The Influence of Meteorology and Air Masses on Daily Atmospheric PCB and PAH Concentrations at a UK Location

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Daily (24 h) air samples were collected on 161 occasions during March−October and December 1994 at a semirural, maritime-influenced site in northwest England and analyzed for PCBs and PAHs. $\sum$PCB and some low molecular weight PAH concentrations followed similar trends, but the magnitude of the daily concentration changes varied between these two sets of compounds. $\sum$PCB concentrations only ranged by a factor of 7, between 54 and 375 pg m^{-3}, with $\sum$PAH varying over a factor of 20 (1.4−40 ng m^{-3}). This is interpreted as evidence that PCBs are becoming well mixed regionally, while PAH concentrations are influenced by ongoing primary sources. A positive relationship between air temperature and concentration was found for some PCB congeners, certain PCB homologue groups, the lighter molecular weight PAHs and $\sum$PCBs; the heavier molecular weight particulate associated PAHs exhibited a negative relationship with temperature, suggesting combustion sources of these compounds which increase as ambient temperature decreases. A range of standard meteorological parameters was also analyzed, but no consistent correlations were found between any of the parameters and the daily concentrations of PCBs or PAHs. Clausius Clapeyron plots for the PCB data produced slopes that were similar to those at urban U.K. sites suggesting that concentrations at this site are influenced by volatilization of PCBs from the earth's surface. However, the correlations were weak, suggesting that advection also plays a role in controlling the concentrations of PCBs at the site. Generally, air masses that originated to the north of the U.K. contained lower concentrations than those originating to the south; masses which had recently passed over land also tended to have concentrations higher than those that had passed over water. Several factors combine together to influence the daily air concentrations at the site, including temperature, passage over marine and land masses source areas, and (presumably) the frequency and intensity of deposition events.

Introduction

Atmospheric transport is the principal pathway for regional and global movement of semivolatile organic compounds (SOCs). The extent to which PCBs and similar compounds with long half-lives have been found in geographically diverse and remote areas is testimony to the importance of atmospheric transport, given that many of these compounds have not been widely used in remote areas (*1−4*). Atmospheric movement and subsequent wet and dry deposition are important sources of SOCs to terrestrial and aquatic systems, where bioaccumulation and entry into the human foodchain through vegetation, fish, and animal products occurs.

Because of the current interest in the global distribution of these compounds, studies have been undertaken to measure the ambient levels of PCBs and PAHs but few have attempted to correlate the concentrations measured with meteorological parameters and to identify the origins of the air masses which predominated at the time of sampling (e.g. *5*, *6*). These studies require a balance between the practical or financial constraints on sample numbers and the analytical detection limit constraints of the short sampling intervals required to monitor specific meteorological conditions and air masses. In other words, if the sampling interval is too long, the development of meaningful correlations between meteorological parameters and air concentrations becomes difficult.

In the U.K. since 1991 the Toxic Organic Micro-Pollutants (TOMPS) program has established the ambient levels of PCBs, PAHs, and PCDD/Fs at selected urban and rural sites (*7−10*), by taking two week long samples consecutively throughout the year. However, this sampling regime is inappropriate to demonstrate the influence of meteorological conditions or air mass origins. Consequently this study was undertaken with sampling every 24 h (09:00 to 09:00 GMT) from March to October and December 1994, when different meteorological conditions and air masses were experienced. Twenty-four h was the minimum practical sampling period with respect to detection limits (for a wide range of PCB congeners), recording of meteorological parameters and the physical maintenance and taking of samples over an 8 month period.

Experimental Section

Field Site and Sampling. The sampling site is at a meteorological station located in a semirural area outside Lancaster, a town of ca. 70 000 inhabitants on the northwest coast of England, approximately 5 km from the Irish Sea (54°2′N, 2°45′W). An air sampler (General Metal Works model GPS1 PUF sampler), set to aspirate approximately 350 m^3 day^{-1}, nominally trapped the particulate fraction on a Whatman glass microfiber filter (GFF) (grade GF/A, 10 cm diameter) and the vapor phase on a polyurethane foam plug (PP) (length 8.0 cm, diameter 6.25 cm, density 0.035 g cm^{-3}). The GFFs were baked out at 450 °C for 12 h and stored in solvent rinsed aluminum packages until used. The PPs were pre-extracted in dichloromethane (DCM) for 18 h, dried under vacuum in a desiccator, placed in solvent rinsed aluminum packages, and stored in plastic bags in a freezer. After baking out/pre-extraction the GFFs and PPs were only handled with solvent rinsed stainless steel tongs and used within 3 weeks. The GFF and PP were held in the sampling module prepared in the laboratory and exchanged in the field. During assembly of the module all the parts which came into contact with the GFF or the PP were routinely solvent rinsed, and periodically the whole sampling module was solvent cleaned. While assembling the modules the GFF was spiked with two PCB congeners (40 and 128) and one PAH (dibenz[*ah*]anthracene) which had not been found in air samples previously taken from the site (*7*, *8*). These were used to indicate the field recoveries of PCBs and PAHs. On return to the laboratory the modules were immediately disassembled, and the GFF and

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PP were stored in a manner similar to the pre-extracted PP.

