

# Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P286

## PCDD/Fs in Archived Historical Soils

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### Introduction

Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) are widespread persistent contaminants released into the environment in low concentrations from various processes (1). Several studies with dated sediment cores have shown that PCDD/F concentrations have greatly increased since 1913-1927 (1,2,3,4). Soil studies have also shown this trend (5), which is largely attributed to an increase in combustion sources and the chlorinated chemical industry. Other accepted sources of PCDD/Fs have been established for many centuries, however there is a lack of historical data for environmental levels of PCDD/Fs. This study presents homologue and congener concentrations from surface soils (0-23cm) from the mid-1800s to 1913 and a soil core from 1893.

### Materials and Methods

Archived Soil Samples. Rothamsted Experimental Station has been conducting agricultural research since the 1840's. The samples analysed in this study were collected from two of their long-term "Classical" experiments, the Broadbalk continuous wheat study and the Hoosfield barley experiment at the Rothamsted farm. Soil was also collected from a woodland adjacent to the Broadbalk agricultural experiment. Samples were air dried and sieved at the time of collection and then stored in glass jars stoppered with cork plugs. In the late 1980's subsamples were removed from the jars, milled to a fine powder and a small amount used for metals analysis (6). The remainder of each milled sample was stored either in glass jars, paper bags or in plastic bags in a closed cupboard since milling. A subsample of one soil (1856) was removed in 1994 for PCDD/F analysis (5). The entire contents of each bag were taken for the current study.

The issue of post-collection contamination is clearly important in studies of this type (7,8). Potential contamination of these samples have been discussed in Alcock *et al.* (9).

PCDD/F Analysis. Between 45 and 100g of sample was taken and spiked with a standard containing 20 <sup>13</sup>C<sub>12</sub> PCDD/Fs. The spiked sample was soxhlet extracted in toluene for 18 h. The cleanup procedure consisted of a multi-layered column containing activated silica, 33% 1N NaOH-silica and 44% H<sub>2</sub>SO<sub>4</sub>-silica followed by fractionation from interfering organochlorine compounds on an alumina column. An injection standard containing <sup>37</sup>Cl<sub>4</sub> 2378-TCDD was added and the sample was analysed by HRGC-HRMS on HP5-ms and SP2331 capillary columns.

The above method was validated by analysing a soil four times and checking recoveries of spiked soils. The replicated soil gave RSDs of 2 to 9%. The spiked soils gave recoveries of 78-125% for congeners spiked between 2% and 2000% of their natural concentrations.

### Results and Discussion

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Table 1 shows the congener data for the archived surface soils, soil core and the lab blank. The lab blank gives significantly lower levels than were found in the samples.

**Table 1 Concentrations of PCDD/Fs in Archived Soil Samples (pg/g)**

YEAR DEPTH(cm)	1856 0-23	1881 0-23	1904 0-23	1913 0-23	1893 0-23	1893 23-46	1893 46-69	1893 231-251	Blank
2,3,7,8-TCDF	0.56	0.45	0.50	1.54	0.50	0.24	0.15	0.11	0.001
1,2,3,7,8-PeCDF	0.76	0.60	0.68	1.18	0.48	0.07	0.05	0.04	0.001
2,3,4,7,8-PeCDF	0.62	0.53	0.65	0.91	0.49	0.06	0.04	0.02	0.001
1,2,3,4,7,8-HxCDF	0.74	0.66	0.81	1.08	0.64	0.07	0.05	0.02	0.004
1,2,3,6,7,8-HxCDF	0.52	0.47	0.64	0.82	0.48	0.05	0.04	0.02	0.004
1,2,3,7,8,9-HxCDF	0.03	0.03	0.06	0.09	0.03	0.01	0.02	0.01	0.001
2,3,4,6,7,8-HxCDF	0.50	0.50	0.66	0.76	0.49	0.05	0.04	0.02	0.002
1,2,3,4,6,7,8-HpCDF	1.75	1.89	2.37	3.34	1.94	0.39	0.42	0.30	0.001
1,2,3,4,7,8,9-HpCDF	0.17	0.13	0.18	0.32	0.18	0.02	0.01	0.01	0.000
OCDF	1.16	1.21	1.51	3.31	1.52	0.15	0.20	0.17	0.003
2,3,7,8-TCDD	0.03	0.03	0.04	0.07	0.04	0.03	0.02	0.03	0.003
1,2,3,7,8-PeCDD	0.15	0.15	0.20	0.31	0.14	0.06	0.06	0.10	0.001
1,2,3,4,7,8-HxCDD	0.17	0.14	0.24	0.32	0.18	0.09	0.09	0.13	0.003
1,2,3,6,7,8-HxCDD	0.16	0.19	0.36	0.50	0.37	0.31	0.25	0.52	0.003
1,2,3,7,8,9-HxCDD	0.18	0.23	0.32	0.46	0.26	0.22	0.25	0.48	0.004
1,2,3,4,6,7,8-HpCDD	1.52	2.47	3.13	4.06	2.09	2.36	3.15	5.68	0.003
OCDD	10.7	14.0	21.9	23.6	10.3	23.0	67.1	121.1	0.029
ΣPCDD/F	45	51	63	84	43	39	83	150	0.055
ΣTEQ	0.79	0.73	0.94	1.4	0.73	0.25	0.27	0.41	0.003

\*blank equivalent to the amount of sample taken.

There is a lack of historical soil data available with which to compare the results obtained here so sediments dating from the mid-1800s to early 1900s have also been drawn upon (2-5,10). Table 2 presents these results and shows that the levels of ΣPCDD/Fs rise through the years presented here. The results of this study are in good agreement with this.

