Environ. Sci. Technol. **1999**, *33,* 2872−2878

Atmospheric Transport of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans (PCDD/Fs) in Air Masses Across the United Kingdom and Ireland: Evidence of Emissions and Depletion

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A sample extraction/cleanup and high-resolution gas chromatography−high-resolution mass spectrometry procedure is described and used to routinely quantify the full range of 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxanes and dibenzofurans (PCDD/Fs) and di- to octa-homologue groups in samples of ∼500−1000 m^3 of remote/rural European air. The relative standard deviations of sum of toxic equivalents (ΣTEQ) and ΣPCDD/F concentrations from five concurrent samples each of 700 m^3 air were 10 and 11%, respectively. Air samples for PCDD/Fs were taken simultaneously at three sites in May 1997: (i) on the remote western Irish coast, (ii) on the northwest coast of England, and (iii) at a regional background site in the northeast of England. For three sampling events where the air passed successively over the two English sites, the increase in air concentrations was used to calculate an emission rate for the mainland United Kingdom land mass; this crude approach gave values of ∼2−12 g ΣTEQ/day, which is broadly in line with annual primary atmospheric source inventory estimates. For another event, when an air mass moved successively over the north of England to the Irish west coast, atmospheric half-lives were calculated to be ∼0.3−4 days for different homologues, which is broadly in line with laboratory and theoretical estimates.

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 (*1*−*3*). Atkinson (*4*) singled out reactions with OH radicals as the only significant destruction mechanism for PCDD/Fs in the atmosphere. Based on laboratory experiments, half-lives of PCDD/Fs with respect to OH radical attack have been estimated and are of the order 1−20 days for the di- to penta/hexa-chlorinated homologues (*5*−*7*). Recently, van Pul et al. (*8*) calculated "overall atmospheric residence times" for two PCDD/Fs, taking into account gaseous and particulate (dry and wet) deposition and depletion/reaction; their values were of the order 37−130 h for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and ∼26 h for octachlorodibenzofuran (OCDF). Residence times for PCDD/Fs have not yet been estimated in the field. Indeed, they are rather difficult to determine, because a particular air mass must be tracked as it moves away from a source region over an area where fresh emissions to the atmosphere are minimal.

Some researchers have argued that the "mixture" or "profile" of PCDD/Fs in air is rather consistent, reflecting the mixture emitted to atmosphere and "weathered" by depletion processes and deposition (see ref *9* for discussion). Indeed, similar (though not identical) homologue profiles to those for air samples from different locations in Europe have been observed (*9*). The typical pattern is characterized by increasing concentrations of the PCDD homologues with increasing degree of chlorination and decreasing concentrations of PCDFs with increasing chlorination (e.g., see refs *9*−*12*). It is not clear, however, to what extent patterns in different places are similar/different, because the analyses have been conducted in different laboratories. One of the aims of this study was, therefore, to investigate the consistency of the mixture or profile of PCDD/Fs within samples taken from the same site. Once this information was available, we hypothesized that we could track changes in the PCDD/F composition of a given air mass by sampling it successively at different sites, separated by a distance of ∼150 km, on its journey across the United Kingdom (UK). To achieve this, we employed three different sites simultaneously. The homologue patterns are compared to each other and those from the literature, and the influence of air mass origin is discussed. The sites for study (see Figure 1) were selected to give: (i) clean European background air from a remote location on the west coast of Ireland (site A: Mace Head; 53° 30′ N, 9° 50′ W); (ii) UK air from a site that—dependent on the air mass movement—can receive "clean" air from the west (off the Irish Sea) or regionally contaminated air from the populated north of England (site B: Lancaster, northwest England, 5 km from the Irish Sea; 54° 2′ N, 2° 45′ W); (iii) air sampled close to the east coast of England, which may either reflect inputs to the UK from mainland European air masses moving from the east or air that has been modified by passing over the UK land mass during its passage from the Irish Sea (i.e., typically areas such as the Lancaster site) to the east (site C: North Yorkshire Moors; 54° 20′ N, 0° 50′ W; near the northeast coast of England). They are therefore contrasting sites that, when sampled concurrently, can give information on how the PCDD/F composition of air is affected either as clean air moves successively from the west to the east over northwest England, where PCDD/F inputs can occur, or as relatively contaminated air moves from the east away from mainland Europe over northwest England to the west of Ireland.