Extraction and Preparation of Samples. The GFF and PP were combined and extracted for 18 h in hexane on a Buchii Soxhlet extractor and prepared for analysis as described previously (*7, 8*). Quantification was by GC-ECD for PCBs and HPLC-fluorescence detection for PAHs. The following PCB congeners were routinely quantified: 30, 18, 28, 52, 104, 40, 61/74, 66, 101, 77/110, 82/151, 149, 118, 188, 153, 105, 138, 187, 183, 128, 185, 180, 170, 198, 201, and 194/205. The following PAHs were routinely quantified: acenaphthene, fluorene, phenanthene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo-[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, and coronene.

Quality Control and Assurance. About 10% of the samples were field blanks (FB), prepared and treated in an identical fashion to the samples; two sets of seven FBs were prepared, separated by a 3 month period. The means of the two sets were very similar, and so they were combined to give a FB mean value. The method detection limits (MDL) defined as the mean plus three times the standard deviation of the FBs were expressed in pg m^{-3} by dividing the sample MDL by the average volume of air aspirated (i.e. 350 m³). The mean FB values were subtracted from the sample values, and the MDL were applied at the end to eliminate any values which were below the detection limits of the method as a whole. FBs were typically 0−4.5 pg m^{-3} (individual PCBs) and 0−0.2 ng m^{-3} (individual PAHs) with MDLs of 1−12 pg m^{-3} for PCBs and 0.018−0.74 ng m^{-3} for PAHs. The recovery of PCBs and PAHs from the PP and GFF was tested by spiking six PP and GFF with a standard containing the full range of PCBs and PAHs. All six PP were extracted and prepared in the same manner as the samples. The resultant recovery values were used in conjunction with recovery values from the field spikes to correct the sample values. The recoveries for the majority of the PCBs were ≥85% and none were <63%. Nine PAH compounds had recovery values >83%, four were >64%, and two >43%. Recoveries for the field spikes were consistently >85%. Periodically a homogenized marine sediment (HS1 Marine Harbor Sediment) was analyzed to give an indication of the consistency of the procedure. The results from nine samples for the PCBs and six for the PAHs were compiled, and the mean, standard deviation, and coefficient of variation (COV) were calculated for individual congeners and the ∑PCBs and ∑PAHs. The results gave the following information: PAH COV ranged from 7.8% (phenanthene) to 18.3% (anthracene), with the COV for the ∑PAH 7.4%. PCB COV ranged from 5.5% (congener 138) to 13.8% (congener 52), with the COV for the ∑PCBs 8.7%. Three air samplers were run simultaneously for 24 h on two occasions. The COV for the ∑PCBs and ∑PAHs for both replicate tests were ∼6% for PAHs and ∼15% for PCBs. Previous work had shown that no breakthrough of the compounds in question occurred at 500 m³; all samples in this study were below 400 m³. The GPS1 PUF sampler was calibrated every 6 weeks but showed no significant variation in flow rates over the period of the study.

Results and Discussion

Typical Concentrations. Table 1 presents a summary of the data for selected PCBs and PAHs. ∑PCB concentrations varied between 54 and 375 pg m^{-3}, with the lighter congeners (e.g. 28 and 52) making major contributions to the total. ∑PAH concentrations varied between 1.4 and 40 ng m^{-3}, with the compounds phenanthene, fluorene, and fluoranthene being particularly important contributors. Comparison with data from elsewhere in Europe and North America supports the view that this site is semirural (e.g. *4, 7, 8, 11, 12*); air in U.K. city centers typically contains annual average ∑PCB and ∑PAH concentrations of ∼1000 pg m^{-3} and ∼100 ng m^{-3}, respectively (*7, 8*). There is a strong marine influence on

TABLE 1. Mean and Range of Selected PCB (pg m^{-3}) and PAH (ng m^{-3}) Concentrations during the Sampling Period

compound/ homologue group	mean	max.	min.
PCB-28	24.7	70	<10
PCB-52	18.4	60	<2.8
PCB-101	6.5	16	<2.0
PCB-153	1.7	12	<1.5
PCB-138	1.5	5.7	<1.2
PCB-180	11	41	<2.2
tri-PCBs	65	180	<1.5
tetra-PCBs	49	139	6.5
penta-PCBs	23	66	5.8
hexa-PCBs	6.3	28	<1.2
hepta-PCBs	16	89	0.4
octa-PCBs	4.1	57	<1.0
∑PCB	164	375	54.0
acenaphthene	0.7	1.4	<0.4
fluorene	2.2	11	<0.3
phenanthrene	4.9	15	0.8
anthracene	0.2	1.2	<0.08
fluoranthene	1.3	4.8	<0.2
pyrene	1.0	1.9	<0.7
benzanthracene	0.3	0.9	<0.09
∑PAH	9.0	40	1.4

many of the air systems which are sampled at Lancaster. It should be noted here that the majority of weather systems influencing the northern U.K. originate in the 50−60°N latitudinal band and that the average daily wind direction during the study period was 270° (i.e. due west of Lancaster). Long-term averaged meteorological information compiled at Stornaway, western Scotland (a national meteorological monitoring site with broadly similar meteorological influences to Lancaster) and at Kew (London) show that ∼50% and ∼35%, respectively, of the air arriving at these sites is derived from 50 to 60°N. Consequently air masses passing over the site have often spent previous days out to the west of the U.K., passing over the Atlantic Ocean, Ireland, and the Irish Sea. However, air masses frequently originate from other areas; during this study air masses from the north, south, and east (i.e. the Arctic, northern Europe, southern Europe, and the U.K.) were all recorded (see below).

