POLYCHLORINATED NAPHTHALENES IN U.K. SOILS: TIME TRENDS AND EQUILIBRIUM STATUS

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Introduction

The production and usage of polychlorinated naphthalenes has paralleled and preceded that of PCBs. The high dioxin-like toxicity contribution of PCNs in various media has raised concerns regarding their persistence and fate in the environment. Results from a recent air study suggest that the U.K. is an important emission region of PCNs [1].

In this study, archived soils are analyzed for PCNs to yield information on historical trends of PCNs in the U.K. Contemporary air and soil concentrations are used to assess the equilibrium status of individual PCN - to determine if the soil acts a "sink" or a "source" of PCNs in the atmosphere.

Methods and Materials

Soils were analyzed from two long-term experiment stations. The first being the Rothamsted Experimental Station (42 km N of London), Broadbalk experiment plots (years 1944, 1956, 1966, 1980, 1986). The second set was obtained from experimental plots at Luddington (in Warwickshire) where an experiment was conducted to investigate the effects of a one-time sewage sludge addition to soil. Samples (1968, 1972, 1976, 1981, 1985 and 1990) were analyzed for the control plot (no sludge treatment). Sludge was applied in 1968 (125 tonnes dry weight of sludge per hectare, mixed to 15 cm) and samples from the treated plots were analyzed for 1972, 1976, 1981, 1985 and 1990. Samples of the original sludge from 1968 were also analyzed. Approximately 10g of soil or 1g of sludge was extracted by soxhlet using dichloromethane. The extracts were concentrated and fractionated twice on alumina/silica-gel columns with PCNs eluting in the first fractions. Analytical details and additional information regarding the samples is presented elsewhere [2]. PCNs were transferred into isooctane and quantified on an HP GC-MS (6890GC, 5973MSD, DB5 column) against technical Halowax 1014 using the method described by Harner and Bidleman [3]. Mirex was used as an internal standard for volume correction. All soil data has been blank corrected. However, recovery factors have not been applied although preliminary tests indicate that recoveries are good.

Results and Discussion

Figure 1 shows the temporal trend of ΣPCN in Broadbalk and Luddington soils. Peak residues were ~12000 pg g^{-1} (dry weight) in 1960, declining to 500-1000 pg g^{-1} in contemporary soils. Previous analysis of the soils indicated that the peak in ΣPCB occurred c.1970, almost 10

years later [4]. This is consistent with analysis of a dated lake sediment core from Northwest England that showed peak PCN concentrations c.1960, about 10-20 years before the PCB peak [5]. Figure 1 also shows good agreement between the two sites – the control plot results from Luddington integrate well with the declining concentrations observed at Broadbalk over the period 1966-1990. There is an apparent outlier in the 1980 Broadbalk soil showing elevated ΣPCN levels. However, duplicate analyses of this sample are in agreement.

The one-time sludge application in 1968 resulted in elevated soil residues of PCNs in the treated plots that were initially ~25% higher than the control plots. This difference has diminished in contemporary samples. Duplicate analysis of the sludge (1968) revealed PCN concentrations of ~200 000 pg g^{-1}, a factor of ~35 higher than measured in soil from the same time period. However, this difference is mostly accounted for by the ~20 times greater organic matter content of the sludge - ~45% versus 2.5% in the soil. The addition of the sludge in 1968 should have resulted in an increase in ΣPCN of approximately 6000 pg g^{-1} soil which is remarkably consistent with the observed ~25% increase. This calculation is based on: 125 tonnes of sludge applied per hectare; plot well-mixed to a depth of 15cm post application; and a soil density of approximately 2500 kg m^{-3}.