To make reliable comparisons of air concentrations and mixtures, we first had to satisfy ourselves that we could sample and analyze air from one site in a sensitive and reproducible manner. We therefore first report on an exercise in which five air samplers were deployed concurrently at the Lancaster site. Then, using back trajectory information, we use measured increases in the PCDD/F concentrations of the same air mass as it moved from site to site to calculate the possible emission of PCDD/Fs into the air between the two sites and compare that with the UK primary atmospheric emissions inventory (*13*, *14*). Finally, another sampling event when air became cleaner as it moved from the English west coast (site B) to the Irish west coast is used to derive atmospheric residence times to compare with those already mentioned that were derived from laboratory/theoretical studies.

10.1021/es981011j CCC: $18.00
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Published on Web 07/22/1999

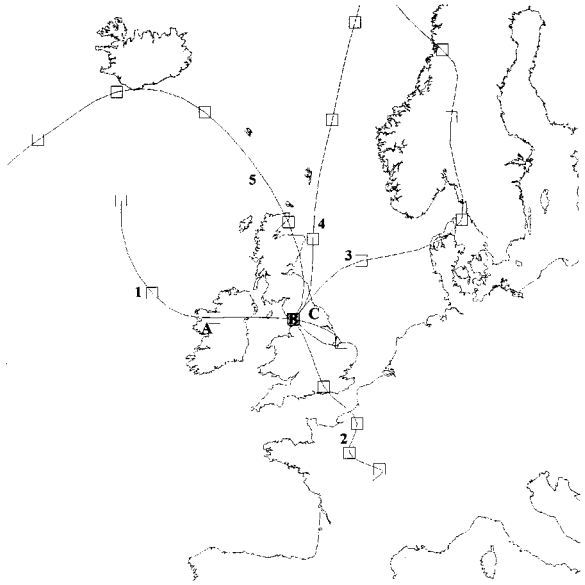

FIGURE 1. Sampling sites (A, western Ireland; B, Lancaster; C, North York Moors) and 5-day back trajectories for five samples taken at site B.

Materials and Methods

Air Sampling and Analysis. All $^{13}C_{12}$-labeled PCDD/Fs standards were obtained from Promochem. Solvents and reagents were pesticide grade/high purity. Silica gel 60 (Merck) was rinsed with dichloromethane (DCM), vacuum-dried, and mixed with sulfuric acid. Super Alumina IB for PCDD/Fs was obtained from ICN. High volume air samplers (PS1; Graseby Anderson) equipped with a glass fiber filter (GFF; 10 cm diameter) and two polyurethane foam plugs (PUFs, 6.25 cm diameter, 5 cm length, density 0.035 g/cm^3) were used to sample the air for PCDD/Fs. The GFFs were precombusted at 450 °C for 12 h, and the PUFs were extracted in DCM for 16 h and vacuum-dried. Samplers were precalibrated and run for 3 days per sample. Flow rates varied from 7 to 14 m^3/h, with the air passing through the GFF followed by PUF1 and PUF2. Our method seeks to quantify the full range of di- to octa-CDD/Fs.

Prior to sampling, the first PUF plug was spiked with all 17 [$^{13}C_{12}$]2,3,7,8-substituted PCDD/Fs plus [$^{13}C_{12}$]2,8-di-CDF, [$^{13}C_{12}$]2,7-di-CDD, and [$^{13}C_{12}$]2,3,7-tri-CDD. [$^{13}C_{12}$]1,2,7,8-TCDF and [$^{13}C_6$]1,2,3,4,6,7,8-HpCDF were spiked onto the filter prior to sampling. Prior to extraction, [$^{13}C_{12}$]1,3,6,8-TCDD was added as a cleanup recovery standard. An injection spike ([$^{37}Cl_4$]2,3,7,8-TCDD) was added to the final extract to act as a retention index for the gas chromatograph (GC), and as a recovery standard to allow the calculation of recoveries of all other spiked compounds. PUFs and filters were combined and extracted in toluene for 16 h; the reduced extract was transferred to *n*-hexane, ensuring complete removal of toluene; and made up to 100 mL in *n*-hexane, to which 30 g of sulfuric acid/silica gel (44%) was added. The mixture was boiled under reflux for 30 min (based on a method published by Höckel et al., ref *15*), then filtered through sodium sulfate, rinsed with 100 mL *n*-hexane, and concentrated to ~1 mL in a rotary evaporator. The extract in *n*-nonane was applied to a pre-rinsed, 4.5-g basic alumina column (diameter 1 cm). The column was eluted with 15 mL of 7% DCM/*n*-heptane (containing ortho-chlorinated polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides), and then with 20 mL of a 1:1 solution of DCM/*n*-heptane to give a fraction containing all PCDD/Fs (mono- through octa-chlorinated congeners). The second fraction was reduced under nitrogen to ~0.5 mL, 15 μL of a solution containing the injection spike was added, and the extract was blown down to ~15 μL. The PCDD/Fs were analyzed by high-resolution gas chromatography−high-resolution mass spectrometry (HRGC−HRMS) using a HP6890 GC connected to a Micromass Autospec Ultima high-resolution mass spectrometer running in SIR mode at a resolution of 10 000. Each sample was analyzed on two different capillary GC columns. Total homologues were quantified on a 30 m DB5-MS (0.25 mm i.d., 0.1 μm film thickness), and the 2,3,7,8-substituted congeners on a 60 m SP2331 (0.25 mm i.d., 0.2 μm film thickness). Quantitation of analytes was achieved by the isotope dilution relative internal standard method using the peak areas of the specific $^{13}C_{12}$-labeled surrogate for each 2,3,7,8-PCDD/F analyte; all concentrations were therefore surrogate-recovery corrected. Recoveries of each surrogate were calculated relative to the injection standard. Peak identification was based on retention time (±2 s) as well as ion ratio of the two masses monitored for each homologue (±15%).

