

Long-Term Changes in the Polychlorinated Biphenyl Content of United Kingdom Soils

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Archived soils collected from five different long-term agricultural experiments in southern England have been analyzed retrospectively for a range of polychlorinated biphenyl (PCB) congeners. The change in soil PCB concentration over time has been similar in each field experiment, namely, that soil samples exhibited a sharp rise in soil PCB concentrations between about 1940 and the early 1960s, reaching a maximum (ca. 140–560 μg of $\Sigma\text{PCB}/\text{kg}$ of soil) during the late 1960s/early 1970s. Since then there has been a dramatic reduction in ΣPCB concentrations, such that contemporary concentrations (ca. 20–30 $\mu\text{g}/\text{kg}$) are now similar to those of the early 1940s soils. If these soil loadings were reflected nationwide, the ΣPCB burden of U.K. soils has fallen from ca. 26 600 t in 1970 to a contemporary burden of ca. 1500 t. This is equivalent to an annually averaged net loss of $\sim 14 \mu\text{g} \Sigma\text{PCB m}^{-2} \text{ day}^{-1}$, but a slower $\sim 1 \mu\text{g} \Sigma\text{PCB m}^{-2} \text{ day}^{-1}$ in recent years. Volatilization and subsequent long-range transport probably account for the bulk of this loss. A total of 67 000 t of PCBs was manufactured in the United Kingdom between 1954 and 1977, with an estimated 40 000 t used within the United Kingdom. There has been a gradual shift in the relative proportion of individual congeners since the peak, with a move toward greater proportions of the heavier homologue groups in the most recent samples.

Introduction

Polychlorinated biphenyls (PCBs) are a group of stable, persistent, lipophilic compounds which adsorb strongly to organic material and accumulate in surface soils. Atmospheric deposition is the major source of PCBs to the terrestrial environment and has resulted in trace levels of PCBs being present in all soils. Their commercial production started in the United States in 1929, with world production reaching a maximum in the early 1960s. More than 2×10^9 kg have been produced worldwide (1). Because of elevated levels found in a range of environmental samples and their suspected toxicity, their industrial use in much of Europe and America has been restricted since the mid 1970s (2). Despite these legislative controls, contemporary PCB concentrations in marine predators are still high enough to be linked to adverse ecotoxicological effects (1, 3).

Reliable quantitative time trend data are important in order to establish how environmental levels have changed over time and to evaluate the progress of strategies designed to limit the release of chemicals into the

environment. Good quality temporal trend data are still limited for this group of compounds. Previous time trend studies have used information based on lake sediment cores and undisturbed sections of peat to infer broad changes in levels (2, 4, 5).

The objective of this study was to establish the long-term temporal trends of PCBs in U.K. soils and to set this in context with contemporary PCB concentrations in U.K. soils. This has been achieved by analysis of a set of archived soil samples from long-term agricultural plots established at the Rothamsted Experimental Station. These samples have been the subject of several studies on long-term trends of heavy metals and other trace organic compounds in agroecosystems (e.g., refs 6–8).

Materials and Methods

Details of Long-Term Experimental Sites. Between 1843 and 1856, Lawes and Gilbert began a series of field-scale experiments at the Rothamsted Experimental Station. Eight of these have continued more or less as originally planned to the present day: these are the 'Rothamsted Classical Experiments'. Their main objective was to measure the effects on crop yields of inorganic fertilizer additions and various organic manures. Rothamsted is a semirural location 42 km north of central London. Soils from two of these experiments (Broadbalk and Hoosfield) have been used here to monitor long-term trends of soil PCBs (see Table I). Samples were collected from untreated 'control' plots which have not received any agricultural amendments during the last 120 years. Details of the history and treatments of these experiments are given in Warren and Johnston (9) and in Johnston and Gardner (10). Over most of the fields, silty clay loams and flinty soil overlies clay with flints at less than 50 cm. Plough-layer soil samples (23 cm) were air-dried, ground, and sieved after collection, then placed in glass containers, and sealed until subsampled for this project. Subsamples were dried at 100 °C to determine dry weight, so that results could be expressed on this basis.

