

# Dioxin '97, Indianapolis, Indiana, USA

## Reconstructing air concentrations and deposition fluxes of PCDD/Fs in the UK

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### Abstract

Information on long-term temporal trends can be obtained from the analysis of dateable deposits, (e.g. sediments) and the retrospective analysis of preserved or archived samples. More recent trends (1970s onwards) have been determined using direct air measurements, archived air filters, archived herbage and human milk.

Human activity is believed to have dominated PCDD/F inputs to the environment this century. Conceptually it is probably appropriate to consider a 'pulse' of PCDD/Fs arising from human activities entering the environment in the 1930/40s, peaking in the 1960/70s and continuing to a lesser degree today. A series of measures introduced in the past, recently and anticipated in the future have reduced emissions to the atmosphere of industrialised countries and are projected to continue to reduce emissions over the coming decade.

### The long-term record

**Sediments:** Dated sediment cores have the potential to provide detailed chronologies of pollutant input, as long as re-suspension, bioturbation, biotransformations, molecular diffusion and transport with infiltrating water are (or may be considered to be) negligible. A recent study of PCDD/F deposition at a remote site in Scotland showed that concentrations started to increase above background pre-industrial levels during the 1860s and 1870s, reaching a peak in the 1950s-1960s and then decreased to the present day (1). The only other UK data published to date present homologue profiles for two dated slices of a core sampled from Lake Windermere in the English Lake District (2). In 1946-50 the PCDFs were a significant fraction of the  $\Sigma$ PCDD/F deposition to the lake, whilst the 1988-92 slice was dominated by OCDD (and HpCDD).

**Soil:** Kjeller et al. (3) analysed archived soils collected from the control plot of the Broadbalk continuous wheat experiment at Rothamsted Experimental Station between 1846 and 1986. The potential for a change in sample composition during storage in the sealed jars is believed to be negligible in these samples (see companion paper). The increase in soil concentrations at Broadbalk between 1846 and 1986 is consistent with an increase in atmospheric deposition inputs to the plot through this century. Concentrations started to increase around the turn of the century and rose from 31 to 92 ng of  $\Sigma$ PCDD/Fs per kg of soil between 1893 and 1986; TCDD concentrations increased from 0.34 to 1.7 ng/kg over the same time period. The net average accumulation rate between 1893 and 1986 was 190 ng m<sup>-2</sup> per year. Concentrations of the individual isomers and the congener groups increased steadily over the last century, by factors of between 1.7 and 18 (3). In summary, there is evidence that UK soils have increased in PCDD/F concentration through this century, as a result of cumulative atmospheric deposition.

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## **The recent record (1970 onwards)**

### Evidence for air trends through the analysis of vegetation

The presence of PCDD/Fs on vegetation surfaces is due almost exclusively to uptake/retention of airborne PCDD/Fs (4). Changes in leaf (i.e. herbage or leafy crops) PCDD/F concentrations and composition can therefore be used to make inferences about changes in air concentrations and hence changing atmospheric source loadings and types. This needs to be done cautiously, however, because the mixture of PCDD/Fs released from a given source is subject to changes during aerial transport, deposition and residence in the environment.

Trends in the  $\Sigma$ PCDD/Fs and  $\Sigma$ TEQ of UK herbage from 1861-1993 have been determined by Kjeller et al., (5). A wide array of PCDD/Fs were detected in all the samples well above the method blanks. Concentrations ranged between 21-310 ng  $\Sigma$ PCDD/F per kg DW, although some individual compounds were sometimes below the detection limits. The most recent sample (1991-93) contained 38 ng/kg, a value typical for contemporary UK vegetation (6), with the OCDD, HpCDD, TCDF and PeCDF homologues dominating.  $\Sigma$ PCDD/F concentrations in the herbage remained essentially constant between 1861-1945, then rose to a peak in 1961-65, declined and then reached a second, lower peak in 1976-80. Since then they have declined and the  $\Sigma$ PCDD/F concentration in the 1991-93 sample was similar to that of the pre-1946 samples. Most individual compounds and homologues peaked in the 1961-65 sample. Kjeller et al. (5) concluded that combustion-derived sources have provided a 'baseline' input to the air throughout the study period (i.e. since 1860), an input which will have presumably changed in intensity and composition over time as combustion sources, types and strengths have altered. Inputs from chloroaromatics production and use are then invoked as supplementing the combustion-derived inputs post-1946.

