

Seasonal, Anthropogenic, Air Mass, and Meteorological Influences on the Atmospheric Concentrations of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans (PCDD/Fs): Evidence for the Importance of Diffuse Combustion Sources

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Sampling programs were undertaken to establish air polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) concentrations at a semirural site on the northwest coast of England in autumn and summer and to investigate factors causing their variability. Changing source inputs, meteorological parameters, air masses, and the impact of a festival when it is customary to light fireworks and bonfires were investigated. Various lines of evidence from the study point to diffuse, combustion-related sources being a major influence on ambient air concentrations. Higher PCDD/F concentrations were generally associated with air masses that had originated and moved over land, particularly during periods of low ambient temperature. Low concentrations were associated with air masses that had arrived from the Atlantic Ocean/Irish Sea to the west of the sampling site and had little or no contact with urban/industrialized areas. Concentrations in the autumn months (~ 1 to 20 pg m^{-3} of $\Sigma_{4-8}\text{CDD/Fs}$) were 2 to 10 times higher than those found in the summer (~ 0.4 to 0.7 pg m^{-3} of $\Sigma_{4-8}\text{CDD/Fs}$). Concentrations in the autumn rose as ambient temperatures decreased; the evidence that diffuse domestic heating (combustion) sources are responsible for this increase is discussed. A sample with concentrations 2 to 3 times above ambient levels was associated with a specific air mass originating from the Mediterranean that moved over Spain and France toward the United Kingdom (UK). Concentrations also increased substantially, by a factor of >10 , during the autumnal festival. It is estimated that $\sim 30 \text{ g}$ of sum of toxic equivalents (ΣTEQ) of PCDD/Fs may have been emitted into the UK atmosphere during a 3-day period at this time. This amount is $\sim 5\text{--}14\%$ of the estimated contemporary annual national primary emissions of PCDD/Fs in the UK and implicates uncontrolled burning of wood, garden refuse, and wastes on the bonfires and/or the lighting of fireworks as diffuse sources of PCDD/Fs.

Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are derived primarily from inefficient combustion pro-

cesses and as unwanted byproducts in the synthesis of various chlorinated products. Primary atmospheric emissions of PCDD/Fs have been estimated for the United Kingdom (UK; 1, 2), the United States of America (USA; e.g., 3) and other industrial countries, but they are subject to many uncertainties and continued refinement (2–4). There are also uncertainties over (i) ambient levels and mixtures of different homologues/compounds in the atmosphere in rural areas, away from local source influences (e.g., 5); (ii) the influence of various factors on homologue/compound specific ambient concentrations, such as regional source inputs, meteorology, air mass origin, and atmospheric degradation/loss processes (i.e., reactions with hydroxyl radicals, photolysis, wet/dry deposition; e.g., 5, 6); and (iii) the balance between atmospheric emissions, air concentrations and deposition (e.g., 2). Unravelling the influences of (i)–(iii) requires measurements of ambient air concentrations in locations away from the influence of local point sources. To date, however, detailed studies have been limited because of the need to couple highly sensitive analytical detection by high-resolution-mass spectrometry (HR-MS) techniques with relatively short sampling times, to allow individual meteorological events and/or air mass movements, etc., to be distinguished. Air concentrations of 2,3,7,8-TCDD, for example, are $\leq 1 \text{ fg m}^{-3}$ in rural areas, requiring the sampling of several hundred cubic meters of air even when the most sensitive MS instrument is available for quantification. We have access to such sensitive analytical methods and therefore undertook this study to (i) measure a full range of PCDD/Fs (di to octa homologues) in air samples at a well-studied semirural/rural location where detailed meteorological information is routinely obtained and other studies on semivolatile organic chemicals (SOCs) in the atmosphere have been carried out (e.g., 7, 8), and (ii) relate variations in PCDD/F concentrations and/or patterns to various anthropogenic and environmental factors, namely, temperature, seasonal and short-term changes in combustion-related inputs, and air mass origin and/or history.

Materials and Methods

Site Description. The sampling site is at Hazelrigg, a meteorological station located in a semirural area outside Lancaster, a town of $\sim 70\,000$ inhabitants on the northwest coast of England, $\sim 5 \text{ km}$ from the Irish Sea ($54^{\circ}2' \text{ N}$, $2^{\circ}45' \text{ W}$). The majority of the air systems that influence the meteorology at the site originate from a 45° sector to the west, between latitudes $\sim 45^{\circ}$ and 70° N , and are often turbulent low pressure systems. Air systems sometimes originate to the east and southeast of the UK over central and southern Europe, and they are often associated with stable high pressure. Low pressure systems are usually dominant during the autumn, winter, and spring periods, but can occur at any time of the year. These systems usually bring unstable, wet, temperate conditions and sometimes snow in winter. High pressure systems occur most often in the summer months and are associated with stable, warm, dry conditions. If they occur in the autumn and winter months, they usually cause a significant drop in the ambient temperature. Although the sampling site is situated in a semirural area, large urban/industrial conurbations are $\sim 90 \text{ km}$ to the south and southeast (i.e., Liverpool, Manchester, Lancashire's industrial belt). To the west is the Irish Sea, Ireland (predominantly rural), and the North Atlantic. The land to the north of the site is predominantly rural northern England and Scotland, except for the urban conurbations of the Scottish lowlands (Glasgow and Edinburgh, $\sim 200 \text{ km}$ to

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the north). Further details of the site are given in refs 7 and 8, and the location is shown on Figure 2.