Seasonal Variations. Broad seasonal variations in PCB concentrations were noted during the study, corresponding to seasonal temperature changes, with summer concentrations tending to be higher than winter ones. This has been noted in temperate regions by other researchers (*6, 8, 13*). In this study the total daily concentrations remained quite stable between March and mid-June and then generally rose (as the mean air temperature increased) until early August. Thereafter, the mean concentration and temperature generally decreased to levels detected before mid-July (see Figure 1). In summary, PCB concentrations were quite stable throughout the study period, ranging only by a factor of ∼7 between March and October. This observation, and generally higher concentrations during warmer periods, supports the view that volatilization/environmental recycling has a dominant influence on the air concentrations of PCBs in rural areas; PCBs are "old" contaminants with few new point source inputs to the environment. The generally quite consistent concentrations between air masses (see below) point to PCBs now being quite uniformly distributed through the northern temperate latitudes where they were produced and widely used in the past (*14*).

PAH concentrations showed greater day-on-day fluctuations than the PCBs, presumably reflecting differences in air mass origins, continuing combustion source inputs, and recent deposition history (*8, 15*) (see Figure 2). In contrast to PCBs, there are ongoing primary atmospheric emissions
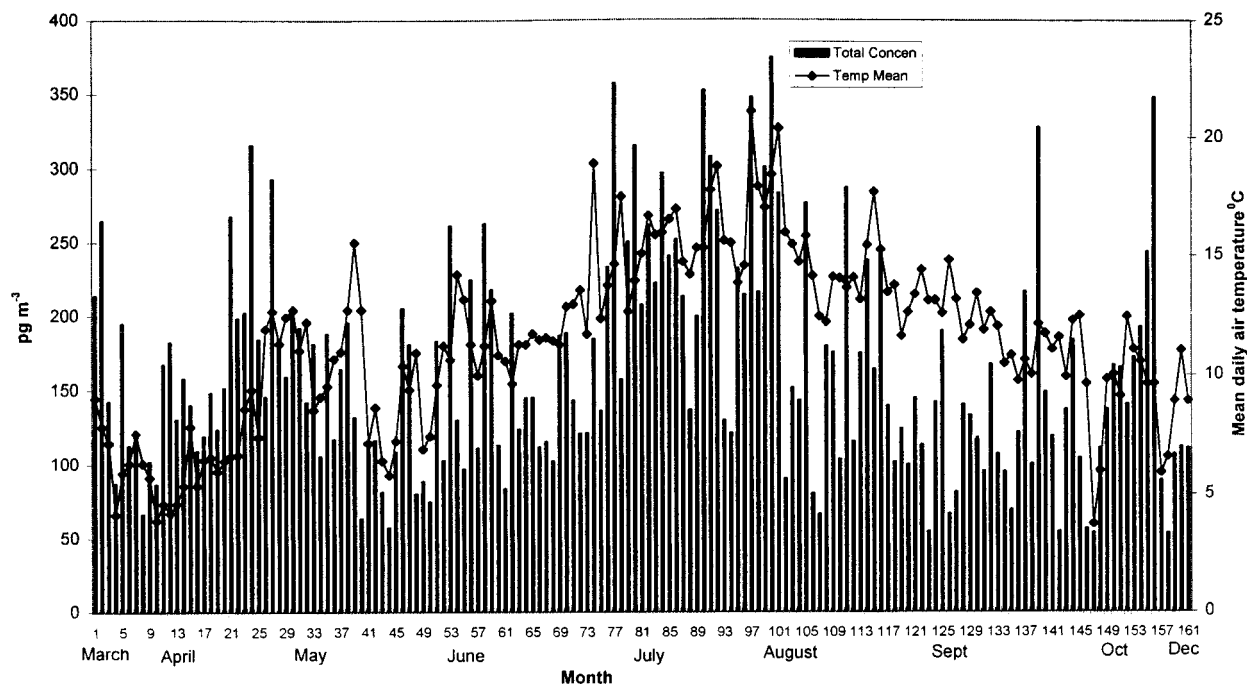
FIGURE 1. Daily PCB concentrations throughout the study period.

of PAHs from a range of combustion sources (*16*). Some PAHs are also quite photoreactive in the atmosphere (*17*). These factors presumably combine with daily temperature variations, air mass origins, and other meteorological parameters to give greater variability in ambient PAH concentrations than those for PCBs. Ambient concentration trends of the relatively volatile, gas-phase dominated compounds (e.g. phenanthrene-Figure 2a) exhibited different behavior from the relatively nonvolatile, higher molecular weight particle associated compounds (Figure 2b). Low concentrations through much of the summer often meant there were nondetectable levels of these higher molecular weight compounds (see Figure 2b).

