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Polychlorinated Naphthalenes in U.K. Soils: Time Trends, Markers of Source, and Equilibrium Status

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Polychlorinated naphthalenes (PCNs) have been analyzed in archived soil from the U.K. to investigate historical trends. Samples were obtained from the Broadbalk experiment plots (1944−1986) and Luddington experiment station (1968−1990). Luddington samples also include a set of soils that received a one-time sludge treatment in 1968, and duplicate samples of this archived sludge were also analyzed. Peak residues of ΣPCN (sum of all PCN congeners quantified) were ∼9000 pg g^{-1} dry weight in 1956, declining to ∼300 pg g^{-1} in contemporary soils. The one-time sludge application resulted in elevated soil residues that were 1.5−6 times higher than the control plot over the time series. This increase is consistent with the known application rate and the amount of ΣPCN in the applied sludge (∼250 000 pg g^{-1} dry wt). Half-lives for the Luddington control soil and the sludge-amended soil for the period 1972−1990 were 5.3 and 9.9 years, respectively. Investigation of time trends revealed differences between homologue groups with the higher molecular weight congeners peaking earlier in the time series (pre-1950) and the lower molecular weight congeners peaking later, ca. 1970. Time trends of individual congeners were investigated in terms of their relative mass percent contribution to the sum of their homologue group. Significant ($p < 0.05$) increasing trends were observed for several congeners associated with combustion sources (CN-29, -51, -52/60, -54, and -66/67) suggesting that combustion related sources are more important now than they were in the past. However, no decreasing trend was observed for congeners that were thought to be susceptible to degradation by photolysis suggesting that this may not be a key elimination pathway of PCNs in the environment. A simple calculation of the fugacity status of PCNs in air and soil showed that the tri-CNs are exhibiting net outgassing, while the penta-CNs are still being deposited to soil. Interestingly, the penta-CNs associated with combustion show the largest gradient for air-to-soil transfer, supporting the notion that combustion sources are important contributors to contemporary air burdens of these congeners.

Introduction

Polychlorinated naphthalenes (PCNs) are a group of compounds with similar physical chemical properties to the polychlorinated biphenyls (PCBs) and have been used in similar applications, such as capacitor fluids, engine oil additives, cable insulation, and wood preservation (*1*). It is estimated that the cumulative global production of PCNs is approximately 10% of the PCBs (*2*). Although the U.S. voluntarily ceased production in 1980, PCNs are not prohibited in most countries (*3*). Weistrand et al. (*4*) found significant contamination of indoor air resulting from leakage from older electrical components. Other sources of PCNs to the atmosphere include chlor-alkali processes (*5*) and thermal processes, particularly emissions from municipal solid waste incinerators (MSWI) (*6*−*8*). PCNs also occur as contaminants in PCB formulations (*9*), and recently Yamashita et al. (*10*) investigated 18 technical PCB mixtures and found high PCN contents in formulations from Russia (Sovol, 150−750 μg g^{-1}) and France (Phenoclors, 150−460 μg g^{-1}).

Polychlorinated naphthalenes are planar compounds and display toxicity similar to that of 2,3,7,8-tetrachlorodibenzodioxin (TCDD), such as ethoxyresorufin *O*-deethylase (EROD), and aryl hydrocarbon hydroxylase (AHH) enzyme induction (*11*). Recently relative potencies (REPs, relative to 2,3,7,8-TCDD) of individual congeners have been reported (*12*, *13*). PCNs exhibit significant TEQ contributions that sometimes compare to or outweigh the contribution of PCBs in air (*14*), sediment (*5*), and biological samples (*15*−*17*). PCNs have also been reported in human milk (*18*) and human adipose tissue (*19*).

In the United Kingdom PCNs were produced by ICI at Runcorn under the trade name Seekay Waxes (*1*). Information on amounts produced is not available, but it is estimated that PCNs were produced in the U.K. from 1919 to the mid-1960s (*1*). Several recent studies in the U.K. have targeted PCNs. Analysis of a dated, rural lake sediment core from northwest England (*20*) showed peak PCN inputs around 1960, consistent with time scales of production in the U.K. Investigations of PCNs in U.K. air (*21*, *22*) show that the U.K. is an important source region for PCNs and that atmospheric burdens are attributed to a combination of diffuse sources (mainly volatilization from soil) and point sources—unlike PCBs that arise mainly from diffuse sources.

Information on concentrations of PCNs in soils is very sparse, and to our knowledge there is only one study that analyzed PCNs in soil. The samples consisted of contaminated soils from waste holding pits near a chlor-alkali plant (*5*). Other studies have looked at PCNs in background sediments (*20*, *23*−*25*) and sediments near pollution sources (*3*, *5*, *15*).

This study contributes to our knowledge of PCNs in the U.K. and is the first study of historical background concentrations of PCNs in soil. Archived soils are analyzed for PCNs to yield information on historical trends of PCNs in the U.K. and the effect of sludge treatment on the long-term residues of PCNs in soils. Time trends of relative contributions of "indicator" congeners are used to investigate the importance of combustion sources and degradation processes. Contemporary air and soil concentrations are used to assess the equilibrium status of individual CN congeners in the soil−air system and thus to determine if the soil acts a net "sink" or a net "source" to the atmosphere.

