Exploration of management options for
Polychlorinated Naphthalenes (PCN)

Paper for the 6th meeting of the UNECE CLRTAP Task Force on Persistent Organic Pollutants,
Vienna, 4-6 June 2007

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For
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Date 25 May 2007
Reference
Status Final
# Table of Contents

Summary ........................................................................................................................................................................................................... 3

1 Introduction................................................................................................................................................................................................. 5

2 Characteristics of PCN ............................................................................................................................................................................... 7

3 Current Sources of Emission .................................................................................................................................................................... 9
   Production and use ....................................................................................................................................................................................... 9
   Emission from production and use ........................................................................................................................................................... 10

4 Management options................................................................................................................................................................................ 13
   Overview of existing legislation in the UN ECE region ........................................................................................................................... 13
   Substitution and alternatives ..................................................................................................................................................................... 13
   Emission Control Techniques ............................................................................................................................................................... 13
   Cost implications......................................................................................................................................................................................... 14

5 References ................................................................................................................................................................................................ 16

Annex: information from questionnaire ............................................................................................................................................................ 17
Summary

Polychlorinated Naphthalenes, or PCNs, are organic chemical compounds based on the naphthalene ring system, where one or more hydrogen atoms have been replaced by chlorine. The generic molecular formula is \( C_{10}H_{8-n}Cl_n \), where \( n = 1–8 \). There are 75 different congeners of PCN with different physical and chemical properties. The congeners and their mixtures have different CAS numbers.

Production, use and emissions
PCNs were commercially produced as mixtures of several congeners with different product names. Until the 1970s PCNs were high volume chemicals. The global production of PCNs is estimated at 150,000 metric tonnes. Production ceased in the UN ECE region in the 1980’s.

Most important uses of PCN were for wood preservation, as additive to paints and engine oils, and for cable insulation and in capacitors. Besides these uses PCNs are present in technical PCB formulations and can be formed in thermal processes, of which waste incineration is the most important.

Current emissions of PCN are caused by unintentional releases from combustion processes to produce heat and power, from industrial processes, solvent use and waste incineration. Total emissions in the UN ECE Europe region are estimated at 1.03 tonnes per year. Emissions in USA/Canada could be estimated to be in the same order of magnitude.

Management options
In order to remediate concerns and risks related to production and use of PCN it is possible to list PCN in annex I of the POPs protocol in order to eliminate its production and use. As PCN is not produced or used in the UN ECE region anymore there are no specific problems with substitution and there are no specific costs involved with a ban on production and use. Listing in Annex 1 is possible and will contribute to the reduction of PCN levels in the environment.

As PCN is not used in the UN ECE region anymore there is no need to allow for certain uses of PCN through a listing in Annex II.

Measures to reduce emissions of PCDD/Fs and of PAH will also reduce unintentional emissions of PCN. Adding of PCN to Annex III will not change the measures already taken. There is no added value in taking up PCN in Annex III.

It is suggested to add PCN as a group of substances to Annex I, in order to eliminate production and use of all PCNs.
1 Introduction

*Polychlorinated naphthalenes regarded as a POP.*
At the 24th session of the Executive Body the Parties to the POP Protocol decided that Polychlorinated naphthalenes (PCNs) are to be considered as a POP as defined under the Protocol. The EB requested the Task Force to continue with the Track B review of the substance and to explore management options for it. The Task Force was invited to complete the reviews preferably in time for presentation to the 40th session of the Working Group on Strategies and Review (WGSR) in September 2007.

*Review of the Protocol*
Also at the 24th session of the Executive Body the Parties to the POP Protocol requested the WGSR to prepare a proposal, as appropriate, for revising the Protocol in the light of the on-going work on management options for PCN. This document “Exploration of Management Options for PCN” is, therefore, an important building stone. First, for the Task Force to report on management options for PCN, and second, together with the report of the Task Force for the WGSR to prepare these proposals.

*Preparation of this document and use of the questionnaire*
This document is based on the information in the dossier that was presented to the Task Force POPs, completed with new information from Parties to the Protocol, from the review of the Gothenburg protocol and that was available in literature and on the Internet.

At its fifth meeting in Tallinn, 2006, the Task Force agreed that a questionnaire was to be sent to all Parties to the Protocol and to other stakeholders. This questionnaire was aimed at gaining a better view on management strategies and options in Europe and North America.

