



**Stockholm Convention  
on Persistent Organic  
Pollutants**

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**Persistent Organic Pollutants Review Committee**  
**Eighth meeting**  
Geneva, 15–19 October 2012

**Report of the Persistent Organic Pollutants Review Committee  
on the work of its eighth meeting**

**Addendum**

**Risk profile on chlorinated naphthalenes**

At its eighth meeting, by its decision POPRC-8/1, the Persistent Organic Pollutants Review Committee adopted a risk profile on chlorinated naphthalenes on the basis of the draft risk profile contained in document UNEP/POPS/POPRC.8/2. The text of the risk profile, as amended, is set out in the annex to the present addendum; it has not been formally edited.

**Annex**

# **CHLORINATED NAPHTHALENES**

## **RISK PROFILE**

Prepared by the ad hoc working group on chlorinated naphthalenes  
under the POPs Review Committee  
of the Stockholm Convention

**19 October 2012**

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## Executive summary

1. Chlorinated naphthalenes (CNs) are halogenated organic compounds. CNs are divided into eight homologue groups, based on the number of chlorine atoms in the molecule. These homologue groups are referred to using the prefixes mono- to octa- (e.g. mono-CNs, di-CNs, etc). Physical-chemical properties vary considerably due to the degree of chlorine substitution. Tri- to octa-CNs are very lipophilic and their water solubility and vapour pressure decrease with the degree of chlorination. Di-CNs are slightly soluble in water while the higher CNs have a water solubility of a few  $\mu\text{g/L}$ .
2. CNs had various uses similar to PCBs, which gradually replaced CNs in many applications. Characteristic functions of CN formulations were electric insulation, flame retardation and biocidal protection of goods. Until known global production virtually stopped in many countries, having drastically decreased already by the late 1970s, some 150–400 kilotons had been produced worldwide (estimates vary widely due to lack of information). However, unintentional releases continued, such as CN-contaminated PCBs, leaching from landfills, or thermal formation, e.g. during waste incineration; with waste incineration being considered the main current source of CN releases. Congener profiles of former commercial CN mixtures differ from those released from incineration or high-temperature industrial processes and have been used to distinguish between sources of release.
3. Atmospheric oxidation by hydroxyl radicals is a possible removal pathway for CNs. Calculated atmospheric half-lives of di-CNs to octa-CNs are between 2.7 to 417 days, indicating sufficient persistence for long-range transport.
4. Model results predict long-range transport for several homologues. Di- to penta-CNs are regarded as multiple hoppers that will be subject to transport by global distillation. A high Arctic contamination potential was also identified for di- to penta-CNs. The modelled transport distance for tetra-CN47 was 2,271 km (atmospheric half-life of ten days). In addition CNs have been repeatedly and globally detected in abiotic and biotic samples even in remote regions like the Arctic.
5. Biota (invertebrates and fish) from the Arctic characteristically contain between 0.3 and 6  $\mu\text{g}$  CNs/kg lipid weight, but individual concentrations of up to 69  $\mu\text{g/kg}$  lipid weight were observed in these remote regions. CN levels from biota in other regions are of the same order of magnitude. Global atmospheric CN levels have a magnitude of tenths of  $\text{pg/m}^3$ , typically 1.6  $\text{pg/m}^3$  with concentrations of 1–8  $\text{pg/m}^3$  measured in Arctic air.
6. CNs are transferred to higher trophic levels and can thus biomagnify in food webs. This transfer was observed in field measurements for higher chlorinated CN congeners (tetra- to hepta-CNs) and attributed to selective metabolism and biomagnification leading to species differences concerning the accumulation of the different congeners. BMFs, FCMFs and TMFs for tetra- to hepta-CNs above 1 were documented for benthic and pelagic food chains/webs. Prey/predator combinations including birds show high BMFs (up to 90) for tetra- to hexa-CNs. The structural similarities and thus the expected similar bioaccumulation and biomagnification of CNs and PCBs were confirmed by several food chain and food web investigations showing a similar or a bit lower bioaccumulation potential of CNs. No data on terrestrial food chains are available so far.
7. Some of these potent congeners have been shown to accumulate and biomagnify in aquatic food webs (e.g. hexa-CN66/67) and penta- hexa- and hepta-CNs are among the most frequent detected homologues in biota. CN levels found in the environment are high enough to induce dioxin-like cellular responses in feral fish as shown by empirical data. In addition, in harbour porpoises, tetra- to hepta-CNs could pass the blood/brain barrier, a mechanism designed to protect the brain from toxins. Calculated contributions of CNs to overall toxic equivalents (TEQ) of dioxin-like compounds indicate a high proportion for the benthic food chain and an important contribution to TEQ in cetaceans in the Arctic environment.
8. It can be concluded that bioaccumulation is confirmed for tetra- to hepta-CNs. Other congeners also meet the bioaccumulation criteria based on a BCF  $>5,000$  for di- and tri-CNs and a log Kow  $>5$  for octa-CN. Monitoring data in biota on di-, tri- and octa-CNs are limited and no field study reported a BMF  $>1$  for these congeners.
9. Several Halowax mixtures are very toxic in acute toxicity studies, also developmental effects in invertebrates and amphibians were observed. Modelled chronic toxicity values for di- to hepta-CNs suggest harmful effects. One major concern for aquatic as well as terrestrial organisms is the possible dioxin-like toxicity of some CN congeners. The toxicity is similar to other chlorinated compounds such as PDDD/Fs and PCBs, PBBs and PBDEs and is mainly mediated via induction of cytochrome P-450 enzymes. Especially hexa- but also penta- and hepta-CNs reveal higher toxicity than lower chlorinated congeners.
10. CNs can be absorbed via all routes of exposure and are distributed in the human body, with a half-life of 1.5 to 2.4 years estimated for hexa-CN congeners. Absorption, distribution, metabolism and toxicity are highly isomer-dependent. Hexa-CNs are among the most frequently detected congeners in human samples. There is a lack of congener-specific chronic toxicity data in laboratory animals. CNs 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.

11. The most important exposure route of the general population is suggested to occur orally via foodstuffs. Exposure via drinking water and air is also reported. CNs have been detected in human blood, milk and adipose tissue. Placental and lactational transfer of hexa-CNs have been demonstrated thus exposing sensitive stages of human life cycles to these pollutants. Consumption of contaminated fish is considered an important route of human exposures to CNs.

12. CNs can contribute substantially to the TEQ of dioxin-like compounds in Arctic air. CNs contribute to the TEQ in Arctic mammals like seals and beluga whales that are part of the diet of indigenous people. It has been demonstrated that seal and whale blubber and meat contribute to up to more than 90% of the dietary source of organochlorine pesticides and PCBs, exceeding tolerably daily intakes in some cases. There is increasing evidence of adverse health effects in Arctic indigenous people. The developing foetus is particularly susceptible to exposure to environmental chemicals, including effects of exposures to a mixture of persistent, bioaccumulative and toxic substances. Therefore it is strongly recommended to reduce the body burden of indigenous people to POPs in general and CNs in particular.

13. Based on the available evidence, CNs (i.e. di- to octa-CNs) 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.

## 1. Introduction

14. The European Union and its Member States submitted a proposal to list chlorinated naphthalenes 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).

15. Chlorinated naphthalenes (CNs) 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.

16. CNs have historically been used as wood preservation, as additive to paints and engine oils, and for cable insulation and in capacitors. While CN uses have been ceased, they are also present in PCB formulations and are unintentionally produced during combustion processes and in industrial installations.

17. This report gathers available information on CN congeners including the environmental behaviour and toxicological properties of specific congeners noting the difficulties due to abundance of various different isomers of diverse toxicity in technical mixtures, commercial preparations and also in environmental samples including foodstuffs.

### 1.1 Chemical identity

#### Names and registry numbers

Common name:	Chlorinated naphthalenes
IUPAC names and numbers and CAS registry numbers of the 75 congeners:	see Annex 1
Synonyms:	PCN, polychlorinated naphthalene, CNs, naphthalene chloro-derivatives <sup>1,2</sup>
CAS registry number:	70776-03-3

18. The system of nomenclature for CNs is similar to that for polychlorinated biphenyls and uses the numbering system shown in Figure 1.1-1. Most of the industrially produced CNs are mixtures of several congeners. Table A2-1 in Annex 2 displays 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).

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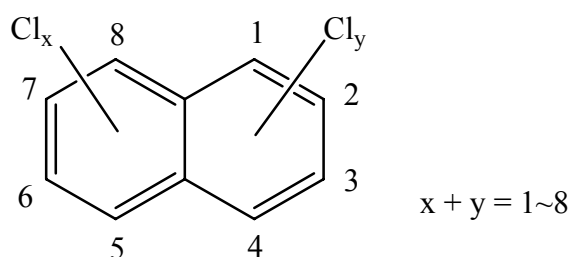
1 UNEP/POPS/POPRC.7/INF/3  
2 ACToR (2012)

19. 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  $^{13}\text{C}$ -labeled tri-CN is available (Kucklick and Helm, 2006).

### Structures

Molecular formula:  $\text{C}_{10}\text{H}_{8-n}\text{Cl}_n$   
Molecular weight: see Table 1.1-1

Figure 1.1-1: 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

20. Physical-chemical properties vary considerable due to the degree of chlorine substitution. Tri- to octa-CNs are very lipophilic with high  $\log K_{ow}$  ( $>5$ ).  $\log K_{ow}$  values in Table 1.1-1 are experimentally determined whereas Annex 1 contains Quantitative Structure–Property Relationship (QSPR) modelled values (Puzyn und Falandysz, 2007). Modelled values were lower for the more chlorinated congeners.

21. 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  $\mu\text{g/L}$ . For chemicals with low water solubility measured values have a higher uncertainty (Environment Canada, 2011) (cf. Table 1.1-1, values in brackets are estimated values with WSKOWWIN version 1.41, EPISUITE). Puzyn et al. (2009) developed a QSPR model to estimate the water solubility,  $\log K_{ow}$ ,  $K_{oa}$ ,  $K_{aw}$  and the Henry's Law Constant for all 75 congeners. The estimates for water solubility are lower than the values given in Table 1.1-1. Values of these modelled endpoints are listed in Annex 1. The range of  $\log K_{oa}$  and  $\log K_{aw}$  are summarized for the different homologue groups in Table 1.1-1.

22. 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).

23. Pure chlorinated naphthalenes are colourless, crystalline compounds (Indian Institute of Science, 2011, submitted Annex E information by Thailand).

**Table 1.1-1. Selected physical and chemical property (table modified from Environment Canada, 2011)**

Congeners	Molecular weight (g/mol)	Solubility ( $\mu\text{g/L}$ ) <sup>a</sup>	Vapour pressure (Pa) <sup>b</sup> (sub-cooled liquid, 25°C)	Henry's law constant ( $\text{Pa}\cdot\text{m}^3/\text{mol}$ , 25°C) <sup>c</sup>	$\log K_{ow}$ <sup>d</sup>	$\log K_{oa}$ <sup>e</sup>	$\log K_{aw}$ <sup>e</sup>	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	Unkno wn
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*

Congeners	Molecular weight (g/mol)	Solubility (µg/L) <sup>a</sup>	Vapour pressure (Pa) <sup>b</sup> (sub-cooled liquid, 25°C)	Henry's law constant (Pa·m <sup>3</sup> /mol, 25°C) <sup>c</sup>	Log K <sub>ow</sub> <sup>d</sup>	Log K <sub>oa</sub> <sup>e</sup>	Log K <sub>aw</sub> <sup>e</sup>	Melting point (°C)	Boiling point (°C)
Hepta-CNs	369.50	0.04* (2.60)	2.78 x 10 <sup>-4</sup> , 2.46 x 10 <sup>-4</sup>	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 <sup>-6</sup>	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 Conclusion of the Review Committee regarding Annex D information

24. The POPs Review Committee evaluated the proposal regarding chlorinated naphthalenes (UNEP/POPS/POPRC.7/2) according to the requirements in Annex D of the Stockholm Convention at its seventh meeting in Geneva. In Decision POPRC-7/2 the Committee reached the conclusion that the polychlorinated naphthalenes (di- to octa- chlorinated naphthalenes) fulfilled the screening criteria specified in Annex D. The Committee also decided to establish an ad-hoc working group to review the proposal further and prepare a draft risk profile in accordance with Annex E of the Convention.

### 1.3 Data sources

25. The draft risk profile is based on the following data sources:

- a) Proposal submitted by the European Community and its member States that are Parties to the Convention Proposal submitted (UNEP/POPS/POPRC.7/2, UNEP/POPS/POPRC.7/INF/3), 2011.
- b) Decision POPRC-7/2 of the POPs Review Committee, 2011.
- c) Information submitted by Parties and observers according to Annex E of the Convention: Azerbaijan, Bulgaria, Cameroon, Canada, China, Costa Rica, Estonia, Germany, Guatemala, Japan, Kiribati, Latvia, Mexico, Monaco, Myanmar, Netherlands, Norway, Romania, Sao Tome and Principe, Sweden, Thailand, United Republic of Tanzania, United States of America, International POPs Elimination Network (IPEN) and Inuit Circumpolar Council (ICC).

This information is available on the Convention's website.

(<http://chm.pops.int/Convention/POPsReviewCommittee/POPRCMeetings/POPRC7/POPRC7Followup/CNAnnexEinformation/tabid/2466/Default.aspx>).

- d) International Programme on Chemical Safety, Chlorinated Naphthalenes, Concise International Chemical Assessment Document 34, World Health Organization. Geneva, 2001. (<http://www.who.int/ipcs/publications/cicad/en/cicad34.pdf>)
- e) Crookes, M. and Howe, P. 1993. Environmental hazard assessment: Halogenated naphthalenes. Building Research Establishment, Toxic Substances Division, Directorate for Air, Climate and Toxic Substances, Department of the Environment Report No TSD/13
- f) Environment Canada 2011, Ecological screening assessment report on chlorinated naphthalene, June 2011 ([http://www.ec.gc.ca/ese-ees/835522FE-AE6C-405A-A729-7BC4B7C794BF/CNs\\_SAR\\_En.pdf](http://www.ec.gc.ca/ese-ees/835522FE-AE6C-405A-A729-7BC4B7C794BF/CNs_SAR_En.pdf))
- g) AMAP 2004, Arctic Monitoring and Assessment Programme 2002: Persistent Organic Pollutants in the Arctic. Oslo, Norway, 2004 (<http://www.amap.no/assessment/scientificbackground.htm>)

26. In addition to these information sources, a literature search of public data bases was conducted that focused on recent scientific literature. The following databases were used: ACToR database (<http://www.epa.gov/actor/>), Pubmed (<http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?DB=pubmed>), SRC databases (<http://www.srcinc.com/what-we-do/free-demos.aspx>), OECD eChemPortal ([http://www.echemportal.org/echemportal/index?pageID=0&request\\_locale=en](http://www.echemportal.org/echemportal/index?pageID=0&request_locale=en)), TOXNET (<http://toxnet.nlm.nih.gov/>), The Carcinogenic Potency Database (<http://potency.berkeley.edu/cpdb.html>), NITE DataBase (<http://www.safe.nite.go.jp/english/db.html>), GESTIS (<http://www.dguv.de/ifa/en/gestis/stoffdb/index.jsp>), WHOLIS WHO (<http://dosei.who.int>), IPCS Inchem (<http://www.inchem.org/>), PAN pesticide database (<http://www.pesticideinfo.org/>), Google scientific search (<http://scholar.google.com>).