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TABLE 1. Concentration of PCNs in Broadbalk Soil (pg/g dw)[a]

IUPAC no.[b]	1944	1956	1966	1980 (1)	1980 (2)	1986
19	120	130	100	330	300	11
24	750	730	780	1700	1600	60
14	180	230	240	610	550	20
15	57	84	57	230	210	4.9
16	38	54	41	130	120	2.8
17/25	87	150	100	370	340	5.9
23	400	770	590	2000	1800	**37**
42	120	110	110	190	180	3.1
33/34/37	690	940	860	1500	1400	**28**
47	230	340	270	560	520	**7.1**
36,45	110	200	150	330	310	**6.3**
28	130	270	180	480	420	**4.5**
43	360	630	540	1100	1000	**18**
29	19	49	34	75	84	1.6
30	36	84	62	150	140	**1.9**
27,39	25	59	38	100	95	**1.8**
32 (48)	29	72	56	130	120	**1.6**
35	330	680	570	1300	1200	**14**
38 (40)	730	1500	1200	2900	2600	**34**
46	290	640	550	1200	1100	**13**
52/60	98	110	120	140	130	4.3
58	13	13	15	16	15	**0.33**
61	170	130	190	150	130	5.8
50	32	31	38	41	37	1.9
51	13	15	16	20	18	0.84
54	1.3	1.6	1.4	2.0	1.8	0.24
57	100	94	100	110	100	2.4
62	140	110	130	130	120	3.8
53/55	120	110	120	140	130	3.4
59	240	190	210	240	210	5.1
49	26	21	25	27	24	0.61
66/67	4.9	3.9	6.2	3.7	3.3	2.0
64/68	12	6.6	12	4.3	3.8	1.1
69	23	10	19	6.6	5.8	1.3
71/72	46	17	32	9.5	8.2	**1.6**
63	9.0	3.7	6.1	2.3	2.1	0.52
65	18	5.9	9.5	4.0	3.3	**0.67**
73	**1.8**	**1.6**	**1.8**	**1.9**	**1.7**	**1.7**
74	**3.3**	**2.8**	**3.2**	**3.4**	**3.1**	**3.1**
ΣPCN	5800	8700	7600	16000	15000	320
ΣTEQ	0.074	0.036	0.061	0.026	0.023	0.008

[a] Bolded numbers are below detection limit. $^1/_2$ LOD has been inserted. [b] Congeners in parentheses are a minor component.

Methods

Sample Information. Archived soils were analyzed from two long-term agricultural experiments. The first set of soils (years 1944, 1956, 1966, 1980, 1986) was obtained from Rothamsted Experimental Station, situated 42 km north of London. The soil samples were taken from untreated control plots from the Broadbalk experiment, which have not received any direct additions of pesticides or fertilizers. The second set was obtained from long-term experiments at Luddington (30 km south of Birmingham) where an experiment was conducted to investigate the long-term effects of sewage sludge additions to soil. Sludge was applied in 1968 (125 tonnes dry weight of sludge per ha, mixed to 15 cm). Samples were obtained for the following years: 1972, 1976, 1981, 1985, and 1990, for both treated and control plots. Samples from the soil in 1968 before sludge addition and of the original sludge applied in 1968 were also included.

The fields were ploughed every year, resulting in a well-mixed soil. Each archived sample was made up of 20 subsamples collected in a grid-like manner, representative of the whole field. The subsamples were mixed, air-dried, ground, and sieved in the year of collection and stored in sealed glass containers with cork lids and wax seals. The samples were not exposed to ambient air until subsampling for this project and great care was taken to avoid contamination during subsampling. The issue of possible contamination of the samples has previously been thoroughly investigated, and additional information can be found elsewhere (*26−28*).

Sample Extraction and Analysis. Approximately 10 g of soil or 1 g of sludge was placed in clean, pre-extracted cellulose thimbles, spiked with a recovery mix, and extracted by Soxhlet apparatus for 16 h using dichloromethane (DCM). The extract was initially cleaned up on an alumina/silica gel column (5 g of alumina (Sigma F-20, 1% deactivated) and 10 g of silica gel (Aldrich 923, 5% deactivated)) using 100 mL of 1:1 DCM: hexane. The sample was then subject to fractionation on a second silica/alumina column containing 3 g of 3% deactivated silica gel (Merck, Silica Gel 60) and 2 g of 6% deactivated alumina (Merck, Beckman Grade 1). The column was eluted with 22 mL of hexane to give fraction 1 (F1), followed by 20 mL of DCM to give fraction 2 (F2). The two fractions were reduced to 100 μL using isooctane as the keeper solvent, and mirex was added as internal standard. Polychlorinated naphthalenes were only detected in F1. Organic matter content (determined by loss on ignition at 450 °C overnight) was 3.1% for the Broadbalk soils. For the Luddington soils, average organic matter content was 2.3% for the 1968 control soil, 45.7% for the sludge, 2.8% for the control plots, and 3.6% for the sludge-amended plots.

Method blanks ($n = 4$) were prepared using the same procedure as for the samples and involved the extraction of

TABLE 2. Concentration of PCNs in Luddington Control Soil (pg/g dw)[a]