Sampling and Analysis. Air samples of $\sim 900 \text{ m}^3$ were taken over periods of 3 or 7 days using General Metal Works GPS1 samplers. The nominally defined particulate fraction was trapped on a Whatman glass microfibre filter (GFF; grade GF/A, 10-cm diameter) and the vapor-phase fraction was trapped on a polyurethane foam plug (PuF; length, 8 cm; diameter, 6.25 cm; density, 0.035 g cm^{-3}). The GFFs were pre-cleaned by baking them in a furnace at 450°C for 24 h and then stored in solvent-rinsed aluminum packages within sealed plastic bags until used. The PuFs were pre-extracted in dichloromethane (DCM) for 18 h on a Büchi Soxhlet system; the DCM was removed by placing the PuFs in a solvent-cleaned desiccator under reduced pressure. The PuFs were then stored in solvent-rinsed glass jars with lids with aluminum surfaces. The GFFs and PuFs were only handled with solvent-rinsed tongs or gloved hands, and were exposed to the laboratory air for the minimum amount of time possible. Sampling modules were assembled with the GFF and PuFs just prior to use. On return to the laboratory, they were immediately disassembled and stored in solvent-rinsed glass jars in a freezer until extracted. The entire sampling modules were periodically solvent cleaned, and any parts that came into contact with the GFF or PuFs were routinely solvent cleaned between each sample. Samples were extracted for 16 h in toluene and cleaned up by refluxing in acid silica, followed by fractionation on a basic alumina column. Cleaned up samples were taken to a final volume of $\sim 15 \mu\text{L}$. Analysis was performed on a Micromass Autospec Ultima HR-MS operated at a resolution of at least 10 000. Details of the cleanup, fractionation, C_{13} spiking, validation, and quantification procedures have been described elsewhere (9). Two sampling programs were undertaken, one in the autumn of 1995 (mid-September to mid-November) and the other in the summer of 1996 (end of May to early August). Total suspended particulate (TSP) concentrations measured in this and other studies at Lancaster range between 14 and $39 \mu\text{g m}^{-3}$ throughout the year. These values are typical of rural areas (10–12).

Quality Assurance/Quality Control (QA/QC). Field and laboratory blanks were extracted with each set of samples and treated in an identical fashion to samples. Blank levels were very low; indeed, levels for individual isomers often had to be based on background noise and the detection limit of the HR-MS [$\sim 0.5 \text{ fg}$]. Method detection limits (MDL) were defined as the mean plus three times the standard deviation of the blanks (there was no consistent difference between levels in field blanks and laboratory blanks). The majority of the MDLs for the individual isomers were $< 0.7 \text{ fg m}^{-3}$, except for 1,2,3,4,6,7,8-HpCDD (0.8), 1,2,3,7,8,9-HxCDF (2.0), 2,3,4,6,7,8-HxCDF (2.1), and OCDD (4.8). The homologue groups generally had MDLs $< 1.0 \text{ fg m}^{-3}$, except the diCDD/Fs, which had MDLs of 39 and 7.3 fg m^{-3} , respectively. A number of studies have been carried out at Lancaster to assess the reproducibility of concurrent air sampling with GPS1 samplers (e.g., 8). In this study, duplicate samples were taken in 1995 for all but one of the sampling periods and, as can be seen in the Supplementary Information (Table S1), there was excellent reproducibility between duplicates. In another study, Lohmann et al. (9) operated five GPS1 samplers concurrently to test sampling and analytical reproducibility. The coefficients of variation (CVs) for the individual 2,3,7,8-substituted isomers were between 5 and 19% (mean, 10%), and those of the homologue groups were between 4 and 20% (mean, 11%). Breakthrough of the nominal vapor phase from the PuF was tested in the 1996 sampling program when higher temperatures would have enhanced the likelihood of it occurring. In two of the duplicate samples, half a PuF was placed behind the normal full PuF, with the other half acting

as a blank for the test. Both halves were treated in a manner similar to the samples and showed levels consistent with blanks. No breakthrough was therefore occurring at volumes of $\sim 1000 \text{ m}^3$ and mean weekly temperatures of 19°C , even for the more volatile di- and triCDD/Fs.

Results and Discussion

Ambient Levels of PCDD/Fs. The concentrations of PCDD/Fs measured at Hazelrigg during this study were typical of those from semirural areas (e.g., 13–15; see ref 5 for review). The full data set is given as Supplementary Information and summarized in Table 1.

Homologues. Concentrations of $\Sigma_{4-8}\text{CDD/F}$ in the autumn 1995 samples ranged from 940 to 7260 fg m^{-3} , except for the sample taken during bonfire weekend, for which the concentration reached $21\,900 \text{ fg m}^{-3}$. The $\Sigma_{4-8}\text{CDD/F}$ concentrations were lower in the summer 1996 samples, ranged between 390 and 790 fg m^{-3} . Typical tetra-to-octa homologue autumn and summer profiles are shown in Figure 1a and are in broad agreement with those found by other workers (see ref 5 for review). Averaged over both seasons, the trend was for decreasing levels with increasing levels of chlorination for the PCDFs and the opposite for the PCDDs. The summer 1996 samples were also analyzed for the di- and triCDD/Fs (see Table 1). These homologues made very sizable contributions to the $\Sigma_{2-8}\text{CDD/F}$, with the diCDDs dominating at concentrations from 29 100 to $112\,000 \text{ fg m}^{-3}$. The di- and triCDD/Fs followed the sequence diCDD \gg diCDF $>$ triCDF $>$ triCDDs. Very little data exist in the literature for these lighter weight PCDD/Fs and yet they contributed $> 99\%$ to the $\Sigma_{2-8}\text{CDD/F}$ burden of air at this site. Although not as toxicologically significant as the 2,3,7,8-substituted congeners, as information is gained about them, they can be used to aid source appointment work (16) and provide information on the partitioning behavior of PCDD/Fs in the environment.