27. In general, search terms include the chemical name or CAS number and/or a combination of technical terms because of the multiplicity of entries. For the same reason specific updated scientific articles were preferentially selected. The reports listed above contained individual references which have not been listed specifically in this draft risk profile unless otherwise stated.

#### **1.4 Status of the chemical under international conventions**

28. Chlorinated naphthalenes are subject to a limited 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 Convention on Long-Range Transboundary Air Pollution. The amendment will come into force when 2/3<sup>rd</sup> of the Parties have adopted the amendment.
  - The OSPAR Commission has included CNs in the List of Chemicals for Priority Action (by June 2003). Further information can be gathered at <http://www.ospar.org/>
  - Waste containing CNs is characterized as hazardous waste under Annex VIII of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal.

## **2. Summary information relevant to the risk profile**

### **2.1 Sources**

#### **2.1.1 Production, trade, stockpiles**

29. It is worth noting that production and use data outside the UNECE region are very scarce. This circumstance impairs the assessment of CN-releases on a global scale considerably.

30. CNs were produced for technical use already in the first decade of the 20<sup>th</sup> century, e.g. as dielectrics, for flame proofing or for the protection of paper and fabrics – including extensive use in paper inlays for gas masks in World War I (Hayward, 1998). Their production declined after the second world war, when they were gradually substituted by plastics (for insulation purposes) and PCBs. Still, CNs remained high volume chemicals until the 1970s (AMAP, 2004) with an annual production of 9000 tonnes worldwide in the 1920s (Jakobsson and Asplund, 2000 as cited in AMAP, 2004). Little accurate information exists about CN production volumes, in contrast to corresponding figures for PCBs: assuming that CN production never exceeded one tenth of PCB productions (Beland and Geer 1973, as cited in: Hayward, 1998), Hayward (1998) approximates a total of between 50,000 and 150,000 tonnes CN having been produced in the US from 1910 until 1960. (Hayward, 1998; Bogdal et al., 2008: 130,000 tonnes). In the US, CN production decreased significantly after 1977, down to an annual output of 320 tonnes in 1978 (IPCS, 2001). The decrease in production volumes was already owed to the growing evidence that CNs turned out to be a pollutant on a global scale (UNEP/POPS/POPRC.7/INF/3). It is interesting to note that atmospheric CN concentrations at numerous locations around the globe are one order of magnitude lower than those of PCB at identical sites (Lee et al. 2007), which corresponds well to the relation between estimated PCB and CN production volumes (see above).

31. Accordingly, sediment cores from the UK indicate a markedly increased emission of CNs from the early 1940s on, with maximum values in the late 1950s–mid 1960s and a fourfold decrease thereafter (Gevao et al., 2000). The findings are in agreement with those from Bogdal et al. (2008) who observed a CN peak at the mid-1950s in sediment cores from a Swiss alpine lake.

32. 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).

33. Commercial PCBs also contained traces of CNs (0.01–0.09%: Falandysz, 1998, Kannan et al., 2000, Yamashita et al., 2000). According to Noma et al. (2005) the impurity chlorodibenzo-p-dioxins has been identified in all Halowax formulations investigated (reported range 1.5 to 370 ng/g).

34. To date, CN production 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), with cases of CN-containing products or technical CN-formulations observed in Japan (Falandysz et al., 2008): Reports from Japan have suggested that CN formulations for laboratory use and research may have been imported from suppliers in Canada and UK in the late 1990s (Yamashita et al. 2003, Falandysz 2003 in Santillo and Johnston, 2004).

35. 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).

#### **2.1.2 Uses**

36. CNs have been used mainly for their chemical inertness, 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, which they were gradually replaced by after WW II (cf. Hayward, 1998).

37. The wide variety of (former) CN uses included (IPCS 2001):

**Less chlorinated congeners:**

Less chlorinated (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.

**Higher chlorinated congeners:**

38. The most important uses, in terms of volume, have been 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. The US Environmental Protection Agency stated that 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. It did note that the most likely possible new uses for CNs would be as intermediates for polymers and as flame retardants in plastics (IPCS, 2001)

**2.1.3 Releases to the environment**

39. As mentioned above, production and use data outside the UNECE region are very scarce.

40. IPCS (2001) *considered waste incineration and disposal of CN-containing items as the major current sources of CNs to the environment*. 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 (Denier Van Der Gon et al., 2007). Most waste is disposed through clinical, municipal and industrial incineration. Weem (2007) gives an estimate of 74% of total CN releases caused by waste combustion in Europe. Similarly, Lee et al. (2007) consider combustion processes as the most important current CN source. 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 by other authors (IPCS, 2001, Falandysz, 1998). Falandysz (1998) gives an annual estimate of 10–100 kg, and a total (ever released) volume of 1–10 tons CN formed during combustion, worldwide.

41. CNs are also suspected to be generated 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). Ba et al. (2010) calculated emission factors of 428.4 ng TEQ per ton secondary copper (aluminium: 142.8, zinc: 125.7, lead: 20.1). 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). Accordingly, in the UNECE industry accounts for ca. 10% and residential, commercial and other combustion for 11% to the total CN releases. The remaining percentage is divided between public heat and power and solvent production and use (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.

42. Another unintentional source is the release from CN-traces in technical PCB which was roughly estimated at 0.1 kt present in all Arochlor and Clophen ever produced worldwide (Falandysz, 1998). Denier Van Der Gon et al. (2007) report CN formation during PCB production as a potential source.

43. There have also been indications (characteristic congener profiles) of CN formation at manufacturing sites producing chlorine by the 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).

44. Table A2-2 in Annex 2 lists characteristic homologue patterns of different CN sources compared to remote atmospheric CN patterns. The most abundant congeners in Arctic air are tri-CN (45–65 % of CN sum) and tetra-CN

(20-47%), followed by some 10% of penta-CNs and the remaining fraction of higher chlorinated homologues. CN concentrations have been found to be elevated in air from high arctic stations (Alert, Canada and Dunai, Russia) in winter, spring and fall, following a trend for arctic haze, (Harner et al., 1998; Helm and Bidleman, 2003, AMAP, 2004, Helm et al. 2004, Bidleman, 2010). Congener analysis indicated that CNs at Alert appeared to be derived from mostly evaporation sources, while a combustion influence was more evident at a subarctic station of Ny Ålesund, Norway. Over the three-month sampling period, combustion CNs amounted to 4.8% of  $\Sigma$ CNs at Alert and 19% of  $\Sigma$ CNs at Ny Ålesund. (Bidleman, 2010).

## 2.2 Environmental fate

45. A level III fugacity model has been used to predict which environmental compartments CNs are most likely to be found in. CNs tend to remain in air or partition to soil when released only into air. CNs tend to remain in water or partition to sediments when released only to water depending on the homologue groups (Environment Canada, 2011; detailed information is compiled in Table A3-1 in Annex 3).

### 2.2.1 Persistence

#### Abiotic degradation

46. According to Lyman et al. 1990 cited in HSDB (2012) halogenated aromatics are generally resistant to aqueous hydrolysis. Therefore it is expected that all congeners do not undergo hydrolysis in water.

47. Experimental data on aqueous photolysis of CNs in a methanol solution at 30°C showed that dechlorination and dimerization were the major reaction pathways (IPCS, 2001) depending on the substitution position (peri-substituted mostly yield dechlorinated products while more unhindered CNs gave dimer products). A free-radical mechanism was proposed to explain the observed products. The reaction was found to be slower for the more highly chlorinated naphthalenes. Järnberg et al. (1999) investigated photolysis of a Halowax 1041-methanol solution using natural sunlight. They found a general shift towards lower chlorinated congeners, particularly a selective loss of 1,8-substituted congeners (especially for CN22, CN35, CN38, CN62, CN53 and CN69).

48. Similar reactions may occur in the environment as stated in IPCS (2001) however, its contribution to the depletion of CNs in aqueous compartments, soil surfaces or air cannot be assessed from this information (e.g. all experiments use methanol, and there is no determination of quantum yield or reaction rates). Järnberg et al. (1999) suggested that photolysis alters the congener pattern and has to be taken into consideration when comparing CN congener profiles and environmental samples. However the finding of Järnberg and co-workers could not be confirmed by a congener-specific analysis of historical U.K. soil samples (Meijer et al., 2001) suggesting photolysis is of minor relevance.

49. Concerning photo-oxidation in the atmosphere Crookes and Howe (1993) in UNEP/POPS/POPRC.7/INF/3 reported a half-life of 2.7 days (assumption of a typical atmospheric hydroxyl radical concentration of  $5 \times 10^5$  molecules/cm<sup>3</sup>) as a result of a smog chamber experiment of di-CN<sub>s</sub>. This finding is below the modelled data by AOPWIN v1.92, EPISUITE of 4 days. For the other compounds the following half-lives (25°C, OH concentration  $5 \times 10^5$  OH/molecules cm<sup>3</sup>) per group were predicted: 4 days for di-CN<sub>s</sub>, 8 days for tri-CN<sub>s</sub>, 18 days for tetra-CN<sub>s</sub>, 39 days for penta-CN<sub>s</sub>, 86 days for hexa-CN<sub>s</sub>, 189 days for hepta-CN<sub>s</sub>, and 417 days for octa-CN. Puzyn et al. (2008a) concluded that the main factors affecting the persistence of CNs in air were the degree of chlorination and the substitution pattern.

50. In addition, semivolatile substances are partitioned by an adsorptive or even absorptive mechanism to particles or aerosol Harner and Bidleman (1998) and thus the real atmospheric-half life could be orders of magnitude higher (European Commission, 2003).

#### Biotic degradation including degradation pathways

51. According to Falandysz (2003), thermodynamic data of CN congeners indicates that persistency towards biotic degradation decrease gradually from octa-CN to di-CN<sub>s</sub>. This is also confirmed by Thailand (2011) that state that the environmental persistence of CNs increase with the degree of chlorination.

52. Environment Canada (2011) performed a QSAR calculation on the ready biodegradability with the BIOWIN model (EPI SUITE). For tetra-CN<sub>s</sub> to octa-CN no biodegradability was predicted and estimated half-lives in water were  $\geq 182$  days. There are conflicting BIOWIN results for di-CN<sub>s</sub> and tri-CN<sub>s</sub>. In general, non ready biodegradability predictions of the BIOWIN model seem to be more certain than ready biodegradability predictions (ECHA, 2008).

53. Vulykh et al. (2005) calculated with the multicompartiment MSCE-POP model<sup>3</sup> the overall persistence expressed as half-life in the environment. It showed that for tetra-CN<sub>47</sub> the half-life in water is most essential for the evaluation of its residence time in the environment. The half-life in the environment was 3.2 months, whereas for the different compartments air, water and soil values of 0.3, 12 and 57 months were calculated.

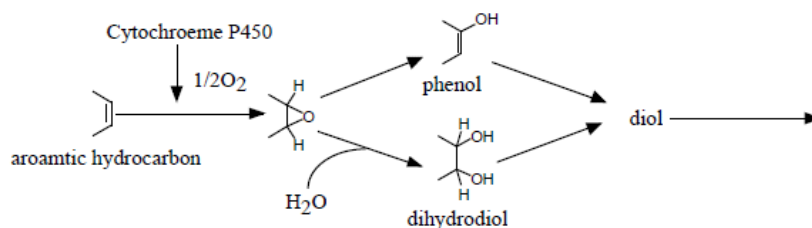
3 [http://www.msceast.org/index.php?option=com\\_content&view=article&id=24&Itemid=36&00abd285a5050fb401a1aac822a594df=6bbabc123f107cde5c62ea15af773e27](http://www.msceast.org/index.php?option=com_content&view=article&id=24&Itemid=36&00abd285a5050fb401a1aac822a594df=6bbabc123f107cde5c62ea15af773e27)

54. According to Fennell (2004) CNs can be reductively dechlorinated by *Dehalococcoides* strains. In the investigation tetra-CN27 was dechlorinated primarily to an unidentified di-CN congener.

55. Kitano et al. (2003) showed aerobic degradation of di-CNs in liquid cultures with the white-rot fungus *Phlebia lindtneri*, an organism well known for its capability to degrade persistent organic pollutants like dioxin, biphenyl derivatives and polyaromatic hydrocarbons. Di-CN was transformed via the formation of an oxide into mono- and/or dihydroxylated CNs and a CN-dihydrodiol (cf. Figure 2.2.1-1). Mori et al. (2009) could also show a 70% degradation of 1,2,3,4-tetra-CN after 14 days by the same organism. No dechlorinated degradation products were formed.

56. These biodegradability studies of CNs (for di-CNs and one tetra-CN) are limited and are focused on the potential degradability under favourable laboratory conditions. These investigations do not meet the standards and procedures of test guidelines used for regulatory assessment on biodegradation. No field degradation studies were available.

Figure 2.2.1-1: Possible pathway for the metabolism of di-CNs (source: Kitano et al., 2003)



57. In a 28 day biodegradation assay with a supernatant sewage sludge inoculum and sediment no change of congener composition of tetra- through hexa-CNs of a Halowax 1041 mixture could be detected. Concerning the lower chlorinated CNs no conclusion could be made due to absence of analytical measurements (Järnberg et al., 1999). According to NITE (2012) tri- to penta-CNs are not readily biodegradable based on OECD TG 301C.

58. Ishaq et al. (2009) showed that the CN congener pattern of anaerobic fjord sediments with former heavy CN input remains nearly constant, regardless of sediment depth, while the absolute contamination increases chronologically with depth. The constancy of the CN pattern suggests that there is no preferential degradation of single congeners as could be expected from biodegradation studies.

59. This finding is further supported by CN analyses from a sediment core of a semirural lake in northwest of England by Gevaio et al. (2000). No significant difference in homologue profiles could be detected. However, the paper does not mention statistical analyses of the different congeners per sediment section. Environment Canada (2011) calculated half lives (first-order kinetic) for tri- to hepta-CNs (no data were available for mono-, di- and octa-CNs) of above one year. The calculation was based on the theoretical DT50 of one year that results in an unrealistic high calculated concentration in 1962 compared to the year of sampling 1995. Thus it was suggested that the DT50 must exceed 1 year.

60. Concerning the soil compartment, Meijer et al. (2001) investigated time trends of CN residues in two UK soils (one soil received a sludge amendment including CNs in 1968). Environment Canada (2011) calculated dissipation half-lives from that data. Samples were taken in 1972 and 1990. The following values were calculated: 7.4 years for tri-CNs, 13.1 years for tetra-CNs and 35.3 years for penta-CNs. Hexa- and hepta-CNs showed no significant concentration decrease. For the calculation first-order kinetic was assumed. However, combustion related congeners showed an increased trend (calculation of mass% relative to the homologue group) in the control soils suggesting continuous loading that may influence the degradation calculations.

61. De Kok et al. (1983) in Crookes and Howe (1993) identified high stability of CN congeners by identical congener distribution of a contaminated soil compared to Halowax 1013 after 10-15 years.

62. There are several lines of evidence available to conclude on the persistence of tri- to octa-CN: resistance to hydrolyses based on the chemical structure, evidence on photolysis with minor relevance under environmental conditions, predicted half-lives in water  $\geq 180$  days, predicted half-lives in soil  $> 1$  year, empirical evidence from historical samples that show half-lives in sediment (tri- to hepta-CNs) and soil (tri- to hepta-CNs)  $> 1$  year. In addition, monitoring data of tri- to octa-CNs in abiotic (and biotic) matrices in the Arctic and Antarctica (cf. section 2.2.3) serve as further evidence that these congeners are persistent, undergo long-range transport and pollute remote regions. Thus it can be concluded that tri- to octa-CNs fulfil the criteria on persistence.

