranging from 2 $10^{-8}$ (di-CN) to 4 $10^{-3}$ (hexa-CN) have been calculated. These TEFs are similar to those for some PCBs.

Data on the sub-acute toxicity of CNs has been centered on the poisoning of cows, causing a disease called bovine hyperkeratosis or X-disease. The toxicity of CNs to cows after oral exposure was found to increase with increasing chlorination, the tetra-CNs and lower chlorinated congeners having little or no effect. (Sub)chronic toxicity tests have been performed with several test species, i.e. rats, guinea pig, sheep and cattle. The most toxic congeners appeared to be penta- and hexa-CNs.

Exposure of CNs has long been known to be associated with chloracne and lethality in occupationally exposed men, however it cannot be ruled out that this was caused by other contaminants such as dioxins or PCBs.

Tests with mono- and di-CNs resulted in L(E)C50 values of 0.69-2.4 mg/l for fish and 0.37-2.82 mg/l for crustaceans. Tests with Halowaxes resulted in LC50 values of 0.0075-0.44 mg/l for *Penaeus aztecus* and Palaemonetes *pugio*.

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3 Falandysz., J. and Rappe, C. (1996). Spatial distribution in plankton and bioaccumulation features of polychlorinated naphthalenes in a pelagic food chain in southern part of the Baltic Proper. Environ. Sci. Technol., **30**, 3362-3370.

4 Mantseva E, S Dutchak, O Rozovskaya, V Shatalov. 2004. EMEP contribution to the preparatory work for the review of the CLRTAP Protocol on Persistent Organic Pollutants. EMEP MSC-E Information Note 5/2004. Meteorological Synthesizing Centre –East, Moscow, Russia (available at http://www.msceast.org/protocols.html)

Sheepshead minnow eggs were exposed to 1-mono-CN from fertilisation to 28 days post-hatch. No effects were observed on survival and growth up to 0.39 mg/l. At 0.79 mg/l all fish died within 28 days.

## 6 Statement of the reasons for concern

According to the available data, CNs are persistent in the environment and are found in environmental compartments. They have a great potential for bioaccumulation. Due to their physical and chemical properties and atmospheric half-life, and based on modelling data and findings in environmental samples, it has been proved that CNs are transported long distances, far from its sources. CNs are toxic for aquatic organisms and their pattern of toxicity resembles that of dioxins.

Although CNs production seems to have ceased in Europe and North America, it is unclear whether it may be still produced and used in other parts of the world. Current emissions of CNs are probably mainly caused by unintentional releases from combustion processes to produce heat and power, from industrial processes, solvent use and waste incineration. Due to their harmful POP properties and risks related to their possible continuing production, use and releases to the environment, international action is warranted to control this pollution.