2,3,7,8-Substituted PCDD/Fs and Toxicity Equivalent Factors ΣTEQ Data. The ΣTEQ values (using the NATO TEFs) ranged between 3.6 and 21 fg m^{-3} in autumn 1995 (except for the sample taken during bonfire weekend, which reached 69 fg m^{-3}) and between 7 and 17 fg m^{-3} in summer 1996. All of the 2,3,7,8-substituted congeners were detected in all of the samples (see Table 1). As expected (see ref 5), 2,3,4,7,8-PeCDF contributed most to the ΣTEQ (15–26%) with 2,3,7,8-TCDD contributing $\sim 5\%$ in autumn 1995 and $\sim 17\%$ in summer 1996. There were also large differences in the absolute concentrations and ΣTEQ contribution of the Hp- and OCDD/Fs, with autumn $>$ summer (see below).

Seasonality in Air Concentrations. Table 1 presents mean 2,3,7,8-substituted congener and homologue ambient air concentrations for the autumn and summer sample sets, together with TEQ information. Concentrations of the homologue groups were all significantly higher during the autumn, as shown clearly in Figure 1a. There was also a seasonal change in the contribution of dioxins and furans to the $\Sigma\text{PCDD/Fs}$, with the PCDDs contributing almost twice as much to the $\Sigma\text{PCDD/Fs}$ in autumn compared with the summer (Table 1). The congener data are plotted in Figure 1b, highlighting the increases of the Hp- and OCDD/Fs in autumn.

Interestingly, within the summer sampling set, two subsets of samples could be identified. The first five samples had similar mean weekly temperatures ($12.2\text{--}13.1^\circ\text{C}$), distinct from the last four samples, which themselves were similar to each other ($14.8\text{--}17.0^\circ\text{C}$). The data for these two sample sets are given in Table 1. The $\Sigma_{4-6}\text{CDD}$ contributed more to the $\Sigma_{4-8}\text{CDD/Fs}$ during the first period of lower temperatures than during the second period with higher temperatures. The PCDDs also contributed more to the $\Sigma\text{PCDD/Fs}$ during the first period when lower temperatures were experienced. Indeed, during the June to mid-August period, quite subtle

TABLE 1. Summary of the Data Set for Autumn 1995 and Summer 1996^a

Isomer/Homologue, fg m ⁻³	summer 1996 (n = 9)				autumn 1995 (n = 15; 7 duplicates, 1 single)					
	first 5 samples		last 4 samples		autumnal ambient		autumnal event 1		autumnal event 2	
	mean	TEQ mean	mean	TEQ mean	mean	TEQ mean	mean	TEQ mean	mean	TEQ mean
2,3,7,8-TCDF	4.1	0.4	3.9	0.4	2.7	0.3	4.4	0.4	15	1.5
1,2,3,7,8-PeCDF	9.1	0.5	7.2	0.4	4.5	0.2	6.4	0.3	31	1.5
2,3,4,7,8-PeCDF	4.6	2.3	4.4	2.2	4.0	2.0	6.1	3.1	26	13
1,2,3,4,7,8-HxCDF	4.9	0.5	5.9	0.6	6.4	0.6	9.4	0.9	43	4.3
1,2,3,6,7,8-HxCDF	4.6	0.5	5.0	0.5	5.5	0.6	8.3	0.8	33	3.3
1,2,3,7,8,9-HxCDF	13	1.3	5.5	0.6	3.1	0.3	4.5	0.5	17	1.7
2,3,4,6,7,8-HxCDF	6.3	0.6	5.8	0.6	8.0	0.8	13	1.3	36	3.6
1,2,3,4,6,7,8-HpCDF	14	0.1	19	0.2	88	0.9	150	1.5	440	4.4
1,2,3,4,7,8,9-HpCDF	5.0	0.05	5.0	0.05	12	0.1	21	0.2	68	0.7
OCDF	25	0.02	25	0.03	100	0.1	180	0.2	650	0.6
2,3,7,8-TCDD	2.5	2.5	1.5	1.5	0.5	0.5	0.7	0.7	2.0	2.0
1,2,3,7,8-PeCDD	4.2	2.1	1.7	0.9	1.7	0.9	3.0	1.5	11	5.5
1,2,3,4,7,8-HxCDD	2.0	0.2	1.2	0.1	2.7	0.3	5.3	0.5	14	1.4
1,2,3,6,7,8-HxCDD	4.8	0.5	3.3	0.3	5.6	0.6	9.8	1.0	32	3.2
1,2,3,7,8,9-HxCDD	9.7	1.0	3.7	0.4	4.8	0.5	8.5	0.9	29	2.9
1,2,3,4,6,7,8-HpCDD	26	0.3	28	0.3	200	2.0	360	3.6	1300	13
OCDD	82	0.1	100	0.1	770	0.8	1500	1.5	5800	5.8
total		13		8.2		11		19		68
di-furans	74000		67000							
tri-furans	270		420							
tetra-furans	110		150		430		730		1900	
penta-furans	57		75		290		420		1900	
hexa-furans	47		59		310		460		1800	
hepta-furans	20		34		160		290		820	
di-dioxins	570		460							
tri-dioxins	46		34							
tetra-dioxins	63		38		330		570		1000	
penta-dioxins	40		19		270		610		1100	
hexa-dioxins	55		39		510		1100		2200	
hepta-dioxins	52		57		410		840		2500	
sum4-8PCDFs	260		340		1300		2100		7000	
sum4-8PCDDs	290		250		2300		4500		13000	
mean air volume m ⁻³	913				844					

^a All homologue groups and 2,3,7,8-substituted isomers were above MDL.

changes in PCDD/Fs patterns occurred. The 3–7CDF homologue groups were positively correlated with temperature ($p < 0.05$ or 0.01), whereas some of the PCDD homologues were negatively correlated, although in general they were not statistically significant. However, it is difficult to unravel the reasons for these comparatively subtle changes because the difference in ambient temperature also reflected, at least in part, differences in air mass origin. Air sampled during the lower temperature periods came almost exclusively from the SW-NW, off the Irish Sea/Atlantic Ocean. In contrast, during the (warmer) second period, the air originated and moved over parts of the UK and Europe (i.e., over land areas) during three of the four sampling periods.