IUPAC no.[b]	1968	1972	1976	1981	1985	1990
19	330	400	380	160	210	15
24	1800	1900	1600	880	110	86
14	420	500	400	220	260	19
15	140	140	110	61	80	3.6
16	94	85	56	30	43	1.6
17/25	250	260	240	400	250	4.2
23	570	560	460	210	340	36
42	40	61	71	29	25	9.7
33/34/37	460	500	390	170	210	51
47	160	160	110	49	68	14
36,45	80	73	47	23	31	**5.9**
28	61	59	43	**5.3**	26	5.6
43	220	210	150	72	91	23
29	17	13	9.4	5.5	7.7	2.4
30	22	21	14	6.4	8.7	**1.7**
27,39	21	19	8.2	4.1	5.9	**1.6**
32 (48)	18	14	9.7	4.9	7.0	1.8
35	160	150	100	55	64	18
38 (40)	530	440	240	120	150	**32**
46	440	320	150	58	74	20
52/60	22	24	21	13	16	6.6
58	2.5	2.4	2.3	1.5	1.4	0.8
61	22	25	25	17	16	8.6
50	6.1	6.4	5.8	4.4	4.5	2.1
51	3.2	3.0	2.7	2.1	2.3	1.0
54	0.37	0.37	0.41	0.39	0.37	0.24
57	17	17	13	12	12	5.1
62	21	21	18	15	17	7.6
53/55	24	24	17	13	16	6.3
59	64	52	42	22	26	11
49	4.6	4.0	4.4	4.2	2.8	1.9
66/67	1.2	1.4	**0.16**	1.3	1.8	1.8
64/68	1.7	2.8	**0.38**	1.7	2.1	1.6
69	2.8	3.0	**0.55**	2.7	3.9	2.1
71/72	3.0	3.7	**1.8**	2.7	4.3	2.5
63	1.0	1.6	**0.46**	**0.47**	1.9	1.6
65	0.78	1.6	**0.77**	**0.78**	2.1	0.87
73	**1.7**	**1.7**	**2.0**	**2.0**	**2.0**	**1.6**
74	**3.1**	**3.0**	**3.6**	**3.7**	**3.6**	**2.9**
ΣPCN	6000	6000	4700	2700	3200	420
ΣTEQ	0.011	0.013	0.004	0.010	0.017	0.012

[a] Bolded numbers are below detection limit. $^1/_2$ LOD has been inserted. [b] Congeners in parentheses are a minor component.

an empty cellulose thimble. Method recoveries were carried out in triplicate and separately for each of the two cleanup columns that were used. Samples, blanks, and recovery checks were quantified by gas chromatography−negative ion mass spectrometry (GC-NIMS) in selected ion mode (SIM) on an HP6890GC-5973MSD using a DB5 column (J&W). Quantification was performed against technical Halowax 1014 using the method and instrument conditions described by Harner and Bidleman (*14*). Briefly, this approach uses predetermined mass contributions of individual CN congeners in Halowax 1014 to assign response factors in NIMS.

Results and Discussion

QA/QC. Method blanks ($n = 4$) had quantifiable levels of tri-CNs and tetra-CNs. The limit of detection (LOD) was calculated as the mean blank value + 3 SD. For the higher molecular weight congeners (penta- to hepta-CNs), no peaks were observed in the method blanks. In these instances an area approximately half the value of the smallest peak that could be integrated was inserted to calculate an amount, and the LOD was determined as usual. Sample data qualified if they exceeded the LOD, and the mean blank value was subtracted. For peaks that were below LOD, half the LOD was inserted. Below LOD values were only observed for the hepta-CNs in most of the soil samples, for some of the tetra- and hexa-CNs in some of the Luddington control soils, and for several tri-, tetra-, penta-, and hexa-CNs in the 1986 Broadbalk sample. Triplicate analysis of the 1990 Luddington sludge amended soil shows good reproducibility with an average RSD of 20%. Duplicate analysis of the 1980 Broadbalk sample and the sludge sample also showed good agreement between replicates (see Tables 1 and 3). Mean method recoveries for F1 were 61.6% and 64.8% for the alumina/silica gel column and the silica/alumina column, respectively. No PCNs were detected in F2. No bias in the recoveries was observed toward the higher or lower molecular weight congeners. Therefore, samples were not recovery corrected. Blank corrected data for all soils and sludge samples are presented in Tables 1−3 with below LOD values bolded.

Temporal Trends of ΣPCN. Tables 1−3 show the concentrations of individual CN congeners in the Broadbalk soils, the Luddington control soils, and the sludge-amended soils as well as the sludge itself, respectively. There is an apparent outlier in the 1980 Broadbalk soil (see Table 1) showing elevated PCN levels, although duplicate analyses of this sample are in agreement. This data point was therefore omitted from Figures 1, 2, 4, and 5 as well as from all calculations. Figure 1 shows the temporal trend of ΣPCN in Broadbalk and Luddington soils. Peak residues were ~9000 pg g^{-1} (dry weight) in 1956, declining to ~300 pg g^{-1} in contemporary soils. Previous analysis of the soils indicated that the peak in ΣPCB occurred ca. 1970, almost 10 years

TABLE 3. Concentration of PCNs in Luddington Sludge Amended Soil and Sludge (pg/g dw)[a]

