POLYCHLORINATED NAPHTHALENES

Authors:
E. van de Plassche and A. Schwegler (Royal Haskoning, The Netherlands)
**CONTENTS**

1. **INTRODUCTION** 3

2. **CHEMICAL IDENTITY** 4

3. **POP CHARACTERISTICS** 6
   3.1 Potential for long-range atmospheric transport 6
   3.2 Persistence 6
   3.3 Bioaccumulation 7
   3.4 Toxicity and Ecotoxicity 7
   3.5 Conclusion on POP characteristics of PCNs 17

4. **EXTENT OF RELEASE TO THE ENVIRONMENT** 17
   4.1 Production 17
   4.2 Uses 17
   4.3 Emissions and pathways to the environment 18
   4.3.1 Emissions from the use of technical PCB formulations 19
   4.3.2 Emissions from thermal and other processes 25
   4.3.3 Emissions from landfills 22

5. **ENVIRONMENTAL LEVELS AND BIOAVAILABILITY** 29
   5.1 Air 29
   5.2 Sediment 24
   5.3 Soil 25
   5.4 Biota 26
   5.5 Human Beings 27
   5.5.1 Human Milk 27
   5.5.2 Adipose Tissues 27

6. **SOCIO-ECONOMIC FACTORS** 29
   6.1 National and international regulation 29
   6.2 Alternatives/substitutes 29
   6.3 Emission control techniques 29
   6.4 Costs and benefits of control 29

7. **REFERENCES** 30
1. INTRODUCTION

Polychlorinated naphthalenes (PCNs) are a group of substances based on the naphthalene ring system. PCNs - commercially produced as mixtures of several congeners e.g. Halowax, Nibren Waxes, Seekay Waxes and Cerifal Materials - became popular chemicals after 1910 but their production decreased in the late 1970s. There is growing evidence that PCNs are widespread pollutants found on a global scale.

Primary sources for information on PCNs are reviews by Crookes and Howe (1993), Falandysz (1998) and Hayward (1998) on toxicity. Recent work – most from the University of Toronto, Canada - on monitoring of PCNs in remote regions is included.
2. CHEMICAL IDENTITY

Polychlorinated naphthalenes are a group of theoretically 75 possible chlorinated naphthalenes, containing one to eight chlorine atoms. They are structurally similar to the PCBs. As an example 1,2,4,5,6,8-hexachloronaphthalene is depicted below.

![Chemical structure of 1,2,4,5,6,8-hexachloronaphthalene](image)

CAS number: All PCNs and their mixtures have different CAS-numbers which can be found in Crookes and Howe (1993);
Chemical formula: $C_{10}H_{8-n}Cl_n$
Synonyms / trade names: Halowax, Nibren Waxes, Seekay Waxes and Cerifal Materials, N-Oil;
Abbreviations: polychlorinated naphthalene: PCN; monochlorinated naphthalene: mono-CN; dichlorinated naphthalene: di-CN etc.

The technical formulations exhibit a wide range of patterns from nearly pure mono-CNs (Halowax 1031) to nearly pure octa-CNs (Halowax 1051). The congener profiles in weight percent for Halowaxes are given in the table below (Hayward, 1998).

<table>
<thead>
<tr>
<th>Halowax</th>
<th>Mono</th>
<th>Di</th>
<th>Tri</th>
<th>Tetra</th>
<th>Penta</th>
<th>Hexa</th>
<th>Hepta</th>
<th>Octa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1031</td>
<td>95</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>60</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1001</td>
<td>10</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1099</td>
<td>10</td>
<td>40</td>
<td>40</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1013</td>
<td>10</td>
<td>50</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1014</td>
<td>20</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1051</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>
PCNs have physical and chemical properties similar to PCBs: hydrophobic, high chemical and thermal stability, good weather resistance, good electrical insulating properties and low flammability. Below the physical chemical characteristics of PCNs are discussed.

Physical state: low viscosity oils to high melting solids with intermediate waxlike solids varying in crystallinity and melting points;
Solubility: soluble in organic solvents (benzene, petroleum ether, alcohol, chloroform, ligroin);
Boiling point: 260 °C for mono to 440 °C octa;
Melting point: -2.3 °C for mono to 192 °C for octa.

In the table below the log Kow, water solubility and log Koa is presented for the different PCN congeners.

Table 2. Physical chemical data for PCNs: log Kow, log Koa and water solubility (mg/L) (Crookes and Howe, 1993; Harner and Bidleman, 1998). Estimated values are indicated with a (*).

<table>
<thead>
<tr>
<th>Congener</th>
<th>water solubility (mg/L)</th>
<th>log Kow</th>
<th>Koa (20 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mono</td>
<td>2.87</td>
<td>3.90</td>
<td>-</td>
</tr>
<tr>
<td>di</td>
<td>0.0314</td>
<td>4.66</td>
<td>1.36 * 10^7</td>
</tr>
<tr>
<td>tri</td>
<td>0.064</td>
<td>5.35</td>
<td>3.35–7.09 * 10^7</td>
</tr>
<tr>
<td>tetra</td>
<td>0.004</td>
<td>6.19</td>
<td>2.29–7.36 * 10^7</td>
</tr>
<tr>
<td>penta</td>
<td>7.3 * 10^{-3} (*)</td>
<td>6.87 (*)</td>
<td>1.10–3.11 * 10^9</td>
</tr>
<tr>
<td>Hexa</td>
<td>1.1 * 10^{-4} (*)</td>
<td>7.58 (*)</td>
<td>1.03–4.19 * 10^10</td>
</tr>
<tr>
<td>Hepta</td>
<td>4.0 * 10^{-6} (*)</td>
<td>8.3 (*)</td>
<td>-</td>
</tr>
<tr>
<td>Octa</td>
<td>8.0 * 10^{-6}</td>
<td>6.42</td>
<td>-</td>
</tr>
</tbody>
</table>

Physical chemical properties and their variation with temperature controls the cycling and transport of POPs. The octanol-air partition coefficient (log Koa) is thought to be the key descriptor of the partitioning of semi-volatile compounds between the atmosphere and terrestrial organic phases. Harner and Bidleman (1998) measured log Koa values for 24 PCNs as a function of temperature over the range of 0 to 50 °C. In Table 2 only the values for 20 °C are presented. The plot of log Koa values for the PCNs at 20 °C showed a clear trend of increasing values with increasing chlorination. Also, the log Koa values increased by more than 3 orders of magnitude from the di- to hexachlorinated homologue groups.

Lei et al. (1999) measured the vapour pressure of the supercooled liquid P_L for 17 PCNs as a function of temperature. Based on the work of Wania and Mackay (1996) who suggested that persistent chemicals have the tendency to be transported as far as, and be preferentially deposited in, polar regions if their log P_L at 298.15 K is between 0 and -2, they conclude that among the PCNs the di- through tetraCNs fall into this range.
3. **POP CHARACTERISTICS**

3.1 **Potential for long-range atmospheric transport**

The properties influencing the long-range transport potential are listed in the table below. All vapour pressure values are estimations as reported by Crookes and Howe (1993). All half-lives are estimated based on a vapour-phase reaction with photochemically bound hydroxyl radicals (Syracuse in HSDB, 2000).

Table 3. Vapour pressure, Henry’s law constant and half-life in air (Crookes and Howe, 1993; Syracuse in HSDB, 2000).

<table>
<thead>
<tr>
<th>congener</th>
<th>vapour pressure (Pa at 25°C)</th>
<th>Henry’s law constant (atm m³/mol; 25°C)</th>
<th>t½ air (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono</td>
<td>2.1</td>
<td>3.55 * 10⁻⁵</td>
<td>1</td>
</tr>
<tr>
<td>Di</td>
<td>0.17</td>
<td>3.15 * 10⁻⁴</td>
<td>1</td>
</tr>
<tr>
<td>Tri</td>
<td>0.13</td>
<td>2.14 * 10⁻⁴</td>
<td>8</td>
</tr>
<tr>
<td>Tetra</td>
<td>0.048</td>
<td>1.59 * 10⁻⁴</td>
<td>18</td>
</tr>
<tr>
<td>Penta</td>
<td>4.3 * 10⁻²</td>
<td>1.17 * 10⁻⁴</td>
<td>40</td>
</tr>
<tr>
<td>Hexa</td>
<td>9.5 * 10⁻⁴</td>
<td>3.55 * 10⁻⁵</td>
<td>89</td>
</tr>
<tr>
<td>Hepta</td>
<td>3.7 * 10⁻⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Octa</td>
<td>1.3 * 10⁻⁴</td>
<td>4.78 * 10⁻⁵</td>
<td>437</td>
</tr>
</tbody>
</table>

Crookes and Howe (1993) report a half-life of 2.7 days based on smog chamber experiments in which the reaction of 1,4-dichloronaphthalene with OH-radicals was studied. Other experimental data on degradation in air of PCNs are not available.