### Evidence from direct air measurements

In the United Kingdom (UK) the Department of the Environment (DoE) has funded the Toxic Organic Micro-Pollutants (TOMPS) Program, to monitor ambient concentrations of PAHs, PCBs and PCDD/Fs. Ambient air concentrations of PCDD/Fs at London and Manchester (sites having a full 5 years of data) are available from the first five years of the program (1991-95). To our knowledge, this is the most comprehensive continuous and ongoing dataset of direct air measurements for PCDD/Fs. We stress that, given the inherent 'noise' in air concentrations, a five year dataset is still insufficient to identify long-term trends with confidence, although some patterns in the behaviour of atmospheric concentrations are emerging.

PCDD/F data in Table 1 were derived assigning half the detection limit values to not detected values. Concentrations were typically in the 50-300 fg  $\Sigma$ TEQ  $m^{-3}$  range, with lowest and highest values of 25 and 1410 fg  $\Sigma$ TEQ  $m^{-3}$ , respectively. This is generally in line with other European and North American (7; 8) data. As Figure 1 shows, the trends at the two sites were similar, with a decline through 1991-1994, followed by an upturn in 1995. As for PAHs and PCBs, there is good evidence that PCDD/F air concentrations have been declining steadily since the 1970s (see above) (8); the downward trend for 1991-94 here may perhaps best be viewed as a continuation of this trend (9). Interestingly, the mixture of 2,3,7,8-substituted PCDD/Fs was quite consistent for the first four years, but rather different in 1995. Several PCDFs congeners, namely 1,2,3,4,7,8- and 1,2,3,6,7,8-HxCDF, 1,2,3,4,6,7,8- and 1,2,3,4,7,8,9-HpCDF and OCDF, became more dominant in the congener mixture in 1995 at both sites. The 1995 data go against the general downward trend and it will be interesting to see if the unusual pattern of compounds in the samples indicate a general shift in sources which will be detected again in later years or if it is a 'one off', perhaps caused by unusual source inputs for that year.

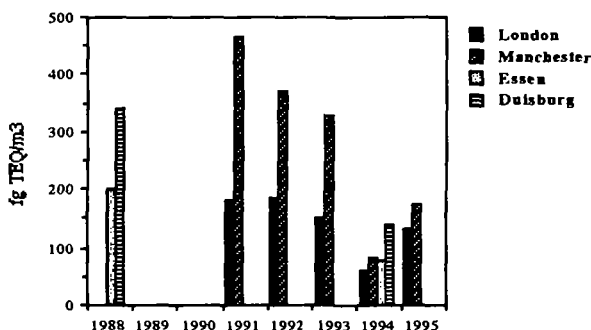
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Table 1: Typical range concentrations and summer:winter ratios for PCDD/Fs ( $\text{fg m}^{-3}$ ) at London and Manchester. The ratios were calculated by dividing the mean concentration in the 3rd quarter (Q3) of the year by the mean from the 1st quarter (Q1).

