

**Historical Record of Polychlorinated Naphthalenes in a Semi-Rural Lake
Sediment, Cumbria UK**

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Introduction

Polychlorinated naphthalenes (PCNs) are a group of 75 congeners with properties similar to those of PCBs and with similar industrial applications. There are three main sources of these compounds in the environment: the technical PCN formulations; their presence as impurities in PCB formulations; and combustion related activities (municipal solid waste incineration, metallurgical processes, water chlorination etc.) in the presence of chlorine ⁽¹⁾. The precise world-wide production of PCNs is not known, but it has been estimated to be approximately 1 500 000 tonnes, which is 10 % of the total global production of PCBs ⁽²⁾. The industrial production of technical PCN formulations began to decline in the 1960s and voluntarily ceased in the United States in 1977 but their production in Europe continued until the mid-1980s ⁽³⁾. PCNs and other persistent organic pollutants (POPs) are delivered to lacustrine and marine systems by atmospheric transport and deposition, direct and indirect discharges, and riverine inputs ⁽⁴⁾. As a result of their low aqueous solubilities they partition preferentially onto abiotic and biotic particles in the water column and are transported to the sediment bed and subsequently buried. Therefore dated lacustrine sediment can provide a reliable historical reconstruction of pollutant inputs provided they are undisturbed, and if diagenetic processes of bioturbation, pore water transport and biotransformation are absent or negligible ⁽⁴⁾. Our objective here is to examine the sedimentary profiles of PCNs in Esthwaite Water (EW), a semi-rural lake in the English Lake District. This study represents the first attempt at reconstructing the historical inputs of PCNs in the UK and -as far as we are aware- is the first such study of these compounds world-wide.

Materials and Methods

A sediment core of approximately 1 metre in length was obtained from the deepest part of EW with a Mackereth mini-corer in July 1995 ⁽⁵⁾. The core was transported to the laboratory, sectioned and stored below 4 °C until analysis. Sediments were extracted and analysed for PCB ⁽⁵⁾ and PAHs ⁽⁶⁾ prior to PCN analysis. A more detailed account of sampling, sectioning of the core, storage and extraction have previously been published ⁽⁵⁾. Samples from the PCB analysis were further fractionated on mini carbon columns ⁽⁷⁾ in order to separate the PCNs from the bulk of the PCBs and to effect further volume reduction for extracts which were stored in dodecane. The samples were loaded onto the column and 5 mL 30% DCM in cyclohexane added. This eluent fraction (Fraction 1) contained the multi-ortho and a portion of the mono-ortho PCBs. The PCNs were then eluted with 5 mL toluene (Fraction 2). The volume was reduced to 25 mL under a gentle stream of nitrogen. PCNs were determined by gas chromatography electron impact mass spectrometry (GC-EIMS, Fisons MD-800) in SIM using a 30 m DB-5 MS column (0.25 mm i.d., 0.25 µm film). The mass of individual PCN congeners present in sediment extracts was determined by comparison to a standard calibration mix containing internal standards 208/209 and Halowax 1014, a commercial

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mixture of 2-Cl to 8 Cl PCNs. The concentrations of PCNs were calculated by dividing their masses by the dry weight of the extracted sediment ($\mu\text{g kg}^{-1}$ dry weight), determined gravimetrically after drying sub-samples of the sediment in an oven at 105 °C to constant weight. Blank levels for the analytical method were based on extractions of 10 g of sodium sulphate ($n=12$). The limit of detection (LOD) was calculated as the blank value + 3 SD. When peaks were not detectable, an area of ~ 2000 was used which corresponds to integration of background noise. Peaks were only quantified if they exceeded the LOD; the mean blank value was then subtracted. Two-thirds of the LOD value was used for peaks which failed this criteria. Recoveries were $>70\%$ for most congeners.

Organic carbon determination and dating of the core

The determination of organic C was carried out by the use of a Carlo Erba 1108 Elemental Analyser. The core has previously been dated using the radioisotopes ^{210}Pb and ^{137}Cs . The detailed methodology used and discussion of the radionuclide profiles is provided elsewhere ⁽⁵⁾. The dates shown in the Figure are based on ^{210}Pb mean sedimentation rates, details of which have been previously reported ⁽⁵⁾. The mean sedimentation rate for the dated portion of the core was determined to be $0.995 \pm 0.153 \text{ kg m}^{-2}\text{yr}^{-1}$.