**Conclusion:** PCNs meet the criterion for long-range atmospheric transport.

3.2 **Persistence**

Almost no information is available on biodegradation of PCNs in water, sediment and soil. The biodegradability has been reported as poor (Koda, Y. et al., 1982 in HSDB 2000). In several studies with bacteria from soil, sewage sludge or river sediment aerobic biodegradation was observed for mono- and di-CNs (several authors in Crookes and Howe, 1993). Only half-lives for 2-mono-CN are presented varying from 38 to 104 days (Kincannon and Lin, 1985 in Crookes and Howe, 1993).

Indirect evidence for the persistence of PCNs is based on the identical congener distribution of contaminated soil compared to Halowax 1013 after 10-15 years being covered by a Dutch landfill (De Kok et al., 1983 in Crookes and Howe, 1993). Other monitoring data showing that PCNs are persistent substances will be presented in the Summary Report.

**Conclusions:** insufficient evidence is available on persistence of PCNs in soil, water and sediment. Indirect evidence from monitoring data presented in the Summary Report will show that PCNs meet the criterion for persistence.
3.3 Bioaccumulation

The results of bioaccumulation studies in fish are reported in the table below (Crookes and Howe, 1993).

Table 4. Bioaccumulation factors for PCNs (Crookes and Howe, 1993)

<table>
<thead>
<tr>
<th>Organism</th>
<th>BCF (L/kg)</th>
<th>Congener</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyprinus carpio</td>
<td>191</td>
<td>Mono-CN</td>
<td>Matsuo (1981)</td>
</tr>
<tr>
<td>Poecilia reticulata</td>
<td>4265</td>
<td>2-mono-CN</td>
<td>Opperhuizen et al. (1985)</td>
</tr>
<tr>
<td>Poecilia reticulata</td>
<td>2290</td>
<td>1,4-di-CN</td>
<td>Opperhuizen et al. (1985)</td>
</tr>
<tr>
<td>Oncorhynchus mykiss</td>
<td>5623</td>
<td>1,4-di-CN</td>
<td>Oliver and Niimi (1984)</td>
</tr>
<tr>
<td>Poecilia reticulata</td>
<td>6166</td>
<td>1,8-di-CN</td>
<td>Opperhuizen et al. (1985)</td>
</tr>
<tr>
<td>Poecilia reticulata</td>
<td>11000</td>
<td>2,3-di-CN</td>
<td>Opperhuizen et al. (1985)</td>
</tr>
<tr>
<td>Poecilia reticulata</td>
<td>11000</td>
<td>2,7-di-CN</td>
<td>Opperhuizen et al. (1985)</td>
</tr>
<tr>
<td>Cyprinus carpio</td>
<td>4677</td>
<td>Tri-CN</td>
<td>Matsuo (1981)</td>
</tr>
<tr>
<td>Poecilia reticulata</td>
<td>26915</td>
<td>1,3,7-tri-CN</td>
<td>Opperhuizen et al. (1985)</td>
</tr>
<tr>
<td>Cyprinus carpio</td>
<td>8710</td>
<td>Tetra-CN</td>
<td>Matsuo (1981)</td>
</tr>
<tr>
<td>Poecilia reticulata</td>
<td>33113</td>
<td>1,2,3,4-tetra-CN</td>
<td>Oliver and Niimi (1985)</td>
</tr>
<tr>
<td>Oncorhynchus mykiss</td>
<td>5130</td>
<td>1,2,3,4-tetra-CN</td>
<td>Oliver and Niimi (1985)</td>
</tr>
<tr>
<td>Poecilia reticulata</td>
<td>3388</td>
<td>1,3,5,7-tetra-CN</td>
<td>Opperhuizen et al. (1985)</td>
</tr>
<tr>
<td>Poecilia reticulata</td>
<td>25118</td>
<td>1,3,5,8-tetra-CN</td>
<td>Opperhuizen et al. (1985)</td>
</tr>
<tr>
<td>Cyprinus carpio</td>
<td>10000</td>
<td>Penta-CN</td>
<td>Matsuo (1981)</td>
</tr>
<tr>
<td>Oncorhynchus mykiss</td>
<td>316</td>
<td>Octa-CN</td>
<td>Oliver and Niimi (1985)</td>
</tr>
</tbody>
</table>

The BCF of PCNs increases with increasing degree of chlorination up to the penta-CNs with values as high as 33113 L/kg. According to Opperhuizen et al. (1985) the uptake depends on the molecular diameter and/or length. This is why no uptake occurs for hepta- and octachloronaphthalene having molecular diameters higher than 0.95 nm. Although the validity of all the experiments presented in Table 4 could not be checked it is clear that the BCF for fish for PCNs is higher than 5000 for several congeners. This is supported by the high log Kow values for PCNs presented in Table 2. Lower BCFs have been found in shrimps, algae and worms (Crookes and Howe, 1993).

Conclusion: PCNs meet the criterion for bioaccumulation.

3.4 Toxicity and Ecotoxicity

PCNs are structurally similar to the PCBs and some congeners may have a similar toxicity as some of the most toxic coplanar congeners of PCBs. Several PCNs exhibit Ah-receptor mediated cytochrome P450 induction. Therefore a separate paragraph is included on the dioxin like toxicity of PCNs.

Toxicity
Acute toxicity
Data on the sub-acute toxicity of PCNs has been centered on the poisoning of cows, causing a disease called bovine hyperkeratosis or X-disease (Hayward, 1998). The disease was of major economic concern in the US in the 1940s and 1950s and was associated with the accidental ingestion by cows of PCNs from lubricants used in machinery making palletised feed, from wood preservatives, from wax used for binding twine and from rubber mats contaminated with PCNs. The toxicity of PCNs to cows after oral exposure was found to increase with increasing chlorination, the tetra-CNs and lower chlorinated congeners having little or no effect. The most toxic congeners appeared to be penta- and hexa-CNs. Oral doses as low as 1 mg/kg bw have been shown to cause systemic effects in cattle. Pigs appear to be less sensitive than cattle.

(Sub)chronic toxicity
(Sub)chronic toxicity tests has been performed with several test species, i.e. rats, guinea pig, sheep and cattle. It appears that penta- and hexa-CNs are the most toxic. Hayward (1998) reports a TLV of 0.2 mg/m³. The two exposure routes were orally and inhalatory. The systemic effect after chronic oral and inhalatory exposure is liver injury. The lowest oral effect dose in guinea pigs was 2.5 mg/kg bw/day after exposure to penta-CNs. After inhalatory exposure the lowest effect dose was 1.16 mg/m³ after long term exposure (134 days, 16 hours/day).

Mutagenicity and carcinogenicity
PCNs have not been tested for their potential to cause cancer in animals (EPA Chemical Fact Sheet, 2000).

Teratogenicity and reproduction
PCNs have not been tested for their potential to adversely affect reproduction (EPA Chemical Fact Sheet, 2000).

Human studies
Exposure of PCNs has long been known to be associated with chloracne and lethality in occupationally exposed men (Hayward, 1998). According to Blankenship et al. (2000) it cannot be ruled out that this was caused by other contaminants such as TCDD or PCBs.

Ecotoxicity

Aquatic toxicity
Only acute toxicity data are available for fish and crustaceans for mono-, di- and octa-CNs and several Halowaxes (mixtures of tetra-, penta- and hexa-CNs). No toxicity was observed in the tests with octa-CNs.

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

Crookes and Howe (1993) report a study of Ward et al (1981) in which sheepshead minnow eggs were exposed to 1-mono-CN from fertilisation to 28 days
post-hatch. No effects were observed on survival and growth up to 0.39 mg/l. At 0.79 mg/l all fish died within 28 days.

