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Evidence for the Presence of PCDD/Fs in the Environment Prior to 1900 and Further Studies on Their Temporal Trends

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This paper presents evidence for the existence of PCDD/Fs in the environment prior to the widespread development of the chloroaromatics and chlorine industry, by the analysis of a previously unopened bottle of soil collected in 1881 from a controlled long-term agricultural experiment at Rothamsted Experimental Station. Great care was taken to avoid contamination of the sample from dust or by exposure to modern air; an experiment was conducted to investigate the potential for contamination of the sample by such exposure. The 1881 soil sample (from the plowed 0−23 cm depth layer) contained 0.7 ng of ΣTEQ/kg soil, and there were no detectable changes in its ΣPCDD/F composition when aliquots of it were exposed over 32 days in a laboratory at Lancaster University. Modern soil sampled from the same field plot (which has never received any fertilizers or amendments) now contains 1.4 ng of ΣTEQ/kg, an increase resulting from cumulative atmospheric deposition of PCDD/Fs retained in the surface layers of the soil. Post-collection contamination issues were also addressed by PCDD/F analysis of dust and paper bags used to store more recent samples. The ΣTEQ concentration of archived herbage samples collected year-on-year from Rothamsted between 1980 and 1995 have trended downward by a factor of 3−4, implying a recent decline in the atmospheric deposition of PCDD/Fs and supporting a previously reported (Kjeller et al. *Environ. Sci. Techol.* **1996**, *31*, 458−463) longer term decline. The significance of these results is discussed.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are released into the environment in ultratrace amounts from various combustion sources or as unwanted byproducts in various chlorinated chemical formulations. Because of concerns over their toxicological significance, considerable resources have been expended in many industrialized countries to identify the most important sources of these compounds to the environment and to introduce source reduction measures. It is therefore important to be able to assess the changing environmental burden and concentrations of PCDD/Fs in key compartments of the environment, to place current burdens/concentrations in context, to assess whether exposure of key species is declining, and to assess the effectiveness and appropriateness of source reduction measures. Importantly, there are continuing uncertainties over whether the key sources of PCDD/Fs have, in fact, been identified and even whether there has been a 'pre-industrial' or historical baseline level of these compounds in the environment (*2*).

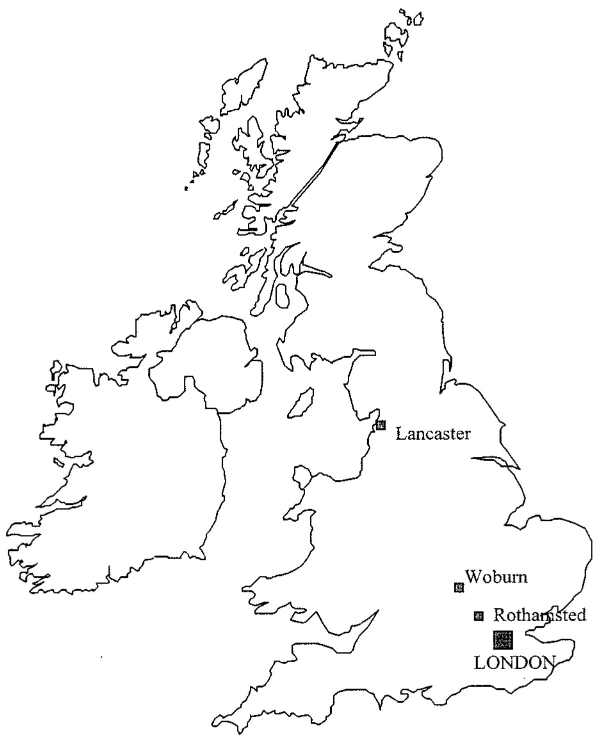

FIGURE 1. Location map of sample sites showing Woburn (soils and herbage collected) and Rothamsted (where Park Grass herbage and Broadbalk soil were collected).

We have been working for a number of years to reconstruct time trends of PCDD/Fs and other organic contaminants, using archived samples of soils and vegetation collected from long-term agricultural experiments in the U.K. (*1, 3*−*7*). This paper extends the data set for PCDD/Fs in the U.K. environment at the sites shown in Figure 1. In addition, a study pertaining to the issue of 'historical' PCDD/Fs is also presented. In this context, it is important to be able to establish whether a sample from the past reflects the environment at that time or whether it has been subject to chemical contamination or alteration since its collection. This could potentially occur during sample storage (a) if the sample is not sealed and comes into contact with 'modern' contaminated air or dust, (b) from contamination associated with the storage medium, (c) or during sampling from the storage vessel and preparation for chemical analysis in the laboratory. Samples of soils collected between 1846 and 1986 from one of the long-term Rothamsted Experimental Station agricultural plots have been analyzed previously and *all* contained the full suite of PCDD/Fs (*6*). However, they were sampled and analyzed before we were as aware of the potential for sample contamination/alteration with trace organics, and there has remained some ambiguity about

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whether some post-collection contamination of the earlier samples had occurred. In a recent review of historical PCDD/F data, we drew attention to the *potential* for sample contamination (*8*). Uncertainties about historical/background concentrations have also confounded attempts to model historical depositional inputs of PCDD/Fs to the U.K. environment (*2*)—namely, whether all PCDD/Fs have entered the environment since the widespread development of the chloroaromatics industry (around the 1930s) or whether some entered the environment prior to this from various combustion sources. The data presented here help to clarify these issues.

Materials and Methods

Archived Samples of Vegetation and Soils. Samples from the Rothamsted collection were obtained from three long-term experiments. Two of these—the Park Grass continuous pasture experiment and the Broadbalk continuous wheat experiment—are both on the Rothamsted site in Harpenden, about 40 km north of central London. They have been described fully in our previous publications (*4*). The third is the Ley Arable experiment, located at Woburn Experimental Station in a semirural site 27 km northwest of Rothamsted (see Figure 1). All the archived soil and herbage samples were collected during two visits to Rothamsted Experimental Station in 1995. Scrupulous attention was paid to cleanliness during subsampling to avoid contamination of the samples with 'modern' dust that had collected on the sealed containers. Subsamples were taken from the Rothamsted collection, transferred into solvent-rinsed storage jars, sealed immediately, and taken to Lancaster University.