Soils from the control plots of three other long-term experiments (Woburn, Luddington, and Lee Valley) were also analyzed (see Table I). These were established more recently to study the long-term effects of sewage sludge additions to soil. Since these soils have been sampled more frequently, they have enabled more detailed recent soil PCB trends to be determined. The Woburn Market Garden Experiment, situated in a rural location lying 27 km northwest from Rothamsted was initiated in 1942. It was originally established to assess the manurial value of various bulky organic manures with additions of organic fertilizer. McGrath (11) has described the historical details of this experiment. The soils at Woburn are free-draining sandy loams developed in drift over Greensand (Cottenham Series) with a 9% clay content and a pH maintained

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Table I. Details of Each Long-Term Experiment

experiment	site and sample details
Broadbalk continuous wheat	established at Rothamsted Experimental Station (RES), Harpenden, Hertfordshire in 1843; rural/semirural location; plough-layer depth (0–23 cm); samples obtained for the following years: 1944, 1956, 1966, and 1986
Hoosfield continuous barley	location and depth as above; samples analyzed for the following years: 1946, 1966, and 1982
Woburn Market Garden	established in 1942 new Woburn village by RES; rural site; depth as above; samples analyzed for the following years: 1942, 1951, 1960, 1967, 1972, 1980, 1984, and 1992
Luddington	established in 1968 near Stratford-upon-Avon, Warwickshire, by the Agricultural and Development Advisory Service (ADAS); rural site; depth 0–15 cm; samples analyzed for the following years: 1968, 1972, 1976, 1985, and 1990
Lee Valley	established in 1968; rural site; depth 0–15 cm; years analyzed: 1968, 1972, 1977, 1981, and 1988

at 6.5–7.0. Again plough-layer (23-cm) samples were bulked, air-dried, and sieved (<2 mm) prior to storage in sealed glass containers. Similar experiments to those at Woburn were set up at Lee Valley and Luddington by the Macaulay Institute for Soil Science (now the Macaulay Land Use Research Institute) and the U.K. Agricultural Development and Advisory Service (ADAS) to investigate the uptake of selected metals by crops on sewage sludge amended soils. Details of these experiments can be found in Berrow and Burridge (12). Luddington soil is a sandy loam (pH 5.8) with a low organic matter content, while the Lee Valley soil has a higher pH (pH 6.5), a higher organic matter content (>5%), a higher cation exchange capacity, and a lower bulk density. Plough-layer (15-cm) samples were bulked, air-dried, and sealed for storage.

Details of Contemporary Soil Survey. Surface soil samples were collected from 39 sites in northwest England. Sample points are located along three transects, running east–west (grid lines 349 E–W, 510 E–W) and north–south (350 N–S) across the region at a spacing of 10 km (see Figure 1). These covered a range of soil types in rural, semiurban, and urban locations. The soils sampled included brown earths, podzols, and peats under a range of land uses such as pasture grassland, forestry, upland bog, recreational, and urban. At each site 20–5-cm cores were taken. After being bulked, air-dried, ground, and sieved (<2 mm), samples were stored at 4 °C prior to analysis.

Sample Extraction and Analysis. Samples (approximately 10–20 g) were weighed into a Whatman extraction thimble, preextracted for 3 h with hexane. The thimbles were then extracted for 16 h with hexane in a six-place Buchi Soxhlet extractor. The samples were gently reduced under nitrogen to ca. 1 mL and cleaned on a 1-g Florisil column. Between two and six subsamples of each soil were analyzed, and analytical blanks (one for each five samples) were prepared using the same procedure. Replicate analysis of soil samples gave an error <±10%. Extracts were analyzed by capillary gas chromatography with electron capture detection (ECD) on a Hewlett Packard 5890A instrument. A Hewlett Packard cross-