	Typical Range	London Q3/Q1	Manchester Q3/Q1
2,3,7,8-TCDD	<5-120	0.91 (0.38-1.42)	0.72 (0.12-1.37)
1,2,3,7,8-PCDD	5-80	0.57 (0.05-0.80)	1.14 (0.16-2.46)
1,2,3,6,7,8-HxCDD	10-170	1.24 (0.10-2.79)	1.36 (0.19-2.87)
1,2,3,4,7,8-HxCDD	10-150	0.88 (0.09-2.3)	1.05 (0.18-2.20)
1,2,3,7,8,9-HxCDD	30-200	0.94 (0.11-2.1)	2.26 (0.21-8.1)
1,2,3,4,6,7,8-HpCDD	250-1100	0.99 (0.24-1.87)	0.87 (0.09-2.3)
OCDD	600-4200	1.11 (0.33-2.38)	0.97 (0.62-1.9)
2,3,7,8-TCDF	50-680	0.80 (0.19-2.3)	1.12 (0.45-2.08)
1,2,3,7,8-PCDF	30-170	1.36 (0.14-5.0)	1.16 (0.17-1.5)
2,3,4,7,8-PCDF	30-190	1.60 (0.28-6.3)	1.53 (0.24-2.4)
1,2,3,4,7,8-HxCDF	150-680	10.1(0.23-47)	1.30 (0.41-1.7)
1,2,3,6,7,8-HxCDF	50-520	9.13 (0.20-43)	1.58 (0.49-2.9)
1,2,3,7,8,9-HxCDF	20-85	2.38 (0.10-9.6)	2.87 (0.34-5.7)
2,3,4,6,7,8-HxCDF	80-390	1.71 (0.24-5.4)	1.74 (0.7-3.9)
1,2,3,4,6,7,8-HpCDF	280-1500	5.40 (0.15-25)	1.25 (0.39-2.4)
1,2,3,4,7,8,9-HpCDF	80-280	8.3 (0.06-39.0)	1.44 (0.22-4.68)
OCDF	50-2070	39.8 (0.07-196)	0.82 (0.49-1.22)

Summer : winter seasonality of PCDD/Fs at both sites has been highly erratic year-on-year and compound-by-compound (see Table 1). This is perhaps best interpreted as a sign that various sources (presumably combustion-derived) have contributed different mixtures of PCDD/Fs of different source strengths at different times to the air at these urban sites.

Figure 1: Annual average concentrations of PCDD/Fs as  $\Sigma\text{TEQ}$  at London, Manchester, Essen and Duisburg. German data from Heister et. al., (10).



The general 1991-94 decline at both Manchester and London was quite marked with the  $\Sigma\text{TEQ}$  falling from 467 to 86 and 180 to 62  $\text{fg } \Sigma\text{TEQ m}^{-3}$  at the two sites, respectively. This general trend is supported by a recent German study in which annual mean air concentrations for 4 cities (Köln, Duisburg, Essen and Dortmund) were measured in 1987/88 and again in 1993/94

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(Heister et al., 1995). During this time annual average  $\Sigma$ TEQs decreased by between 46 - 69% for the four locations. It should be noted, however, that in this study the sampling regime was not the same in the two years; there were differences in the number of samples taken and the length of the sampling intervals. The authors attributed the decline to abatement measures introduced between the two sampling intervals, notably the prohibition of halogenated scavengers in petrol in 1992, a 'ban of PCBs' in 1989 and the upgrading/shutdown of 12 out of 26 waste incinerators in the region. An inventory of contemporary PCDD/F emissions to the UK atmosphere highlighted municipal solid waste incineration (MSWI) as the major primary source, accounting for an estimated 70% of the annual  $\Sigma$ TEQ emissions in the early 1990s. However, unlike Germany where MSWI source reduction measures for PCDD/Fs began in the late 1980's, the downward trend between 1991-94 appears to have occurred in the absence of such a stated primary emission source reduction policy. UK MSWI emission policy controls for PCDD/Fs were intended to come into force at the beginning of 1996 (11). It seems unlikely, therefore, that these improvements in UK air quality can be ascribed solely to a reduction in MSWI emissions during the early 1990s. Questions must therefore remain over our understanding of PCDD/F sources to the atmosphere, our ability to quantify sources accurately at the present time, and our understanding of the factors which control the PCDD/F concentrations of air

