Air concentrations and atmospheric transport of PCDD/Fs across the UK and Ireland

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Introduction

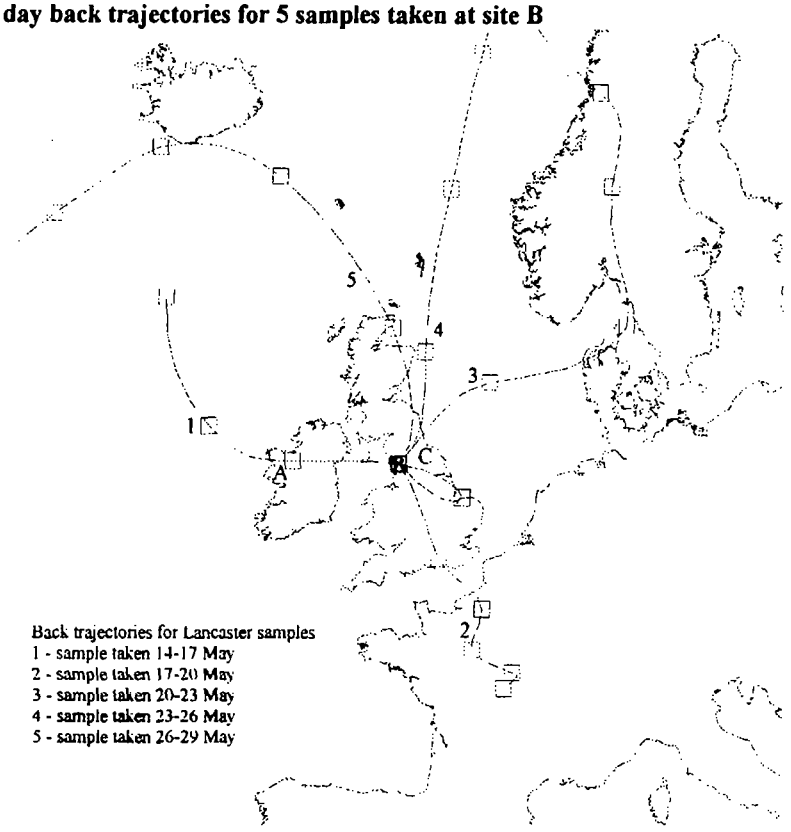
Atmospheric transport is the primary distribution pathway moving PCDD/Fs from atmospheric emission sources via deposition to terrestrial and aquatic ecosystems. We are therefore studying the spatial and temporal variability in atmospheric PCDD/Fs at various sites in the UK and one in Ireland to improve our understanding of their sources, atmospheric behaviour and fate.
In the particular study reported here, PCDD/Fs were sampled simultaneously at three sites in May 1997. The sites are close to the north-east and north-west coasts of England and on the west coast of Ireland. The PCDD/F homologue patterns are compared to other background patterns and the influence of air mass origin discussed. Finally, measured increases in ΣTEQ of the same air mass measured on the west and east coast are compared to a UK estimate of emissions of PCDD/Fs into the air and found to be in reasonable agreement.

Experimental Section

Five air samples (500 - 1000 m^3) were taken simultaneously at each of three sites during May 1997. Each sample took 3 days to collect. The sites were selected to be a regional background area on the north east and north west coast of the UK and on the remote western Irish coast (site A - Mace Head 53°30'N, 9°50'W; site B - Lancaster 54°2'N, 2°45'W; site C -North York Moors 54°20'N, 0°50'W) (see Figure 1). Site selection was made with a view to studying the similarities/ differences in PCDD/F concentrations and composition as air masses move over the Ireland/UK land masses, either for 'clean Atlantic' air to the west, or from European land mass air to the east. Polyurethane foam plugs and glass fibre filters were combined, extracted with toluene for 16 hrs and cleaned up by acid silica refluxing followed by fractionation on basic alumina. The samples were spiked with all $^{13}C_{12}$-2,3,7,8-substituted congeners prior to sampling. Analysis was performed on a Micromass Autospec Ultima, operated at a resolution of at least 10,000. Homologue groups were quantified together on a DB5-column and congener-specific data was obtained using an SP-2331 column. Recoveries ranged between 50 - 150% with an average of 90%. The reproducibility of our air sampling method has been described elsewhere (1). Standard deviations on the concentrations measured for five air samplers operated concurrently at the

Lancaster University field station (site B) averaged 10% for the homologue groups and the 2,3,7,8-substituted congeners with sample volumes of ~700m^3.

Figure 1: Sampling sites (A-western Ireland; B-Lancaster; C-North York Moors) and 5-day back trajectories for 5 samples taken at site B



Results and Discussion

Air concentrations - PCDD/F homologue groups

The PCDD/F concentrations found in the 15 samples are summarised in Table 1, together with the calculated ΣTEQ values, the ΣPCDD/Fs and the ratio of PCDDs/PCDFs for the tetra- to octa-chlorinated PCDD/Fs. Tri-chlorinated congeners, which are routinely quantified as part of our analytical method, are also included in Table 1.