Figure 1. Location map of the long-term experiments and the contemporary soil samples.

linked 5% phenyl methyl silicone column (50 m × 0.2 mm, film thickness 0.11 μm) was used. The GC conditions were as follows: carrier gas, He at 0.32 mL/min; makeup gas, N₂ at 60 mL/min; temperature program, 100 °C for 2 min, 5 °C/min to 200 °C for 6 min, 4 °C/min to 280 °C for 12 min; injector temperature, 280 °C; detector temperature, 380 °C. (Total run time 60 min.) The following IUPAC congener numbers in elution order were screened: 3, 6, 8, 10, 14, 15, 18, 28, 30, 37, 40, 44, 52, 54, 61/72, 66, 77/110, 82/151, 99, 101, 104, 105, 118, 119, 126, 128, 138, 149, 153, 156, 169, 170, 180, 183, 185, 187, 188, 194/205, 198, 201, 202, 204, 206, 208, and 209. GC-ECD detection limits were typically 2–20 pg/g of soil. Congener 209 was used as a retention time marker and added to each extract prior to GC-ECD analysis. Relative retention times (RRT) of unknown peaks were identified and quantified with respect to congener 209 using a VG Minichrom data handling system. Analytical recoveries of PCB congeners were monitored with the aid of three recovery standards (congeners 54, 155, and 185), spiked into each sample prior to extraction. Recoveries of congener 54, 155, and 185 (three congeners not routinely found in environmental samples) averaged 87, 92, and 96%, respectively. All data reported is based on dry weight and has been corrected for recoveries with the individual congener recoveries applied to homolog groups of congeners (i.e., up to and including the tetra-CBs corrected with respect to congener 54; penta- and hexa-CBs corrected to 155; hepta- and octa-CBs to 185). A subset of samples was also analyzed by

GC-mass spectrometry on an HP5970B MSD operated in selected ion mode, using an identical column. Soil organic matter was determined by loss on ignition at 450 °C. Standards and certified reference materials were obtained individually as solutions from the National Bureau of Standards in the United States and from Promochem, U.K.

The following congeners were routinely detected and quantified in all the samples: 6, 8, 14, 18, 28, 52, 104, 44, 40, 61, 66, 101, 99, 110, 151, 149, 118, 188, 153, 105, 138, 183, 180, 170, 201, and 194/205. Σ PCB refers to the sum of these congeners.

Results

Possible PCB Contamination of Soil Samples or Losses during Storage. All the samples had been air-dried at the time of sampling from the field. All necessary precautions were taken for this project during subsampling of these stored samples to ensure samples did not become contaminated. Each soil had been stored in sealed glass containers until subsampled for this project and was therefore not in contact with ambient air which could have been a source of contamination. Subsamples were transferred carefully into new hexane-rinsed glass jars and taken to Lancaster where they were kept sealed until removed for analysis. PCB contamination from the glass storage jars is highly unlikely, and it is considered that the only time any contamination could have occurred was either during the initial air-drying or the extraction procedure. To ensure against the latter, all glassware was thoroughly rinsed with hexane, thimbles were preextracted, and analytical blanks were run with each five samples. Blank levels were insignificant, with the congeners quantified present well above the limits of detection. Both the GC-ECD and GC-MSD traces showed good agreement and were largely free from interferences.

The likelihood of losses from samples during storage and processing should also be considered before the data set can be interpreted. Potentially PCB losses could occur by photooxidation, volatilization, and microbial degradation. Photooxidation is unlikely since all samples have been stored in darkness in glass throughout. Microbial degradation has been limited because each sample was stored dry and completely sealed. Losses due to volatilization during the air-drying phase would have been more likely to lead to a reduction of low molecular weight PCB congeners. However, low molecular weight congeners dominate the congener composition particularly in the earlier samples.