Exploring the Relationships between Concentrations and Meteorological Parameters, Notably Temperature. Data for a number of meteorological variables (mean, maximum, and minimum ambient temperatures; relative humidity; rainfall; wind speed and direction; atmospheric pressure) were recorded at the site where the GPS1 sampler was situated. This is a meteorological station, part of a nationwide network that records a range of meteorological parameters using standard techniques for the U.K. Meteorological Office. Readings are taken at 09:00 GMT for some parameters, and for others the readings reflect the conditions over the previous 24 h. Product moment correlation coefficients were then determined when compound concentration was plotted against these variables. Individual compounds, sum of compounds, homologue groups and sum of compounds nominally in the vapor or particulate phase were tested against all the meteorological parameters, resulting in the calculation of over 280 correlation coefficients.

As mentioned above, PCBs were positively correlated against air temperature; correlations were generally significant at the $P \leq 0.01$ level for individual congeners. Phenanthrene, fluoranthene, and pyrene were also positively correlated (also at the 0.01 level), while the higher molecular weight benzo[*b*]- and benzo[*k*]fluoranthene were negatively correlated. It made no systematic difference to the strength of the correlation whether the mean, maximum, or minimum daily temperature value was used. None of the other meteorological parameters regularly gave a significant correlation with compound concentrations (although several

of the more volatile compounds e.g. phenanthrene, anthracene, PCB-28, and -52 were inversely correlated with average daily wind speed). Wania et al. (*18*) have discussed how the relationship between temperature and air concentration (or partial pressure), as described by Clausius Clapeyron plots, begins to break down as wind speed increases and advection from source areas or cleaner regions becomes the dominant force governing ambient concentrations at a given site. These results for the lighter weight PCBs may therefore reflect the increased dominance of advection which is associated with increased wind speeds and unstable cyclonic weather systems arriving at the Lancaster site from the west.

The relationship between temperature and PCB concentrations was therefore investigated further with the aid of Clausius Clapeyron (CC) plots, namely the natural logarithm of partial pressure against inverse absolute temperature (ln (P^o) versus $1000/^oK$). These plots allow the energy of phase transition to be calculated and inferences drawn about the source(s) of PCBs at the site (i.e. the relative importance of "local" volatilization or long-range advective transport) (*18*). Figure 3 gives CC plots for a tetrachlorinated (PCB-66) and hexachlorinated (PCB-82/151) biphenyl and the sum of all those congeners which correlated ($p > 0.05$) with temperature. Table 2 presents the slopes and energy of phase transitions for a selection congeners. Slopes were in the range -2300 to -6800, similar to those noted by Halsall et al. (*19*) for two U.K. urban centers. In a separate study at Lancaster described elsewhere (*20*), intensive diurnal sampling of the air was undertaken every 6 h during a period in the summer when stable air conditions were observed. The PCB concentrations were closely correlated with ambient temperature through day–night cycles (*20*). CC plots from that data set were therefore also calculated and gave much steeper slopes in the range -7100 to $-14\,100$. These are similar to those derived from vapor pressure measurements (*21*) or experimentally derived K_{oa} slopes for individual PCB congeners (see ref *19*). The larger data set of the present (daily) study and the greater range of meteorological conditions gave much greater scatter in the CC plots and hence weaker (though still statistically significant) correlations than the diurnal data set. Our interpretation of the shallower daily slopes than the
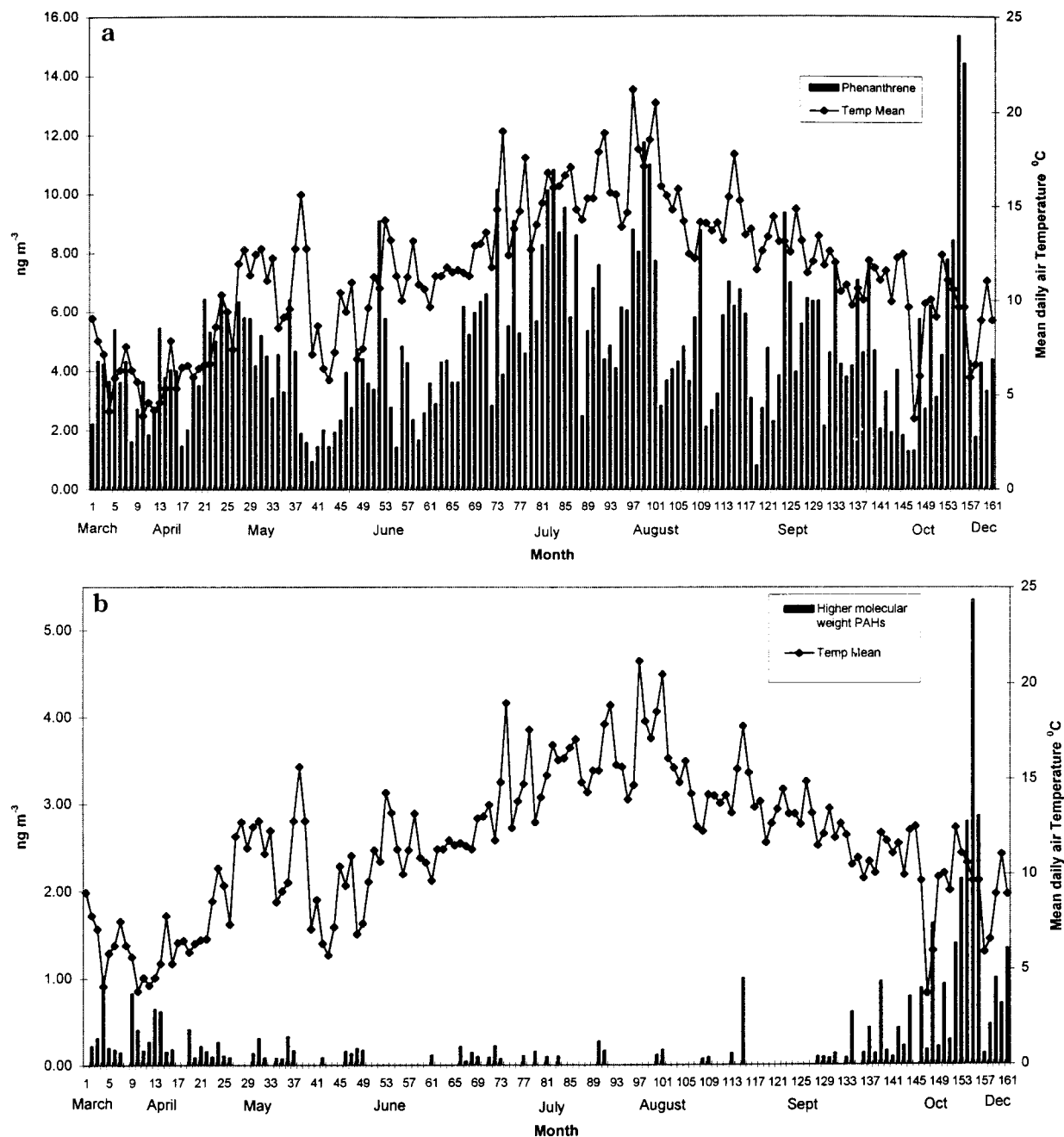
FIGURE 2. Daily PAH concentrations throughout the study period: (a) phenanthrene and (b) sum of selected high molecular weight compounds (benzanthracene, chrysene, benzo[*b*]- and benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo(*ghi*)perylene, and coronene).