63. Concerning the persistence of di-CNs, model predictions were equivocal and experimental investigations show a susceptibility to biodegradation, though the data are not conclusive for an in-depth assessment. Few monitoring data of these congeners has been reported, partly because it has not been included in the analytical detection. However, based on the weight of evidence and expert judgement, it can be considered that di-CNs are also persistent.

### 2.2.2 Bioaccumulation

64. Several information sources were used to assess the bioaccumulation potential of CNs.

#### Screening assessment based on physical-chemical properties

65. The log  $K_{ow}$  values for CNs range from 4.2 to 8.5. Thus these values clearly indicate a potential for bioaccumulation. In addition to log  $K_{ow}$  information, log  $K_{oa}$  (octanol-air partition coefficient) is available for all 75 congeners (cf. Annex 1). As suggested by Kelly et al. (2004) for air-breathing organisms, respiratory elimination occurs via lipid-air exchange, and such exchange declines as  $K_{oa}$  increases, with biomagnifications predicted to occur in many mammals at a log  $K_{oa}$  above 5. Based on a log  $K_{ow}$  range of 4.2 to 8.5 and a log  $K_{oa}$  range of 5.9 to 11.6 for CNs a high bioaccumulation potential in both air-breathing organisms and aquatic organisms can be expected (log  $K_{ow}$  higher than 2 and a log  $K_{oa}$  higher than 5 according to ECHA, 2008).

#### Bioconcentration and bioaccumulation studies in aquatic organisms

66. Experimental BCF studies were available for several CN congeners (except for hexa-CNs) and range from 2,300 to 34,000 (Crooke and Howard, 1993, IPCS, 2001 and Environment Canada, 2011).

67. Opperhuizen et al. (1984) reported in their investigation BCF values in *Paecilia reticulata* for di-CNs of 2,300 to 11,000, for tri-CN21 27,000, for tetra-CN27 33,000, for tetra-CN42 34,000 and for tetra-CN43 25,000. No up-take for hepta- and octa-CN was observed. The experiment was accompanied by a high mortality (50% after 7 day). For tetra-CNs no steady-state could be achieved within 7 days thus the BCF values are probably underestimates.

68. BCFs in *Oncorhynchus mykiss* for di-CN5 were 5,600, tetra-CN27 5,100 and for octa-CN 330 according to Oliver and Niimi (1984, 1985) Methanol was used as a co-solvent. Matsuo (1981) reported for tri-, tetra- and penta-CN log BCF values of 3.76, 9.94 and 4.00 (tested species *Cyprinus carpio*). However no experimental details were given and the quoted source did also not contain any further information. According to NITE (2012) BCF values of tri-CNs to penta-CNs for Carp (*Cyprinus carpio*) of 5,600 – 11,800 for the concentration of 0.05 ppm and 4,400 – 8,500 for the concentration of 0.005 ppm during 8 weeks exposure period were reported.

69. Opperhuizen et al. (1985) suggested for hepta- and octa-CN a lack of uptake by fish based on the molecular diameter of >0.95 nm (influence of membrane permeation on the mechanism of bioconcentration). However, the second result of Oliver and Niimi (1985) indicates possible uptake. In addition, ECETOC (2005) recommends that molecular mass and size should not be used in isolation as confirmatory evidence of lack of bioaccumulation. Falandysz and Rappe (1996) showed that biological membranes are permeable even for higher molecular weight CNs such as hepta-CNs.

70. Bioaccumulation was also studied in sediment-dwelling invertebrates (*Tubifex tubifex* and *Limnodrilus hoffmeisteri*) using spiked sediment (1300 ng tetra-CN27/g dw) for 79 days following depuration. A BCF of 21,000 and a depuration half-life of 30 days were measured (Crookes and Howe, 1993). However, the BAF was calculated as ratio of concentration in worms and the pore water concentration instead of, as recommend by the OECD test guideline, the concentration of the test substance in the sediment. Thus the result is probably an overestimate.

71. In conclusion, the experimental derived BCFs for di- tri-, tetra- and penta-CNs are above 5,000. A BCF value for hepta-CNs of 0 and a BCF <5,000 for octa-CN were determined. No information concerning BCF for hexa-CNs is available. However, uptake via diet of the two homologue groups is possible and monitoring data (Gewurtz, 2009) confirmed hepta-CNs and octa-CN residues in fish (rainbow trout) tissues. In general for substances with a log  $K_{ow}$  >5 it is predicted that dietary uptake is likely to be much more significant than uptake from water (Arnot and Gobas 2003 cited in Environment Canada, 2011).

72. Tysklind et al. (1998) studied the dietary accumulation of CNs in salmon (*Salmo salar*) at different doses of Halowax 1001, 1014 and 1051 (0.1 µg/g, 1 µg/g, 2 µg/g and 10 µg/g feed) for 17 weeks. The levels of CNs increased in a dose dependent manner and were dominated by penta-, hexa- and hepta-CNs. CN42, CN58, CN61, CN66, CN 67 and CN69 showed BMFs >1 and <2 at a dietary dose of 2 µg/g. Akerblom et al. (2000) found highest BMFs for penta- and hexa-CNs (BMF for CN66/67 2.1) after 41 weeks of dietary exposure of Baltic salmon (*Salmo salar*).

#### Toxicokinetic and metabolism studies

73. Uptake efficiencies of CN66, CN67, CN71, CN73 and CN75 from diet (rainbow trout) have been investigated in northern pike and reached 63% to 78% for hexa-CNs, 68% for hepta-CN and 35% for octa-CN (Burreau et al. 1997 cited in Jakobsson and Asplund, 2000).

74. Metabolism of CNs is congener and organism specific according to the analyses of homologue patterns in food chains by several investigators (e.g. Lundgren et al. 2002, Helm et al. 2008, Falandysz, 1998).

75. As summarized in Falandysz et al. (2003) CNs without adjacent carbons unsubstituted with chlorine (CNs-NVC) are more resistant to biotransformation and thus have a tendency to bioaccumulate through the food chain. In other words, the susceptibility of metabolic degradation of CNs increases with the number of unsubstituted adjacent carbon atoms. The following congeners belong to CNs-NVC: CN no. 42, 52, 58, 60, 61, 64, 66, 67, 68, 69, 71, 72, 73, 74, 75. Helm et al. (2008) suggested excluding from this relationship CN 73, 74 and 75 based on their data (Lake Ontario food web study).

76. Opperhuizen et al. (1985) calculated half-lives in fish of 4 to 6 days for di-CN, 8 days for tri-CN21, and 7 to 30 days for tetra-CN. According to IPCS (2001) half-lives in humans are several years, suggesting high bioaccumulation. Further information on ADME (adsorption, distribution, metabolism and elimination) is compiled in section 2.4.

#### **Assessment of field data**

77. A food chain study (zooplankton-small char-large char) in an Arctic environment of a freshwater lake on Bear Island, showed similar accumulation of four CNs in biota compared to PCBs (Evenset et al., 2005). CN concentrations increased significantly from zooplankton to small char with BMFs for CN42, CN52 and CN66/67 of 10, 5.3 and 3.6, respectively. The BMF of penta-CN52 between large char-small char was 6.4, for the other congeners <1.

78. Lundgren et al. (2002) studied a benthic food chain (surface sediment-amphipod-isopod-fourhorned sculpin) in the Bothnian Bay, Baltic Sea. BSAF (biota to sediment accumulation factors) were 2.9 for tetra-CN, 1.4 for penta-CN and 0.9 for hexa-CN (average values of the homologue groups). Although the sum of CNs declined per trophic level, specific tetra-, penta- and hexa-CN showed BMFs >1. Calculated BMFs were low, suggesting many congeners are excreted or eliminated at higher trophic level. Hexa-CN accumulated more than other homologues. CN66/67 and CN69 biomagnified in isopod-sculpin. Highest BMFs (0.09-1.4) were found for 2,3,6,7-substituted congeners and those lacking adjacent hydrogen-substituted carbon atoms.

79. Another study in the Baltic Sea of a benthic and a pelagic food chain included trophic levels. Food chain magnification factors (FCMFs) <1 for all tetra-CN indicated no biomagnification, whereas FCMFs for penta-CN ranged from 0.66 to 1.29 in the pelagic food chain. Hexa-CN biomagnified in the benthic food chain with highest FCMFs for CN63 and CN72 of 1.5 (Nfon et al., 2008).

80. Corsolini et al. (2002) found higher concentrations of CNs (sum) in predatory animals such as Weddell seal, skua and polar bear compared to lower trophic organisms, suggesting biomagnification. No selective CN accumulation could be shown and no BMFs values were determined. However, the concentration increases per trophic level of CNs were comparable to those determined for PCBs in the Antarctic organisms in the same study.

81. In a food web study of Lake Ontario (plankton, mysids and amphipods, forage fish and trouts) trophic magnification factors (TMF) for CNs (sum) was 1.25 and comparable, though slightly lower, to the TMF of 1.44 for *n/m-o*-PCB (sum). Highest TMF (1.23 to 1.42) were found for tetra-CN42, penta-CN52, 60, 58, 61, hexa-CN66, 67, 64, 68, 69 and hepta-CN73. CNs tend to biomagnify to a lesser extent in the benthic pathway than in the pelagic food web (Helm et al., 2008).

82. Reported BMFs for tetra- to hepta-CN from a benthic food between algae/zebra mussel in the Great Lakes system ranged from 3 to 10. However, not all CNs that were detected in mussel showed quantifiable levels in their diet, benthic algae (e.g. octa-CN). No further increase for most congeners were found in round goby, which prey on the zebra mussels. The exceptions were CNs 52/60 and 66/67, which showed BMFs of 1.6 and 2.2. (Hanari et al., 2004).

83. Falandysz and Rappe (1996) found a BMF of 1.2 for CN66/67 as the only two biomagnifying congeners for harbour porpoise/herring in a pelagic food chain in the southern part of the Baltic Sea.

84. Järnberg et al. (1993) reviewed in Bidleman et al. (2010) found that several CN congeners biomagnified from herring to guillemot. BMFs were <5 for most tetra-, penta- and hexa-CN, but as high as 25 for CN66/67 and 15 for CN73. A food chain including fishes and black cormorants of the Baltic Sea showed highest BMFs in black cormorants for tetra-CN42 of up to 10 and hexa-CN of up to 14 (Falandysz et al. (1997) in Bidleman et al. (2010)).

85. Falandysz et al. (1997) (cited in Environment Canada (2011)) studied bioaccumulation of CNs in other predator/prey combinations from the Baltic Sea: herring/plankton, stickleback/plankton, sand eel/plankton, flounder/mussel, white tailed sea eagle/fish and harbour porpoise/herring. Almost all of these were found to have BMFs greater than 1 for at least one of the tetra-CN (95 maximum for the white-tailed sea eagle/fish) Penta-CN were found to biomagnify to a lesser extent than tetra-CN except for harbour porpoise. Hexa-CN66/67 was found to biomagnify from their food for all studied organisms in addition to other CNs biomagnification from the same homologue group in some predators. Hepta-CN biomagnified in herring/plankton, flounder/mussel, eagle/cormorant and white-tailed eagle/fish (maximum BMF 5.7). White-tailed sea eagles/fish were found to have the highest BMFs >30 for some tetra-, penta- and hexa-CN congeners.

86. According to Sweden (2011) the long term time-trend and short-term temporal variations of CNs resembles those of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) they may thus share the same

bioaccumulation/biomagnification pathways. Several authors conclude in their biomagnification studies that the biomagnification potential of CNs appears to be similar to PCBs (Hanari et al.(2004), Corsolini et al. (2002), Evenset et al.(2005), Helm et al.(2008)).

87. No food chain studies in the Arctic Ocean and no data on terrestrial food chains are available so far. Most of the studies were performed in lower food chains/webs, higher biomagnification was observed in birds.

88. There are several lines of evidence available for the assessment of the bioaccumulation potential of CNs:  $\log K_{ow} > 5$  for tri- to octa-CN, experimental derived BCFs for di- to penta-CN above 5000 and below 5000 for octa-CN; and high dietary uptake for hexa- to octa-CN. Concerning field derived measurements, BMFs and FCMFs as well as TMFs for tetra- to hepta-CN were above 1 for benthic and pelagic food chains/webs, thus demonstrating trophic transfer and accumulation in food webs. Additional studies on several prey/predator combinations including birds and mammals showed biomagnification of tetra- to hepta-CN. Monitoring data on octa-CN are limited and no field study reported a BMF  $> 1$  for this congener. This might be due to lower levels of emissions, the predicted lower mobility and/or selective absorption and metabolism. Taken together, it can be concluded that bioaccumulation potential is confirmed for di- to octa-CN.

### 2.2.3 Potential for long-range environmental transport

89. Under Annex D, an atmospheric half-life  $> 2$  days is recognized as a criterion for long-range transport potential. Calculated half-lives in air including one experimentally determined value, are between 3 and 417 days for di-CN to octa-CN. The potential of CNs for long-range environmental transport is further substantiated by both model predictions and by the occurrence of CNs in abiotic and biotic environmental media in remote regions, as illustrated below.

#### LRT model predictions

90. According to a partitioning map based on the multimedia Globo-POP model (Wania, 2006 in Puzyn et al., 2008b) four categories were defined according to their partitioning behaviour that corresponded to various modes of environmental transport: “fliers” ( $\log K_{aw} > 0$ ;  $\log K_{oa} < 6.5$ ), “multiple hoppers” ( $-4 < \log K_{aw} < 0$ ;  $6 < \log K_{oa} < 10$ ) and “single hoppers” ( $\log K_{aw} < 0$ ;  $\log K_{oa} > 10$ ) as well as “swimmers” ( $\log K_{aw} < -2$ ;  $\log K_{ow} < 7$ ). According to this scheme Puzyn et al. (2008b) characterized di- to tetra-CN and penta- to hepta-CN as multiple hoppers. However, di- to tetra-CN are suggested to show higher mobility based on their partitioning coefficients than penta- to hepta-CN. These substances can readily exchange between the atmosphere and the surface depending on temperature. Octa-CN was qualified as single hopper implying considerable less mobility compared to the other homologues.

91. Environment Canada (2011) calculated a high Arctic contamination potential (ACP) based on the partitioning characteristics for di- to penta-CN.

92. Vulykh et al. (2005) used the MSCE-POP model (a three-dimensional Eulerian multicompartiment chemistry transport model) to predict the transport of CN congener 47, a representative of the tetra-CN, the widest-spread homologue group in congener profiles of environmental and source samples (Vulykh et al., 2005). CN47 is removed from the atmosphere to almost equal parts by degradation (54%) and deposition (46%). The authors predict an atmospheric half-life of 10 days (cf. section 2.2.1), and, allowing for removal by deposition, an atmospheric residence half-time of 7 days. They model an atmospheric transport distance TR (distance from source to a point where the concentration has dropped to 1/1000 of its initial value) of 2271 km. The authors conclude that both atmospheric residence time and TR suffice to cause CN47 pollution in remote areas (Vulykh et al., 2005).

