

Ecological Screening Assessment

Chlorinated Naphthalenes

Environment Canada

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Synopsis

Pursuant to section 74 of the *Canadian Environmental Protection Act, 1999*, the Minister of the Environment has conducted an ecological screening assessment of chlorinated naphthalenes. “Naphthalene, chloro derivatives”, Chemical Abstracts Service Registry Number 70776-03-3, was identified as meeting the ecological categorization criteria for persistence, bioaccumulation potential and inherent toxicity to non-human organisms. “Naphthalene, chloro derivatives” is a variable chemical mixture that covers the chemical class of chlorinated naphthalenes.

Chlorinated naphthalenes were not considered to be a high priority for assessment of potential risks to human health, based upon application of the simple exposure and hazard tools developed by Health Canada for categorization of substances on the *Domestic Substances List*. Therefore, this assessment focuses on information relevant to the evaluation of ecological risks.

Chlorinated naphthalenes (CNs) have the molecular formula $C_{10}H_{8-n}Cl_n$ ($n = 1-8$). There are 75 possible chlorinated naphthalenes in 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). The number and, to a lesser extent, the positions of the chlorine atoms within the CN molecule are the key determinants of the physical and chemical properties of the CN congeners.

Key physical and chemical properties are useful when predicting the environmental fate of CNs. The values for water solubility, vapour pressure and Henry’s law constant tend to decrease when progressing from mono- to octa-CNs, while the values for $\log K_{ow}$, melting point and boiling point tend to increase when progressing from mono- to octa-CNs.

Sources of CNs in the environment are mainly anthropogenic. Beginning around 1910, mono- to octa-CNs were produced commercially for a variety of uses. CNs were likely never manufactured in Canada but they were imported from manufacturers in the USA. Although CNs are not currently in commercial use in Canada, they are likely to be produced unintentionally as a by-product of some industrial processes involving chlorine, especially in the presence of heat, such as waste incineration, cement and magnesium production, and the refining of metals such as aluminium. Releases resulting from some of these processes have not been well characterized. Other sources of CNs in the environment include products containing CNs disposed of in landfill sites and old industrial sites where CNs were used. There are reports of CNs being released into the atmosphere from the domestic combustion of wood. A possible non-anthropogenic (i.e., natural) source of CNs is the combustion of wood during forest fires.

Fugacity modelling 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.

CNs have been detected in Canada, specifically, in: Arctic and urban air, Lake Ontario water, fish and birds from the Great Lakes and environs, seals and whales from the Canadian Arctic, and Vancouver Island marmots. The data on environmental concentrations of CNs in Canada are limited. Much more data on CN levels in environmental media, including sediments and soils, are available for the USA and Europe.

Di- through octa-CNs are persistent in air. The potential for long-range transport has been estimated to be moderate for di-CNs and high for tri- through octa-CNs, indicating that some CNs may be subject to atmospheric transport to remote regions such as the Arctic. In addition, di- through octa-CNs are predicted to be persistent in water, and tri- through hepta-CNs are persistent in both sediments and soil. Based on the weight of evidence, including, in particular, measured log K_{ow} values for di- to octa-CNs, the measured bioconcentration values for di- to penta-CNs in fish, measured biomagnification factors for tetra- to hepta-CNs, the high dietary uptake efficiencies of hexa- to octa-CNs in northern pike and the very slow elimination of hexa-CNs from rats, it is concluded that di- to octa-CNs are also bioaccumulative.

The available empirical and modelled aquatic toxicity data for CNs indicate that di-, tri-, tetra- and penta-CNs may be harmful to aquatic organisms at relatively low concentrations (below 1 mg/L for acute tests, and 0.1 mg/L for chronic tests). Hexa-, hepta- and octa-CNs were found to cause harmful effects in mammals (particularly cattle) after short term exposure at relatively low doses – as low as 0.69 mg/kg body weight per day.

Evidence that a substance is highly persistent and bioaccumulative, as defined in the Persistence and Bioaccumulation Regulations under the *Canadian Environmental Protection Act*, 1999, when taken together with potential for environmental release or formation and potential for toxicity in organisms, provides a significant indication that the substance may be entering the environment under conditions that may have harmful long-term ecological effects. Substances that are persistent remain in the environment for a long time after being released, increasing the potential magnitude and duration of exposure. Substances that have long half-lives in air and water and partition into them in significant proportions have the potential to cause widespread contamination. Releases of small amounts of bioaccumulative substances may lead to high internal concentrations in exposed organisms. Highly bioaccumulative and persistent substances are of special concern, since they may biomagnify in food webs, resulting in very high internal exposures, especially for top predators.

There is international consensus on the dangers posed by CNs and the need for international action. In December 2009, CNs were added to the Protocol on Persistent Organic Pollutants under the Convention on Long-Range Transboundary Air Pollution.

Based on the lines of evidence presented above, particularly the evidence for persistence, bioaccumulation and potential to cause acute and chronic harm at low exposure levels,

and taking into account the limitations of existing quantitative risk estimation methods when applied to such substances, and recognizing that although CNs are no longer in commercial use in Canada they continue to enter the Canadian environment from unintentional production as well as through transboundary movement of air, and have been identified as a concern by international consensus, it is concluded that releases of di-through octa-CN_s have the potential to cause environmental harm in Canada.

Therefore, it is concluded that di-through octa-CN_s are entering the environment in quantities or concentrations, or under conditions that have or may have immediate or long-term harmful effects on the environment or its biological diversity.

Based on the information available, it is concluded that di-through octa-CN_s meet one or more of the criteria set out in section 64 of the *Canadian Environmental Protection Act*, 1999. These substances are persistent and bioaccumulative in accordance with the regulations, their presence in the environment results primarily from human activity, and they are not a naturally occurring radionuclide or a naturally occurring inorganic substance.

These substances will be considered for inclusion in the Domestic Substances List inventory update initiative. In addition and where relevant, research and monitoring will support verification of assumptions used during the screening assessment and, where appropriate, the performance of control measures identified during the risk management phase.

Introduction

The *Canadian Environmental Protection Act, 1999* (CEPA 1999) (Canada 1999) requires the Minister of the Environment and the Minister of Health to conduct screening assessments of substances that have met the categorization criteria set out in the Act to determine whether these substances present or may present a risk to the environment or to human health.

Based on the information obtained through the categorization process, the Ministers identified a number of substances as high priorities for action. These include substances that

- met all of the ecological categorization criteria, including persistence (P), bioaccumulation potential (B) and inherent toxicity to aquatic organisms (iT), and were believed to be in commerce in Canada; and/or
- met the categorization criteria for greatest potential for exposure (GPE) or presented an intermediate potential for exposure (IPE) and had been identified as posing a high hazard to human health based on classifications by other national or international agencies for carcinogenicity, genotoxicity, developmental toxicity or reproductive toxicity.

Screening assessments involve analyzing available information about substances, sometimes using reasonable worst case assumptions, to determine whether the substances are “toxic” or capable of becoming so, as defined in CEPA 1999. During screening assessments, various pieces of scientific and technical information are examined and conclusions are developed based on the weight of evidence and the application of precaution, as required under CEPA 1999. Screening assessments do not present an exhaustive review of all available data; rather, they present the most critical studies and lines of evidence pertaining to the conclusions.

An ecological screening assessment of chlorinated naphthalenes (CNs) was undertaken, in part, because “Naphthalene, chloro derivatives”, Chemical Abstracts Service Registry Number 70776-03-3, was identified as a high priority for assessment of ecological risk as it had been found to meet the categorization criteria, as set out in the Act, including persistence (P), bioaccumulation potential (B) and inherent toxicity to aquatic organisms (iT). “Naphthalene, chloro derivatives” can be described as a variable chemical mixture that covers the chemical class of CNs. Although CNs are not currently in commerce in Canada, there are still unintentional releases occurring and recent scientific studies demonstrated the presence of CNs in the Arctic and Antarctica, indicating that CNs are persistent in air and subject to long-range atmospheric transport. Additionally, CNs were assessed because their production and usage have been banned or restricted in various OECD (Organisation for Economic Co-operation and Development) countries, including Switzerland, Germany and Japan. As well, these substances were recently added to the Protocol on Persistent Organic Pollutants (POPs) under the international Convention on Long-Range Transboundary Air Pollution (CLRTAP) based on international consensus

that the presence of CNs in the environment poses a concern and due to their long-range transport, there is a need for coordinated international action on these substances.

Although CNs were found to be a high priority for assessment with respect to the environment, they did not meet the criteria for greatest potential for exposure or intermediate potential for exposure, and were not identified as posing a high hazard to human health, based on classifications by other national and international agencies for carcinogenicity, genotoxicity, developmental toxicity and reproductive toxicity. Therefore, this assessment only deals with information relevant to the evaluation of ecological risk.

The number of chlorine atoms within the CN structure is a key determinant of a CN's physical and chemical properties. Consequently, the potential for each CN homologue group to cause environmental harm is evaluated separately in this report. Furthermore, because of the unique concerns relating to substances that are persistent and bioaccumulative, and given that current science is unable to accurately predict the ecological effects of such substances, the assessments of the CN homologue groups with these properties were performed using a less quantitative, more conservative (precautionary) approach than might otherwise have been taken.

Data relevant to the ecological screening assessment of CNs were identified in original literature and review documents that summarize current scientific information about them (e.g., CICAD No. 34: Chlorinated Naphthalenes; IPCS 2001). Searches of online literature databases were conducted. As well, direct contacts were made with researchers, academics and industry to obtain information about CNs. The final screening assessment does not represent an exhaustive or critical review of all available data. Rather, it presents the most critical studies and lines of evidence pertinent to the conclusion.

Scans were conducted of the open literature, conference proceedings and the Internet for relevant information. Data obtained up to March 2010 were considered in this document. In addition, a voluntary industry survey about CNs was conducted by Environment Canada in 2003, to collect data on the Canadian manufacture, import and use of CNs.

This final screening assessment was prepared by staff in the Existing Substances Program at Environment Canada. This assessment has undergone external written peer review/consultation. Additionally, the draft of this screening assessment was subject to a 60-day public comment period. While external comments were taken into consideration, the final content and outcome of the screening assessment remains the responsibility of Environment Canada.

The critical information and considerations on which the assessment is based are presented below.

Identity, Uses, Sources and Releases to the Environment

Substance Identity

The generic structure of a chlorinated naphthalene molecule is shown in Figure 1.

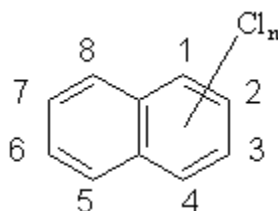


Figure 1. Generic structure of a chlorinated naphthalene molecule showing the naphthalene ring structure, carbon atom numbering system and potential for chlorine substitution

CNs are formed by substituting chlorine for hydrogen atoms that are attached to the numbered carbon atoms, as shown in Figure 1. CNs have the molecular formula $C_{10}H_{8-n}Cl_n$ ($n = 1-8$). There are 75 possible chlorinated naphthalenes. The system of nomenclature for CNs is similar to that for polychlorinated biphenyls and uses the numbering system shown in Figure 1. 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). CNs are commonly referred to in the scientific literature as polychlorinated naphthalenes (PCNs). The term “CNs” is used in this report because it more accurately describes the entire class of chlorinated naphthalenes, including the mono-CN congeners. The number and, to a lesser extent, the positions of the chlorine atoms within the CN molecule are the key determinants of the physical and chemical properties of the CN congeners.

CNs were produced for commercial use as mixtures. In North America, Halowax® was a common brand that was manufactured by Koppers Inc. in the USA until 1977 (Kirk-Othmer 1980). The Halowax mixtures have commonly been used in toxicity testing of CNs; however, researchers have reported varying proportions of CN homologue groups in these mixtures.

The key physical and chemical properties of CNs and of the Halowax mixtures that are useful in predicting their environmental fate are listed in Tables 1 and 2, respectively. Water solubility estimated using WSKOWWIN (version 1.41) is consistently higher than measured values, typically by a factor of about 10. For chemicals with low water solubility (i.e., less than 1000 $\mu\text{g/L}$), there can be appreciable error in measured solubility values (Mackay et al. 1999), so the water solubility values obtained from WSKOWWIN have been used as conservative upper-bound solubility estimates.

Table 1. Key physical and chemical property values or ranges of CNs

	Molecular weight (g/mol)	Solubility (µg/L) ^a	Vapour pressure (Pa) ^b (subcooled liquid, 25°C)	Henry's law constant (Pa·m ³ /mol, 25°C) ^c	Log K _{ow} ^d	Melting point (°C)	Boiling point (°C)
Mono-CNs	162.61	924; 2870 (10 300)	5.59; 2.53	22.21–24.48	3.90–4.19	-2.3; 59.5–60	259–260
Di-CNs	197.00	137–862 (2713)	0.198–0.352	3.67–29.15	4.19–4.88	37–138	287–298
Tri-CNs	231.50	16.7–65 (709)	0.0678–0.114	1.11–51.24	5.12–5.59	68–133	274*
Tetra-CNs	266.00	3.70–8.30 (177)	0.0108–0.0415	0.87–40.66	5.76–6.38	111–198	Unknown
Penta-CNs	300.40	7.30 (44)	0.00275–0.00789	0.46–12.45	6.80 (1,2,3, 5,8-penta); 7.00(1,2,3, 4,6-penta)	147–171	313*
Hexa-CNs	335.00	0.11* (11)	0.00157–0.000734	0.31–2.27	7.50 (1,2,3, 5,7,8-hexa); 7.70(1,2,3, 4,6,7-hexa);	194	331*
Hepta-CNs	369.50	0.04* (2.60)	2.78 x 10 ⁻⁴ ; 2.46 x 10 ⁻⁴	0.11–0.19	8.20	194	348*
Octa-CNs	404.00	0.08 (0.63)	6.84 x 10 ⁻⁵	0.02	6.42–8.50	198	365*

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

^a Values outside of brackets were experimentally determined by aqueous saturation method (Oppehuizen 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 K_{ow} sources: Oppehuizen (1987), Oppehuizen et al. (1985) (shake flask method, Bruggeman et al. (1982)), Lei et al. (2000) (reversed phase HPLC method).

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

Table 2. Key physical and chemical properties of Halowax mixtures

Halowax mixture	CAS number	Chlorine content (%)	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)	Aqueous solubility	Henry's law constant (Pa·m ³ /mol)
Halowax 1031	25586-43-0	22	250 ^a	-25	1.9 ^b	Insoluble ^a	31.9
Halowax 1000	58718-66-4	26	250 ^a	-33	No value available	Insoluble ^a	No value available
Halowax 1001	58718-67-5	50	308 ^a	98	No value available	Insoluble ^a	No value available
Halowax 1099	39450-05-0	52	315 ^a	102	No value available	Insoluble ^a	No value available
Halowax 1013	12616-35-2	56	328 ^a	120	No value available	Insoluble ^a	No value available
Halowax 1014	12616-36-3	62	344 ^a	137	No value available	Insoluble ^a	No value available
Halowax 1051	2234-13-1	70	NA	185	No value available	No value available	No value available

Data source: IPCS (2001).

^a Brinkman & De Kok (1980).

^b Estimated value.

Table 3a. Composition of Halowax mixtures (% weight) as reported in IPCS (2001)

	Halowax 1031	Halowax 1000	Halowax 1001	Halowax 1099	Halowax 1013	Halowax 1014	Halowax 1051
Mono-CN _s	95	60	0	0	0	0	0
Di-CN _s	5	40	10	10	0	0	0
Tri-CN _s	0	0	40	40	10	0	0
Tetra-CN _s	0	0	40	40	50	20	0
Penta-CN _s	0	0	10	10	40	40	0
Hexa-CN _s	0	0	0	0	0	40	0
Hepta-CN _s	0	0	0	0	0	0	10
Octa-CN _s	0	0	0	0	0	0	90

Table 3b. Composition of Halowax mixtures (% weight) as reported by other sources^{1,2}

	Halowax 1031	Halowax 1000	Halowax 1001	Halowax 1099	Halowax 1013	Halowax 1014	Halowax 1051
Mono-CN _s	65	15	0.06	0.04	0.04	0.04	0.08
	(65–70.1)	(6.7–69)	(0.01–0.3)	(0 - 1.1)	(0–0.2)	(0–0.066)	(0–0.25)
Di-CN _s	30	76	4.4	3.6	0.45	0.66	0.11
	(24.8–30)	(28–76.5)	(3.5–6.1)	(0 - 35.7)	(0–12.7)	(0–1.9)	(0–0.34)
Tri-CN _s	2.6	6.4	51.7	38.7	13.1	6.0	0.13
	(0.8–2.6)	(1.2–44.1)	(48.1–54)	(38 - 54.6)	(8.2–53.2)	(2.8–17.1)	(0–0.4)
Tetra-CN _s	2.2	1.3	40.7	48	53.3	16	0.26
	(0–2.2)	(1.2–47.4)	(38–44.7)	(9.5 - 52)	(26.3–56)	(12–18.2)	(0–0.77)
Penta-CN _s	0.38	0.44	3.3	9.0	30	47.7	0.10
	(0–0.38)	(0.21–8.44)	(2.2–4.7)	(0.3 - 9.7)	(3–38)	(32.2–55)	(0–0.22)
Hexa-CN _s	0.054	0.33	0.12	0.50	3.2	25.3	0.31
	(0–0.054)	(0.006–0.33)	(0–0.18)	(0 - 0.6)	(2.6–4.75)	(21–35.3)	(0–0.82)
Hepta-CN _s	0.016	0.073	0.02	0.05	0.12	3.0	7.6
	(0–0.016)	(0.017–0.073)	(0–0.04)	(0 - 0.061)	(0.1–0.154)	(1.6–4.24)	(6.2–18.1)
Octa-CN _s	0.03	0.015	0.01	0.02	0.01	0.13	91.4
	(0–0.03)	No range	(0–0.024)	(0 - 0.037)	(0.0089–0.013)	(0–6.6)	(81.8–93.5)

1. The percentage compositions reported represent the average and range of values reported in Falandysz et al. (2006a and 2006b). The percentage homologue composition of the Halowax mixtures may vary, however, and different percentage compositions are given in Wiedmann and Ballschmiter (1993), Imagawa and Yamashita (1994), Harner and Bidelman (1997), Falandysz et al. (2006a), Falandysz et al. (2006b), Helm and Bidleman (2003), Espadaler et al. (1997), and Noma et al. (2004).