The information received from this survey was used to compile this document. In general it can be stated that the questionnaire did not yield much new data. Because the time between the preparation of the dossiers for the Task Force and the questionnaire was relatively short (2 to 4 years) not much new research was done and not many new inventories were made. Furthermore, data on emissions are scarce because the production and use of most of the POPs under consideration has decreased significantly or was completely stopped.

The questionnaire was sent to the Parties to the protocol and to a group of stakeholders from industry. 61 questionnaires were sent and in total 19 responses were returned. Eight of these 19 questionnaires contained answers to the questions about PCN. The information in the answers to the questionnaires is taken up in this document. A summary of the results of the questionnaire is presented as an annex to this document.
About this document
This document gives information on the substance under consideration (chapter 2),
gives an overview of the known use and sources of emissions in the UN ECE region
(chapter 3), and presents information on management options (chapter 4).
2 Characteristics of PCN

Polychlorinated Naphthalenes, or PCNs, are organic chemical compounds based on the naphthalene ring system, where one or more hydrogen atoms have been replaced by chlorine. The generic molecular formula is $C_{10}H_{8-n}Cl_n$, where $n = 1–8$.

**Chemical and physical properties**
There are 75 possible congeners of PCN in eight homolog groups with one to eight chlorines substituted around the planar aromatic naphthalene molecule. While PCN are considered as a class, physical-chemical and toxicological properties vary by congener and homolog group. The chlorinated naphthalenes are usually identified using this numbering system.

Polychlorinated naphthalenes are structurally similar to the PCBs.

Chemical formula: $C_{10}H_{8-n}Cl_n$

All PCNs and their mixtures have different CAS-numbers.

Synonyms and trade names are: Halowax, Nibren Waxes, Seekay Waxes and Cerifal Materials, N-Oil.

Abbreviations: polychlorinated naphthalene: PCN; monochlorinated naphthalene: mono-CN; dichlorinated naphthalene: di-CN etc.

Example of a PCN congener.

The technical formulations exhibit a wide range of patterns from nearly pure mono-CNPs (Halowax 1031) to nearly pure octa-CNPs (Halowax 1051). PCNs have physical and chemical properties similar to PCBs: hydrophobic, high chemical and thermal stability, good weather resistance, good electrical insulating properties and low flammability.

PCNs and mixtures are low viscosity oils to high melting solids with intermediate wax like solids varying in crystallinity and melting points. They are soluble in organic solvents (benzene, petroleum ether, alcohol, chloroform, ligroin).
3 Current Sources of Emission

Production and use

PCNs were commercially produced as mixtures of several congeners with different product names e.g. Halowax, Nibren Waxes, Seekay Waxes and Cerifal Materials. Until the 1970s PCNs were high volume chemicals, e.g. in the 1920s the worldwide production was approximately 9000 tonnes per year. The most important uses, in terms of volume, have been in:

- cable insulation
- wood preservation
- engine oil additives
- electroplating masking compounds
- feedstocks for dye productions
- dye carriers
- capacitors
- refracting index oils

Besides these uses PCNs are also present in technical PCB formulations and can also be formed in thermal processes, of which waste incineration is the most important (see emissions).

Production of PCNs decreased significantly since 1977. The production of PCNs in the USA stopped in 1980. Main producers were Bakelite Corporation and Koppers Company Inc. in the USA (Halowax). The production of technical PCNs by Koppers Company ceased in 1977. In the USA only small amounts of PCNs – approximately 15 tonnes per year – were used in 1981, mainly as refractive index testing oils and capacitor dielectrics.

In the UK the production stopped in the mid 60s, although it was reported that in 1970 small amounts of PCNs were still being produced. In Germany around 300 tonnes were produced in 1984, mainly for use as dye intermediates. It was reported that that there was use as casting materials until 1989 in Germany and former Yugoslavia.

In Europe, Bayer produced PCNs in a range of 100 to 200 tonnes per year between 1980 and 1983 and ceased PCN production in 1983.

Based on the assumption that the PCN production was 10% of the PCB production the global production was estimated to be approximately 150,000 metric tons. As PCNs were mainly used between 1920 and 1980 it is probably impossible to obtain a more exact figure on the global production volume. There is growing evidence that PCNs are widespread pollutants found on a global scale.
As already stated in the USA only small amounts were used in 1981 as refractive index testing oils and capacitor dielectrics. Possible new uses according to the US-EPA would be as intermediate for polymers and flame-retardants in plastics (Crookes and Howe, 1993). However, more information on these uses is not presented.

