Polychlorinated Naphthalenes in the United Kingdom – Present and Past

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Introduction

New attention has been given to an "old" class of persistent organic pollutants - polychlorinated naphthalenes (PCNs). Because they are chemically and thermally stable, the use-history of PCNs has paralleled that of the polychlorinated biphenyls (PCBs). Studies have shown that several of the 75 possible PCN congeners have dioxin-like toxicity *(1)*.

Recent measurements of PCN concentrations in urban and Arctic air show that their toxicity contribution (TEQ value) sometimes outweighs the contribution of the coplanar PCBs – the most toxic of the PCB congeners *(2)*. Back trajectory analysis for the Arctic samples has related episodes of elevated PCN and PCB concentrations to air trajectories that pass over the United Kingdom and other European regions in the five-day period prior to collection, implicating these regions as potential sources. This study investigates this hypothesis by examining air concentrations at a semi-rural site in the North West of England. Air concentrations of PCNs are interpreted with the use of 5-day air parcel back trajectories and atmospheric burdens are compared to PCBs. Preliminary results are presented for PCNs residues in contemporary grass, soil, lake sediment and sewage sludge samples. Historical trends are discussed based on analysis of archived soils and a dated sediment core.

Experimental

Air

High volume air samples were collected daily over the period Mar.-Oct. and Dec. in 1994 at a semirural location just outside of Lancaster (pop. 70 000), about 5 km inland from the northwest coast of England. Analytical details and results for PCBs and PAHs are presented elsewhere *(3)*.

Sediment

Two 1 m deep sediment cores were extracted from Esthwaite Water, a semi-rural lake in the English Lake District. The cores were sectioned and dated and analyzed for residues of PCBs and PAHs *(4)* prior to analysis for PCNs in this study. A more detailed account of collection, storage, sectioning, dating and sample extraction and cleanup methodology is presented elsewhere *(4)*.

Soil

Archived (1951-1974) and contemporary soils (1993) were collected at several sites across the U.K. and analyzed for PCB residue concentrations *(5)*. The archived soils were originally collected as profiles for surveys of soil type and the contemporary soils were collected at the same locations and to the same depth 0-2.5 cm and 0-25 cm. For this study samples were analyzed from 2 locations (pasture soils, loam type) in the west and southwest of the U.K.

Grass

Grass samples after 2 weeks of growth were taken from a field plot of improved pasture at a semi-rural field station site in the northwest of England. The samples were previously analyzed for PCBs, the analytical procedure and results for which have already been reported *(6)*.

Sewage Sludge

Sewage sludge samples were collected from representative metropolitan, urban, and rural catchments from the northwest of England during 1998 as part of an organic contaminant assessment exercise. The metropolitan sludge was analyzed for PCNs as this wastewater treatment plant receives urban, light industrial, and other specific industrial inputs.

Analysis

The F1 portions ("PCB fractions") from the above samples were further fractionated on mini carbon columns (see ref. 2 for details) in order to separate the PCNs from the bulk of the PCB congeners and to allow further reduction in volume for extracts stored in dodecane. The first fraction (F1-1) was eluted with 5 mL 30% dichloromethane in cyclohexane and contained the multi-ortho and a portion of the mono-ortho PCBs. The second fraction (F1-2) was eluted using 5 mL toluene and contained the PCNs, non-ortho PCBs and the remainder of the mono-ortho congeners. PCB congeners 208 and 209 in dodecane were added as internal standards for volume correction. Fraction F1-2 was volume reduced to 25 μL using 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-5MS column (0.25 mm i.d., 0.25 μm film). Peaks were quantified against Halowax 1014, a commercial mixture of 2-Cl to 8-Cl PCNs. All results have been blank corrected according to air blanks but not recovery corrected. Preliminary recovery tests indicate >70% recovery for most 3-Cl to 5-Cl congeners.