2. The values inside brackets represent the range for each congener.

As can be seen from Tables 3a and 3b, the reported proportions of the homologue groups present in the Halowax mixtures vary.

Natural Sources

The presence of CNs in the environment is likely to result mainly from human activity (see, for example, Gevao et al. 2004, and Horii et al. 2000). A possible non-anthropogenic (i.e., natural) source of CNs is combustion of wood, for example during forest fires. Although CNs have been reported to be released into the atmosphere from domestic combustion of wood (see, for example, Lee et al. 2005), no studies documenting release from natural combustion were identified.

Manufacture and Import

Mono- and di-CNs, and “naphthalene, chloro derivatives” (a variable chemical mixture that covers the chemical class of CNs, CAS RN 70776-03-3) are on the Canadian Domestic Substances List, which indicates that these substances were in commercial use in Canada between January 1, 1984, and December 31, 1986. It does not appear that CNs were ever manufactured in Canada (Holliday et al. 1982), but they were likely imported from manufacturers in the USA.

According to responses to a voluntary industry survey carried out by Environment Canada in 2003, there was no manufacturing of CNs in Canada from 2000 to 2002. Only one company reported importing CNs (tri- and tetra-CNs) from 2000 to 2002. These imports have since been discontinued.

It is known that, in the 1990s, Sumitomo 3M Ltd. in Japan imported, from Canada, 54 tonnes of an adhesive material containing Neoprene FB, a product that contains 3% tri-CNs and 1% tetra-CNs (Yamashita et al. 2003).

Two Canadian industry associations indicated that mono-CNs were used in manometer fluid in very small quantities in a laboratory setting. These associations stated that the CN-containing material in the manometers was replaced with non-CN material in 2004.

Wellington Laboratories of Guelph, Ontario, is a supplier of CN standard materials for analytical purposes (e.g., the series of Halowax mixtures and single congeners), and these materials are purchased by laboratories around the world, including in Japan (Wellington Laboratories 2005; Takasuga et al. 2004). It is not known whether any other laboratory supply companies in Canada sell CN standard materials for analytical purposes.

Uses

Domestic Substances List data (1984-1986) indicate that CNs were used for organic chemicals, abrasives, polymers, components of plastic and synthetic resins.

CNs are not currently in commercial use in Canada, the USA and many other countries that belong to the Organisation for Economic Co-operation and Development (OECD). Production of CNs in the USA had ceased completely by 1980 (IPCS 2001). Around 15

tonnes a year of CNs were still being imported into the USA as of 1981, mainly for use in refractive index testing oils and capacitor dielectrics (IPCS 2001).

Beginning around 1910, CNs were produced commercially as mixtures of several homologue groups for a variety of uses. Mono-CNs, and mixtures of mono- and di-CNs, have been used for chemical-resistant gauge fluids and instrument seals, as heat exchange fluids, as high-boiling-point specialty solvents, for colour dispersions, as engine crank case additives and as ingredients in motor tune-up compounds. Mono-CNs have also been used as raw materials for dyes and as wood preservatives with fungicidal and insecticidal properties (Crookes and Howe 1993).

Products made with tri- and more highly chlorinated CNs have been used as impregnants for condensers, capacitors and dipping-encapsulating compounds in electronic and automotive applications, as temporary binders in the manufacture of ceramic components, in paper coating and impregnation, in precision casting of alloys, in electroplating stop-off compounds, as additives in gear oils and cutting compounds, in flame-proofing and insulation for electrical cable and conductors, as moisture-proof sealants, as separators in batteries, in refractive index testing oils, as masking compounds for electroplating, and in grinding wheel lubricants (Kirk Othmer 1980, US EPA 1983).

Until the early 1970s, General Motors of Canada used automotive capacitors containing CNs, which were imported from the USA (Holliday et al. 1982). Dow Chemical Canada reported that it did not use CNs at its Canadian chlorine manufacturing facility (Holliday et al. 1982).

Unintentional Production and Releases to the Environment

CNs are produced unintentionally as a by-product of many industrial processes involving chlorine atoms, especially in the presence of heat, such as waste incineration, cement and magnesium production (Falandysz 1998; SFT 2001; Takasuga et al. 2004) and the refining of metals such as aluminium with chlorine (Vogelgesang 1986; Aittola et al. 1994). It is also thought that CNs may be produced as a by-product in the chloralkali process (Falandysz 1998; Kannan et al. 1998) as well as by the slow combustion (at 600 degrees celcius) of dichlorophenols (DCPs) (Kim et al. 2007). The amount of CNs released into the environment from these sources has not been well characterized.

With respect to the presence of CNs in cement ash (i.e., cement kiln dust), cement kiln dust may be managed by either introduction into cement products or it may be disposed at a provincially licensed landfill. Landfills accepting cement kiln dust, as part of their operating permits, are typically required to be lined and groundwater in its vicinity is to be monitored.

Although one older study reported that mono- and di-chlorinated naphthalenes are formed at low concentrations as by-products in the chlorination of drinking water (Shiraishi et al. 1985), no evidence has been found in the recent literature to support this finding.

CNs are also a contaminant found in commercial polychlorinated biphenyl (PCB) formulations, such as Aroclor. The mean concentration of CNs in technical Aroclor formulations is reported as 67 µg/g by Falandysz (1998) and a reported range of 5.2–67 µg/g (Yamashita et al. 2000). Based on the amount of PCBs in use or stored as waste in Canada (Environment Canada 2003), and assuming a mean value of 67 µg CNs/g of PCBs, it is estimated that these PCBs contain less than one tonne of CNs.

Domestic burning of coal and wood in the U.K. was estimated to emit only 2 kg of CNs per year, including a wide range of tri- through octa-CN congeners; mono- and di-CNs were not monitored as part of the study (Lee et al. 2005). The tri- and tetra-CN homologue groups were the dominant ones detected. In comparison, CN emissions from PCBs were roughly estimated to produce 300 kg of CN emissions in the U.K. each year (Lee et al. 2005).

Emissions from both municipal and special waste incinerators are likely a significant source of CNs in the atmosphere, both in Canada and around the world.

- Helm et al. (2003) analyzed fly ashes from a medical waste incinerator, a cement kiln, a municipal solid waste incinerator and an iron sintering plant, all in Canada. The samples from the municipal solid waste incinerator, cement kiln and iron sintering plant contained 1.3–2.0 ng ΣCN/g of ash, while the medical waste incinerator sample contained 3600 ng ΣCN/g of ash.
- Helm and Bidelman (2003) found the average ΣCNs (tri- to octa-) in Canadian samples of fly ash to be 1.82 ng/g (municipal solid waste incinerator), 2.09 ng/g (cement kiln), 2.66 ng/g (iron sintering plant) and 5439 ng/g (medical waste incinerator).
- Helm et al. (2003) found CN congeners that are typically associated with combustion sources in Great Lakes air and around industrial sites in Toronto.

Elsewhere, Schneider et al. (1998) found that all CN homologue groups were found in fly ash from a municipal waste incinerator in Germany. Di- through penta-CNs were found in the largest amounts, and mono- through tri-CN congeners were also found in high amounts during the gas phase of incineration. 1,2,3,5,6,7-Hexa-CN was also formed in large amounts, together with other hexa-CN isomers (Schneider et al. 1998). Takasuga et al. (2004) examined unintentional CN production in municipal waste incinerators in Japan and found that all CN homologue groups are produced in flue gas, with mono- through tetra-CN congeners being the predominant by-products. The formation of CNs from waste incineration and its occurrence in ambient air during start-up, steady operation and shutdown of municipal solid waste incineration machinery were examined (Takasuga et al. 2004). In 1992, mono- through octa-CN congeners were measured in ambient air samples from three incineration sites in western Japan. Total CN concentrations in flue gas were 15 000, 4300 and 13 000 ng/m³ during start-up, steady operation and shutdown, respectively. Concentrations of CNs in air samples collected in winter were slightly higher than in those collected in summer (Takasuga et al. 2004). It should be noted that incinerators in Japan operate at lower temperatures than those required in Canada, which can affect CN production. A study of CNs in dated sediment cores in Switzerland

concludes that thermal reactions are gaining in importance relative to technical formulations as a source of CNs in the environment (Bogdal et al. 2006).

CNs in the environment could also result from disposal of products containing CNs in landfill sites and from old industrial sites where CNs were used. The releases from these sources to the Canadian environment have not been characterized.

Environmental Fate

The fate of the individual CN homologue groups has been evaluated separately because, as noted previously, the number of chlorine atoms in the CN structure is a key determinant of a CN's physical and chemical properties (see Table 1). Air-only release is the most likely scenario based on information about current use patterns, although direct release to water could also occur.

Partitioning

Level III fugacity modelling (Table 4) was used to predict into which environmental compartments CNs would partition. CNs tend to remain in air or to partition into soil when released only into the air. CNs tend to remain in water or to partition into sediment when released only into the water.

Table 4. Predicted environmental distribution of CNs in the environment *

	Compartment receiving 100% of emissions	Percentage of Substance Partitioning into Each Compartment			
		Air	Water	Soil	Sediment
Mono-CN _s	Air	97.50	0.61	1.84	0.068
	Water	5.37	85.10	0.10	9.44
	Soil	0.62	0.08	99.30	0.01
Di-CN _s	Air	96.60	0.94	2.26	0.20
	Water	9.44	74.70	0.22	15.60
	Soil	0.43	0.05	99.50	0.01
Tri-CN _s	Air	64.80	0.21	34.50	0.49
	Water	4.59	28.00	2.45	65.00
	Soil	0.22	0.01	99.80	0.02
Tetra-CN _s	Air	33.40	0.12	65.50	0.99
	Water	1.59	10.60	3.12	84.70
	Soil	0.19	0.27	97.40	2.13
Penta-CN _s	Air	3.99	0.09	91.80	4.09
	Water	0.08	2.05	1.72	96.20
	Soil	0.00	0.00	99.90	0.11
Hexa-CN _s	Air	56.20	0.17	34.00	9.62
	Water	0.02	1.77	0.01	98.20
	Soil	0.00	0.00	99.90	0.12
Hepta-CN _s	Air	36.40	0.22	50.90	12.50
	Water	0.00	1.71	0.01	98.30
	Soil	0.00	0.00	99.90	0.13
Octa-CN _s	Air	14.60	0.40	70.20	14.80
	Water	0.20	2.61	0.97	96.20
	Soil	0.69	1.50	42.40	55.40

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

Persistence in Air and Long-Range Atmospheric Transport

All CNs, with the exception of mono-CN, have estimated atmospheric half-lives that are longer than two days. This is based on their reaction with hydroxyl radicals, modelled using rate constants predicted with the Syracuse Research Corporation AOPWIN computer program (version 1.75) model and a daily (24-hour) hydroxyl radical concentration of 5×10^5 molecules/cm³, a typical value for the northern hemisphere (Table 5). There exists a measured hydroxyl radical reaction rate constant for 1,4-di-CN only, which would also give an atmospheric half-life of longer than two days (Klöpffer et al. 1988). The AOPWIN-estimated atmospheric half-life does not consider the chlorine position on the naphthalene rings; therefore, individual isomers may have somewhat higher or lower reaction rates than predicted for their congener group.

Table 5. Estimated atmospheric half-lives for CNs calculated using AOPWIN (the Syracuse Research Corporation (SRC) computer program)

	Estimated k_{OH} (cm ³ /mol per second)	Estimated atmospheric half-life (days)
Mono-CN	15.2×10^{-12}	1.06
1,4-di-CN	4.44×10^{-12}	3.62
2,7-di-CN	4.44×10^{-12}	3.62
Tri-CN	2.01×10^{-12}	7.98
Tetra-CN	9.11×10^{-13}	17.6
Penta-CN	4.13×10^{-13}	38.8
Hexa-CN	1.87×10^{-13}	85.7
Hepta-CN	8.48×10^{-14}	189
Octa-CN	3.84×10^{-14}	417

The TaPL3 model was used to estimate characteristic travel distance (CTD), defined as the maximum distance travelled by 63 percent of the substance after being released into the environment. Beyer et al. (2000) have proposed that CTDs that are greater than 2000 km represent high long-range transport potential (LRTP), 700–2000 km as moderate, and less than 700 km as low. The LRTP for CNs after release into the air was estimated to be low for mono-CN, moderate for di-CN and high for tri- through octa-CN. Based on these model predictions, mono-CN are expected to remain primarily in the areas close to their emission sources, while tri- through octa-CN may be subject to transboundary transport in the atmosphere and may be carried to remote regions such as the Arctic.

Tri- and greater CNs have been detected in air and biota in the Arctic, Antarctic and other regions that lack significant local sources of CNs, which indicates that long-range atmospheric transport of CNs is occurring (Helm et al. 2004). The tri- and tetra-CN congeners accounted for 90% to 95% of the total mass of CNs in the Canadian Arctic air samples collected by Harner et al. (1998), with the penta- and hexa-CN comprising the remainder. Given that tetra-, penta- and hexa-CN are the homologue groups most

dominant in wildlife in polar regions (Corsolini et al. 2002, Helm et al. 2002), penta- and hexa-CN_s may also be transported in the air to those regions in significant quantities.

Helm and Bidelman (2005) report the particle/gas distribution in Arctic air and show that the distribution is consistent with that predicted by the octanol-air partition coefficient (K_{OA}). Distributions on particles in the winter ranged from 5% or less for tri- and tetra-CN_s, to 20 to 35% for penta-CN_s, and 80 to 100% for hexa-, hepta- and octa-CN_s. Herbert et al. (2005) reported the sum of all CN congeners detected (Σ CN_s) at Ny Ålesund and Tromsø, Norway, was equal to 27–48 pg/m³ and 9–47 pg/m³, respectively. Lee et al. (2007) measured Σ CN_s in the Arctic air at levels of 1–8 pg/m³. Tri- and/or tetra-CN_s dominated.

Wania (2003) used the octanol-air partition coefficients (K_{OA}) and the air-water partition coefficients (K_{AW} , the dimensionless Henry's law constant) to derive the Arctic contamination potential (ACP) of persistent organic chemicals. The two sets of partitioning characteristics with elevated ACP overlap in the range of $6.5 < \log K_{OA} < 10$ and $-0.5 > \log K_{AW} > -3$, which also corresponds to a $\log K_{OW}$ range of 5 to 8 (i.e., substances that also have a potential for bioaccumulation) (Wania 2003). The $\log K_{AW}$ ranges at 25°C for each homologue group (except the di- and octa-CN_s) were estimated based on the Henry's law constant ranges presented in Table 1, using the following formula: $K_{AW} = \text{Henry's Law Constant} / (R \times T)$. The $\log K_{OA}$ values were measured by Harner and Bidleman (1998) or estimated for mono-CN based on the following formula: $K_{OA} = K_{OW} / K_{AW}$

This information is presented in Table 6. The values that fall in the ranges specified by Wania (2003) are shaded. Based on these criteria, at least some of the congeners from the di-, tri-, tetra-, and penta-CN homologue groups appear to have elevated ACP.

Table 6. Arctic contamination potential characteristics of CNs

	Log K_{AW} at 25°C	Log K_{OA} at 25°C ¹
Mono-CN _s	-2.05–2.01	4.61–4.96 *
Di-CN _s	-2.83–1.93	6.93
Tri-CN _s	-3.35–1.68	7.27–7.56
Tetra-CN _s	-3.45–1.78	8.08–8.64
Penta-CN _s	-3.73–2.3	8.73–9.15
Hexa-CN _s	-3.9–3.04	9.70–10.37
Hepta-CN _s	-4.35–4.12	8.18–8.24 *
Octa-CN _s	-5.09	9.25 *

1. Measured values from Harner and Bidleman (1998)

*These values calculated based on $K_{OA} = K_{OW}/K_{AW}$ using a median K_{OW} value, and the estimated K_{AW} from the above-mentioned formula.

Persistence in Water, Soil, and Sediments

There are limited data on abiotic and biotic degradation of CNs. Some aerobic biodegradation of mono- and di-CNs does occur: after five days in liquid culture medium, 100% of 2-CN, 95% of 1,4-di-CN and 50% of 2,7-di-CN were converted to several hydroxylated products (Kitano et al. 2003). There is also evidence that certain CNs (1,4-di-CN, 2,7-di-CN, and 1,2,3,4-tetra-CN) are degraded to hydroxylated compounds by wood-rotting fungi in liquid culture medium (Mori et al. 2009). For example, 1,2,3,4-tetra-CN was found to degrade by 70% after 14 days; using first order rate equations, the calculated half-life is 8.06 days.

