Atmospheric concentrations and partitioning of PCDD/Fs at a semi-rural site in the north west of England

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Introduction

The atmosphere is an important pathway for the movement of PCDD/Fs into the human food chain. However, relatively little data exist for ambient concentrations and the vapour:particle partitioning in rural areas. In this study we report data from two separate sampling programmes at a semi-rural site in the north-west of England. The first samples were taken in the autumn of 1995 and provide data on: i. ambient levels of PCDD/Fs; ii. the increase in levels as anthropogenic sources increase during the winter months; and iii. a marked increase in concentrations that is linked to an autumnal festival when it is customary to light bonfires and set off fire works (1). The second sampling programme was carried out in the summer of 1996 and provides data on ambient summer concentrations and vapour/particle partitioning.

Experimental Section

The sampling site is at a meteorological station located in a semi-rural area outside Lancaster, a town of ca. 70,000 inhabitants on the north west coast of England, approximately 5 km from the Irish Sea ($52^0$2'N,$2^0$45'W). Air samples of ca. 900 m^3 were taken over 7 days using a General Metal Works GPS1 sampler. The nominal particulate fraction was trapped on a Whatman glass microfibre filter (GFF) (grade GF/A, 10 cm diameter) and the vapour fraction on a polyurethane foam plug (PP) (length 8 cm, diameter 6.25 cm). Samples were extracted for 16 hours in toluene and then cleaned up by refluxing in acid silica, followed by fractionation on a basic alumina column. Particulate samples were further cleaned using a carbon column. Analysis was performed on a Micromass Autospec Ultima high-resolution mass spectrometer operated at a resolution of at least 10,000. Details of the clean up, fractionation and spiking procedures have been described elsewhere(2). Breakthrough of the nominal vapour phase from the PP was tested in the 1996 sampling programme; no breakthrough was observed at volumes of 1000 m^3.

Results and Discussion

The concentrations measured during both sampling programmes are summarised in Table 1. They compared well with other available values (3), confirming that the sampling site can be classed as rural/semi-rural with respect to PCDD/F concentrations. All but one of the 1995 samples were one of a pair, the results show good consistency between the paired samples with only minor variations. ΣPCDD/F and ΣTEQ concentrations generally follow the trend summer < winter.

Noticeable in Table 1 is the high concentrations for the paired samples 12 and 13. These samples were taken between 03/11/95 and 06/11/98 which coincided with bonfire weekend, a time when bonfires containing a variety of vegetation (tree-cuttings, leaves) and sometimes domestic (maybe illegal industrial) waste are lit around the country. Fireworks containing gunpowder are also set off throughout this period. After bonfire weekend the levels drop dramatically, but still show a continuation of the upward trend already mentioned. The change in the homologue profiles during this period can be seen in Figure 1. During bonfire weekend there is a rise in the percentage contribution of the higher molecular weight PCDDs (particularly HpCDD and OCDD) to the ΣPCDD/F when compared to a typical autumnal profile. This in turn has a higher percent contribution of HxCDD, HpCDD and OCDD than the summer samples.

In Table 2 the percentage of the different homologue groups in the particle phase during summer 1996 is shown. The OCDD/F and HpCDD/F were almost exclusively in the particulate fraction, while only 16-44% of the PeCDD/F and 4-17% of the TCDD/Fs were associated with the particulate phase. The vapour/particle partitioning was investigated with a plot of the Log Kp (temperature dependent partitioning constant) vs. Log p_L (Log of the subcooled liquid vapour pressure) (4). Each of the weekly samples is plotted separately on figure 2. Slopes of the lines averaged -0.5 and intercepts averaged -5.4. Other data of this kind are presented for daily samples at the same site (5). Clearly there is variability in the partitioning behaviour of PCDD/Fs between sampling events. It will be interesting to explore the factors responsible for this.

Acknowledgements
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Table 1: Ambient air concentrations of PCDD/Fs from bulked (gas+particulate)samples taken in the autumn of 1995, (two samples were taken during each sampling period except for the first period) and the summer of 1996.