		sludge-amended soil					sludge	
IUPAC no.[b]	1972	1976	1981	1985	(mean) 1990	(SD) 1990	(1)	(2)
19	550	670	480	300	94	28	8700	10000
24	2700	3000	2400	1600	490	134	46000	50000
14	690	790	620	370	120	36	13000	14000
15	180	210	140	100	24	7.9	2900	3100
16	120	85	87	54	16	7.4	1600	1700
17/25	330	360	950	280	33	12	3500	3600
23	780	770	710	440	210	69	20000	20000
42	120	150	110	59	56	14	4800	4500
33/34/37	770	730	610	390	270	66	26000	25000
47	230	210	190	120	83	21	8100	7500
36/45	100	98	80	53	40	11	4000	3600
28	88	87	70	42	28	6.7	4500	4100
43	340	350	310	190	150	38	15000	13000
29	21	20	16	11	9.9	3.0	830	710
30	30	28	25	15	11	3.0	1500	1300
27/39	21	17	15	9.3	7.1	2.0	860	750
32 (48)	26	24	24	14	11	2.1	1300	1200
35	280	280	280	140	140	35	14000	12000
38 (40)	620	570	510	330	250	63	28000	30000
46	420	360	250	160	130	33	14000	15000
52/60	53	61	64	43	35	5.0	2700	2700
58	6.4	8.7	8.4	6.4	4.6	0.50	340	370
61	68	83	84	51	50	7.2	4200	4400
50	16	19	20	13	11	1.4	840	830
51	6.9	8.1	9.1	6.0	5.1	0.74	340	340
54	0.8	1.0	1.1	0.68	0.70	0.10	32	31
57	41	53	51	34	29	4.4	2300	2300
62	53	69	75	48	41	6.3	3000	3000
53/55	52	63	69	43	37	6.2	2900	3000
59	95	120	110	72	62	9.8	5000	5100
49	14	16	16	10	9.9	1.5	790	780
66/67	3.6	5.2	5.6	4.0	4.5	0.22	120	120
64/68	6.7	8.1	8.8	7.8	6.5	0.40	298	287
69	9.6	12	15	11	11	1.0	470	470
71/72	12	24	19	16	14	1.3	730	720
63	3.1	9.4	6.5	4.3	4.6	0.56	190	190
65	5.2	9.2	9.5	6.1	5.1	0.49	250	260
73	**1.7**	**1.9**	**2.1**	**2.0**	**1.9**	0.09	56	52
74	**3.1**	**3.4**	**3.9**	**3.5**	**3.4**	0.16	88	87
ΣPCN	8900	9400	8500	5000	2500		240000	250000
ΣTEQ	0.033	0.053	0.054	0.039	0.040		1.6	1.6

[a] Bolded numbers are below detection limit. $^1/_2$ LOD has been inserted. [b] Congeners in brackets are a minor component.

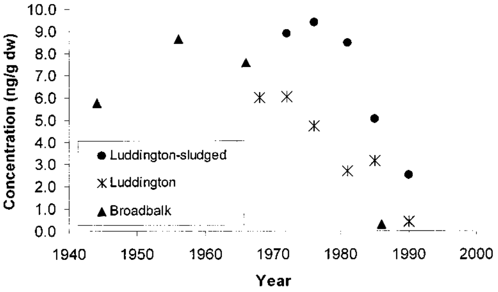

FIGURE 1. Concentration of ΣPCN in Luddington and Broadbalk soils (ng/g dw)

later (*26*). This is consistent with analysis of a dated lake sediment core from Northwest England that showed peak PCN concentrations ca. 1960, about 10–20 years before the PCB peak (*20*). 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.

Half-lives of PCNs in the Luddington control soil and the sludge-amended soil for the period 1972–1990 were 5.3 and 9.9 years, respectively. ANOVA carried out on the regressions (natural log of concentration vs time) showed $p < 0.05$.

Comparison with other studies is difficult, as only one (contaminated) soil has been analyzed for PCNs before (*5*). In that study, excavated soil from a former chlor-alkali plant was found to contain about 18 μg/g of ΣPCN, 3–4 orders of magnitude higher than what was found in the present study. However, concentrations of ΣPCN reported in sediments (10 cm depth or less) from various background sites, or sites with no known pollution source, were between 230 and 7600 pg g^{-1} dry weight (*3,24*), comparable to what was found here.

Effect of Sludge Addition. The one-time sludge application in 1968 resulted in elevated soil residues of PCNs in the treated plot that were 1.5–6 times higher than the control plot over the time series. Duplicate analysis of the sludge (1968) revealed ΣPCN concentrations of ~250 000 pg g^{-1}, a factor of ~40 higher than measured in soil from the same time period. However, this difference is partly 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 a factor 4. This calculation is based on a one-time application of 125 tonnes of sludge applied per hectare to a soil that is routinely mixed to a depth of 15 cm. This expected increase is consistent with what is observed in Figure 1.