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. Detection limits were derived from the blanks and quantified as the sum of the baseline plus three times the standard deviation of the noise.

Isobaric 5-day air mass back trajectories for site B were calculated with Trajplot four times per day at 925 mbar. The mean trajectories for each sampling event are shown in Figure 1.

Study on Replicate Air Sampling. To demonstrate the reproducibility of the sampling and analytical procedure, five high-volume air samplers were set running concurrently over a 3-day period at site B (yielding ~700 m^3/sample). All samples, including a field blank and a laboratory blank underwent the standard extraction and cleanup method already detailed. The analytical method is unsuitable for monochlorinated CDD/Fs, for which no $^{13}C_{12}$-labeled standard is available. The PCDD/F concentrations in the blanks were generally <5% of the concentrations found in the air samples. Recoveries ranged from 65 to 126%, with an average of 85%.

The results for the 2,3,7,8-substituted congeners are shown in Figure 2, with error bars representing single standard deviations. The average reproducibility values for the 2,3,7,8-substituted congeners were 10% and 11% for the homologue groups, clearly within the strict limits suggested by Oehme et al. (*16*). A similar degree of reproducibility (12%) has been reported for 30-day samples of considerably higher air volumes (7000−8000 m^3) by Maisel and Hunt (*17*).

Results and Discussion

Air Concentrations and Patterns. The PCDD/F concentrations found in the 15 samples are summarized in Table 1, together with the calculated ΣTEQ values (sum of toxic equivalents, I-TEQ, ref *18*), the Σ_{4-8}CDD/Fs, and the PCDDs/PCDFs ratio for the tetra- to octa-chlorinated PCDD/Fs. Di- and tri-chlorinated congeners, which are routinely quantified as part of the analytical method, are also included in Table 1.

The contribution of the different congeners to the ΣTEQ is shown in Figure 3, with error bars representing single standard deviations. The ΣTEQ pattern was fairly constant at the three sites, with 2,3,4,7,8-PeCDF the most important compound and contributing >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 >10%. 2,3,7,8-TCDD was detected in the blanks (~1 pg/sample), with breakthrough from the injection spike ([$^{37}Cl_4$]2,3,7,8-TCDD) found as the cause. The concentration of 2,3,7,8-TCDD for the calculation of the ΣTEQ was therefore taken