**Dioxin like toxicity of PCN**

Holm et al. (1993) exposed female three-spined sticklebacks (*Gasterosteus aculeatus*) to food contaminated with Halowax 1014 at two doses for 3.5 months. Induction of EROD activity was found for both doses (measured concentrations in fish: 861 and 1929 mg PCN/kg fat. No effects were found on spawning success. Induction of EROD activity was also found by Pesonen et al. (2000) who exposed rainbow trout sac fry for two weeks to Hallowax 1014, a mixture of hexa- and hepta-CN and hepta-CN. EROD induction was also found in a rat hepatoma H4IIE cell assay and in egg injection studies with chickens and eider ducks (Hayward, 1998). Blankenship et al. (2000) determined relative potencies (REPs) compared to TCDD of PCNs in the rat hepatoma H4IIE cell assay. REPs of the most potent PCNs - all penta-, hexa- and hepta-CNs - varied from 0.001 to 0.004. These REPs are in the same range as some PCBs, mono-ortho as well as non-ortho. Villeneuve et al. (2000) used three in-vitro assays to characterize the dioxin-like potency of 18 PCN congeners. The PLHC-1 fish hepatoma assay was relatively insensitive compared to the EROD and luciferase assays using rat hepatoma cells. Hexa- and pentaCNs were most potent with REPs between $10^{-3}$ and $10^{-7}$. These REPs were similar to those for some PCBs. In Table 5 a summary is given of the TEFs determined in several studies.

**Table 5. Relative potencies of individual PCNs related to 2,3,7,8,-TCDD.**

<table>
<thead>
<tr>
<th>Congener</th>
<th>TEF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-di-CN</td>
<td>$3.5 \times 10^{-8}$</td>
<td>Villeneuve et al. (2000)</td>
</tr>
<tr>
<td>2,4-di-CN</td>
<td>$2.0 \times 10^{-8}$</td>
<td>Villeneuve et al. (2000)</td>
</tr>
<tr>
<td>1,2,6,8-tetra-CN</td>
<td>$1.7 \times 10^{-5}$</td>
<td>Blankenship (submitted) in Kannan et al. (1998)</td>
</tr>
<tr>
<td>1,2,3,6,7-penta-CN</td>
<td>$1.7 \times 10^{-4}$</td>
<td>Blankenship et al. (2000)</td>
</tr>
<tr>
<td>1,2,3,7,8-penta-CN</td>
<td>$4.6 \times 10^{-5}$</td>
<td>Villeneuve et al. (2000)</td>
</tr>
<tr>
<td>1,2,4,5,6-penta-CN</td>
<td>$1.6 \times 10^{-6}$</td>
<td>Villeneuve et al. (2000)</td>
</tr>
<tr>
<td>1,2,3,4,6,7-hexa-CN</td>
<td>$4.0 \times 10^{-3}$</td>
<td>Blankenship et al. (2000)</td>
</tr>
<tr>
<td>1,2,3,5,6,7-hexa-CN</td>
<td>$1.0 \times 10^{-2}$</td>
<td>Blankenship et al. (2000)</td>
</tr>
<tr>
<td>1,2,3,5,6,8-hexa-CN</td>
<td>$2.0 \times 10^{-2}$</td>
<td>Hanberg (1990) in Villeneuve et al. (2000)</td>
</tr>
<tr>
<td>1,2,3,6,7,8-hexa-CN</td>
<td>$2.1 \times 10^{-3}$</td>
<td>Villeneuve et al. (2000)</td>
</tr>
<tr>
<td>1,2,4,5,6,8-hexa-CN</td>
<td>$7.0 \times 10^{-5}$</td>
<td>Hanberg (1990) in Villeneuve et al. (2000)</td>
</tr>
<tr>
<td>1,2,3,4,5,6-hexa-CN</td>
<td>$2.0 \times 10^{-3}$</td>
<td>Hanberg (1990) in Villeneuve et al. (2000)</td>
</tr>
<tr>
<td>1,2,3,4,5,7-hexa-CN</td>
<td>$2.0 \times 10^{-3}$</td>
<td>Hanberg (1990) in Villeneuve et al. (2000)</td>
</tr>
<tr>
<td>1,2,3,5,7,8-hexa-CN</td>
<td>$2.0 \times 10^{-3}$</td>
<td>Hanberg (1990) in Villeneuve et al. (2000)</td>
</tr>
<tr>
<td>1,2,3,4,5,6,7-hepta-CN</td>
<td>$3.0 \times 10^{-5}$</td>
<td>Blankenship et al. (2000)</td>
</tr>
</tbody>
</table>

**Conclusion**

Based on the acute toxicity data it can be concluded that PCNs are toxic to cattle. From results from subchronic studies on guinea pigs and rats it can be concluded that especially penta- and hexa-CNs are very hepatotoxic chemicals. Ecotoxicity data are scarce and are also mainly acute. Based on the results with Halowax it can be concluded that PCNs are toxic to aquatic organisms.
The pattern of toxicity of PCNs resembles that of TCDD. Recent work has been done to determine the relative potency of PCNs - mixtures as well as individual congeners - in fish, birds and mammals. The potency of several PCN congeners is in the same range as some PCB congeners.
Table 6. Summary of toxicity tests with PCNs.

<table>
<thead>
<tr>
<th>Testresult</th>
<th>Exposure period</th>
<th>Observation period</th>
<th>Dose</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acute oral toxicity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cattle</td>
<td>LDLo= 11 mg/kg</td>
<td></td>
<td></td>
<td>Hexa-CNs</td>
<td>NTP Chemical repository, 2000</td>
</tr>
<tr>
<td>Pig</td>
<td>No effect</td>
<td>8-10 days</td>
<td>36-64 days</td>
<td>11.0-16.5 mg/kg bw/day</td>
<td>Hexa-CNs; gelatine capsule</td>
</tr>
<tr>
<td>Pig</td>
<td>Depressed vitamin A levels</td>
<td>8-10 days</td>
<td>36-64 days</td>
<td>17.1-17.6 mg/kg bw/day</td>
<td>Hexa-CNs; gelatine capsule</td>
</tr>
<tr>
<td>Pig</td>
<td>All moribund or dead</td>
<td>8-10 days</td>
<td>36-64 days</td>
<td>19.8-22.0 mg/kg bw/day</td>
<td>Hexa-CNs; gelatine capsule</td>
</tr>
<tr>
<td>Pig</td>
<td>Degeneration of liver and kidney</td>
<td>8-9 days</td>
<td></td>
<td>22 mg/kg bw day</td>
<td>Hexa-CNs; gelatine capsule</td>
</tr>
<tr>
<td>Cattle</td>
<td>No effect</td>
<td>7 days</td>
<td>Several months</td>
<td>4.4 mg/kg/day</td>
<td>Di-CNs; gelatine capsule</td>
</tr>
<tr>
<td>Cattle</td>
<td>No effect</td>
<td>7-10 days</td>
<td>Several months</td>
<td>2.4-2.6 mg/kg/day</td>
<td>Tri-CNs; gelatine capsule</td>
</tr>
<tr>
<td>Cattle</td>
<td>Slight hyperkeratosis</td>
<td>10 days</td>
<td>Several months</td>
<td>1.6-2.7 mg/kg/day</td>
<td>Tetra-CNs; gelatine capsule</td>
</tr>
<tr>
<td>Cattle</td>
<td>No effect</td>
<td>13 days</td>
<td>Several months</td>
<td>3.4 mg/kg/day</td>
<td>Tetra-CNs; gelatine capsule</td>
</tr>
<tr>
<td>Cattle</td>
<td>Severe systemic disease</td>
<td>5-10 days</td>
<td>Several months</td>
<td>1.7-3.3 mg/kg/day</td>
<td>Penta-CNs; gelatine capsule</td>
</tr>
<tr>
<td>Cattle</td>
<td>Severe systemic disease</td>
<td>5-10 days</td>
<td>Several months</td>
<td>1.1-3.2 mg/kg/day</td>
<td>Hexa-CNs; gelatine capsule</td>
</tr>
<tr>
<td>Cattle</td>
<td>Severe systemic disease</td>
<td>7-9 days</td>
<td>Several months</td>
<td>0.69-2.4 mg/kg/day</td>
<td>Hepta-CNs; gelatine capsule</td>
</tr>
</tbody>
</table>

