Persistent Organic Pollutants Review Committee

Working group on chlorinated naphthalenes

**Chlorinated Naphthalenes**

**Draft risk management evaluation**

Second draft

1 April 2013

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# Executive summary

1. The European Union and its Member States submitted a proposal to list chlorinated naphthalenes (CNs) in Annex A, B or C of the Stockholm Convention pursuant to paragraph 1 of Article 8 of the Convention. The risk profile on CNs was adopted on the eighth meeting of the Persistent Organic Pollutants Review Committee in October 2012. The Committee decided (1) that dichlorinated naphthalenes, trichlorinated naphthalenes, tetrachlorinated naphthalenes, pentachlorinated naphthalenes, hexachlorinated naphthalenes, heptachlorinated naphthalenes and octachlorinated naphthalene (di- to octachlorinated naphthalenes = polychlorinated naphthalenes = PCNs), are likely, as a result of their long‑range environmental transport, to lead to significant adverse human health and environmental effects such that global action is warranted, (2) to prepare a risk management evaluation that includes an analysis of possible control measures for chlorinated naphthalenes and (3) to invite parties and observers to submit to the Secretariat the information specified in Annex F before 11 January 2013, as well as additional information relevant to Annex E in particular data on sources of emissions such as the production of chlorinated naphthalenes and/or unintentional releases.
2. CNs comprise of 75 possible congeners in eight homologue groups with one to eight chlorine atoms substituted around the planar aromatic naphthalene molecule. CNs have historically been used as wood preservative, as additive to paints and engine oils, and for cable insulation and in capacitors. To date, intentional production of CNs is assumed to have ended and CNs have been substituted by other chemicals, however, remaining use is still possible. To limit possibly remaining uses and to prevent re-introduction of other uses, listing of PCNs in Annex A without any specific exemptions could be the primary control measure for intentional sources under the Convention. As a consequence PCNs would be submitted to the provisions of Article 3 of the convention and the objective to eliminate their production, use, import and export. Health and environment could benefit from listing PCNs in Annex A as the re-introduction of PCNs and related risks would be prevented. A beneficial effect could be expected as any currently unidentified production and use around the world should end. Relevant negative impacts on health, environment and society are not expected from the listing of PCNs.
3. CNs are unintentionally generated during high-temperature industrial processes. Of the known releases, combustion (primarily waste incineration) is considered the most significant current source. CNs are also unintentionally generated with similar mechanisms as PCDD/Fs during other industrial processes such as smelting in the secondary non-ferrous metal industry, cement and magnesia production, aluminum refining and coking. Listing of PCNs in Annex C would subject this substance group to the measures under Article 5 of the Convention and establish the goal of continuing minimization and, where feasible, ultimate elimination of PCNs releases. This would include an obligation to promote best available techniques (BAT) and best environmental practices (BEP) for CNs sources. Measures that reduce the release of PCDD/F emissions will also reduce CNs emissions. BAT and BEP relevant to unintentionally produced PCDD/Fs for various types of incinerators are available and already widely applied. Measures to reduce unintentional releases of PCNs through listing in Annex C would positively impact human health and the environment. Additional costs for monitoring, enforcement and supervision are considered to be low as the control measures for other PCDD/Fs are already applied.
4. CNs can be unintentionally released from landfills or old appliances (stockpiles). Listing of PCNs in Annex A or C would subject PCNs to the measures under Article 6 of the Convention and establish the goal of identifying stockpiles consisting of or containing PCNs and managing them in a safe, efficient and environmentally sound manner. Stocks of CNs are particularly occurring in conjunction with PCBs (i.e. in PCB containing waste disposals and PCB containing equipment). Parties to the convention have already introduced measures to identify and manage PCB stockpiles. Measures in place with respect of PCB stockpiles will also efficiently reduce releases of PCNs from stockpiles. Health and environment would benefit from reduced releases. Additional costs would not arise.
5. Having prepared a risk management evaluation and considered the management options, in accordance with paragraph 9 of Article 8 of the Convention, the Committee recommends the Conference of the Parties to the Stockholm Convention to consider listing and specifying the related control measures for PCNs in Annexes A and C.

# Introduction

## 1.1 Chemical identity of the proposed substance (source: UNEP/POPS/POPRC.8/16/Add.1)

1. The European Union and its Member States submitted a proposal to list PCNs in Annex A, B or C of the Stockholm Convention on 10 May 2011 (UNEP/POPS/POPRC.7/2) together with a detailed dossier to support the proposal (UNEP/POPS/POPRC.7/INF/3).
2. Chlorinated naphthalenes comprise of 75 possible congeners in eight homologue groups with one to eight chlorine atoms substituted around the planar aromatic naphthalene molecule. The homologue groups considered in this report are dichlorinated naphthalene (di-CNs), trichlorinated naphthalene (tri-CNs), tetrachlorinated naphthalenes (tetra-CNs), pentachlorinated naphthalenes (penta-CNs), hexachlorinated naphthalene (hexa-CNs), heptachlorinated naphthalenes (hepta-CNs), octachlorinated naphthalenes (octa-CN). They are structurally similar to the polychlorinated biphenyls (PCBs), which were listed in the Stockholm Convention upon its adoption in 2001.
3. CNs have historically been used as wood preservation, as additive to paints and engine oils, and for cable insulation and in capacitors. While CNs uses have been ceased, they are also present in PCB formulations and are unintentionally produced during combustion processes and in industrial installations.