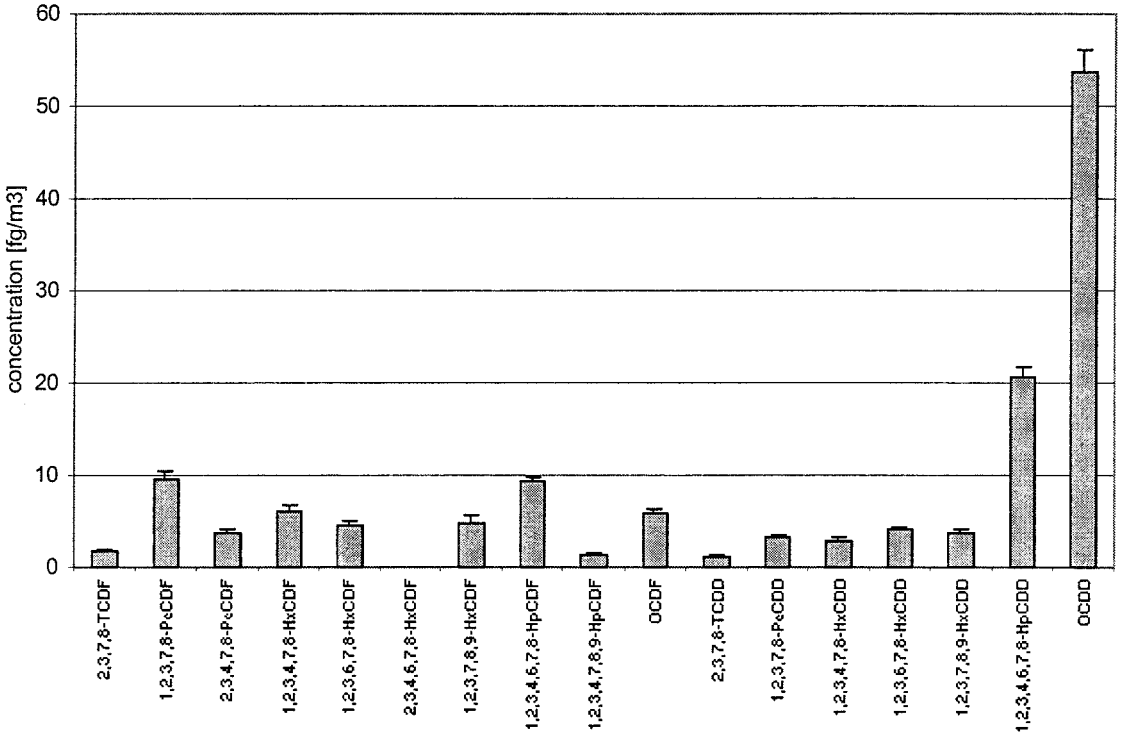

FIGURE 2. Replicate measurements of the 2,3,7,8-substituted congeners at Hazelrigg, Lancaster from 5 samplers running concurrently.

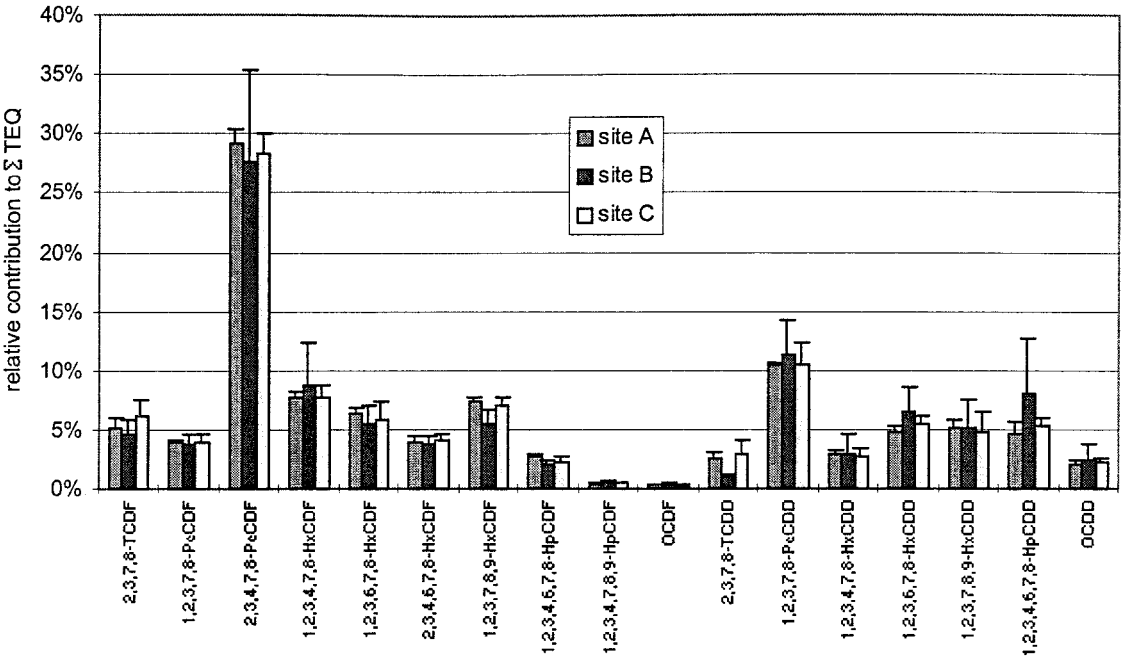

FIGURE 3. Comparison of the relative contribution to the overall TEQ at the three sites.

as half the detection limit. The average contribution of PCDDs to the ΣTEQ was 33%; only the site B (Lancaster) samples 1 and 4 were different, with PCDDs contributing ~50% of the ΣTEQ.