Results and Discussion

The depth profiles for ΣPCN together with that for ΣPCBs ⁽⁵⁾ for the same core are shown in Figure 1. The two profiles have similar features. They are typical of profiles for many banned anthropogenic chemicals, characterised by low fluxes at depth, followed by an exponential rise to a sub-surface peak and a gradual decrease to the sediment-water interface. Background ΣPCN fluxes varied between $0.4\text{-}0.6 \mu\text{g m}^{-2}\text{yr}^{-1}$ until about the mid 1940s, rose to a well defined maximum of $\sim 12 \mu\text{g m}^{-2}\text{yr}^{-1}$ in the late 1950s to mid-1960s and a decrease to present fluxes of $\sim 3 \mu\text{g m}^{-2}\text{yr}^{-1}$. The ΣPCB sediment maximum occurs at a depth corresponding to 1979 (± 2 yr) and is broadly consistent with PCB production data ⁽⁵⁾. The input maximum for ΣPCNs predates that of ΣPCBs by ~ 20 years. This is consistent with the time difference in the production and wide use of PCBs and PCNs ^(3,8). PCN usage was reduced when suitable alternatives were found. PCBs were the primary replacements for PCNs because of their markedly similar properties (thermal stability and inertness). Another remarkable similarity between the two profiles is the presence of a smaller but distinct peak over the period of maximum input of the other. This secondary peak is possibly due to the presence of PCNs as an impurity during the production of PCBs and *vice versa* ⁽¹⁻³⁾. The homologue profiles of PCNs closely tracked that of the ΣPCN profile and generally decreased in abundance in the order: Tetra-CN > Tri-CN > Penta-CN > Hexa-CN > Hepta-CN. The mass percent contribution of individual congeners showed no significant down-core variation. This suggests that the compounds are well preserved and that no significant post-depositional diagenesis might have occurred. One interesting observation in the congener profiles was that for the Hepta-CNs, CN-73 was a factor of 3 higher in concentration than CN-74, the reverse of which is in the technical Halowax mixtures. This suggests a preferential degradation of CN-74 relative to CN-73. Whether this degradation is occurring pre- or post- deposition is not known. Alternatively, it may be due to a different PCN source other than the technical PCN mixture released in the UK or differences in physico-chemical properties which may have resulted in preferential preservation of CN-73 over CN-74.

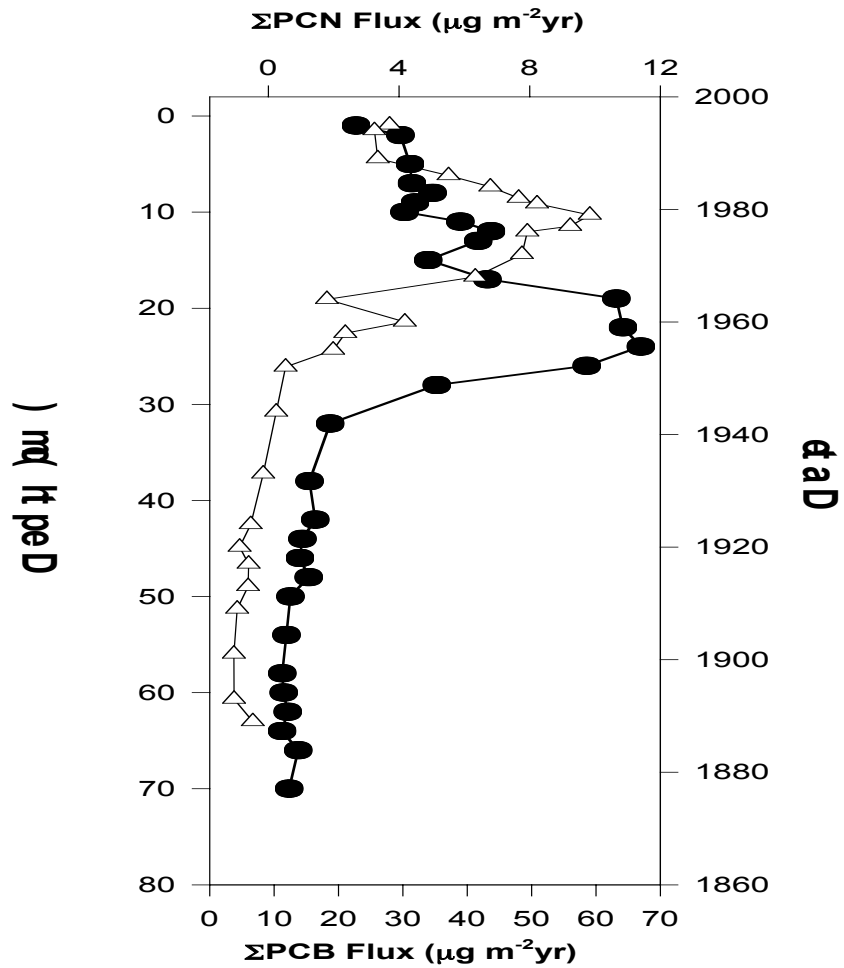


Figure 1: Fluxes of PCBs and PCNs ($\mu\text{g m}^{-2}\text{yr}^{-1}$) in Esthwaite Water Sediments. Circles represent PCNs and open triangles represent PCBs (Ref. 5)

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Another interesting feature of the EW core is the presence of these compounds in pre-1900 sediments. This has been observed before for PCBs in EW and other lake sediments and reasons for their presence in these sediment sections for PCBs have previously been discussed at length⁽⁵⁾. PCNs on the other hand, are known to be by-products of combustion processes and in metal smelting activities. There is a long combustion history in the Lake District associated with metal exploration. Wood burning (ash and hazel) for the production of charcoal for use in iron ore smelting was locally common in the eighteenth century⁽⁹⁾. The so-called 'bloomery' method in open hearths was used before 1709, after which it was replaced by furnaces. Some of the bloomeries and subsequent furnaces were located within 1 km of EW. Between 1855 and 1877, a smelting works was built in Coniston, alongside copper mines, about 3 km from EW. Until about 1970, there were 32 blast furnaces operational between Barrow and Millom, utilising wood burning methods in iron smelting. EW is along the SW-NW direction of the prevailing winds and rain. It is expected therefore that carbon debris associated with the process is likely to enter the lake. It is therefore likely that the metal mining and smelting in the Lake District environment before and during the early period of industrialisation, may have contributed to the pre-industrial levels observed in the study.

In summary, this study presents evidence that the input maximum of PCNs predates that of PCBs by ~20 years. Secondly, it provides evidence that PCB and PCN inputs to the environment have declined in recent years in response to the bans imposed on their use in the mid-1970s.

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