Tetra- through hexa-CNs did not degrade during a 28-day aerobic biodegradation test using spiked natural lake sediment (Järnberg et al. 1999). As Geva et al. (2000) have noted, anaerobic dechlorination of CNs (similar to that of PCBs) cannot be ruled out, although it has not yet been reported. It is therefore possible that some lesser chlorinated CNs found in anaerobic sediment are degradation products of more highly chlorinated congeners.

Since there are few experimental data for the degradation of CNs, a QSAR-based weight-of-evidence approach (Environment Canada 2007) was also applied using the BIOWIN model (BIOWIN 2000). Table 7 summarizes the BIOWIN results.

Table 7: Biodegradation of CNs as predicted by BIOWIN (2000)

Homologue Group	Sub-model 4 (Primary Degradation)		Sub-model 3 (Ultimate Degradation)		Sub-model 5 (MITI linear)		Sub-model 6 (MITI Non-linear)	
	Result	Estimated Half-life (days)	Result	Estimated Half-life (days)	Result	Estimated Half-life (days)	Result	Estimated Half-life (days)
Mono-CN	3.448	< 182	2.633	< 182	0.292	≥ 182	0.175	≥ 182
Di-CN	3.233	< 182	2.351	< 182	0.188	≥ 182	0.053	≥ 182
Tri-CN	3.018	< 182	2.068	< 182	0.083	≥ 182	0.015	≥ 182
Tetra-CN	2.803	≥ 182	1.785	≥ 182	-0.022	≥ 182	0.004	≥ 182
Penta-CN	2.588	≥ 182	1.502	≥ 182	-0.126	≥ 182	0.001	≥ 182
Hexa-CN	2.373	≥ 182	1.220	≥ 182	-0.231	≥ 182	0.0003	≥ 182
Hepta-CN	2.158	≥ 182	0.937	≥ 182	-0.335	≥ 182	0.0001	≥ 182
Octa-CN	1.943	≥ 182	0.654	≥ 182	-0.440	≥ 182	0.0000	≥ 182

There are conflicting BIOWIN results for mono and di-CN. The two ready biodegradation sub-models (5 and 6) indicate that biodegradation is relatively slow and that the half-lives in water would be ≥182 days, whereas sub-model 3 indicates ultimate degradation half-lives of <182 days. The primary biodegradation sub-model (BIOWIN sub-model 4) result indicates that mono- and di-CN have primary half-lives of <182 days.

For tri-CN, the three BIOWIN sub-models relating to ultimate degradation (3, 5, and 6) indicate that biodegradation is slow and that the half-life in water would be ≥182 days.

However, the primary biodegradation sub-model (BIOWIN sub-model 4) result indicates that tri-CNs have a primary half-life of <182 days.

For tetra to octa-CNs, all four biodegradation sub-models (3,4,5, and 6) indicate that the biodegradation of these homologue groups is slow and that the half-life in water would be ≥ 182 days.

Using an extrapolation ratio of 1:1:4 for a water: soil: sediment biodegradation half-life (Boethling et al. 1995), the half-lives in soil for tetra to octa-CNs are also ≥ 182 days and the half-lives in sediments are ≥ 365 days. This indicates that tetra to octa-CNs are expected to be persistent in soil and sediments.

Tri- to hepta-CNs have been detected in lake sediments dating back about 33 years (Gevao et al. 2000), in quantities suggesting that the half-lives of CNs in sediments are greater than one year (mono-, di- and octa-CNs were not analyzed in these studies). The calculations supporting this conclusion are included in Appendix A. In a study of CNs in Norwegian sediments, it was further found that the tetra- to octa-CN isomer composition was unchanged when comparing samples from different sediment core layers and it was concluded that essentially no degradation had occurred in approximately fifty years (Ishaq et al. 2009).

Using the data from Meijer et al. (2001), it is possible to estimate the following degradation half-lives for soils that had been amended with CN-containing sewage sludge, based on analysis of an archived sample from 1972 and subsequent sampling in 1990: 7.4 years for tri-CNs, 13.1 years for tetra-CNs and 35.3 years for penta-CNs. Since concentrations of hexa- and hepta-CNs did not decrease significantly, half-lives could not be calculated.

Based on the weight of evidence, including the predicted persistence of di- to octa-CNs in the air, the high characteristic travel distances for tri- to octa-CNs, the high predicted Arctic contamination potential of di- to penta-CNs, the empirical evidence of the long-range transport of several CNs in Arctic air, the empirical evidence for persistence of tri- to hepta-CNs in sediments and soils, and the estimated degradation half-lives of tetra- to octa-CNs in water, it is concluded that di- to octa-CNs are persistent, as defined in the Persistence and Bioaccumulation Regulations of CEPA 1999 (Canada 2000).

Bioaccumulation

Lipophilic organic substances with log K_{ow} values equal to or greater than 5, and/or bioconcentration factor (BCF) and bioaccumulation factor (BAF) values equal to or greater than 5000, such as PCBs, DDT and chlordane, have been shown in the field to bioaccumulate and to biomagnify into the tissues of wildlife in the upper trophic levels (Canada 1995). Therefore, if a substance has a biomagnification factor (BMF) significantly greater than 1, this may be an important supporting line of evidence indicating that the substance has the potential to bioaccumulate, especially when relevant BCF and BAF data are limited. Information on biomagnification of CNs in food chains

will therefore be considered as part of the weight of evidence that CNs are bioaccumulative substances, as understood in the context of the Persistence and Bioaccumulation Regulations of CEPA 1999 (Canada 2000).

Tri- to octa-CNs are neutral organic substances, and log K_{ow} values equal to or greater than 5 have been measured for these substances using either the shake flask method (Opperhuizen 1987; Opperhuizen et al. 1985) or the reversed phase-HPLC method (Lei et al. 2000), as summarized in Table 1.

BCFs greater than 5000 have been measured for di- to penta-CNs in aquatic biota, as summarized in Table 8. No measured BCF values were available for hexa-CNs. The BCF studies by Oliver and Niimi (1984, 1985) are deemed to be acceptable, even though a solubilizer (methanol) was used in one of the studies, because the exposure concentrations (low ng/L range) were within the reported range of water solubilities of the CNs being studied (see Table 1). The BCF values reported by Matsuo (1981) are included in Table 8; however, this is a secondary reference, and the primary reference that Matsuo (1981) cites for this BCF data (Kawasaki 1980) does not appear to report these values or the methodology employed. However, no other reports of measured BCF values were found for penta-CNs.

Based on this BCF information, di-, tri-, tetra- and penta-CNs appear to bioconcentrate to a high degree in fish. Octa- and hepta-CNs do not appear to bioconcentrate significantly (Opperhuizen et al. 1985); however, the time of exposure to octa- and hepta-CNs in the experiments was short (seven days). No studies of the bioconcentration of hexa-CNs are available. However, because the log K_{ow} values for the higher chlorinated CNs are greater than 5, it is predicted that dietary uptake is likely to be much more significant than uptake from water (Arnot and Gobas 2003). Hexa- and hepta-CNs have been found in relatively large amounts in harbour porpoises (Falandysz and Rappe 1996) and in white-tailed sea eagles (Falandysz et al. 1996). Hexa-CN congeners 66/67 were also found to biomagnify in many aquatic and bird predator species (Falandysz 1997c), as is discussed below.

Table 8. Bioconcentration factors for CNs in fish and other aquatic species (after IPCS 2001)

	Species	Exposure concentration (µg/L)	Duration of exposure (depuration)	BCF	Reference
	<i>Fish</i>				
Mono-CN	Common carp (<i>Cyprinus carpio</i>)	Not indicated	Not indicated	191	Matsuo (1981)
2-CN	Fancy guppy (<i>Poecilia reticulata</i>)	100–1000 ^a	7 days (84 days)	4300	Opperhuizen et al. (1985)
1,4-Di-CN	Fancy guppy (<i>Poecilia reticulata</i>)	10–1000 ^a	7 days (84 days)	2300	Opperhuizen et al. (1985)
1,4-Di-CN	<i>Oncorhynchus mykiss</i> (rainbow trout)	1.7×10^{-3}	Not indicated	5600	Oliver and Niimi (1984)
1,8-Di-CN	Fancy guppy (<i>Poecilia reticulata</i>)	10–100 ^a	7 days (84 days)	6100	Opperhuizen et al. (1985)
2,3-Di-CN	Fancy guppy (<i>Poecilia reticulata</i>)	10–100 ^a	7 days (84 days)	11 000	Opperhuizen et al. (1985)
2,7-Di-CN	Fancy guppy (<i>Poecilia reticulata</i>)	10–100 ^a	7 days (84 days)	11 000	Opperhuizen et al. (1985)
Tri-CN	<i>Cyprinus carpio</i> (common carp)	Not indicated	Not indicated	4677	Matsuo (1981)
1,3,7-Tri-CN	Fancy guppy (<i>Poecilia reticulata</i>)	1–100 ^a	7 days (84 days)	27 000	Opperhuizen et al. (1985)
Tetra-CN	Common carp (<i>Cyprinus carpio</i>)	Not indicated	Not indicated	8710	Matsuo (1981)
1,2,3,4-Tetra-CN	Fancy guppy (<i>Poecilia reticulata</i>)	0.1–10 ^a	7 days (84 days)	33 000 ^b	Opperhuizen et al. (1985)
1,2,3,4-Tetra-CN	<i>Oncorhynchus mykiss</i> (rainbow trout)	5.6×10^{-3}	Not indicated	5100	Oliver and Niimi (1985)
1,3,5,7-Tetra-CN	Fancy guppy (<i>Poecilia reticulata</i>)	0.1–1 ^a	7 days (84 days)	34 000 ^b	Opperhuizen et al. (1985)
1,3,5,8-Tetra-CN	Fancy guppy (<i>Poecilia reticulata</i>)	1–10 ^a	7 days (84 days)	25 000 ^b	Opperhuizen et al. (1985)
Penta-CN	Common carp (<i>Cyprinus carpio</i>)	Not indicated	Not indicated	10 000	Matsuo (1981)
Hepta-CN	Fancy guppy (<i>Poecilia reticulata</i>)	Not indicated	7 days (84 days)	0	Opperhuizen et al. (1985)
Octa-CN	Fancy guppy (<i>Poecilia reticulata</i>)	Not indicated	7 days (84 days)	0	Opperhuizen et al. (1985)
Octa-CN	<i>Oncorhynchus mykiss</i> (rainbow trout)	1.3×10^{-2}	Not indicated	330	Oliver and Niimi (1985)

^a Exposure concentrations are estimated ranges from a graphical presentation of results.

^b Equilibrium was not reached within the duration of the experiment.

Tysklind et al. (1998) and Åkerblom et al. (2000) studied the bioaccumulation of CNs in salmon fry (*Salmo salar*). The fish were fed food to which Halowax 1001, 1014 and 1051 were added at concentrations of 0.1–10 µg Halowax/g of food. The study lasted 41 weeks. BMFs after 17 weeks that ranged from 0.73 to 2.5 were reported for single-eluting congeners, calculated for salmon fed 2 µg CNs/g of food (Tysklind et al. 1998). The congeners tetra-CN 42, penta-CNs 58 and 61 and hexa-CNs 65 and 69 were observed to have BMFs ranging from 1.0 to 2.5. A QSAR model based on the results of this study

predicted that hexa-CNs 66, 67 and 68 would have BMFs ranging from 1.0 to 1.5, while hexa-CNs 64, 70 and 71 would have BMFs ranging from 0.90 to 0.97. Log BMFs for total tri- to octa-CNs after 41 weeks ranged from 3.34 to 3.54 (Åkerblom et al. 2000).

Tetra- to hepta-CNs were found to have BMFs greater than 1 in several aquatic food chains. Hanari et al. (2004) found CN levels in the St. Clair River near Marine City, Michigan, suggesting a BMF of approximately 3 for benthic algae, zebra mussels and round gobies. BMFs for hexa-CNs 66/67 and 69 in a benthic marine food chain in the Baltic Sea were found to be 1.1 and 1.4, respectively (Lundgren et al. 2002). The BMF for the hexa-CN 66/67 congeners in a Baltic Sea pelagic food chain was found to be 1.2 for harbour porpoise/herring (Falandysz and Rappe 1996a).

Falandysz (1997c) calculated BMFs for tetra- through hepta-CN congeners in many types of aquatic biota (predator/prey combinations) from the Baltic Sea. All exposure was considered to be through food (prey). The predator/prey pairings included herring/plankton, stickleback/plankton, sand eel/plankton, flounder/mussel, black cormorant/fish, white-tailed sea eagle/fish, white-tailed sea eagle/cormorant and harbour porpoise/herring. Almost all of these were found to have BMFs greater than 1 for at least some of the tetra-CN congeners, including a maximum of 95 for the white-tailed sea eagle/fish. For almost all of the predators at least some penta-CN congeners were found to be biomagnified from their food, with the exception of harbour porpoise/herring; the maximum observed BMF being 150 for white-tailed sea eagle/fish. For all of the predators, hexa-CN congeners 66/67 were found to be biomagnified from their food, while for some of the predators other hexa-CN congeners were also biomagnified. The white-tailed sea eagles were found to have the highest biomagnification from fish, with BMFs greater than 30 for some tetra-, penta- and hexa-CN congeners. The pairings that biomagnified one or both of the hepta-CN congeners included herring/plankton, flounder/mussel, eagle/cormorant, with the BMF for the white-tailed eagle/fish the largest at 5.7.

Additional evidence for the biomagnification of CNs – i.e., increasing total CN concentration as trophic level increases - is shown in Table 9. The relative level of CNs/PCBs is comparatively stable throughout the Arctic marine food chain studied (krill, icefish and south polar skua). Since PCBs are known to be significantly biomagnified, this suggests that CNs are also significantly biomagnified (Corsolini et al. 2002).

Table 9. Concentration of total CNs and PCBs (ng/g) at increasing trophic levels

Species	CNs	PCBs	Relative level (CN/PCB)
Krill	1.5×10^{-3}	1.9	7.9×10^{-4}
Crocodile icefish	3.4×10^{-3}	8.4	4.0×10^{-4}
South polar skua liver	2.55	11 150	2.30×10^{-4}
South polar skua muscle	9.7×10^{-2}	2630	4.00×10^{-5}

Data source: Corsolini et al. 2002.

In addition, the dietary uptake efficiencies of hexa-, hepta- and octa-CNs in northern pike were found to be 35% for octa-CNs, 66% for hepta-CNs and 63% and 78% for hexa-CNs,

depending on the congener. This is much higher than predicted by the empirical model of Gobas et al. (1988) for molecules of this size (Burreau et al. 1997), and indicates enhanced uptake potential.

The half-lives of certain hexa-CN congeners in rats and humans were found to be similar to those of recalcitrant compounds such as polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) that are known to accumulate in organisms and magnify in food chains (Asplund et al. 1994a, 1994 b; Ryan et al. 1993). Asplund et al. (1994a) studied the retention of a mixture of hexa-CN congeners 66/67 and one unidentified hexa-CN congener in rats. The half-lives were calculated to be 41 days in the adipose tissue and 36 days in the liver, which are comparable with those reported for the most slowly eliminated 2,3,7,8-substituted PCDF congeners (Asplund et al. 1994a). Human blood samples from three individuals exposed in 1979 to CN-contaminated rice oil in Taiwan were monitored for the 1,2,3,4,6,7/1,2,3,5,6,7-hexa-CNs over a period of about 10 years. The measured concentrations resulted in calculated half-lives of 1.5–2.4 years (Ryan and Masuda 1994). These long half-lives in humans are similar to those reported for selected PCDFs (Ryan et al. 1993).

Based on the weight of evidence, including in particular measured log K_{ow} values for tri- to octa-CNs (Table 1) and measured BCF values for di- to penta-CNs in fish (Table 7), and taking into account supporting information on measured BMFs for tetra- to hepta-CNs, the high dietary uptake efficiencies of hexa- to octa-CNs in northern pike, and the very slow elimination of hexa-CNs from the bodies of rats and humans, it is concluded that di to octa-CNs are bioaccumulative, as defined in the Persistence and Bioaccumulation Regulations of CEPA 1999 (Canada 2000).

Environmental Effects

Aquatic Organisms

There are only limited measured, reliable aquatic toxicity data for most CN homologue groups, so the toxicity of these groups was modelled using ECOSAR (version 0.99h). The log K_{ow} and water solubility values were estimated using WSKOWWIN (version 1.41). The estimated K_{ow} values were generally similar to available measured K_{ow} values, but the estimated water solubility values were generally higher than available measured values (see Table 2). ECOSAR has log K_{ow} cut-offs of 5.0 and 8.0 for acute effect and chronic effect estimations, respectively, so toxicity estimations for homologues with K_{ow} values greater than these cut-off values were not included in Table 10. As well, any predicted toxicity values greater than the predicted water solubility values were not included in Table 10.

Table 10. ECOSAR estimated toxicity values for CNs (results given in $\mu\text{g/L}$)

	Acute invertebrate LC_{50}	Fish LC_{50} ¹ median (range)	Green algae 96-hour LC_{50} /chronic toxicity	Fish 30-day chronic value	Daphnid 16-day EC_{50} ² chronic value
Mono-CNs	190	1858 (1318–2911)	2020/575	413	330

Di-CN _s	35	624 (536–712)	651/270	136	136
Tri-CN _s ^a	7	212 (209–215)	208/125	44	55
Tetra-CN _s	NA	NA	63/55	14	22
Penta-CN _s	NA	NA	19/25	4	8
Hexa-CN _s	NA	NA	NA	1.3	3
Hepta-CN _s	NA	NA	NA	0.4	1.2
Octa-CN	NA	NA	NA	NA	NA

¹LC₅₀ – The concentration of a substance that is estimated to be lethal to 50% of the test organisms.