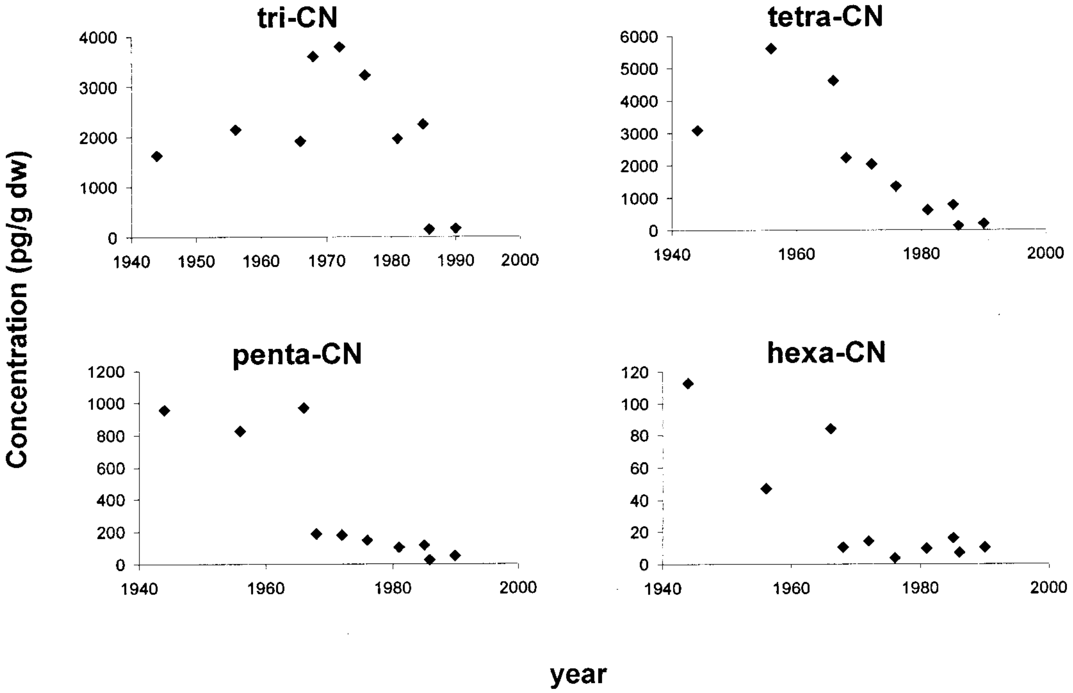

FIGURE 2. Concentration of tri- to hexa-CNs (sum homologue group, pg/g dw) in Broadbalk and Luddington control soils (Luddington sludge-amended soils and the 1980 Broadbalk outlier have been omitted).

Detailed PCN Temporal Trends. Figure 2 shows time trends of CN homologue groups in Luddington and Broadbalk archived soils. This analysis excludes the sludge treated soils and the 1980 suspect value for Broadbalk. Figure 2 reveals that the higher molecular weight homologue groups exhibit peak residues earlier in the time series. For instance, peak residues for the penta- and hexa-CNs seems to have occurred prior to 1944, while the peak for the tetra-CNs is delayed until the 1950s. The peak for the tri-CNs is further retarded, occurring around 1970. In comparison, the data on CN homologue groups from Gevao et al. (*20*) for a dated sediment core do not show this shift in homologue time trends. Intuitively we expect that because the lower molecular weight PCNs are more volatile, they should be the first to revolatilize from soil and readjust to lower atmospheric burdens. The apparent differences in the time of peak soil residues for the different CN homologue groups could be attributed to a number of factors: (1) a shift in usage of PCNs in the U.K. from a technical mixture with higher degree of chlorination to a technical mixture with lower degree of chlorination over this time period, (2) early, industrial, or combustion inputs of the higher molecular weight (penta- and hexa-CN) congeners that may have been a dominant source of these congeners prior to 1950, and (3) a time-dependent degradation of the higher molecular weight congeners to the lower ones. An indication toward possibility (1) is given by Jakobsson and Asplund (*29*), who estimate that contemporary use consists mainly of lower chlorinated PCNs, for example, as glues for plywood. However, this possibility cannot be thoroughly investigated because of the lack of production and usage data in the U.K. Possibilities (2) and (3), however, can be addressed more closely by examining temporal trends of key “indicator” congeners (see also Figure 3).

Combustion Indicators. Several CN congeners are produced as byproducts during combustion processes (Table 4). For example, Schneider et al. (*6*) found preferred synthesis of CN-44, -45/36, -39, -38/48, -51, -54, -66/67, and -73 on fly ash compared to the Halowax mixture. Nakano et al. (*7*) detected several congeners in ambient air that are not present in the Halowax mixture and therefore could be indicative of combustion sources. These are CN-25, -39, and -54. Järnberg et al. (*3*) found and increase in CN-52/60, -66/67, and -73 in both a fly ash and a chloralkali sample compared to the other peaks. In addition, they found several other congeners that showed abundance in fly ash compared to technical PCB and PCN mixtures. These were mainly substituted in the 2,3,6,7-positions and included CN-39, -44, -48, -54, -60, and -70. Helm et al. (*30*) found an enrichment of CN-51 and -54 in medical waste fly ash and urban air relative to Halowax 1014. They also found an enrichment of CN-44 in urban air, while this congener is absent from the Halowax 1014 mixture, indicating a possible combustion source. Imagawa et al. (*8*) collected fly ash samples from stoker type and fluidized bed incinerators. Stoker incinerator samples were found to contain CN-39, -54, and -66/67 as dominant congeners, whereas the samples from fluidized bed incinerators contained mainly CN-18, -27, -35, -62, and -49 as dominant congeners. In all samples, concentration of CN-73 was higher than that of CN-74. Table 4 summarizes combustion related CN congeners found in the different studies.

If industrial or combustion-related emission were responsible for a premature peak in soil residues of the 5-Cl and 6-Cl congeners (Figure 2), these samples should also be enriched in these “indicator” congeners. To investigate whether the relative importance of certain congeners changes with time, we can calculate a normalized mass % relative to the homologue group of that particular congener. Table 5 summarizes the trends and their statistical significance found for all individual PCN congeners when plotting the normalized mass % for their homologue group against time. From this table it follows that the combustion indicator congeners CN-29, -51, -52/60, -54, and -66/67 all show a statistically significant trend with time ($p < 0.05$). In all cases the proportion of these congeners steadily increased with time (see also Figure 4). This is opposite to what we expected and suggests that combustion-related sources of PCNs to the atmosphere are more important now than they were in the past. The other combustion-related congeners mentioned in Table 4 show no trend with time, except for CN-38(40) ($p < 0.1$). However, in the one study where CN-38 is reported as linked to combustion (*6*), it coelutes with CN-48; therefore, we cannot say with certainty that CN-38 is formed in