In Australia PCN-1 and PCN-2 (1-chloronaphthalene and 2-chloronaphthalene) are still used in small amounts for scientific research (NICNAS 2002).

**Emission from production and use**

As there is no production of PCN anymore there are no intentional emissions. Because the production has stopped there is a lack of data on several aspects. For the same reason there is no need for additional data.

Only unintentional emissions still contribute to PCN levels in the environment. The emissions of PCNs in UNECE-Europe were calculated for the year 2000 by TNO. The total emission was estimated to be 1.03 tonnes/year (Denier van der Gon et al 2005). This value is based on data from individual countries and expert estimates where detailed data were missing.

*Estimated annual emissions of PCNs per source category for the year 2000*

<table>
<thead>
<tr>
<th>Source category</th>
<th>Emission of PCN, tonnes/year.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Public power and heat</td>
<td>0.01</td>
</tr>
<tr>
<td>Residential combustion</td>
<td>0.10</td>
</tr>
<tr>
<td>Industrial combustion and processes</td>
<td>0.11</td>
</tr>
<tr>
<td>Solvent and product use</td>
<td>0.06</td>
</tr>
<tr>
<td>Waste incineration</td>
<td>0.74</td>
</tr>
<tr>
<td>Total emissions est.</td>
<td>1.03</td>
</tr>
</tbody>
</table>

The environmental levels in air measured at 71 locations in 22 countries across the European continent indicate that there are emissions from technical mixtures of PCNs. It was estimated that PCB mixtures like the Arochlor or Clophen series can contain PCNs. A median value of 0.0067% PCNs with a maximum of 0.087% was reported. This could be a pathway for PCN emissions to the environment. This is elaborated below.

*Additional information resulting from the questionnaire*

The questionnaire that was sent out by The Netherlands to the Parties to the Convention and to the stakeholders resulted in 13 responses regarding PCNs. None of the countries reported current production or use of PCN. The only production of PCN could occur as a by product of the production of PCBs. The total emission of PCN as a by product is estimated for Canada to be about one tonne in 2003.
Illegal production and use
This overall picture may not be totally correct. There are indications of possible ongoing illegal sale and use of PCNs. Recent reports from Japan suggested that PCN formulations may have been imported very recently from suppliers in North America and Europe as recently as the late 1990s. It is not known whether these reported illegal activities represent isolated incidents or hint at more widespread illegal trade and use of PCN stockpiles. However, further investigations on the scale of these unknown but indicated production and uses of PCNs is not needed in order to evaluate the overall impact of management options.

Based on the information in the dossier and the additional information from the questionnaire it is concluded that there is no commercial use of PCNs any more.

The concentrations measured in the environment nowadays originate from unintentional emissions from the following sources:
- historical use of PCNs;
- historical and present use of PCBs;
- thermal processes and waste incineration;
- landfills.

Emissions of PCN as a by-product in PCB
The total amount of production of PCNs as a by product of PCB production was estimated to be <0.1% of the total estimated global production of PCNs of 150,000 tons.
For Europe the emissions of PCNs from the use of PCBs were estimated to be 6% of the yearly emissions of 1 tonne. For Canada the total emission of PCN as a by-product of PCB production is estimated at about one tonne in 2003.

Emissions from thermal and other processes
PCNs are known to be formed in thermal processes, of which waste incineration is the most important. The formation mechanism of PCNs in incineration plants is not exactly known. Total emissions of PCN from thermal processes and incineration were estimated to be 74% of the total PCN emissions in Europe in the year 2000. Incineration of waste is probably the most important source of remaining emissions of PCNs.

Other thermal processes possibly resulting in PCN emissions are copper ore roasting and aluminium reclamation. Also the chlor-alkali industry was mentioned as a possible source of unintentional release of PCNs, but there is no information available.