Crookes and Howe (1993)
<table>
<thead>
<tr>
<th>Testresult</th>
<th>Testdetails</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exposure period</td>
<td>Observation period</td>
</tr>
<tr>
<td>Cattle Mild systemic disease</td>
<td>11 days</td>
<td>Several months</td>
</tr>
<tr>
<td>Cattle Severe systemic disease</td>
<td>9 days</td>
<td>Several months</td>
</tr>
</tbody>
</table>

**(sub)chronic oral toxicity**

<table>
<thead>
<tr>
<th></th>
<th>Testresult</th>
<th>Exposure period</th>
<th>Observation period</th>
<th>Dose</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rat</td>
<td>Liver damage</td>
<td>84 days</td>
<td></td>
<td>20 mg/kg/day</td>
<td>Hexa-CNs; in food</td>
<td>Crookes and Howe (1993)</td>
</tr>
<tr>
<td>Rat</td>
<td>Liver damage</td>
<td>84 days</td>
<td></td>
<td>63 mg/kg/day</td>
<td>Hexa-CNs; in food</td>
<td></td>
</tr>
<tr>
<td>Rat</td>
<td>All dead</td>
<td>56 days</td>
<td></td>
<td>200 mg/kg/day</td>
<td>Hexa-CNs; in food</td>
<td></td>
</tr>
<tr>
<td>Rat</td>
<td>9 of 10 died, severe liver injury</td>
<td>1 month</td>
<td></td>
<td>3000 mg/kg/day</td>
<td>Penta-CNs/hexa-CNs</td>
<td>Clayton and Clayton</td>
</tr>
<tr>
<td>Guinea pig</td>
<td>Severe weight loss and liver damage and death</td>
<td>48 days</td>
<td></td>
<td>2.5 mg/kg/day</td>
<td>Penta-CNs</td>
<td>Crookes and Howe (1993)</td>
</tr>
<tr>
<td>Sheep</td>
<td>Severe liver damage or death</td>
<td>90-135 days</td>
<td></td>
<td>1.1 mg/kg/day</td>
<td>Tetra-, penta-, hexa-CNs; by gelatine capsule</td>
<td></td>
</tr>
<tr>
<td>Sheep</td>
<td>All dead</td>
<td>23-35 days</td>
<td></td>
<td>11 mg/kg/day</td>
<td>Tetra-, penta-, hexa-CNs; by gelatine capsule</td>
<td></td>
</tr>
<tr>
<td>Sheep</td>
<td>All dead</td>
<td>7-25 days</td>
<td></td>
<td>27.6 mg/kg/day</td>
<td>Tetra-, penta-, hexa-CNs; by gelatine capsule</td>
<td></td>
</tr>
<tr>
<td>Testresult</td>
<td>Testdetails</td>
<td>Reference</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------------------</td>
<td>------------------------------</td>
<td>----------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cattle, Severe systemic disease</td>
<td>20-60 days</td>
<td>Hexa-CNs; by gelatine capsule</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.9-13.9 mg/kg bw/day</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cattle, Severe systemic disease</td>
<td>13-18 days</td>
<td>Octa-CNs; by gelatine capsule</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.9-12.3 mg/kg/day</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**(sub)chronic inhalation toxicity**

<table>
<thead>
<tr>
<th>Animal</th>
<th>Type of damage</th>
<th>Duration</th>
<th>Dose</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rat</td>
<td>Very slight liver damage</td>
<td>134 days</td>
<td>1.31 mg/m3</td>
<td>Tri- and tetra-CNs; 16 hours/day</td>
<td>Crookes and Howe (1993)</td>
</tr>
<tr>
<td>Rat</td>
<td>Moderate liver damage</td>
<td>102 days</td>
<td>10.97 mg/m3</td>
<td>Tri- and tetra-CNs; 16 hours/day</td>
<td>Crookes and Howe (1993)</td>
</tr>
<tr>
<td>Rat</td>
<td>Slight to moderate liver damage</td>
<td>143 days</td>
<td>1.44 mg/m3</td>
<td>Penta- and hexa-CNs; 8 hours/day</td>
<td>Crookes and Howe (1993)</td>
</tr>
<tr>
<td>Rat</td>
<td>Slight to moderate liver damage</td>
<td>134 days</td>
<td>1.16 mg/m3</td>
<td>Penta- and hexa-CNs; 16 hours/day</td>
<td>Crookes and Howe (1993)</td>
</tr>
<tr>
<td>Rat</td>
<td>All moribund or dead</td>
<td>52 days</td>
<td>8.88 mg/m3</td>
<td>Penta-and hexa-CNs; 16 hours/day</td>
<td>Crookes and Howe (1993)</td>
</tr>
</tbody>
</table>
### Table 7. Summary of ecotoxicological tests with PCNs.

<table>
<thead>
<tr>
<th>Test result</th>
<th>Test details</th>
<th>Water quality</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exposure period</strong></td>
<td><strong>Experimental details</strong></td>
<td><strong>Hardness</strong></td>
<td><strong>Remarks</strong></td>
<td><strong>Reference</strong></td>
</tr>
<tr>
<td><strong>Acute aquatic toxicity</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fish</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lepomis macrochirus</td>
<td>LC$_{50}$ = 2.3 mg/l</td>
<td>96 hours</td>
<td>weight 0.32-1.2g, static, nominal</td>
<td>20-24°C, hardness 28-44mg CaCO$_3$/l</td>
</tr>
<tr>
<td>Cyprinodon variegatus</td>
<td>LC$_{50}$ = 2.4 mg/l</td>
<td>96 hours</td>
<td>8-15 mm, static</td>
<td>25-31°C, salinity 10-31%o</td>
</tr>
<tr>
<td>Cyprinodon variegatus</td>
<td>LC$_{50}$ &gt; 560 mg/l</td>
<td>96 hours</td>
<td>8-15 mm, static</td>
<td>25-31°C, salinity 10-31%o</td>
</tr>
<tr>
<td>Cyprinodon variegatus</td>
<td>LC$_{50}$ = 0.690 mg/l</td>
<td>96 hours</td>
<td>age &lt; 20 days, flow-through</td>
<td>29-31°C</td>
</tr>
<tr>
<td>Mugil cephalus</td>
<td>LC$_{50}$ &gt; 0.263 mg/l</td>
<td>96 hours</td>
<td>juvenile</td>
<td></td>
</tr>
<tr>
<td><strong>Crustaceans</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daphnia magna</td>
<td>LC$_{50}$ = 1.6 mg/l</td>
<td>48 hours</td>
<td>age &lt; 24 hour, static</td>
<td>hardness 173 mg CaCO$_3$/l</td>
</tr>
<tr>
<td>Daphnia magna</td>
<td>LC$_{50}$ &gt; 530 mg/l</td>
<td>48 hours</td>
<td>age &lt; 24 hour, static</td>
<td>hardness 173 mg CaCO$_3$/l</td>
</tr>
<tr>
<td>Daphnia magna</td>
<td>LC$_{50}$ = 0.82 mg/l</td>
<td>48 hours</td>
<td>age 4-6 days, static</td>
<td>21-25°C</td>
</tr>
<tr>
<td>Daphnia magna</td>
<td>LC$_{50}$ = 1.99 mg/l</td>
<td>48 hours</td>
<td>age 4-6 days, static</td>
<td>21-25°C</td>
</tr>
<tr>
<td>Artemia salina</td>
<td>LC$_{50}$ = 1.84 mg/l</td>
<td>24 hours</td>
<td>nauplii, static</td>
<td>19-21°C</td>
</tr>
<tr>
<td>Artemia salina</td>
<td>LC$_{50}$ = 2.82 mg/l</td>
<td>24 hours</td>
<td>nauplii, static</td>
<td>19-21°C</td>
</tr>
<tr>
<td>Artemia salina</td>
<td>LC$_{50}$ = 0.91 mg/l</td>
<td>24 hours</td>
<td>nauplii, static</td>
<td>19°C</td>
</tr>
<tr>
<td>Test result</td>
<td>Test details</td>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>--------------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mysis bahia</td>
<td>LC₅₀ = 0.37 mg/l, 96 hours, static, 1-mono-CN, US-EPA, 1980</td>
<td>Crookes and Howe (1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Penaeus aztecas</td>
<td>LC₅₀ = 0.0075 mg/l, 96 hours, flow-through, Halowax 1014, US-EPA, 1980</td>
<td>Crookes and Howe (1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palaemonetes pugio</td>
<td>LC₅₀ = 0.44 mg/l, 96 hours, post-larva, static, 19-24°C, Halowax 1000, Green and Neff, 1977</td>
<td>Crookes and Howe (1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palaemonetes pugio</td>
<td>LC₅₀ = 0.325 mg/l, 96 hours, adult, static, 19-24°C, Halowax 1000, Green and Neff, 1977</td>
<td>Crookes and Howe (1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palaemonetes pugio</td>
<td>LC₅₀ = 0.074 mg/l, 96 hours, post-larva, static, 19-24°C, Halowax 1013, Green and Neff, 1977</td>
<td>Crookes and Howe (1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palaemonetes pugio</td>
<td>LC₅₀ = 0.069 mg/l, 96 hours, post-larva, static, 19-24°C, Halowax 1099, Green and Neff, 1977</td>
<td>Crookes and Howe (1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palaemonetes pugio</td>
<td>LC₅₀ = 0.09 mg/l, 96 hours, adult, static, 19-24°C, Halowax 1099, Green and Neff, 1977</td>
<td>Crookes and Howe (1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palaemonetes pugio</td>
<td>LC₅₀ = 0.248 mg/l, 96 hours, flow-through, 19-24°C, Halowax 1014, USEPA, 1980</td>
<td>Crookes and Howe (1993)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.5 Conclusion on POP characteristics of PCNs