*Name and registry number*

|  |  |
| --- | --- |
| Common name:  | Chlorinated naphthalenes |
| IUPAC names and numbers and CAS registry numbers of the 75 congeners: | see Annex 1 of UNEP/POPS/POPRC.8/16/Add.1 |
| Synonyms: | PCN, polychlorinated naphthalenes, CNs, naphthalene chloro- derivatives[[1]](#footnote-1),[[2]](#footnote-2)  |
| CAS registry number: | 70776-03-3  |

1. The system of nomenclature for CNs is similar to that for polychlorinated biphenyls. Most of the industrially produced CNs are mixtures of several congeners. Table A2-1 in Annex 2 of UNEP/POPS/POPRC.8/16/Add.1displays the composition of several Halowaxes according to analytical measurements (data adapted from Environment Canada, 2011 and Falandysz et al., 2008). Other commercial mixtures and trade names are Basileum SP‑70, Nibren wax D88, Nibren wax D116N, Nibren wax D130, Seekay wax R68, Seekay wax R93, Seekay wax R123, Seekay wax R700, Seekay wax RC93, Seekay wax RC123, Chlonacire wax 115, Chlonacire wax 95, Chlonacire wax 130 (Jakobsson and Asplund, 2000) and Cerifal Materials (Falandysz, 1998). The physical state ranges from thin liquids to hard waxes (IPCS, 2001).
2. While several analytical challenges are associated with the exact determination of CNs the current methods are similar to analytical methods used for PCBs. It is based on carbon clean-up (from matrices) and fractionation followed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) for low levels CNs/high selectivity. However fewer than half of the possible congeners are available commercially and isotopically labelled CNs are available for only a few congeners e.g. no 13C-labeled tri-CNs is available (Kucklick and Helm, 2006).

*Structures*

|  |  |
| --- | --- |
| Molecular formula: | C10H8-nCln |
| Molecular weight: | see  |
| Chemical structure showing the carbon atom numbering system and the potential positions for chlorine atom substitution (source: UNEP/POPS/POPRC.7/INF/3)  |

*Physical and chemical properties of different homologue groups*

1. Physico-chemical properties vary considerable due to the degree of chlorine substitution. Tri- to octa-CNs are very lipophilic with high log Kow (>5). Log Kow values in are experimentally determined whereas Annex 1 (note: of UNEP/POPS/POPRC.8/16/Add.1) contains Quantitative Structure–Property Relationship (QSPR) modelled values (Puzyn and Falandysz, 2007). Modelled values were lower for the more chlorinated congeners.
2. Water solubility and vapour pressure decrease with the degree of chlorination. Di-CNs are slightly soluble in water while the higher chlorinated naphthalenes have a water solubility of a few µg/L. For chemicals with low water solubility measured values have a higher uncertainty (Environment Canada, 2011) (cf. , values in brackets are estimated values with WSKOWWIN version1.41, EPISUITE). Puzyn et al. (2009) developed a QSPR model to estimate the water solubility, log Kow, Koa, Kaw and the Henry´s Law Constant for all 75 congeners. The estimates for water solubility are lower than the values given in . Values of these modelled endpoints are listed in Annex 1 (note: of UNEP/POPS/POPRC.8/16/Add.1). The range of log Koa and log Kaw are summarized for the different homolog groups in .
3. CNs in the gas phase are attached to particles due to their semivolatility. Based on the Henry´s Law constant volatilization from moist soil surfaces and water is expected for di-CNs to hexa-CNs (HSDB, 2012). The UV spectra of CNs show strong absorbance maxima between 220 and 275 nm and weaker maxima between 275 and 345 nm. The absorption maxima are shifted towards longer wavelengths as the chlorine degree increases (according to Brinkman and Reymer, 1976 in Jakobsson and Asplund, 2000).
4. Pure chlorinated naphthalenes are colourless, crystalline compounds (lndian Institute of Science, 2011, submitted Annex E information by Thailand).

Table 1: Selected physical and chemical property (table modified from Environment Canada, 2011)

| **Congeners** | **Molecular weight** **(g/mol)** | **Solubility****(μg/L) a** | **Vapour pressure** **(Pa)b (sub-cooled liquid, 25**°**C)**  | **Henry’s law constant** **(Pa·m3/mol, 25**°**C)c** | **Log Kow d** | **Log Koae** | **Log Kawe** | **Melting point** **(°C)** | **Boiling point (°C)** |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Di-CNs  | 197.00  | 137–862 (2713)  | 0.198–0.352  | 3.7–29.2  | 4.2–4.9  | 6.55 to 7.02 | -2.83 to -1.98 | 37–138  | 287–298  |
| Tri-CNs  | 231.50  | 16.7–65 (709)  | 0.0678–0.114 | 1.11–51.2  | 5.1–5.6  | 7.19 to 7.94 | -3.35 to -2.01 | 68–133  | 274\*  |
| Tetra-CNs  | 266.00  | 3.7–8.3 (177)  | 0.0108–0.0415  | 0.9–40.7  | 5.8–6.4  | 7.88 to 8.79 | -3.54 to -2.02 | 111–198  | Unknown  |
| Penta-CNs  | 300.40  | 7.30 (44)  | 0.00275–0.00789  | 0.5–12.5  | 6.8 - 7.0 | 8.79 to 9.40 | -3.73 to -2.3 | 147–171  | 313\*  |
| Hexa-CNs  | 335.00  | 0.11\* (11)  | 0.00157–0.000734  | 0.3–2.3  | 7.5 - 7.7  | 9.62 to 10.17 | -4.13 to -3.04 | 194  | 331\*  |
| Hepta-CNs  | 369.50  | 0.04\* (2.60)  | 2.78 x 10-4, 2.46 x 10-4  | 0.1–0.2  | 8.2  | 10.68 to 10.81 | -4.34 to -4.11 | 194  | 348\*  |
| Octa-CN  | 404.00  | 0.08 (0.63)  | 1.5 x 10-6  | 0.02  | 6.42–8.50 | 11.64 | -5.21 | 198  | 365\*  |

Data source: IPCS (2001), unless otherwise noted.

a Values outside of brackets were experimentally determined by aqueous saturation method (Opperhuizen et al. 1985) for the solid congeners; values in brackets are predicted using WSKOWWIN 2000.

b Source: Lei et al. (1999).

c Values obtained from Puzyn and Falandysz (2007).

d Measured Kow sources: Opperhuizen (1987), Opperhuizen et al. (1985) (shake flask method, Bruggeman et al. (1982)), Lei et al. (2000) (reversed phase HPLC method).

e estimates from Puzyn et al. (2009)

\*Estimated value, using methodologies laid out in Lyman et al. (1982).