General PCB Trends in Archived Soil Samples. Figure 2 shows the temporal trend of Σ PCB concentrations found in the archived soil samples between 1944 and 1992. The pattern is similar in each soil series analyzed, namely, that soil samples exhibit a sharp rise in soil PCB concentrations between about 1940 and the early 1960s, reaching a maximum during the late 1960s/early 1970s. Since then there has been a dramatic reduction in Σ PCB concentrations at these sites, so that contemporary concentrations are now close to those of the early 1940s soils. This trend broadly mirrors peat and sediment core data (2, 4, 5). The Σ PCB burden of each soil sample was dominated by the tri- and tetrachlorinated congeners, particularly congeners 18 and 28 (Table II). These two congeners consistently made up >20% of the Σ PCB load.

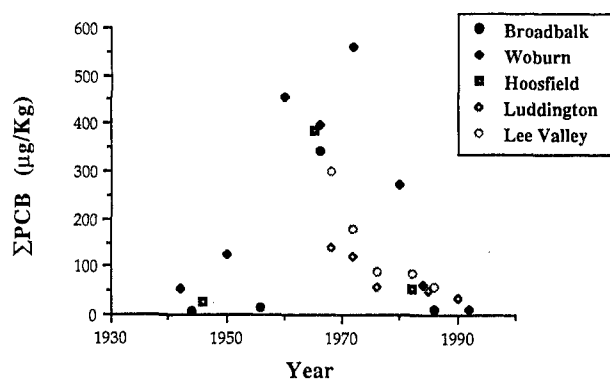


Figure 2. Temporal trends in the PCB content of archived soils.

PCB Increases between the 1940s and the 1960/70s. Σ PCB concentrations on Broadbalk, Hoosfield, and Woburn soils had begun to rise during the late 1940s and continued rising until the late 1960s/early 1970s (Figure 1 and Table II). Soils sampled from the Luddington and Lee Valley experiments confirmed maximum levels at around this time. Soil concentrations peaked at between 140 (Luddington) and 560 μ g of Σ PCB/kg (Woburn) at the five sites, with the tri- and tetrachlorinated congeners dominating the composition (Table III). These two homolog groups consistently account for >75% of Σ PCB in these samples. Congeners 28, 44, and 66 were most abundant in the Broadbalk, Hoosfield, Lee Valley, and Woburn samples, accounting for >25%, >10%, and >12% of the Σ PCB load for each congener, respectively (Table II). At Luddington, maximum levels in 1968 were slightly different, being dominated by congeners 28 (24%), 52 (13%), and 101 (11%). Peak PCB concentrations occurred between 1966 and 1972.

The sharp increase in soil Σ PCB content between the 1940s and the early 1960s coincides with trends in the industrial manufacture of these chemicals, both in the United Kingdom and on a global scale (1). Nonetheless, it is interesting to note that environmental levels had probably started to increase during the 1940s, prior to U.K. production of PCBs in 1954. Between 1954 and 1977, when all U.K. sales were discontinued, a total of 66 748 t of PCBs were manufactured in the United Kingdom, with an estimated 40 000 t used within the United Kingdom (13, 14). Global trends follow a similar pattern (1). Their widespread use in 'open' systems, (e.g., hydraulic fluids, plasticizers, adhesives) during this time is probably responsible for the observed substantial rise in soil levels. However, the fact that levels had begun to rise prior to U.K. production of PCBs suggests that they may have undergone long-range transport across the Atlantic from the United States in predominantly westerly winds or perhaps from mainland Europe.

More Recent Declines. An interesting feature of this time trend data is that Σ PCB concentrations on Broadbalk and Hoosfield have declined substantially since their maximum values in the late 1960s. Contemporary Σ PCB levels in Woburn soil samples are lower than those found in the 1942 sample. Levels at Luddington and Lee Valley exhibit a similar substantial decline. At each of the sites, the concentrations declined at a greater rate during the early 1970s and then more slowly up to the present.