The three sites had similar ΣTEQs, most notably sites A (2.9−4.2 fg m^{-3}) and C (2.1−6.1 fg m^{-3}), with site B tending to be somewhat higher (7.1−17.6 fg m^{-3}). Air mass back trajectories explain the similarities for sites A and C quite well (see later). Similar low concentrations have been reported from Sweden, rural Germany, Australia, and rural parts of the United States (*19*−*23*). The similarities in profile (2,3,7,8-substituted and homologue) are clearly seen in Figures 3 and 4.

Homologue group profiles taken in coastal areas of Australia and Sweden also show very similar profiles to the averaged ones in Figure 4; namely, generally decreasing concentrations for the PCDFs with increasing chlorination level and increasing concentrations for the PCDDs with increasing chlorination level (*19*, *20*, *23*). This trend is continued through the tri-CDFs, although the tri-CDDs and TCDDs are more abundant than PeCDDs (see Figure 4). A comparison of these 'coastal' homologue patterns to ones

TABLE 1. Air Concentrations (fg/m^3) of the Homologue Groups Measured Simultaneously at Three Sites

homologue group[a]	A, Ireland (west coast)					B, Lancaster (northwest coast)					C, North York Moors (northeast coast)				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Di-CDFs	1100	1700	1400	1200	1400	17000	24000	15000	27000	38000	2700	3500	1600	1500	1300
Tri-CDFs	160	220	140	180	210	280	590	310	350	480	330	500	150	280	270
TCDFs	99	130	84	110	130	72	270	140	130	300	110	170	49	53	160
PeCDFs	41	46	32	40	49	43	110	89	65	210	39	72	20	23	58
HxCDFs	31	32	25	26	34	36	70	63	52	150	17	48	12	12	38
HpCDFs	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
Di-CDDs	75	130	64	66	97	76	240	140	200	250	90	130	120	43	68
Tri-CDDs	43	47	26	42	45	15	81	35	40	55	18	28	11	9	41
TCDDs	47	42	27	30	39	25	130	55	55	89	17	19	13	7	120
PeCDDs	26	29	8	26	28	31	76	31	39	56	14	8	11	3	86
HxCDDs	42	49	29	40	49	100	78	43	94	87	20	43	16	13	36
HpCDDs	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
ΣTEQ[b]	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
Σ_{4-8}CDD/Fs	450	520	360	390	530	880	1080	710	1090	1500	360	650	240	230	690
Σ_{4-8}CDDs/CDFs	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

[a] Homologue group is a group of PCDD/Fs having the same molecular weight but differing with respect to the chlorine substitution pattern. [b] 2,3,7,8-TCDD taken as half the detection limit.

typical for continental Europe (*9*−*12*) indicates a difference in the relative importance of TCDDs and PeCDDs. Samples from continental Europe have TCDD concentrations < PeCDD concentrations (*9*−*12*). Interestingly, TCDFs are present at similar/slightly higher concentrations than OCDD, whereas other studies have shown that OCDD is generally the most abundant homologue (*9*).

The profiles shown in Figure 4 represent air masses in which PCDD/F compositions have been changed by deposition and atmospheric removal processes ('weathered') away from source regions. In summary, the most important finding from the comparison of sites and sampling times is the *consistency in the mixture* of PCDD/Fs observed within a given time period. This consistency is despite differences in proximity to source regions and air mass origins (see next section).

Air Mass Origins. Air masses passing over site B originated from different areas (see Figure 1). The air mass of the first sampling event had traversed Ireland and northern England, the second central Europe, with the last three coming from the north, Scandinavia, and the North Atlantic. 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 alone cannot satisfactorily explain the differences in ΣTEQ for site B. Other factors will likely play a part in controlling air concentrations, including differences in atmospheric removal via deposition and depletion in the atmosphere. Table 2 shows the meteorological conditions during the five sampling periods; for sampling events 3 to 5, dry, warm weather prevailed over the UK. Thus, no one factor of those measured appears to determine air PCDD/Fs concentrations measured at site B.

The Irish site had air coming from the Atlantic and western France over southern Ireland for the first and second sampling events. The third and fifth events were marked by air masses coming from northern Europe/Atlantic and passing over England before being sampled at the site A. The 'clean' sites A and C therefore basically sampled the same air masses on these occasions, PCDD/F levels being influenced by different residence times over England/continental Europe. The fourth sampling event was special insofar as the air mass moved from the north Atlantic over England, moving broadly on a trajectory encompassing site C, then B, and finally A. This fourth event is considered further later.