A more detailed analysis of time trends of PCN homolog groups is presented in Figure 2. This analysis excludes the sludge treated soils and the 1980 suspect value for Broadbalk. Soil concentrations are normalized against the peak concentration for the homolog group and are fitted with a third order polynomial trendline. Figure 2 reveals that the higher molecular weight homolog groups exhibit peak residues earlier in the time series – c.1955 for the 4-Cl and c. 1950 for the 5-Cl PCNs. The data suggests that the peak in the 6-Cl occurred prior to or near 1940. Conversely, peak residues for the lower molecular weight 3-Cl group occurs much later, in1970. These results are not consistent with the fact that the lower molecular weight PCNs are more volatile and should therefore be depleted from soil more quickly. However, Figure 2 indicates that the 3-Cl PCNs continued to increase in the period 1955-1970 while the residues of the 4-6 Cl PCNs declined substantially. This anomalous behaviour may be attributed to a shift in usage of PCNs in the U.K. from a "heavier" to a "lighter" technical mixture over this time period.

In light of these differences in time trends for the different homolog groups it is interesting to investigate the contemporary soil-air equilibrium status of PCNs in the U.K. This was done in a manner explained by Harner et al. [6]. Soil residues of individual congeners from 1990 (this study) and average air data from four TOMPS monitoring sites (1998-1999, 1 urban and three semi-rural sites) were used to calculate fugacities (Pa) in air and soil [1]. Soil fugacity was calculated using a K_{OA}-based expression for soil-air partitioning and measured K_{OA} values for PCNs [7,8].

Figure 3 shows the soil-air fugacity ratio (fs/fa) for several 3-5 Cl PCN congeners. Six-Cl congeners were excluded since no air data was available [1]. Fugacity ratios greater than unity indicate that the soil is a source with net outgassing from soil while values less than unity suggest that net transfer is from air to soil. A fugacity ratio near unity (within a factor of about two) indicates that the chemical is near soil-air equilibrium. Based on these criteria the 5-Cl PCNs are fairly close to soil-air equilibrium suggesting that soils have already adjusted to declining air concentrations. However, the results suggest that the 4-Cl and especially the 3-Cl PCNs are saturated in soil with respect to the air. The high fugacity ratios of ~50 for the 3-Cl PCNs and ~2-4 for the 4-Cl PCNs would indicate that net volatilization of these congeners from soil contributes

to atmospheric burdens. In fact, diurnal surface-air exchange studies suggest that PCNs in the U.K. are released from terrestrial surfaces to the atmosphere with an atmospheric signature dominated by the 3-Cl and 4-Cl congeners [9,1].

References

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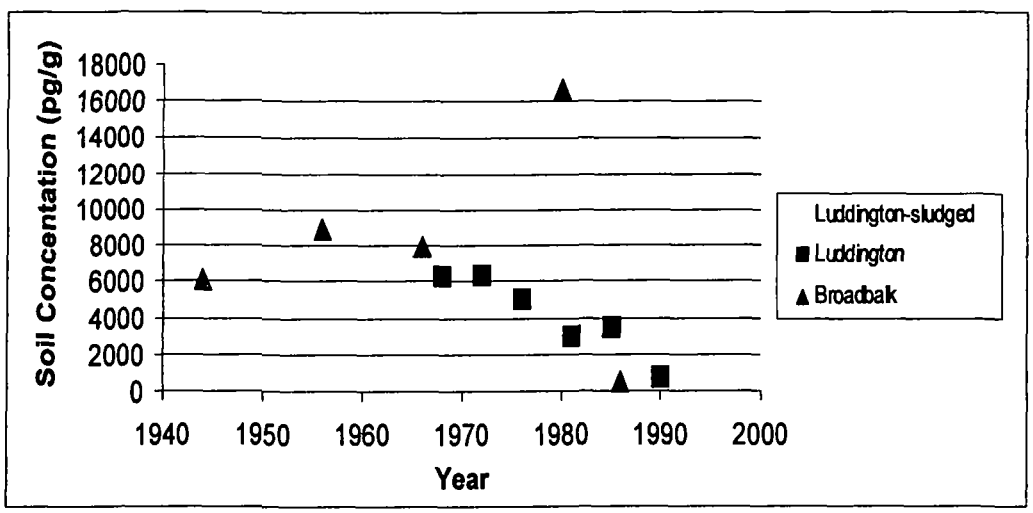

Figure 1. Historical trends of PCNs in U.K. soils, 1944-1990.