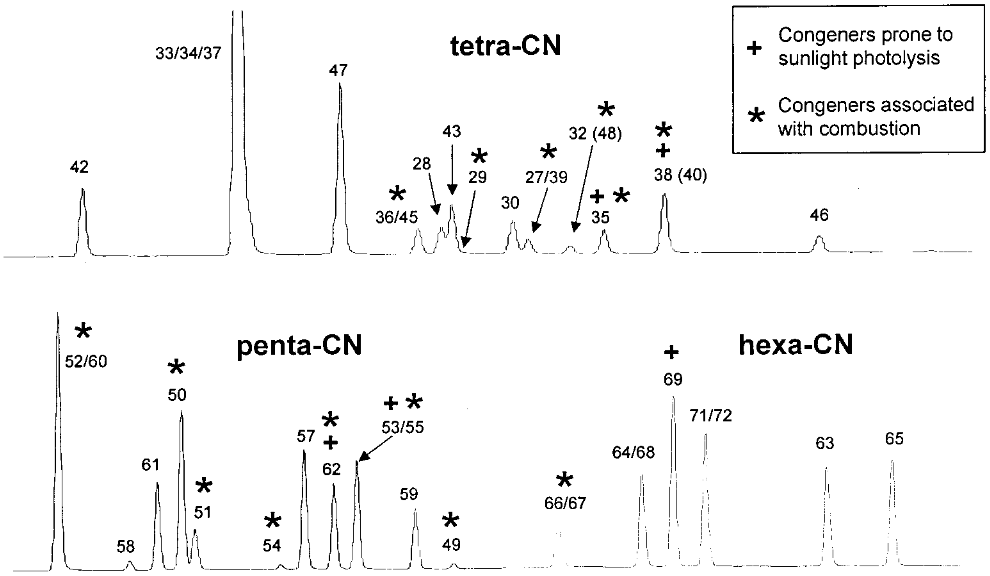

FIGURE 3. Chromatogram of Halowax 1014 (tetra-, penta-, and hexa-CNs) showing "combustion-indicator" and "photolysis-indicator" congeners.

TABLE 4. Summary of PCNs Found in Combustion Related Samples[h]

IUPAC no.	Schneider et al. (*6*)[a]	Nakano et al. (*7*)[b]	Järnberg et al. (*3*)[c]	Helm et al. (*30*)[d] and (*35*)[e]	Imagawa et al. (*8*)[f]
18					X
25		X			
27					X
29				X	
35					X
39	X	X	X		X
44	X		X	X	
45/36	X				
48	X[g]		X		
49					X
50				X	
51	X			X	
52/60			X		
54	X	X	X	X	X
62					X
66/67	X		X		X
70			X		X
73	X		X		

[a] Fly ash. [b] Ambient air. [c] Fly ash and a chloralkali sample. [d] Medical waste fly ash and urban air. [e] Fly ash. [f] Fly ash samples from stoker type and fluidized bed incinerators. [g] Coelutes with CN-38. [h] Bolded CN congeners have been found in more than one study.

TABLE 5. Results of ANOVA Analysis on Time Trends of Relative Concentrations (Mass % Relative to the Homologue Group) for All CN Congeners

IUPAC no.[b]	slope	*p*-value	significant trend ($p < 0.1$)
19	0.062	0.196	
24	0.152	0.225	
14	0.030	0.203	
15	−0.017	0.160	
16	−0.025	0.016	down
17/25	0.056	0.654	
23	−0.257	0.191	
42	0.030	0.360	
33/34/37	0.175	0.077	up
47	0.015	0.614	
36/45	0.009	0.423	
28	−0.039	0.101	down
43	0.030	0.206	
29	0.012	0.015	up
30	−0.005	0.329	
27/39	0.0007	0.884	
32 (48)	−0.003	0.586	
35	−0.047	0.292	
38 (40)	−0.148	0.066	down
46	−0.028	0.736	
52/60	0.070	0.011	up
58	−0.002	0.595	
61	0.010	0.876	
50	0.034	0.112	
51	0.020	0.027	up
54	0.010	0.030	up
57	−0.027	0.307	
62	0.008	0.806	
53/55	−0.013	0.569	
59	−0.124	0.296	
49	0.012	0.422	
66/67	0.312	0.043	up
64/68	0.061	0.418	
69	0.004	0.971	
71/72	−0.360	0.031	down
63	0.081	0.269	
65	−0.098	0.258	
73		na[a]	
74		na[a]	

[a] na: not applicable (relative contribution remained constant over time). [b] Congeners in brackets are a minor component.

combustion. Lee et al. (*22*) by measuring temperature coefficients for surface-air exchange for PCNs also postulated that atmospheric burdens of PCNs in the U.K. have an important contribution from point sources such as combustion sources. In summary, the early soil residue peak for the penta- and hexa-CNs cannot be attributed to combustion-related sources prior to 1950. At first this seems to contradict the information on total coal consumed in the U.K. between the mid-1800s and the late 1900s, which shows that the peak in coal consumption was between 1910 and 1960 (*31*). However, even though more combustion occurred before 1950 in total amounts than after 1950, the relative contribution of combustion toward PCN emissions would have been small compared to direct sources from usage. In present times, however, as usage has declined, combustion sources are most likely the only direct sources of PCNs to the environment, and, therefore, their relative contribution toward PCN emissions will be larger now than in the past.