²EC₅₀ – The concentration of a substance that is estimated to cause some toxic sublethal effect on 50% of the test organisms.

^a Acute results are presented, even though the calculated K_{ow} value for tri-CN_s (5.10) was slightly above the cut-off value of 5.00.

NA: Results not valid, since log K_{ow} value was too high or the water solubility too low.

The toxicity of CN_s, mostly tested as commercial Halowax mixtures, has been studied in a variety of aquatic species, including aquatic plants, invertebrates, fish and frogs. A summary of most of these studies is given in IPCS (2001). The more recent studies not included in IPCS (2001) were reviewed and key studies are noted below. Some of the tests involved using solubilizers such as acetone, with resulting test concentrations being potentially greater than the water solubility of some CN homologues or mixtures. It should, however, be noted that the solubilities of the Halowax mixtures have not been well characterized: all Halowax products are described as “insoluble” in the IPCS (2001) report, rather than actual solubilities being reported, as is done for some of the individual CN isomers (refer to Table 1 for solubility estimates for homologue groups). Therefore, the solubilities of the Halowax mixtures were roughly estimated based on the solubilities listed (see Table 1) for the dominant congener groups found in the mixtures (refer to Table 3b), in order to compare the solubilities to the concentrations tested in the toxicity studies. The most sensitive aquatic toxicity values for each homologue group of CN_s are summarized below. Generally, these toxicity values are considered acceptable, being within a factor of 10 of measured solubilities and below the solubility values predicted by ECOSAR.

Mono-CN_s

The most sensitive invertebrate test with mono-CN_s was a 96-hour LC₅₀ of 370 µg/L with mysid shrimp (US EPA 1980). No chronic aquatic studies were identified. This value is higher than the ECOSAR 96-hour LC₅₀ for mysid shrimp of 190 µg/L, and is very similar to the chronic ECOSAR 16-day EC₅₀ for daphnids. The most sensitive vertebrate test was a 96-hour LC₅₀ of 690 µg/L with sheephead minnows (Ward et al. 1981).

The most sensitive chronic toxicity result with Halowax 1000 was 100 µg/L, which caused an 11% reduction in the growth of the marine alga *Dunaliella tertiolecta* in a seven-day study (Walsh et al. 1977). This effect value is lower than the ECOSAR-predicted chronic value for algae of 575 µg/L, but is in the same range as other ECOSAR acute values for invertebrates. These toxicity values are all below the measured and estimated solubility values of mono-CN_s (Table 1). Halowax 1000 is reported in IPCS

(2001) to be comprised of 60% mono-CNs and 40% di-CNs (see Table 3a), although these values do not agree with the mean (and ranges) of the experimental percentages (see Table 3b): 15 (6.7–69), 76 (28–76.5) and 6.5 (1.2–44.1) for mono-, di- and tri-CNs, respectively.

Di-CNs

No toxicity studies of di-CNs alone were identified. The most sensitive acute toxicity result with Halowax 1000, comprised of 76% di-CNs and 15% mono-CNs, based on averages reported by Falandysz et al. (2006b) (see Table 3b), was 100 µg/L. This caused an 11% reduction in the growth of the marine alga *Dunaliella tertiolecta* in a seven-day study (Walsh et al. 1977). This effect value is lower than the ECOSAR-predicted chronic value for algae of 270 µg/L but is in the same range as other ECOSAR acute and chronic values for invertebrates and fish. These toxicity values are generally below the measured and estimated solubility values of di- and mono-CNs (Table 1).

Tri-CNs

No toxicity studies of tri-CNs alone were identified. However, based on averages reported by Falandysz et al. (2006b), tri-CNs comprise approximately 38.7% of Halowax 1099 (see Table 3b). In a study with Halowax 1099 (which also contains about 48% tetra-CN), the 96-hour LC₅₀ with the grass shrimp *Palaemonetes pugio* was 69 µg/L (Green and Neff 1977). Neff and Giam (1977) exposed juvenile horseshoe crabs (*Limulus polyphemus*) to Halowax 1099 for 96 days. They found that 50% mortality of the late T₁ stage crabs occurred at 27 days at the highest exposure concentration of 80 µg/L (nominal). Significant effects on the length of the intermoult period were observed at 80 µg/L. Acetone was used as a solubilizer in both studies. These toxicity values are within approximately 10 times the measured solubility limit for tri- and tetra-CN but are below the solubility values predicted by ECOSAR. They are also within the range of acute and chronic values predicted for invertebrates and fish using ECOSAR.

Tetra-CNs

No toxicity studies of tetra-CN alone were identified. However, based on averages reported by Falandysz et al. (2006b), tetra-CNs comprise approximately 48% of Halowax 1099 and 53.3% of Halowax 1013 (see Table 3b). Studies conducted with Halowax 1099 are described above (see tri-CN). Halowax 1013 (which also contains about 30% penta-CN) reduced the growth of the marine alga *Nitzschia sp.* at 500 µg/L (Walsh et al. 1977). A 96-hour LC₅₀ of 74 µg/L was obtained with grass shrimp with Halowax 1013 (Green and Neff 1977). These values are generally within about 10 times the measured solubility limit for tetra-CN and below the solubility predicted by ECOSAR. Acetone was used as solubilizer in this study. The measured grass shrimp toxicity value is higher than, but within the same range as, the chronic values for invertebrates and fish predicted with ECOSAR. The measured marine algae toxicity value is an order of magnitude higher than the ECOSAR-predicted algae values.

Penta-CNs

No toxicity studies of penta-CNs alone were identified. However, based on averages reported by Falandysz et al. (2006b), penta-CNs comprise approximately 47.7% of Halowax 1014 (see Table 3b). Halowax 1014 also contains 25.3% hexa-CNs, some of which have been found to be quite toxic to mammals, since they have a dioxin-like mode of action. Penta-CNs comprise approximately 30% of Halowax 1013 (which also contains 53.3% tetra-CNs and 13.1% tri-CNs). A 96-hour LC₅₀ of 74 µg/L was obtained with grass shrimp (*Palaemonetes pugio*) and Halowax 1013 (Green and Neff 1977). This toxicity value is within about 10 times the measured solubility value and is slightly more than the WSKOWWIN-predicted solubility of penta-CNs and below the WSKOWWIN-predicted solubility values for tri- and tetra-CNs. The ECOSAR-predicted chronic toxicities of penta-CNs in fish and daphnids, and green algae are less than 10 µg/L and 25 µg/L, respectively.

The US EPA (1980) conducted acute studies with Halowax 1014 (tetra-, penta-, hexa-CNs = 16: 47.7: 25.3) and brown shrimp (*Penaeus aztecus*), grass shrimp (*Palaemonetes pugio*), sheepshead minnows (*Cyprinodon variegatus*) and striped mullets (*Mugil cephalus*). The 96-hour LC₅₀ values for these studies (in µg/L) were 7.5, 248, greater than 343 and greater than 263, respectively; however, the experimental details have not been published. Halowax 1014 was not found to have a significant effect on the growth of any of four species of marine algae at concentrations of up to 1000 µg/L during seven-day studies (Walsh et al. 1977). A concentration of 100 µg/L of Halowax 1014 was fatal to 52% of frog larvae (*Rana agilis*) after 18 hours, while the metamorphosis of the rest of the treated tadpoles was delayed for three weeks (Buggiani 1980). Only the toxicity value of 7.5 µg/L LC₅₀ for brown shrimp is comparable to or below the measured and WSKOWWIN-predicted solubility values for penta-CNs.

Talykina et al. (2003) studied the effects of Halowax 1014 on the erythrocytes (red blood cells) of adult medaka fish (*Oryzias latipes*) exposed *in ovo*. Fragmented nuclei (micronucleated erythrocytes) were induced by Halowax 1014 at the lowest concentration tested, 300 ng of Halowax 1014/g of egg.

Villalobos et al. (2000) conducted partial lifecycle toxicity tests in which medaka fish eggs (*Oryzias latipes*, early gastrula) 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 1013 caused 64% mortality of the eggs at a dose of 10 ng/egg, with half of those deaths occurring on day 3; the greatest dose (30 ng/egg) caused 28% mortality late in development (Villalobos et al. 2000). Halowax 1013 also caused premature hatching of embryos at all doses (0.3–30 ng/egg). LD₅₀ measurements could not be calculated for the Halowax 1013 tests since they did not elicit monotonic dose-response relationships. Therefore, the threshold dose of Halowax 1013 in this study appears to be 0.3 ng/egg.

Hexa-CNs

No toxicity studies of hexa-CNs alone were identified. The only Halowax mixture containing a significant proportion of hexa-CNs is Halowax 1014, which contains approximately 25.3% (21–35.3%) hexa-CNs based on data reported by Falandysz et al. (2006b) (see Table 3b). Acute studies with Halowax 1014 are described above, with LC₅₀ values ranging from 7.5 µg/L to more than 343 µg/L for invertebrates, fish and frogs. The lowest of the toxicity values (7.5 µg/L LC₅₀ for brown shrimp) is within a factor of 100 of the measured solubility and below the WSKOWWIN-predicted solubility of hexa-CNs. ECOSAR predicted chronic toxicity values for hexa-CNs with fish/daphnid are 1–3 µg/L.¹

Hepta-CNs

No toxicity studies of hepta-CNs alone were identified. The ECOSAR-predicted chronic toxicity of hepta-CNs to fish and daphnids is in the low µg/L range (see Table 9). The only Halowax mixture containing a significant proportion of hepta-CNs is Halowax 1051, which, based on data reported by Falandysz et al. (2006b), contains only about 7.6% hepta-CNs and 91.4% octa-CNs (see Table 3b). Toxicity studies with Halowax 1051 are described below.

Villalobos et al. (2000) injected medaka embryos with Halowax 1051, as described earlier. Halowax 1051 was the least toxic of the three Halowax mixtures tested; embryo mortality did not exceed 20% for all doses after 8–16 days of exposure. However, Halowax 1051 caused significantly decreased gonadosomatic indices for females after 122 days at all four doses (0.3–10 ng/egg), with no evident dose-response trend.

Talykina et al. (2003) studied the effects of Halowax 1051 on the erythrocytes (red blood cells) of adult medaka exposed *in ovo*. Fragmented nuclei (micronucleated erythrocytes) were induced by Halowax 1051 at the lowest concentration tested, 300 ng of Halowax 1051/g of egg (0.3 ng/embryo).

¹ Because of the uncertainties associated with measuring water solubility, especially at very low levels, toxicity values were accepted if they were within a factor of 100 of reported measured values.

Octa-CNs

Three acute studies of octa-CN were identified: with water fleas (*Daphnia magna*) (LeBlanc 1980), sheepshead minnows (*Cyprinodon variegatus*) (Heitmuller et al. 1981), and mysid shrimp (*Mysidopsis bahia*) (US EPA 1980). In the first two of these tests, no effects were seen at the highest concentrations tested (530 mg/L and 560 mg/L, respectively). In the third study, the 96-hour LC₅₀ was greater than 500 mg/L (no further experimental results were available). This indicates that octa-CNs are of relatively low acute toxicity to aquatic organisms. These effect concentrations are far above both the measured and predicted solubilities of octa-CNs. No ECOSAR toxicity predictions for octa-CN were available, since the K_{ow} value of octa-CNs is outside of the acceptable range for this model.

Toxicity studies with Halowax 1051, which is comprised of approximately 91.4% octa-CNs, are described for hepta-CNs, above.

Terrestrial Wildlife

This section focuses on the toxicity of hexa- to octa-CNs, with particular emphasis on exposure via food, since food ingestion is expected to be the principal exposure pathway for these high log K_{ow} (7.5–8.5) homologue groups.

Mammalian studies with CNs are summarized in IPCS (2001), and some additional studies were also reviewed. No long-term mammalian studies were identified. A study lasting up to 135 days was conducted with ewes (Brock et al. 1957). Most studies were short-term, and many were conducted with laboratory animals such as rats, rabbits and guinea pigs. Cattle, however, appear to be more sensitive to CNs than laboratory rodents and are also more sensitive to CNs than sheep (IPCS 2001). No studies with mono- or di-CNs have been conducted with cattle.

Avian and Mammalian studies: Mixtures of penta- and hexa-CNs

Only two studies of the toxicity of CNs to birds have been identified. These studies involved turkey poults and chickens fed a diet containing Halowax 1014 (25.3% hexa-, 47.7% penta- and 16% tetra-CNs; see Table 3b) for 40 days (Pudelkiewicz et al. 1958, 1959). A dose of 20 mg/kg feed caused 50% mortality of the turkeys but had little effect on the chickens. At 5 mg/kg feed, the CNs caused 6.5% turkey mortality, and their weight gain was reduced by 33%.

In a rabbit study, Flinn and Jarvik (1936) administered two CNs mixtures subcutaneously. After daily administration of the mixtures, which consisted mainly of tetra- and penta-CNs, and of penta- and hexa-CNs at doses of 30 mg (in paraffin oil) per day per rabbit, all the rabbits died (5/5 per group) by days 12–26. Autopsies found that the livers had many yellow areas and a wide zone of necrosis (Flinn and Jarvik 1936).

Rats fed a mixture of penta- and hexa-CNs (125 mg/rat on alternate days) for 26 days showed moderate liver changes (swollen and vacuolated liver cells, as well as necrosis and degeneration of scattered cells). All other organs (no specifics given) were found to be normal after microscopic examination (Bennett et al. 1938). Groups of 10 rats fed penta- and hexa-CNs in feed, dosed at either 100 mg/rat per day for 55 days or 300 mg/rat per day for 33 days, all died or were moribund (Drinker et al. 1937, Bennett et al. 1938).

Gastrointestinal lesions and severe liver damage or death were reported in sheep orally administered 1.1 mg/kg body weight per day of Halowax 1014 for 90–135 days (Brock et al. 1957).

Decreased sperm production occurred in bulls fed penta- and hexa-CNs (50 to 200 mg daily for approximately seven weeks) (Vlahos et al. 1955).

Mammalian studies: Hexa-CNs

Oral exposure of pigs to hexa-CNs at 19–22 mg/kg body weight per day for up to 10 days caused degeneration of the liver and kidneys, and mortality, while 17.1–17.6 mg/kg body weight per day caused depressed vitamin A levels (Link et al. 1958, Huber and Link 1962). Oral exposure of rats to hexa-CNs at doses of 0.3–2.3 mg/day over a period of 56–84 days caused dose-dependent increases in relative liver weights, and doses of 20 and 60 mg/day caused liver damage (Weil and Goldberg 1962). Oral doses of 1.1 mg/kg body weight per day of hexa-CN congeners administered to cattle via gelatine capsules for 5–10 days resulted in severe systemic disease (hyperkeratosis) (Bell 1953).

Mammalian studies: Hepta-CNs

Oral doses of 0.69–2.4 mg/kg body weight per day of hepta-CNs administered to cattle via gelatine capsules for seven to nine days resulted in severe systemic disease (hyperkeratosis) (Bell 1953). A single oral dose of 500 mg/kg body weight of hepta-CNs resulted in the death of all three rabbits during a seven-day period (Cornish and Block 1958).

Mammalian studies: Octa-CNs

A single oral dose of 500 mg/kg body weight of octa-CNs resulted in the death of all three rabbits during a seven-day period (Cornish and Block 1958). An oral dose of 2.4 mg/kg body weight per day of octa-CNs administered to cattle via gelatine capsules for nine days resulted in severe systemic disease (hyperkeratosis), while an oral dose of 1.0 mg/kg body weight per day for 11 days resulted in mild hyperkeratosis (Bell 1953).

Assessment of Potential to Cause Ecological Harm

The approach taken in this ecological screening assessment was to examine various pieces of scientific and technical information, and to develop conclusions based on a weight-of-evidence approach and using precaution as required under CEPA 1999. Since there are unique concerns about di- through octa-CN_s, because they are persistent and bioaccumulative substances, the potential for these homologue groups to cause environmental harm has been evaluated separately from that of mono-CN_s.

Environmental Exposure

There is a small dataset of environmental concentrations of CN_s in Canada. Much more environmental data on CN_s, including data from sediments and soils, have been collected in the USA and Europe. CN_s have been detected in the following media in Canada: Arctic and urban air, water from Lake Ontario, fish and birds from the Great Lakes and environs, seals and whales from the Canadian Arctic, and Vancouver Island marmots. Key environmental exposure data from Canada, the USA and elsewhere are presented below.

It should be noted that the validity of some older monitoring data for CN_s has been questioned. Concerns about methodology, specifically that PCBs could co-elute with PCNs and interfere with their detection, if gas chromatography (GC) alone was used, have been expressed (Crookes and Howe 2002). Most of the studies used in this assessment are recent (1990s and later).

CN_s have been measured in air in Canada in Toronto (Harner and Bidleman 1997, Helm and Bidleman 2003), around the Great Lakes and near Cornwall, Ontario (Helm et al. 2003). The highest total-CN concentration measured in Canada was 84.5 pg/m³, measured in suburban Toronto (Helm and Bidleman 2003). The dominant homologue group found over western Lake Ontario and Toronto was tetra-CN_s, with smaller proportions of penta- and hexa-CN congeners (Helm et al. 2003; Helm and Bidleman 2003). The percentage of tetra-CN_s was significantly higher over Lake Superior than Lake Ontario, while the percentage of penta- and hexa-CN_s was higher over Lake Ontario. This is consistent with the greater number of sources of CN_s in close proximity to Lake Ontario and the greater influence of transport of the lighter tetra-CN congeners to the Lake Superior region (Helm et al. 2003).