## Evidence from archived air filters

The Harwell Laboratory of AEA Technology near Oxford started the collection of air filters for the analysis of trace elements in air on a monthly basis at various rural UK sites in 1972. Cellulose filters (Whatman 40) are used to retain air particulates at 1.5 m above ground. Portions of these filters have been retained, stored in petri dishes and sealed in plastic bags in a dark cupboard at room temperature at the Harwell Laboratory. Samples were selected from two sites in the UK, at Styrrup near Sheffield and Trebanos, south Wales. For this study, monthly filters from the winter months (October, November, December and January) were bulked. Samples for the winters of 1975/76, 1978/79, 1981, 1983/84, 1988/89, 1991/92 and 1994/95 at Styrrup and 1974/75, 1977/78, 1980/81, 1983/84, 1986/87, 1989/90, 1992/93 and 1994/95 at Trebanos were analysed for this project. The samples have been collected, stored and handled in the same way over time. Sample integrity questions are therefore thought to relate primarily to the stability of PCDD/Fs on the filters in the sealed glass containers and possible take up or loss of vapour phase PCDD/Fs. This second factor would have influenced the lower chlorinated congeners, if it occurred. Sixteen filter samples were analysed in all, together with one filter blank and two laboratory blanks.

$\Sigma$ PCDD/F concentrations on the filters at Styrrup and Trebanos ranged between 5 - 19 pg/m<sup>3</sup> and 3 - 5 pg/m<sup>3</sup>, respectively.  $\Sigma$ PCDD/F concentrations on filter + polyurethane foam (i.e. particulate + vapour phase components) at the London, Manchester and Cardiff TOMPS urban network sites typically averaged (medians) ~3 - 4 pg/m<sup>3</sup> in the early 1990s, using less sensitive analytical procedures (12). The mixture of PCDD/Fs on the filters was typical of the composition of air, with highest levels of the hepta- and octa-CDD homologues.

Surprisingly, given the evidence for declines presented earlier, there were no consistent changes in either the winter PCDD/F concentrations or the mixture of PCDD/Fs at either site between the mid-1970s and the mid-1990s.

One possibility for the absence of an observed decline is that the archived filters have, over time, either lost PCDD/Fs to the indoor air during storage or become contaminated by it. However: a). the consistency of the compound and homologue mixture of the samples from both sites, and; b). the fact that the air concentrations derived from the filters are in line with contemporary data suggests that neither of these problems have been significant and that the samples maintained their integrity during storage. Any systematic error in assembling filters (such as low particle mass concentrations or filters exposed during/directly following rain events for the early samples) are also highly unlikely.

## Evidence from cows milk

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The composition of meat and milk can be considered to give a broad 'integration' of PCDD/F recent atmospheric inputs over large areas. Milk provides a particularly valuable indication of regional deposition, since dairy cattle effectively bioaccumulate PCDD/Fs and can 'process' PCDD/Fs recently deposited onto vegetation into a homogenous, readily sampled and analysed matrix. The MAFF Total Diet Study in the UK provides extremely useful data on the PCDD/F content of milk, milk products, carcase meat and offals collected in 1982, 1988 and 1992 (13; 14). The 1982, 1988 and 1992 samples have all been analysed by the same laboratory in Norwich which regularly participates in inter-laboratory comparison exercises. Average dietary intakes were estimated to be 250 pg of TEQ per person<sup>-1</sup> day<sup>-1</sup> in 1982, 145 pg/day in 1988 and 88 pg of TEQ per person<sup>-1</sup> day<sup>-1</sup> in 1992. Clearly, this study has important implications for human exposure. Given the importance of the pathway: emissions - air - deposition - grass/feed - livestock ingestion - milk/meat, these data provide good evidence that there has been an underlying decline in the PCDD/F emissions in the UK since the early 1980s.

## Concluding remarks

UK sediments, archived vegetation and soil, major food groups and comparisons with direct air measurements all consistently suggest that air concentrations and deposition fluxes were much higher in the 1950-70s and have shown a sustained decline since that time. The weight of evidence suggests that even if there were PCDD/Fs formed pre-industrially, the PCDD/F burden of the contemporary environment far exceeds any historical burden. As long as uncertainties remain over the significance, or otherwise, of natural and anthropogenic sources, the effectiveness of emission control and source reduction measures introduced by the regulatory authorities will remain unclear.

The UK Government has implemented a series of measures to control releases of PCDD/Fs, which aims to reduce primary atmospheric emissions of PCDD/Fs by 70%. The continuation of various monitoring programs will show if the declining trends in PCDD/Fs discussed here are sustained and whether future controls bring about the desired reductions in air concentrations intended to ultimately further reduce human exposure to these compounds.

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