Broadbalk. Air-dried and sieved (<2 mm) soil samples collected between 1846 and 1986 from Broadbalk have been analyzed for PCDD/Fs previously by Kjeller et al. (*6*). PCDD/Fs were detected in all these samples, but they would have had contact with modern air during their preparation for analysis. Given the significance of sample contamination due to air contact from an earlier PCB study (*9*), we needed to clarify if a similar effect could result in PCDD/F contamination of soil. The objective here was to analyze a sample from a *previously unopened* jar of soil collected in 1881 (0−23 cm depth) to investigate the possibility of sample contamination in the laboratory. Subsamples were taken very carefully from the center of the glass jar (which contained several kilograms of soil), ensuring that any dust from the top of the jar was removed prior to sampling. One sample was taken and prepared immediately for analysis (the $T = 0$ sample). Further subsamples (10 g) of the soil were transferred to solvent-rinsed aluminum foil trays and spread out as a thin layer (~1−2 mm) to maximize the potential for sample contamination from the modern atmosphere. These were left in a general laboratory at Lancaster University, exposed to the laboratory air for either 1, 2, 4, 8, 16, or 32 days. After these exposure times, each sample was transferred to separate solvent-rinsed glass jars and sealed to await analysis.

Park Grass. The Park Grass experiment, established in 1856, has plots subject to different fertilizers and amendments. The herbage is cut usually twice each year for hay in June and September/October. Annually harvested (unwashed) herbage samples (dried at 80 °C on aluminum trays) have been stored in sealed glass jars or metal tins in the Rothamsted archive. Bulked (5 or 10 year) samples of herbage collected between 1893 and 1986 from this experiment were analyzed for PCDD/Fs previously (*6*). For this study, a herbage sample from the first cut of each year 1980−1994 was subsampled and analyzed for PCDD/Fs to provide a clearer picture of recent atmospheric inputs/trends of PCDD/Fs over a time frame relevant to certain source reduction measures (such as municipal solid waste incineration emission abatement controls and pentachlorophenol usage restrictions).

Woburn. The Ley Arable experiment was established in 1938, originally to test the effect of 3-year grass and lucerne leys on the yields of the following arable crops. Archived surface soils (0−23 cm) were collected in 1957, 1962, 1967, 1972, 1977, 1982, 1987, and 1992 using a semicylinder auger and transferred to plastic bags in the field. Following collection, they were transported to Rothamsted, air-dried on cardboard trays for a few days, ground in a steel roller mill, and sieved to <2 mm prior to storage in paper bags inside boxes.

Rothamsted Dust and Storage Bags. Two samples of dust were collected in July 1996 from two buildings used to store the archived samples at Rothamsted Experimental Station. Both buildings have been used for sample storage since the early 1950s. Dust (~15 g) that had accumulated on the surface of storage shelves was collected. Dust sample A originated from the building containing the majority of the older samples (pre-1960s) while sample B was collected from the building housing more recent samples (1960s onward).

Five representative samples of paper storage bags used to hold the Woburn soil samples were collected in September 1997 from Rothamsted Experimental Station. These represent bags used for soil storage in 1956, 1966, 1967, 1976, and 1986 and do not coincide with the soil collection years 1957, 1962, 1967, 1972, 1977, 1982, 1987, and 1992. A modern paper bag was also extracted for comparative purposes. It was hypothesized that if samples have been significantly contaminated during storage from either dust in the storage building or—in the case of Woburn soil—from the paper bags that held the samples, the congener/homologue profile within the samples should reflect this contamination.

PCDD/F Analysis. During November and December 1995 and in August 1996 the herbage, soil, and dust samples detailed above were transferred to the University of Bayreuth for extraction and analysis. Between 7 and 20 g of herbage and 5−10 g of soil or dust were used for each analysis. Samples of paper storage bags (4−8 g) were analyzed in October 1997 in the PCDD/F laboratory at Lancaster University. Samples were Soxhlet extracted in toluene for 18 h. The toluene was spiked with a mixture of 12 isotopically labeled PCDD/F standards prior to extraction. The extract was reduced to 2 mL on a rotary flask evaporator prior to cleanup. The cleanup was conducted using a mixed H_2SO_4−silica/NaOH−silica column and an alox column. A glass column (30 mm i.d.) filled from the bottom with 9 cm of 33% NaOH-silica, 1 cm of activated silica, 10 cm of 44% H_2SO_4−silica, and 2 cm of 22% H_2SO_4−silica was used for the first step in the cleanup. The extract was applied to the column, and the PCDD/Fs were eluted with 300 mL of *n*-hexane. A second glass column (30 mm i.d.) was filled with 25 g of Al_2O_3 and 20 g of Na_2SO_4 and prewashed with 50 mL of *n*-hexane. After evaporation to 2 mL, the extract was transferred to the column and eluted with the following solvents: 80 mL of benzene (discarded), 200 mL of *n*-hexane/CH_2Cl_2 (98:2) (discarded), and 170 mL of *n*-hexane/CH_2Cl_2 (1:1). The last fraction contained the PCDD/F and was evaporated to 2 mL. An isotope recovery standard was added to the sample directly before it was transferred to a vial and reduced to a volume of 15 μL in toluene. The HRGC/HRMS analysis was conducted on a VG Autospec Ultima using EI ionization at a resolution of 10 000 in selected ion mode. The following parameters were used for the analysis:

(a) Analysis of the Tetra- to Octa-CDD/F Homologue Sums. GC parameters: carrier gas helium; injector 280 °C splitless; temperature 130 °C for 1 min, 20 °C/min to 240 °C, 10 °C/min to 300 °C, hold for 6 min; interface 280 °C; column pressure 10 psi; column DB-5-MS, length 30 m, film thickness 0.10 μm; i.d. = 0.25 mm.