Results

Air parcel 5-day back trajectories were determined at 850 and 925 hPa for all air samples collected in 1994. Samples were divided into four groups (see Fig. 1) according to sectors of air mass origin. Samples from each sector (n=3-4) were then analyzed for PCNs. Figure 1 summarizes the mass contribution of the 3-, 4-, 5- and 6-Cl PCN homologs. The air samples showed a lower molecular weight profile than the Halowax 1014 technical mixture and are dominated by the 3- and 4-Cl congeners. Mean values for the 13 samples were ΣPCN=72 pg m^{-3} and ΣPCB=165 pg m^{-3} *(3)*. Highest concentrations were observed for air samples with back trajectories that originated in the "U.K." and mainland "Europe" sectors supporting the hypothesis that these regions may be significant emission sources of PCNs to the atmosphere. It is interesting to note that a greater range of air concentrations was observed for PCNs than PCBs. The ratio of highest concentration observed / lowest concentration observed was greater for ΣPCNs than ΣPCBs – 44 versus 6 respectively. This suggests that atmospheric burdens of PCNs in the U.K. may be attributed to a mixture of "diffuse" and "non-diffuse" sources whereas PCB are primarily due to "diffuse" sources e.g. re-emission from terrestrial surfaces. Very little is known of the production and use-history of PCNs in the U.K.

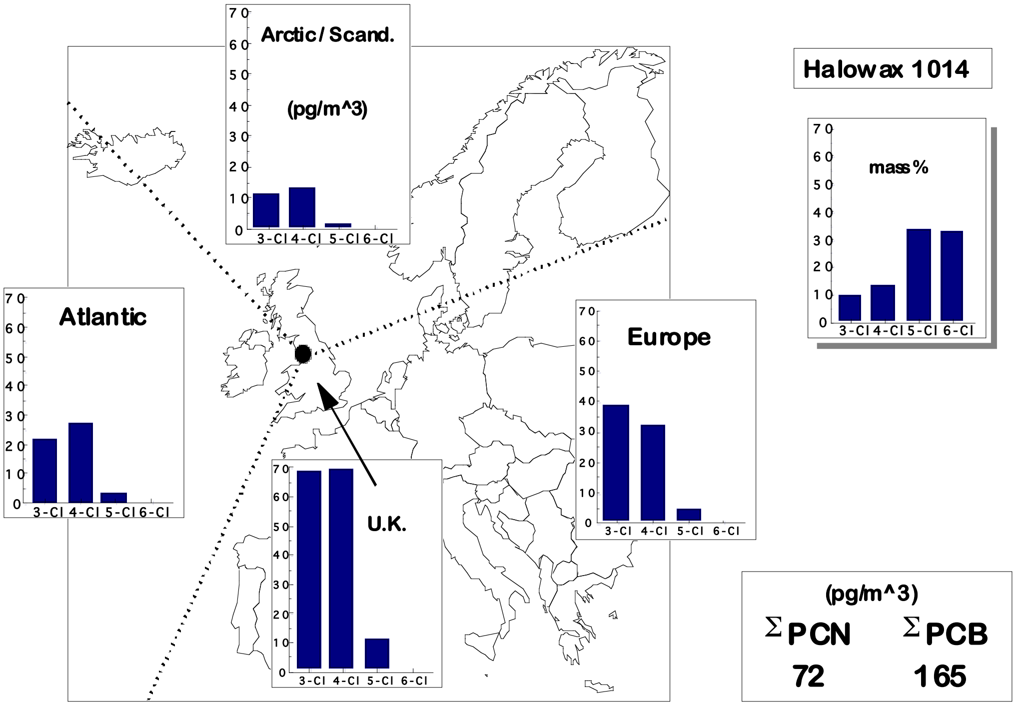

Figure 1. PCN homolog concentrations (pg m^{-3}) for air arriving at the sampling location from different sectors. The U.K. sector refers to air that spent a significant portion of its 5-day history over the U.K.

PCN homolog concentration profiles in grass, soil, metropolitan sewage sludge, and top sediment (Esthwaite Water) are shown in Figure 2. Values (pg g^{-1} dry wt.) were 350 for soil (n=2), 2120 for grass, 3540 for sediment, and 15 100 for sewage sludge. Concentrations in Esthwaite Water sediment are comparable to levels recently reported for contaminated Mediterranean lagoons *(8)*.