diurnal slopes is that the Lancaster site is subject to regional advective inputs, which often have more influence over concentrations at the site than temperature (*18*). The similarity of the slopes to those found in urban areas of the U.K. is the result of regional influence/advection from the general urbanized conurbations of the north west of England (e.g. within 10−70 km are the towns/cities of Lancaster, Blackpool, Preston, Blackburn, Bolton, Manchester, and Liverpool) as well as localized recycling/volatilization of PCBs. In other words, advection results in lower gradients on the CC plots (*18*). The dominance of either local temperature-driven volatilization or advection/long-range transport on the concentrations found at the site will be governed by the meteorology prevalent at the time of sampling and the air mass history.

Energy of phase transition derived from the data set values ranged between 19 and 57 kJ mol^{-1}. Wania et al. (*18*) suggested

that without ideal conditions (heavily contaminated source and stable atmospheric conditions) the inference of the energy of phase transition from these plots can be open to error. The results from the diurnal intensive sampling experiment carried out at the same site but under ideal sampling conditions (*20*) gave energies of phase transition (59−122 kJ mol^{-1}) similar to theoretical values derived from plots of K_{oa} or vapor pressure (*21*). This difference demonstrates that under ideal meteorological conditions temperature is the dominant factor controlling the concentrations of PCBs in the air at this site; under these conditions the energy of phase transition can be determined from the CC plots.