There are multiple studies measuring CN_s in the Canadian and other Arctic regions. Harner et al. (1998) and Helm et al. (2004) measured CN_s in air at Alert and Tagish in the Canadian Arctic and found Σ CN_s in a concentration of less than 0.01–55 pg/m³; tri- and tetra- CN_s were the primary congeners found. Herbert et al. (2005) reported Σ CN concentrations equal to 27–48 and 9–47 pg/m³ in air at Ny Ålesund and Tromsø, Norway, respectively.

Lee et al. (2007) measured Σ CNs, from the Global Atmospheric Passive Sampling (GAPS) survey, at several Arctic locations: Barrow, Alaska; Alert, Nunavut; and Ny Ålesund, Norway. The CN concentrations ranged from 1–8 pg/m³. Tri- and tetra-CNs were the dominant congeners at these Arctic sites. The combustion-related congeners 52/60, 50, 51, 54 and 66/67 were enriched at most sites, indicating the influence of combustion emissions on global levels.

The concentration of CN congeners in Canadian urban air and their transboundary movements was discussed in Harner et al. (2006). The study states that congeners (tri- to octa-CNs) have been found to migrate from Detroit to Point Pelee and Toronto, Ontario.

Certain CN congeners that are absent in technical Halowax formulations (i.e., CNs 44 and 54) and other congeners that are present in much higher concentrations in combustion sources, such as flue gas and fly ash, than in Halowax mixtures (e.g., CNs 52/60 and 73) are used as indicators of combustion-related CN sources in the environment. Combustion-marker congeners were found to be enriched in the air in suburban and industrial Toronto, as compared to downtown Toronto, suggesting that there are current combustion-related sources in the Toronto suburbs, with evaporative emissions from past Halowax uses being more predominant downtown (Helm and Bidleman 2003).

Although mono- and di-CNs have not been reported in air, this mostly reflects the fact that these homologue groups are typically not measured in air samples.

Few concentrations of CNs have been measured in water, in Canada or elsewhere. In various locations of Lake Ontario, 16.4–24.5 pg/L of tri- and tetra-CNs were measured (Helm et al. 2003). CNs were not detected (at a concentration less than 10 ng/L) near an industrial plant in Owen Sound, Ontario, which is on Lake Huron (Kauss 1991), despite the fact that CNs were detected in a concentration of 13 ng/L in the effluent discharged from this facility (Kauss 1991). CNs were also detected sporadically in final effluent discharges on shore at levels of 20–50 ng/L, possibly due to purging of residual contamination from the sewer system. The only other CN measured in water in North America was 2-CN, found in Miami-Dade County, Florida, in concentrations of 740 ng/L (in 2002) and 10 000 ng/L (in 2003), respectively. These measurements may have originated near Superfund sites contaminated with PCBs or near old landfill sites.

There is only one known case of an attempt to measure CNs in Canadian sediments. CNs were not detected in surficial sediments (less than 20 ng/g) in the harbour in Owen Sound, Ontario, near an industrial plant (Kauss 1991). The highest identified concentration of CNs in sediment (61 000 ng/g dry wt.) was measured in the Trenton Channel of the Detroit River (Furlong et al. 1988). This level is even higher than that measured near a former chloralkali plant in the state of Georgia, which is known to have caused CN contamination (Kannan et al. 1998). In surficial and suspended sediment samples, penta- to hepta-CNs were dominant in most cases.

No data were found for CNs in Canadian soil. Only one measured value for soil in the USA was found: 17 900 ng/g dry wt., which was measured in soil near a former

chloralkali plant in Georgia (Kannan et al. 1998). This concentration is very high compared to values measured in agricultural, residential and industrial soils in England, Spain and Germany (less than 0.01–15.4 ng/g dry wt.) (Meijer et al. 2001; Schumacher et al. 2004; Krauss and Wilcke 2003).

No data were found for CNs in Canadian sewage sludge. Only two values were found for CNs in sewage sludge elsewhere. An average of 83 ng/g dry wt. (range: 50–190 ng/g dry wt.) of di- to penta-CNs were measured in sewage sludge from 14 wastewater treatment plants in the U.K. (Stevens et al. 2003). Concentrations of 3.2 ng/g dry wt. and 5.8 ng/g dry wt. of tetra- and penta-CNs were measured in sewage sludge from a sewage treatment plant in Gothenburg, Sweden (Nylund et al. 1992).

There are few studies of levels of CNs in Canadian biota. No data are available for aquatic invertebrates. Data exist for fish, birds and aquatic mammals from the Great Lakes area and the Arctic. Only one Canadian value exists for terrestrial wildlife (the endangered Vancouver Island marmot). Data are also available for a variety of fish and bird species from Sweden and the Baltic Sea near Poland. The Canadian data, as well as levels in biota in the USA and Europe are included in Table 11. Canadian data are listed first, with USA data second followed by the European data.

In general, tetra-, penta- and hexa-CNs are the dominant homologue groups found in wildlife. The proportions of these congeners found in various species depend on the sources of CNs (i.e., old industrial sources (Halowax) versus combustion sources) and also on the species, since species vary in their ability to metabolize CNs. For example, tetra-CNs dominated (79–82%) in phytoplankton from the Baltic Sea, whereas in herring, the penta-CNs were dominant (50%) (Falandysz and Rappe 1996). In the Canadian Arctic, penta-CNs (33–57%) and hexa-CNs (22–45%) were dominant in beluga whales, whereas in ringed seal, tetra-CNs were dominant (58–83%) (Helm et al. 2002). These differences were attributed to selective metabolism, as is observed in these species with PCDDs (Helm et al. 2002).

There is evidence from dated sediment cores collected in the United Kingdom and Japan that environmental concentrations of CNs have decreased by several-fold in recent decades (Yamashita et al. 2000; Gevao et al. 2000; Horii et al. 2004). Peak concentrations of tri- to hepta-CNs were recorded in the 1960s in profundal lake sediments of Esthwaite Water, a seasonally anoxic lake in a rural part of northwest England (Gevao et al. 2000). In both Tokyo Bay and a freshwater lake in rural Japan, peak concentrations of total CNs were associated with sediment deposited in the 1980s. However concentrations of CNs in recently deposited sediments in both regions remain well above pre-1900 background levels – by several-fold in the United Kingdom (Gevao et al. 2000) and approximately 100-fold in Tokyo Bay (Horii et al. 2004).

There is similar evidence that the concentration of CNs in the Canadian environment is decreasing. A 2009 study of temporal trends reported that the concentration of CNs in Lake Ontario trout had declined eightfold from 1979 to 2004 (Gewurtz et al. 2009). However, the decline was congener-specific, being most marked for the higher

chlorinated congeners. The authors suggested that CN concentrations in whole lake trout may still be relatively high (i.e., sufficient to trigger consumption restrictions).

A downward trend in ambient concentrations of CNs is not surprising, given the declining uses of CNs. However, the level of CNs in the environment may still be relatively high due to their resistance to degradation and possibly because of continuing releases from sources of unintentional production such as incineration.

Table 11. Total CN concentrations in biota

Organism and tissue type	Location	Sample year	Number of samples	Mean (range) ng/g lipid weight, unless noted otherwise	Reference
Aquatic invertebrates					
Zebra mussel (<i>Dreissena polymorpha</i>)	Raisin River, Michigan, river mouth and Port of Monroe	1998–1999	More than 100, homogenized	46.4–54.8 (1.12–1.75 wet wt.)	Hanari et al. (2004)
Zebra mussel (<i>Dreissena polymorpha</i>)	Marine City, St. Clair River, Michigan	1998–1999	More than 100, homogenized	1.09 (0.002 wet wt.)	Hanari et al. (2004)
Amphipod (unidentified sp.)	Raisin River, Michigan, river mouth	1999	Ns	85.9 (1.1 wet wt.)	Hanari et al. (2004)
Fish					
Lake trout (<i>Salvelinus namaycush</i>) and lake whitefish (<i>Coregonus clupeaformis</i>)	Thunder Bay, Lake Huron, Michigan	1996	2	0.98–1.1 wet wt.	Kannan et al. (2000)
Lake trout (<i>Salvelinus namaycush</i>)	Siskiwit Lake, Isle Royale, Lake Superior	1996	4	0.041–0.25 wet wt.	Kannan et al. (2000)
Smallmouth bass (<i>Micropterus dolomieu</i>)	Raisin River, Michigan, Hwy. 24	1998	Ns, fillet homogenate	2.26–4.21	Hanari et al. (2004)
Largemouth bass (unidentified sp.)	Raisin River, Michigan, river mouth to Lake Erie	1999	Ns, fillet homogenate	22.7	Hanari et al. (2004)
Round gobies (<i>Neogobius melanostomus</i>)	Raisin River, Michigan, river mouth and Port of Monroe	1998–1999	Ns, whole body	12.1–43.6 (0.264–1.14 wet wt.)	Hanari et al. (2004)
Round gobies (<i>Neogobius melanostomus</i>)	Near Belle River mouth and Marine City, St. Clair River, Michigan	1998–1999	Ns, whole body	2.13–4.81	Hanari et al. (2004)
Carp (<i>Cyprinus carpio</i>) and walleye (<i>Sander vitreus</i>)	Grassy Island, Detroit River, Michigan	1996	3	1.31–31.4 wet wt.	Kannan et al. (2000)
Fourhorned	Five locations, Gulf	1991–	14	0.54–1.5 ^b (range	Lundgren et al.

Organism and tissue type	Location	Sample year	Number of samples	Mean (range) ng/g lipid weight, unless noted otherwise	Reference
sculpin (<i>Triglopus. quadricornis</i>)	of Bothnia, northern Baltic Sea, off Swedish coast	1993		of averages)	(2002)
Pike (<i>Esox. lucius</i>) muscle and liver	Lake and river in Sweden with point sources of CNs	1988	3	210–360 ^b (0.48–33.0 wet wt.)	Järnberg et al. (1997)
Pike (<i>Esox. lucius</i>) liver and muscle	Other lakes, Sweden	1988	5	13–170 ^b	Järnberg et al. (1997)
Burbot (<i>Lota. lota</i>) liver and muscle	Various locations, Sweden	1988	6	0.98–4.9 ^b	Järnberg et al. (1997)
Cod (<i>Gadus morrhua</i>)	Karlskrona archipelago, southern Sweden	1988	2	9.8–10 ^b	Järnberg et al. (1997)
Whitefish (<i>Coregonus clupeaformis</i>)	Lake Störvindeln, Lapland, Sweden	1986	35 pooled, muscle	2.58 ^c	Jansson et al. (1993)
Arctic char (<i>Salvelinus alpinus</i>)	Lake Vättern, central Sweden	1987	15 pooled, muscle	40.8 ^c	Jansson et al. (1993)
Herring (<i>Clupea harengus</i>)	Baltic Proper	1987	60 pooled, muscle	34.8 ^c	Jansson et al. (1993)
Herring (<i>Clupea. harengus</i>)	Gulf of Bothnia, Baltic Sea, two locations	Ns	13, whole body	0.49 [0.41–0.58]	Lundgren et al. (2003)
Perch (<i>Perca fluviatilis</i>)	Gulf of Bothnia, Baltic Sea, four locations	Ns	9, whole body	0.48 [0.22–1.20]	Lundgren et al. (2003)
Perch (<i>Perca fluviatilis</i>)	Gdańsk	1992	8, pooled	69	Falandysz et al. (1997b)
Flounder (<i>Platichthys. flesus</i>)	Mikoszewo, Gulf of Gdańsk, Baltic Sea	1992	5, pooled	83	Falandysz et al. (1997b) ^b
Flounder (<i>Platichthys flesus</i>)	Gdynia, Gulf of Gdańsk	1992	5, pooled	36	Falandysz et al. (1997b) ^b
Lamprey (<i>Lampetra. fluviatilis</i>)	Gdańsk	1992	3, pooled	8.9	Falandysz et al. (1997b) ^b
Lamprey (<i>Lampetra. fluviatilis</i>)	Gdynia, Gulf of Gdańsk, Poland	1992	3, pooled	6.3	Falandysz et al. (1997b) ^b
Crocodile icefish (<i>Chionodraco hamatus</i>); Sharp-spined notothen (<i>Trematomus pennelli</i>),	Ross Sea, Antarctica	1994–1996	4	(0.0015–0.0047 wet wt.)	Corsolini et al. (2002)

Organism and tissue type	Location	Sample year	Number of samples	Mean (range) ng/g lipid weight, unless noted otherwise	Reference
Silverfish (<i>Pleuragramma antarcticum</i>)	Ross Sea, Antarctica	1994–1996	3	0.086 wet wt.	Corsolini et al. (2002)
Arctic cod (<i>Gadus. callarias</i>), liver	Vestertana, Arctic coast of Norway	1987–1994	Composites of 5 livers	[0.132–1.06] ^g	Sinkkonen and Paasivirta (2000)
Birds					
Double-crested cormorant eggs (<i>Phalacrocorax auritus</i>)	Saginaw Bay and Thunder Bay, Lake Huron, Michigan; Whitefish Bay, Lake Superior, Ontario (no point sources nearby)	1998	9	1.13 [0.38–2.40] wet wt.	Kannan et al. (2001)
Herring gull eggs (<i>Larus argentatus</i>)	Same as above	1998	6	0.565 [0.083–1.30] wet wt.	Kannan et al. (2001)
Northern fulmar (<i>Fulmarus glacialis</i>)	Prince Leopold Island and Cape Vera, Ellesmere Island, Nunavut	2003	5 eggs each location	1.33, 1.40	Muir et al. (2004)
Double-crested cormorant eggs (<i>Phalacrocorax auritus</i>)	Gull Island, Green Bay, Lake Michigan	Ns	Ns	Max. = 22 wet wt.	Kannan et al. (2001)
Black cormorants (<i>Phalacrocorax carbo sinensis</i>)	Gulf of Gdańsk, Baltic Sea	1992	3	Breast muscle: 122 [75–160] Liver: 159 [68–240]	Falandysz et al. (1997a)
White-tailed sea eagle (<i>Haliaeetus albicilla</i>)	Various locations, Poland	1991–1992	5 birds, varying ages	Breast: 516 [25–1400] ^b Liver: 646 [30–2400] ^b Fat: 61 [56–66] ^b	Falandysz et al. (1996)
White-tailed sea eagle (<i>Haliaeetus albicilla</i>)	Baltic proper, Sweden, two locations	1985	2	120 ^b	Järnberg et al. (1997)
Osprey (<i>Pandion haliaetus</i>)	Sweden, various locations	1982–1986	35 pooled, muscle	50.0 ^c	Jansson et al. (1993)
Aquatic mammals					
Harbor seal (<i>Phoca vitulina</i>)	Gulf of Alaska	2000–2001	-	0.3–27	Wang et al. (2007)
Ringed seal (<i>Phoca hispida</i>)	Pangnirtung, Baffin Island, Northwest Territories	1993	6, varied sex and age	0.049 [0.035–0.071] lipid wt. ^d	Helm et al. (2002)
Ringed seal (<i>Phoca hispida</i>)	Grise Fiord, Ellesmere Island, Northwest Territories	2003	7 female	0.277 ± 0.149	Muir et al. (2004)
Beluga whale (<i>Delphinapterus</i>)	Hudson Strait, Canada	2003	8 male,	0.421 ± 0.258	Muir et al. (2004)

Organism and tissue type	Location	Sample year	Number of samples	Mean (range) ng/g lipid weight, unless noted otherwise	Reference
<i>leucas</i>)					
Beluga whale (<i>Delphinapterus leucas</i>)	Nastapoka, Hudson Bay, Canada	2003	6 female	0.156 ± 0.094	Muir et al. (2004)
Beluga whale (<i>Delphinapterus leucas</i>)	Kimmirut, Northwest Territories	1994	6, varied sex and age	0.253 [0.036–.383] lipid wt. ^d	Helm et al. (2002)
Otter (<i>Lutra lutra</i>) homogenate	Several sites in Sweden with low PCB levels	1980s	6 individuals	7.0 ^b	Järnberg et al. (1997)
Otter (<i>Lutra. lutra</i>) homogenate	Several sites in Sweden with high PCB levels	1980s	9 individuals	2.6 ^b	Järnberg et al. (1997)
Grey seal (<i>Halichoerus grypus</i>)	Baltic Sea		7	0.05–0.2 wet wt.	Koistinen (1990)
Grey seal (<i>Halichoerus grypus</i>)	Baltic Sea	1979–1985	8, pooled	0.89 ^c	Jansson et al. (1993)
Harbour porpoise (<i>Phocoena phocoena</i>)	South Baltic Sea	1991–1993	4	1.7–2.8 lipid wt. ^a	Falandysz and Rappe (1996)
Harbour porpoise (<i>Phocoena phocoena</i>)	Kattegatt		3	0.524–0.729 wet wt.	Ishaq et al. (2000)
Weddell seal (<i>Leptonichotes weddelli</i>)	Ross Sea, Antarctica	1994–1996	1	Liver 0.044 wet wt.; blubber 0.077	Corsolini et al. (2002)
Seal	Antarctica	?	?	1.2–58	Schiavone et al. (2009)
Terrestrial mammals					
Vancouver Island marmot (<i>Marmota vancouverensis</i>)	Mount Washington, Vancouver Island	2001	1, female	0.063	Lichota et al. (2004)
Polar bear (<i>Ursus maritimus</i>)	Alaska	Ns	5	Liver 0.370 [<0.0001 –0.945]	Corsolini et al. (2002)
Rabbit (<i>Oryctolagus cuniculus</i>)	Revingehed, southern Sweden	1986	15 pooled, muscle	1.4 ^c	Jansson et al. (1993)
Moose (<i>Alces. alces</i>)	Grimsö, Sweden	1985–1986	13 pooled, muscle	1.3 ^c	Jansson et al. (1993)

Ns: Not stated

^a Only CNs with four to eight chlorines analysed^b Only CNs with four to seven chlorines analysed^c Concentration qualitatively estimated by comparing heights of ion traces with the ion trace of the ¹³C instrumental standard (1,2,3,4-TCDD).