TABLE 1. PCDD/F Exposure Experiment Using Broadbalk 1881 Soil (ng/kg dry wt)[a]

	$t = 0$	$t = 32$	1893 soil[b]	1986 soil[b]	lab blank (pg/g dry wt)
TCDD	0.91	1.2	0.34	1.7	0.18
PeCDD	1.9	1.5	0.97	3.9	0.19
HxCDD	3	3	2.2	8.6	0.12
HpCDD	5.1	5.1	3.2	4.4	0.08
OCDD	18	19	11	25	0.25
TCDF	7	7.1	3.2	9.3	0.19
PeCDF	6.1	6.7	3.5	11	0.07
HxCDF	4	4.3	3.9	9.3	0.11
HpCDF	2.5	2.5	1.9	6	0.06
OCDF	1.1	1.2	1.1	4.6	0.06
$\sum$PCDD/F	50	52	31	84	
2,3,7,8-TCDD	<0.03	<0.04	0.03	0.11	0.01
1,2,3,7,8-PCDD	0.12	0.12	0.09	0.29	<0.01
1,2,3,6,7,8-HxCDD	0.17	0.2	0.1	0.37	0.01
1,2,3,4,7,8-HxCDD	0.17	0.19	0.12	0.62	<0.01
1,2,3,7,8,9-HxCDD	0.22	0.21	0.13	0.48	0.01
1,2,3,4,6,7,8-HpCDD	2.1	2.2	1.5	6.3	0.04
2,3,7,8-TCDF	0.44	0.46	0.29	0.95	0.02
1,2,3,7,8-PCDF	0.63	0.57	0.32	1.1	0.01
2,3,4,7,8-PCDF	0.53	0.52	0.35	0.93	0.01
1,2,3,4,7,8-HxCDF	0.61	0.59	0.43	1.3	0.01
1,2,3,6,7,8-HxCDF	0.41	0.4	0.34	0.82	0.01
1,2,3,7,8,9-HxCDF	<0.08	<0.09	0.01	0.01	<0.01
2,3,4,6,7,8-HxCDF	0.46	0.45	0.54	0.73	0.02
1,2,3,4,6,7,8-HpCDF	1.9	1.8	1.5	4.1	0.02
1,2,3,4,7,8,9-HpCDF	0.1	0.14	0.09	0.38	0.01
$\sum$I-TEQ	0.7	0.71	0.5	1.4	

[a] t = days. See text for details. [b] From ref 6.

(b) Analysis of the 2,3,7,8-Substituted Congeners. GC parameters: carrier gas helium; injector 270 °C splitless; temperature 120 °C for 1 min, 30 °C/min to 200 °C, 2 °C/min to 248 °C, 20 °C/min to 270 °C, hold for 11 min; interface 260 °C; column pressure 35 psi; column RTX 2330, length 60 m, film thickness 0.10 μm; i.d. = 0.25 mm.

Results and Discussion

1881 Soil Sample and the Potential for Its Contamination. The large volume of congener-specific and homologue data generated during this study precludes inclusion of it all; selected data are presented to highlight discussion points in the text. Data from the sample contamination experiment are presented in Table 1. The $\sum$TEQ and individual congener concentrations in the 1881 soil are in excellent agreement with those obtained in a previous study by Kjeller et al. (*6*) in Prof. Christoffer Rappe's laboratory at the University of Umeå. Compound-specific and homologue data from an 1893 soil analyzed by Kjeller et al. (*6*) are compared in Table 1 with the 1881 soil analyzed in Bayreuth. The agreement is within a factor of 2 for all of the 2,3,7,8-substituted PCDD/Fs.

The key findings from this exercise are that (a) the previously unopened bottle of 1881 Broadbalk soil contained a full array of PCDD/Fs or (b) exposure to laboratory air in Lancaster for up to 32 days did not affect the concentrations detected in the samples. Table 1 shows this by a comparison of just the $t = 0$ and $t = 32$ days samples, but the $t = 2$, 4, 8, and 16 day samples are consistent with these.

The 1986 soil data obtained by Kjeller et al. (*6*) and presented in Table 1 show that modern soils contain higher concentrations of PCDD/Fs than a century ago. The homologue profiles for soil collected in 1881 and 1986 are plotted in Figure 2. The striking feature about these data is the similarity in the profile, suggesting perhaps (a) the long-term persistence of PCDD/Fs deposited to the soil many decades ago or (b) similarities in the atmospheric deposition homologue input over time. Clearly, however, the concentrations of PCDD/Fs have increased in the soil from this rural site, with the homologue groups HxCDD, OCDD, and PeCDFs increasing most markedly (see Figure 2). The homologue pattern in this soil is typical of that noted in U.K. soils generally (*10*) and has often been called a 'combustion pattern' with high HxCDD, HpCDD, and OCDD homologues. In short, the data imply that pre-1900 soils had been subject