Degradation Indicators. Preferential degradation of CN congeners may also explain the shift in peak soil residues for the different homologue groups, especially if the higher

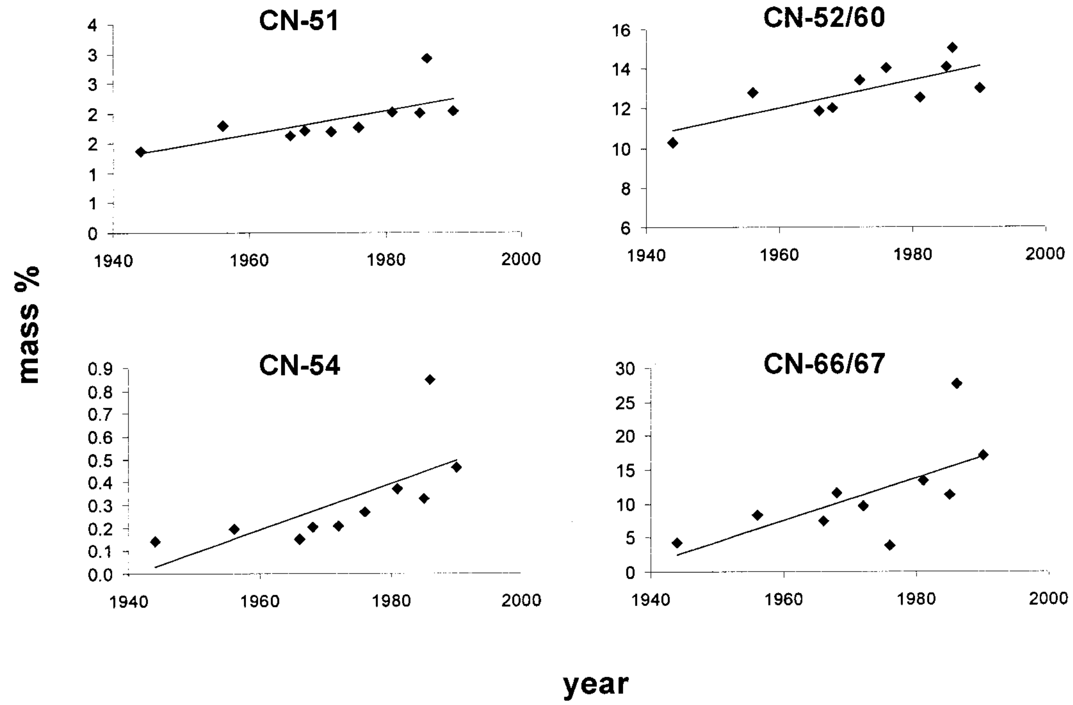

FIGURE 4. Time trends of selected "combustion-indicator" congeners (mass % relative to sum of homologue group).

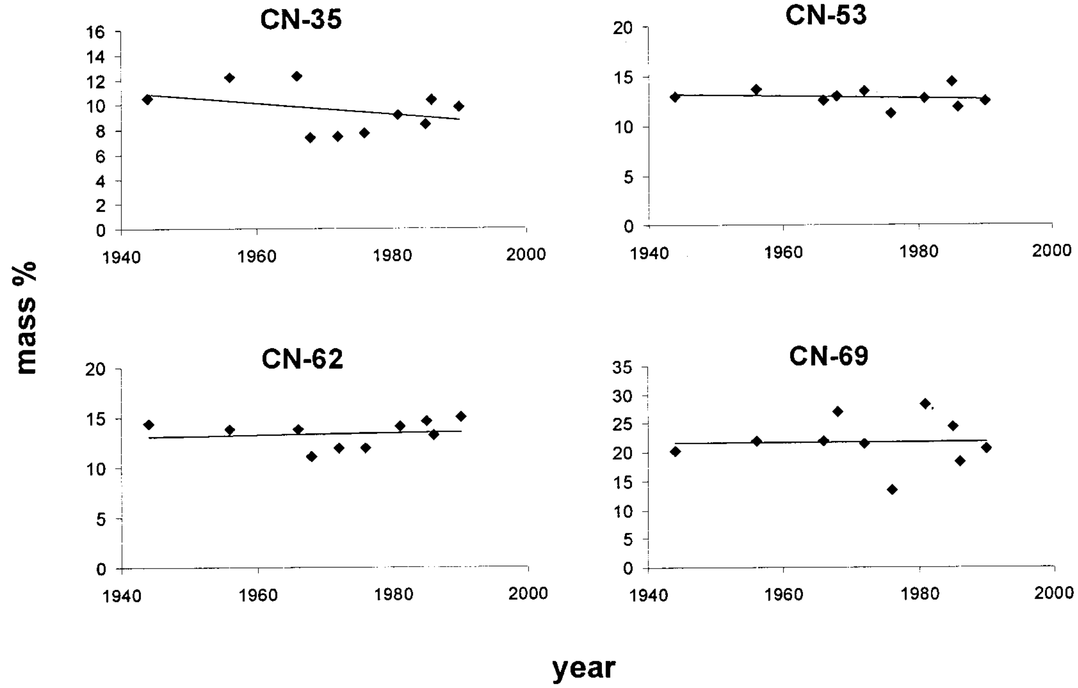

FIGURE 5. Time trends of selected "photolysis-indicator" congeners (mass % relative to sum of homologue group).

molecular weight congeners are degraded and converted to lower molecular weight congeners. Järnberg et al. (*25*) investigated the alteration of the PCN pattern (Halowax 1014) by aerobic microbial degradation and sunlight photolysis (in methanol solution). They found no significant microbial breakdown of PCNs but did see a marked change in the sunlight photolysis experiment that yielded a lower chlorinated congener profile after only 28 days. Congeners with chlorine atoms in the 1,8 positions were most susceptible. These included congeners CN-35, -38, -53, -62, and -69. If photolysis is occurring in the atmosphere that delivers the PCNs to the soil or in the surface soil itself, we should be able to see a time-dependent depletion of these "photolysis-indicator" congeners. Although CN-38 shows a slight downward trend ($p < 0.1$), no significant trend is observed for CN-35, -53, -62, and -69 (see also Figure 5). This indicates that the apparent delay in peak residues of the lower molecular weight PCNs is not attributed to alteration of the profile by sunlight photolysis.