^d Only CNs with three to seven chlorines analysed

^e Only CNs with four to six chlorines analysed

^f Hexa-CN congeners plus one penta-CN congener analysed

^g Only penta- and hexa-CN congeners analysed. No significant time trends evident in the data.

Mono-CNs

Risk Quotient Calculations

Toxicity data for potential receptor organisms were reviewed to find the most sensitive assessment endpoint for each environmentally relevant compartment. A conservative predicted exposure concentration (PEC) was selected for each potential receptor, based on empirical data from monitoring studies. Exposure data for the Canadian environment were used. PECs usually represent reasonable worst-case conditions.

A predicted no-effects concentration (PNEC) was determined, for each assessment endpoint by dividing a critical toxicity value (CTV) by an application factor. CTVs typically represented the lowest acceptable ecotoxicity value. Preference is generally for chronic toxicity data, since long-term exposure is a concern.

Application factors were used to account for various sources of uncertainty associated with, for example, making extrapolations from acute to chronic effects, from a test species to a different, potentially more sensitive, species, from effects observed in a laboratory to a field setting, and from a single-species test to ecosystems.

Since mono-CNs are relatively soluble in water (see Table 1) and have been detected in water at high concentrations near contaminated sites internationally, risk quotients for pelagic organisms were calculated. Since mono-CNs have not been detected in air or soil internationally, and relevant effects data are lacking, risks to soil biota and terrestrial wildlife through exposure to contaminated air or soil were not considered.

The CTV for pelagic organisms was conservatively set at 100 µg/L, which is the lowest concentration of Halowax 1000 (containing from 6.7–69% mono-CN) (see tables 3a and 3b) that significantly reduced the growth of the marine algae *Dunaliella teriolecta* under chronic exposure conditions (Walsh et al. 1977). The PNEC was determined by dividing the CTV by an application factor of 10 to account for extrapolation from laboratory to field conditions and inter- and intra-species variability. Therefore, the PNEC is 10 µg/L.

Near an industrial plant located in Owen Sound, Ontario, total CNs were detected in final effluent discharge on the shore of Owen Sound at levels of 20–50 ng/L (Kauss 1991). However, the CNs identified in the final effluent from the plant were mainly tri- and tetra-CNs closely resembling Halowax 1099 (Kauss 1991). 1-CN and 2-CN were not detected at a method detection limit of 20 ng/L in the final effluent. Nevertheless, for the purposes of this conservative risk quotient, it will be assumed that the final effluent contained 10 ng/L of mono-CNs (one half the detection limit). This effluent discharge was diluted by a factor of 10 to give a concentration of mono-CNs of 1 ng/L (0.001 µg/L), which is used as the PEC.

The PEC is divided by the PNEC to estimate the risk quotient. The quotient is therefore calculated as follows:

$$\begin{aligned}\text{Quotient for pelagic organisms} &= \frac{\text{PEC}}{\text{PNEC}} \\ &= \frac{0.001 \mu\text{g/L}}{10 \mu\text{g/L}} \\ &= 0.0001\end{aligned}$$

The quotient is much less than 1, suggesting that there is negligible risk associated with the presence of mono-CN_s in Canadian waters.

Other Lines of Evidence

Mono-CN_s are not expected to be persistent in air, or in any other environmental medium. They are furthermore not expected to have significant potential for long-range transport.

Based on available evidence, including in particular the measured log K_{ow} values and measured BCF values in fish, mono-CN_s are not bioaccumulative. However, the available empirical and modelled aquatic toxicity data indicate that mono-CN_s may be harmful to aquatic organisms at relatively low concentrations: less than 1 mg/L for acute tests, and 0.1 mg/L for chronic tests.

Mono-CN_s have never been detected in the environment in Canada, and CN_s are not currently in commercial use in Canada.

Di- to Octa-CN_s

Di- through octa-CN_s are persistent in air. Di- through hexa-CN_s have been shown to have elevated Arctic contamination potentials. In addition di- through octa-CN_s are predicted to be persistent in water and tri- through hepta-CN_s are persistent in both sediment and soil.

Based on the weight of evidence, including in particular measured log K_{ow} values for di- to octa-CN_s, the measured BCF values for di- to penta-CN_s in fish, and taking into account the supporting information on measured BMFs for tetra- to hepta-CN_s, the high dietary uptake efficiencies of hexa- to octa-CN_s in northern pike, and the very slow elimination of hexa-CN_s from the bodies of rats and humans, it is concluded that di- to octa-CN_s are also bioaccumulative.

There are special concerns about persistent and bioaccumulative substances that are also potentially harmful to organisms at low concentrations in controlled toxicity tests.

Although current science is unable to accurately predict the ecological effects of these substances, they are generally acknowledged to be highly hazardous. Assessments of such substances may thus be performed using a more conservative (precautionary) approach.

Evidence that a substance is highly persistent and bioaccumulative, as defined in the *Persistence and Bioaccumulation Regulations* of CEPA 1999 (Canada 2000), when taken together with potential for environmental release or formation and potential for toxicity to organisms, provides a significant indication that it may be entering the environment under conditions that may have harmful long-term ecological effects. Substances that are persistent remain in the environment for a long time after being released, increasing the potential magnitude and duration of exposure. Substances that have long half-lives in mobile media (air and water) and partition into these media in significant proportions have the potential to cause widespread contamination. Releases of small amounts of bioaccumulative substances may lead to high internal concentrations in exposed organisms. Highly bioaccumulative and persistent substances are of special concern, since they may biomagnify in food webs, resulting in very high internal exposures, especially for top predators.

The available empirical and modelled aquatic toxicity data for CNs indicate that di-, tri-, tetra- and penta-CNs may be harmful to aquatic organisms at relatively low concentrations: less than 1 mg/L for acute exposures, and less than 0.1 mg/L for chronic exposures. Hexa-, hepta- and octa-CNs were found to cause harmful effects to mammals (particularly cattle) at relatively low doses of 2.4 mg/kg body weight per day and less.

Beginning around 1910, mono- to octa-CNs were produced commercially as Halowax mixtures for a variety of uses. Although CNs are not currently in commercial use in Canada, CNs may be produced unintentionally as a by-product of industrial processes involving heat and/or chlorine, such as waste incineration, cement and magnesium production, and the refining of metals such as aluminium.

Even though CNs are no longer used in Canada, because of their historical use and continued incidental releases, CNs continue to be detected in a variety of environmental samples over wide areas of Canada. For example, they have been detected in Arctic and urban air, in water from Lake Ontario, in fish and birds from the Great Lakes and environs, in seals and whales from the Canadian Arctic, and in Vancouver Island marmot. Their widespread presence in biota demonstrates that uptake and bioaccumulation are occurring and therefore there is the potential for adverse effects.

Finally, there is international consensus on the concerns posed by CNs and the need for coordinated international action due to their long-range transport in the atmosphere.

Based on the lines of evidence presented above, particularly the evidence for persistence, bioaccumulation and potential to cause both acute and chronic harm at low exposure values in controlled toxicity tests, and taking into account the limitations of existing quantitative risk estimation methods when applied to such substances, and recognizing

that, although CNs are no longer in commercial use in Canada, they continue to enter the Canadian environment from unintentional production as well as transboundary movement of air, and have been identified as a concern by international consensus, it is concluded that di- through octa-CNs have the potential to cause environmental harm in Canada.

Sources of Uncertainty

The amount of CNs unintentionally emitted in Canada – e.g., into the air during incineration – is not known.

The environmental fate of CNs is not well understood, since only a few empirical studies have been performed, for example on the environmental partitioning and degradation of CNs. Limited data are available on the solubility of individual CN congeners and Halowax mixtures. Available empirical information was therefore supplemented with model predictions. Since these model predictions were based on representative structures for each homologue group, there may be congeners within each group that show higher or lower property values.

The data on environmental concentrations of CNs in Canada are limited and incomplete. There are no Canadian soil or sewage sludge data for CNs and very little data exist for the lower chlorinated CNs in other environmental samples in Canada (none exists for mono-CN). The few studies of levels of CNs in Canadian biota do not include aquatic invertebrates. Consequently information on concentrations in environmental media from other countries has been considered in this assessment.

While available information generally indicates significant potential for bioconcentration and bioaccumulation of CNs, relatively few studies have been performed to ascertain bioconcentration factors or bioaccumulation factors for the various homologue groups.

For mono-CNs, no chronic aquatic studies were identified for the pure substance, and some of the experimentally derived data do not agree with the modelled data. For di-through hepta-CNs, no aquatic toxicity studies were identified for any of these congeners alone. Aquatic toxicity of the CN homologue groups was thus modelled using ECOSAR and extrapolated from toxicity testing of Halowax mixtures. This extrapolation of toxicity from a mixture of CN homologues to a single CN homologue group is problematic, since there are uncertainties about the composition of the Halowax mixtures themselves. In addition, mixtures of compounds can have cumulative effects that are additive, antagonistic or synergistic, and hence different from those of the individual compounds. For octa-CNs, experimental effect concentrations were found to be above both the measured and predicted solubilities. No ECOSAR toxicity predictions for octa-CNs were available because the log K_{ow} value is outside of the acceptable range for this model. Due to the lack of appropriate long-term mammalian studies and the absence of empirical information on effects to soil- and sediment-dwelling organisms, the toxicological behaviour of CNs is experimentally not very well characterized.

Conclusion

Based on the information presented in this assessment report, it is concluded that di- through octa-CNs are entering or may enter the environment in a quantity or concentration, or under conditions that have or may have immediate or long-term harmful effects on the environment or its biological diversity.

It is therefore concluded that di- through octa-CNs meet one or more criteria under section 64 of CEPA 1999.

Di- through octa-CNs are persistent and bioaccumulative in accordance with the *Persistence and Bioaccumulation Regulations* (Canada 2000), their presence in the environment results primarily from human activity, and they are not naturally occurring radionuclides or naturally occurring inorganic substances. Production and usage of chlorinated naphthalenes have been banned or restricted in various countries of the Organisation for Economic Co-operation and Development (OECD), including Switzerland, Germany and Japan. Additionally, in December 2009, CNs were added to the Protocol on Persistent Organic Pollutants (POPs) under the Convention on Long-Range Transboundary Air Pollution (LRTAP) based on international consensus that the presence of CNs in the environment poses a concern and due to their long-range transport, there is a need for coordinated international action on these substances.

These substances will be considered for inclusion in the Domestic Substances List inventory update initiative. In addition and where relevant, research and monitoring will support verification of assumptions used during the screening assessment and, where appropriate, the performance of control measures identified during the risk management phase.

References

- Ahotupa M, Aitio A. 1980. Effect of chlorinated naphthalenes and terphenyls on the activities of drug metabolizing enzymes in rat liver. *Biochem Biophys Res Commun* 93(1):250–257. [cited in IPCS 2001].
- Aittola J-P, Paasivirta J, Vattulainen A, Sinkkonen S, Koistinen J, Tarhanen J. 1994. Formation of chloroaromatics at a metal reclamation plant and efficiency of stack filter in their removal from emission. *Organohalogen Compounds* 19:321–324.
- Åkerblom N, Olsson K, Berg AH, Andersson PL, Tysklind M, Förlin L, Norrgren L. 2000. Impact of polychlorinated naphthalenes (PCNs) in juvenile Baltic salmon, *Salmo salar*: Evaluation of estrogenic effects, development, and CYP1A induction. *Arch Environ Contam Toxicol* 38:225–233.
- Arnot JA, Gobas FACP. 2003. A generic QSAR for assessing the bioaccumulation potential of organic chemicals in aquatic food webs. *Quant Struct Act Relat* 22: 1–9.
- Asplund L, Jakobsson E, Haglund P, Bergman A. 1994a. 1,2,3,5,6,7-Hexachloronaphthalene and 1,2,3,4,6,7-hexachloronaphthalene selective retention in rat liver and appearance in wildlife. *Chemosphere* 28 (12):2075–2086.
- Asplund L, Svensson BG, Nilsson U, Jansson B, Widequist U, Skerfving S. 1994b. Levels of polychlorinated naphthalenes (PCN) in human blood plasma with reference to fish intake. In: Asplund L, Development and application of methods for determination of polychlorinated organic pollutants in biota. Stockholm, University of Stockholm. 9 pp. (Thesis). [cited in IPCS 2001].
- Bell WD. 1953. The relative toxicity of the chlorinated naphthalenes in experimentally produced bovine hyperkeratosis (X-disease). *Vet Med* 48:135–146.
- Bennett GA, Drinker CK, Warren MF. 1938. Morphological changes in the livers of rats resulting from exposure to certain chlorinated hydrocarbons. *J Ind Hyg Toxicol* 20(2):97–123. [cited in IPCS 2001]
- Beyer A, Mackay D, Matthies M, Wania F, and Webster E. 2000. Assessing long-range transport potential of persistent organic pollutants. *Environ Sci Technol* 34 (4): 699-703.
- Bogdal C, Kohler M, Schmid P, Sturm M, Grieder E, Scheringer M, Hungerbühler K. 2006. Polychlorinated naphthalenes: congener specific analysis and source identification in a dated sediment core from Lake Thun, Switzerland. *Organohalogen Compounds* 68: 300-303.
- Brinkman UAT, De Kok A. 1980. Production, properties and usage. In: Kimbrough RD, ed. Halogenated biphenyls, terphenyls, naphthalenes, dibenzodioxins and related products. Vol. 26. New York, Elsevier/North-Holland Biomedical Press.
- Brock WE, Jones EW, MacVicar R, Pope LS. 1957. Chlorinated naphthalene intoxication in sheep. *Am J Vet Res* 18:625–630.
- Bruggeman WA, Steen Jvd, Hutzinger O. 1982. Reversed-phase thin-layer chromatography of polynuclear aromatic hydrocarbons and chlorinated biphenyls. Relationship with hydrophobicity as measured by aqueous solubility and octanol–water partition coefficient. *J Chromatogr* 238:335–346.
- Brunström B, Engwall M, Hjelm K, Lindqvist L, Zebuhr Y. 1995. EROD induction in cultured chick embryo liver: A sensitive bioassay for dioxin-like environmental pollutants. *Environ Toxicol Chem* 14(5):837–842. [cited in IPCS 2001].

- Buggiani SS. 1980. The effects of polychlorinated naphthalenes (PCN) on metamorphosis of *Rana agilis* tadpoles. *Developments in Animal Vet Sci* 6: 326. [in Holliday et al. 1982].
- Bureau S, Axelman J, Broman D, Jakobsson E. 1997. Dietary uptake in pike (*Esox lucius*) of some polychlorinated biphenyls, polychlorinated naphthalenes and polybrominated diphenyl ethers administered in natural diet. *Environ Toxicol Chem* 16(12):2508–2513.
- Campbell MA, Bandiera S, Robertson L, Parkinson A. 1983. Hepta-, hexa-, tetra-, and dichloronaphthalene congeners as inducers of hepatic microsomal drug-metabolizing enzymes. *Toxicology* 26:193–205. [cited in IPCS 2001]
- Campbell MA, Bandiera S, Robertson L, Parkinson A, Safe S. 1981. Octachloronaphthalene induction of hepatic microsomal aryl hydrocarbon hydroxylase activity in the immature male rat. *Toxicology* 22:123–132.
- Canada. 1995. Toxic Substances Management Policy, persistence and bioaccumulation criteria. Minister of Supply and Services, Ottawa, Ontario (ISBN 0-662-23524-X; Catalogue No. En 40-499/2-1995E).
- Canada. 1999. Canadian Environmental Protection Act, 1999. S.C., 1999, c. 33, Canada Gazette. Part III, vol. 22, no. 3. Available from: <http://www.gazette.gc.ca/archives/p3/1999/g3-02203.pdf>
- Canada. 2000. Canadian Environmental Protection Act, 1999: Persistence and Bioaccumulation Regulations, P.C. 2000-348, 23 March, 2000, SOR/2000-107, Canada Gazette, Part II, vol. 134, no. 7, p. 607–612. Available from: <http://www.gazette.gc.ca/archives/p2/2000/2000-03-29/pdf/g2-13407.pdf>
- Cockerline R, Schilling M, Safe S. 1981. Polychlorinated naphthalenes as hepatic microsomal enzyme inducers in the immature male rat. *General pharmacology* 12:83–87. [cited in IPCS 2001].
- Cornish HH, Block WD. 1958. Metabolism of chlorinated naphthalenes. *J Biol Chem* 231:583–588. [cited in Crookes and Howe 1993].
- Corsolini S, Kannan K, Imagawa T, Focardi S, Giesy JP. 2002. Polychloronaphthalenes and other dioxin-like compounds in Arctic and Antarctic marine food webs. *Environ Sci Technol* 36: 3490–3496.
- Crookes MJ, Howe PD. 1993. Environmental hazard assessment: Halogenated naphthalenes. Report prepared for the Toxic Substances Division, Directorate for Air, Climate and Toxic Substances, Department of the Environment, United Kingdom. Building Research Establishment, Garston, Watford, U.K.
- Drinker CK, Warren MF, Bennett GA. 1937. The problem of possible systemic effects from certain chlorinated hydrocarbons. *J Ind Hyg Tox* 19(7):283–311. [cited in IPCS 2001]
- Dyke PH. 1998. PCB and PAH Releases from Incineration and Power Generation Processes. R&D Technical Report P4-052 published by Environment Agency. ISBN 185705895 X. Accessed July, 2007. Available from: <http://www.pops.int/documents/guidance/NIPsFinal/techrep.pdf>
- Engwall M, Brundström B, Jakobsson E. 1993. EROD- and AHH-inducing potency and lethality of chlorinated naphthalenes in chicken (*Gallus domesticus*) and eider duck (*Somateria mollissima*) embryos. *Organohalogen Compounds* 14:151–154. [cited in IPCS 2001].
- Engwall M, Brundström B, Jakobsson E. 1994. Ethoxyresorufin O-deethylase (EROD) and aryl hydrocarbon hydroxylase (AHH)-inducing potency and lethality of chlorinated naphthalenes in chicken (*Gallus domesticus*) and eider duck (*Somateria mollissima*) embryos. *Arch Toxicol* 68:37–42. [cited in IPCS 2001].
- Environment Canada. 2003. National inventory of PCBs in use and PCB wastes in storage in Canada. 2002 annual report. Prepared for Canadian Council of Ministers of the Environment by Toxics Pollution

Prevention Directorate, Environmental Protection Service, Environment Canada. Gatineau, Quebec. May 2003. 14 pp.