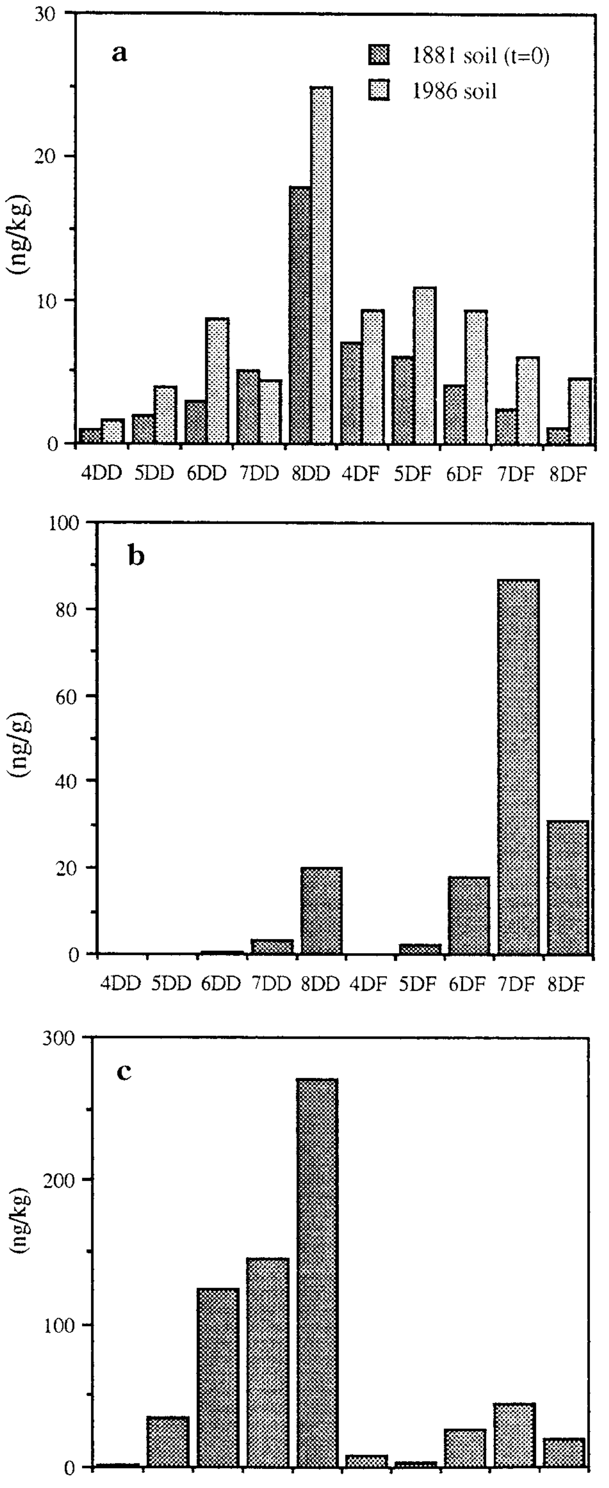

FIGURE 2. Homologue profiles for a) Broadbalk soil (1881 and 1986), (b) indoor dust, and (c) the mean concentration of Rothamsted paper bags used for Woburn soil storage.

TABLE 2. PCDD/Fs in Dust Samples (ng/kg) from Sample Archive Buildings at Rothamsted[a]

homologue	dust sample A	dust sample B
TCDD	120 (0.3)	70 (0.04)
PeCDD	450 (1.1)	220 (0.14)
HxCDD	3,000 (7.3)	670 (0.41)
HpCDD	5,300 (13)	3,300 (2.1)
OCDD	8,000 (19)	20,000 (12)
TCDF	340 (0.8)	160 (0.09)
PeCDF	480 (1.2)	2,300 (1.4)
HxCDF	1,600 (3.9)	18,000 (11)
HpCDF	11,000 (27)	87,000 (54)
OCDF	11,000 (27)	31,000 (19)
∑PCDD/F	41,300	163,000

[a] Values in parentheses represent each homologue as a percentage of ∑PCDD/F.

TABLE 3. Comparison of PCDD/Fs (ng/kg) in a Typical Archived Soil and Average Dust[a]

homologue	typical soil concn	av dust concn	g of dust to double soil
TCDD	0.91	95	9.6
PeCDD	1.9	335	5.7
HxCDD	3	1,835	1.6
HpCDD	5.1	4,300	1.2
OCDD	18	14,000	1.3
TCDF	7	250	28
PeCDF	6.1	1,390	4.4
HxCDF	4	9,800	0.41
HpCDF	2.5	49,000	0.05
OCDF	1.1	21,000	0.05
∑PCDD/F	49.6	102,150	0.49

[a] The mass of dust needed to double the concentrations of 1 kg of soil is also given.

to cumulative inputs of atmospherically derived PCDD/Fs over quite long periods of time (given the concentrations detected), if the assumption that PCDD/Fs present in soil are derived only from atmospheric deposition is correct.

In summary, therefore, the data presented in this section provide strong evidence of the presence of PCDD/Fs in the sealed pre-1900 sample stored in glass. The only potential source of contamination of these samples during handling is therefore considered to be the transfer of small amounts of dust from the outer surface of the glass jar during subsampling. This was considered very unlikely because the jar was scrupulously cleaned prior to opening. However, as a precaution, the dust samples described earlier were analyzed; the results are presented below.

Dust Samples. Results from the analysis of dust samples are given in Table 2. ∑PCDD/F concentrations in the two samples were elevated (~41 000 and ~163 000 ng/kg) and >1000 times higher than for the Broadbalk soil (soils typically contained of the order of 100 ng of ∑PCDD/F kg^{-1}). The dust homologue profile is different from that of the soils and very distinctive (Figure 2b), with the hepta- and octa-CDFs dominating and comprising >50% of the ∑PCDD/F. The dust concentrations and profiles are not typical of Rothamsted soils but reflect a pattern mirrored in other modern indoor dust samples (e.g., refs *11* and *12*). Table 3 shows the amount of dust required to double the concentration of each homologue group in 1 kg of archived soil *if* it were to have been exposed to the dust. In some cases it is relatively small (e.g., 50 mg for HpCDF), and in other cases it is very large (e.g., 28 g for TCDF). These wide ranging values suggest that not even small amounts of dust could have contaminated the sample either during storage or during transfer of the subsample to Lancaster and that dust contamination cannot explain the presence of the full range of homologues/congeners in the soil. The profile in the Rothamsted dust sample may indicate an important PCP source component, perhaps related to treatment of the building timbers in the early 1950s when these old farm buildings, which were converted to army mess rooms during the war, were converted to house the archive. However, we have not been able to confirm any specific use of PCP compounds in the Rothamsted records. In conclusion, therefore, dust contamination is not considered to be a factor influencing the full range of PCDD/Fs present in the sealed 1881 soil sample. As discussed below, it could potentially have influenced the homologue composition of some later samples stored in cardboard boxes/paper.

The presence of PCDD/Fs in the 1881 soil sample is important evidence for their environmental occurrence prior to the widespread development of the chloroaromatics (CA) industry in the 1930s. Our data are not unique in this respect. It is appropriate to briefly review other published data supporting the pre-CA environmental occurrence of PCDD/Fs.

