

Polychlorinated naphthalenes: congener specific analysis and source identification in a dated sediment core from Lake Thun, Switzerland

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Introduction

Polychlorinated naphthalenes (PCNs) are persistent, lipophilic substances. An estimated amount of 150,000 t of PCNs was produced between 1910 and 1970 under different trade names such as Halowax, Nibren Wax, Seekay Wax or Clonacire Wax. Due to their high chemical stability, inertness, water-proofness, flame resistance, fungicidal and insecticidal properties, PCN formulations were used as capacitor fluids, engine oil additives, cable insulation, protective coatings, underwater paints and for impregnating wood or paper^{1,2}. Besides the release from formerly used technical formulations, environmental sources of PCNs include chlor-alkali processes and thermal reactions, particularly emissions from municipal solid waste incinerators, metal ore roasting or refining and metal reclamation¹. PCNs also occur as impurities in formerly used polychlorinated biphenyl (PCB) formulations, representing another source of PCNs³. Theoretically, there are 75 possible planar congeners with 1-8 chlorine atoms substituted to the naphthalene skeleton (Figure 1). In technical PCN products, up to 67 congeners were reported. In toxicological studies, several of the PCN congeners have been shown to be toxic, and dioxin-like toxicity with a relative potency similar to that of mono-*ortho* PCBs is exhibited, especially for the 2,3,6,7-chlorine substituted PCNs⁴. Additionally, effects on the reproductive systems of rats, shown for the 1,2,3,4,6,7-CN congener, indicate the potential for endocrine disruption of PCNs⁵. Similar to other persistent organic pollutants, PCNs have been detected in a wide range of abiotic and biotic environmental samples². While many studies have reported on the occurrence of PCNs in the environment, congener specific data relating to their historical time trends and particularly to their possible sources are relatively sparse^{6,7,8}.

This study presents concentrations of PCNs in a dated sediment core from a Swiss lake and investigates possible sources to PCN load. Tracking the origin of PCNs by comparing congener patterns of technical PCN mixtures to those of secondary combustion sources contributes to the assessment of the possible sources of PCNs.

Materials and methods

A sediment core of 1.1 m in length and 56 mm in diameter was collected on July 11, 2005 from the deepest point (Beatenbucht, 217 m depth, 7°44'48.5''E, 46°40'28.8''N) of Lake Thun. Lake Thun is an oligo-mesotrophic lake situated in the alpine region of the Canton Bern in the centre of Switzerland. Lake Thun has a surface area of 47.69 km², a mean depth of 136 m, a volume of 6.42 km³ and a hydraulic residence time of 684 days. The catchment area is 2451 km² with mean and maximum altitudes of 1748 and 4272 m, respectively.

The core was sectioned in slices of 1 cm that were freeze-dried, weighted and stored in glass jars in the dark. Based on ¹³⁷Cs dating of 34 slices, the sedimentation rate was estimated to be 0.39 cm/y. Sediments were Soxhlet extracted for 8 hours using acetone/hexane (1:1 v/v). Extracts were spiked with ¹³C₁₂-PCNs (¹³C₁₂-PCN-42/27/52/67/73/75, purchased from Cambridge Isotope Laboratories) and after evaporation of the solvents to 0.5 ml, the volume was adjusted to 5 ml with cyclohexane/ethylacetate (1:1). This solution was purified by gel permeation chromatography (Biobeads S-X3) to eliminate sulfur and high molecular weight compounds. The purified fraction was reduced to nearly dryness, adjusted to 1 ml with hexane and subsequently cleaned on an acidic silica column (44% H₂SO₄-modified silica) eluted with 10 ml of hexane. The extracts were reduced to approximately 25 µl under a gentle stream of N₂ and ¹⁵N₃-musk xylene (1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene, synthesized in our laboratories) was added to check for recovery of the internal standards. Tetra-CN to octa-CN were quantified using gas chromatography electron impact high resolution mass spectrometry (GC/EI-MS), recording the two most abundant signals of the molecular ion clusters.

Ambient levels and trends

Qualitative identification of individual congeners was achieved by comparing elution order and relative abundances of PCNs with published chromatograms of Halowax mixtures⁹. GC/MS analysis was carried out on a high resolution mass spectrometer (MAT95, Thermo Finnigan MAT, Bremen, Germany) at a mass resolution of 10,000.