There has been a gradual shift in the relative proportion of individual congeners during this decline, with a move toward greater proportions of the heavier homolog groups

Table II. Total PCB Concentrations and Percentage of Selected Individual Congeners in Samples from Long-Term Experimental Plots

	congener																				ΣPCB (μg/kg)				
	6	8	14	18	28	52	44	40	61	66	101	99	119	110	149	118	188	153	105	138		180	170	201	206
Broadbalk																									
1944	<1	6	5	12	9	4	4	1	1	7	6	2	3	3	12	2	2	7	4	3	4	1	1	2	8.8
1956	2	12	4	17	23	8	6	2	2	5	3	1	2	2	4	1	1	2	1	<1	1	2	<1	<1	14.9
1966	1	5	<1	8	31	9	10	4	6	12	3	2	<1	3	1	2	<1	1	1	1	<1	<1	<1	<1	341
1980	<1	9	13	13	18	8	6	2	2	6	4	1	<1	1	4	2	1	2	2	2	2	<1	<1	1	10.5
Hoosfield																									
1946	3	14	18	10	22	8	6	2	4	1	2	1	<1	2	2	1	<1	1	1	1	<1	<1	1	<1	27.2
1966	<1	3	<1	5	25	9	11	4	13	19	3	1	<1	2	1	1	<1	1	1	1	<1	<1	<1	<1	382
1982	<1	3	<1	11	31	14	14	4	14	1	2	1	<1	1	1	1	<1	1	1	1	1	<1	<1	<1	54.4
Woburn																									
1942	<1	4	9	13	16	17	14	6	8	4	3	2	1	1	2	1	<1	<1	1	1	<1	<1	<1	<1	60.4
1951	2	6	3	14	41	10	8	2	5	4	1	<1	<1	1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	123
1960	<1	1	<1	7	34	10	9	3	7	12	2	1	<1	4	1	1	2	1	2	1	<1	<1	<1	<1	454
1966	1	1	1	8	37	10	9	3	6	11	2	1	<1	4	1	1	1	<1	2	1	<1	<1	<1	<1	394
1972	1	1	<1	7	33	9	9	4	6	12	3	2	<1	4	1	1	0	1	3	1	<1	<1	<1	<1	555
1980	<1	2	2	11	41	11	10	3	6	6	2	1	<1	3	1	<1	<1	<1	1	1	<1	1	<1	<1	269
1984	<1	2	9	12	7	8	8	3	9	2	4	3	1	14	3	<1	<1	1	7	4	1	1	1	<1	58.8
1992	<1	<1	<1	<1	3	10	6	<1	<1	19	12	<1	1	<1	9	1	10	3	9	8	2	<1	5	<1	12.8
Luddington																									
1968	2	3	5	7	25	14	8	>1	<1	7	11	3	1	3	3	1	2	1	1	1	1	<1	2	<1	132
1972	2	1	4	6	26	14	9	3	1	4	7	3	1	4	3	1	1	1	1	3	1	1	2	1	113
1976	3	2	19	13	3	20	8	1	1	5	1	2	1	3	4	<1	2	1	1	2	1	1	5	<1	54.5
1985	<1	2	7	7	3	15	5	1	<1	6	7	4	1	3	3	<1	1	9	2	7	4	2	7	2	48.7
1990	<1	2	18	4	3	4	2	1	>1	4	10	4	2	5	13	<1	<1	4	<1	7	3	1	5	5	31.2
Lee Valley																									
1968	1	6	9	8	13	11	10	3	3	11	5	2	<1	6	3	2	1	1	2	1	<1	1	1	<1	298
1972	<1	6	17	8	12	9	7	2	3	9	5	2	<1	6	3	2	1	1	2	1	1	1	1	<1	181
1977	1	9	25	9	10	8	5	1	2	6	4	1	<1	4	3	1	1	1	2	2	1	2	2	<1	92.6
1981	<1	2	7	7	3	16	6	1	<1	6	8	4	1	3	3	<1	1	9	2	8	4	<1	7	2	47.9
1988	<1	2	19	5	3	4	2	1	<1	4	10	4	2	6	13	<1	<1	4	<1	7	3	<1	5	5	30.9