Wania et al. (*18*) noted a difference in the gradients of CC plots between urban/industrial areas (−6000 to −8000) and rural/remote sites (−4000 to −5000). As noted above, the slope for the $\sum$PCB found in this study is similar to the slopes
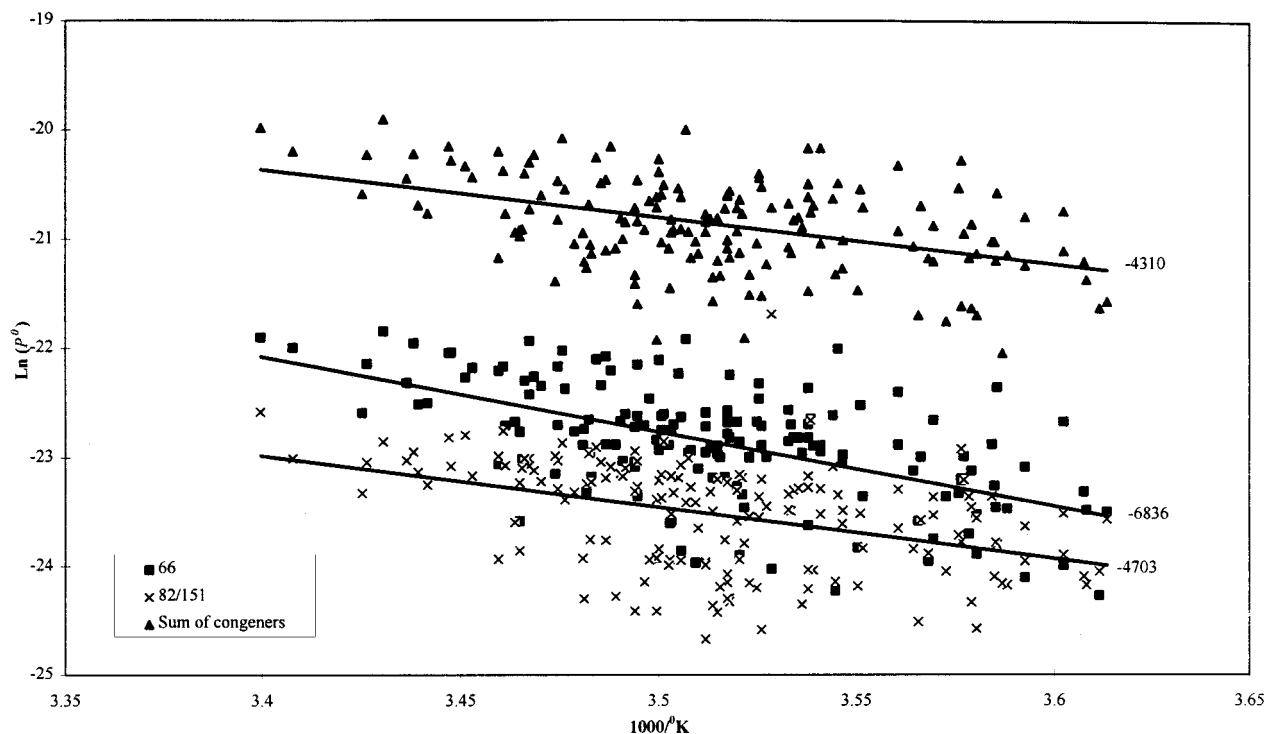
FIGURE 3. Plot of ln P^o vs 1000/^{o}K for congeners 66, 82/151, and the sum of those congeners which correlated with temperature.

TABLE 2. Data from the Clausius Clapeyron Plots for Eight Congeners and the Sum of PCBs from This Study

congener	this study slope m	r value	$n = 161$ significance	kJ mol^{-1}
18	-3351 ± 852	0.30	$p < 0.01$	28
52	-4659 ± 704	0.47	$p < 0.01$	39
61/74	-3791 ± 836	0.35	$p < 0.01$	31
66	-6836 ± 786	0.57	$p < 0.01$	57
101	-2468 ± 869	0.23	$p < 0.01$	20
77/110	-2289 ± 761	0.26	$p < 0.01$	19
151	-4703 ± 803	0.42	$p < 0.01$	39
118	-3282 ± 919	0.28	$p < 0.01$	27
Σ congener	-4310 ± 654	0.45	$p < 0.01$	36

found in U.K. urban sites (*19*). However, this corresponds with slopes found in rural areas of the U.S. This may reflect differences in general meteorology between inland areas of the U.S. and coastal regions of the U.K. As has already been stated, in the west of the U.K. the weather is dominated by unstable cyclonic systems which are associated with high winds. These may be influencing concentrations of PCB in the urban areas of the U.K. through advection and "diluting" the volatilization effect common in urban areas. This assertion is supported by the diurnal study (*20*), where the steeper slopes were associated with stable conditions.

Clearly factors other than temperature will play a role in influencing the daily concentrations of PCB/PAH (see also ref *22*). The influence of the source and area over which a particular air mass had moved was therefore investigated in more detail.

Back Trajectories and Air Masses. As noted earlier, the majority of the weather systems which influence the UK originate to the west (southwest to northwest). However, during the study period air masses originating from the north, south, or east of the U.K. were sampled. These episodes allowed air to be sampled which had very different origins from the air usually reaching the study site, namely, air masses which had originated in the Arctic, central/northern Europe, and the Mediterranean. Trajectories were therefore calculated

for those samples/days which had the highest and lowest concentrations and with interesting meteorological conditions. The choice was primarily based on PCB data, with a focus on the 10 highest and 10 lowest concentration events. An event is one or more consecutive samples/days when concentrations were extreme and or unusual meteorological conditions were experienced. Back trajectories were calculated based on near-surface geostrophic wind speed estimated every 6 h from surface isobars/pressure gradients on synoptic charts. Pressure gradients at this height gave a realistic representation of ground level air movements. The basic concept and some of the problems associated with this method are outlined in Sykes and Hatton (*23*) and Smith and Jeffrey (*24*). The movement of air mass parcels 4–5 days prior to their arrival at Lancaster was traced (*6*). It was assumed, based on other studies, that the concentrations of PCBs and PAHs in the air arriving at Lancaster would be a function of events/processes occurring in the hours/days preceding arrival at Lancaster (*6, 11, 20, 25*).