Analytical quality control included method blank samples for every 4 sediment samples (blank $\Sigma(\text{PCN}) \leq 0.024$ ng/g dw based on typical sample amount). Analysis of spiked sediment samples showed an accuracy of 98-111%. Limits of detection (LOD) based on a signal-to-noise ratio > 3 in the chromatogram were 0.002-0.008 ng/g dw for each PCN congener. Recovery of isotope-labelled internal standards was $> 60\%$, except for octa-CN ($> 40\%$). The coefficient of variation for replicate analysis was 5.6%.

Results and discussion

Concentration time trend. The sum of tetra-CN to octa-CN concentrations $\Sigma(\text{PCN})$, given in ng/g dry weight (dw) as a function of time is shown in Figure 1. The profile is characterized by very low concentrations of 0.1 ng/g dw in deeper, pre-industrial, sediments; followed by a maximum in the late 1920s (2.1 ng/g dw) and a lower maximum around 1957 (1.0 ng/g dw). Since the 1960s, concentrations gradually decreased to 0.3 ng/g dw, representing the current $\Sigma(\text{PCN})$ concentration in the surface sediments. For all samples, the $\Sigma(\text{PCN})$ concentrations in Lake Thun are low when compared to literature, where typical concentrations for surface sediments in remote areas of the Baltic Sea in the range of 1-7 ng/g dw are reported¹⁰. In Lake Thun sediments, the maximum $\Sigma(\text{PCN})$ concentration of 2.0 ng/g dw was found at a depth of 29-30 cm, corresponding to the year 1928. This first major peak reflects the time of production and use of PCN formulations at the first quarter of the 20th century. Additionally, production of PCNs by combustion processes may have taken place before this time, as well. This is reflected by total PCN levels being distinctly above the detection limit in the period from 1865 to 1905. Other studies report different temporal trends for PCNs for England and Japan. In previous studies, the maximum concentrations of tetra-CN to octa-CN in dated sediment cores from England⁶ and Japan^{7,8} were 9.1, 4.4 and 1.1 ng/g dw, respectively, and occurred in samples from 1962, 1980 and 1984, respectively. These discrepancies of the peaking time suggest different usage and phase-out scenarios in these countries and different impact of possible local sources.

Figure 1 also shows a less distinctive peak around 1957 representing a concentration of 1.0 ng/g dw. The increasing concentrations after World War II could be rationalized by an increased demand for technical products during this period or reflect the presence of impurities of PCNs in PCB products that were introduced later on the market following the PCNs. Although PCN contamination of PCB formulations can not be ruled out as a reason for this second peak, the concentration of PCNs in technical PCB mixtures is low (2-870 ppm according to literature³) and residual PCNs in technical PCB mixtures can hardly account alone for this peak.

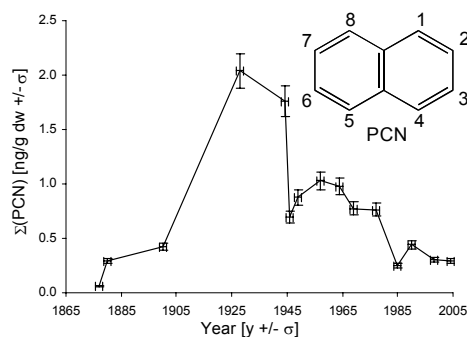


Figure 1: Concentrations $\Sigma(\text{PCN})$ in Lake Thun sediments. Error bars indicate standard deviations (σ) for horizontal and vertical axes.

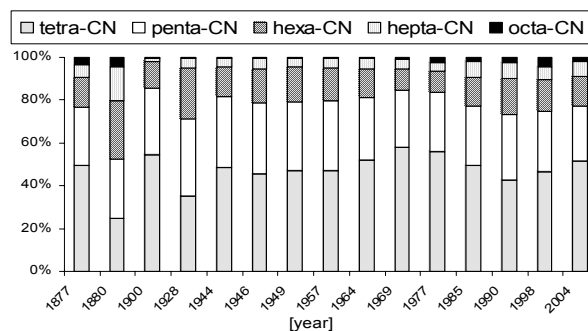


Figure 2: Relative contribution of homologue groups to $\Sigma(\text{PCN})$ in Lake Thun sediments.

Congener pattern. The homologue pattern (Figure 2) remains fairly constant throughout the core. Relative contributions of the homologue groups decrease in the order: tetra-CN $>$ penta-CN $>$ hexa-CN $>$ hepta-CN $>$ octa-CN. The only congener distribution not following this scheme is that of the sample of 1880, showing a shift

towards a pattern dominated by higher chlorinated PCN congeners. The reason for this shift is not clear yet (levels are clearly above typical blank concentrations). A constant homologue pattern was also observed by Gevao *et al.*⁶ in sediments from northwest England.