Sample ID	Start Date	Finish Date	$\Sigma P_{4-8}CDD/F$ ($fg\ m^{-3}$)	OCDD % of Σ	PCDD/PCDF ratio	ΣTEQ ($fg\ m^{-3}$)	2,3,7,8-PCDF [% of ΣTEQ]
1	19/09/95	26/09/95	1030	30.4	2.32	3.0	19.8
2	26/09/95	03/10/95	1280	20.4	1.29	3.0	22.4
3	26/09/95	03/10/95	1040	17.6	1.16	3.0	23.6
4	03/10/95	10/10/95	2280	21.6	2.01	5.0	21.6
5	03/10/95	10/10/95	2210	21.7	2.07	5.0	21.1
6	10/10/95	17/10/95	7840	20.4	2.18	15.0	22.9
7	10/10/95	17/10/95	6450	20.3	2.19	12.0	22.3
8	17/10/95	24/10/95	2540	20.6	1.48	6.0	25.5
9	17/10/95	24/10/95	1960	17.5	1.45	5.0	24.8
10	27/10/95	03/11/95	5330	18.7	1.93	12.0	22.5
11	27/10/95	03/11/95	6110	18.9	1.91	11.0	22.6
12	03/11/95	06/11/95	18800	27.6	1.84	47.0	26.6
13	03/11/95	06/11/95	24000	26.7	1.85	54.0	25.4
14	06/11/95	13/11/95	6690	19.0	1.53	16.0	25.8
15	06/11/95	13/11/95	5710	20.1	1.45	14.0	26.3
Summer 1996 results.							
1	30/05/96	06/06/96	630	20.7	1.35	11.0	19.1
2	06/06/96	13/06/96	790	11.9	1.11	10.0	23.2
3	20/06/96	27/06/96	490	13.4	1.10	7.0	19.6
4	27/06/06	04/07/96	460	13.3	1.12	7.0	20.0
5	04/07/96	11/07/96	380	16.1	0.84	5.0	23.4
6	11/07/96	18/07/96	660	30.9	1.42	4.0	26.5
7	18/07/96	25/07/96	730	11.1	0.63	5.0	26.7
8	25/07/96	01/08/96	410	12.1	0.61	4.0	25.5
9	01/08/96	08/08/96	780	8.9	0.33	5.0	28.6

Table 2: % PCDD/Fs found in the particulate fraction.

PCDD/Fs - % particle bound [p/(g+p)]

Homologue group	Sample ID 1	2	3	4	5	6	7	8	9
F4	10	5	7	4	6	5	6	6	5
F5	40	22	28	27	33	15	14	18	16
F6	81	58	65	68	72	47	35	55	50
F7	100	83	88	97	87	83	63	87	81
F8	99	97	99	98	98	95	90	96	98
D4	17	5	18	13	10	8	7	10	10
D5	25	33	53	30	44	22	38	23	41
D6	85	65	78	74	81	45	47	60	54
D7	97	89	95	95	95	81	76	95	89
D8	95	90	94	94	81	93	91	91	95
Temp °C	12	13	12	12	12	14	16	14	15

Figure 1: PCDD/F homologue profiles for selected samples from 1995 and 1996.

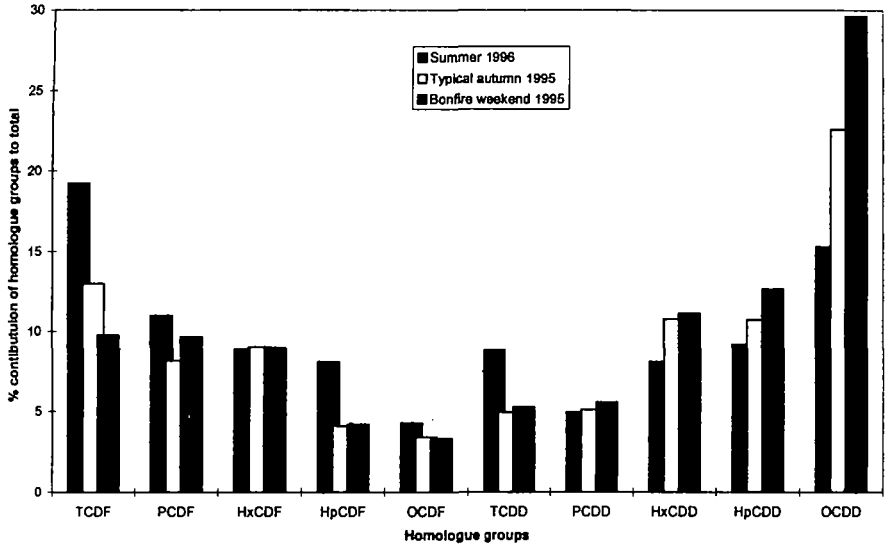

Figure 2: Gas-particle partitioning of PCDD/F in the 1996 summer samples.