For each daily sample two back trajectories (BTs) were calculated: one at the start of sampling period and one at the end; some BTs were therefore common to two samples. If an event consists of two consecutive 24 h samples, then three BTs described the air movements for both samples, and three source areas were identified, because one BT was common to both 24 h periods. If an event consists of three consecutive 24 h periods (which occurred on only a few occasions), then four BTs described the air movements, and four source areas were identified because two BTs were common to two of the four samples. Therefore one event may not result in only two source areas.

Illustrative Air Masses from the North and Southwest of the U.K. Figure 4a shows source areas (position of the air mass 4–5 days before arriving at Lancaster) derived from back trajectories (see below) for some of the lowest and highest PCB air concentration events. The larger circles represent the source area for an event containing more than one 24 h sample. All the "low concentration events" (in the range 54–90 pg ΣPCB m^{-3}, substantially below the mean of 164) were associated with the air masses that originated to
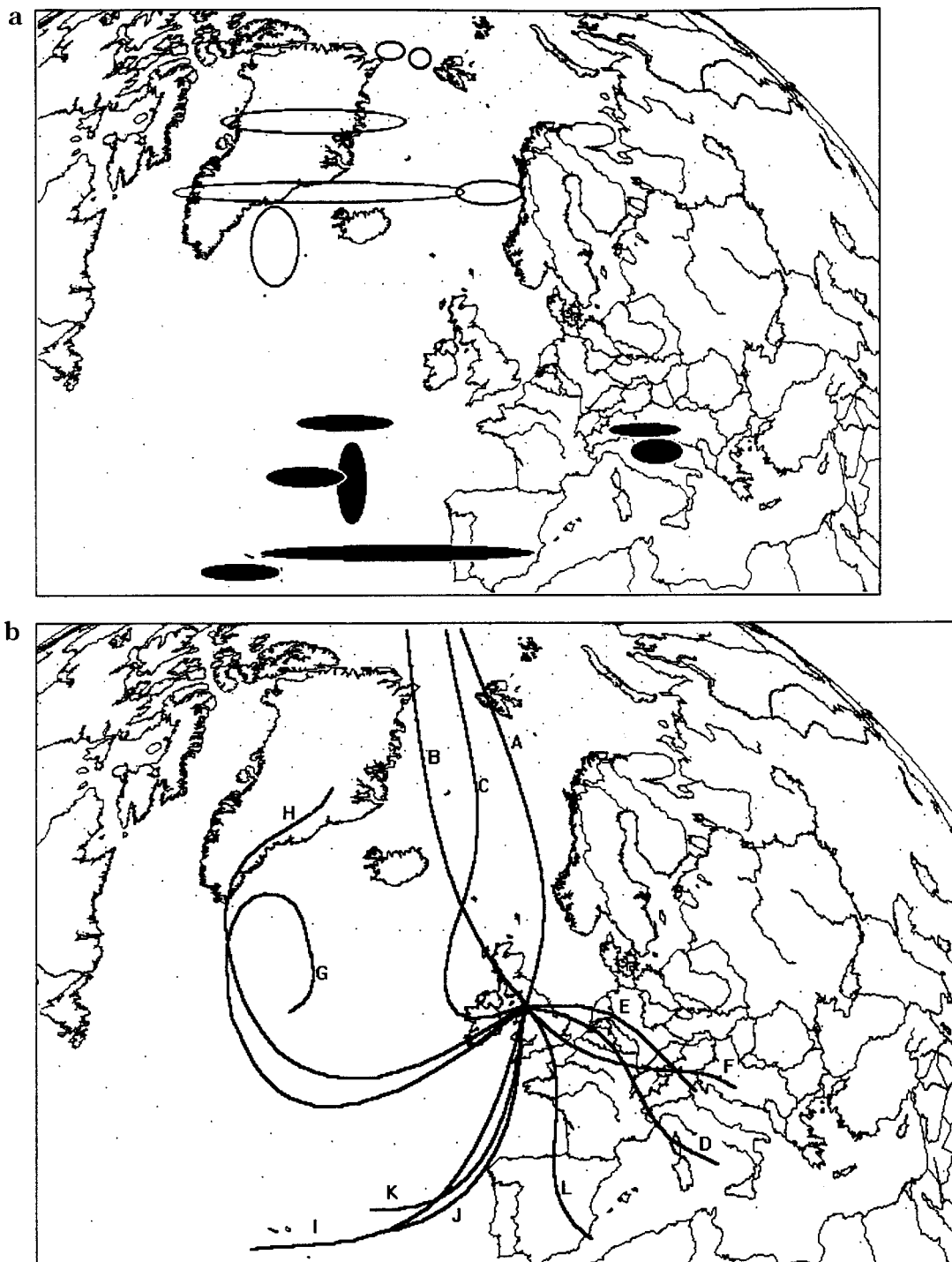
FIGURE 4. (a) Air mass source origins for selected events during the study period. Open circles show the origins of "low PCB" events, shaded circles the origins of "high PCB" events. (b) Air mass back trajectories for selected events during the study period (see text for details of the coded events).

the north of the U.K. and occurred at *different* times of the year (i.e. March, July/August, December). They also tended to have low PAH (5.2−7.5 ng ΣPAH m^{-3}) concentrations. All originated in regions to the north of the UK, at latitudes >60° N (and usually >65° N). High PCB concentrations (200−315 pg ΣPCB m^{-3}) and somewhat higher PAH concentrations (8.6−14 ng m^{-3}) were recorded in events originating from the south/southwest of the U.K. At these times the air had moved from the west and south of the U.K., starting at <60°N and usually <55° N. As noted above, individual events within the "northern low PCB" and "south/south west high PCB" subsets were often separated by several months, yet the

concentrations were very similar. Air from the north in August and December events, for example, showed little difference in the PCB concentrations, despite differences in the ambient temperatures.

