Detailed studies of the factors controlling short-term variations of atmospheric PCDD/F concentrations

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Introduction

Atmospheric transport is the primary distribution pathway moving polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) from atmospheric emission sources via deposition to terrestrial and aquatic ecosystems. During their transport in the atmosphere, PCDD/Fs can be removed by reactions or by deposition, which will ultimately alter ('weather') the atmospheric PCDD/F profile (1 -3). However, very few sampling programs have been undertaken with short sampling periods (4). This comprehensive study with 37 short-term (either 2 or 3 days) air samples was therefore undertaken at a semi-rural site near Lancaster, UK, from September to December 1997. Total PCDD/F concentrations were correlated with meteorological parameters; homologue patterns and air mass origin were used to discuss the relative importance of local PCDD/F releases, long-range transport and atmospheric loss processes of PCDD/Fs.

Materials and Methods

Analytical procedure: The method employed has been described elsewhere (5). Briefly, air samples were taken with PS-1 air samplers (Graseby Andersen) equipped with a glass fibre filter (GFF) and 2 polyurethane foam plugs (PUF). The PUF plugs were spiked with all $^{13}C_{12}$-2,3,7,8-substituted congeners prior to sampling. PUFs and GFFs were combined and extracted in toluene for 16 hours, refluxed in hexane with sulphuric acid/silica gel and fractionated on a basic alumina column. Our method seeks to quantify the full range of di-to octa-CDD/Fs. All samples were analysed by HRGC-HRMS using an HP6890 GC connected to a Micromass Autospec Ultima high resolution mass spectrometer at 10,000 resolving power. Total homologues were quantified on a 30m DB5-MS, and the 2,3,7,8-substituted congeners on a 60m SP2331.

Quality Control: Method detection limits were 0.5 pg/sample for the 2,3,7,8-substituted tetra- to hexa CDD/Fs, 1 pg/sample for the hepta-congeners and OCDF and 5 pg/sample for OCDD. Mean recoveries for the tetra- to octa-2,3,7,8-substituted CDD/Fs were between 74% and 104%, 45% for 2,8-DiCDF, 42% for 2,7-DiCDD and 58% for 2,3,7-TriCDD.

Results and discussion

ΣTEQ (I-TEQ) concentrations varied from 5.5 to 220 fg/m^3, with a mean of 38 fg TEQ/m^3, typical of rural/semi-rural sites (see 6). Σ $P_{3\text{-}8}$CDD/Fs (Σ $P_{4\text{-}8}$CDD/Fs) ranged from 690 (410) to 47,000 (45,000) fg/m^3, with a mean of 4,500 (3,700) fg/m^3 (see Table 1). Major contributors to the total were TriCDFs and OCDD. The averaged tetra- to octa-CDD/Fs homologue profile mirrors a 'typical' profile discussed in the literature (6). Concentrations of P_2CDFs were at least an order of magnitude higher than other homologue groups, varying from 2,700 to 180,000 fg/m^3, with a mean of 32,000 fg/m^3.

Table 1: Minimum, maximum and mean concentrations (fg/m^3) of the homologue groups, the 2,3,7,8-substituted congeners and ΣTEQ (fg TEQ/m^3)

homologues	min	max	mean	congener	min	max	mean
P_2CDFs	2,700	180,000	35,000	2,3,7,8-TCDF	3.0	59	12
P_3CDFs	200	2200	680	1,2,3,7,8-PeCDF	3.6	180	24
P_4CDFs	80	2,400	410	2,3,4,7,8-PeCDF	2.7	140	20
P_5CDFs	40	2,200	300	1,2,3,4,7,8-HxCDF	3.2	210	28
P_6CDFs	23	1,900	260	1,2,3,6,7,8-HxCDF	2.8	170	23
P_7CDFs	16	1,000	150	1,2,3,7,8,9-HxCDF	<0.5	15	3
OCDF	8.8	420	72	2,3,4,6,7,8-HxCDF	4.0	180	28
P_2CDDs	84	1,300	300	1,2,3,4,6,7,8-HpCDF	9.6	590	88
P_3CDDs	22	330	84	1,2,3,4,7,8,9-HpCDF	1.4	83	13
P_4CDDs	33	740	160	2,3,7,8-TCDD	0.2	7.7	1.7
P_5CDDs	26	1,200	200	1,2,3,7,8-PeCDD	1.4	55	10
P_6CDDs	22	2,200	340	1,2,3,4,7,8-HxCDD	1.3	100	12
P_7CDDs	44	5,800	510	1,2,3,6,7,8-HxCDD	1.8	180	28
OCDD	92	30,000	1,300	1,2,3,7,8,9-HxCDD	1.7	160	22
TEQ (I-TEQ)	5.5	220	38	1,2,3,4,6,7,8-HpCDD	22	2,900	260

Influence of meteorology: All homologue groups and 2,3,7,8-substituted congener concentrations were log-normalised and regressed with the meteorological parameters (see Table 2).

