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Confirmation of the presence of PCDD/Fs in UK soils prior to 1900

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Abstract
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 ploughed 0-23 cm depth layer) contained 0.7 ng ΣTEQ/kg with the Cl8DD, Cl7DD and Cl5DF homologs dominating. There was no change in the ΣPCDD/F composition of the soils 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 fertilisers or amendments) now contains 1.4 ng ΣTEQ/kg, an increase resulting from cumulative atmospheric deposition of PCDD/Fs retained in the surface layers of the soil.

Introduction

Because of concerns over their toxicological significance, considerable effort and money has been expended in many industrialised countries to identify the most important sources of PCDD/Fs 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 and media, to place current burdens/concentrations in context, to assess whether exposure in 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.

In a recent review of historical PCDD/F data we drew attention to the potential for sample contamination in our data and that reported by other workers (1). This also resulted in uncertainties when we attempted to model historical depositional inputs of PCDD/Fs to the UK 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.

We have been working for a number of years to re-construct time trends of PCDD/Fs and other organic contaminants, using archived samples of soils, vegetation and air filters collected from long-term agricultural experiments and measurement programmes in the UK (e.g. 3,4,5). This paper extends the dataset for PCDD/Fs in the UK environment.

Materials and Methods

Archived samples of soils

Air-dried and sieved (<2 mm) soil samples collected between 1846 and 1986 from Broadbalk have been analysed for PCDD/Fs previously by Kjeller et al. (4). PCDD/Fs were detected in all these samples, but they would have had contact with modern air during their preparation for analysis. Given the potential for sample contamination due to air contact noted in an earlier PCB study (6), we needed to clarify if a similar effect could result in PCDD/F contamination of soil. The objective here was to use a sample of a previously unopened jar of soil collected in 1881 (0-23 cm depth) to investigate the possibility of sample contamination in the laboratory. A sub-sample was taken very carefully from the jar, after ensuring 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 sub-samples (10 g) of the soil were transferred to solvent rinsed aluminium foil trays and spread out as a thin veneer, to maximise the potential for sample contamination. 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 they were transferred to solvent rinsed glass jars and sealed, awaiting analysis.

Rothamsted dust

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) which 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 1950s) while sample B was collected from a sample area containing more recent samples (1950s onwards). It was hypothesised that if samples have been significantly contaminated during storage, the congener profile within the samples should reflect this contamination.

PCDD/F analysis

During November and December 1995 and in August 1996 the samples detailed above were transferred to the University of Bayreuth for extraction and analysis. Between 5-10 g of soil and 0.1g of dust was used for each analysis. The samples were Soxhlet extracted in toluene for 18 hours. The toluene was spiked with a mixture of 12 isotopically labelled PCDD/F standards prior to extraction. The extract was reduced to 2 ml on a rotary flask evaporator prior to clean-up. The clean-up 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 33% NaOH-silica, 1 cm activated silica, 10 cm 44% H_2SO_4-silica and 2 cm 22% H_2SO_4-silica was used for the first step in the clean-up. The extract was applied to the column and the PCDD/Fs were eluted with 300 ml n-hexane. A second glass column (30 mm i.d.) was filled with 25 g Al_2O_3 and 20 g Na_2SO_4 and pre-washed with 50 ml n-hexane. After evaporation to 2 ml the extract was transferred to the column and eluted with the following solvents: 80 ml benzene (discarded), 200 ml n-hexane/CH_2Cl_2 (98:2) (discarded) and 170 ml 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 ionisation at a resolution of 10,000 in selected ion mode.

Results and Discussion

The 1881 soil sample and the potential for its contamination

Data from the sample contamination experiment are presented in Table 1. The ΣTEQ and individual congener concentrations in the 1881 soil are in excellent agreement with those obtained in the previous study by Kjeller et al. (4) for Broadbalk soil. The Kjeller et al. data was obtained in Prof. Christoffer Rappe's laboratory at the University of Umeå, whilst these data were obtained at the University of Bayreuth. Compound-specific data from an 1893 soil analysed by Kjeller et al. (4) are compared in Table 1 with the 1881 soil analysed in Bayreuth. There is good agreement (within a factor of 2) for all of the 2,3,7,8-substituted PCDD/Fs.

The key findings are that: 1). the previously unopened bottle of 1881 Broadbalk soil contained

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a full array of PCDD/Fs; 2). 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.