## 1.2 Conclusions of the Review Committee regarding Annex E information

1. The Committee has conducted and evaluated a risk profile in accordance with Annex E at the eighth meeting in Geneva 15- 19 October 2012. The Committee adopted decision POPRC-8/1, by which it adopted the risk profile for chlorinated naphthalene (UNEP/POPS/POPRC.8/16/Add.1) and

decided, in accordance with paragraph 7 (a) of Article 8 of the Convention, that dichlorinated naphthalenes, trichlorinated naphthalenes, tetrachlorinated naphthalenes, pentachlorinated naphthalenes, hexachlorinated naphthalenes, heptachlorinated naphthalenes and octachlorinated naphthalene, are likely, as a result of their long‑range environmental transport, to lead to significant adverse human health and environmental effects such that global action is warranted;

also decided, in accordance with paragraph 7 (a) of Article 8 of the Convention and paragraph 29 of decision SC-1/7 of the Conference of the Parties, to establish an ad hoc working group to prepare a risk management evaluation that includes an analysis of possible control measures for chlorinated naphthalenes in accordance with Annex F to the Convention;

invited, in accordance with paragraph 7 (a) of Article 8 of the Convention, parties and observers to submit to the Secretariat the information specified in Annex F before 11 January 2013, as well as additional information relevant to Annex E in particular data on sources of emissions such as the production of chlorinated naphthalenes and/or unintentional releases.

## 1.3 Data sources

1. The Risk Management evaluation is primarily based on

information that has been provided by Parties and observers to the Convention. Responses regarding the information specified in Annex F of the Stockholm Convention (risk management) have been provided by the following Parties and observers [[3]](#footnote-3):

1. Parties: Croatia, Estonia, Nigeria, Romania, Slovakia, Sri Lanka
2. Observers: no information submitted

decision POPRC-8/1 (see UNEP/POPS/POPRC.8/16)

the risk profile for chlorinated naphthalene (UNEP/POPS/POPRC.8/16/Add.1)

the exploration of management options for PCN [UNECE 2007]

1. In addition information has been gathered from other open information sources and literature. Such Information sources are listed under “References” in addition to the above mentioned sources.

## 1.4 Status of the chemical under international conventions

1. Chlorinated naphthalenes are subject to a number of international treaties and conventions:

In December 2009 CNs were proposed according to Decision 2009/2 to amend Annex I (prohibition of production and use) of the Aarhus Protocol on Persistent Organic Pollutants (POPs) under the UNECE (United Nations Economic Commission for Europe) Convention on Long-Range Transboundary Air Pollution. The amendment will come into force when 2/3rd of the Parties have adopted the amendment.

The OSPAR Commission has included PCNs in the List of Chemicals for Priority Action (by June 2003). Further information can be gathered at <http://www.ospar.org/>

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

1. Additional information on the status of the chemical under international conventions has not been provided by parties or observers who submitted Annex F information.

## 1.5 Any national or regional control actions taken

1. Information on CNs considered in regional and national substance lists is scarce. Additional information on national or regional control actions has not been provided by parties or observers who submitted Annex F information.
2. Canada has prohibited production and use of PCNs through the Canadian Environmental Protection Act , 1999 in 2012 (Canada, 2012). No actions have been undertaken in the United States as the production of PCNs ceased in the 1980s. The import and manufacture of PCNs has been banned in Japan since 1979. All halogenated naphthalenes, including PCNs, are legally banned in Switzerland. Within the European Union, the Netherlands reported that PCNs were listed as a National Priority Substance for possible future regulatory control.[[4]](#footnote-4)
3. In Japan, tri-CNs and more chlorinated congeners are designated as Class I Specified Chemical Substances under the Chemical Substances Control Law (CSCL). A person who intends to operate a business of manufacturing, import or use of a Class I Specified Chemical Substance shall obtain permission (Manufacture, import or use of these chemical substances is prohibited in principle.)

# 2. Summary information relevant to the risk management evaluation

## 2.1 Additional relevant information on sources, releases and measures

Production

1. Sources of CNs are possible due to anthropogenic activities: (1) intentional production, (2) unintentional generation and (3) stockpiles (for details see UNEP/POPS/POPRC.8/16/Add.1, section 2.1 on sources):
2. (1) Within the UNECE region CN is not intentionally produced anymore. Production and use data outside the UNECE-region are very scarce and largely unknown. Known global production has virtually stopped in many countries, having drastically decreased already in the 1970s. Present production of PCNs cannot be excluded.

Estimates for the total global CN production so far vary between 200,000–400,000 tonnes (AMAP, 2004) and 150,000 tonnes (about one tenth of the PCBs ever produced (Brinkman & De Kok, 1980 as cited in: Falandysz, 1998).