Tri- to octa-CDD/Fs All the 2,3,7,8-substituted congeners and tri- to octa-CDD/Fs were negatively related to the meteorological variables studied. However, statistically significant negative correlations (P≤0.05 or P≤0.01) were only seen against temperature for most of the congeners/homologues and with wind direction for some of the congeners/homologues. With few exceptions (i.e. HpCDDs, OCDD/F) correlations were stronger with the minimum than the

Table 2: Correlations between meteorological parameters and the homologue groups

homologue group	T max	T min	rainfall	sunshine	wind dir.	Wind speed
P_2CDFs	+0.38*	+0.48**	+0.43**	-0.24	+0.63**	-0.27
P_3CDFs	-0.30	-0.35*	-0.095	-0.088	-0.27	-0.12
P_4CDFs	-0.41*	-0.45**	-0.048	-0.12	-0.25	-0.23
P_5CDFs	-0.44**	-0.48**	-0.11	-0.10	-0.26	-0.26
P_6CDFs	-0.37*	-0.41*	-0.16	-0.070	-0.28	-0.21
P_7CDFs	-0.27	-0.30	-0.14	-0.052	-0.27	-0.17
OCDF	-0.23	-0.23	-0.044	-0.13	-0.14	-0.15
P_2CDDs	+0.22	+0.28	+0.60**	-0.29	+0.32	-0.10
P_3CDDs	-0.21	-0.28	-0.058	-0.010	-0.28	-0.23
P_4CDDs	-0.24	-0.29	-0.053	-0.045	-0.27	-0.19
P_5CDDs	-0.34*	-0.39*	-0.15	-0.026	-0.34*	-0.29
P_6CDDs	-0.35*	-0.38*	-0.22	-0.015	-0.41*	-0.20
P_7CDDs	-0.44**	-0.41*	-0.11	-0.15	-0.36*	-0.22
OCDD	-0.40*	-0.35*	-0.075	-0.20	-0.33*	-0.22

significant at * P≤0.05; ** P≤0.01

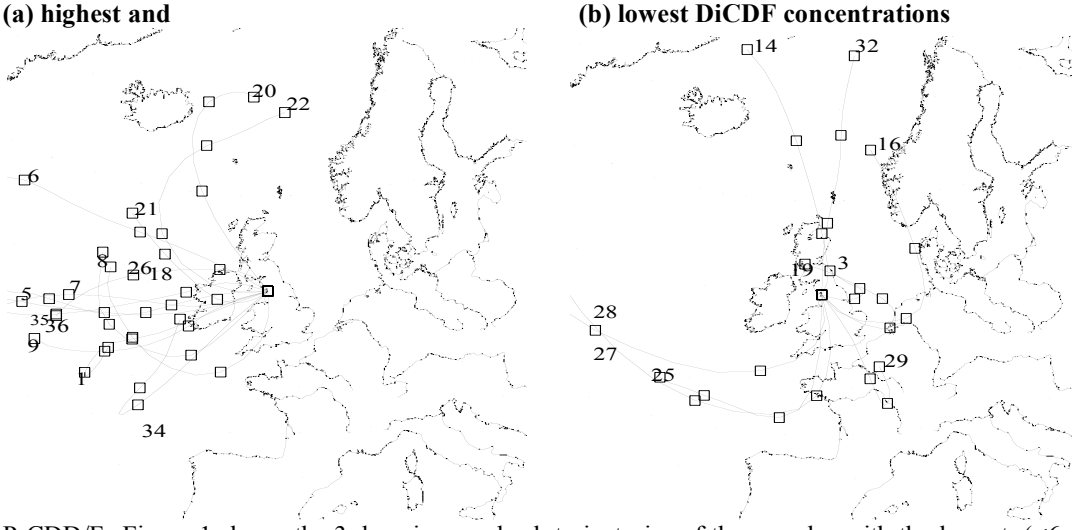
maximum temperature. Correlations with rainfall and sunshine were weakly negative and not statistically significant. Wind direction was the only parameter which effectively discriminated between PCDDs and PCDFs; it was significantly correlated ($P \leq 0.05$) with all 2,3,7,8-substituted CDDs (except 2,3,7,8-TCDD) and all CDD homologue groups (except $P_{3/4}$CDDs), but with none of the PCDFs. Of course, wind direction links meteorological observations to air mass origin. Air masses arriving from the west (i.e. centred around 270°, off the Irish Sea) had lower PCDD/F concentrations than air masses arriving from between the east and south (i.e. 90-180°), where the most densely populated/industrial areas of the UK can be found.