Sediment Cores: the Evidence for pre-1900 PCDD/Fs. There is an increasing body of evidence for the existence of pre-1900 levels of PCDD/Fs in the environment provided by deep sediment core data from both Europe and the United States, although some studies have been ambiguous about these findings (e.g., refs *13* and *14*). Analytical constraints may relate to some of these uncertainties in the form of detection limit improvements that have been made over the last 10−15 years or because of greater appreciation of the need for ultraclean sample handling and preparation procedures required. This highlights the need for strict sampling and analytical protocols using high-resolution instruments that maintain low limits of detection and enable trace concentrations of individual congeners to be reported with confidence. Interestingly, studies that support the existence of PCDD/Fs prior to 1900 have generally used a more sensitive HRGC−MS analytical proceedure (*15*−*18*) than other comparative studies using low-resolution instrumentation (*13*, *14*). It is appropriate to briefly summarize the evidence for pre-1900 PCDD/F concentrations.

U.S. Evidence. Smith and co-workers have published a series of papers on the historical record of PCDD/F deposition preserved in the sediments of northeastern United States (*19*−*21*). Their early work (*19*, *20*) focused on Green Lake in New York State, located in a rural setting with no known sources of local PCDD/F contamination. In the sediment deposited prior to 1900, Smith et al. noted that there was little or no PCDD/F in the Green Lake sediments—values were ≤10 ng/kg. These workers later published a somewhat more detailed account of their data from Green Lake (*20*). Here they noted that PCDD/F "were present in sediment from 1860, although the concentrations were very low". They also adjusted the dating profile, indicating that they now believed the onset of the rise in concentrations commenced after 1916−1923. Later work on the Hudson River (*21*) supported the earlier trend data from Green Lake. The oldest sediment (~1907−1924) contained <1100 ng of ∑PCDD/F kg^{-1}. Recently, in Lake Ontario sediments, Pearson et al. (*14*) measured detectable concentrations in the deepest sediment cores analyzed, dated about 1900, but suggested this may be a function of "core-specific bias".

European Studies. Kjeller and Rappe (*18*) obtained a laminated marine core from the Baltic Proper, off the coast of Sweden. The core was sliced into nine dated disks (average dates 1882, 1906, 1922, 1938, 1954, 1962, 1970, 1978, and 1985). PCDD/Fs were detected in all the 1882−1962 slices at 92−234 ng of ∑PCDD/F kg^{-1} and did not increase until the 1970−1985 slices (520−1800 ng/kg). Vartiainen et al.

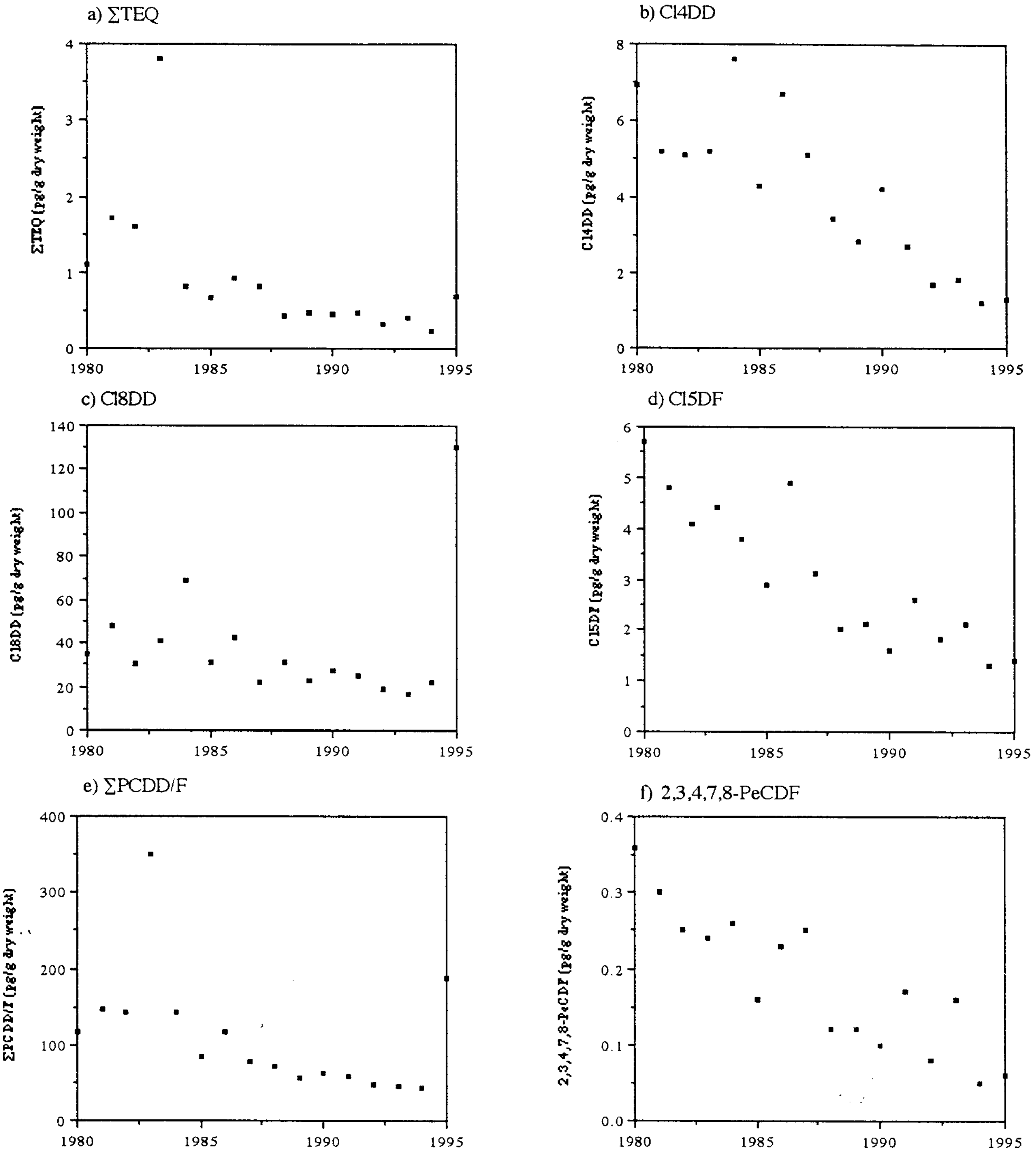

FIGURE 3. Selected congener specific and homologue data for Park Grass herbage samples.