Espadaler I, Eljarrat E, Caixach J, Rivera J, Martí I, Ventura F. 1997. Assessment of polychlorinated naphthalenes in aquifer samples for drinking water purposes. *Rapid Commun. Mass Spectrom* 23-4:410–414.

Falandysz J, Rappe C. 1996a. Spatial distribution in plankton and bioaccumulation features of polychlorinated naphthalenes in a pelagic food chain in southern part of the Baltic proper. *Environ Sci Technol* 30(11):3362–3370.

Falandysz J, Strandberg L, Kulp SE, Strandberg B, Bergqvist PA, Rappe C. 1996b. Congener-specific analysis of chloronaphthalenes in white-tailed sea eagles *Haliaeetus albicilla* breeding in Poland. *Chemosphere* 33(1):51–69.

Falandysz J, Strandberg B, Strandberg L, Bergqvist PA, Rappe C. 1997a. Concentrations and biomagnification of polychlorinated naphthalenes in black cormorants *Phalacrocorax carbo sinensis* from the Gulf of Gdansk, Baltic Sea. *The Science of the Total Environment* 204(1):97–106.

Falandysz J, Strandberg L, Bergqvist PA, Strandberg B, Rappe C. 1997b. Spatial distribution and bioaccumulation of polychlorinated naphthalenes (PCNs) in mussel and fish from the Gulf of Gdansk, Baltic Sea. *The Science of the Total Environment* 203(2):93–104.

Falandysz J. 1997c. Bioaccumulation and biomagnification features of polychlorinated naphthalenes. *Organohalogen Compounds* 32:374–379.

Falandysz J. 1998. Polychlorinated naphthalenes: an environmental update. *Environ Pollut* 101:77–90.

Falandysz J, Nose K, Ishikawa Y, Lukaszewicz E, Yamashita N, Noma Y. 2006a. Chloronaphthalenes composition of several batches of Halowax 1051. *Journal of Environmental Science and Health—Part A Toxic/Hazardous Substances and Environmental Engineering* 41(3):291–301.

Falandysz J, Nose K, Ishikawa Y, Lukaszewicz E, Yamashita N, Noma Y. 2006b. HRGC/HRMS analysis of chloronaphthalenes in several batches of halowax 1000, 1001, 1013, 1014 and 1099. *Journal of Environmental Science and Health—Part A Toxic/Hazardous Substances and Environmental Engineering* 41(10):2237–2255.

Flinn FB, Jarvik NE. 1936. Action of certain chlorinated naphthalenes on the liver. *Proceedings of the Society for Experimental Biology and Medicine* 35:118–120. [cited in IPCS 2001].

Furlong ET, Carter DS, Hites, RA, 1988. Organic contaminants in sediments from the Trenton Channel of the Detroit River. *J. Great Lakes Res* 14:451–489. [cited in Marvin et al. 2002].

Gevao B, Harner T, Jones KC. 2000. Sedimentary record of polychlorinated naphthalene concentrations and deposition fluxes in a dated lake core. *Environ Sci Technol* 34(1):33–38.

Gewurtz SB, Lega R, Crozier PW, W M, Fayez L, Reiner EJ, Helm PA, Marvin CH, Tomy GT. 2009. Factors influencing trends of polychlorinated naphthalenes and other dioxin-like compounds in Lake Trout (*Salvelinus Namaycush*) from Lake Ontario, North America (1979-2004). *Environmental Toxicology and Chemistry* 28(5): 921-930.

Gobas, FAPC, Muir DCG, Mackay D. 1988. Dynamics of dietary bioaccumulation and faecal elimination of hydrophobic organic chemicals in fish. *Chemosphere* 17:943–962.

Goldstein JA, Safe S. 1989. Mechanism of action and structure–activity relationships for the chlorinated dibenzo-p-dioxins and related compounds. In: Kimbrough RD, Jensen AA, eds. *Halogenated biphenyls*,

terphenyls, naphthalenes, dibenzodioxins and related products. Amsterdam, Elsevier Science Publishers B.V. (Biomedical Division), pp. 239–293. [cited in IPCS 2001].

Green FA, Neff JM. 1977. Toxicity, accumulation and release of three polychlorinated naphthalenes (Halowax 1000, 1013 and 1099) in postlarval and adult grass shrimp, *Palaemonetes pugio*. Bulletin of Environmental Contamination and Toxicology 17(4):399–407.

Hanari N, Kannan K, Horii Y, Taniyasu S, Yamashita N, Jude DJ, Berg MB. 2004. Polychlorinated naphthalenes in benthic organisms of a Great Lakes food chain. Arch Environ Contam Toxicol 47:84–93.

Hanberg A, Stahlberg M, Georgellis A, De Wit C, Ahlborg UG. 1991. Swedish dioxin survey: Evaluation of the H-4-II E bioassay for screening environmental samples for dioxin-like enzyme induction. Pharmacology and toxicology 69(6):442–449. [cited in IPCS 2001].

Hanberg A, Waern F, Asplund L, Haglund E, Safe S. 1990. Swedish dioxin survey: determination of 2,3,7,8-TCDD toxic equivalent factors for some polychlorinated biphenyls and naphthalenes using biological tests. Chemosphere 20:1161–1164. [cited in IPCS 2001].

Harner T, Bidleman TF. 1997. Polychlorinated naphthalenes in urban air. Atmospheric environment 31(23):4009–4016.

Harner T and Bidleman TF. 1998. Measurements of octanol-air partition coefficients for polycyclic aromatic hydrocarbons and polychlorinated naphthalenes. Journal of Chemical and Engineering Data 43:40–46.

Harner T, Kylin H, Bidleman T, Halsall C, Strachan W, Barrie L, Fellin P. 1998. Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in Arctic air. Environ Sci Technol 32:3257–3265.

Harner T, Shoeib M, Gouin T, Blanchard P. 2006. Polychlorinated naphthalenes in Great Lakes air: assessing spatial trends and combustion inputs using PUF disk passive air samplers. Environ Sci Technol 40:5333–5339.

Heitmuller PT, Hollister TA, Parrish PR. 1981. Acute toxicity of 54 industrial chemicals to sheepshead minnows (*Cyprinodon variegatus*). Bulletin of Environmental Contamination and Toxicology 27:596–604. [cited in IPCS 2001].

Helm P, Bidleman T, Jantunen TF, Ridal J. 2000. Polychlorinated Naphthalenes in Great Lakes Air: Source and Ambient Air Profiles. Organohalogen Compounds 47:17–20.

Helm PA, Bidleman TF. 2003. Current combustion-related sources contribute to polychlorinated naphthalene and dioxin-like polychlorinated biphenyl levels and profiles in air in Toronto, Canada. Environ Sci Technol 37:1075–1082.

Helm PA, Bidleman TF. 2005. Gas–particle partitioning of polychlorinated naphthalenes and non- and mono-ortho-substituted polychlorinated biphenyls in arctic air. Science of the Total Environment 342(1):161–173.

Helm PA, Bidleman TF, Li HH, Fellin P. 2004. Seasonal and spatial variation of polychlorinated naphthalenes and non-/mono-ortho-substituted polychlorinated biphenyls in arctic air. Environ Sci Technol 38(21):5514–5521.

Helm P, Bidleman T, Sternand G, and Koczanski K. 2002. Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in beluga whale (*Delphinapterus leucas*) and ringed seal (*Phoca hispida*) from the eastern Canadian Arctic. Environmental Pollution 119:69–78.

Helm P, Jantunen L, Ridal J, Bidleman T. 2003. Spatial distribution of polychlorinated naphthalenes in air over the Great Lakes and air-water gas exchange in Lake Ontario. *Environ Toxicol Chem* 22:1937–1944.

Herbert BMJ, Halsall CJ, Villab S, Fitzpatrick L, Jones KC, Lee RGM, Kallenborn R. 2005. Polychlorinated naphthalenes in air and snow in the Norwegian Arctic: a local source or an Eastern Arctic phenomenon? *Science of the Total Environment* 342(1):145–160.

Holliday MG, Engelhardt FR, Young AMK. 1982. Chloronaphthalenes: an environmental-health perspective. Report 83-EHD-96, Environmental Health Directorate, Health Protection Branch, Health and Welfare Canada. 117 pp.

Holm G, Lundström J, Andersson T, Norrgren L. 1994. Influences of halogenated organic substances on ovarian development and hepatic EROD activity in the three-spined stickleback, *Gasterosteus aculeatus*, and rainbow trout, *Oncorhynchus mykiss*. *Aquatic toxicology* 29(3–4):241–256. [cited in IPCS 2001].

Holm G, Norrgren L, Andersson T, Thuren A. 1993. Effects of exposure to food contaminated with PBDE, PCN or PCB on reproduction, liver morphology and cytochrome P450 activity in the three-spined stickleback, *Gasterosteus aculeatus*. *Aquatic toxicology* 27:33–50. [cited in IPCS 2001].

Horii Y, Falandysz J, Hanari N, Rostkowski P, Puzyn T, Okada M, Amano K, Naya T, Taniyasu S, and Yamashita N. 2004. Concentrations and fluxes of chloronaphthalenes in sediment from Lake Kitaura in Japan in past 15 centuries. *Journal of Environmental Science and health, A39* (3): 587-609.

Huber WG, Link RP. 1962. Toxic effects of hexachloronaphthalene on swine. *Toxicology and applied pharmacology*, 4:257–262. [cited in IPCS 2001, Crookes and Howe 1993].

Imagawa T, Yamashita N. 1994. Isomer specific analysis of polychlorinated naphthalenes in Halowax and fly ash. *Organohalogen Compounds* 19:215–218. [cited in Falandysz 1998, 1997a].

[IPCS] International Programme on Chemical Safety. 2001. Concise International Chemical Assessment Document (CICAD) No. 34, Chlorinated Naphthalenes. World Health Organization, Geneva.

Ishaq R, Karlsson K, Näf C. 2000. Tissue distribution of polychlorinated naphthalenes (PCNs) and non-ortho chlorinated biphenyls (non-ortho PCBs) in harbor porpoises (*Phocoena phocoena*) from Swedish waters. *Chemosphere* 41(2):1913–1925. [cited in Jakobsson and Asplund 2000].

Ishaq R, Persson NJ, Zebuhr Y, Broman D, Naes K. 2009. PCNs, PCDD/Fs, and non-orthoPCBs, in water and bottom sediments from the industrialized Norwegian Grelandsfjord. *Environmental Science and Technology*. 43(10): 3442-3447.

Jakobsson E, Asplund L. 2000. Polychlorinated Naphthalenes (PCNs). In: J. Paasivirta, ed. *The Handbook of Environmental Chemistry*, Vol. 3 Anthropogenic Compounds Part K, New Types of Persistent Halogenated Compounds. Berlin, Springer-Verlag.

Jansson B, Andersson R, Asplund L, Litzen K, Nylund K, Sellström U, Uvemo U-B, Wahlberg C, Wideqvist U, Odsjö T, Olsson M. 1993. Chlorinated and brominated persistent organic compounds in biological samples from the environment. *Environ Toxicol Chem* 12:1163–1174.

Järnberg U, Asplund L, De Wit C, Egebäck AL, Wideqvist U, Jakobsson E. 1997. Distribution of polychlorinated naphthalene congeners in environmental and source-related samples. *Archives of Environmental Contamination and Toxicology* 32(3):232–245.

Järnberg U, Asplund L, Egebäck AL, Jansson B, Unger M, Wideqvist U. 1999. Polychlorinated naphthalene congener profiles in background sediments compared to a degraded Halowax 1014 technical mixture. *Environ Sci Technol* 33(1):1–6. [cited in IPCS 2001].

- Kannan K, Imagawa T, Blankenship AL, Giesy JP. 1998. Isomer-specific analysis and toxic evaluation of polychlorinated naphthalenes in soil, sediment and biota collected near the site of a former chlor-alkali plant. *Environ Sci Technol* 32:2507–2514.
- Kannan K, Yamashita N, Imagawa T, Decoen W, Khim YS, Day RM, Summer CL, Giesy JP. 2000. Polychlorinated naphthalenes and polychlorinated biphenyls in fishes from Michigan waters including the Great Lakes. *Environ Sci Technol* 34:566–572.
- Kannan K, Hilscherova K, Imagawa T, Yamashita N, Williams LL, Giesy JP. 2001. Polychlorinated naphthalenes, -biphenyls, -dibenzo-p-dioxins, and -dibenzofurans in double-crested cormorants and herring gulls from Michigan waters of the Great Lakes. *Environ Sci Technol* 35(3):441–447.
- Kauss PB. 1991. Polychlorinated naphthalenes survey at Goodyear (Owen Sound Harbour) October 16–19, 1990. Great Lakes Section, Water Resources Branch, Ontario Ministry of the Environment. ISBN 0-7729-8747-5, pp. 1–49.
- Kawasaki M. 1980. Experiences with the test scheme under the Chemical Control Law of Japan: an approach to structure-activity correlations. *Ecotox and Environ Safety* 4:444–454.
- Kim DH, Mulholland JA, Ryu J-Y. 2007. Chlorinated naphthalene formation from the oxidation of dichlorophenols. *Chemosphere* 67(9):135–143.
- Kirk-Othmer. 1980. *Encyclopaedia of Chemical Technology*, 3rd Edition. John Wiley and Sons Inc., USA. [cited in Crookes and Howe 1993].
- Kitano S, Mori T, Kondo R. 2003. Degradation of polychlorinated naphthalenes by the lignin-degrading basidiomycete *Phlebia lindtneri*. *Organohalogen Compounds* 61:369–372.
- Klöpffer W, Haag F, Kohl EG, Frank R. 1988. Testing of the abiotic degradation of chemicals in the atmosphere: The smog chamber approach. *Ecotoxicology and Environmental Safety* 15:298–319.
- Koistinen J. 1990. Residues of planar polychloroaromatic compounds in Baltic fish and seal. *Chemosphere* 20:1043–1048. [cited in Helm et al. 2002].
- Krauss M, W Wilcke. 2003. Polychlorinated naphthalenes in urban soils: analysis, concentrations and relation to other persistent organic pollutants. *Environmental Pollution* 122:73–89.
- LeBlanc GA. 1980. Acute toxicity of priority pollutants to water flea (*Daphnia magna*). *Bull Environ Contam Toxicol* 24:648–691. [cited in IPCS 2001].
- Lee RGM, Coleman P, Jones JL, Jones KC, Lohmann R. 2005. Emission factors and importance of PCDD/Fs, PCBs, PCNs, PAHs and PM10 from the domestic burning of coal and wood in the U.K. *Environ Sci Technol* 39:1436–1447.
- Lee SC, Harner T, Pozo K, Shoeib M, Wania F, Muir D, Barrie L, Jones K. 2007. Polychlorinated Naphthalenes in the Global Atmospheric Passive Sampling (GAPS) Study. *Environ. Sci. Technol.* 41(8):2680–2687.
- Lei YD, Wania F, Shiu WY. 1999. Vapor pressures of the polychlorinated naphthalenes. *J Chem Eng Data* 44:577–582.
- Lei YD, Wania F, Shiu WY, Boocock DGB. 2000. HPLC-based method for estimating the temperature dependence of n-octanol-water partition coefficients. *J Chem Eng Data* 45:738–742.