The conclusions on the POP characteristic of PCNs according to the UN-ECE criteria are presented in Table 8.

Table 8. POP characteristics of PCNs according to the UN-ECE POP criteria.

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Meets the criterion (Yes/No)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential long-range atmospheric transport</td>
<td>Yes</td>
<td>Confirmed by monitoring data in remote areas (see Summary Report).</td>
</tr>
<tr>
<td>Persistence in water, soil and sediment</td>
<td>Yes</td>
<td>No experimentally determined half lives. Indirect evidence from monitoring data and studies using sediment cores (see Summary Report).</td>
</tr>
<tr>
<td>Bioaccumulation</td>
<td>Yes</td>
<td>Especially tetra-, penta-, and hexa-CNs show high BCFs.</td>
</tr>
<tr>
<td>Toxicity and ecotoxicity</td>
<td>Yes</td>
<td>Some congeners show a dioxin like toxicity.</td>
</tr>
</tbody>
</table>

It can be concluded that PCNs clearly meet the UN-ECE POP criteria.
1. EXTENT OF RELEASE TO THE ENVIRONMENT

1.1 Production

PCNs are manufactured by the meta-halide catalysed chlorination of molten naphthalene at a temperature slightly above the melting point of the desired product. The crude chlorinated naphthalenes are then treated with soda ash or caustic soda, fractionated under reduced pressure and purified with activated clay.

Until the 1970s PCNs were high volume chemicals, e.g. in the 1920s the worldwide production was approximately 9000 tonnes per year. Production of PCNs decreased significantly since 1977. The production of PCNs in the USA stopped in 1980. In the USA only small amounts of PCNs – approximately 15 tonnes per year – were used in 1981, mainly as refractive index testing oils and capacitor dielectrics.

In the UK the production stopped in the mid 60s, although Crookes and Howe (1993) report that in 1970 small amounts of PCNs were still being produced. In Germany around 300 tonnes were produced in 1984, mainly for use as dye intermediates. Falandysz (1998) reports use as casting materials until 1989 in Germany and former Yugoslavia.

Main producers were Bakelite Corporation and Koppers Company Inc. in the USA (Halowax). The production of technical PCNs by Koppers Company ceased in 1977 (e-mail d.d. 19-6-2001 of T. Self from Koppers Industry).

In Europe, main producers were Bayer (Nibren waxes) and Imperial Industries (Seekay waxes) (Hayward, 1998). Bayer produced PCNs in a range of 100 to 200 tonnes per year between 1980 and 1983 and ceased PCN production in 1983 (e-mail d.d. 7-8-2001 of Mr. Finzenhagen from Bayer).

Falandysz (1998) is the only author who estimated the global production of PCNs. Based on the assumption that the PCN production was 10% of the PCB production he estimated the global production to be approximately 150,000 metric tons. As PCNs were mainly used between 1920 and 1980 it is probably impossible to obtain a more exact figure on the global production volume.

1.2 Uses

The use and application of PCNs is rather diverse. The most important uses, in terms of volume, have been in: cable insulation, wood preservation, engine oil additives, electroplating masking compounds, feedstocks for dye production, dye carriers, capacitors and refracting index testing oils.

A brochure from Koppers Company Inc. contains information on the Halowaxes presented below. The Halowax PCNs were also available as crude products.
Table 9. Use profile of Halowaxes as produced by Koppers Company Inc. in the past.

<table>
<thead>
<tr>
<th>Halowax</th>
<th>Composition</th>
<th>Chlorine content</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>Mono- and di-CN</td>
<td>26</td>
<td>Dissolve sludge and varnish formed by petroleum oils; ingredient in motor tune-up compounds and upper cylinder lubricants; solution polymerisation solvent; gauge fluids; inert liquid seals for instruments; photoelastic immersion fluids.</td>
</tr>
<tr>
<td>1001</td>
<td>Tri- and tetra-CN</td>
<td>50</td>
<td>Capacitor impregnant; binder for electrical grade ceramics. Used - not specified - in paper coating, precision casting and chemical processing industries.</td>
</tr>
<tr>
<td>1031</td>
<td>Mono-CN</td>
<td>22</td>
<td>Raw material for dyes and similar products where Halowax 1000 cannot be used.</td>
</tr>
<tr>
<td>1099</td>
<td>Tri- and tetra-CN</td>
<td>52</td>
<td>Capacitor impregnant where higher operating temperatures are encountered.</td>
</tr>
<tr>
<td>1099B</td>
<td>Tri- and tetra-CN</td>
<td>52</td>
<td>Capacitor impregnant with operating temperatures higher than 110°C.</td>
</tr>
<tr>
<td>1013</td>
<td>Tetra- and penta-CN</td>
<td>56</td>
<td>Electrical insulating compounds; electroplating stop-off compounds; additive in automobile and industrial gear oils and cutting oils.</td>
</tr>
<tr>
<td>1014</td>
<td>Penta- and hexa-CN</td>
<td>62</td>
<td>Idem Halowax 1013.</td>
</tr>
<tr>
<td>1051</td>
<td>Octa-CN</td>
<td>70</td>
<td>Unknown.</td>
</tr>
<tr>
<td>2141</td>
<td>Blend</td>
<td>54</td>
<td>High temperature and flame resistant seal for condensers and coils.</td>
</tr>
<tr>
<td>2148</td>
<td>Blend</td>
<td>61</td>
<td>Binder for manufacture of electrical grade ceramics and sintered metals.</td>
</tr>
</tbody>
</table>

As already stated in the USA only small amounts were used in 1981 as refractive index testing oils and capacitor dielectrics. Possible new uses according to the US-EPA would be as intermediate for polymers and flame-retardants in plastics (Crookes and Howe, 1993). More information on these uses is not presented, however.

1.3 Emissions and pathways to the environment

It can be concluded that there is no commercial use of PCNs any more. The concentrations measured in the environment nowadays comes from the following sources (Crookes and Howe, 1993; Falandysz, 1998):
- historical use of PCNs;
- historical and present use of PCBs;
- thermal and other processes;
- landfills.
The last three sources are discussed in the next paragraphs.
1.3.1 Emissions from the use of technical PCB formulations

Many studies focused on the formation of PCNs during PCB production, the amounts of PCNs and the PCN congener profiles in PCB mixtures. The mechanism of formation of PCNs during PCB production is not fully known. Based on combined PCN- and PCB-chlorination patterns, it is expected that naphthalenes in the biphenyl mixtures are chlorinated simultaneously with the chlorination of biphenyl. The average degree of chlorination of PCNs is higher than the corresponding chlorination of the PCBs. This can be explained by the higher reactivity of naphthalenes than biphenyls, caused by the greater mean electron localisation energy reactivity (Haglund et al. 1993).