The comparison of "low" and "high" PCB concentration events is explored further in Table 3 by comparing the source areas of the 10 highest and 10 lowest PCB events according to the latitude of the source area at the start and end of each 24 h period within the event (see below). The Σ of the numbers in the columns in Table 3 is dependent on how many 24 h periods make up an event and how many BTs are common to the 24 h samples within an event. Therefore the 10 events

TABLE 3. Comparison of the Latitudinal Source Areas of the 10 Highest and 10 Lowest PCB and PAH Concentration Events during the Study Period[a]

latitude of source area (°N)	highest PCB events	lowest PCB events	highest PAH events	lowest PAH events
35–39	1	0	1	0
40–44	6	0	9	0
45–49	7	0	6	1
50–54	3	0	2	1
55–59	3	5	1	7
60–64	2	5	3	9
65–69	0	7	0	0
70–74	0	0	0	0
75–79	0	1	0	0
80–84	0	1	0	1
85–89	0	3	0	3

[a] Refer to text for explanation.

do not necessarily result in 20 source areas. As stated previously the majority of weather systems influencing the northern U.K. originate in the 50–60°N latitudinal band with the average wind direction during the study period 270° (i.e. due west of Lancaster). Table 3 clearly shows the general distinction between the "high PCB events", always originating from <65°N and often from <50°N, and the "low PCB events", which never occur from <55°N and are sometimes from >75°N. However, low PCB events most usually came from the 55–70°N latitudes. The matching sample PAH data generally followed the PCB trends in this table.

Back Trajectories for Selected Events. Figure 4b shows trajectories for a number of events which showed interesting features with respect to air concentrations and/or source area. The air sampled will have moved between the BTs estimated at the start and end of that 24 h sample and will have originated between the end points of these BTs. For example, the air sampled during the first 24 h sample of event one will have originated between the end points of BTs A and B and moved between these BTs to reach Lancaster, with air from the second 24 h sample of this event originating and moving between BTs B and C. This principle is common to all the events in Figure 4b.

Event 1 relates to an occasion which rarely occurs in the U.K. Air traveled directly down from >85° N in just 2 days in early October 1994 and gave rise to the lowest PCB concentrations recorded in any of the samples (57 and 54 pg m^{-3}). PAHs were also very low (6 and 4 ng m^{-3}). In contrast, just 10 days later two of the highest PCB concentrations (243 and 348 pg m^{-3}) and the two highest PAH concentrations (40 and 31 ng m^{-3}) recorded during the study were associated with an air mass which originated over northern Italy and the Mediterranean (event 2, see trajectories D, E, and F in Figure 4b). It traveled slowly over industrialized areas of central Europe and the UK. The BTs at the start and end of each sampling period in events 1 and 2 followed very similar paths, adding confidence to their reliability.

Figure 4b also shows events 3–5. Event 3 comprised a single sample (see trajectories G and H) taken on 27 June which had relatively low levels of PCBs (120 pg m^{-3}) and PAHs (8 ng m^{-3}) and originated from the north western Atlantic, around Greenland/Iceland. Both events 4 and 5 comprised of a single sample (31 July–1 August and 3–4 August) which had the highest PCB values recorded in the study (348 and 375 pg m^{-3}) and relatively high PAHs (16 and 19 ng m^{-3}). The first of these samples/event (the lower of the two) originated over the sea to the south west and the BTs at the start and end were very similar (see trajectories I and J). The second sample/event (with the highest PCB concentration) had a BT at the start which was very similar to that

for the first sample (trajectory K), but by the end shows the origin of the air to have changed substantially, traveling up from the Mediterranean over northern France and the southern U.K. (trajectory L). We interpret this as evidence that land-based sources continue to influence regional/global atmospheric PCB concentrations. These sources are believed to be principally secondary recycling/volatilization from terrestrial ecosystems and urban centers (8, 26, 27). In contrast, PAH primary sources are ongoing (16), so that ambient concentrations remain susceptible to continuing sources/regional inputs as air masses pass over cities/conurbations and localized combustion inputs.

As a final comment, it is important to note that some of the samples clearly contained a "residue" of the air mass history from several days previously. However, conditions can arise where ambient concentrations at a given site are influenced over shorter time frames (e.g. few hours/diurnally) by recent deposition events or volatilization/inputs from the surface. Studies by others over the Great Lakes water bodies (e.g. 25), the North American land mass (28), and by ourselves at this site provide clear evidence of such short-term/diurnal cycling for selected SOCs (20).

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