In summary, this section has shown that there were clearly large variations in the concentrations and mixtures of PCDD/Fs during the study, reflecting complex differences in sources, environmental processes, meteorology, and air mass history. We will now systematically address these factors, to make inferences about the key factors controlling ambient PCDD/F concentrations in the semirural UK atmosphere. It is appropriate to first consider the general observation that autumn/winter concentrations exceed those measured in the summer.

General Observations on Factors that Could Influence Seasonality. A number of direct and indirect factors could influence seasonality, and may be responsible for differences between and within the two sampling programs.

Photolytic Degradation and Reaction with Hydroxyl Radicals. Increasing sunlight results in the potential for greater photolytic degradation and reactions with hydroxyl radicals generated by sunlight (6, 17, 18). There is uncertainty in the

literature about the significance of these processes (5, 6), but it is known that lower chlorinated species are more susceptible to atmospheric degradation than the higher chlorinated species (6, 17, 18). If atmospheric reactions were solely responsible for the differences between summer and autumn noted in this study, it would be expected that summer concentrations, especially of the lower chlorinated species, would be lower than those in the autumn. The data show the opposite trend, implying that atmospheric reactivity is not the most important factor operating here.

Precipitation. Wet deposition is a major removal process for many SOCs (5). It is more frequent in the autumn than summer at the site and could alter the concentrations and profiles measured. However, samples from both sampling periods (summer and autumn), that experienced similar rainfall during the sampling periods still had significantly different concentrations and profiles. This result implies that other factor(s) exhibit a stronger influence on seasonality.

Vegetation. Hites and co-workers have drawn attention to the role that vegetation can play in scavenging compounds from the atmosphere, although estimates as to its significance vary sharply (19, 20). The autumn 1995 sampling started in September and continued to November. Trees still had leaf cover at the time. However, toward the end of the growing season, vegetation may have a lower capacity to retain gas-phase PCDD/Fs deposited by dry gaseous deposition because fresh biomass is not produced (21). Vegetation could still scavenge particulate-bound PCDD/Fs, although some leaves are obviously shed during the autumn. The capacity of vegetation to directly scavenge PCDD/Fs and other SOCs from the atmosphere is small relative to the emissions into

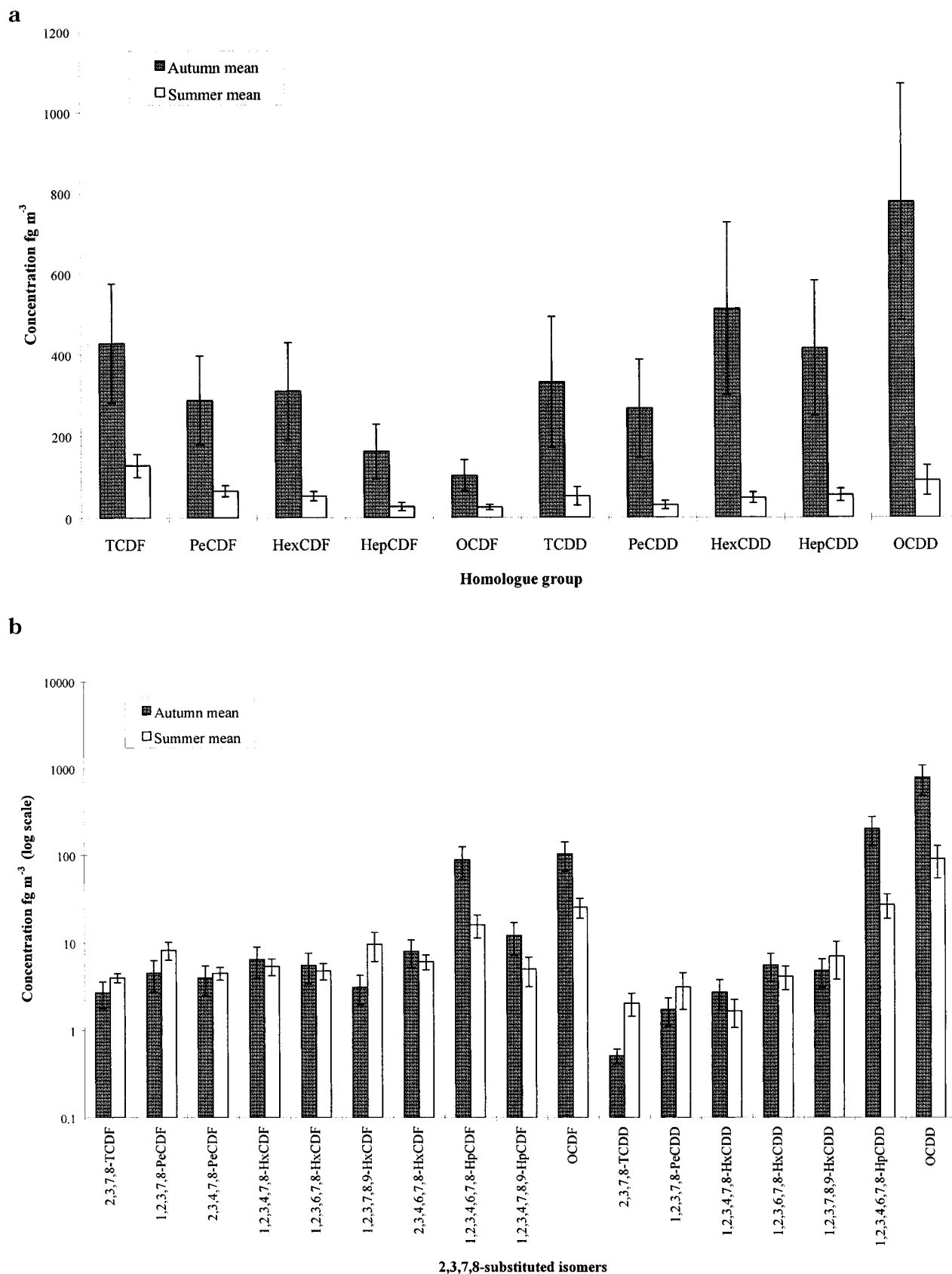


FIGURE 1. Comparison of the autumn and summer data sets: (a) tetra to pentahomologues; (b) 2,3,7,8-substituted congeners (note the logarithmic scale)