#### LONG-RANGE TRANSPORT: POLAR REGIONS

93. Environmental samples show that CNs are widespread in the Arctic, with higher concentrations found in the European Arctic. In samples from arctic Canada and Russia, CNs contribute more to the TEQ than PCB pollution (Bidleman et al. 2010).

#### Arctic Air

94. Bidleman et al. (2010) compile atmospheric CN data from seven studies for the Arctic region. Air concentrations, observed between 1990 and 2005, vary by two orders of magnitude, from 0.66 to 40  $\text{pg}/\text{m}^3$  (these are sums of different congeners, mainly of the tri- to octa-CN). Bidleman et al. (2010) point out that  $\Sigma\text{CN}$  concentrations in air are much higher at most European arctic-subarctic locations than at sites in Siberia, Iceland, Alaska and the Canadian Arctic. One study could attribute higher CN levels in the Barents Sea to air masses arriving from Europe. The global GAPS monitoring program with passive samplers yielded air concentrations of 1–8  $\text{pg}/\text{m}^3$  for Arctic sites (Lee et al., 2007). Comparison of Arctic with urban sites shows that Arctic air is dominated by the tri-CN, followed by tetra- and penta-CN, with 2% or less being made up by heavier CNs (Harner et al. 1998, Helm 2002, Helm et al. 2004). The urban homologue profiles are markedly shifted towards the heavier congeners with sizeable fractions of penta- and even hexa-CN (Lee et al., 2007).

95. Various authors (as cited in Bidleman et al., 2010) observed the dominating contribution of tri- to tetra-CN to atmospheric CN levels in Arctic air.

96. Helm et al. (2004) conclude from measurements at remote Arctic Canadian and Russian sites that evaporative emissions from source regions were likely the dominant CN source at these stations, although during winter there was an additional contribution of combustion sources (as indicated by combustion marker congeners).

#### Arctic Sediment

97. There is only little information on CN levels in subarctic (not arctic) sediment. Concentrations in surface sediment reached 1.9 ng/g dw in the northern Baltic Sea and 0.23 ng/g in a Swedish lake (Bidleman, 2010).

#### Arctic and Antarctic Biota

98. Bidleman et al. (2010) give an extensive inventory of CN levels in Arctic, Subarctic and Antarctic biota (see above). As can be seen from Table A4-1 and Table A4-2, CNs have been detected in various species across all trophic levels and over a large range of remote areas – showing the importance of long-range transport on CN pollution of remote areas. According to Bidleman et al. (2010) CN54 may have been overlooked in studies that use Halowax mixtures as standards, because it is contained in these mixtures only in trace amounts. CN54 is usually considered a combustion marker.

### **2.3 Exposure**

99. Global atmospheric sampling studies, among others, show that atmospheric CNs are ubiquitous (Lee et al. 2007). Atmospheric CNs reach highest levels in urban or industrial environments, but they are also found in very remote regions like the Arctic (Bidleman et al., 2010). Bidleman et al. (2010) point out that no significant trends in CN concentration were found during a 1987–98 monitoring of cod liver from a Norwegian fjord. Atmospheric levels observed in UK from the mid-1990s until 2001 do not indicate a decline, either (Lee et al., 2005 as cited in Bidleman et al., 2010). AMAP (2009) report that there are no studies to assess the temporal trends of CNs in the Arctic.

100. Laboratory and monitoring data show that CNs are bioavailable and uptake of CNs from several routes of exposure occur. Persson et al. (2005) showed that a high proportion of CNs is particle associated (soot and organic matter) in a marine environment thus probably lower bioavailability of CNs. However no further studies are available.

101. Falandysz (2003) reviewed the contamination of the food chain in 2003. Highest CN concentrations were found in fish of the species *Neogobius melanogaster* (14,000 pg/g ww) and Blue crab (13,000 pg/g ww). Liver of cod from Norway contained 45,000 pg/g ww and from the North Sea 210,000 pg/g ww.

102. In 2004 Domingo reviewed human exposure to CNs through the diet and estimated the daily CN intake. The total daily intake calculated for a male person with 70 kg body weight from Spain was estimated to be 45.78 ng/day; with cereals and fat and oils as main contributors. CNs were found also in milk, eggs, meat, meat and dairy products, potatoes, vegetables and fruits. The author concluded that the contribution of CNs to sum TEQ was similar or greater than that contributed by coplanar PCBs and that in some industrialized locations contributions of CNs to TEQ might be high enough to be of concern (Domingo, 2004). Recently, Fernandes and coworkers have measured CNs in 100 commonly consumed Irish foods (Fernandes et al., 2011). CNs were detected in milk, fish, dairy and meat products, eggs, animal fat, shellfish, offal, vegetables and cereal products ranging from 0.09 ng/kg whole weight for milk to 59.3 ng/kg whole weight for fish for the sum of measured CNs. penta-CN52, hexa-CN66/67 and the hepta-CN73 were the most frequently detected congeners. Marti-Cid et al. (2007) investigated the intake of chemical contaminants through fish and seafood consumption by children in Spain. The highest concentrations of CNs were found in salmon with 227 ng/kg wet weight for the sum of tetra to octa-CN. The calculated intakes from fish and seafood consumption were estimated to be 0.52 ng/day for girls and 0.97 ng/day for boys (Marti-Cid et al. 2007). Compared to the intake of a male adult of 70 kg body weight (ranging from 0.004 to max. 0.41 ng/day) by consumption of various fish species calculated by Domingo et al. (2007) it can be seen that intake by children is considerably higher.

103. Measurements of CNs in human adipose tissue in 1979 were in the ppb range (3 to 17 ppb), about 500-1,000 times below PCB concentrations. 1-3 ng/g lipid was detected in human milk samples (Hayward, 1998). AMAP (2003) states that concentrations in human liver and adipose tissue indicate CN levels 200 to 500 times lower than the total PCB burden (Weistrand and Norén, 1998 cited in AMAP, 2003). This may reflect to a certain extent the lower emissions reported in chapter 2.1.1. More recently Park et al (2010) measured PCDDs, PCDFs and PCBs and CNs in 61 healthy human volunteers. The mean CN concentration detected in blood serum was 2.1 ng/g lipid, the dominating congener was hepta-CN73 and according to the authors the sum of CNs contributed to 26.8% of the total TEQ (Park et al., 2010). CNs have also been measured in human placenta. Leino and Coworkers detected hexa-CN66/67 in almost all samples (126 from 130 above the LOQ); the 95<sup>th</sup> percentile was 0.022 ng/g fat. The 95<sup>th</sup> percentile of the sum of 14 measured CNs were 0.14 ng/g fat. By comparison to other halogenated compounds CNs were about the factor 50 below the sum of 15 PBDEs (95<sup>th</sup> percentile), 350 fold lower than the sum of 37 PCB congeners (95<sup>th</sup> percentile) but fourfold the sum of PBBs, which were mostly detected below the limit of quantification (95<sup>th</sup> percentile: sum of all PBBs (polybrominated biphenyls): 0.039). PCDD/F were detected in the pg/g fat range (95<sup>th</sup> percentile: sum of all 17 PCDD/F: 256) (Leino, et al., 2011). The review of Falandysz (2003) summarized studies from different countries (Germany, Canada, Sweden, Japan, Russia, Kazakhstan) ranging from not detected (Fukuoka, Japan) up to 250,000 pg/g lipid in human adipose tissue (Osaka, Japan). In conclusion exposure of CNs of

the general public via food is considered to be most important route, though no calculated estimates concerning the different exposure scenarios are available.

### 2.3.1 Environmental monitoring data

#### Air

104. The global study GAPS yielded an overall atmospheric CN concentration of 1.6 pg/m<sup>3</sup> (geometric mean of 40 urban, industrial and background sites from both hemispheres and all continents). Observations ranged between not detectable and 32 pg/m<sup>3</sup>, the highest levels occurring in industrial and urban locations, while ca. 90% of the remote (“background”) / rural/ agricultural sites stayed below air concentrations of 2.5 pg/m<sup>3</sup> (Lee et al., 2007). CNs were detected primarily in the northern hemisphere, with the highest levels at urban/industrial sites in Eastern Europe and Asia. Another passive sampling campaign across Europe in summer 2002 turned out congeners no. CN 23, 24, 57 and 59 as the CN species with the highest measured reported ranges: CN23 <1.3-4, CN24 <1.4-9, CN 57<0.5-5.4, CN59 <0.3-4.2, all pg/m<sup>3</sup> (Jaward et al., 2004a). Congeners no. 24 and 59 were part in commercial Halowax mixtures. However, CN 24 is also regarded as a marker congener for combustion. Jaward et al. (2004b) reported in a study along the north-south Atlantic transect a concentration range of 13 quantified CN congeners of 0.3–86 pg/m<sup>3</sup> air. The comparative concentrations of CNs in the maritime background of the northern and southern hemispheres are 1-30 pg/m<sup>3</sup> and 0.3–5 pg/m<sup>3</sup> indicating higher levels of CNs in maritime air in the northern hemisphere. Substantial concentrations of CNs were measured off the coast of South Africa (at latitude 33.88° S) (Jaward et al. 2004b). Air monitoring in Japan, China, and Republic of Korea revealed CN concentrations of 9.5 ± 1.5, 61 ± 6, and 16 ± 2.4 pg/m<sup>3</sup> respectively (Hogarh et al., 2002a). Harner et al. (2006) measured CNs at the in rural and urban sites. The high concentrations at urban sites (up to 52 pg/m<sup>3</sup>) Laurentian Great Lakes were attributed to continued emissions of historically used technical CN. Contributions from combustion-derived CNs seemed to be more important at rural locations where CN24 and 50, associated with wood and coal burning, were elevated (Harner et al. 2006).

105. CNs between 1–8 pg/m<sup>3</sup> were also detected in Arctic air, indicating long-range transport of these compounds (Lee et al., 2007). Harner et al. (1998) reported that dioxin like CNs contribute 13–67 % to the toxic equivalents caused by polychlorinated biphenyls (PCB) and PCN in Arctic air.

106. A nationwide monitoring of atmospheric POPs (persistent organic pollutants) was conducted in Ghana between May and July 2010, and observed a significant level of fractionation of CNs across the breadth of the country. The percentage composition of the lowly chlorinated homologues increased northwards, probably because of their transportation in the direction of prevailing winds. From congener profile analysis, CN45/36 is proposed as a possible source marker for emissions preempted by uncontrolled waste burning activities. Dioxin-like toxicity of air CNs in Ghana was estimated to range 0.49–5.6 fg TEQ/m<sup>3</sup> (Hogarh et al., 2012b)

#### Sediment

107. Pan et al. (2011) compiled sediment CN concentrations in various regions under different pollution regimes, including original data from the authors: while most concentrations were below 10 µg/kg, industrial influence could raise the order of magnitude of CN concentrations to mg/kg (cf. Table A4-1).

108. Bogdal et al. (2008) calculated an atmospheric deposition of 29 g CN per year onto the 47.7 km<sup>2</sup> surface area of the Swiss Lake Thun (corresponding to 6.08 mg/hectare/year) although CN were banned in Switzerland already in 1972 (Bogdal et al., 2008).

#### Biota in and outside (sub)polar regions

109. In a 1993 compilation, CN levels in fish from the boreal zone ranged between 0–10 µg/kg ww (7 studies 1984–1990 as cited in Crookes & Howe, 1993). A more recent meta-survey (Bidleman et al., 2010), covering studies from 1981–2005 in the Arctic, shows that characteristic levels (geometric means of single studies’ arithmetic means) in biota range from 0.3 to 6 µg/kg lipid, with lowest concentrations occurring in seal, and highest concentrations in invertebrates and seabirds. Mean concentrations from individual studies could be as high as 74 µg/kg lipid (Glaucous gull plasma). The studies summarised by Bidleman et al. (2010) are listed in the tables in Annex 4, together with supplementary evidence from non (sub)polar regions. A case of unusually high CN levels of 0.69–2.6 mg/kg (*sic*) was reported for White tailed sea eagle (Falandysz, 1998). Falandysz 1998 summarized concentrations of CNs in fish of up to 360 ng tetra- to hepta-CN/g lipid wt (flesh and liver) from lakes and rivers in Sweden and 9 to 290 ng/g lipid wt for whole fish from the Baltic Sea (Gulf of Gdansk).

110. Bidleman et al. (2010) investigated congener patterns in biota from (sub)polar regions, distinguishing between a) invertebrates and fish, b) seal, c) whales and polar bear and d) seabirds (see Figure A4-1 in Annex 4). Patterns vary considerably between and within these biota groups and even within organs/compartments of the same species, but there are some regularities:

- a) hepta-CNs are absent in seal and marine birds (with exceptions). They were found in some invertebrates/fish but even there they contribute less than 10% to the CN content (one exception).
- b) Seal had the strongest shift towards the lighter congeners of all groups since the samples contained only tri- to penta-CNs except for one sample.



- c) Seal also differed from the other samples by the sizeable levels of tri-CN. In contrast, tri-CN contributed little to nothing to the congener profile found in whales, polar bear, seabirds and invertebrates/fish (except Krill, which was dominated by tri-CN and single fish samples)
- d) The homologue profile of seabirds resembled that of fish, but with a shift towards the heavier hexa-CN, which were the main homologues in some cases. Hexa-CN were also the main homologues in pilot whale blubber and polar bear fat.

111. Rotander et al. (2012) found CN concentrations (sum CNs) between 0.1 and 5.2 ng/g lipid weight in blubber from subarctic/arctic seal and whale species. The highest concentrations were found in the toothed whale species which feed on a higher trophic level. Average concentrations in pilot whale and two seal species were lower in 2006/07 than 20 years earlier in the same regions, although for two species, and also for white-sided dolphin observed 1997-2006, average concentrations were highest between first and last of the three observation time points (i.e. peaking at the intermediate observation 1997-2002, depending on time series). A clear and statistically significant decrease 1990–2007 of sum CNs was only found for hooded seal from the West Ice (Rotander et al., 2012).

112. Kannan et al. (2002) reported for the year 1999 for the Mediterranean region levels in bluefin tuna up to 552 ng/kg ww, for swordfish 15-63 ng/kg ww, for cormorant 130-795 ng/kg and for swallow from Milano 700-1510 ng/kg ww. For porpoise at the west coast of Sweden 0.52-0.72 µg/kg ww were detected (Ishaq et al., 2000). In an alpine environment (Lake Thun in Switzerland) measured concentrations in white fish were approximately 1-3 µg/kg lipid (from figure in Bogdal et al., 2008).

#### **2.4 Hazard assessment for endpoints of concern**

##### **Aquatic and terrestrial organisms**

113. The ecotoxicity of CNs has been reported for several species representing different trophic levels: algae, aquatic plants, invertebrates, fish, birds and rats (cf. section on adverse effects on human health). Many studies used Halowax mixtures and this can make the results difficult to interpret due to possible toxicological interactions and dioxin impurities (Noma et al., 2005).

114. Environment Canada (2011) predicted acute and chronic toxicity data for di- to hepta-CN for green algae, daphnids and fish with the ECOSAR v0.99 (EPISUITE) model. According to the model result algae were the least sensitive group, chronic values were considerably lower for all taxa and for the higher chlorinated congeners (range for chronic endpoints EC50 or chronic value: 575 µg/L to 0.4 µg/L). Chronic toxicity was predicted to increase to <0.1 mg/L for tri- to hepta-CN for fish and daphnids.