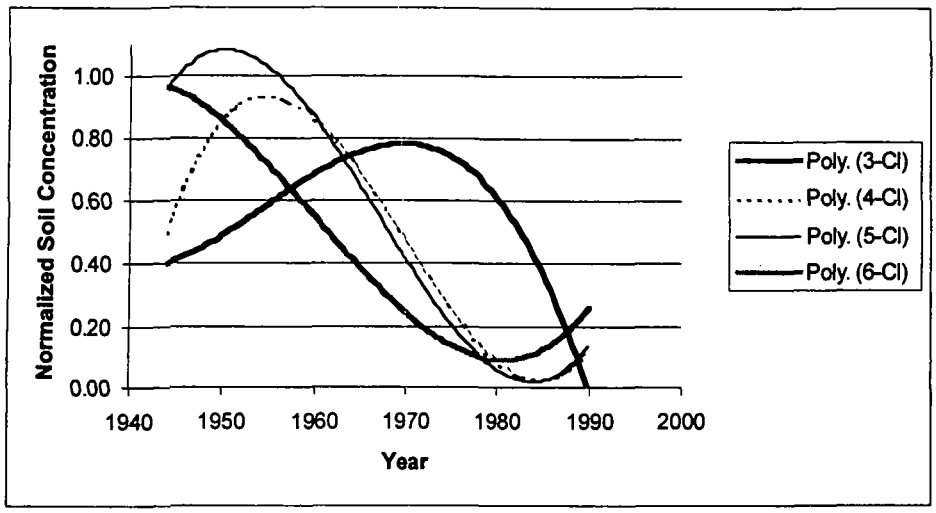

Figure 2. Time trends for PCN homolog groups over the period 1944-1990.

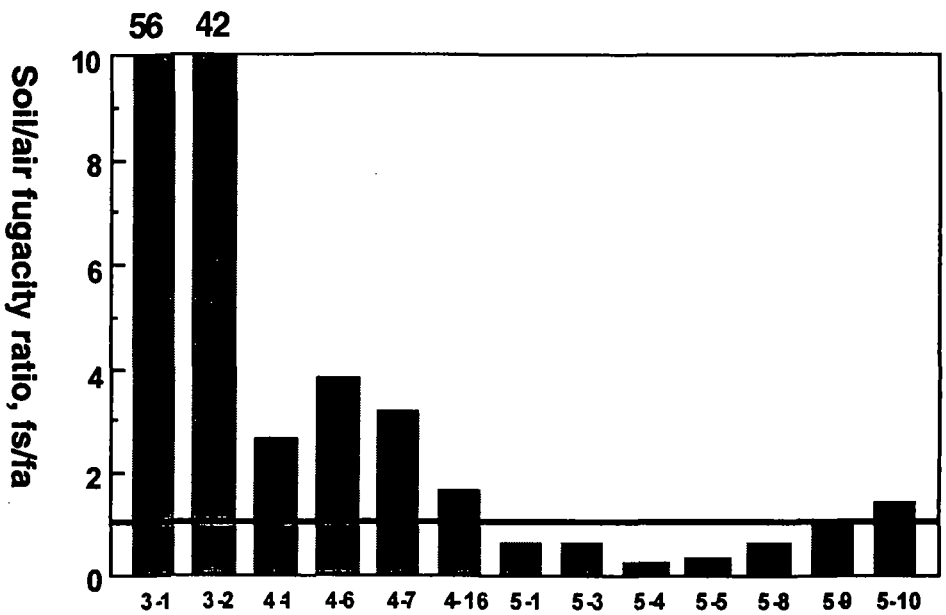

Figure 3. Contemporary soil-air fugacity status of PCNs in the U.K.