Falandysz (1998) states that PCB mixtures like the Arochlor or Clophen series can contain PCNs. He reports a median value of 0.0067% PCNs with a maximum of 0.087% and derives a potential release of 100 tonnes based on the worldwide production of PCBs.

Kannan (2000) reports concentrations of total PCNs in Arochlors from 3.5 to 170 μg/g. ∑PCN in Aroclors 1254 and 1260 were 197 and 155 μg/g respectively in the study of Helm et al. (2000a).

Yamashita et al. (2000b) conducted a comparative study on PCN concentrations and profiles in 18 different PCB mixtures. From that study it appeared that the PCN concentration is the lowest in Aroclor, ranging from 5.2 to 67.2 μg/g. In Solvol, from Russia, the PCN concentration was 730.8 μg/g. The total PCN concentration in Aroclor and Kanechlor increased with increasing chlorine content. That trend was not observed in Phenoclors. Lower total PCN concentrations compared to former studies were explained by the possibility of volatilisation of the lower chlorinated congeners (mono-, di- and tri-CNs). Volatilisation can also be a reason for varying PCN concentrations as well as congener spectra in three different lots of Aroclor 1254. From the PCN concentrations in the analysed PCB mixtures the world production of PCN as a by-product of PCBs was estimated to be approximately 169 tons.

The concentration of PCNs in PCBs measured by Haglund et al. (1993) varied from 1.8 to 870 μg/g. In this study the PCN concentrations were 5 to 8 fold higher in Clophen than in Aroclor 1232 and 1242. In this study, the amount of PCNs as by-product in PCB mixtures was calculated to be approximately 120 metric tonnes.

Summarizing, several authors measured the PCN content in commercial PCBs leading to a potential release of 100-169 tons. This amount is <0.1% of the total global production of PCNs of 150,000 tons estimated by Falandysz (1998).

1.3.2 Emissions from thermal and other processes

PCNs are known to be formed in thermal processes, of which waste incineration is the most important. Other thermal processes possibly resulting in PCN emis-
sions are copper ore roasting, aluminium reclamation and chlor-alkali industry (Crookes and Howe, 1993).

The formation mechanism of PCNs in incineration plants is not exactly known. Iino (1999) sets the first step in the clarification of this mechanism. In that study it was shown that PCNs can directly be formed from PAHs when heated at 400 ºC for 2 hours in the presence of copper(I)chloride. It was stated that there are other possible precursors or pathways for PCN formation.

Schneider et al. (1998) analysed PCNs on fly ash. Concentrations were measured in genuine fly ash as well as thermal treated fly ash for 2 hours at 300 ºC. After analysing the concentrations these were compared to concentrations and congener spectra in Halowax. It was observed that in fly ash different congeners are found compared to Halowax, especially the strongly accumulating and toxic 1,2,3,6,7-tetra-CN and 1,2,3,5,6,7-tetra-CN. Congener specific PCN concentrations before and after thermal treatment of the fly ash are shown in Table 10.

### Table 10. Congener specific concentration of PCNs before and after thermal treatment of fly ash.

<table>
<thead>
<tr>
<th>Congener</th>
<th>Initial concentration (ng/g)</th>
<th>Concentration after thermal treatment (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-CN</td>
<td>19.1</td>
<td>189.6</td>
</tr>
<tr>
<td>Di-CN</td>
<td>36.0</td>
<td>658.4</td>
</tr>
<tr>
<td>Tri-CN</td>
<td>60.1</td>
<td>1027.2</td>
</tr>
<tr>
<td>Tetra-CN</td>
<td>84.2</td>
<td>1687.8</td>
</tr>
<tr>
<td>Penta-CN</td>
<td>87.0</td>
<td>1442.0</td>
</tr>
<tr>
<td>Hexa-CN</td>
<td>32.4</td>
<td>319.3</td>
</tr>
<tr>
<td>Hepta-CN</td>
<td>5.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Octa-CN</td>
<td>0.4</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>

In genuine fly ash mainly di- to hexa-CN's were observed. Mono-CN's are volatile and partly evaporate while hepta- and octa-CN's mostly degrade under MWI-thermal conditions. After thermal treatment of the fly ash mono- to di-CN's are partly in the gas phase while tetra- to hexa-CN's are available on the particles. Hepta-CN's are formed in very low concentrations, and octaCN's nearly completely disappeared.

The increase in PCN amounts after thermal treatment is remarkable but thermal treatment of fly ash is probably no common event. The differences in congener spectra indicate different formation mechanisms between production of PCNs in Halowax by chlorination with molten naphthalene and chlorine gas in presence of e.g. FeCl₆ and de-novo-formed PCNs from the organic macromolecular organic carbon and inorganic chlorine under catalytic influence of transition metal ions, such as CuCl₂.

Abad et al. (1999) analysed emission samples collected from five different municipal waste incinerators in Spain. The total material incinerated by these MWIs represented 70% of the total Spanish waste incinerated in that year. The total levels of PCNs varied from 1.08 up to 21.36 ng/Nm³ for mono- to octa-CN's and 0.33 to 5.72 ng/Nm³ for tetra- to octa-CN's. In this study, no information was given on differences between MWIs. Therefore it is impossible to relate the different PCN concentrations and congener spectra to incineration circumstances.
The samples in the Abad study (1999) were from MWIs in Spain. The fly ash in the studies of Schneider (1998) was probably obtained from a MWI in Europe (not mentioned in the publication). Because European standards have been set for waste incineration (latest Directive 2000/76/EC) it can be assumed that the samples in both studies were derived from waste incinerated at at least 850 ºC. Because the European maximum limit of 0.1 ng I-TEC/Nm³ is then still exceeded for at least dioxins the stack gas must always be cleaned afterwards. The situation in the United States and Canada can differ from these European regulations, but waste incineration is not as common in these countries as it is in Europe. In some eastern countries waste incineration is applied like in European countries.

For the results of the Spanish samples a calculation was made of the I-TEQ concentration contributed by PCNs. The calculation was not complete because no TEQs are available for tri-CNs, which were available in relative high concentrations in the samples. Based on the available TEQs presented in Table 5, the highest calculated TEQ concentration was 0.00187 ng-TEQ/Nm³. Based on that concentration it is unlikely that the total concentration of TEQs, including the tri-CNs, will exceed the limit value of 0.1 ng-TEQ/Nm³.

When PCNs are compared with dioxins, because of the resemblance in effects and formation circumstances, it might be assumed that PCNs are, like dioxins, formed directly after the incineration. Dioxins are mainly formed at cooling down of the fly ash, and the formation rate appears to be highest at 300 ºC. For PCNs it can only be concluded that at a temperature of 300 ºC the amount of PCNs is multiplied.

Imagawa and Lee (2001) analysed PCNs formed from waste incineration. They analysed 12 samples from Japanese MWIs. These MWIs were already confronted with the limit value of 0.1 ng-TEQ/Nm³. Besides the MWI samples, emission samples produced from soot and copper-deposit experiments conducted at the US-EPA were analysed. The comparison of these two types of sources showed a similar difference as the comparison of fly ash with Halowax by Schneider et al (1998). The PCNs in the fly ash samples also included 1,2,3,6,7-CN and 1,2,3,5,6,7-CN, while these congeners were not available in the samples from the soot and copper-deposit experiments.

Helm et al. (2000a) analysed ashes from a medical waste incinerator, a cement kiln, a municipal solid waste incinerator and an iron sintering plant, all in Canada. These samples contained 1.3-2.0 ng \( \Sigma \)PCN/g ash for the municipal solid waste incinerator, cement kiln and iron sintering ash, while the medical waste incinerator ash contained 3600 ng \( \Sigma \)PCN/g.

Meijer et al. (2001) analysed PCN concentrations in United Kingdom soils in a time range from 1944 to 1986. Time trends drawn in the study for the different PCN homologue groups, showed that the higher chlorinated groups exhibit peak concentrations earlier. For penta- as well as hexa-CNs a peak was shown in 1944, while the peak for the tetra-CNs was delayed until the 1950s. The tri-CNs peak appeared in 1970. Possible causes for these differences are searched in changing production process of technical mixtures, increasing share of industrial or combustion sources to PCN emissions and differences in degradation rates for
the different homologue groups. The first possibility cannot be further examined because of the lack of information on production processes in the past.