Calculation of PCDD/F Emissions and Fate and the Assumptions Made. Prior to making some calculations of the relationship between air concentration changes observed as a given air mass moved between sites and potential emissions to the atmosphere and/or losses from it, it is appropriate to clearly state the assumptions made for the calculations. These are as follows:

(i) The air masses moved with an average speed calculated from the back-trajectories (see Figure 1).

(ii) The average traveling distance for the air masses from the coast (site C) to site B is 150 km. This assumption seems reasonable from the trajectories shown in Figure 1 and given the uncertainty inherent in estimating back trajectories (20−30%, refs *24*, *25*).

(iii) The atmosphere was well mixed with respect to PCDD/Fs up to a height of 750 m, both for air masses arriving at site C and for air traveling between the sites. Air masses arriving from the North Sea are likely to be 'weathered' and free from major concentration gradients within the well mixed atmosphere. Most PCDD/F emissions are likely to occur from the densely populated regions of northern England over which the air masses passes; namely, within the first 30 km from the east coast (e.g., over conurbations such as Newcastle and Middlesbrough). However, while traversing the upland Pennines, which run north−south through the middle of northern England, air will become mixed and is known to

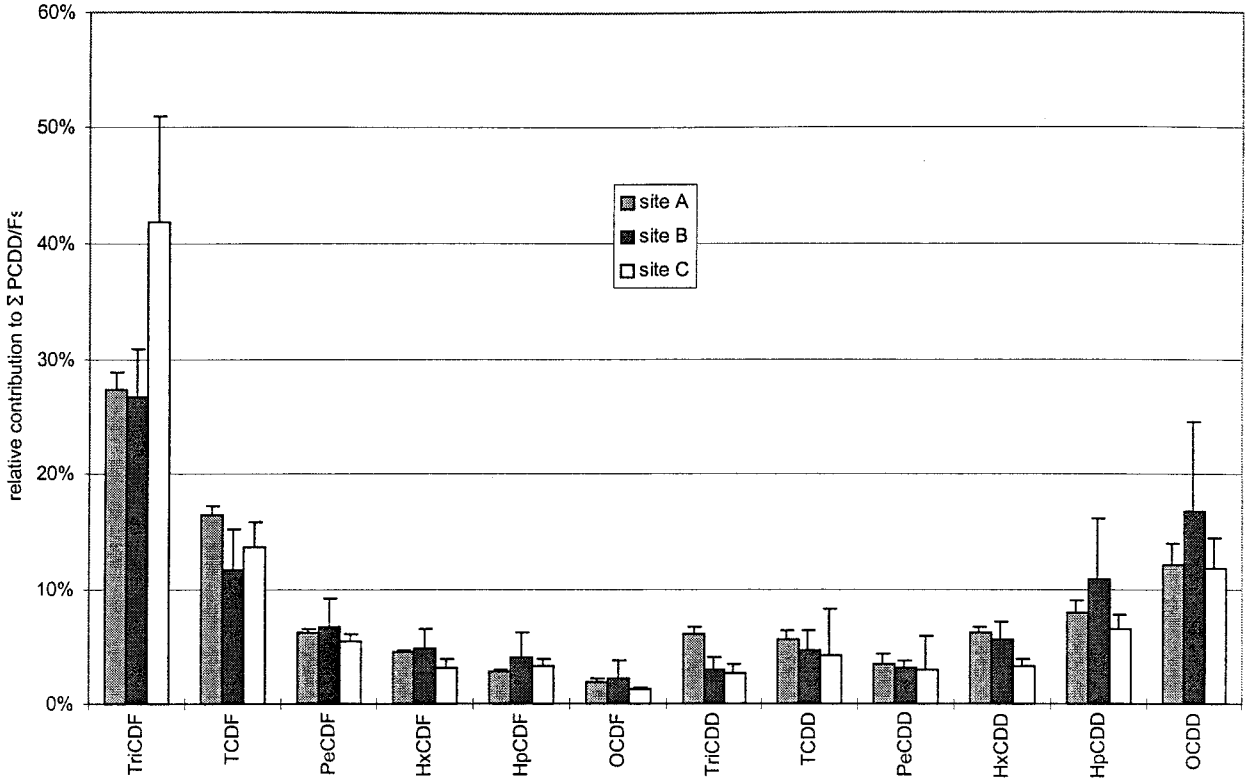

FIGURE 4. Comparison of the averaged PCDD/F homologue patterns from the three sites.