the air (2, 20, 21). The effects of vegetation growth, scavenging, and boundary layer resistance on the seasonal deposition of PCDD/Fs to the earth's surface would presumably be greater in spring/summer than autumn/winter. However, in the 1995

study, large differences in concentrations were found between samples at a time of the year when vegetation growth/cover was at its lowest and could not play a significant role in influencing the concentrations measured. In conclusion,

although vegetation scavenging undoubtedly influences atmospheric concentrations of PCDD/Fs, it is unlikely to be the dominant factor responsible for the seasonal differences noted in this study.

Atmospheric Boundary Layer (ABL). There is a broad seasonality in the height of the mixed atmosphere. Generally it is greater in summer than winter and is usually between 100 and 1000 m. Some authors have speculated that the lower ABL during winter may result in less dispersal of PCDD/Fs emitted at the surface, giving locally elevated concentrations (22, 23). However, Hippelein et al. (24) concluded that increased levels of PCDD/Fs in the winter months in Germany were due to increased emissions and not to a lower ABL and/or longer residence time/lower deposition rates. The ABL may be significantly reduced during specific meteorological conditions but these are unlikely to be sustained for more than a few days. It is therefore unreasonable to suggest that the increased levels of PCDD/Fs during the whole of the 1995 autumnal sampling program were due to a prolonged reduction in the ABL.

Seasonally Consistent Sources. The major sources that have been estimated to dominate the UK primary atmospheric emissions inventory will essentially be consistent throughout the year and not display seasonality (i.e., emissions from municipal solid waste and clinical waste incinerators, the iron and steel industry, and metal smelting, 1–4). Power stations burning fossil fuels increase their activities during the darker, colder months of winter, but PCDD/F emissions from these high temperature, clean combustion sources are thought to be minor (1–4). It is therefore unlikely that any of the major primary sources just mentioned are responsible for the differences noted in this study.

Seasonally Variable Sources. The seasonally consistent emission sources identified in the previous section have been estimated to contribute the majority of the UK national annual primary PCDD/F and Σ TEQ inventory (1, 2, 4). However, there are clearly other diffuse sources that could make an important contribution to emissions that are seasonally dependent and that have been less easy to quantify. Foremost among these are inputs associated with domestic heating during colder conditions; namely, domestic burning of coal, wood, and gas (22, 24–27). Indeed, the use of domestic heating systems and open fires is very temperature dependent, and there is clear evidence in the data set that these sources make a sizable contribution to the ambient PCDD/F concentrations at Hazelrigg. During autumn there was a strong, significant ($p \leq 0.01$), inverse correlation between the average weekly temperature and the ambient air concentrations of all individual PCDD/Fs and homologue groups. In other words, it is hypothesized that as air temperature declines, combustion sources are used for space heating and emit PCDD/Fs to the atmosphere. This increase in ambient Σ PCDD/F concentrations was quite systematic through the autumn period, increasing from 940 fg m⁻³ in mid- to late September to 5730 fg m⁻³ by mid-November. Minimum average weekly temperatures during the autumnal sampling weeks varied between 9.8 and -0.4 °C, tending downward with time and becoming sufficiently low for residents to increasingly need home heating. The use of domestic heating and open fires is very temperature dependent, with the lowest daily temperature influential in controlling whether heating systems/fires are used, and capable of producing rapid changes in PCDD/F emissions. In contrast, ambient PCDD/F concentrations were not inversely correlated with temperature in the early summer sampling campaign, when minimum weekly temperatures ranged between 9.4 and 14.3 °C and domestic heating systems are not widely used. The PCDD/F profile in chimney soot and the combustion products varies widely with the fuel type (i.e., coal, wood, gas) and the combustion conditions (16, 28, 29), and can be

indicative of a source type (30, 31). Increased ambient levels of PCDD/Fs during the winter months have been noted by others (22, 25–27) and, in some studies, this increase has been associated with domestic heating (24).

In summary, the data show a marked seasonality in PCDD/F concentrations at Hazelrigg. Several factors have been identified that could exert a seasonally dependent influence on ambient PCDD/F concentrations, but we interpret the strong inverse temperature dependency in autumn as powerful evidence for diffuse inputs from domestic heating. We now consider general meteorology and specific events that provide further evidence linking the increase in PCDD/Fs concentrations in the autumn with the burning of wood and waste on domestic fires in populated areas.

General Correlations with Meteorological Parameters.

The determination of relationships between meteorological parameters and compound concentrations is complicated by the source inputs, properties of the sorbing surfaces (e.g., soils, vegetation), the dynamic nature of the micro- and macrometeorology at a site, and confounding factors that exist between variables (8, 32, 33). Very large numbers of samples and/or very high resolution data taken under relatively stable conditions (7) are needed to be able to show significant correlations. In this study, the number of samples and the sampling duration were necessarily limited and correlations therefore required careful interpretation. Product moment correlation coefficients were derived from mean weekly meteorological parameters (mean, maximum, and minimum temperatures; relative humidity; pressure; rainfall; run of wind; hours of sunshine) and the concentrations of the individual isomers and homologue groups.