Comparison of the specific individual congeners, with those found in fly ash experiments, could also not explain the shift in homologue groups, but increasing mass contributions of combustion related congeners did suggest that the combustion sources are more important now than they were in the past. From the congener specific analysis it was also concluded that the delayed peak of lower chlorinated homologues was not caused by photodegradation.

Meijer et al. (2001) finishes with the determination of fugacity gradients between air and soil. This determination showed that the tri-CNs are exhibiting net outgassing, while the pentac-CNs are still being deposited to soil. The fugacity gradients support the theory of combustion sources being more and more important contributors to air burdens of penta-CNs, because of the combustion related penta-CNs showing the largest gradient for air-to-soil transfer.

According to the Norwegian Pollution Control Authority there is still emission and discharge of PCNs from cement kiln industry, municipal waste incineration and magnesium production in Norway. Data for one cement kiln plant showed an emission of 60.5 g/year (SFT, 2001).

1.3.3 Emissions from landfills

Landfills are a potentially large source for PCNs due to the historical use pattern and laboratory data showing that PCNs are released from old capacitors and wires from electronic equipment (Weistrand et al., 1992 in Crookes and Howe, 1993). Data are very scarce, however. The only data are for a Dutch landfill (see section 3.2 of the Risk Profile), where concentrations of PCNs were 31-38 and 1180-1290 mg/kg dw. (De Kok et al., 1983 in Crookes and Howe, 1993).
2. ENVIRONMENTAL LEVELS AND BIOAVAILABILITY

A substantial amount of monitoring data is available for PCNs, also in remote regions. Old data should be interpreted with care according to Crookes and Howe (1993) due to difficulties in the analytical methods applied. Especially in GC-ECD PCNs and PCBs interfere with each other. The development and application of new analytical techniques - especially mass spectrometry - has lead to more insight into the fate of PCNs in the environment. For example, Harner et al. (1998) use GC-NIMS to measure PCNs in air samples.

PCNs have been detected in air, sediment, soil, water, biota (freshwater and marine organisms as well as birds and otters) and human beings. Overviews are presented by Crookes and Howe (1993) and Falandysz (1998). In the past few years PCNs have also been monitored in arctic air and in some other remote regions. In this section, an overview will be given of these data.

2.1 Air

Harner et al. (1998) reports the first measured concentrations of PCNs in arctic air. These concentrations are the result of several monitoring studies carried out in 1993 at the Barents Sea, Eastern Arctic Ocean, Norwegian Sea and two land-based monitoring stations at Alert, Canada and Dunai Island in eastern Siberia, Russia. The results are listed in Table 11.

<table>
<thead>
<tr>
<th>Location</th>
<th>number of samples</th>
<th>( \Sigma \text{PCN range (pg/m}^3 )</th>
<th>mean ( \Sigma \text{PCN} ) (pg/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barents Sea</td>
<td>2</td>
<td>32.0 - 48.7</td>
<td>40.4</td>
</tr>
<tr>
<td>Eastern Arctic Ocean</td>
<td>10</td>
<td>7.6 - 16.0</td>
<td>11.6</td>
</tr>
<tr>
<td>Norwegian Sea</td>
<td>2</td>
<td>5.8 - 8.3</td>
<td>7.1</td>
</tr>
<tr>
<td>Alert</td>
<td>7</td>
<td>0.1 - 3.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Dunai</td>
<td>3</td>
<td>0.31 - 1.2</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Helm et al. (2000) measured PCNs at Alert, Dunai and the Great Lakes in 1994/1995. Combining these measurements with the ones from Harner et al. (1997 and 1998) a comparison can be made between concentration in urban and rural areas.
For the Great Lakes higher concentrations were measured near industrial and urban centres while lower concentrations were measured near rural areas. PCN concentrations in urban areas are obviously significantly higher than in remote areas, the difference being more than one order of magnitude.

Most PCNs found in air are the lighter congeners: tri- and tetra-CN account for approximately 80% and 90-95% of the total mass in ambient and arctic air, respectively. Harner et al. (1998) explain the depletion of the higher chlorinated congeners compared to their standard Halowax 1014 with preferential volatilisation of the lower chlorinated naphthalenes or differences in source signatures.

Helm et al. (2000) reports higher concentrations of PCNs in Alert and Dunai in colder months; a higher portion being associated with the particle phase.

Harner et al. (2000) reports on air sampling of PCNs in the UK. They conclude that air masses from the UK and Europe may be influencing PCN burdens more than PCBs and suggest a mixture of diffuse and non-diffuse sources in the UK. A $\Sigma$PCN/$\Sigma$PCB ratio of 0.2-0.25 is characteristic for “background air”. Mean $\Sigma$PCN concentrations were 59 pg/m$^3$ in one study while in the other study concentrations decreased from 138-160 pg/m$^3$ at urban sites to 22-35 pg/m$^3$ at rural sites.

The $\Sigma$PCN/$\Sigma$PCB ratio of 0.2-0.25 should reflect to a certain extent the use volumes of both compounds. The ratio is higher than the estimation made by Falandysz (1998) that PCN production was approximately 10% of the PCB production, although the uncertainty of this estimation is high.

### 2.2 Sediment

Sediment studies are frequently used to follow up the environmental fate of POPs. They are also well-suited to studies of historical patterns in the environment, since they reflect the original composition better than biological samples.

Gevao et al. (2000) measured PCNs and PCBs in sediment cores of a lake in north-west England. Before 1940 the yearly flux of PCNs was about 0.5 µg/m$^2$.y, Between 1940 and 1965 the flux increased up to 12 µg/m$^2$.y and decreased since then to about 3 µg/m$^2$.y. Early emissions were attributed to iron and copper smelters. Later emissions were not correlated with fluxes of PCBs.
PCNs in sediment have also been measured by Kannan et al. (1998). Based on their measurements Blankenship et al. (2000) conclude that at some contaminated sites the contribution of PCNs to the total TEQs by PCNs, PCBs and PCDD/Fs can be up to 58%.

Järnberg et al. (1997) reported PCN concentrations in sediments of Swedish lakes. A concentration of 0.23 ng/g dw was the lowest of all samples. This concentration was concluded to be the background concentration for Swedish sediments. The concentrations in the other sediment samples varied from 0.62 to 270 ng/g. The highest concentrations were measured in PCB polluted areas and near chlor-alkali industries. Congener profiles were studied and resulted in two types of profile. One (containing low to medium chlorinated congeners) seemed to be related to profiles of PCB and PCN mixtures while the other (dominated by higher chlorinated congeners) was similar to profiles found in graphite sludge from one chloralkali-process.

In an Italian study of Eljarrat et al. (1999) sediments of two lakes were analysed resulting in concentration ranging from 34 to 1515 pg/g dry weight. The lowest concentration was measured at a control site far from industrial areas. The highest concentration was measured at a sewage treatment plant using chlorine.

PCNs – emitted by a magnesium plant - were measured in Norway in the Grenland fjords in 1997. Tetra- to octa-CNs were measured up to concentrations of somewhat lower than 1 μg/g ∑PCNs (Naes, 1999).

2.3 Soil

Meijer et al. (2001) analysed archived soil samples from two different locations in the United Kingdom (see also paragraph 1.3.2 from the Summary Report). The first series of samples were obtained at Rothamsted Experimental Station 42 km north of London, from the Broadbalk experiment. The second location was Luddington at 30 km south of Birmingham.

The samples of the Broadbalk experiment only included control samples, without any additions of pesticides of fertilisers. These samples originated from 1944, 1956, 1966, 1980 and 1986. The samples from Luddington included control samples as well as samples from soil treated with sewage sludge, both originating from 1972, 1976, 1981, 1985 and 1990. The original sewage sludge applied in 1968 was also included.

In the Broadbalk samples the ∑PCN concentration varied between 6.0 μg/g dw in 1944 to 8.64 μg/g dw in 1956, subsequently declining to 317 pg/g dw in 1986. Although both samples resulted in the same concentration the peak from 1980 of ~16 μg/g dw was considered to be a remarkable outlier.