1. Cases of illegal trade of Halowax-like CN formulations were reported in 2002, and information about CN production and use is scarce for many countries. To date, intentional production of CN is assumed to have ended although contaminated products were still found on the market in 2003 (Yamashita et al., 2003 as cited in: Bidleman et al., 2010). According to Yamashita et al., 2003, illegal imports to Japan around 2000 were about 18 tons of a PCNs mixture (Halowax 1001) from the UK used to manufacture a wide spectrum of industrial materials and commercial goods including sealants, putty, shock absorbing materials, adhesive materials, insulating materials and rubber belts and another 10.6 tons of PCNs contained in 54 tons of PCNs contaminated raw rubber which was imported for industrial use.
2. According to a comment from the Netherlands, production was still possible in the UNECE region until 2012 when PCNs were incorporated in the EU POP regulation. Canada prohibited production and use already earlier. However, a number of UNECE countries have not yet organised legal prohibition. So production is still possible within the UNECE as well[[5]](#footnote-5). Specific information on ongoing production is not available. Present use of PCNs cannot be excluded.
3. A recent study by Chinese authors states that there is no information available about the production of technical CN formulations in China (Pan et al., 2011), however a small quantity production (not specified) of octa-CN for scientific purposes was reported for Jiangsu province lately (China, 2011).
4. CNs are currently not produced in Nigeria and have never been produced in the country (Annex F, Nigeria, 2013). Also Slovakia and Sri Lanka reported that there is no production of CNs within these countries (Annex F, Slovakia and Sri Lanka, 2013). Additional information on the intentional production of the chemical has not been provided by parties or observers who submitted Annex F information.
5. (2) CNs are still unintentionally generated during high-temperature industrial processes. Of the known releases, combustion (primarily waste incineration) is considered the most significant current source, at 10-100 kg per year, worldwide. For Europe, waste incineration contributed an estimated 74% to total CN emissions in 2000 [UNECE 2007].
6. CNs are also suspected to be generated unintentionally with similar mechanisms as PCDD/Fs: they are formed during the smelting in the secondary non-ferrous metallurgical industry (where production conditions include heat, chlorine-containing recyclates and the catalytic function of metals like, e.g. copper). Cement and magnesia production and aluminum refining have been reported as further unintentional CN sources. Also coking can release CNs and there have also been indications of CN formation at manufacturing sites producing chlorine by the chlor-alkali process and at low concentrations as by-products in the chlorination of drinking water.
7. (3) Commercial PCBs also contained traces of CNs (0.01–0.09%; Falandysz, 1998, Kannan et al., 2000, Yamashita et al., 2000). CNs were unintentionally released as contaminants in PCBs. Releases from former uses (CN or impurities of technical PCB) contained in landfills or old appliances (stockpiles) are plausible but difficult to assess. In urban sites emissions of suggested historically used technical CN have been reported (Harner et al., 2006 cited from UNEP/POPS/POPRC.8/16/Add.1).

Use

1. CNs have been used mainly for their chemical stability, including low flammability, their (electrically) insulating properties and recalcitrance including resistance to biodegradation and biocidal function; they share these properties and their scope of application with the PCBs, by which they were gradually replaced after WW II.
2. Less chlorinated congeners (mono-CN and mixtures of mono- and di-CN) have been used for chemical-resistant gauge fluids and instrument seals, as heat exchange fluids, as high boiling specialty solvents, for colour dispersions, as engine crankcase additives, and as ingredients in motor tune-up compounds. Mono-CN has also been used as a raw material for dyes and as a wood preservative with fungicidal and insecticidal properties (IPCS, 2001).
3. Higher chlorinated congeners have been used mostly, in terms of volume, for cable insulation and flame-proofing, wood preservation, engine and gear oil additives, electroplating masking compounds, feedstock for dye production, dye carriers, dielectric impregnates for capacitors/condensers, and refractive index testing oils. The use of CNs as wood preservatives was popular in the 1940s and 1950s, but they are no longer used for this purpose in the USA. Further uses were (NICNAS 2002) dipping encapsulating compounds in electronic and automotive applications, temporary binders in paper coating and impregnation, binders for ceramic components, casting materials for alloys, grinding and cutting lubricants, separators in batteries, moisture proofing sealant. In the USA, only very small amounts of CNs (about 15 tons/year in 1981) were still being used, mainly as refractive index testing oils and as capacitor dielectrics. The most likely possible new uses for CNs would be as intermediates for polymers and as flame retardants in plastics (IPCS, 2001).
4. CNs have historically been used for several purposes, which are cable insulation, wood preservation, as additive in engine oils, electroplating masking compounds, feedstock for dye productions, dye carriers, capacitors and refracting index oils. Thereof, in the UNECE region, application in wood preservation, as additive in paints and engine oils, for cable insulation and in capacitors have been the most important ones [UNECE 2007]. They were also applied in technical PCB formulations. PCNs have been used in pyrotechnic applications. It cannot be excluded that such use is still ongoing[[6]](#footnote-6). CNs were mainly used between 1920 and 1980. Afterwards use declined considerably. In Europe, last data on use available have been reported for Germany and former Yugoslavia, where small amounts were used as casting material until 1989. [ESWI 2011]
5. The ECHA (European Chemicals Agency) classification and labelling inventory indicates that there are notifiers for a limited number of specific CN congeners[[7]](#footnote-7) (CN congeners 1, 2, 5, 9, 27 and 75). Specific congeners are furthermore listed in the ECHA inventory of pre-registered substances (CN congeners 1 to 5, 7 to 12, and 75 with envisaged registration deadlines in 2010 or 2013). So far no registration has been submitted to ECHA. This suggests that there are no EU companies which produce or import CNs in high volumes. The entries in the C&L inventory and the fact that pre-registrations have been submitted to ECHA at least indicates that CNs are of certain interest for EU companies although pre-registrations could also have been submitted due to strategic reasons instead of real registration obligations.
6. Within the Annex F submissions Nigeria reported that there are documented uses[[8]](#footnote-8) of CNs as cable insulation, capacitor fluids, casting material for alloys, dye carriers, electroplating masking compounds, engine oil additives, feedstock for dye production, flame proofing, lubricants, moisture proofing sealant, preservatives, refractive index testing oils, temporary binders for ceramic component manufacture and wood preservatives (Annex F, Nigeria, 2013). Additional relevant information on uses has not been provided by parties or observers who submitted Annex F information.
7. Halowax can still be purchased via internet. E.g. octachloronaphtalene can be bought from almost 27 Chinese suppliers or 27 global suppliers. The website does not provide information on the amounts for sale.[[9]](#footnote-9)