Autumn 1995 Data Set. The ambient 1995 sample set excluded two specific events because they yielded unrepresentatively high ambient concentrations that will be discussed later. However, the general trend in autumn was for strong significant negative correlations ($p \leq 0.05$ to $p \leq 0.01$) between PCDD/F concentrations and ambient temperature, run of wind (ROW, km day⁻¹), and rainfall. There were no significant correlations with the hours of sunlight. Reduced temperature is a confounding factor for increased source inputs. Increased rainfall may cause an increase in the deposition of PCDD/Fs (i.e., lowering air concentrations, 34, 35), whereas higher ROW is symptomatic of turbulent low pressure systems resulting in greater atmospheric mixing and a possible increase in the ABL. It should be noted, however, that these meteorological variables are confounders for two different types of weather systems that were prevalent at different times during the sampling period. Low pressure systems are associated with mild, wet, and turbulent conditions and generally bring cleaner (oceanic) air from the west, whereas high pressure systems usually bring more stable, rain-free conditions with lower temperatures in the autumn. Meteorological conditions for the first seven samples were influenced by turbulent low pressure systems, whereas the last four samples were taken when high pressure systems and ridges affected the site, resulting in lower temperatures and possibly increased anthropogenic inputs. Meteorological conditions can undoubtedly influence concentrations of PCDD/Fs at a site, but the results from this study suggest that the meteorological conditions monitored here were confounding factors that could be related to anthropogenically mediated combustion sources that increased as the autumn progressed. These arguments are highlighted in the following discussion of specific meteorological events.

1996 Data Set. No consistent significant correlations were found between any of the meteorological parameters and ambient PCDD/Fs concentrations in the 1996 data set.

General Comments on the Back Trajectories and Air Masses Influencing the Site. Back trajectories (BTs) were calculated using a commercial software program every 6 h

for 5-day periods at a height of 925 mb. For SOCs that have ongoing emissions to the atmosphere and hence strong source areas, the air mass origin is important (36–38), together with the route the air has travelled to reach a site and the prevailing meteorological conditions in those areas (39). Up to this point we have considered general trends and influences on ambient PCDD/F concentrations. However, in this section we show how specific events can influence the pattern and concentrations of PCDD/Fs and how this information implicates diffuse combustion sources as a key factor in controlling ambient levels. Two examples are considered, one relating to large-scale air mass movements and the other to an unusual diffuse emission input event. However, it is first appropriate to consider the commonly occurring situation at the Hazelrigg site (8) of air masses arriving from the Atlantic Ocean/Irish Sea to the west, the clean sector. Figure 2a shows air mass BTs for every 6 h for the samples taken between September 26 and October 3, 1995, and clearly shows the arrival of air predominantly from the clean sector to the southwest, west, and northwest. The minimum temperature during this period was 3.4 °C, and concentrations under these conditions were 1070 fg m⁻³ for Σ_{4-8} PCDD/F and 4 fg m⁻³ for Σ TEQ (i.e., low ambient concentrations). The BTs for the samples taken between October 17 and 24, 1995, and October 27 and November 3, 1995, were very similar to those in Figure 2a; however, the minimum air temperatures were lower (0.6 and -0.3 °C) and Σ_{4-8} PCDD/F concentrations were correspondingly somewhat higher at 2080 and 5270 fg m⁻³, respectively. The systematic rise in concentrations through these autumnal samples can therefore be readily related to the overall drop in ambient temperature and increased local combustion sources discussed earlier. The ambient autumnal profile in Figure 3 is representative of both these samples.

Bonfire Weekend. November the fifth is a festival in the UK when it is customary to set alight bonfires, set off fireworks containing gunpowder, and celebrate the ritual burning of human effigies (40). This is an old tradition, and a high proportion of the UK population participate, either by burning a bonfire in their own garden or by attending large public fireworks and bonfire displays. If November 5th falls on a week day, the celebrations may be deferred to the weekend, but November 5, 1995 (Bonfire day) was on a Sunday. As a consequence, most of the celebrations took place on Friday, Saturday, and Sunday (i.e., 11/3–5/1998). Bonfires usually consist of wood and leaves (garden refuse) gathered from the local area, but many people (illegally) supplement the fire with domestic waste and other materials that they wish to dispose of, including plastics, textiles, PCP-treated wood, etc. As a result, there are many tens of thousands of diffuse and uncontrolled fires lit across the UK at this time, providing an important, unique input of combustion-derived products into the atmosphere over a short period of time (40). Samples were obtained between November 3 and 6, 1995, and contained very high PCDD/F concentrations (20 000 fg m⁻³, Σ_{4-8} PCDD/F; 68 fg m⁻³, Σ TEQ; see Table 1). The homologue pattern is shown in Figure 3, along with the autumnal and summer averages for comparison. What is clearly distinctive about this sample is that all of the 2,3,7,8-substituted isomers and homologues show very marked increases and that the pattern is very similar to the autumnal mean. For example, with the exception of the tetrachlorinated species, all the other congeners and homologues increased in the air during Bonfire weekend by a factor of 10–14. Only 2,3,7,8-TCDD (factor of 5), 2,3,7,8-TCDF (9.7), Σ TCDF (8), and OCDD (16) showed any variation from this increase. Back trajectory data and mass balance calculations for Bonfire weekend (see below) show how important many small-scale diffused sources can be in influencing the atmospheric concentrations of PCDD/Fs.