In the Luddington soils the ∑PCN concentrations declined as well varying from 6.0 μg/g dw to 417 pg/g dw in the control soils and from 8.9 μg/g dw to 2.5 μg/g dw in the sludge amended soils. The ∑PCN concentration in the applied sludge was > 240 μg/g dw.
The difference between sludge concentrations and sludge treated soil concentrations (factor of 40) were partly related to the difference in organic matter being 45% in sludge and 2.5% in soil. The addition of the sludge resulted in 4 times higher PCN concentrations.

2.4 Biota

PCNs being strong bioaccumulators are also measured in biota. Some of the measured concentrations in biota are listed below in Table 13.

Table 13. ΣPCN concentrations in biota at several remote areas.

<table>
<thead>
<tr>
<th>location</th>
<th>species</th>
<th>ΣPCN concentration</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pangnirtung, Canada</td>
<td>Beluga whale</td>
<td>52.6 - 372.4 pg/g</td>
<td>Helm et al. (2000)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(wet weight)</td>
<td></td>
</tr>
<tr>
<td>Pangnirtung, Canada</td>
<td>Ringed Seal Blubber</td>
<td>46.3 - 66.4 pg/g</td>
<td>Helm et al. (2000)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(wet weight)</td>
<td></td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>Fish</td>
<td>0.98 - 26 ng/g</td>
<td>Järnberg et al. (1997) in Falandysz (1998)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(lipid weight)</td>
<td></td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>Guillemot (Urea aalgae)</td>
<td>84 - 220 ng/g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(lipid weight)</td>
<td></td>
</tr>
<tr>
<td>Sweden</td>
<td>White tailed sea eagle (Haliaeetus albicilla)</td>
<td>120 - 130 ng/g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(lipid weight)</td>
<td></td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>Herring</td>
<td>8.9 - 290 ng/g</td>
<td>Falandysz et al. (1996)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(lipid weight)</td>
<td></td>
</tr>
</tbody>
</table>

Concentrations of PCNs in ringed seal and beluga blubber are lower than levels detected in the Baltic Sea. In ringed seal tetra- and penta-CN were the dominant congeners, while for beluga this was tetra-, penta- and hexa-CN (Helm et al., 2000).

PCNs and PCBs were measured in fish samples of the Great Lakes during 1996 and 1997 (Kannan et al., submitted). Fishes from the Detroit River contained the greatest concentrations. Concentrations of PCNs were up to 31.4 ng/g ww. Although concentrations of PCBs in fish were 100-1000 fold greater than that of total PCNs, PCNs contributed to 2-57% of the sum of TEQs of PCBs and PCNs.

Ishaq et al. (2000) reported on measurements of PCNs in harbour porpoises from the west coast of Sweden. PCNs and non-ortho PCBs were measured. Highest concentrations up to 730 pg/g ww were detected in blubber, nuchal fat and liver. In the liver PCNs - mainly hexaCNs - contributed to about 50% of total TEQs while in the other organs the contribution was less than 20%.

Concentrations in livers from cod were measured in Grenland fjords from 1995 to 2000 (see also section 2.2) (Knutzen, J. et al., 2000). At three sited mean concentrations over this period were 158 ± 93, 34.8 ± 11.9 and 12.7 ± 5.6 μg ΣPCN/kg ww. Concentrations were high over background levels.
2.5 Human Beings

The main route of exposure of humans to PCNs is probably by ingestion of fish. The elimination of compounds like PCNs and their lipophilic metabolites from body fat is very low. PCNs can be traced in adipose tissues as well as breast milk. The levels in the milk are strongly correlated to the fat content of the milk and reflect the accumulated levels in the adipose tissues.

2.5.1 Human Milk

Norén and Meironyté (2000) reported PCN concentrations in Swedish human milk in the past 20-30 years. The results are shown in Table 14 and show an obvious decrease. Because the documentation of usage of PCNs in Sweden is scarce, contribution of different sources to the total exposure is unknown. However, PCNs were used in capacitors and wires in Sweden according to the authors.


<table>
<thead>
<tr>
<th>Year</th>
<th>PCN concentration (ng/g lipid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1972</td>
<td>3.08</td>
</tr>
<tr>
<td>1976</td>
<td>1.73</td>
</tr>
<tr>
<td>1980</td>
<td>1.23</td>
</tr>
<tr>
<td>1984/1985</td>
<td>0.89</td>
</tr>
<tr>
<td>1990</td>
<td>0.71</td>
</tr>
<tr>
<td>1991</td>
<td>0.50</td>
</tr>
<tr>
<td>1992</td>
<td>0.48</td>
</tr>
</tbody>
</table>

2.5.2 Adipose Tissues

Witt and Niessen (2000) measured PCNs in adipose tissue of children in Germany and Russia. These measurements resulted in concentrations varying from 0.9 to 34.6 ng/g fat. Identified PCNs were exclusively tetra-, penta- and hexa-CN. The distribution of the congeners varied between samples from different locations.

Although commercial PCN products consist of mainly higher chlorinated compounds, octa- and hepta-CN were not found in human adipose tissues. A possible explanation is that the lower PCNs accumulate stronger or that PCNs are dechlorinated before ingestion. Remarkable is that hepta-CN have been found in the environment, in sediment, fish and birds. The lack of these congeners in humans was explained by low absorption (Birnbaum, 1985 in Weistrand and Norén, 1998).
Weistrand and Norén (1998) measured PCN concentrations in human liver and adipose tissues. In both tissues, 1,2,5,7-, 1,2,4,6- and 1,2,4,7-tetra-CNs, 1,2,3,5,7- and 1,2,4,6,7-penta-CNs and 1,2,3,4,6,7- and 1,2,3,5,6,7-hexa-CNs were the most abundant. This result was compared and confirmed with the result of two other studies in Sweden and Japan. Ranges of concentrations of those congeners in liver and adipose tissue are listed in the Table 15.

Table 15. PCN concentrations in liver and adipose tissues (Weistrand and Norén, 1998).

<table>
<thead>
<tr>
<th>Congener</th>
<th>Liver ng/g lipid</th>
<th>Adipose ng/g lipid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,5,7/1,2,4,6/1,2,4,7-tetra-CNs</td>
<td>0.11-0.45</td>
<td>0.04-0.42</td>
</tr>
<tr>
<td>1,2,3,5,7/1,2,4,6,7-penta-CNs</td>
<td>0.17-2.64</td>
<td>0.19-0.22</td>
</tr>
<tr>
<td>1,2,3,4,6,7/1,2,3,5,6,7-hexa-CNs</td>
<td>0.44-21.49</td>
<td>0.44-1.09</td>
</tr>
<tr>
<td>ΣPCN</td>
<td>1.38-26.13</td>
<td>0.10-3.91</td>
</tr>
</tbody>
</table>

The comparison of liver concentrations and concentrations in adipose tissues showed a strong correlation with the distribution over congeners.
3. SOCIΟ-ECONΟMIC FACTORS

3.1 National and international regulation

Although a formal questionnaire has not been sent out by the UN-ECE Secretariat on behalf of the Ad-hoc Expert Group on POPs, it can be argued that there is probably no specific regulation with respect to PCNs in most UN-ECE countries other than PCNs being part of the class organohalogen compounds. Production of PCNs stopped in the seventies and eighties of the last century. From reviews like Crookes and Howe (1993) and Falandysz (1998) it is unclear if industry voluntarily stopped production after negotiations with national authorities or that national regulations banning PCNs were needed.

There are no international regulations with respect to PCNs.

3.2 Alternatives/substitutes

PCNs have been replaced by other chemicals as the production of PCNs stopped in the seventies and eighties of the last century – and use probably several years or a decade later. There may still be some minor uses but no information is available for the UN-ECE region.

3.3 Emission control techniques

In the POP Protocol already several emission control techniques are given which will also lead to a reduction of PCN emissions; for example:

- Annex II (Substances scheduled for restrictions on use) where implementation requirements are given for PCBs. As technical PCBs also contain PCNs the conditions given in Annex II will also lead to a reduction of the (potential) PCN emission;
- Annex V (Best Available Techniques to control emissions of persistent organic pollutants from major stationary sources): PCNs are emitted from the same sources as described for PCDD/F in Annex V: waste incineration, thermal metallurgic processes and combustion plants providing energy. The approaches described in Annex V to control the emissions of PCDD/F will subsequently also lead to a reduction of the emissions of PCNs.

3.4 Costs and benefits of control

PM


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.