Releases

1. As mentioned above, production and use data outside the UNECE region are very scarce. This circumstance impairs the assessment of CN-releases on a global scale considerably. PCNs are not mentioned in the European Pollutant Release and Transfer Register[[10]](#footnote-10). Hexa- and octachloronaphthalenes are mentioned in the Toxics Release Inventory (TRI) database of US, but no releases have been reported[[11]](#footnote-11).
2. IPCS considered waste incineration and disposal of CN-containing items as the major current sources of CNs to the environment (IPCS, 2001). Bolscher et al. (2005) conclude on the combustion of clinical, municipal and industrial waste as a key source of environmental CNs. For the UNECE-region, unintentional CN releases from waste disposal through incineration are assumed to be the most important current source. Most waste is disposed through clinical, municipal and industrial incineration. It is estimated that 74% of total CN releases in Europe are caused by waste combustion. Denier Van der Gon et al. (2007) report one ton annual CN emissions from UNECE-Europe back in 2000, more than 80 % of which were due to combustion. Incineration of municipal and special waste, and more generally, thermal processes like combustion, roasting and metal reclamation are also regarded significant sources (IPCS, 2001, Falandysz, 1998). It is estimated that annually 10–100 kg, and a total (ever released) volume of 1–10 tons CN are and have been formed during combustion, worldwide (Falandysz, 1998). In the UK, commercially produced PCNs are thought to be the most important source of PCNs in the atmosphere, with the other source sectors being thermal sources, other industrial processes and contamination in PCB industrially produced mixtures [Dore et al. 2008].
3. Due to common practices in clinical waste incineration under uncontrolled conditions it is likely that in developing countries there are significant PCN releases from clinical waste incineration in these countries[[12]](#footnote-12).
4. CNs are also suspected to be produced unintentionally with similar mechanisms (NICNAS, 2002, Bolscher et al., 2005) as dibenzodioxins and -furans: they are formed during the smelting in the secondary non-ferrous metallurgical industry (where production conditions include heat, chlorine-containing recyclates and the catalytic function of metals like, e.g. copper; Kannan et al., 1998, Ba et al., 2010). Calculated emission factors suggest 428.4 ng TEQ per ton secondary copper (aluminium: 142.8, zinc: 125.7, lead: 20.1; Ba et al., 2010). Cement and magnesia production and aluminium refining have been reported as further unintentional CN sources (Environment Canada, 2011). Coking can release CNs, too, with emissions of 0.77–1.24 TEQ per ton coke ( Liu et al., 2010). Within the UNECE, CNs are thus unintentionally released by industry, but these emissions amount to only about 1/7 of those from waste incineration and are of approximately the same size as releases from other combustion processes (Denier van der Gon et al., 2007).
5. Accordingly, in the UNECE, about 79% of the CN releases result from public heat and power and industrial solvent production and use, about 11% result from residential, commercial and other combustion and about 10% from other industrial activities (Denier van der Gon et al., 2007). There are potential releases from former uses (CN or impurities of technical PCBs) contained in landfills or old appliances, but their contribution to current CN releases are difficult to assess (UNEP/POPS/POPRC.8/16/Add.1).
6. Although official release data are lacking, there is literature available on emissions from PCNs from various industries, specifically on unintentional emissions. For instance, Brack et al (2003) report on past emissions in Germany Sediments were isomerspecifically analysed. The isomer pattern suggests chloralkali industry as the major source of PCN contamination. There have also been indications (characteristic congener profiles) of CN formation at manufacturing sites producing chlorine by the use of graphite anodes in mercury cell chlor-alkali process, as indicated by the high concentrations of CNs reported in fish collected near a former chlor-alkali plant (Kannan et al., 1998). Although one older study reported that di-CNs are formed at low concentrations as by-products in the chlorination of drinking water (Shiraishi et al. 1985 in Environment Canada, 2011), no evidence has been found in the recent literature to support this finding ( Environment Canada, 2011).
7. Nie et al. 2012 report on PCN emissions from thermal wire reclamation at industrial scrap metal parks in China.
8. Another unintentional source is the release of CN-traces from technical PCB production which was roughly estimated at 0.1 kt present in all Arochlor and Clophen ever produced worldwide (Falandysz, 1998). CN formation during PCB production was reported as a potential source (Denier van der Gon et al., 2007).
9. Nigeria reported that no coordinated survey has been conducted in Nigeria, however, considering the use pattern of CNs, unintentional production of CNs, may be linked to metal refining, waste incineration, wood combustion, open municipal waste dump, historical use of CNs, contaminated sites, abandoned stockpiles, old formulation facilities, historical and present use of PCBs, open burning practices, etc. (Annex F, Nigeria, 2013). Additional information on releases has not been provided by parties or observers who submitted Annex F information.
10. Data on the concentrations in sediment cores presented in Gevao et al (2000) indicate that peak production of PCNs precede that of PCBs by 20-30 years. A summary of concentration patterns in sediment cores is provided in Gewurz et al (2009), which suggest that peak concentrations of PCNs were reached about 20 years earlier in UK than in Japan, in the late 1950s to mid-1960s and in the 1980s respectively.
11. Data on markers in soil or sediment cores may indicate the importance of the various sources. E.g. data presented in Meijer et al (2001) show significant increasing trends for several congeners associated with combustion sources suggesting that combustion related sources are more important than they were in the past. This indicates that the relative importance of combustion sources may increase.
12. In conclusion the information available indicates that most important releases result from (1) past intentional production of PCNs and remaining products, stockpiles and landfills (estimates for global production range between 150,000 and 400,000 tonnes), (2) unintentional generation during waste incineration (e.g. municipal, clinical and industrial waste) and (3) other thermal and industrial processes (e.g. public heat and power, industrial solvent production and use, chloralkali industry, non-ferrous metal industry, cement industry, coking, metal reclamation).