Table III. Contribution of Different Homolog Groups in Samples from Long-Term Experimental Plots*

	Σdi-CBs	Σtri-CBs	Σtetra-CBs	Σpenta-CBs	Σhexa-CBs	Σhepta-CBs	Σocta-CBs
Broadbalk							
1944	1(11)	2(19)	1(16)	2(22)	2(20)	1(7)	<1(2)
1956	3(18)	6(40)	3(22)	2(11)	1(6)	1(4)	<1(1)
1966	20(6)	132(39)	139(41)	37(11)	10(3)	3(1)	1(1)
1980	2(22)	3(31)	2(23)	1(12)	1(8)	<1(4)	<1(1)
Hoosfield							
1946	9(34)	8(32)	6(22)	2(8)	1(3)	ND	<1(1)
1966	11(3)	114(30)	211(55)	34(9)	8(2)	3(1)	1(<1)
1982	2(3)	23(42)	25(46)	3(6)	1(2)	<1(1)	ND
Woburn							
1942	7(12)	17(29)	29(48)	5(8)	2(3)	ND	ND
1951	13(11)	67(55)	35(28)	4(3)	2(2)	1(1)	ND
1960	9(2)	181(40)	192(42)	51(11)	11(2)	10(2)	1(<1)
1966	12(3)	177(45)	150(38)	43(11)	8(2)	4(1)	ND
1972	15(3)	221(40)	223(40)	75(14)	17(3)	4(1)	ND
1980	10(4)	138(51)	95(35)	20(7)	4(2)	3(1)	ND
1984	6(11)	11(19)	18(30)	18(30)	5(9)	1(1)	1(1)
1992	ND	<1(3)	5(35)	3(24)	3(20)	2(13)	1(5)
Luddington							
1968	12(9)	42(32)	38(29)	26(20)	7(5)	4(3)	3(2)
1972	9(8)	35(31)	34(30)	19(16)	8(7)	4(4)	3(3)
1976	13(24)	9(17)	19(35)	4(7)	4(7)	2(4)	3(5)
1985	4(9)	4(9)	14(28)	9(18)	9(19)	4(8)	3(7)
1990	6(20)	2(8)	3(11)	7(23)	7(24)	2(5)	2(5)
Lee Valley							
1968	48(16)	62(21)	110(37)	55(19)	14(5)	6(2)	2(1)
1972	43(24)	36(20)	53(30)	33(18)	10(5)	4(2)	1(1)
1977	32(35)	18(19)	20(21)	12(13)	5(6)	4(4)	2(2)
1981	4(9)	4(9)	14(28)	9(18)	9(19)	3(6)	3(7)
1988	6(20)	2(8)	3(11)	7(24)	7(24)	1(4)	2(5)

* Numbers in parentheses are % contribution of each homolog group. Σdi-CBs = congeners 6, 8, and 14. Σtri-CBs = congeners 18 and 28. Σtetra-CBs = congeners 40, 44, 61, and 66. Σpenta-CBs = congeners 99, 101, 105, 118, and 110. Σhexa-CBs = congeners 138, 149, and 153. Σhepta-CBs = congeners 170, 180, 183, and 188. Σocta-CBs = congeners 194/205 and 201. ND = not detected.

in the most recent/contemporary samples. Table III shows that tri- and tetrachlorinated congeners are present in the most recent samples from Broadbalk and Woburn at <3%

of their peak levels in the early 1970s. In contrast, the relative proportion of higher molecular weight congeners (particularly hepta- and octachlorinated) increases in the