115. A compilation of aquatic toxicity data is given in Table 2.4-1. As mentioned in Environment Canada (2011) some tests used a solubilizer such as acetone, thus test concentrations being potentially greater than the water solubility of the reported test material. Particular Halowax mixtures have no well characterized water solubility. Generally toxicity values (except for octa-CN) are considered acceptable since water solubility corresponds by a factor of 10 of measured values and are below prediction of WSKOWIN (cf. Table 1.1-1). Though the reported data have deficiencies, the results of several studies are consistent.

116. No toxicity data on sediment dwelling organisms are available according to the sources in section 1.3, although these organisms are exposed given the high log  $K_{ow}$  of CNs as well as detected levels of up to mg/kg for polluted regions (cf. section 2.3.1). Kannan et al. (2001) measured several contaminants in sediments from Michigan (including CNs, PCBs and PCDDs and PCDFs). The relative contributions of PCBs, CNs, PCDDs, and PCDFs to the concentrations of TEQ were estimated using H4IIE cell line-specific TEFs. The CNs contributed the greatest TEQ (42–84% of the total), followed by PCDFs (8–39%), PCDDs (5–16%), and then PCBs (2–3%).

**Table 2.4-1: Aquatic toxicity of CNs (Table modified from IPCS, 2001, Environment Canada, 2011)**

Chlorinated naphthalene	Species	Duration/End-point (effect)	Concentration (mg/litre)	Reference
Octa-CN	Water flea ( <i>Daphnia magna</i> )	48h LC50 /NOEC	>530/530 n	LeBlanc, 1980
Octa-CN	Mysid shrimp ( <i>Mysidopsis bahia</i> )	96h LC50	>500 n	US EPA (1980)
Octa-CN	Sheepshead minnow ( <i>Cyprinodon variegatus</i> )	96h LC50/NOEC	560 n	Heitmuller et al. (1981)
Hallowax 1000	Algae ( <i>Dunella tertiolecta</i> )	7d EC10	0.1	Walsh et al. 1977
Halowax 1099	Gras shrimp ( <i>Palaemonetes pugio</i> )	96h LC50	0.069 m, s	Green and Neff (1977)
Halowax 1099	Juvenile Horseshoe crab ( <i>Limulus polyphemus</i> )	96days LC50	0.08 n, s Significant effects on intermoult period	Neff and Giam (1977)
Halowax 1014	Brown shrimp ( <i>Penaeus aztecus</i> )	96h LC50	0.0075 m	US EPA (1980)
Halowax 1014	Gras shrimp ( <i>Palaemonetes pugio</i> )	96h LC50	0.248 m	US EPA (1980)
Halowax 1014	Sheepshead minnow ( <i>Cyprinodon variegatus</i> )	96h LC50	>0.343 m	US EPA (1980)
Halowax 1014	Frog larvae ( <i>Rana agilis</i> )	18h LC50	0.1 survivors showed delayed metamorphosis for 3 weeks	Buggiani (1980)
Halowax 1014	Striped mullet ( <i>Mugil cephalus</i> )	96h LC50	>0.343 m	US EPA (1980)
Halowax 1013	Gras shrimp ( <i>Palaemonetes pugio</i> )	96h LC50	0.074 m, s	Green and Neff (1977)

n = based on nominal concentrations; m = based on measured concentrations, s = Solubilizer was used

117. Information concerning chronic toxicity in fish is limited to a non-standard partial life-cycle assessment in medaka (*Oryzias latipes*) (Villalobos et al., 2000). Medaka fish eggs were injected with Halowax 1013, 1014 or 1051 dissolved in triolein. Following exposure, embryos developed and fry were reared to sexual maturity (four months), at which time they were euthanized. Halowax 1014 was the most toxic mixture with a dose-response relationship. The LD50 for medaka embryos was 4.2 ng/egg and compared to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin 5.5 less potent. The most significant lesion at the LOAEL of 3 ng/egg was the inability of newly hatched embryos to inflate their swim bladders. In early adult life-stage female had significantly reduced gonadosomatic indexes (GSI). In addition Halowax 1051 caused significantly decreased GSI for females after 122 days at all tested doses (0.3–10 ng/egg, no dose-response relationship could thus be shown). These results indicate that adverse effects (and possible endocrine disrupting effects) similar to dioxins on sensitive stages of aquatic organisms may occur upon exposure of CNs.

118. Genotoxicity (micronucleated erythrocytes) was observed after injection of Halowax 1013, 1051 and 1013 in Medaka fish eggs after 122 days in adults (Talykina et al., 2003). The lowest exposure concentration at which this effect was measured (0.3 ng/egg which is equivalent to 300 ng/g egg) is 5-10 fold greater than that observed in field-collected fish tissues from highly contaminated sites (Belfroid et al., 2006).

119. Some CNs show toxic activities similar to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and co-planar PCBs by binding to the Ah-receptor, and consequently CNs have been assigned relative effect potencies (REPs) similar to the co-planar PCBs (penta-, hexa- and hepta-CN) (Villeneuve et al., 2000). Akerblom et al. (2000) found that in a dietary feeding study with duration of 41 weeks (Halowax 1014) induction of ethoxyresorufin-O-deethylase (EROD) activity occurred at the low-dose group at 0.1 µg CN/g food. After 8 weeks of exposure fish contained 304 ng tetra-CN to hepta-CN/g fat that is comparable to levels found in the environment (cf. para. 108). At the highest test level (10 µg/g food), female gonad development was delayed.

120. Corsolini et al. (2002) found that contribution of CNs to toxicity equivalency quotients (TEQ) was negligible in polar organisms including polar bear due to the absence of toxic higher chlorinated congeners (i.e. CN63, CN69, CN70). In contrast CNs contribute significantly to the burden of dioxin-like compounds in Lake Ontario biota, contributing between 12 and 22% of total CN and PCB TEQ in lake trout and up to 69% in benthic organisms (Helm et al. 2008). This could be explained by the presence and accumulation of penta-, hexa- and hepta-CN (CN52, CN60, CN66, CN67, CN73).

121. CNs contributed an additional 11% (mean, range of 7-19%) to the total TEQ of measured dioxin and dioxin-like compounds in beluga blubber (AMAP 2004) and up to 6-15% in longfinned pilot whale blubber (Bidleman et al. 2010). In sub-Arctic and Arctic mammals the highest calculated TEQ concentration for CN66 ranged between 4 and 17 pg/g lw in pilot whales (Rotander et al., 2012). The TEQ values are lower than those considered to elicit toxicological effects in birds and marine mammals (Kannan et al. 2001 cited in Rotander et al. 2012). However, the calculated TEQ concentration in Rotander et al. was based on CN66 only and did not include other dioxin-like compounds.

122. In a dietary study on chicken and turkeys a LC50 of 20 mg Halowax 1014/kg food was determined for turkeys while chicken showed little effects (Pudelkiewicz et al., 1958 in IPCS, 2001). Adverse effects were also reported for 5 mg/kg food (reduced body weight of 33%, lethality 7%). Gross histological examinations of the turkeys revealed enlarged and darkened livers. Octa-CN at a dose of 125 mg/kg food caused no significant effects on the turkeys.

123. In conclusion, several Halowax mixtures are very toxic in acute toxicity studies, and developmental effects in invertebrates and amphibians were observed. Modelled chronic toxicity values for di- to hepta-CN suggest harmful effects. Chronic toxicity was predicted to increase from 136 to 0.4 µg/L for di- to hepta-CN for fish and daphnids. Results from a partial life-cycle study in fish suggest possible endocrine disrupting effects. Genotoxicity was demonstrated in a non-standard test protocol in fish.

124. One major concern for aquatic as well as terrestrial organisms is the possible dioxin-like toxicity of some CN congeners. Some of these potent congeners have been shown to accumulate and biomagnify in aquatic food webs (e.g. CN66/67). CN levels found in the environment are high enough to affect feral fish as shown by empirical data. In addition, Ishaq et al. (2000) showed that in harbour porpoises, tetra- to hepta-CN could pass the blood/brain barrier, a mechanism designed to protect the brain from toxins. Calculated contributions of CNs to overall TEQ indicate a high proportion for the benthic food chain and an important contribution to TEQ in cetaceans in the Arctic environment.

#### **Assessment of adverse effects on human health**

125. Toxicological assessment of CNs implies difficulties due to abundance of various different isomers of diverse toxicity in technical mixtures, commercial preparations and also in environmental samples including foodstuffs. While CNs have not yet been included in the official development of TEFs, toxicity studies of CNs have shown that similar to other halogenated compounds such as PCBs, PCDD/Fs the toxicity level depends upon the number and the location of the halogen atoms (Mc.Conell 1989 in Kimbrough and Jensen, 1989). Particularly the CNs with the planar structure similar to TCDD, may exert a toxicity comparable to the more toxic PCBs (IPCS, 2001). Also, similar to PCDDs, PCDFs, and PCBs, CNs are thought to interact with the Ah receptor and it has been confirmed in part that exposure to CNs can result in a pattern of biochemical and toxic responses typical for dioxin-like compounds (IPCS, 2001). Some CNs have enzyme-inducing properties (AHH, EROD, luciferase) comparable to PCDDs, PCDFs, and PCBs. For the most active and persistent CN congeners, relative potencies were similar to those of some PCBs. Therefore, IPCS (2001) conclude that CNs should be included in the development of TEFs (IPCS, 2001).

126. IPCS (2001) state that possible long-term effects of CNs are of most concern, and that exposure to CNs should be minimized as much as possible, in part because effects on endocrine functions have been shown to occur at very low doses.

#### **Metabolism**

127. CNs can be absorbed via all routes of administration. The distribution of commercial CN congener mixtures (Halowax 1014 and 1051) was investigated after 1, 10, 30 and 120 days of oral exposure of rats by analysis in liver and adipose tissue. After 10 days the dominating compound in the liver was hexa-CN67, which was the only detectable compound after 120 days (Asplund et al, 1986). Also in studies with FireMaster BP-6, which is known to be contaminated with hexa-CN67, this CN was found to be the major persisting congener (Birnbaum et al. 1983, Birnbaum and Mac Kinney, 1985: in Kimbrough and Jensen, 1989). Studies on metabolism with different CN congeners have shown that higher chlorinated compounds (penta-octa-CN) were not metabolised, whereas lower CNs formed hydroxylated CNs (Kimbrough and Jensen, 1989).

128. Hexa-CNs are also persistent in humans; half-lives of 1.5-2.4 years were calculated based on monitoring results of three individuals exposed to CN-contaminated rice oil in Taiwan, half-lives very similar to those for selected PCDFs (Ryan & Masuda, 1994 and Ryan et al., 1993 in IPCS, 2001).

129. Similar to TCDD and related compounds a transfer of hexa-CN66 via placental and lactational routes was demonstrated (Omura et al. 2000).

#### **Toxicity in laboratory animals**

##### **Acute and subacute toxicity**

130. As for other known chlorinated compounds, chronic exposures to low levels lead to a significant lower cumulative lethal dose compared to single acute lethal exposure doses. According to Mc.Conell (1989) (cited in Kimbrough and Jensen, 1989) the mean time to death for these kinds of substances is 2-3 weeks after a single exposure for most small laboratory animals and longer for larger domestic animals, dogs and non-human primates.

131. The LD<sub>50</sub> values of chlorinated naphthalenes are highly isomer- specific: e.g. >3mg/kg bw for tetra-CN48 (IPCS, 2001). In guinea pigs the relative toxicity of tetrachlorinated congeners of dioxins, furans, biphenyls, naphthalenes and brominated naphthalenes was evaluated by comparing their respective LD<sub>50</sub> values. The toxic potency in terms of LD<sub>50</sub> was estimated for tetra-CN48 to be one compared to 1883 (2,3,7,8 TCDD), 505 (2,3,7,8 TCDF), 21 (2,3,6,7 TBN) and 8 respectively (3,3',4,4',5,5'-hexachlorobiphenyl). Toxicity for all these classes of compounds is highly species specific, with high susceptibility in poultry, guinea pigs, mink and nonhuman primates. Studies in laboratory rodents suggest gender differences i.e. higher female susceptibility and especially high susceptibility in young animals (Mc.Conell 1989 in Kimbrough and Jensen, 1989).

132. To date, CNs are not included in an internationally agreed toxic equivalency factor (TEF) system. *In vitro* bioassays were used to describe the relative potency of CNs compared to TCDD in terms of EROD induction in fish cell lines and rat cell lines as well as activation of a Dioxin-Responsive-Elements (DRE)-luciferase reporter gene within the same rat cell line. The intention was to determine the relative contribution of CNs to the total dioxin – like activity associated with environmental samples. Hexa-CN exhibited relative potencies around  $10^{-3}$ , followed by penta-CN with potencies between  $10^{-3}$  to  $10^{-7}$  (lower than TCDD) comparable to those of some PCBs, whereas lower chlorinated congeners (di-,tri-, tetra-CN) were less active (Villeneuve et al., 2000). Blankenship et al. also used a DRE-luciferase reporter-gene assay to show that the most potent congeners were hexa-CN66, hexa-CN67 and hepta-CN73 with TCDD relative potencies of  $4 \times 10^{-3}$  and  $10^{-3}$  respectively. Halowax mixtures revealed activity between  $8.9 \times 10^{-3}$  (Halowax 1051),  $3.8 \times 10^{-5}$  (Halowax 1014); and  $1.8 \times 10^{-3}$  (Halowax 1013) relative to TCDD (Blankenship et al, 2000).

133. Olivero-Verbel et al. (2004) used QSARs (quantitative structure activity relationships) to evaluate the potency of CNs with regard to AhR mediated reactivity. From 75 CNs 14 were of predicted activity, all of them have also been tested positively in *in vitro* experiments. Among these were mainly the higher chlorinated congeners : tetra-CN39; penta-CN50; penta-CN51; penta-CN52; penta-CN54; penta-CN60; hexa-CN63; hexa-CN64; hexa-CN66; hexa-CN67; hexa-CN68; hexa-CN69; hexa-CN70; hepta-CN73.

134. Acute exposure of rats to CNs caused an increase in the level of total cytochrome P-450 as well as the activity of CYP 1A (12-15 fold increase) in the liver after 24, 72 and, most pronounced, at 240 hours (Galoch et al., 2006).

135. Short term exposure to CNs (penta- and hexa-CN) of 125 mg/rat per alternate day for 26 days showed liver changes and necrosis. Rabbits treated subcutaneously with a hexa-hepta CN mixture (30 mg/day) died within 12-26 days, showing liver changes and necrosis, whereas none of the rabbits treated with a tri/tetra-CN mixture died (IPCS, 2001).

136. The subacute toxicity of a CN mixture and its effect on cytochrome P-450 levels in rats was investigated by Kilanowicz et al. (2009). Male Wistar rats were treated 7, 14 and 21 times with 10 and 100 mg/kg bw mixture of CN (containing 54% tetra-, 8% penta-, 23% hexa- and 14% hepta-CN similar to Halowax 1014). Beside an increase in lipid peroxidation, increase in malondialdehyde MDA levels, decrease in glutathione (GSH) levels and induction of Cytochrome P450, CYP 1A (10-21-fold) a significant loss of body mass was reported (Kilanowicz et al., 2009). In a later study the toxicity of hexa-CN and its potential to induce CYP 1A in the rat after single and repeated exposure was shown. Even the lowest dose of 1 mg/kg bw induced CYP 1A significantly; substantial body mass loss was observed after a single dose of 250 mg/kg bw and after repeated doses of 10 mg/kg bw. Due to a dose-dependent increase in lipid peroxidation the generation of oxidative stress was assumed. Tetra-CN given at the same repeated dose as that in the previous mentioned experiment used mixture neither showed evident toxicity nor alterations in biological parameters (Kilanowicz and Skrzypinska-Gawrysiak, 2010).