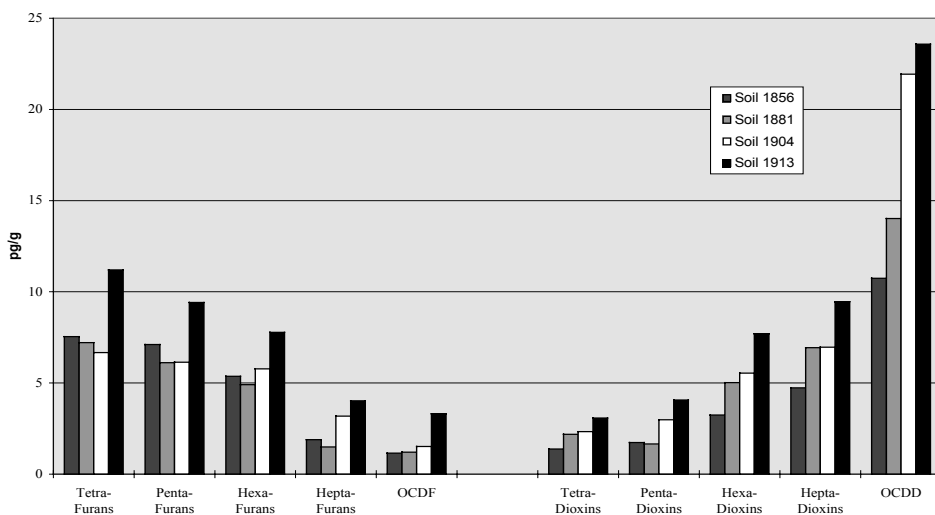
Figure 1 shows the homologue concentrations for the surface soils. The patterns are consistent with one another and resembles that of modern day UK air (11). Although the homologue patterns resemble modern day air it is unlikely that they arose from modern day contamination. Each soil sample would need to have absorbed the entire PCDD/F burden of  $\sim 100\text{m}^3$  to produce the measured concentrations. Furthermore the patterns are different to those seen in the soil core sections, although all samples have been handled similarly.

**Table 2 Comparison of ΣPCDD/Fs in historical samples**

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Year	$\Sigma$ PCDD/Fs(pg/g)	Matrix	Reference
1856	31	Soil	Kjeller L-O, et al,1991 (5)
1865 -1872	9	Sediment	Bruckmeier B.F.A.et al,1997 (3)
1878 - 1884	30	Sediment	Bruckmeier B.F.A.et al,1997 (3)
1882 -1962	92-234	Sediment	Kjeller and Rappe, 1995 (10)
1893	31	Soil	Kjeller L-O, et al,1991(5)
1907 - 1924	<1100	Sediment	Smith R.M. et al, 1992 (4)
1911 - 1918	121	Sediment	Bruckmeier B.F.A.et al,1997 (3)
1913 - ??	451	Sediment	Schramm K.W. et al, 1997 (2)
1927 - 1913	1508	Sediment	Schramm K.W. et al, 1997 (2)

Figure 2 shows the normalised profile of the four sections of soil core. This shows each homologue group decreasing with depth except for the HpCDD and OCDD. The HpCDDs and OCDD rise markedly in the two deepest core segments with 80% of the tetra- to octa-furans and dioxins being made up of OCDD. The overall effect is a smooth change of pattern from the surface to the deep core segment.



**Figure 1. Homologue Concentrations in Surface Soils**

High HpCDD and OCDD levels also cause the  $\Sigma$ PCDD/F to increase with the depth of the soil. This could be due to a variety of reasons such as historical exposure, percolation(migration) or manual disturbance. However none of these are satisfactory explanations. The depth of the deepest core section (2.3m) is such that it may never have been exposed to the atmosphere. Percolation by

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OCDD is unlikely and the site was chosen because manual disturbance had never occurred. Further investigations are underway to replicate and elucidate these findings.

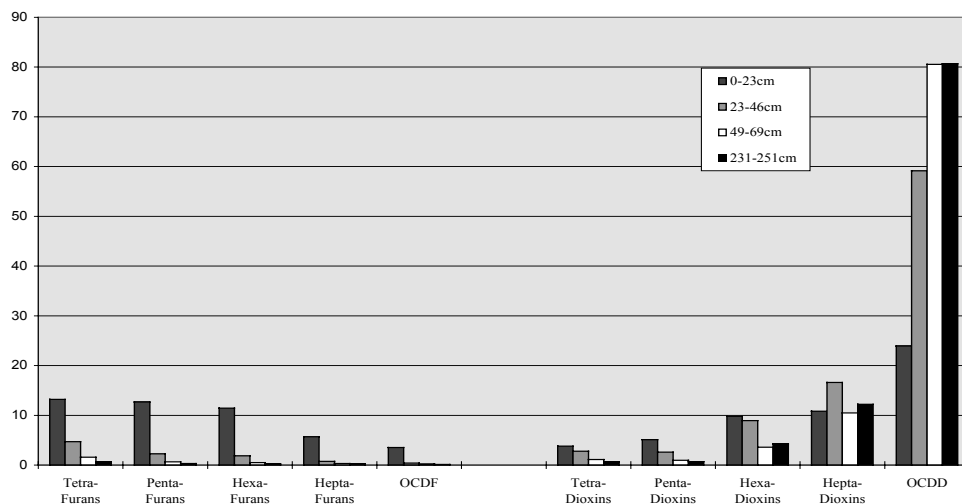


Figure 2. Normalised Pattern of Soil Core Sections

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