Possible measures

1. Possible measures can be directed at the relevant anthropogenic sources of CN: (1) intentional production, (2) unintentional generation and (3) stockpiles. illustrates relevant sources and possible control measures for CN.

Anthropogenic sources

Natural sources

Stockpiles

Unintentional generation

Natural generation

Intentional production

Considerable quantities through thermal processes (especially waste incineration) and by-production

Production still possible outside UNECE

Considerable releases from waste landfills and/or old appliances are possible

No natural sources

Control measures relevant

Control measures relevant

Control measures relevant

Control measures not relevant

Inventories, Emission reduction measures (BAT); Legislation

Prohibit or restrict production and use;
Legislation

Emission reduction measures (BAT);
Legislation

Listing in Annex A or C

Listing in Annex C

Listing in Annex A (prohibition) or B (restriction)

Figure 1: Relevant sources and possible control measures for CN
(note: use for laboratory-scale research or as a reference standard is not considered; such use is excluded from the Convention according to Article 3(5))

## 2.2 Identification of possible control measures

*Control measures for releases from intentional production*

1. Production of CNs has ceased in the UNECE-region and known global production has virtually stopped in many countries. The use of CNs has been substituted by the use of other chemicals [UNECE 2007]. To date, intentional production of CNs is assumed to have ended, however, remaining use is still possible.
2. To limit possibly remaining uses and to prevent re-introduction of other uses, listing of PCNs in Annex A without any specific exemptions could be the primary control measure for intentional sources under the Convention. As a consequence PCNs would be submitted to the provisions of Article 3 of the convention and the objective to eliminate their production, use, import and export.

*Control measures for releases from unintentional generation*

1. The use of PCBs and waste incineration are considered to be the most important remaining sources of unintentional emissions of CNs. Possible measures to control such releases include measures for PCBs outlined in Annex A, Part II of the Stockholm Convention and measures to reduce releases of PCBs and dioxins from incineration (see [UNECE 2007] and the Stockholm Convention BAT/BEP Guidelines [UNEP 2007]).
2. Annex V of the POP protocol contains the BAT to control emissions of POPs from major stationary sources including waste incinerators. Further thermal processes covered are thermal metallurgic processes and combustion plants providing energy. As these installations have to reduce the emissions of PCDD/F by using BAT included in Annex V, this will also lead to a reduction of the emissions of CNs from waste incineration. CNs emissions from these sources are expected to be reduced with ~70% upon full implementation of the POP protocol. Further, cement kilns can be a source of CNs not listed in Annex V [UNECE 2007].
3. Corresponding BAT and BEP is also described in the Stockholm Convention BAT/BEP Guidelines [UNEP 2007] in Section V on guidance/guidelines by source categories Part II of Annex C relevant BAT for various types of incinerators (including waste incinerators in section V.A and cement kilns firing hazardous waste in section V.B) and other thermal sources (including thermal processes in the non-ferrous metal sector in section V.D) and in the relevant EU BAT reference documents (BREFs; particularly the BREFs on waste incineration [EC BREF WI 2006] and on non-ferrous metal industries [EC BREF NFM 2009].

The application of corresponding BAT reduces CN releases.

1. Listing of PCNs in Annex C would subject this substance group to the measures under Article 5 of the Convention and establish the goal of continuing minimization and, where feasible, ultimate elimination of CN releases. This would include an obligation to promote BAT and BEP for PCN sources.

*Control measures for releases from stockpiles*

1. Releases from former uses (CN or impurities of technical PCBs) contained in landfills or old appliances (stockpiles) are plausible but difficult to assess. The use of PCBs is considered the most important remaining source of unintentional emissions of CNs besides waste incineration (see above). Possible measures to control releases from stockpiles are
* to establish inventories of relevant landfills and control and sound management of releases (particularly leachate) from relevant waste disposals or restoration/decontamination of waste disposals.
* to establish inventories of stocks of relevant old appliances and their sound management.
1. For engineering standards of landfills, including management of leachate, and further information on sustainable waste management the technical guidelines of the Basel Convention are recommended (technical guidelines: on specially engineered landfill (D5); [BC 1997] ). As there is a direct relation between the occurrence of PCBs and CNs in old appliances, stocks of CNs in old appliances are particularly occurring in PCB stockpiles (waste disposals and PCB containing equipment).
2. Listing of PCNs in Annex A or C would subject PCNs to the measures under Article 6 of the Convention and establish the goal of identifying stockpiles consisting of or containing chemicals listed in Annex A or C and managing them in a safe, efficient and environmentally sound manner.

## 2.3 Efficacy and efficiency of possible control measures in meeting risk reduction goals

*Intentional production*

1. On a global scale intentional production of CN is assumed to have ended, however, remaining use is still possible. Nigeria reported that there are no additional costs for eliminating the production and use of CNs, since industry has substituted this use already (Annex F, Nigeria, 2013). Additional costs for eliminating the production and use of CNs are not expected as alternative chemicals for the same uses are available and already in use and it seems that intentional production and use of CNs have already stopped. Health and environment would benefit from a ban of PCNs as their re-introduction and related risks would be prevented. A beneficial effect could be expected as any currently unidentified production and use around the world should end. Relevant negative impacts on health, environment and society are not expected from a ban of PCNs.