(*22*) presented data from two small sub-Arctic lakes in Lapland, northern Finland. The trends noted here were similar to those reported by Kjeller and Rappe (*18*), with extremely low (2−20 ng of PCDD/F kg^{-1}) concentrations between 1880 and 1965. Recently, Jütter et al. (*15*) reported a wide range of PCDD/Fs in sediment slices deposited in the 17th and 18th century in lakes in the Black Forest, Germany. PCDD/F concentrations were also reported in cores from Lake Stechlin, Germany, prior to 1913 (*16*). The only U.K. data published to date that reports measured concentrations in pre-1900 sediments is that of Rose et al. (*17*) for remote lakes in Scotland. Low concentrations of PCDD/Fs were measured in sediments dated from the early to mid-1800s. Hashimoto et al. (*23, 24*) present data from Japanese sediments, reporting the presence of PCDDs in deep samples, dated over many thousands of years old.

Summary Comments on the Pre-1900 Occurrence of PCDD/Fs. The balance of evidence from both the Rothamsted archived soil and the recent literature supports the existence of PCDD/Fs in the environment before the widespread development of the CA and chlorine industry during this century. In this context, it is important to remember that the U.K. has a long industrial history, involving combustion activity in the form of wood and coal burning. For example, over 65 million ton of coal was being burned each year nationally in the 1850s (*3*). The smelting of metals and the production of iron and steel also have a long history in the U.K. and Europe, processes known to have significant

TABLE 4. PCDD/F Concentrations (pg/g dry weight) in Selected Archived Herbage from the Park Grass Experiment

	1980	1985	1988	1990	1992	blank[a]
TCDD	6.9	4.3	3.4	4.2	1.7	0.97
PeCDD	8.5	11	5.7	2.6	1.9	1.1
HxCDD	21	12	7.4	5.1	3.2	0.93
HpCDD	15	12	12	9.8	8.2	2.2
OCDD	35	31	31	27	19	4.7
TCDF	11	4.5	3.5	4.3	3.1	1.5
PeCDF	5.7	2.9	2	1.6	1.8	1
HxCDF	5.2	2.7	2.1	1.9	2.5	0.74
HpCDF	5.3	2.9	2.5	3.7	3.8	0.8
OCDF	3.1	1.3	1.3	2.2	1.8	0.74
ΣPCDD/F	117	85	71	62	47	15
2,3,7,8-TCDD	<0.04	<0.06	<0.03	<0.05	<0.05	<0.07
1,2,3,7,8-PCDD	0.18	0.11	0.08	0.05	0.06	0.05
1,2,3,6,7,8-HxCDD	2.3	1.6	0.76	0.55	0.25	0.03
1,2,3,4,7,8-HxCDD	0.22	0.14	0.1	0.06	0.07	0.03
1,2,3,7,8,9-HxCDD	1.3	0.86	0.37	0.32	0.13	0.03
1,2,3,4,6,7,8-HpCDD	7.1	5.5	5.8	5.2	4.1	1.3
2,3,7,8-TCDF	0.49	0.39	0.21	1	0.29	0.16
1,2,3,7,8-PCDF	0.44	0.18	0.15	0.08	0.13	0.1
2,3,4,7,8-PCDF	0.36	0.16	0.12	0.1	0.08	0.12
1,2,3,4,7,8-HxCDF	0.48	0.2	0.14	0.12	0.12	0.08
1,2,3,6,7,8-HxCDF	0.39	0.18	0.12	0.09	0.13	0.03
1,2,3,7,8,9-HxCDF	<0.09	<0.05	<0.05	<0.03	<0.05	<0.08
2,3,4,6,7,8-HxCDF	0.49	0.24	0.19	0.13	0.16	0.24
1,2,3,4,6,7,8-HpCDF	3.4	1.8	1.5	1.6	1.9	0.31
1,2,3,4,7,8,9-HpCDF	0.21	0.08	0.07	0.07	0.07	0.05
ΣI-TEQ	1.1	0.68	0.44	0.46	0.33	

[a] Blank units = pg/sample.

PCDD/F emissions. It is important to remember that the history of PCDD/F environmental inputs/burdens in the U.K. and Europe may therefore not be mirrored in other regions of the world.

Other Trend Data at Rothamsted. (a) Park Grass Herbage. Selected congener and homologue Park Grass annual herbage data are plotted in Figure 3 and given in Table 4. Given that these samples have been stored in either glass or sealed metal tins, we can be confident of their integrity. The ΣPCDD/F and ΣTEQ concentrations generally decline by a factor of 3−4 over the 15 years. For example, the ΣPCDD/F (and ΣTEQ concentrations) average 136 (1.5) ng/kg in 1980−1982 and 45 (0.44) ng/kg in 1993−1994. This is good evidence for a general improvement in air quality because grass concentrations reflect air concentrations/deposition fluxes (*17*), supporting the general trends found in long-term bulked grass analyzed from this experiment by Kjeller et al. (*1*) and—more recently—for measured air concentrations from a long-term U.K. air monitoring program (*7*). Some constituents in the herbage show quite clear and consistent declines, e.g., the TCDD and PeCDF homologue groups (see Figure 3). Other constituents are influenced by some highly erratic data points. For example, the OCDD concentration of the 1995 sample was 130 ng/kg, while for all the other years it was between 17 and 69 ng/kg. The 1983 sample was also strongly influenced by a spurious HxCDD signal. The 1,2,3,6,7,8-HxCDD:1,2,3,4,7,8-HxCDD ratio was highly variable through the time series, as in the soils from Woburn (see Table 5).