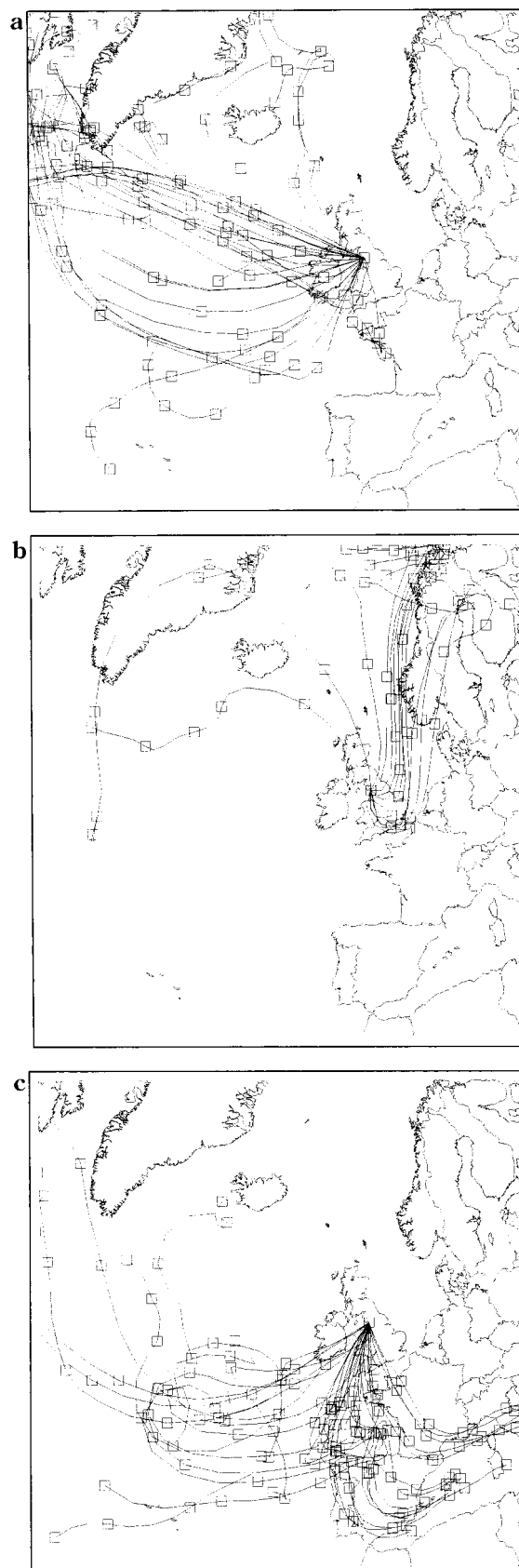


FIGURE 2. Air mass trajectories for specific events. (a) Air mass originating from the west of the UK, typical of the majority of air masses/systems experienced at the site. (b) Air movements over the Bonfire weekend. (c) Air mass originating from the south of the UK in October 1995, that gave unseasonably high PCDD/F concentrations.

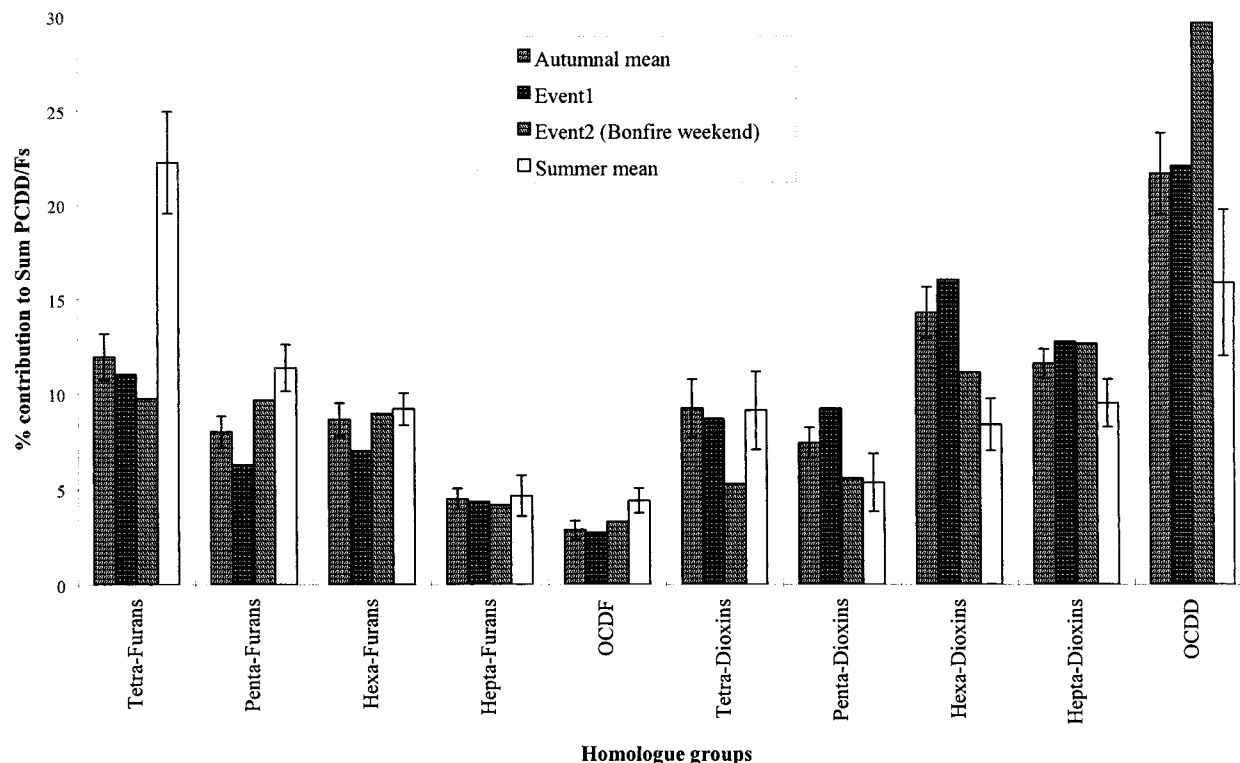


FIGURE 3. Comparison of the homologue profile for Bonfire night and the autumnal and summer averages.