137. Medium-term experiments with technical mixtures of CNs in rats and guinea-pigs have shown weight loss, liver damage and death after oral, dietary and inhalative exposures (Hayward, 1998).

138. It has been observed that domestic animals react more sensitively to CNs than laboratory rodents. Sheep treated with a 1.1 mg/kg bw/day CN mixture for 90-135 days suffered from severe liver damage leading to deaths (IPCS, 2001).

#### **Skin irritation, dermal lesions and acne**

139. CNs caused skin irritations and hyperkeratotic activity was observed with penta- and hexa-CN. Bovine hyperkeratosis was described after a 5-10 day oral exposure period to 0.69-2.4 mg/kg bw/day of penta-, hexa-, hepta- or octa-CN. Among the symptoms of this severe systemic disease were deaths, severe weight loss, and liver damage was reported. Accidental ingestion by cows of CNs led to bovine hyperkeratosis in the USA in the 1940s and 1950s. Similar symptoms were also observed in laboratory animals during medium term oral or inhalation exposure (IPCS, 2001).

#### **Oxidative stress and lipid peroxidation**

140. CNs have been shown to induce oxidative stress, lipid peroxidation and decreasing activities of detoxifying enzymes. In the liver of rats treated with Halowax 1014 an increase in conjugated dienes (suggesting lipid peroxidation) and decreasing activities of superoxide dismutase and catalase in the liver and in the testes was reported. 3 months after treatment a decrease of glutathione peroxidase and glutathione transferase in the testes was observed, the only change in lipid peroxidation was a decrease in thiobarbituric acid reactive species. Also in the liver an increase in thiobarbituric acid has been observed after treatment of rats with a CN-mixture containing tetra- to hepta-CN (IPCS, 2001).

#### **Genotoxicity and Carcinogenicity**

141. Limited data are available concerning genotoxicity of CNs. 1,2,3,4-tetra-CN were not mutagenic in the Ames test with *Salmonella typhimurium* TA 98, and TA 100 with and without metabolic activation. No genotoxicity studies with the more toxic congeners have been identified. A non-guideline study in erythrocytes of medaka fish demonstrated genotoxicity of several Halowax mixtures (Talykina et al. 2003, see section above).

142. No long term and carcinogenicity studies with laboratory animals have been performed with CNs.

143. Therefore no overall conclusions on genotoxicity and carcinogenicity of CNs can be derived.

#### **Effects on fertility, reproduction and development**

144. Effects on male fertility were reported for hexa-CN66 after gestational administration of a dose of 1 µg/kg/bw/day in rats (IPCS, 2001). Developmental toxicity of CNs was investigated by Kilanowitz and coworkers. Groups of 15-19 mated female Wistar rats were treated with 0.3, 1.0, 3.0 and 9.0 mg/kg bw of an CN mixture (containing 54% tetra-, 8% penta-, 23% hexa- and 14 % hepta-CNs similar to Halowax 1014). CNs administration in the organogenesis period within the range of 0.3 to 9 mg/kg bw lead to significantly enhanced intrauterine mortality manifested by a larger number of postimplantation losses in the litters, as also observed in earlier studies. A dose-dependent foetotoxic effect has been found, i.e. decreased body weight and length of foetuses, disorders of intrauterine development, delayed process of ossification and retarded development of internal organs. Foetotoxic effects were also observed at the lowest dose, in the absence of maternal toxicity giving clear-cut evidence of teratogenicity (Kilanowitz et al., 2011). Also in domestic animals reproductive effects were observed: squamous metaplasia of seminal vesicles and epididymides, testicular degeneration and decreased sperm production, squamous metaplasia of vaginal wall, uterine, congestion and haemorrhage, abortion and decreased milk production after administration of doses in the mg/kg dose range over days or weeks (IPCS, 2001).

145. No embryotoxic effects have been observed after administration of 1 µg hexa-CN66/kg bw /day on days 14,15 and 16 of gestation, but acceleration of the onset of spermatogenesis in male offspring has been reported. Maximum levels of luteinizing hormone (LH) and follicle stimulating hormone (FSH) were observed earlier in the treated group as in the control group. Therefore it was considered that the onset of LH and FSH secretion from the pituitary gland was accelerated and further that this endocrine disruption had been the cause for the acceleration of spermatogenesis. An increase in testis weight (postnatal day 31 and 48) and increase in postmeiotic tubules (postnatal day 31) as well as increase in seminal vesicle weight was observed. On postnatal day 89, the sperm count was not significantly different from the control (Omura et al., 2000).

#### **Neurotoxicity**

A study of hexa-CN exposure in male Wistar rats demonstrated impaired long-term memory, reduced pain sensitivity and stress-induced analgesia at hexa-CN levels low enough to avoid any signs of overt toxicity (Kilanowicz et al., 2012).

#### **Toxicity in humans**

146. First reports of workers developing chloracne after exposure with CNs were published in the early 1940s. Systemic symptoms included digestive problems, anorexia, nausea and vertigo (Touraine et al. 1934 cited in Hayward, 1998). Crow (1970) reported large chloracne outbreaks in Germany during World War I and after the 1930s due to use of CNs in cable manufacture, wood preservation and additives in oil grew. Outbreaks of chloracne were then frequently reported in the United States, Britain and Germany (Crow 1970, cited in Hayward, 1998). According to Hayward (1998) three men died in 1936 within weeks of becoming ill with acute cases of hepatic jaundice after exposure with a tetra- and penta-CN mixture or tetrachloro and PeCNs mixed with chlorobiphenyl. A series of fatal poisonings occurred in the first half of the 20<sup>th</sup> century. Several cases of deaths after CN exposure were reported, some of them after acute yellow atrophy of the liver (Hayward, 1998).

147. A cohort mortality study was conducted in the population employed at a cable manufacturing plant during World War II. Excess mortality from cirrhosis of the liver was observed and related to the chronic effect of chlorinated naphthalene exposure (Ward et al., 1996). Popp et al. (1997) found liver dysfunction in 6 of 16 CN exposed workers, elevated GGT values and also in some cases fatty livers.

148. 31 men aged 25 to 35 years were intentionally exposed to Halowax 1014 (containing mainly penta- and hexa-CN) in mineral oil to different locations of the skin for two months. Chloracne appeared after 4-6 weeks and continued to spread and develop after the treatment period. Metaplasia of the epithelial lining of the follicle to a keratin producing membrane and sebaceous gland loss was described as well as inflammatory response. Hyperpigmentation and scarring remained evident 1 year after treatment. Halowaxes 1000, 1001, 1052 and 1051 containing mainly di-,tri-, tetra-, hepta-and octa-CNs were described as not acnegenic (Shelley and Kligman, 1957 referenced in Hayward, 1998).

149. 95% of workers (56 out of 59) exposed to tetra- and penta-CN via dermal contact and inhalation of fumes in the application of a wax insulation to wire coils at an electrical plant developed dermatoses diagnosed as chloracne and systemic effects such as headache, fatigue, vertigo and anorexia (Kleinfeld et al., 1972).

150. Results of a cohort study among 9,028 workers, including approximately one- third women, suggest an association of CN exposure with excess of malignant neoplasms. An association of tumours of the connective tissue was suggested with workers with over 1 year of CN exposure and 25 years latency. Concordant excesses were also reported for malignant neoplasms of the stomach, rectum and trachea, bronchus and lung. Significant excesses in two rare causes of death were reported among 460 individuals with chloracne within the cohort: oesophagus and benign and unspecified neoplasms, without an overall increase of the mortality rate. Limitations of the study include short

duration of exposure to CNs (max. 5 years, 80% of the population max. 2 years) and co-exposure with asbestos (Ward et al. 1994).

### 3. Synthesis of information

151. CNs were produced for a large variety of uses from the early 20th century, peaking between the late 1950s and mid 1960s and strongly decreasing thereafter. Total global production is estimated at 150,000–400,000 tonnes in the period 1920–1965. CNs were unintentionally released as contaminants in PCBs and are still generated during high-temperature industrial processes. Releases from former uses (CN or impurities of technical PCB) contained in landfills or old appliances are plausible but difficult to assess. In urban sites continued emissions of suggested historically used technical CNs have been reported. 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. Of the known releases, combustion (primarily waste incineration) is considered the most important current source, at 10–100 kg per year, worldwide. For Europe, waste incineration contributed an estimated 74% to total CN emissions in 2000.

152. CN concentrations in Eastern Asia were found to reach up to 61 pg/m<sup>3</sup>. The global GAPS study revealed a characteristic value of 1.6 pg/m<sup>3</sup> across continents and source distances. Concentrations between 1–8 pg/m<sup>3</sup> have been found in the Arctic, where CNs can contribute substantially to the toxic equivalents (TEQ) presented by dioxin-like contaminants. CN levels in sediments range from 0.01–10 µg/kg dw (order of magnitude) but can reach several milligrams/kg dw in polluted areas. Levels in (sub)arctic biota range from typically between 0.1 and 1 µg CNs/kg lipid weight but concentrations beyond 10 µg/kg have repeatedly been measured.

153. In addition to the evidence of long-range transport by monitoring data model results predict long-range transport for several homologues. Di- to penta-CNs are regarded as multiple hoppers that will be subject to transport by global distillation. A high Arctic Contamination Potential was also identified for di- to penta-CNs. The modelled transport distance for tetra-CN47 was 2,271 km (atmospheric half-life of 10 days).

154. CNs are not expected to hydrolyse due to the absence of hydrolysable functional groups. Photolysis may occur under environmental conditions. Its role is considered minor based on historical collected environmental samples from soil. CNs can also be oxidized in the atmosphere by OH-radicals. However, the rate decreases with increasing chlorine substitution and the calculated half-lives including one experimentally determined value are between 2.7 and 417 days for di-CN to octa-CN.

155. Biodegradation for di-CN and one tetra-CN was demonstrated under favourable laboratory conditions, the tests were performed with specialised xenobiotic degrading fungi. No field degradation (simulation) studies were available. However, analyses of historical samples in soil and the comparison of the homologue profile in soil and sediment cores allowed the determination of half-lives for both compartments >1 year for tri- to hepta-CN.

156. CNs are transferred to higher trophic levels and can thus biomagnify in food webs. This transfer was observed in field measurements for higher chlorinated CN congeners (tetra- to hepta-CN) and attributed to selective metabolism and biomagnification leading to species differences concerning the accumulation of the different congeners. BMFs, FCMFs and TMFs for tetra- to hepta-CN above 1 were documented for benthic and pelagic food chains/webs. Prey/predator combinations including birds show high BMFs (up to 90) for tetra- to hexa-CN. The structural similarities and thus the expected similar bioaccumulation and biomagnification of CNs compared to PCBs was confirmed by several food chain and food web investigations showing a similar or a bit lower bioaccumulation potential. No data on terrestrial food chains are available so far.

157. It can be concluded that bioaccumulation is confirmed for tetra- to hepta-CN. Other congeners also meet the bioaccumulation criteria based on a BCF >5000 for di- and tri-CN and a log K<sub>ow</sub> >5 for octa-CN. Monitoring data in biota on di-, tri- and octa-CN are limited and no field study reported a BMF >1 for these congeners.

158. Several Halowax mixtures are very toxic in acute toxicity studies, and developmental effects in invertebrates and amphibians were observed. Modelled chronic toxicity values for di- to hepta-CN suggest toxic effects. Chronic toxicity was predicted to increase to <0.1 mg/L for tri- to hepta-CN for fish and daphnids. One major concern for aquatic as well as terrestrial organisms is the possible dioxin-like toxicity of some CN congeners.

159. The dioxin-like mechanism of toxicity of CNs is depending on the degree of chlorination. QSAR estimations as well as in vitro and in vivo experiments have shown that toxicity increases with the number of chlorine-atoms and is structure related; the highest toxicity has been demonstrated for hexa-CN, and to some extent, penta- and hepta-CN.

160. Some of these potent congeners have been shown to accumulate and biomagnify in aquatic food webs (e.g. CN66/67) and penta- hexa- and hepta-CN are among the most frequent detected homologues in biota. CN levels found in the environment are high enough to induce dioxin-like cellular responses in fish as shown by empirical data. In addition tetra- to hepta-CN could pass the blood/brain barrier of harbour porpoises, a mechanism designed to protect the brain from toxins. Calculated contributions of CNs to overall TEQ indicate a high proportion for the benthic food chain and an important contribution to TEQ in cetaceans in the Arctic environment.

161. CNs are proven to interact with the Ah receptor and therefore can induce toxic effects typical for dioxin-like compounds. A number of short and medium term tests prove high acute toxicity, i.e. weight loss, liver damage and delayed deaths at relatively low concentrations (>3mg/kg), but considerably higher than TCDD (approximately three orders of magnitude) have been reported. Also dermal lesions irritation and hyperceratotic symptoms have been observed in laboratory and domestic animals. Evidence for teratogenic effects and endocrine disrupting effects and effects on fertility have been described in rats. Reproductive abnormalities have been also observed in domestic animals after daily CN exposure in the mg/kg bw range. Neurotoxicity has been observed in rats. However congener specific experimental data in laboratory animals are scarce.

162. Apart from negative test results with mono- and tetra-CNs, there are no genotoxicity data for CNs available. Genotoxicity was demonstrated for Halowax mixtures in a non-guideline fish study. No long term carcinogenicity studies have been performed in laboratory animals. Also no studies on possible immunotoxic effects have been identified. Occupational studies have proven negative effects on human health; some of them were also experienced in animal studies (dermal effects, liver disease, death). Some evidence for an association with the excess of specific cancers has been shown.

163. CNs have been concluded to be potent foetotoxic and teratogenic agents producing effects similar to those of other toxic dioxin-like compounds. CN-exposed fish had delayed gonadal development. Hexa-CN66 has been found to accelerate the onset of spermatogenesis in male offspring of rats when given to young animals at 1 µg/kg bw/day on days 14-16 of gestation, suggesting potential for endocrine disruption at very low exposure concentrations.

164. Exposure of the general population occurs primarily through foodstuffs (e.g. fish). Exposure via drinking water and air is also reported. CNs have been detected in human blood, milk and adipose tissue. CNs contribute to the TEQ in Arctic mammals like beluga whales that are part of the diet of Arctic indigenous peoples. It has been demonstrated that seal whale blubber and meat contribute to up to more than 90% of their dietary source of organochlorine pesticides and PCBs, leading to exceeding tolerably daily intakes in some cases. There is increasing evidence of adverse health effects in Arctic indigenous peoples. The developing foetus is particularly susceptible to exposure to environmental chemicals, effects of exposures to a mixture of persistent, bioaccumulative and toxic substances (AMAP, 2003).

#### **4. Concluding statement**

165. While the commercial CN manufacture in the UNECE region has drastically declined since their large-volume production in the first half of the 20<sup>th</sup> century, the major current source of CNs is probably waste incineration. Releases from former uses of CNs or as impurities of technical PCB contained in landfills or old appliances are plausible but difficult to assess. Moreover, former and current production and unintentional releases outside the UNECE-region are largely unknown.