P_2CDD/Fs In marked contrast to the tri-to octa- congeners/homologues the P_2CDD/Fs were positively correlated to temperature, rainfall and wind speed. They were significantly correlated with minimum temperature ($P \leq 0.01$). One possible explanation for the positive correlation with temperature could be that they are susceptible to a temperature dependent re-cycling between terrestrial/aquatic surfaces and air already observed for PCBs and pesticides (7). P_2CDD/Fs were also positively related to wind direction ($P < 0.01$), i.e. higher levels reached Lancaster when the air came from the west and lower concentrations from the east/south. This points to a source(s) west of the sampling site.

Back trajectories and air masses

ΣTEQ and Σ tri- to octa CDD/Fs The lowest ΣTEQ samples with ≤ 10 fgΣTEQ /m^3 and Σ $P_{3\text{-}8}$CDD/Fs ≤ 1,400 fg/m^3 were when air masses arrived from the west. Samples with high PCDD/F concentrations came mainly from the south-east to south west (ΣTEQ > 40 fg/m^3 and Σ $P_{3\text{-}8}$CDD/Fs ≥ 3,800 fg/m^3) and from the north to north-east. The air masses for two samples moved gradually over central England, resulting in very high concentrations (90 and 60 fg ΣTEQ/m^3, ≥ 6,200 fg Σ $P_{3\text{-}8}$CDD/Fs/m^3). 'Clean' air with respect to the Σ $P_{3\text{-}8}$CDD/Fs and ΣTEQs generally originated from the west, off the Irish Sea-Ireland and the Atlantic Ocean. Air masses that had spent any time travelling over relatively populated areas of the UK tended to be higher.

Figure 1: 3-day back-trajectories for the samples (numbered) with the
(a) highest and **(b) lowest DiCDF concentrations**



P_2CDD/Fs Figure 1 shows the 3 day air mass back trajectories of the samples with the lowest (<6 pg/m^3) and highest (>30 pg/m^3) P_2CDF concentrations. The P_2CDD/Fs clearly exhibit differences

from the tri- to octa-CDD/Fs. None of the samples with relatively low P_2CDF levels came from the west, whilst all of the highest P_2CDF concentrations did. Elevated P_2CDDs were generally - though not always - linked to elevated P_2CDFs; 11 of the 14 highest ($\geq$ 290 fg/m^3) and 7 of the 13 lowest ($\leq$ 200 fg/m^3) P_2CDD levels coincided with the samples shown in Figure 1. In this respect, air mass origin clearly determined the levels of P_2CDFs (P_2CDDs). It is therefore hypothesised that either the incoming air masses picked up their P_2CDD/F 'burden' over the Irish Sea (following water-air transfer) and/or there was a specific source on land west of our sampling site.

Homologue patterns and air mass origin

The relative contribution of the tri- to octa-CDD/Fs was used to gain clues about the processes altering the PCDD/F composition of a given air mass, namely emissions and/or loss processes. A principal component analysis (PCA) was performed with $P_{3\text{-}8}$CDD/Fs of all samples and 4 factors extracted. Many samples were clustered centrally on the plot and this cluster contained samples with a range of air mass histories. However, some samples fell outside the main cluster; four sample groups are highlighted on the plot depending on their source regions: 'north-west' , 'south-west', 'south' and 'centre'. The 'north-west' group was dominated by high contributions from the $P_{4\text{-}8}$CDFs and low contributions from the $P_{4\text{-}8}$CDDs, suggestive of a 'weathered' profile, preferably losing PCDDs. The 'south-west' group was distinguished by higher contributions of $P_{3\text{-}4}$CDD/Fs and lower contributions of $P_{5\text{-}8}$CDDs than the average pattern. These are truly 'clean', oceanic air samples with a low ΣTEQ. The 'south' group samples had lower contributions of $P_{3\text{-}4}$CDFs and higher $P_{5\text{-}8}$CDFs; they originated from Central Europe during their 3-day trajectory, prior to moving over the southern UK. The 'centre' samples had generally moved slowly over the UK mainland and had a higher contribution of $P_{5\text{-}8}$CDDs and lower $P_{3\text{-}4}$CDD/Fs than the average pattern. Sample 20 was taken at the time of the 'Bonfire Night', a UK festival on or around the 5th November, where it is customary to light fireworks and open outdoor fires.

In summary, several factors - some of them confounding - act to control/influence ambient PCDD/F concentrations. For the majority of air masses, its origin / recent movement over the UK was more important than wet deposition and degradation during the time the air mass spent over northern England.

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