Table IV. Summary of Congener Data from Northwest Soil Survey

congener	mean ($\mu\text{g}/\text{kg}$)	median ($\mu\text{g}/\text{kg}$)	min ($\mu\text{g}/\text{kg}$)	max ($\mu\text{g}/\text{kg}$)	SD
8	2.0	1.3	n/d	12	2
18	1.9	1.7	0.1	15	3
28	2.9	1.9	0.1	20	4
52	1.5	1.1	0.1	6	1
104	2.4	0.3	n/d	76	12
44	1.3	0.9	n/d	15	2
40	0.7	0.2	n/d	12	2
61	1.6	0.8	n/d	24	4
66	4.2	3.5	0.1	34	5
101	2.3	1.8	n/d	11	2
99	0.8	0.4	n/d	11	2
119	0.7	0.5	n/d	5	1
110	3.3	0.6	0.2	28	21
82/151	2.0	1.3	0.1	16	3
149	4.8	3.8	0.2	40	7
118	1.2	0.5	0.1	11	2
188	0.9	0.5	n/d	7	2
153	2.4	1.7	0.1	17	4
105	0.9	0.5	n/d	6	1
138	2.8	1.1	0.1	33	6
187	2.5	0.5	n/d	58	9
183	0.8	0.3	n/d	16	3
180	5.3	0.8	n/d	128	21
170	0.6	0.3	n/d	10	2
201	2.4	0.2	n/d	76	12
194/205	1.4	0.4	n/d	43	7
206	2.6	1.2	n/d	84	13
ΣPCB	65	30	14	669	122

most recent samples (Table III). This shift in the dominance of congeners reflects the greater soil residence time of higher chlorinated compounds.

Changes in the levels of soil ΣPCB have mirrored changes in the ΣPCB content of herbage harvested at Rothamsted. Annual herbage PCB concentrations have declined substantially since the late 1960s, so that ΣPCB in samples from the late 1980s were just 2% of those between 1965 and 1969 (7). Interestingly, the timing of the peak and the pattern of decline in both soil and herbage at Rothamsted are similar. Vegetation harvested annually would be expected to reflect short-term temporal variations in air quality. It is therefore interesting that the rate of decline in the soils is similar to that in the herbage, implying relatively short residence times of PCBs at the soil surface.

The declines in all of the long-term experiments suggest that there has been a substantial reduction in the source of PCBs to the environment in rural southern England during the past 20–25 years, presumably because their use in 'open' systems has been limited. While ΣPCB concentrations have declined in these soils since the late 1960s/early 1970s, concentrations of PAHs and PCDD/Fs at Rothamsted have increased (6, 8).

Contemporary U.K. Soil Concentrations. The survey of 39 contemporary surface (0–5-cm) soil samples in northwest England suggests that contemporary ΣPCB concentrations from the long-term experimental plots are broadly representative of U.K. soils nationally. Data from this survey are summarized in Table IV (mean, median, range, and standard deviation for each congener). ΣPCB concentrations ranged from 14 to 670 (median = 30) μg of $\Sigma\text{PCB}/\text{kg}$. However, a statistical evaluation of the data reveals a distinct subgroup, comprising 85% of the samples with ΣPCB levels below 60 $\mu\text{g}/\text{kg}$. The mean and range for this group are 28 and 14–53 $\mu\text{g}/\text{kg}$, respectively. Highest

ΣPCB levels (>200 μg of $\Sigma\text{PCB}/\text{kg}$) were found in samples collected from the industrial centers of Manchester and Liverpool. Sample location is therefore an important factor affecting soil ΣPCB concentrations.