Historical Trends

The historical record for PCNs in Esthwaite Water sediment has been determined *(7)*. The results suggest that peak concentrations of PCN occured c.1960 (ΣPCN=11 400 pg g^{-1}) and for PCB c.1979 (ΣPCB=62 000) *(7)*. Since then ΣPCN and ΣPCB values have decreased by a factor of 2-3 to contemporary levels. Residues of ΣPCN and ΣPCB in archived (1964) soils were 12 900 and 1 500 000 pg g^{-1} dry wt. respectively; compared to contemporary values of 350 and 2850 respectively. Here the difference between 1964 and contemporary concentrations is much greater – a factor of ~30 for PCN and ~500 for PCBs. The excessive values for archived soils may be due to contamination by indoor air while these soils were being dried (at the time of collection) in preparation for storage.

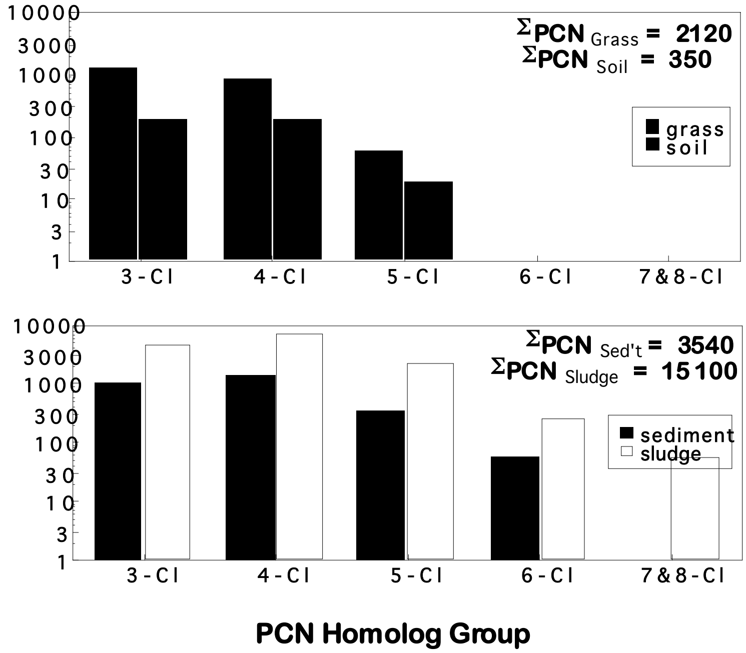

Figure 2. PCN homolog concentrations (pg g^{-1} dry wt.) in: contemporary rural grass and soil (top), Esthwaite Water lake sediment and metropolitan sewage sludge (bottom).

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References

1. Hanberg, A.; Wern, F.; Asplund, L.; Haglund, P.; Safe, S. *Chemosphere* **1990**, 20, 1161-1164.
2. Harner, T.; Bidleman, T. F. *Environ. Sci. Technol.* **1998**, 32, 3357-3265.
3. Lee, R.G.M; Jones, K. C. *Environ. Sci. Technol.* **1999**, 33, 705-712.
4. Gevao, B.; Hamilton-Taylor, J.; Murdoch, C.; Jones, K.C.; Kelly, M.; Tabner, B.J. *Environ. Sci. Technol.* **1997**, 31, 3274-3280.
5. Lead, W.A.; Steinnes, E.; Bacon, J.R.; Jones, K.C. *Sci. Total Environ.* **1997**, 193, 229-236.
6. Thomas, G.; Sweetman, A.J.; Ockenden, W.A.; Mackay, D.; Jones, K.C. *Environ. Sci. Technol.* **1998**, 32, 936-942.
7. Gevao, B.; Harner, T.; Jones, K. C. *Organohalogen Compd* **1999** (submitted)
8. Eljarrat, E.; Caixach, B.; Jiménez, B.; González, M. J.; Rivera, J. *Chemosphere* **1999**, 38, 1901-1912