According to the Norwegian Pollution Control Authority there is still emission and discharge of PCNs from cement kiln industry, municipal waste incineration and magnesium production in Norway. Data for one cement kiln plant showed an emission of 60.5 g/year (SFT, 2001).
Total current emissions of PCN
The emissions of PCN for the UN ECE Europe region are estimated at 1.03 tonnes/year. The emissions in the USA/Canada can be estimated to be in the same order of magnitude. Total emissions of PCN in the UN ECE region are expected to decline with decreasing use of PCB and with increasing use of emission abatement technology on high temperature processes.
4 Management options

Overview of existing legislation in the UN ECE region

National and international regulation
Production of PCNs stopped in the seventies and eighties of the last century. From reviews it is unclear whether industry voluntarily stopped production after negotiations with national authorities or that national regulations banning PCNs were needed.
In response to the questionnaire Switzerland reported that the use of PCNs was prohibited. The Netherlands reported that PCNs were listed as a National Priority Substance and that an emission limit value was given in a guideline. Canada reported that industry voluntarily stopped the production and use of PCNs.

There are no international regulations with respect to PCNs. However, wastes containing PCN are characterised as hazardous waste under category A3180 under the new Annex VIII of the Basel Convention.

Substitution and alternatives
The information in this section is extremely limited. The main reason for this lack of information is that PCNs are not in use anymore.
The only available information is that since the production of PCNs has been stopped as early as in the seventies and eighties, PCNs have been substituted by other chemicals. These chemicals have not been identified and further described in the dossier.

Emission Control Techniques
The use of PCBs and waste incineration are assumed to be the most important remaining sources of emissions of PCNs. The emissions of PCNs from these sources are reduced by the same measures that are already taken to reduce the emission of PCBs from the use of PCBs and to reduce emissions of PCBs and dioxins from incineration.
PCN emissions from these sources are expected to be reduced with ~70% upon full implementation of the POP protocol (Denier van der Gon et al 2005).

In the POP Protocol already several emission control techniques are given which will lead to a reduction of PCN emissions. Annex V gives the Best Available Techniques to control emissions of persistent organic pollutants from major stationary sources.
Most of the high temperature sources emitting PCNs are the same as those mentioned in Annex V as a possible source for emitting PCDD/F: waste incineration, thermal
metallurgic processes and combustion plants providing energy. Cement kilns can also be a source of PCN but are not mentioned in Annex V. Emissions of PCDD/F by these installations have to be reduced by using the Techniques mentioned in Annex V. These approaches will subsequently also lead to a reduction of the emissions of PCNs.

**Cost implications**

*Costs of eliminating production and use*
There are no additional costs for eliminating the production and use of PCN, since industry has substituted this use already. There are alternatives which are judged to be less environmentally damaging.

*Costs of controlling unintentional emissions*
No specific information is available on cost and benefits of control. PCNs are emitted as unintentional release from the same sources as the POP compounds dioxins and furans. Hence measures that reduce the release of PCDD/F emissions will also reduce PCN emissions. There are no extra costs involved for industry.

*Costs for consumers*
Price increases are not expected since the substitutes are already in use and the measures against unintentional emissions have to be taken to reduce other emissions.

*Costs for state budgets*
Control costs will be very low and could consist of extra costs for measuring of PCN content in products or from unintentional emissions, and for making emission inventories. These costs are regarded as negligible.

**Possible management options under the UN ECE POPs protocol**
The objective of the POPs protocol is to control, reduce or eliminate discharges, emissions and losses of persistent organic pollutants.

*Options*
In order to remediate concerns and risks related to production and use of PCN it would be possible to:
- list PCN in annex I of the POPs protocol in order to eliminate its production and use,
- list PCN in annex II of the POPs protocol in order to eliminate certain uses,
- list PCN in annex III of the POPs protocol in order to reduce total annual unintentional emissions.
Discussion of the options

As PCN is not produced or used in the UN ECE region anymore there are no specific problems with substitution and there are no specifics costs involved with a ban on production and use. Listing in Annex 1 is possible and will contribute to the ongoing reduction of PCN levels in the environment.

As PCN is not used in the UN ECE region anymore there is no need for a listing in Annex II to allow for certain uses of PCN.

The unintentional emissions of PCN are for the largest part caused by thermal processes like waste incineration and high temperature production processes. With exemption of cement kilns the most relevant of these processes are mentioned in Annex VIII to the protocol. Measures to reduce emissions of PCDD/Fs and of PAH will also reduce emissions of PCN. These measures are given in Annex V to the protocol. Adding of PCN to Annex III will not change the measures mentioned in Annex V. There is no added value in taking up PCN in Annex III.