Throughout the core, the dominant congeners within every homologue group remain mostly the same and closely resemble the congener pattern of technical Halowax formulations⁹. Coeluting congeners are indicated here with a slash: PCN-33/34/37, PCN-47, PCN 28/43 and PCN-38/40 dominate the tetra-CN_s; PCN-52/60, PCN-61, PCN-62, PCN-53/55 and PCN-59 dominate the penta-CN_s; PCN-69, PCN-71/72, PCN-63 and PCN-65 dominate the hexa-CN_s and PCN-73 dominates the hepta-CN_s. These congeners represent $\geq 70\%$ of their homologue group.

Source identification. The similarity between the congener pattern observed in this study and the composition of technical mixtures suggests that formerly used technical PCN products are the main source of PCNs in Lake Thun sediments. However, PCNs may also be formed as byproducts of thermal processes, such as waste incineration. This includes PCN congeners with chlorine substitution in the lateral 2,3,6,7-positions. PCN congeners reported as markers for thermal sources and that are only minor constituents or even absent in technical Halowax formulations are congeners number 27, 30, 36, 39, 45, 50, 51, 54, 66/67, 73 (Abad *et al.*¹¹); 27, 29, 35, 39, 41, 49, 51, 54, 56, 66/67, 70 (Imagawa and Lee¹²) and 39, 45/36, 48, 52/60, 54, 66/67, 73 (Schneider *et al.*¹³).

To investigate whether the relative contribution of these congeners changed with time, the normalized mass ratio of each congener relative to its homologue group was calculated. For some congeners this procedure was not possible since they were either coeluting or since their concentrations were below the detection limits. For those congeners where the calculation was possible and where a time trend could be observed (for PCN-45/36, PCN-52/60 and PCN-73 no time trend could be noticed), the results are shown in Figures 3-8.

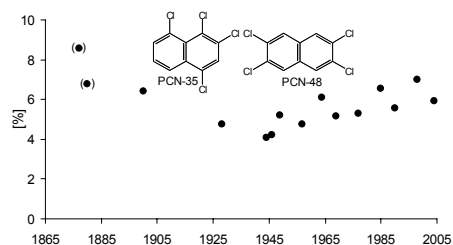


Figure 3: Relative contribution of 1,2,4,8/2,3,6,7-CN (PCN-35/48) to Σ (tetra-CN) between 1877 and 2004.

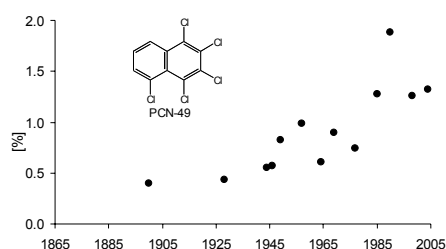


Figure 4: Relative contribution of 1,2,3,4,5-CN (PCN-49) to Σ (penta-CN) between 1900 and 2004.

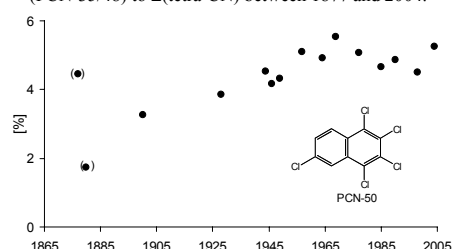


Figure 5: Relative contribution of 1,2,3,4,6-CN (PCN-50) to Σ (penta-CN) between 1877 and 2004.

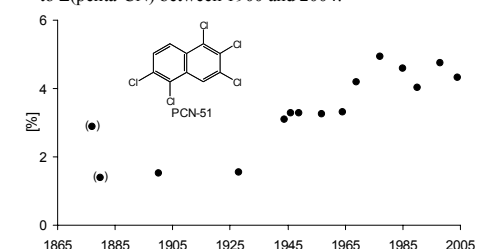


Figure 6: Relative contribution of 1,2,3,5,6-CN (PCN-51) to Σ (penta-CN) between 1877 and 2004.

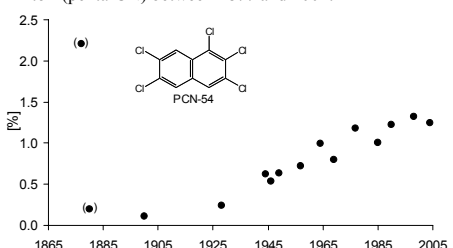


Figure 7: Relative contribution of 1,2,3,6,7-CN (PCN-54) to Σ (penta-CN) between 1877 and 2004.