*Unintentional generation*

1. CNs are unintentionally released from the same sources as the POP compounds dioxins and furans. Therefore, measures that reduce the release of PCDD/F emissions will also reduce CN emissions. BAT and BEP relevant to unintentionally produced POPs for various types of incinerators and other thermal sources are very well documented in the Stockholm Convention BAT/BEP Guidelines [UNEP 2007] and the relevant EU BAT reference documents (BREFs) and are widely applied.
2. There are no extra costs involved for industry of the UNECE region for controlling unintentional emissions. 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. 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 [UNECE 2007]. Outside the UNECE region the situation is similar because it seems that substitutes are already in use and the measures against unintentional emissions have already to be taken to reduce other emissions. As a consequence no extra costs are expected for industry and consumers in the countries who are parties to the Stockholm Convention due to the measures that are already taken to reduce releases of PCDD/F emissions. Costs for authorities/the state are considered to be low; they may consist of additional costs for measuring of PCN contents in products or from unintentional emissions (monitoring, preparation of emission inventory). Corresponding cost impacts are also expected by Nigeria (Annex F, Nigeria, 2013)

*Stockpiles*

1. As a consequence of listing PCNs in Annex A or C, parties to the convention would have to identify existing stockpiles of PCNs (including both, relevant waste disposals and old appliances), and to manage them in a safe, efficient and environmentally sound manner.
2. There is a specific relation between the occurrence of PCBs and PCNs (see above). According to Article 6 of the Convention, Parties are already obliged to identify existing stockpiles consisting of or containing PCBs, and to manage these in a safe, efficient and environmentally sound manner. As a consequence, CN stockpiles which are part of the PCB stockpiles, are already identified and managed in an environmentally sound manner together with any remaining PCB stockpiles. Additional costs for PCNs contained in PCB stockpiles will not arise.

## 2.4 Information on alternatives (products and processes) where relevant

1. Within the UNECE-region the information on substitution and alternatives is extremely limited as PCNs are not in use anymore. The only available information is that since the production of CNs has been stopped in the seventies and eighties, CNs have been substituted by other chemicals. These chemicals have not been identified and described [UNECE 2007].
2. Hayward 1998 reports that production of PCNs began to decline with the advent of plastic substitutes for insulation and the use of polychlorinated biphenyls (PCBs) for dielectrics in transformers (Hayward 1998). This indicates that PCNs have been replaced by PCBs as dielectrics and by plastics as insulating material. PCBs are nowadays largely substituted by other alternatives.
3. No requests have been received nor particular needs identified for specific exemptions on PCNs. No additional information on alternative chemicals being used to substitute PCNs was provided by the parties within the questionnaire on Annex F.

## 2.5 Summary of information on impacts on society of implementing possible control measures

*Intentional production*

1. No negative impacts on society have been reported from prohibition or phasing-out CNs within the UNECE region [UNECE 2007]. Most uses seem to have stopped worldwide, however, the information provided does not allow to draw a concrete conclusion on this. Health and environment could benefit from listing PCNs in Annex A as the re-introduction of PCNs and related risks would be prevented. A beneficial effect on health, environment and society could be expected as any currently unidentified production and use around the world should end. Relevant negative impacts are not expected.

*Unintentional generation*

1. CNs are unintentionally released from the same sources as the POP compounds dioxins and furans. Measures that reduce the release of PCDD/F emissions will also reduce CNs emissions. BAT and BEP relevant to unintentionally produced PCDD/Fs for various types of incinerators are available and already widely applied. Measures to reduce unintentional releases of PCNs through listing in Annex C would positively impact human health and the environment. Additional costs for monitoring, enforcement and supervision are considered to be low as the control measures for other PCDD/Fs are already applied.

*Stockpiles*

1. CNs are unintentionally released from existing stockpiles (waste disposal sites and old appliances). Listing of PCNs in Annex A or C would require developing strategies to identify existing stockpiles, and to manage them in an environmentally sound manner. Parties to the convention have already introduced such measures to manage PCB stockpiles. Measures in place with respect of PCB stockpiles will also efficiently reduce releases of CNs from stockpiles. Health and environment would benefit from reduced releases. Additional costs would not arise.

## 2.6 Other considerations

1. Specific relevant information on information and public education and on the status of the control and monitoring capacity has not been provided by parties or observers who submitted Annex F information.

# 3. Synthesis of information

*Risks and need for action*

1. According to the risk profile, PCNs meet all screening criteria, i.e. long-range environmental transport, bioaccumulation, persistence and toxicity. The POPRC decided that PCNs are likely, as a result of their long‑range environmental transport, to lead to significant adverse human health and environmental effects such that global action is warranted.

*Sources*

1. CNs have been used mainly for their chemical stability, including low flammability, their (electrically) insulating properties and recalcitrance including resistance to biodegradation and biocidal function. They share these properties and their scope of application with the PCBs by which they were gradually replaced since the 1950s. They have been used for several technical applications and as wood preservative. To date, intentional production of CNs is assumed to have ended, however, remaining use is still possible.
2. CNs are still unintentionally generated during high-temperature industrial processes. Of the known releases, combustion (primarily waste incineration) is considered the most significant current source. CNs are also generated in industrial processes with similar mechanisms as PCDD/Fs: They are formed during the smelting in the secondary non-ferrous metallurgical industry (where production conditions include heat, chlorine-containing recyclates and the catalytic function of metals like, e.g. copper), cement and magnesia production, aluminum refining and coking have been reported as unintentional CNs sources. There have also been indications of CNs formation at manufacturing sites producing chlorine by use of graphite anodes in mercury cell in chlor-alkali process and at low concentrations as by-products in the chlorination of drinking water.
3. Commercial PCBs contained traces of CNs. CNs were unintentionally released as contaminants in PCBs. Releases from former uses (CNs or impurities of technical PCB) contained in landfills or old appliances (stockpiles) are plausible but difficult to assess.