166. CNs are atmospherically transported to Arctic and subarctic regions far from local sources. Several CNs homologues are persistent in the environment and investigations on food webs and food chains confirm CNs selectively accumulate in invertebrates, fish, seabirds and marine mammals.

167. CNs show a dioxin-like mechanisms of toxicity thus contributing to the overall toxicity of dioxins and dioxin-like compounds such as coplanar PCBs. Some of the potent penta- hexa- and hepta-CN congeners are among the most frequent detected homologues in addition to the confirmed bioaccumulation in biota thus exposing predators to high levels of these toxic compounds. Especially endocrine disrupting effects at low exposure concentrations and possible long term effects on wildlife and future generations are of concern. Despite the lack of experimental data for endpoints of concern such as carcinogenicity and immunotoxicity these effects cannot be excluded based on toxicological and structural similarities to the known toxicity of polychlorinated biphenyls. Possible long-term effects of CNs are of most concern, and exposure to CNs should be minimized as much as possible.

168. The general public, and in particular Arctic indigenous peoples, are exposed to CNs in addition to a wide array of other contaminants, including already regulated dioxin-like compounds such as PCBs, adding to the overall body burden. Several of these contaminants (including PCBs), already exceed guideline levels in Arctic aboriginal peoples, and new evidence indicates that POPs and heavy metals such as mercury and lead can affect the health of people and especially children at lower levels of exposure than previously thought (AMAP, 2009).

169. Therefore it can be concluded that CNs (specifically di- to octa- chlorinated naphthalenes) 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.

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## Annex 1

Identity and QSPR modelled data of CNs <sup>4</sup>							
#CN	CN congener	CAS no. <sup>5</sup>	Log10 Water solubility [ $\mu\text{g}\cdot\text{dm}^{-3}$ ]	Log $K_{ow}$	Log $K_{oa}$	Log $K_{aw}$	Henry's Law constant [ $\text{Pa m}^3 \text{mol}^{-1}$ ]
1	1-chloronaphthalene	90-13-1	3.29	3.97	6.02	-2.05	22.21
2°	2-chloronaphthalene	91-58-7	3.10	3.93	5.93	-2.01	24.48
3	1,2-dichloronaphthalene	2050-69-3	2.58	4.47	6.85	-2.38	10.26
4	1,3-dichloronaphthalene	2198-75-6	2.40	4.61	6.68	-2.07	21.00
5	1,4-dichloronaphthalene	1825-31-6	2.48	4.67	6.76	-2.09	20.15
6°	1,5-dichloronaphthalene	185-30-5	2.40	4.58	6.61	-2.03	23.24
7	1,6-dichloronaphthalene	2050-72-8	2.43	4.63	6.56	-1.93	29.15
8	1,7-dichloronaphthalene	2050-73-9	2.52	4.59	6.77	-2.18	16.22
9	1,8-dichloronaphthalene	2050-74-0	2.87	4.20	7.02	-2.83	3.67
10	2,3-dichloronaphthalene	2050-75-1	2.41	4.47	6.79	-2.32	11.95
11	2,6-dichloronaphthalene	2065-70-5	2.27	4.45	6.55	-2.10	19.64
12°	2,7-dichloronaphthalene	2198-77-8	2.22	4.63	6.61	-1.98	25.95
13°	1,2,3-trichloronaphthalene	50402-52-3	1.81	5.07	7.63	-2.57	6.72
14	1,2,4-trichloronaphthalene	50402-51-2	1.78	5.41	7.50	-2.09	19.99
15	1,2,5-trichloronaphthalene	55720-33-7	1.71	5.31	7.37	-2.06	21.70
16	1,2,6-trichloronaphthalene	51570-44-6	1.74	5.25	7.34	-2.09	19.98
17	1,2,7-trichloronaphthalene	55720-34-8	1.75	5.23	7.60	-2.37	10.65
18	1,2,8-trichloronaphthalene	55720-35-9	2.11	4.59	7.94	-3.35	1.11
19	1,3,5-trichloronaphthalene	51570-43-5	1.61	5.41	7.33	-1.92	29.96
20	1,3,6-trichloronaphthalene	55720-36-0	1.44	5.50	7.19	-1.68	51.24
21	1,3,7-trichloronaphthalene	55720-37-1	1.60	5.31	7.32	-2.01	24.21
22	1,3,8-trichloronaphthalene	55720-38-2	1.92	4.95	7.59	-2.63	5.75
23	1,4,5-trichloronaphthalene	2437-55-0	1.90	4.86	7.57	-2.71	4.84
24	1,4,6-trichloronaphthalene	2737-54-9	1.60	5.29	7.31	-2.02	23.64
25	1,6,7-trichloronaphthalene	55720-39-3	1.72	4.95	7.49	-2.54	7.19
26	2,3,6-trichloronaphthalene	55720-40-6	1.55	5.16	7.38	-2.23	14.75
27°*	1,2,3,4-tetrachloronaphthalene	20020-02-4	1.09	5.71	8.44	-2.72	4.68
28°	1,2,3,5-tetrachloronaphthalene	53555-63-8	0.99	5.85	8.25	-2.40	9.78
29	1,2,3,6-tetrachloronaphthalene	149864-78-8	0.85	5.80	8.10	-2.31	12.24
30	1,2,3,7-tetrachloronaphthalene	55720-41-7	0.92	5.62	8.29	-2.68	5.22
31	1,2,3,8-tetrachloronaphthalene	149864-81-3	1.27	5.16	8.62	-3.45	0.87
32	1,2,4,5-tetrachloronaphthalene	6733-54-6	1.09	5.63	8.35	-2.72	4.76
33	1,2,4,6-tetrachloronaphthalene	51570-45-7	0.88	6.04	8.06	-2.02	23.54
34	1,2,4,7-tetrachloronaphthalene	67922-21-8	0.81	6.01	8.09	-2.08	20.72
35	1,2,4,8-tetrachloronaphthalene	6529-87-9	1.27	5.61	8.43	-2.83	3.69
36°	1,2,5,6-tetrachloronaphthalene	67922-22-9	0.95	5.79	8.05	-2.26	13.72
37	1,2,5,7-tetrachloronaphthalene	67922-23-0	0.81	5.95	7.97	-2.03	23.36
38	1,2,5,8-tetrachloronaphthalene	149864-80-2	1.30	5.51	8.17	-2.66	5.47
39	1,2,6,7-tetrachloronaphthalene	149864-79-9	0.99	5.72	8.28	-2.56	6.81
40	1,2,6,8-tetrachloronaphthalene	67922-24-1	1.18	5.33	8.33	-3.01	2.44
41	1,2,7,8-tetrachloronaphthalene	149864-82-4	1.50	5.25	8.79	-3.54	0.71
42	1,3,5,7-tetrachloronaphthalene	53555-64-9	0.72	6.10	7.88	-1.78	40.66

4 Puzyn and Falandysz (2007), Puzyn et al. (2009)

5 From IPCS (2001) and Jacobsson &amp; Asplund (2000)

#CN	CN congener	CAS no. <sup>5</sup>	Log10 Water solubility [ $\mu\text{g}\cdot\text{dm}^{-3}$ ]	Log $K_{ow}$	Log $K_{oa}$	Log $K_{aw}$	Henry's Law constant [ $\text{Pa m}^3 \text{mol}^{-1}$ ]
43	1,3,5,8-tetrachloronaphthalene	31604-28-1	1.08	5.63	8.13	-2.50	7.87
44	1,3,6,7-tetrachloronaphthalene	55720-42-8	0.80	5.91	7.99	-2.08	20.61
45	1,3,6,8-tetrachloronaphthalene	150224-15-0	0.93	5.81	8.00	-2.18	16.25
46°	1,4,5,8-tetrachloronaphthalene	3432-57-3	1.28	5.14	8.42	-3.29	1.28
47	1,4,6,7-tetrachloronaphthalene	55720-43-9	0.95	5.90	8.08	-2.19	16.15
48°	2,3,6,7-tetrachloronaphthalene	34588-40-4	0.77	5.71	8.16	-2.45	8.75
49	1,2,3,4,5-pentachloronaphthalene	67922-25-2	0.57	6.03	9.33	-3.30	1.24
50°	1,2,3,4,6-pentachloronaphthalene	67922-26-3	0.21	6.34	9.00	-2.66	5.48
51	1,2,3,5,6-pentachloronaphthalene	150224-18-3	0.18	6.25	8.92	-2.67	5.28
52°*	1,2,3,5,7-pentachloronaphthalene	53555-65-0	0.13	6.49	8.79	-2.30	12.45
53°	1,2,3,5,8-pentachloronaphthalene	150224-24-1	0.55	5.98	9.11	-3.13	1.83
54	1,2,3,6,7-pentachloronaphthalene	150224-16-1	0.17	6.21	8.95	-2.74	4.55
55	1,2,3,6,8-pentachloronaphthalene	150224-23-0	0.37	6.02	8.98	-2.96	2.73
56	1,2,3,7,8-pentachloronaphthalene	150205-21-3	0.66	5.67	9.40	-3.73	0.46
57	1,2,4,5,6-pentachloronaphthalene	150224-20-7	0.43	6.16	9.03	-2.87	3.34
58	1,2,4,5,7-pentachloronaphthalene	150224-19-4	0.13	6.24	8.85	-2.61	6.13
59	1,2,4,5,8-pentachloronaphthalene	150224-25-2	0.66	5.91	9.23	-3.32	1.19
60	1,2,4,6,7-pentachloronaphthalene	150224-17-2	0.10	6.42	8.82	-2.40	9.89
61	1,2,4,6,8-pentachloronaphthalene	150224-22-9	0.33	6.14	8.94	-2.80	3.95
62	1,2,4,7,8-pentachloronaphthalene	150224-21-8	0.54	6.03	9.12	-3.09	2.03
63	1,2,3,4,5,6-hexachloronaphthalene	58877-88-6	-0.19	6.32	10.03	-3.71	0.49
64*	1,2,3,4,5,7-hexachloronaphthalene	67922-27-4	-0.38	6.53	9.84	-3.31	1.21
65	1,2,3,4,5,8-hexachloronaphthalene	103426-93-3	-0.01	6.04	10.17	-4.13	0.19
66°	1,2,3,4,6,7-hexachloronaphthalene	103426-96-6	-0.51	6.68	9.73	-3.04	2.24
67*	1,2,3,5,6,7-hexachloronaphthalene	103426-97-7	-0.53	6.59	9.62	-3.04	2.27
68	1,2,3,5,6,8-hexachloronaphthalene	103426-95-5	-0.29	6.50	9.86	-3.36	1.07
69°	1,2,3,5,7,8-hexachloronaphthalene	103426-94-4	-0.20	6.31	9.81	-3.50	0.78
70	1,2,3,6,7,8-hexachloronaphthalene	17062-87-2	-0.24	6.02	9.93	-3.91	0.31
71	1,2,4,5,6,8-hexachloronaphthalene	90948-28-0	-0.16	6.26	9.86	-3.60	0.62
72	1,2,4,5,7,8-hexachloronaphthalene	103426-92-2	-0.16	6.25	9.88	-3.64	0.57
73°*	1,2,3,4,5,6,7-heptachloronaphthalene	58863-14-2	-0.95	6.57	10.68	-4.11	0.19
74	1,2,3,4,5,6,8-heptachloronaphthalene	58863-15-3	-0.72	6.48	10.81	-4.34	0.11
75°*	1,2,3,4,5,6,7,8-octachloronaphthalene	2234-13-1	-1.35	6.43	11.64	-5.21	0.02

° ... native (indicated commercial availability by 2012)

\* ... <sup>13</sup>C-Isotope labeled (indicated commercial availability by 2012)

**Annex 2**
**Table A2-1: Composition of selected commercial mixtures identified by analytical measurements (Falandysz, 2008 and Environment Canada, 2011)**

Congeners	Halowax 1031	Halowax 1000	Halowax 1001	Halowax 1099	Halowax 1013	Halowax 1014	Halowax 1051	Seekay wax R93**
Mono-CNs	65	15	0	0	0	0	0.1	-
Di-CNs	30	76	2.7-4.3*	3.6	0.5	0.7	0.1	1
Tri-CNs	7.6	6.4	36-52	38.7	13	6	0.1	27-41*
Tetra-CNs	6.4	1.3	40-58*	48	53.3	16	0.3	52-62*
Penta-CNs	1.1	0.4	3.3 -3.9*	9	30	48	0.1	6.2-9.8*
Hexa-CNs	0.2	0.3	0.1	0.5	3.2	25	0.3	0.1-0.2*
Hepta-CNs	0.1	0.1	0	0.1	0.1	3	8	0
Octa-CN	0.1	0	0	0	0	0.1	91	0

\* range corresponds to different separation procedures

\*\* suggested identity

**Table A2-2: Characteristic homologue patterns of different CN sources compared to remote atmospheric CN patterns.**

CN source	characteristic homologue pattern	Source
coking	less chlorinated, most abundant: mono-CNs	Liu et al., 2010
secondary non-ferrous metallurgy	less chlorinated in gas phase: mono- to tri-CNs; in fly ash: highly chlorinated congeners dominate	Ba et al., 2010
thermally generated	abundant: tri- CN45/CN36, penta- CN54, hexa- CN66/CN67, hepta-CN73	cited in Liu et al., 2010
Halowax series combustion sources	See Annex 2 tetra-CNs: CN29, CN44, penta-CN54 (these congeners are absent in Halowax mixtures); moreover: tri-CNs: CN13, CN18, CN17/25, CN24, CN26, tetra-CNs: CN27, CN35, CN36, CN39, CN36/45, CN48, penta-CNs: CN50, CN51, CN52/60, CN62, hexa-CNs: CN66/67, CN70 and hepta-CN73	summarized in Bidleman et al., 2010
municipal waste incineration	2,3,6,7-substituted congeners tri-CNs	Järnberg et al., 1999 Helm et al., 2004
<b>environmental CN pattern remote from sources</b>	<b>characteristic homologue pattern</b>	<b>Source</b>
Arctic air	tri-CNs: 58–64%, tetra-CNs: 25–40%, penta-CNs: 2–3%; heavier CNs: 0–7%  tri-CNs: 48–65%, tetra-CNs: 6–47%, penta-CNs: 8–10%, heavier CNs: 1–2%	three Arctic stations (Dunai, Alert, Tagish); calculated from Helm et al., 2004  Resolute and Canadian Archipelago; Helm et al., 2002 as cited in: ICC IPEN, 2011



## Annex 3

Table A3-1 Partitioning of CNs between environmental media (source: Environment Canada, 2011)

	Compartment receiving 100% of emissions:	Percentage of substance partitioning into:			
		Air	Water	Soil	Sediment
<b>di-CN</b> s	Air	96.6	0.94	2.26	0.2
	Water	9.44	74.7	0.22	15.6
	Soil	0.43	0.05	99.5	0.01
<b>tri-CN</b> s	Air	64.8	0.21	34.5	0.49
	Water	4.59	28	2.45	65
	Soil	0.22	0.01	99.8	0.02
<b>tetra-CN</b> s	Air	33.4	0.12	65.5	0.99
	Water	1.59	10.6	3.12	84.7
	Soil	0.19	0.27	97.4	2.13
<b>penta-CN</b> s	Air	3.99	0.09	91.8	4.09
	Water	0.08	2.05	1.72	96.2
	Soil	0	0	99.9	0.11
<b>hexa-CN</b> s	Air	56.2	0.17	34	9.62
	Water	0.02	1.77	0.01	98.2
	Soil	0	0	99.9	0.12
<b>hepta-CN</b> s	Air	36.4	0.22	50.9	12.5
	Water	0	1.71	0.01	98.3
	Soil	0	0	99.9	0.13
<b>octa-CN</b> s	Air	14.6	0.4	70.2	14.8
	Water	0.2	2.61	0.97	96.2
	Soil	0.69	1.5	42.4	55.4