A survey of PCBs in soils (0–5 cm) from central and southern England reported levels of 2.3–444 μg of $\Sigma\text{PCB}/\text{kg}$ in soils (15). However, statistical analysis suggested that true background levels, comprising more than 80% of samples, ranged from 2.3 to ~ 20 μg of $\Sigma\text{PCB}/\text{kg}$. Another survey covering central and southern Wales (16) reported that levels of up to ~ 30 μg of $\Sigma\text{PCB}/\text{kg}$ were representative of the background. The results of the present survey are somewhat higher than these earlier studies. However, we believe this is most likely due to differences in analytical methods used by different laboratories. This survey quantified more congeners and involved the use of activated Florisil during the cleanup, which increases the recovery efficiency of the lower chlorinated congeners that make a significant contribution to the ΣPCB burden of soils (Table II).

General Comments

The soil trends provide a record of long-term temporal trend data for PCBs, clearly showing the timing and magnitude of the peak and subsequent decline in concentrations for sites in rural southern England and allowing contemporary levels to be set in context. These results provide a new perspective on the measures that would be needed to further reduce the environmental burden of PCBs, the likely success of current strategies based on controlling Aroclor releases, and the likely future trends in environmental levels. They suggest that the contribution of Aroclor inputs to the current U.K. environmental burden has been substantially reduced in the last 20 years and that this reduction had commenced prior to the cessation of U.K. production and the introduction of use restrictions in the late 1970s.

One fascinating feature of the time trend data is that ΣPCB concentrations at these sites have now apparently reverted to levels close to those in the mid-1940s, albeit with a somewhat different congener composition, with the heavier homologs constituting a greater proportion of the ΣPCB content. Clearly, manufactured Aroclor inputs now exert a far less significant influence on ΣPCB levels at these sites than during the years of peak use. As an illustration of the scale of the reduction in levels of PCBs, if we assume that concentrations at the five study sites were/are representative of those in the United Kingdom generally (total surface area is 2.475×10^{11} m^2), that the soil density at the five sites averages 1300 kg/m^3 , and that the soils were sampled to plough-layer depth (23 cm), the ΣPCB burden of U.K. soils has declined from ca. 26 600 t (using a mean of 360 μg of $\Sigma\text{PCB}/\text{kg}$) to ca. 1500 t (mean of 20 μg of $\Sigma\text{PCB}/\text{kg}$) in the last 2 decades. Surface (0–5-cm) soils in northwest England contained between 14 and 670 (median = 30) μg of $\Sigma\text{PCB}/\text{kg}$, suggesting that the contemporary PCB concentrations in the long-term experiments studied are indeed broadly representative of soils nationally.

It is interesting to speculate on the ultimate fate of the PCBs lost from these soils. The most likely loss process is volatilization (17). Biodegradation is likely to be minor, since it has already been established that aerobic degradation is slow, especially for the more recalcitrant con-

generators (18). Moza *et al* (19) showed that volatilization losses of ^{14}C -labeled tri-, tetra-, and pentachlorinated PCBs from soils were substantial and accounted for the majority of the compound lost. Volatilization fluxes are temperature-dependent (20) and may result in PCBs from temperate latitudes, such as the United Kingdom, migrating by 'cold condensation' process to the sub-Arctic and Arctic regions, where high concentrations have been observed far from local sources (7, 21).

If we assume that volatilization has been the *only* loss mechanism over the last 20 years, the above estimates of 26 600 t in U.K. soils in 1970 reducing to a burden of 1500 t in 1990 imply that the *net annually averaged* volatilization flux over this 20-year period has been $\sim 5 \text{ mg m}^{-2} \text{ year}^{-1}$ or $\sim 14 \mu\text{g m}^{-2} \text{ day}^{-1}$. To put this in context, Achman *et al.* (23) reported volatilization rates to the air above the highly contaminated Green Bay, Lake Michigan sediment-water system of $0.013\text{--}1.3 \mu\text{g m}^{-2} \text{ day}^{-1}$. Clearly this implies that soil outgassing is potentially a major contributor to the atmospheric burden of PCBs, which possibly accounts for the majority of PCBs entering U.K. air at the present time (14). It is therefore of considerable interest to establish the equilibrium partitioning between the soil and that in the overlying atmosphere. This will enable predictions of future trends to be made.

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