- Lichota GB, McAdie M, Ross PS. 2004. Endangered Vancouver Island marmots (*Marmota vancouverensis*): sentinels of atmospherically delivered contaminants to British Columbia, Canada. *Environ Toxicol Chem* 23(2):402–407.
- Link RP, Smith JC, Newton DI. 1958. Toxic effect of chlorinated naphthalenes in pigs. *Journal of the American Veterinary Medical Association* 133:83–85. [cited in IPCS 2001, Crookes and Howe 1993].
- Lundgren K, Ishaq R, Bavel Bv, Broman D, Tysklind M. 2003. Polychlorinated naphthalene (PCN) levels and distribution pattern in fish from the Baltic Sea. *Organohalogen Compounds* 62:399–403.
- Lundgren K, Tysklind M, Ishaq R, Broman D, Bavel Bv. 2002. Polychlorinated naphthalene levels, distribution, and biomagnification in a benthic food chain in the Baltic Sea. *Environ Sci Technol* 36(23):5005–5013.
- Lyman WJ, Rosenblatt DH, Reehl WJ. 1982. *Handbook of Chemical Property Estimation Methods*, McGraw-Hill, New York.
- Mackay D, Shiu WY, Ma KC. 1999. *Physical-Chemical Properties and Environmental Fate and Degradation Handbook*. CRCnetBASE 1999. Chapman & Hall CRCnetBASE, CRC Press LLC, Boca Raton, Florida (CD-ROM).
- Mäntylä E, Ahotupa M. 1993. Polychlorinated biphenyls and naphthalenes: long-lasting induction of oxidative stress in the rat. *Chemosphere* 27:383–390. [cited in IPCS 2001].
- Marvin C, Alae M, Painter S, Charlton M, Kauss P, Kolic T, MacPherson K, Takeuchi D, Reiner E. 2002. Persistent organic pollutants in Detroit River suspended sediments: polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls and polychlorinated naphthalenes. *Chemosphere* 49:111–120.
- Matsuo M. 1981. *i/o**-characters to describe bioconcentration factors of chlorobenzenes and naphthalenes — meaning of the sign of the coefficients of *i/o* in the correlating equations. *Chemosphere* 10(9):1073–1078.
- Meijer SN, Harner T, Helm PA, Halsall CJ, Johnston AE, Jones KC. 2001. Polychlorinated naphthalenes in U.K. soils: time trends, markers of source, and equilibrium status. *Environ Sci Technol* 35(21):4205–4213.
- Mori T, Nakamura K, Kondo R. 2009. Fungal hydroxylation of polychlorinated naphthalenes with chlorine migration by wood rotting fungi. *Chemosphere*. 77(2009): 1230–1235.
- Muir D, Alae M, Braune B, Butt C, Chan L, Helm P, Mabury S, Stock N, Tomy G, Wang X. 2004. New contaminants in arctic biota. Project summary, pp. 139–148. *Synopsis of Research Conducted Under the 2003–2004 Northern Contaminants Program*, Indian and Northern Affairs Canada, Gatineau, Quebec.
- Neff JM, Giam CS. 1977. Effects of Aroclor 1016 and Halowax 1099 on juvenile horseshoe crabs *Limulus polyphemus*. In: Vernberg F, Calabrese A, Thurberg F, Vernberg W, eds. *Physiological responses of marine biota to pollutants*. New York, NY, Academic Press, pp. 21–35.
- Noma Y, Yamamoto T, Sakai S. 2004. Congener-specific composition of polychlorinated naphthalenes, coplanar PCBs, dibenzo-p-dioxins, and dibenzofurans in the Halowax series. *Environ Sci Technol* 38(6):1675–1680.
- Norrgrén L, Andersson T, Björk M. 1993. Liver morphology and cytochrome P450 activity in fry of rainbow trout after microinjection of lipid-soluble xenobiotics in the yolk-sac embryos. *Aquatic toxicology* 26:307–316. [cited in IPCS 2001].

- Nylund K, Asplund L, Jansson B, Jonsson P, Litzén K and Sellström U. 1992. Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. *Chemosphere* 12:1721–1730.
- Oliver BG. 1987. Biouptake of chlorinated hydrocarbons from laboratory-spiked and field sediments by oligochaete worms. *Environ Sci Technol* 21:785–790.
- Oliver BG, Niimi AJ. 1984. Rainbow trout bioconcentration of some halogenated aromatics from water at environmental concentrations. *Environ Toxicol Chem* 3:271–277.
- Oliver BG, Niimi AJ. 1985. Bioconcentration factors of some halogenated organics for rainbow trout: Limitations in their use for prediction of environmental residues. *Environ Sci Technol* 19:842–849.
- Oppenhuizen A. 1987. Relationships between octan-1-ol/water partition coefficients, aqueous activity coefficients and reversed phase HPLC capacity factors of alkylbenzenes, chlorobenzenes, chloronaphthalenes and chlorobiphenyls. *Toxicol Environ Chem* 15:249–264.
- Oppenhuizen A, Velde E, Gobas F, Liem D, Steen J. 1985. Relationship between bioconcentration in fish and steric factors of hydrophobic chemicals. *Chemosphere* 14:1871–1896.
- Pudelkiewicz W, Boucher R, Callenbach E, Miller R. 1959. Some physiological responses of New Hampshire chickens to a mixture of penta- and hexachloro-naphthalenes. *Poultry science* 38:424–430. [cited in IPCS 2001].
- Pudelkiewicz WJ, Boucher RV, Callenbach EW, Miller RC. 1958. Some physiological responses of broad breasted bronze poult to chlorinated naphthalene. *Poultry Science* 37:185–187.
- Puzyn T, Falandysz J. 2007. QSPR modeling of partition coefficients and Henry's law constants for 75 chloronaphthalene congeners by means of six chemometric approaches—A comparative study. *J Phys Chem Ref Data* 36(1):203–214.
- Ryan JJ, Levesque D, Panoplia LG, Sun WF, Masuda Y, Kuroki H. 1993. Elimination of polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) from human blood in the Yusho and Yu-Cheng rice oil poisonings. *Arch Environ Contam Toxicol* 24:504–512. [cited in IPCS 2001].
- Ryan JJ, Masuda Y. 1994. Polychlorinated naphthalenes (PCNs) in the rice oil poisonings. *Organohalogen Compounds* 21:251–254. [cited in IPCS 2001].
- Safe S, Robertson L, Parkinson A, Shilling M, Cockerline RC, Campbell MA. 1981. Polybrominated biphenyls, polychlorinated naphthalenes and polychlorinated terphenyls as microsomal enzyme inducers. In: Khan MAQ, ed. *Toxicology of halogenated hydrocarbons: health and ecological effects*. New York, NY, American Chemical Society, Environmental Chemistry Division, pp. 97–105. [cited in IPCS 2001].
- Schiavone A, Kannan K, Horii Y, Focardi S, Corsolini S. 2009. Occurrence of brominated flame retardants, polycyclic musks, and chlorinated naphthalenes in seal blubber from Antarctica: Comparison to organochlorines. *Marine Pollution Bulletin* 58(9): 1415–1419.
- Schneider, M, Stieglitz L, Will R, Zwick G. 1998. Formation of polychlorinated naphthalenes on fly ash. *Chemosphere* 37(9-12):2055–2070. [cited in Helm and Bidleman 2003].
- Schumacher M, Nadal M, Domingo JL. 2004. Levels of PCDD/Fs, PCBs, and PCNs in soils and vegetation in an area with chemical and petrochemical industries. *Environ Sci Technol* 38(7):1960–1969.
- [SFT]. 2001. Letter of L. Säll from the Norwegian Pollution Control Authority (SFT) to the Ministry of Housing, Spatial Planning and the Environment, 18-12-2001. [in van de Plassche and Schwegler 2002].

- Shiraishi H, Pilkington NH, Otsuki A and Fuwa F. 1985. Occurrence of chlorinated polynuclear aromatic hydrocarbons in tap water. *Environ Sci Technol* 19(7):585–590.
- Sinkkonen S, Paasivirta J. 2000. Polychlorinated organic compounds in the Arctic cod liver: trends and profiles. *Chemosphere* 40:619–626.
- Stevens JL, Northcott GL, Stern GA, Tomy GT, Jones KC. 2003. PAHs, PCBs, PCNs, organochlorine pesticides, synthetic musks and polychlorinated n-alkanes in U.K. sewage sludge: survey results and implications. *Environ Sci Technol* 37: 462–467.
- Takasuga T, Tsuyoshi I, Ohi E, Kumar KS. 2004. Formation of polychlorinated naphthalenes, dibenzo-p-dioxins, dibenzofurans, biphenyls and organochlorine pesticides in thermal processes and their occurrence in ambient air. *Arch Environ Contam Toxicol* 46:419–431.
- Talykina MG, Papoulias DM, Allert JA, Izyuov YU, Villalobos SA, Giesy JP, Tillitt DE. 2003. The effect of polychlorinated naphthalenes and tributyltin on the occurrence of aberrant nuclei in erythroid cells of *medaka*. *Environ Sciences* 10(6):337–348.
- Tysklind M, Nyström M, Åkerblom N, Andersson PL, Van Bavel B, Norrgren L. 1998. Determination and modelling of biomagnification factors for polychlorinated naphthalenes (PCNs) in salmon (*Salmo salar*). *Organohalogen Compounds* 39:13–16.
- [US EPA] United States Environmental Protection Agency. 1980. Ambient water quality criteria for chlorinated naphthalenes. Washington, DC, US Environmental Protection Agency (EPA 440/5-80-031; PB81-117426). [cited in IPCS 2001].
- [US EPA] United States Environmental Protection Agency. 1983. Category of chemical substances known as chlorinated naphthalenes proposed determination of significant new uses. *Federal Register*, 48(89), 20668-79. [cited in Crookes and Howe 1993].
- van de Plassche E, Schwegler A. 2002 Preliminary Risk Profile for Polychlorinated Naphthalenes. Ministry of VROM/DGM. Royal Haskoning, The Netherlands. Available from: <http://www.unece.org/env/lrtap/TaskForce/popsxg/2000-2003/pcn.pdf>
- Villalobos SA, Papoulias DM, Meadows J, Blankenship AL, Pastva SD, Kannan K, Hinton DE, Tillitt DE, Giesy JP. 2000. Toxic responses of *medaka*, d-rR strain, to polychlorinated naphthalene mixtures after embryonic exposure by in ovo nanoinjection: a partial life-cycle assessment. *Environ Toxicol Chem* 19(2):432–440.
- Vlahos K, McEntee K, Olafson P, Hansel W. 1955. Destruction and restoration of spermatogenesis in a bull experimentally poisoned with highly chlorinated naphthalene. *Cornell Veterinarian* 45:198. [cited in IPCS 2001].
- Vogelgesang J. 1986. Hexachlorobenzene, octachlorostyrene and other organochlorine compounds in waste water from industrial high-temperature processes involving chlorine. *Wasser- und Abwasser-Forschung* 19:140–144.
- Wagstaff DJ. 1973. Effects of chlorinated naphthalenes on liver levels of detoxication enzymes and vitamin A. *Toxicol Appl Pharmacol* 25:490–491. [cited in IPCS 2001].
- Walsh GE, Ainsworth KA, Faas L. 1977. Effects of uptake of chlorinated naphthalenes in marine unicellular algae. *Bull Environ Contam Toxicol* 18:297–302.
- Wania F. 2003. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in polar regions. *Environ Sci Technol* 37(7):1344–1351.

- Wang D, Shannon A, Hoover-Miller A, Qing X. 2007. Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in tissues of harbour seals (*Phoca vitulina*) from the northern Gulf of Alaska. *Chemosphere*. 67(10): 2044-2057.
- Ward GS, Parrish PR, Rigby RA. 1981. Early life stage toxicity tests with a saltwater fish: effects of eight chemicals on survival, growth, and development of sheepshead minnows (*Cyprinodon variegatus*). *J Toxicol Environ Health* 8:225–302. [cited in IPCS 2001].
- Weil CS, Goldberg ME. 1962. Toxicological and pharmacological criteria of repeated doses of a hepatotoxic agent. *Acta Pharmacologica* 19:129–138. [cited in IPCS 2001].
- Wellington Laboratories. 2005. 2003–2004 Catalogue (online). Accessed April 5, 2005 at www.well-labs.com/catalogue/catalogue.html
- Wiedmann T, Ballschmiter K. 1993. Quantification of chlorinated naphthalenes with GC-MS using the molar response of electron impact ionization. *Fresenius J Anal Chem* 346(6–9):800-804
- [WSKOWWIN] Water Solubility for Organic Compounds Program for Microsoft Windows [Estimation Model]. 2000. Version 1.41. Washington (DC): US Environmental Protection Agency, Office of Pollution Prevention and Toxics; Syracuse (NY): Syracuse Research Corporation. Available from: www.epa.gov/oppt/exposure/pubs/episuite.htm
- Yamashita N, Kannan K, Imagawa T, Villeneuve D, Hashimoto S, Myazaki A, Giesy JP. 2000. Vertical profile of polychlorinated dibenzo-p-dioxins, dibenzofurans, naphthalenes, biphenyls, polycyclic aromatic hydrocarbons, and alkylphenols in a sediment core from Tokyo Bay, Japan. *Environ Sci Technol* 34:3560-3567.
- Yamashita N, Kannan K, Imagawa T, Myazaki A, Giesy JP. 2000. Concentrations and profiles of polychlorinated naphthalene congeners in eighteen technical polychlorinated biphenyl preparations. *Environ Sci Technol* 34:4236–4241.
- Yamashita N, Taniyasu S, Hanari N, Horii Y, Falandysz J. 2003. Polychlorinated naphthalene contamination of some recently manufactured industrial products and commercial goods in Japan. *J Environ Sci Health Part A*(9):1745–1759.

Appendix A

Persistence in Sediments

Tri- to hepta-CNs can be shown to meet the criterion under Persistence and Bioaccumulation Regulations of the *Canadian Environmental Protection Act, 1999* (CEPA 1999) for persistence in sediment (half-life in sediment of one year or more) using monitoring data from a dated sediment core. Gevaio et al. (2000) measured CNs in a sediment core from Esthwaite Water, a semi-rural lake in northwest England. Using the lowest homologue group concentration found in the sediments of this lake—0.619 µg hexa-CN/kg (dated from 1962 and measured in 1995)—and assuming a half-life of one year, one can calculate the concentration of CNs that would have had to have been deposited in the sediments in 1962 for this concentration to currently be there. Using a first-order decay scenario, the following calculation is made:

$$C(t) = C_0 e^{-kt}$$

- $C(t)$ is the concentration, measured in 1995, from sediments dated from 1962 (0.619 µg/kg);
- C_0 is the original concentration deposited in 1962;
- k is the reaction rate, which is equal to 0.693, assuming a half-life of one year ($t_{1/2} = \ln 2/k$); and
- t is the number of years from 1962 to 1995: 33.

Therefore,

$$\begin{aligned} 0.619 &= C_0 e^{-(0.693)(33)} \\ C_0 &= 5.32 \times 10^9 \text{ µg/kg} \\ &= 5.32 \text{ kg/kg} \end{aligned}$$

Therefore, 5.32 kg/kg of hexa-CNs would have had to have been deposited in the sediments in 1962 for a concentration of 0.619 µg/kg to exist in 1995, assuming a half-life of one year. Since that amount of deposition was not possible, it shows that the half-life of hexa-CNs in sediment must be longer than one year. Similar calculations were also carried out for the other homologue groups that Gevaio et al. (2000) had measured (tri- to hepta-CNs). Higher C_0 values were estimated for each of these homologue groups, suggesting that these groups also have half-lives of longer than one year, thus meeting the CEPA criterion for persistence in sediment.

Persistence in Soils

Using the data from Meijer et al. (2001), who measured the concentration of CNs over time in archived agricultural soil from the U.K., it is possible to show that CNs meet the criterion for persistence in soil specified in the Persistence and Bioaccumulation

Regulations of CEPA 1999 (half-life equal to or greater than 182 days (0.5 year) in soil; Canada 2000). Sewage sludge containing 245 ng/g dry wt. of CNs was applied to the subject agricultural soil in 1968 and mixed in to a depth of 15 cm. The soil received no other inputs of CNs over the years, other than atmospheric deposits. An archived sample of the soil from 1972 was found to contain 0.4061 ng/g dry wt. of penta-CN_s. In 1990, a sample from this same soil was found to contain 0.2853 ng/g dry wt. penta-CN_s. The half-life of CNs in this soil can be calculated using the first-order decay equation:

$$C(t) = C_0 e^{-kt}$$

- $C(t)$ is the concentration of 0.2853 ng/g, measured in 1990;
- C_0 is the concentration of 0.4061 ng/g, measured in 1972;
- k is the reaction rate; and
- t is the number of years from 1972 to 1990: 18.

Therefore, to solve for k ,

$$k = [\ln (C(t) / C_0)] / -t$$

$$k = [\ln (.2853/.4061)] / -18$$

$$k = 0.0196$$

$$t_{1/2} = \ln 2/k$$

$$t_{1/2} = \ln 2/0.0196$$

$$= 35.33$$

Therefore, the half-life of penta-CN_s in the soil is 35.33 years, demonstrating that the penta-CN homologue group meets the CEPA 1999 criterion for persistence in soil (half-life in soil of 182 days or more).

Based on the data of Meijer et al. (2001), who analyzed 39 CN congeners or groups of congeners (ones that could not be analytically separated) in the soil samples, the hexa- and hepta-CN congeners 66/67, 64/68, 69, 71/72, 63, 65, 73 and 74 were found to be very persistent, since their concentrations did not change significantly over the 18-year period from 1972 to 1990. All of the other homologue groups analyzed, which included tri-, tetra- and penta-CN_s, were also found to meet the CEPA criterion for persistence in soil, with half-lives in the soil ranging from 7 to 9.5 years for the tri-CN_s and from 10.6 to 18 years for the tetra-CN_s, and with a half-life of 35.3 years for the penta-CN_s as a group.