Numbers have been rounded to two decimal places so row totals do not necessarily add to 100 percent

## Annex 4

Table A4-1: CN concentration ranges in sediment from various regions

location	min-max [ $\mu\text{g}/\text{kg d.w.}$ ]	source
Sweden	0.14–7.6 *	Järnberg et al. (1993)
Venice lagoon	0.03–1.51 *	Eljarrat et al. (1999)
Batic Sea	6.7 *	Falandysz et al. (1996)
Gulf of Bothnia	0.27–2.8 *	Lundgren et al. (2002)
Barcelona coast	0.17–3.27 *	Castells et al. (2008)
Qingdao coast	0.2–1.2 *	Pan et al. (2007)
Lake Ontario	21–38 *	Helm et al. (2008)
Tokyo bay	1.81 *	Yamashita et al. (2000)
Bitterfeld, industrial area	2 540 *	Brack et al. (2003)
Georgia coast, former industrial area	23 400 *	Kannan et al. (1998)
Lhaizhou Bay, receiving high loads of domestic and industrial wastewater	0.05–5.1	Pan et al. (2011)
10 lake and sea sites	0.14–7.6	Järnberg et al. 1999
Esthwaite Water, UK, 1962	12.15	Gevao et al. 2000
Esthwaite Water, UK, 1995	2.821	Gevao et al. 2000

\* as cited in Pan et al. (2011)

Table A4-2: CN concentrations [ $\mu\text{g}/\text{kg lipid}$ ] in invertebrates and fish as compiled from ten independent sources in Bidleman et al. (2010)

biota	location	year	range	mean
<b>Arctic biota</b>				
Zooplankton	Bear Island, Ellasjøen, Norway	1999	0.14–0.16	0.15
Arctic char ( <i>S. alpinus</i> ), small		1999–2001		0.81
Arctic char ( <i>S. alpinus</i> ), large		1999–2001	0.45–1.4	0.85
Arctic char ( <i>S. alpinus</i> ), small	Bear Island, Øyangen, Norway	1999–2001		0.29
Arctic char ( <i>S. alpinus</i> ), large		1999–2001	0.32–0.68	0.5
Phytoplankton	Central/northern Baltic	1991–1993		17.1
Zooplankton		1991–1993		4
Amphipod ( <i>M. affinis</i> )		1991–1993		28.5
Mysis ( <i>Mysis sp.</i> )		1991–1993		4
Isopod ( <i>S. entomon</i> )		1991–1993		8.4
Herring ( <i>C. harengus</i> )		1991–1993		1.9
Fourhorned sculpin ( <i>O. quadricornis</i> )		1991–1993		1.9
Amphipod ( <i>M. affinis</i> )		Bothnian Bay/Sea	1991–1993	12–69
Isopod ( <i>S. entomon</i> )	1991–1993		3.9–16	9.2
Fourhorned sculpin ( <i>O. quadricornis</i> )	1991–1993		0.54–1.5	1.1
Whitefish ( <i>Coregonus sp.</i> )	Lake Störvindeln, Sweden	1986		2.6
Arctic cod ( <i>C. callarias</i> )	Vestertana Fjord, Norway	1987–1998	0.13–1.06	0.42
Herring ( <i>C. harengus</i> )	Bothnian Bay/Sea	1999	2.6–5.6	
		2001–2003	0.53–3.4	2.4
Salmon ( <i>S. salar</i> )		2001–2003	1.6–2.5	2
Burbot ( <i>L. lota</i> )		2001–2003	1.6–1.8	1.8
Pike ( <i>E. lucius</i> )		2001–2003	2.3–5.0	3.6
Perch ( <i>P. fluviatilis</i> )		2001–2003	1.0–3.0	1.7
Whitefish ( <i>C. lavaretus</i> )		2001–2003	1.0–4.6	1.9

biota	location	year	range	mean
Vendace ( <i>C. albula</i> )	Bothnian Bay	2001–2003	0.16–0.32	0.24
River lamprey ( <i>L. fluviatilis</i> )		2001–2003	0.88–1.0	0.93
Herring ( <i>C. harengus</i> )	Bothnian Sea	2002	0.3–2.9	1.7
Burbot ( <i>L. lota</i> )	Pajala, Finland	1988		2.9
		1988		2
	Etukrunni, Finland	1988		4.9
		1988		2
	Seskarø, Sweden	1988		4.4
		1988		0.98
Pike ( <i>E. lucius</i> )	Lake Störvindeln,	1988		2.6
Burbot ( <i>L. lota</i> )	Lake Oulujärvi, Finland	2001–2003		1.3
Pike ( <i>E. lucius</i> )		2001–2003	1.0–1.2	1.1
Perch ( <i>P. fluviatilis</i> )		2001–2003	0.6–0.6	0.6
Pike-perch ( <i>S. lucioperca</i> )		2001–2003	0.16–0.24	0.2
Whitefish ( <i>C. lavaretus</i> )		2001–2003	0.29–0.33	0.31
Vendace ( <i>C. albula</i> )		2001–2003	0.53–0.68	0.6
Bream ( <i>A. brama</i> )		2001–2003	0.24–0.73	0.49
<b>Antarctic biota</b>				
Krill ( <i>E. superba</i> )	Ross Sea	1994		0.1
Sharp spined notothen ( <i>T. pennelli</i> )	Terra Nova Bay	1995	0.081–0.13	0.1
Crocodile fish ( <i>C. hamatus</i> )		1995	0.12–0.15	0.12
Silverfish ( <i>P. antarcticum</i> )	Ross Sea	1994		0.91

**Table A4-3: CN concentrations [ $\mu\text{g}/\text{kg}$  lipid] in marine mammals and birds as compiled from ten independent sources in Bidleman et al. (2010)**

biota	location	year	range	mean
<b>Arctic</b>				
Ringed seal ( <i>P. hispida</i> )	Pangnirtung, Canada	1993	0.035–0.071	0.051
		1993	0.045–0.049	0.047
		2002	0.12–0.54	0.32
		1999–2002	0.09–0.42	0.23
	Grise Fiord, Canada	2003	0.15–0.59	0.27
	Sachs Harbour, Canada	2001	0.023–0.18	0.072
	Kongsfjorden, Svalbard	1981		0.038
	Ittoqqortoormiit, Greenland	2002	all congeners n.d.	0.13*
Qeqertarsuaq, Greenland	2002	all congeners n.d.	0.12*	
Harbour seal ( <i>P. vitulina</i> )	Gulf of Alaska, U.S.A.	2000–2001	0.92–27	4.8
		2000–2001	0.38–1.4	1.1
		2000–2001	0.31–0.90	0.59

biota	location	year	range	mean
Beluga ( <i>D. leucas</i> )	Kimmirut, Canada	1994	0.036–0.26	0.18
		1994	0.30–0.38	0.33
	Hudson Strait, Canada	1999	0.20–0.89	0.42
		1999		0.56
	Nastapoka, Canada	2000	0.11–0.21	0.16
		2000	0.081–0.33	0.16
Minke whale ( <i>B. acutorostrata</i> )	Greenland	1998	all congeners n.d.	0.18*
Longfinned pilot whale ( <i>G. melas</i> )	Faroe Islands	2001		3.66
		2001		0.99
		2001		2.22
Polar bear ( <i>U. maritimus</i> )	Alaska, U.S.A.	1997–1999		3.2
	Ittoqqortoormiit, Greenland	1999–2002	0.49–0.53	0.51
Glaucous gull ( <i>L. hypoboreus</i> )	Bear Island, Norway	2002–2004	1.8–162	49
		2002–2004	1.34–126	74
		2002–2004	1.34–119	62.8
	Ny Ålesund, Svalbard	2002		0.88
	Festningisfjord, Svalbard	2002		0.97
	Northwater Polynya, Canada	1998	4.1–17.1	10.6**
		1998	3.1–9.1	6.1**
Black legged kittewake ( <i>R. tridactyla</i> )	Prince Leopold Island, Canada	1998	8.0–29.5	18.8**
Black guillemot ( <i>C. grylle</i> )		1998	1.7–8.7	5.2**
Thick-billed murre ( <i>U. lomvia</i> )		2005	1.27–2.12	1.68
Great black-backed gull ( <i>L. marinus</i> )	Vardø, Norway	2001		see <i>L. argentatus</i>
	Kongsfjord, Norway	2001		2.16
	Rolvøya in Valfjord, Norway	2002		1.35
	Alta, Norway	2001		see <i>L. argentatus</i>
	Sommarøy, Norway	2001		2.45
	Lyngøyen in Øksnes, Norway	2002		see <i>L. argentatus</i>
	Kirkjubøreyni, Faroe Islands	2002		0.96
Lesser black-backed gull ( <i>L. fuscus</i> )	Góðadular, Faroe Islands	2002		0.5
Herring gull ( <i>L. argentatus</i> + <i>L. marinus</i> )	Vardø, Norway	2001		1.39
Herring gull ( <i>L. argentatus</i> )	Rolvøya in Valfjord, Norway	2002		2.06
Herring gull ( <i>L. argentatus</i> + <i>L. marinus</i> )	Alta, Norway	2001		1.06
Herring gull ( <i>L. argentatus</i> )	Lyngøyen in Øksnes, Norway	2002		1.6
	Saltstraumen, Norway	2002		2.44
	Givaer, Norway	2002		4.65

<b>biota</b>	<b>location</b>	<b>year</b>	<b>range</b>	<b>mean</b>
Northern fulmar ( <i>F. glacialis</i> )	Faroe Islands	1998–1999		2.55
		1998–1999		3.75
	Prince Leopold Island, Canada	2005	1.64–2.56	2
		2003		1.3
	Cape Vera, Canada	2003		1.4
	Northwater Polynya, Canada	1998	17.6–48.2	32.9**
<b>Antarctic biota</b>				
South polar skua ( <i>C. macormicki</i> )	Terra Nova Bay	1994		6.07
		1994		5.71
Weddell seal ( <i>L. weddelli</i> )		1996		0.077
		1997		1.6

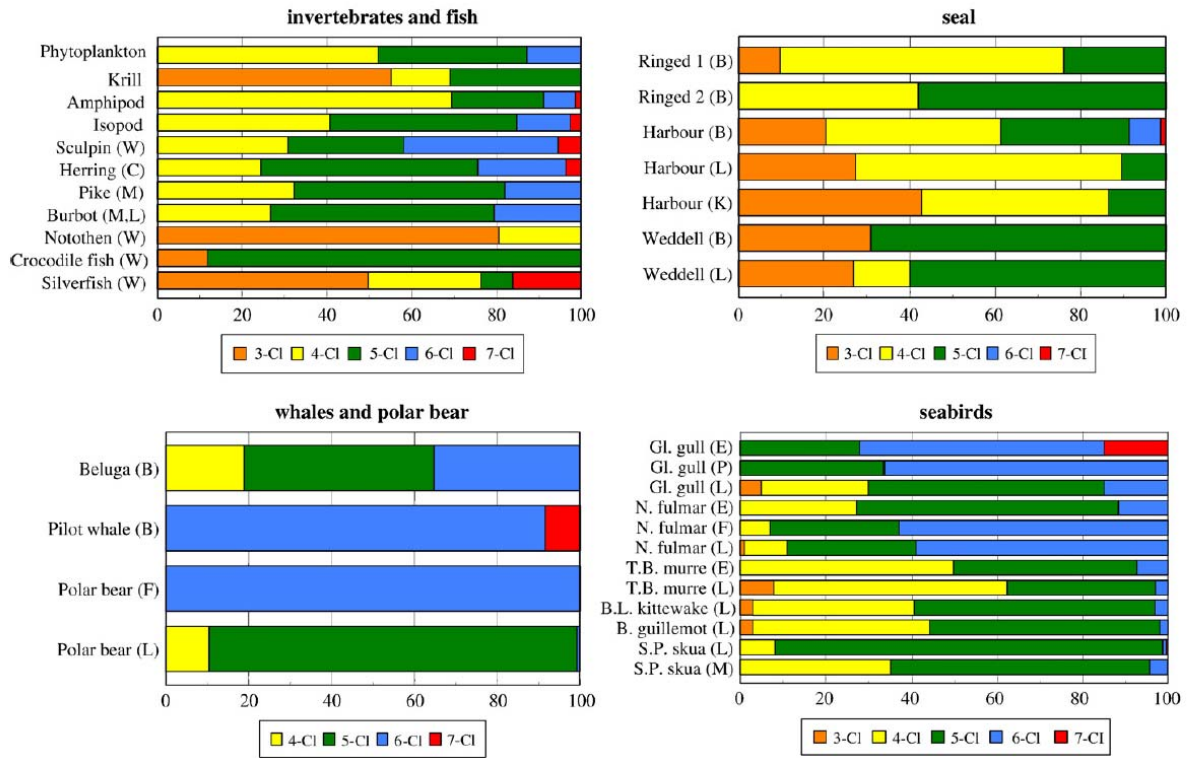
\* All congeners not detectable (below LOQs), upper limit estimated by substituting 1/2 LOQ values

\*\* Midpoint of range

**Table A4-4: CN concentrations in Arctic biota from other sources than compiled in Bidleman et al. (2010):**

biota	compartment	unit	min-max (mean ± s.d.)	year	location	source
polar bear	adipose tissue (56.3±15.1 % lipid)	µg/kg w.w.	0.7–29.3 (4.4±7.3)	2002	Svalbard	Gabrielsen et al., 2004
seal	blubber	µg/kg lipid w.	1.2–58 (16.3±28)	2004	Livingston Island, <i>Antarctica</i>	Schiavone et al., 2009

**Figure A4-1: congener patterns found in biota from (sub)polar regions. Source: Bidleman et al., 2010**



Explanation of figure (taken from Bidleman et al. 2010): CN homologues (% of ΣCNs) in arctic, subarctic and antarctic biota. Symbols in parentheses: W=whole, M=muscle, L=liver, C=cleaned (head and guts removed), B=blubber, F=fat, P=plasma. Reports containing three or more homologues were included; those containing only upper limits were excluded. Lack of a homologue may indicate not found or not measured, see original study. When ranges were given, the midpoints of the range were taken, resulting in central values for homologue percentages which did not always sum to 100%. In these cases, figure data were normalized to 100%. Organisms studied (homologues analysed) and data sources are listed. Invertebrates and fish: phytoplankton (4–6-CN); krill (3–8); isopod, fourhorned sculpin (4–7); herring (4–8); pike, burbot (4–8); notothen, crocodile fish, silverfish (3–8). Seal: ringed seal 1 (3–7), ringed seal 2 (4–6); harbour seal (3–8); Weddell seal (3–8). Whales and polar bear: beluga whale (3–7); longfinned pilot whale (4–7); polar bear (3–8). Seabirds: glaucous gull (4–7), (3–6); northern fulmar (4–7), (3–8); black-legged kittewake (3–8); black guillemot (3–8); thick-billed murre (4–6) and (3–8); south polar skua (3–8)