(b) Woburn Soil Trends. Soils from another long-term experimental site at Woburn have been analyzed for PCDD/Fs to compare with trends already seen in the Broadbalk (see ref *6*) soil series. As noted earlier, however, these soils were stored differently from those at Broadbalk—in paper bags and cardboard boxes. The Woburn soils data are presented in Table 5. There is evidence for an increase in the concentrations of PCDD/Fs in the soils between 1957 and 1992 (see Table 5). The ΣTEQ increased from 1.1 ng/kg in 1957 to 1.5 ng/kg in 1992, in line with the Rothamsted data from the Broadbalk experiment (*6*). In general, the congeners/homologues that showed the greatest increase between 1957 and 1992 are HxCDD, HpCDD, and OCDD. There is some noise in the data; notably, the sample from 1967 is consistently lower across the PCDD/Fs than other samples,

TABLE 5. PCDD/F Concentrations (ng/kg dry weight) in Archived Soils from the Woburn Ley Arable Experiment

	1957	1962	1967[a]	1972[a]	1977[a]	1982	1987	1992	blank 1[b]	blank 2[c]	blank 3[d]
TCDD	2.7	3.3	2.7 (3.0)	4.6 (4.2)	4.3 (4.5)	6	5.8	4.6	0.45	1	0.09
PeCDD	3.8	3.9	3.3 (4.2)	5.6 (5.3)	7.6 (7.5)	13	7.5	5.9	1.3	1.1	0.13
HxCDD	6	6.9	5.5 (6.0)	14 (13)	15 (15)	17	11	9.8	0.86	0.66	0.08
HpCDD	7.5	9.4	7.6 (8.7)	10 (10)	13 (13)	14	16	14	1	1.8	0.06
OCDD	14	18	16 (18)	17 (17)	25 (28)	28	40	32	2.2	6	0.21
TCDF	12	14	13 (14)	22 (23)	16 (17)	13	16	17	1.3	1.5	0.11
PeCDF	7.8	8.2	7.4 (8.8)	9.4 (9.3)	9 (10)	8.8	9.2	9.8	1.3	1.3	0.09
HxCDF	5.9	7.3	6.5 (6.9)	7.9 (7.9)	8.5 (8.5)	8.3	8.2	8.6	0.86	0.83	0.08
HpCDF	4.6	5.6	4.6 (4.5)	5.7 (5.7)	7 (6.5)	6.4	6.8	7.1	0.34	0.63	0.04
OCDF	3.5	3.4	2.8 (3.0)	3.5 (3.4)	4.3 (4.1)	4	4.2	4.5	0.81	0.6	0.05
ΣPCDD/F	67.8	80.0	69.4	99.7	110.0	118.5	124.7	113.3	10.4	15.4	0.9
2,3,7,8-TCDD	<0.04	<0.07	<0.05 (<0.05)	<0.11 (<0.11)	<0.09 (<0.09)	<0.1	<0.08	<0.07	0.03	0.04	0.01
1,2,3,7,8-PCDD	0.21	0.23	0.19 (0.2)	0.27 (0.26)	0.29 (0.31)	0.29	0.3	0.29	0.03	0.02	0.01
1,2,3,6,7,8-HxCDD	0.48	0.56	0.44 (0.54)	1.4 (1.4)	1.5 (1.4)	1.7	0.95	0.82	0.05	0.08	<0.01
1,2,3,4,7,8-HxCDD	0.37	0.35	0.35 (0.35)	0.31 (0.37)	0.47 (0.34)	0.47	0.52	0.51	0.11	0.05	<0.01
1,2,3,7,8,9-HxCDD	0.66	0.65	0.65 (0.63)	1.2 (1.2)	1.3 (1.4)	1.4	1.1	0.93	0.02	0.03	<0.01
1,2,3,4,6,7,8-HpCDD	4.6	5.2	4.4 (4.7)	5.7 (5.8)	7.5 (7.3)	7.8	9.4	8.1	0.65	1.1	0.04
2,3,7,8-TCDF	0.55	0.86	0.47 (0.62)	1.1 (1.2)	1.1 (1.2)	1.1	1	0.86	0.15	0.17	0.01
1,2,3,7,8-PCDF	0.87	0.97	0.75 (0.83)	1.1 (1.1)	1 (1.2)	1	1.1	1.2	0.06	0.09	0.01
2,3,4,7,8-PCDF	0.7	0.69	0.58 (0.62)	0.84 (0.80)	0.84 (0.84)	0.81	0.89	0.94	0.14	0.13	0.01
1,2,3,4,7,8-HxCDF	0.77	0.89	0.72 (0.77)	0.97 (0.88)	0.94 (1.0)	0.99	1.1	1.1	0.03	0.05	<0.01
1,2,3,6,7,8-HxCDF	0.55	0.62	0.52 (0.52)	0.65 (0.6)	0.65 (0.68)	0.72	0.72	0.77	0.04	0.03	<0.01
1,2,3,7,8,9-HxCDF	<0.25	<0.22	<0.22 (<0.24)	<0.26 (<0.22)	<0.25 (<0.3)	<0.28	<0.27	<0.33	<0.04	<0.01	<0.01
2,3,4,6,7,8-HxCDF	0.64	0.64	0.57 (0.57)	0.73 (0.67)	0.76 (0.83)	0.82	0.83	0.92	0.31	0.19	0.02
1,2,3,4,6,7,8-HpCDF	3.4	3.7	3 (3.1)	3.6 (3.6)	4.3 (4.4)	4.3	4.7	4.9	0.19	0.3	0.01
1,2,3,4,7,8,9-HpCDF	0.23	0.24	0.19 (0.2)	0.28 (0.28)	0.28 (0.31)	0.31	0.37	0.37	0.06	0.05	0.01
ΣI-TEQ	1.1	1.2	1 (1)	1.5 (1.5)	1.6 (1.6)	1.6	1.6	1.5	0.21	0.2	0.03

[a] Numbers in parentheses represent results of sample re-analysis. [b] Blank 1 = for samples 1957−1977 (pg/sample). [c] Blank 2 = for samples 1982−1992 (pg/sample). [d] Blank 3 = pg/g dry weight.