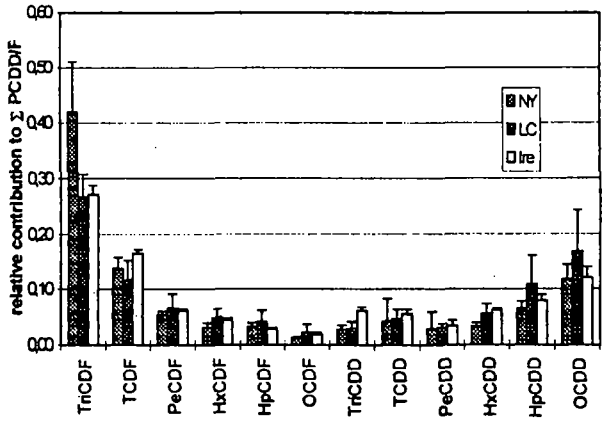
The contribution of the different congeners to the ΣTEQ was fairly constant at the three sites - 2,3,4,7,8-PeCDF was the most important compound, contributing over 25% to the ΣTEQ; the contribution of the other congeners to the ΣTEQ was minor, with only 1,2,3,7,8-PeCDD generally contributing more than 10%. The average contribution of PCDDs to the ΣTEQ was 33%; only the Lancaster samples 1 and 4 were different with PCDDs contributing roughly 50% of the ΣTEQ.

Table 1: Air concentrations (fg/m^3) of the homologue groups measured simultaneously at three sites

Homologue Groups	Ireland (west coast)					Lancaster (north west coast)					North York Moors (north east coast)				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Tri-CDF	160	220	140	180	210	280	590	310	350	480	330	500	150	280	270
TCDF	99	130	84	110	130	72	270	140	130	300	110	170	49	53	160
PeCDF	41	46	32	40	49	43	110	89	65	210	39	72	20	23	58
HxCDF	31	32	25	26	34	36	70	63	52	150	17	48	12	12	38
HpCDF	20	20	15	17	20	21	53	62	37	150	24	39	11	22	23
OCDF	10	21	9	11	11	21	21	20	16	100	10	16	5	5	12
Tri-CDD	43	47	26	42	45	15	81	35	40	55	18	28	11	9	41
TCDD	47	42	27	30	39	25	130	55	55	89	17	19	13	7	120
PeCDD	26	29	8	26	28	31	76	31	39	56	14	8	11	3	86
HxCDD	42	49	29	40	49	100	78	43	94	87	20	43	16	13	36
HpCDD	51	63	49	35	63	230	110	79	200	140	34	87	32	32	62
OCDD	78	90	77	54	100	300	170	120	400	220	72	140	65	58	92
Σ TEQ	3.8	4.2	2.9	3.0	4.1	8.3	9.1	7.1	8.3	17.6	2.9	6.1	2.1	2.3	4.9
$\Sigma_{4\text{-}8}$ PCDD/Fs	450	520	360	390	530	880	1080	710	1090	1500	360	650	240	230	690
$\Sigma_{4\text{-}8}$ PCDD/ $\Sigma_{4\text{-}8}$ PCDF	1.32	1.17	1.29	0.99	1.25	4.21	1.20	0.98	2.94	0.73	0.87	0.99	1.58	1.13	1.47

Concentrations were generally low, at 2.1-6.1, 7.1-17.6 and 2.9-4.1 fg ΣTEQ /m^3 on the north east English coast, north west English coast and west Irish coast, repectively. Similar low concentrations have been reported from Sweden, rural Germany, Australia and rural parts of the United States (see ref. 2). The PCDD/F homologue group profiles taken in coastal areas of Australia and Sweden show very similar profiles to the averaged ones in Figure 2, namely generally decreasing concentrations for the PCDFs with increasing chlorination level and increasing concentrations for the PCDDs with increasing chlorination level. This trend is continued through the tri-CDFs, but Tri-CDDs and TCDDs are more abundant than PeCDDs (see Figure 2). The PCDD:PCDF ratio is ~1 for all but two samples. Interestingly TCDFs are present at similar/ slightly higher concentrations than OCDD; other studies have shown that

Figure2: Comparison of the averaged PCDD/F homologue patterns from the three sites



OCDD is generally the most abundant homologue (2). The profiles shown in Figure 2 represent 'weathered' air masses from rural areas, having spent several days over water/land surfaces. In summary, the most important finding from the comparison of sites and sampling times is the consistency in the mixture of PCDD/Fs observed. This is despite differences in proximity to source regions and air mass origins (see next section).

Air mass origins

Air masses passing over Lancaster (the north west England site) originated from different areas (see Figure 1). The first two sampling events had air masses traversing Ireland and central Europe, with the later three coming from Scandinavia and the North Atlantic. Rather surprisingly, the lowest and highest concentrations of ΣPCDD/Fs and ΣTEQ were measured in air masses coming from Scandinavia and the North Atlantic. Thus air mass origin cannot satisfactorily explain the differences in ΣTEQ. 'Clean' air will have different concentrations of PCDD/Fs depending on the time it spends over a terrestrial surface. This probably explains the differences found for ΣPCDD/Fs and ΣTEQ for the last three sampling events.

A mass balance assessment of the different air concentrations between sites and potential source inputs

During sampling periods 3 to 5 the predominant air mass over northern England came from the north-east. Thus we were able to sample 'clean Atlantic' air at site C, while the air sampled at site B had moved over northern England. ΣTEQ values were at least three times higher at Lancaster than at the North York Moors site during these sampling periods, indicating the PCDD/F input occurring in northern England at this time. Taking the average wind speed, the distance between the two sites (150km), assuming a well mixed atmosphere of 750 m and taking an area of 200,000 km^2 for the UK, we can estimate the ΣTEQ output of the UK.
The total increase in ΣTEQ was calculated to be 1.1-2.0 g/day, which compares well with national atmospheric source estimates of 1.5-3.0 g ΣTEQ/day released from emissions (3). Obviously, these approximations rely very much on parameters for the height of the well mixed atmosphere and a representative ('average') transect; nevertheless this is an encouraging approach.

Acknowledgements

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Literature Cited

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