Apart from the combustion-indicator and photolysis-indicator congeners mentioned above, several other congeners displayed statistically significant ($p < 0.1$) increasing or decreasing trends with time (when expressed as mass % relative to their homologue group). These include CN-16, -33/34/37, -28, and -71/72.

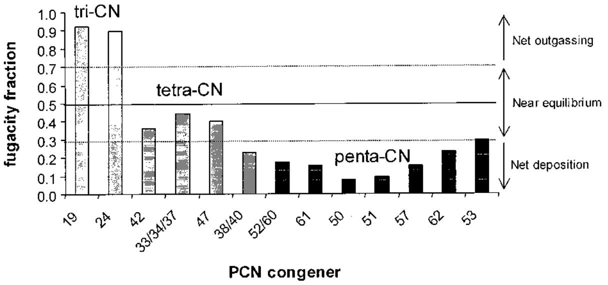

FIGURE 6. Fugacity fractions ($ff = f_{soil}/(f_{soil} + f_{air})$) of selected PCN congeners.

Soil−Air Equilibrium Status. Some insight into the temporal profile of PCNs in soil can be gained by investigating the relative chemical fugacity of CN congeners in soil and air. Fugacity represents the partial pressure of chemical in a particular medium and controls the movement of chemical between media. Chemicals strive to establish an equal fugacity (equilibrium) in the soil−air system. The equilibrium partitioning of chemical between soil and air is described by the dimensionless soil−air partition coefficient, K_{SA} (*32*). K_{SA} can be approximated using the octanol−air partition coefficient, K_{OA}, and the relationship

$$K_{SA} \sim \phi'_{SOC} K_{OA}, \tag{1}$$

where ϕ'_{SOC} is the mass fraction of soil organic carbon. Temperature-dependent K_{OA} values for PCNs have been reported (*33*). K_{SA} can also be expressed as a ratio of the fugacity capacity (Z-value, mol m^{-3} Pa^{1-}) for soil and air

$$K_{SA} = Z_{soil}/Z_{air} \tag{2}$$

Z_{air} is calculated as $1/RT$ where R is the ideal gas constant and T is in Kelvin. Concentrations (C, mol m^{-3}) in air can easily be converted to fugacities (f, Pa) using the relationship $f = C/Z$. When performing this conversion for soil we assume that most of the chemical is associated with the organic portion of the soil. This is a valid assumption for PCNs, which partition strongly into organic phases. Combining eq 1, eq 2, and $Z_{air} = 1/RT$ we obtain the expression $Z_{soil} = \phi'_{SOC} K_{OA}/RT$ which can be converted to a fugacity with knowledge of the chemical concentration in soil in mol m^{-3}. A more detailed explanation of this calculation is presented elsewhere (*34*).

Ideally, when determining fugacity gradients between media the measurements should be coupled and conducted at the same time. Unfortunately in this study air measurements were not made over the fields that were sampled or at the time of collection. Our fugacity estimates are a compromise, and we realize that our comparison is not ideal. Here we use soil residues from 1990 (Luddington, control plot) and compare this to average air data from three semirural TOMPS monitoring sites (1998−1999, only results for tri- to penta-CNs were reported) (*21*).

Figure 6 shows the soil−air fugacity fraction ($ff = f_{soil}/(f_{soil} + f_{air})$) calculated as discussed above for several tri- to penta-CNs. Fugacity fractions greater than 0.5 indicate that the soil is a source with net revolatilization from soil; values less than 0.5 indicate that the soil is a "sink" and net transfer occurs from air to soil. A ff near 0.5 (realistically, within ∼0.3−0.7 considering the built-in uncertainties in the calculations (*34*)) indicates that the chemical is near soil−air equilibrium. Figure 6 shows that tri-CNs are oversaturated in the soil relative to the air ($ff = \sim 0.9$) resulting in net soil−air transfer. This is supported by diurnal surface-air exchange studies which showed that much of the PCNs in the U.K. atmosphere originate from terrestrial surfaces and have a profile that is dominated by the tri- and tetra-CNs (*22*). The tetra-CNs are near equilibrium ($ff = \sim 0.3−0.4$), and the penta-CNs ($ff = \sim 0.2−0.4$) vary considerably with some near equilibrium with the soil and others showing a relative overabundance in the air. It is interesting to note that some of the lowest ff for the penta-CNs are observed for "combustion-indicator" congeners (e.g. CN-50 and -51) suggesting that their abundance in air relative to soil is due to contemporary atmospheric emissions from thermal processes.

In summary, ΣPCN temporal trends in archived soil from the U.K. show peak concentrations in the 1950s/1960s. Detailed investigation of homologue time trends shows a shift in peak concentrations from the heavier to the lighter homologue groups, with the penta- and hexa-CNs peaking before 1950 and the tri-CNs peaking in 1970. This might be explained by a shift in usage, although information lacks to support this theory. Investigation of time trends of relative contributions of combustion- and degradation "indicator" congeners did not explain the shift in homologue time trends. However, increasing mass contributions of several combustion related congeners with time suggest combustion related sources are more important now than they were in the past. This theory is supported by calculated fugacity fractions (ff) showing net outgassing of the tri-CNs and net deposition of the penta-CNs with the combustion related congeners showing the greatest net deposition.

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