TABLE 6. PCDD/Fs in Paper Bag Samples (ng/kg) from the Woburn Soil Archive at Rothamsted[a]

homologue	1956	1966	1967	1976	1986	1997
TCDD	0.8	0.5	0.6	4.7	2.0	0.4
PeCDD	nd[b]	nd	1.7	132	37.2	nd
HxCDD	31.1	165	3.1	928	79.1	13.0
HpCDD	6.1	290	34.0	320	75.5	18.4
OCDD	16.6	396	91.2	738	115	31.0
TCDF	1.3	12.0	4.0	12.8	8.2	0.2
PeCDF	0.9	4.9	2.1	6.1	5.7	0.0
HxCDF	6.3	46.3	9.6	60.7	4.3	0.1
HpCDF	10.3	60.9	19.9	124	4.6	0.8
OCDF	4.5	12.0	9.5	66.8	3.6	2.4
$\sum$PCDD/F	78	988	176	2393	335	66

[a] The 1997 sample is a contemporary bag from Rothamsted.

suggestive of a sampling artifact. Other irregularities were observed, particularly a different isomer pattern for the TCDDs and PeCDDs in the 1982 sample. Given the stability and persistence of PCDD/Fs in soils (*16*) and the dominance of higher chlorinated PCDD/Fs in indoor dust (see earlier), it was considered that these differences could be due to sample contamination, either during sample collection or during drying. The possibility of sample contamination via the paper storage bags was therefore investigated.

(c) Paper Storage Bag Samples. Results from the analysis of paper bag samples are given in Table 6. $\sum$PCDD/F concentrations in the five archived bags showed a wide range (~80 and ~2400 ng/kg) and were between 1 and ~20 times higher than the Woburn soils (between 70 and 125 ng of $\sum$PCDD/F kg^{-1}). The paper homologue profiles contained high proportions of HxCDD, HpCDD, and OCDD. The pattern is more representative of the soil itself than the indoor dust. Samples of paper from 1966 and 1976 also contain elevated concentrations of HxCDDs and HxCDFs (between ~20% and 40% of the $\sum$PCDD/F concentration). Of course, it is not clear if the bags themselves could be influenced by the soil concentrations or vice versa. Presumably PCDD/Fs in one matrix could potentially transfer to the other in close proximity to it to approach an equilibrium controlled essentially by the PCDD/F:paper fiber and the PCDD/F:soil organic matter partition coefficients. Soil contamination from the bags themselves could have arisen as a result of both contact with the bag and disintegration of the paper material itself. If a "worst case" paper bag $\sum$PCDD/F concentration is assumed (2400 ng/kg), then only between 2 and 5 wt % of such a bag would have to transfer into the soil inside it to then double the soil $\sum$PCDD/F concentration, given that each bag would typically contain ca. 400 g of soil. Table 7 shows the amount (ng) of degraded paper bag required to double the concentration of each homologue group in soil contained in a bag. The most contaminated and least contaminated paper bag and its corresponding soil have been used for comparative purposes.The amount needed varies for different homologues. In some cases the amount is relatively small (e.g., 0.81 g for HxCDD) and in other cases very large (e.g., up to 60−460 g for TCDF). These wide ranging values suggest that for certain homologues (notably HxCDD, HpCDD, and OCDD) even small amounts of paper could potentially have contaminated the sample either during storage or during subsampling of the bag contents. The integrity of certain congeners in the soil samples (notably TCDD, TCDF, PeCDF) is confirmed by their very low concentrations in the paper bag samples. No visible evidence of degradation of the paper bag was observed at the time of sampling. In summary then, these results suggest that soil archived in paper bags *could* become contaminated from the paper storage medium over time and that these samples are more likely to be compromised by post-collection contamination than those stored in glass containers. It is stressed, however, that this evidence does not affect the issue of PCDD/Fs found in pre-1900 samples since all these older samples have been stored sealed in glass.

Concluding Remarks. The integrity of the Broadbalk soil collection and the herbage samples stored in sealed glass jars is demonstrated by this study. This allows us to state with a high degree of confidence that PCDD/Fs were present in the U.K. environment in the late 1800s at readily detectable levels in soils. This is not surprising given the reliance on coal and wood combustion for energy at that time and the widespread smelting of a variety of metals. Furthermore, the Broadbalk soil data set shows that the soil has acted as a sink for atmospherically derived PCDD/Fs in recent decades (*2*), with certain homologue groups/compounds slowly increasing in concentration. This implies, of course, that the net rate of deposition has exceeded the net rate of disappearance for PCDD/Fs in these semirural/rural locations. However, the rates of change are slow and can only be detected in soils from known plots that have been carefully managed and sampled for long periods of time. In contrast, the recent (1984−1994) herbage samples show clear evidence of declining atmospheric concentrations of PCDD/Fs in recent years, in line with other air samples and atmospherically impacted media. Storage of other samples from the Woburn collection in paper bags/cardboard boxes could have potentially compromised the historical record of some homologues (notably HxCDD, HpCDD, and OCDD) but not others (notably TCDD, TCDF, and PeCDF). This draws attention to the need to consider sample storage issues in maintaining the integrity of environmental samples used for trace organic analysis. In addition, more complete sets of environmental media should be analyzed before definitive observations can be made.

TABLE 7. Mass of Paper from Most Contaminated (1976) and Least Contaminated (1956) Bags Needed To Double the Concentrations of PCDD/F Homologues in Soil Contained within a Given Bag

homologue	total mass of PCDD/F in the 1976 bag (ng)	total mass of PCDD/F in the 1977 soil (ng)	g of bag to double soil	total mass of PCDD/F in the 1956 bag (ng)	total mass of PCDD/F in the 1957 soil (ng)	g of bag to double soil
TCDD	37.6	1720	45.74	6.40	1080	168.75
PeCDD	1056	3040	2.88	0.00	1520	nd
HxCDD	7424	6000	0.81	248.80	2400	9.65
HpCDD	2568	5200	2.02	48.80	3000	61.48
OCDD	5904	10000	1.69	132.80	5600	42.17
TCDF	104	6400	61.54	10.40	4800	461.54
PeCDF	48	3600	75.00	7.20	3120	433.33
HxCDF	488	3400	6.97	50.40	2360	46.83
HxCDF	984	2800	2.85	82.40	1840	22.33
OCDF	536	1720	3.21	36.00	1400	38.89

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