*Existing control*

1. In 2009 PCNs were proposed to amend Annex I (prohibition of production and use) of the Aarhus Protocol on POPs under the UNECE Convention on Long-Range Transboundary Air Pollution. The amendment will come into force when 2/3rd of the Parties have adopted the amendment. The OSPAR Commission has included PCNs in the List of Chemicals for Priority Action (by June 2003) and waste containing PCNs is characterized as hazardous waste under Annex VIII of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal.

*Releases and control measures and their efficacy and efficiency*

1. In the present document an overview of release sources of CNs from current activities and related possible control measures is given. Possible release sources are (a) intentional production (seems to have ceased), (b) unintentional production (particularly from waste incineration and other activities potentially generating PCDD/Fs) and (c) release from stockpiles (particularly waste disposals and old appliances).
2. (a) To date, intentional production of CNs is assumed to have ended, however, remaining use is still possible. To limit possibly remaining uses and to prevent re-introduction of other uses, listing of PCNs in Annex A without any specific exemptions could be the primary control measure for intentional sources under the Convention. As a consequence PCNs would be submitted to the provisions of Article 3 of the convention and the objective to eliminate their production, use, import and export.
3. Additional costs for eliminating the production and use of PCNs are not expected as alternative chemicals for the same uses are available and already in use. Health and environment could benefit from a ban of PCNs as their re-introduction and related risks would be prevented. A beneficial effect on health, environment and society could be expected as any currently unidentified production and use around the world should end. Relevant negative impacts are not expected from a ban of PCNs.
4. (b) CNs are unintentionally generated during high-temperature industrial processes. Of the known releases, combustion (primarily waste incineration) is considered the most significant current source. CNs are generated unintentionally with similar mechanisms as PCDD/Fs during other industrial processes such as smelting in the secondary non-ferrous metal industry, cement and magnesia production, aluminum refining and coking. Listing of PCNs in Annex C would subject this substance group to the measures under Article 5 of the Convention and establish the goal of continuing minimization and, where feasible, ultimate elimination of CN releases. This would include an obligation to promote best available techniques (BAT) and best environmental practices (BEP) for PCN sources.
5. Measures that reduce the release of PCDD/F emissions will also reduce PCNs emissions. BAT and BEP relevant to unintentionally produced PCDD/Fs for various types of incinerators are available and already widely applied. Measures to reduce unintentional releases of PCNs through listing in Annex C would positively impact human health and the environment. Additional costs for monitoring, enforcement and supervision are considered to be low as the control measures for other PCDD/Fs are already applied.
6. (c) CNs can be unintentionally released from landfills or old appliances (stockpiles). Possible measures to control releases from stockpiles are (1) to establish inventories of relevant landfills and control and sound management of releases (particularly leachate) from relevant waste disposals or restoration/decontamination of waste disposals, and (2) to establish inventories of stocks of relevant old appliances and their sound management. Listing of PCNs in Annex A or C would subject PCNs to the measures under Article 6 of the Convention and establish the goal of identifying stockpiles consisting of or containing PCNs and managing them in a safe, efficient and environmentally sound manner.
7. Commercial PCBs contained traces of PCNs and CNs can be unintentionally released as contaminants in PCBs. As there is a direct relation between the occurrence of PCBs and CNs in old appliances, stocks of CNs are particularly occurring in conjunction with PCBs (i.e. in PCB containing waste disposals and PCB containing equipment). Parties to the convention have already introduced measures to identify and manage PCB stockpiles. Measures in place with respect of PCB stockpiles will also efficiently reduce releases of PCNs from stockpiles. Health and environment would benefit from reduced releases. Additional costs would not arise.

# 4. Concluding statement

1. Having evaluated the risk profile on PCNs the POPs Review Committee concludes that these chemicals are likely, as a result of long-range environmental transport, to lead to significant adverse effects on human health and/or the environment, such that global action is warranted.
2. The Committee prepared this risk management evaluation and concluded that although PCNs are not known to be currently intentionally produced or used, it is important to prevent their re-introduction.
3. CNs are unintentionally generated during high-temperature industrial processes (particularly waste incineration but also in other processes known to generate PCDD/Fs). Measures that reduce the release of PCDD/Fs will also reduce PCNs releases.
4. CNs are released to an unknown extent from waste disposals and stocks of old appliances. CNs in stockpiles are particularly occurring in conjunction with PCBs (i.e. in PCB containing waste disposals and PCB containing equipment). Parties to the convention have already introduced measures to identify and manage PCB stockpiles. Measures in place with respect of PCB stockpiles will also efficiently reduce releases of PCNs from stockpiles.
5. The Stockholm Convention, through the Persistent Organic Pollutants Review Committee aims to protect human health and the environment from POPs, while being mindful of the Precautionary Approach as set forth in Principle 15 of the Rio Declaration on Environment and Development. It seeks to adopt measures to eliminate releases from intentional POP production and use, to reduce or eliminate releases from unintentional POP production, and to reduce or eliminate POP releases from its stockpiles and wastes in support of the goal agreed at the 2002 Johannesburg World Summit on Sustainable Development of ensuring that by the year 2020, chemicals are produced and used in ways that minimize significant adverse impacts on the environment and human health.
6. Having prepared a risk management evaluation and considered the management options, in accordance with paragraph 9 of Article 8 of the Convention, the Committee recommends the Conference of the Parties to the Stockholm Convention to consider listing and specifying the related control measures for PCNs in Annexes A and C.

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