Table 1: PCDD/F concentrations in Broadbalk soil - ng/kg dry weight (see text for details)

	T=0	T=32	1893 soil*	1986 soil*	lab blank
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
OCDD	18	19	11	25	0.25
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
OCDF	1.1	1.2	1.1	4.6	0.06
I-TEQ	0.7	0.71	0.5	1.4	

* from Kjeller et al., 1991

The 1986 soil data obtained by Kjeller et al. (4) and presented in Table 1 clearly show that modern soils contain higher concentrations of PCDD/Fs than a century ago. The homolog profiles for soil collected in 1881 and 1986 are plotted in Figure 1. The striking feature about this data is the similarity in the profile, suggesting perhaps a). the long-term persistence of PCDD/Fs deposited to the soil many decades ago; b). similarities in the atmospheric deposition homolog input over time. Clearly, however, the concentration of PCDD/Fs have increased in the soils at this rural site, with the homolog groups Cl8DD, Cl6DD, and Cl5DF increasing most markedly (see Figure 1). The homolog pattern in this soil is typical of that noted in UK soils generally (7) and has often been called a 'combustion pattern' with high Cl6DD, Cl7DD and Cl8DD homologs. This implies that pre-1900 soils had been subject to cumulative inputs of atmospherically-derived PCDD/Fs over time.

Although there have been some observations of PCDD/Fs found prior to 1900 within deep sediment layers (e.g. 8, 9), studies have often been ambiguous in their interpretation of these findings (9). Recently however, Jütter et al., (10) have reported a wide range of PCDD/Fs in sediment slices deposited in the 17th and 18th century. Unlike a surface soil, sediment cores used to study time trends do not reflect <u>cumulative</u> deposition over a long timescale in a thin layer of sediment, but in successive layers of 'new' deposition; consequently sediment concentrations of individual PCDD/F congeners may be below the analytical limit of detection in individual sediment 'slices'.

<u>The dust samples</u>
ΣPCDD/F concentrations in the two samples were elevated (~41,000 and ~163,000 ng/kg) and

>1000 x higher than for the Broadbalk soil (soils typically contained of the order of 100 ng ΣPCDD/F/kg). The dust homolog profile is different from that of the soils and very distinctive (Figure 1), with the hepta- and octa-CDFs dominating and comprising >50% of the ΣPCDD/F.

Figure 1:Homolog profiles for Broadbalk soil (1881 and 1986) and indoor dust (note differences in the concentration units)
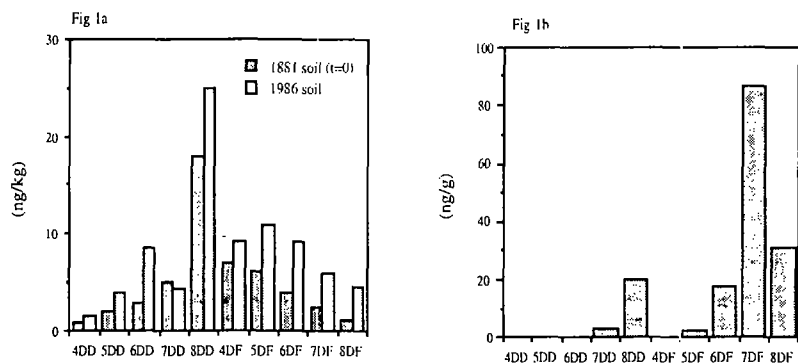

Table 2 shows the amount of dust which would be required to double the concentrations of each homolog group in a kg of archived soil if it were to have been exposed to it. In some cases it is relatively small (e.g. 50 mg for Cl7DF) and in other cases very large (e.g. 28 g for Cl4DF). However, we stress that we believe that even the smallest amounts could not have been incorporated into the sealed jar during storage or have transferred into the sub-sample taken to Lancaster.

Table 2: A comparison of PCDD/Fs (ng/kg) in a typical archived soil, average dust and the mass of dust needed to double the concentration in 1 kg of soil.

Homolog Group	Typical soil conc.	Average dust conc.	g of dust to double soil
ΣCl4DD	0.91	95	9.6
ΣCl5DD	1.9	335	5.7
ΣCl6DD	3	1,835	1.6
ΣCl7DD	5.1	4,300	1.2
Cl8DD	18	14,000	1.3
ΣCl4DF	7	250	28
ΣCl5DF	6.1	1,390	4.4
ΣCl6DF	4	9,800	0.41
ΣCl7DF	2.5	49,000	0.05
Cl8DF	1.1	21,000	0.05
ΣPCDD/F	49.6	102,150	

The distinctive dust congener profile confirms our earlier assertion that the sealed archived soil discussed above has not been contaminated with PCDD/Fs during storage because it is very

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different from that seen in the soil. These findings support the view that soil in sealed glass containers at Rothamsted has maintained its integrity during storage. These results provide valuable information with which to further reconstruct changing PCDD/F environmental burdens in the UK (2). Indeed, they point to important PCDD/F sources to the environment prior to the widespread development of the chloroaromatics and chlorine industry.

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