TABLE 2. Minimum and Maximum Temperatures (°C), Cumulative Rainfall (mm), Hours of Sunshine, and Speed of the Air Mass, v_{air} (km/day), for the Five Samples at the Three Sites

	Ireland			Lancaster					North York Moors			
sample (dates)	T_{min}	T_{max}	rain	T_{min}	T_{max}	rain	sun	v_{air}	T_{min}	T_{max}	rain	sun
1 (14.−17.5)	10.1	16.7	1.2	7.1	18.0	14.5	12.6	465	6.3	14.3	7.2	13
2 (17.−20.5)	10.7	14.4	18.6	10.6	18.6	9.6	8.7	375	9.7	15.7	6.8	8
3 (20.−23.5)	9.0	13.7	4.6	7.8	12.0	0	11.3	500	3.7	11.3	1.2	8.2
4 (23.−26.5)	8.7	15.1	0	3.6	14.4	0	29.8	330	3.0	17	0.2	23
5 (26.−29.5)	10.2	19.7	0	7.6	18.4	0	32.4	300	6.3	18.7	0	31

have a mixed height ≥1000 m during the day and ≤500 m during the night (*26*). Furthermore, it was assumed that PCDD/Fs remained in the well-mixed layer up to 750 m and were not dispersed to greater heights. However, there are no data on the vertical atmospheric distribution of persistent organic pollutants with which to test this assumption.

(iv) The transect between sites B and C contains both rural and urban/industrial regions in approximate proportion to that for the whole of the UK (i.e. 94% rural; 6% urban). This assumption is used to relate the national emission estimates made by others (*13*, *14*) to the changes in PCDD/F air concentrations observed as the air masses moved between the sites.

(v) The sites are representative of their regions (i.e., that they are not influenced by local PCDD/F sources). This assumption is believed to be reasonable; indeed the sites were deliberately selected with this criterion in mind. If this assumption is indeed the case, then it can be assumed for the sake of mass balance calculations that the effects of horizontal mixing during the passage of air masses to the west coast of Ireland are minimal.

A Mass Balance Assessment of the Different Air Concentrations between Sites and Potential Source Inputs. During sampling periods 3−5, the predominant air mass over northern England came from the northeast. Thus, 'clean Atlantic' air was sampled at site C, whereas the air sampled at site B had moved over northern England. The ΣTEQ values were at least three times higher at site B than at site C during these sampling periods, indicating that PCDD/F inputs had occurred during the passage of air over northern England at this time. It is therefore possible to derive a simple mass balance for this event, with the assumptions already discussed. Taking the average speed of the air mass (x km/day), and the distance between site B and the east coast of England (150 km), assuming a well mixed atmosphere of 750 m height (*26*), and taking an area of 200 000 km^2 for the UK, a crude estimate of the ΣTEQ output of the UK can be made, assuming that the regions passed over by this air mass are representative of the UK as a whole [input estimation (in g TEQ/day) = ΔTEQ·height·area·speed of air mass movement/distance]. The total increases were calculated to be 2.0, 2.5, and 3.8 g ΣTEQ/day for individual events 3, 4, and 5, respectively; this result compares well with national atmospheric source inventory estimates of 1.5−3.0 g ΣTEQ/day (*13*) or, more recently, 0.7−1.9 g ΣTEQ/day (*14*). Of course, this calculation has not taken into account atmospheric removal of the PCDD/Fs. If the removal data derived in the next section is included, the emission of ΣTEQ is of the order 5.8−12 g ΣTEQ/day, which is somewhat higher than estimations based on source emissions. This difference between the source inventory estimates and the estimates in our calculations derived here could, of course, be due to an underestimation of the

TABLE 3. Derived Atmospheric Half-Lives for the Homologue Groups and the 2,3,7,8-Substituted Congeners during One Sampling Event Compared with Theoretical OH Radical Reaction Half-Life Times (Days)

	PCDFs			PCDDs		
$t_{1/2}$, no chlorines	homologue group	2,3,7,8-substituted	$t_{1/2}$ due to OH depletion[a]	homologue group	2,3,7,8-substituted	$t_{1/2}$ due to OH depletion[a]
2	0.3	—	2.8−3.9	1.0	—	1.4−1.7
3	1.6	—	3.9−6.7	—	—	1.7−2.2
4	3.6	1.5	5.3−13 (3.5)[b]	1.6	n.d.[c]	2.5−5.0
5	1.4	1.0−1.2	10−20	3.0	0.9	2.7−5.9
6	1.2	1.0−1.2	—	1.8	0.6−0.9	4.0−8.5
7	0.9	1.1−1.2	—	0.7	0.6	—
8	1.9	—	(1.1)[b]	0.6	—	—

[a] From ref 7. [b] From ref 8, based on the air mass passing over 220 km of sea and 220 km of land for 2,3,7,8-TCDF and OCDF [c] n.d., Not detected.