Back Trajectory and Mass Balance Calculation. Figure 2b presents the BTs for the Bonfire weekend samples. It can be seen that the air arriving at Lancaster during this weekend came from 40° to 160° and represented air that had moved over the southern UK before reaching Lancaster. Given the mean distance of the UK downwind of the site between 40° to 160° is 240 km, with a mean ROW of 252 km day⁻¹ during the sampling period, the air over the UK would have been replaced approximately every 24 h. During this period, the $\Sigma_{4-8}\text{CDD/F}$ concentration was 20 000 fg m⁻³ (68.5 fg m⁻³; ΣTEQ). If various assumptions are made (i.e., a daytime ABL of 1000 m; nighttime mean ABL of 300 m; land area of the UK of 2.34×10^{11} m²) it is possible to calculate the PCDD/F inputs to the UK atmosphere during Bonfire weekend, assuming no losses. Inputs would therefore have been ~ 3 kg day⁻¹ of $\Sigma_{4-8}\text{CDD/F}$ and ~ 10 g day⁻¹ of ΣTEQ over the 3 days of Bonfire weekend (i.e., a total emission of ~ 30 g of ΣTEQ during the event). Estimates of the contemporary primary atmospheric emissions inputs of PCDD/Fs to the UK environment range from 220 to 660 g year⁻¹ of ΣTEQ (4). Bonfire weekend is only 0.8% of the year, but this event accounted for ~ 5 to 14% of those inputs. This simple calculation demonstrates how the widespread, inefficient combustion of domestic/garden waste and old wood (and possibly illegal waste) can have a significant effect on the concentrations of PCDD/Fs in the air. As stricter controls over municipal waste incinerators and other major primary sources have come into effect in recent years, it is evident that the diffuse uncontrolled burning of domestic waste and emissions from domestic fires have become major contributors to the atmospheric burden of PCDD/Fs in the UK.

Air Mass from the South. As just noted, the general trend through the autumn was increasing PCDD/F concentrations later in the sampling period as ambient temperatures tended to decline. However, the sample taken between October 10 and 17, 1995, was an obvious exception to this (see Table 1). This sample was taken when the average temperature was unusually high for autumn at 14.3 °C (9.8–18.4 °C), yet the air concentration was ~ 6 times higher (6600 fg m⁻³ of Σ_{4-8}

PCDD/F; 19 fg m⁻³ of ΣTEQ) than in samples taken immediately before or after. The homologue profile for this event is shown in Figure 3. The explanation lies in the unusual source area for the air during the sampling event, shown in Figure 2c. The majority of the air sampled during this period had passed over southern Europe, moving predominantly over the west side of the UK, and passing over urban and industrialized areas of the UK before reaching Lancaster. This path demonstrates how air mass movements over urbanized/industrialized areas may result in increased concentrations of PCDD/Fs. The similarity between the homologue profiles for this sample, the autumnal mean, and Bonfire weekend would suggest a similar source; that is, diffuse, low-temperature burning of wood and domestic waste. Although the differences in concentration are not as great when the 1996 samples are compared with each other, they showed that increased levels of PCDD/Fs tend to be associated with air masses that originated and/or moved over land, particularly urban/industrial areas. Both samples 7 and 9 (see Supplementary Information) from the 1996 sampling program had seasonally high levels of $\Sigma_{4-8}\text{PCDD/Fs}$ (730 and 585 fg m⁻³, respectively), and the BTs for both samples show that for all or some of the week the air originated and moved over urbanized/industrialized land areas. Samples 5 and 8 had almost half the concentrations of samples 7 and 9 (i.e., 391 and 410 fg m⁻³, respectively). The BTs for both these samples show the air to have originated over the North Atlantic to the west and north of the UK. For the majority of the time the air moved over the ocean and for only short periods did it move over remote/rural areas of the UK. The difference between the summer and autumnal homologue profiles and concentrations would suggest that, although populated areas are still acting as a source during the summer, a reduction and change in the emissions of PCDD/Fs has taken place between the winter and summer. As discussed earlier, this reduction implicates seasonally variable sources, such as domestic heating.

Inferences from the Bonfire Weekend and Back Trajectory Data. Because of the similarities in patterns between the

Bonfire weekend sample and the autumnal mean, it is tempting to conclude that the large-scale uncontrolled burning of wood, textiles, plastics, etc. produces emissions of PCDD/Fs that are quite similar to those of domestic fire/heating systems implicated earlier in the paper as providing a major input to the UK atmosphere nationally. It is also interesting to note the similarities with the profile from the BT event originating from southern Europe, just discussed (see Table S2 of Supplementary Information). We conclude, therefore, that there are similar sources of PCDD/Fs throughout autumn/winter that vary in strength. The increase in concentrations that occurs over Bonfire weekend can be identified as being primarily due to the low-temperature burning of domestic waste (wood, textiles, garden refuse). The similarities between the profile during this period and the ambient autumnal profile (Figure 3) further suggests that the diffuse, low-temperature burning of old wood, coal, and household waste on domestic fires/heating systems may be an important source of PCDD/Fs during the autumn/winter period.

Concluding Remarks. A number of factors may be responsible for changes in the atmospheric PCDD/F burden and mixture experienced at a site at a given time. Most important among these at this semirural UK site are seasonally dependent inputs from diffuse combustion sources and the history of a given air mass. Other factors operate at a finer scale to influence the air concentration and composition through loss processes. Different meteorological conditions, for example, can cause changes in the degradation and deposition rates and routes for airborne PCDD/Fs.

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Supporting Information Available

Supplemental information (Tables S1 and S2) is available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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