It is suggested to add PCN as a group of substances to Annex I, and to eliminate production and use of all PCNs.
5 References

Reference list


## Annex: information from questionnaire

<table>
<thead>
<tr>
<th>PCN</th>
<th>Production</th>
<th>Consumption</th>
<th>Alternatives</th>
<th>Releases</th>
<th>Emission control</th>
<th>Additional notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgium</td>
<td>stopped, year unknown</td>
<td>no</td>
<td>no info</td>
<td>no info</td>
<td>no info</td>
<td>No Government of Canada Regulations are in place at this point, however, industry has voluntarily stopped using and importing PCN. An Ecological Screening Assessment Report on PCN will be published shortly</td>
</tr>
<tr>
<td>Canada</td>
<td>unclear. It does not appear as if PCN has ever been manufactured in Canada, but it was likely imported from manufacturers in the United States.</td>
<td>no</td>
<td>no info</td>
<td>PCN by product in Aroclor, est. 1 tonne emission in 2003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyprus</td>
<td>never produced</td>
<td>PCN is not imported in Cyprus. No data is available at the moment whether PCN is contained in any products imported in Cyprus.</td>
<td>no info</td>
<td>no info</td>
<td>no info</td>
<td></td>
</tr>
<tr>
<td>Denmark</td>
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<td>never used</td>
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<td>no info</td>
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<tr>
<td>Italy</td>
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<td>no info</td>
<td>no info</td>
<td></td>
</tr>
<tr>
<td>The Netherlands</td>
<td>never produced</td>
<td>never used</td>
<td>no info</td>
<td>no info</td>
<td>PCBs, PCTs and PBBs are classified under Category A3180 under the new Annex VIII of the Basel Convention. A3180 Wastes, substances and articles containing, consisting of or contaminated with polychlorinated biphenyl (PCB), polychlorinated PCNs are identified as national priority substance. Limited qualitative information on emissions is available within the project Priority substances. There is an emission limit for PCNs within the NeR, the Dutch</td>
<td></td>
</tr>
<tr>
<td>Country</td>
<td>Status</td>
<td>Reason</td>
<td>Reporting Information</td>
<td>Notes</td>
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<td>----------------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Czech Republic</td>
<td>never produced</td>
<td>unclear</td>
<td>no info</td>
<td>no info</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UK</td>
<td>stopped in 1960's-1970's</td>
<td>no use anymore</td>
<td>no info</td>
<td>Not possible to make estimate (NAEI, 2004)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>Unclear. Chlorinated derivatives of naphthalene plus 16 PCN congeners are listed on the TSCA Inventory with no production and import information reported for the 2002 reporting year. Production and import volume of 38,700 lbs (17.5 metric tons) for chlorinated derivatives of naphthalene (CAS No. 70776-03-3) was last reported for the 1990 reporting year.</td>
<td>unclear. PCN is listed on the TSCA Inventory with no production and import information reported for the 2002 reporting year. See question 1a.</td>
<td>Only 2 PCN congeners are on the Toxics Release Inventory list yet have no reported TRI.</td>
<td>no info</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switzerland</td>
<td>never produced</td>
<td>no use</td>
<td>no info</td>
<td>no info</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Terphenyl (PCT), polychlorinated naphthalene (PCN) or polybrominated biphenyl (PBB), or any other polybrominated analogues of these compounds, at a concentration level of 50 mg/kg or more.

http://www.chem.unep.ch/pops/POPs_inc/proceedings/lusaka2k/lusaka2k.pdf

Emission Directive on Air.

Czech Republic never produced

UK stopped in 1960's-1970's

USA Unclear. Chlorinated derivatives of naphthalene plus 16 PCN congeners are listed on the TSCA Inventory with no production and import information reported for the 2002 reporting year. Production and import volume of 38,700 lbs (17.5 metric tons) for chlorinated derivatives of naphthalene (CAS No. 70776-03-3) was last reported for the 1990 reporting year.

Switzerland never produced

According to the Ordinance relating to Environmentally Hazardous Substances of 9 June 1986 Art. 11 and Annex 3.1 (replaced by ORRChem of 19 July 2005): The manufacture,
Supply, import and use of the following a) substances and b) products which contain these substances other than as unavoidable impurities are prohibited. PCNs belong to this list among other substances.