'real' releases by the source-based emission inventories and/or due to inappropriate assumptions. However, the approach gives an encouragingly close agreement and suggests that the sampling/analytical procedures are sufficiently rigorous to support this type of experimental approach.

Assessment of Atmospheric Depletion and Deposition during Transport between Two Sites. Sampling period 4 involved an air mass moving from the west coast of England (site B) toward the west coast of Ireland (site A). This event allows information about PCDD/F losses to be derived as the air mass moves from a 'source region' to a remote location, assuming no dilution/concentration processes in the air mass and no further PCDD/F inputs into the air during its passage between the two sites. Southern Ireland is very rural, and we believe major industrial sources of PCDD/Fs are unlikely to influence air concentrations. The air mass traveled ~450 km between the two sites, and the wind speed at site B during that event was 330 km/day. As the air took roughly one and a half days to pass from one site to another, average air concentrations from site B for sampling periods 3 and 4 were used. Compound differences between sampling events 3 and 4 were generally <25% (see also Table 1). A first-order atmospheric loss constant (k_{loss}) was therefore calculated:

$$k_{loss} = \ln([B]/[A]) \cdot \text{wind speed/distance} \qquad (1)$$

with [B] and [A] the PCDD/F air concentrations at sites B and A. For mono- to tri-chlorinated congeners, it is believed k_{loss} will be dominated by depletion (reaction) in the atmosphere, whereas particulate deposition will dominate for the hexa- to octa-CDD/Fs (*4*, *8*). The tetra- and penta-CDD/Fs are present in both the gas and the particulate phase and will thus be prone to depletion in the gas phase, and to dry gaseous and dry particulate deposition (*25*−*27*).

Atmospheric residence half-lives are obtained by dividing ln 2 by k_{loss}. Table 3 shows the calculated half-life times (varying between 0.3 and 3.6 days for different homologues) and the predicted half-lives based on OH radical depletion by Kwok et al. (*6*, *7*; varying between 1.4 and 20 days for the di- to hexa-CDD/Fs). As the data in Table 3 are based on one sampling event only, very careful evaluation of the numbers is needed. However, certain trends of the calculated data are encouraging and worth noting. For the PCDDs, half-life times increase from the di- to the PeCDDs, suggesting that OH radical reactions are strongly influencing the atmospheric behavior of these compounds that are mostly in the gas phase. Gas particle distribution studies have reported <50% of PeCDDs particle-bound for warm temperatures (see discussion in refs *9*, *27*). There is very good agreement between the field estimations with the predicted half-lives based solely on OH radical depletion. The higher chlorinated homologues and 2,3,7,8-substituted congeners show shorter half-lives, which is expected for these primarily particle-bound species.

The PCDFs show less clear-cut behavior. The TCDFs appear to have the longest atmospheric residence time (3.6 days) of the PCDFs for the sampling event. A trend can again be seen for the 2,3,7,8-substituted congeners, where half-lives decrease with increasing levels of chlorination. The derived half-lives for 2,3,7,8-TCDF (1.5 days from this study compared with estimated 3.5 days) and OCDF (1.9 days compared with 1.1 days) were very similar to those estimated by van Pul et al. (*8*). However, van Pul's estimate assumed that wet deposition events strongly influenced the atmospheric residence time; our estimate was not affected by a rain event.

Clearly the *absolute* numbers will be influenced by the assumptions made in the calculations, for example, of wind speed/mixing height, etc. However, an encouraging aspect of the data presented here is the general trend of atmospheric half-lives derived in Table 3 across the homologue groups and the 2,3,7,8-substituted congeners. Furthermore, sampling site A (Ireland) showed very similar concentrations and profiles for different air mass origins, suggesting that atmospheric removal mechanisms are effective across water surfaces.

Acknowledgments

We thank Leonie Robertson for operating the air sampler at Mace Head, the Mace Head Research Station and Atmospheric Environment, Canada, for supplying back trajectories, and Addo van Pul (RIVM, The Netherlands) for constructive comments on an earlier version of this manuscript.

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Received for review September 30, 1998. Revised manuscript received May 18, 1999. Accepted June 7, 1999.

ES981011J