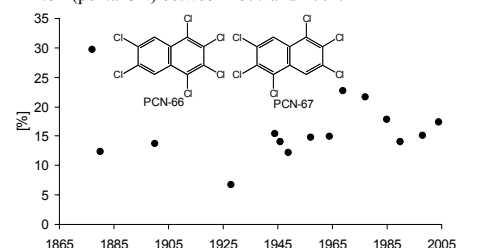


Figure 8: Relative contribution of 1,2,3,4,6,7/1,2,3,5,6,7-CN (PCN-66/67) to Σ (hexa-CN) between 1877 and 2004.

Ambient levels and trends

In Figures 3, 5, 6, 7, the first two points are put in brackets to indicate that the concentrations of these congeners in these two early samples are equal or slightly above the limit of detection. Thus interpretations should be considered with care for the two first samples. As PCN-49 could not be detected in the two earliest samples, these samples are omitted in Figure 4.

Natural and/or anthropogenic combustion sources could explain the presence of PCNs in deeper sediments, as already mentioned in literature^{6,7,8}, where PCNs in sediments deposited in the 18th or even 5th century are reported. The selected congeners, especially PCN-49, 50, 51, 54, which are absent in technical Halowax mixtures⁹, clearly indicate that the relative contribution of thermal reactions to the PCN load in Lake Thun sediments is increasing during the last decades. The contribution of combustion sources is the lowest around 1930 when $\Sigma(\text{PCN})$ peaks. This allows the conclusion that the peak of $\Sigma(\text{PCN})$ is largely due to technical PCN products released in the environment. Since the late 1920s, thermal processes seem to gain more importance as PCN sources relatively to technical formulations. This observation is in accordance with Meijer *et al.*¹⁴, who observed a similar trend in archived U.K. soils. Nevertheless, the congener pattern strongly resembles that of technical formulations throughout the years, signifying that these formulations remain the main source of PCNs in Lake Thun.

Conclusions

The decreasing trend of concentrations of tetra-CN to octa-CN in the dated sediment core shows that the environmental burden of PCNs is declining during the last decades. The fairly constant congener pattern suggests that release of formerly used technical PCN formulations remains the main source of PCNs in these sediments. However, a closer investigation of combustion related congeners shows that the decrease of total PCN concentrations is slower for combustion markers. Thus, thermal reactions are gaining in importance relatively to technical formulations as a source of PCNs in the environment.

Acknowledgements

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References

1. Brinkman UAT, Reymer HGM. *J Chromatography* 1976; 127: 203-243.
2. Falandysz J. *Environ Pollution* 1998; 101: 77-90.
3. Haglund P, Jakobsson E, Asplund L, Athanasiadou M, Bergman A. *J Chromatography* 1993; 634: 79-86.
4. Villeneuve DL, Kannan K, Khim JS, Falandysz J, Nikiforov VA, Blankenship AL, Giesy JP. *Arch Environ Contam and Toxicology* 2000; 39: 273-281.
5. Omura M, Masura Y, Hirata M, Tanaka A, Makita Y, Ogata R, Inoue N. *Environmental Health Perspectives* 2000; 108: 539-544.
6. Gevao B, Harner T, Jones KC. *Environ Sci & Technol* 2000; 34: 33-38.
7. Yamashita N, Kannan K, Imagawa T, Villeneuve D, Hashimoto S, Miyazaki A, Giesy JP. *Environ Sci & Technol* 2000; 34: 3560-3567.
8. Horii Y, Falandysz J, Hanari N, Rostkowski P, Puzyn T, Okada M, Amano K, Naya T, Taniyasu S, Yamashita N. *J Environ Sci and Health* 2004; A39: 587-609.
9. Noma Y, Yamamoto T, Sakai S-I. *Environ Sci & Technol* 2004; 38: 1675-1680.
10. Lundgren K, Tysklind, M, Ishaq R, Broman D, van Bavel B. *Environ Pollution* 2003; 126: 93-105.
11. Abad E, Caixach J, Rivera J. *Chemosphere* 1999; 38: 109-120.
12. Imagawa T, Lee CW. *Chemosphere* 2001; 44: 1511-1520.
13. Schneider M, Stieglitz L, Zwick G. *Chemosphere* 1998; 37: 2055-2070.
14. Meijer S, Harner T, Helm P, Halsall CJ, Johnston AE, Jones KC. *Environ Sci & Technol* 2001; 35: 4205-213.