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Measurement and Modeling of the Diurnal Cycling of Atmospheric PCBs and PAHs

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PCBs and PAHs were quantified in air samples taken every 6 h over a 7 day period in August 1995 at a rural site in northwest England. For the first 5 days, a stable high-pressure system moved slowly across northern England from the east. During this time, PCB air concentrations responded very closely to the changes in ambient temperature, following a clear diurnal cycle. All PCB congeners correlated well with temperature, but the correlation was strongest for lower chlorinated species. Daily PCB concentration maxima exceeded minima by a factor of 2.1—3.7 for different congeners; in contrast, daily maxima:minima ratios for different PAHs were in the range 0.47—1.44. These data are interpreted as providing evidence that rapid, temperature-controlled air-terrestrial surface exchange of PCBs influencing air concentrations and, hence, regional/global scale cycling of these compounds occurs. Toward the end of the study period, the stable air conditions were replaced by a turbulent (windy), unstable low-pressure system, when day/night temperature differences were small and the diurnal PCB congener pattern was not discernible. Diurnal PAH concentration changes were not correlated with temperature, but groups of compounds were strongly correlated with each other (e.g., phenanthrene, fluoranthene, and pyrene; benzo(*k*)fluoranthene, benzo(*a*)pyrene, benzo-(*ghi*)perylene). It is therefore hypothesized that short-term PAH air concentrations are controlled by ongoing recent local/regional source inputs (rather than air-surface recycling), atmospheric reactions, and deposition processes. The air—surface exchange of PCBs is satisfactorily modeled by a sine curve describing ambient temperatures and controlled by a temperature-dependent air—terrestrial surface (K_{TA}) partition coefficient.

Introduction

Semivolatile organic contaminants (SOCs), like polychlorinated biphenyls (PCBs) and other organochlorine (OCs) compounds, continue to be detected in the environment far from areas where they were originally used and despite efforts to restrict their use/emissions. It is believed that a major reason for this is the persistence of these compounds and their propensity to recycle, such that material that has been released to the environment in the past can evaporate to the atmosphere and become subject to long-range atmospheric transport (*1*, *2*). Virtually all of the studies which have attempted to quantify surface—atmosphere exchange of SOCs have dealt with large-scale aquatic systems, notably the Great Lakes (*3*, *4*) and air—ocean exchange (*5*, *6*). However, there is evidence for a net supply of many SOCs, including PCBs, to the atmosphere from *terrestrial* systems where they were used in the past and became deposited to and stored in soils and vegetation. This evidence takes the form of environmental budgets and inventories, which show that the bulk of the environmental burden of many SOCs continues to reside in the soil (*7*—*11*), soil-air fugacity calculations (*11*—*13*), and air concentration data which are higher for PCBs and other OCs in the areas where they were widely used in the past (e.g., urban areas for PCBs and agricultural areas for many OC pesticides) (*13*—*16*). Terrestrial ecosystems, including agroecosystems, are also of key importance in supplying atmospherically derived SOCs to human and other food chains (e.g., ref *13*). Hence, it is important to investigate the nature, extent, and rate of processes which govern the air—surface exchange of SOCs in terrestrial systems and to build upon the limited database and process understanding in this area (e.g., refs *17* and *18*).

This paper reports one such study, in which we quantified short-term changes in the air concentrations of PCBs and polynuclear aromatic hydrocarbons (PAHs) at a rural site in the U.K. We were testing the hypothesis that temperature-controlled short-term changes in air concentrations may be apparent for those SOCs for which primary sources are now limited, but there is active recycling through the environment, "driven by" air—terrestrial surface exchange phenomena (i.e., secondary atmospheric sources). The site selected is a meteorological station and has been used previously to help define rural U.K. air concentrations and to study the influence of meteorology and air mass origin/history for these compounds (*19*, *20*).

Experimental Section

Field Site and Sampling. The sampling site is at a meteorological station located in a rural area outside Lancaster, a town of ca. 70 000 inhabitants on the northwest coast of England, approximately 5 km from the Irish Sea (54°N, 3°W). An air sampler (General Metal Works model GPS1 PUF sampler) was set to aspirate ~100 m³ in every 6 h period, nominally trapping 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). The air sampler operated ca. 1.5 m above the soil surface at the field station. The site itself is on a gentle westerly facing hillslope of rough grazing pastureland, as described elsewhere (*19*). Given the relatively small volumes of air involved, particular attention was paid during pre-extraction and handling to ensuring low sample blanks.

Air sampling commenced on August 17, 1995, at 12:00 p.m. and continued until 12:00 p.m. on August 24, 1995. Samples were taken every 6 h precisely, i.e., at 6:00 p.m., 12:00 a.m., 6:00 a.m., and 12:00 p.m. every day. Field blanks were also prepared and handled in a manner identical to the samples. It is recognized that air concentrations recorded at the site would be a function of many factors and that any influence of surface—air exchange would be broadly a function of surface features, temperature, and concentrations

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over an area far wider than just the field station itself. The local maximum and minimum air temperatures were all recorded for each 6 h sampling interval (see later).

Extraction and Analysis of Samples. The GFF and PP were combined and extracted for 18 h in hexane on a Buchi Soxhlet extractor and prepared for analysis. Cleanup and fractionation of PCBs and PAHs were achieved using a 3 g activated silica column of 7 mm internal diameter. The samples were reduced to 200 μL and placed on the column with the minimum of washings. The PCBs were eluted first with 28 mL of hexane, the PAHs were then eluted with 20 mL of 1:3 hexane/DCM. Both fractions were reduced under nitrogen and solvent exchanged, the PAHs to acetonitrile and the PCBs into dodecane; at this stage a retention time marker and internal standard were added to the PCB fraction (see ref *16*). Quantification was by GC-ECD for PCBs and HPLC-fluorescence detection for PAHs (*16*). The following congeners were routinely quantified: 30, 18, 54, 31, 28, 33, 52, 49, 47, 104, 44, 37, 40, 61/74, 66, 155, 60, 101, 81/87, 77/110, 82, 151, 123/149, 118, 114, 153, 105, 141, 138, 187, 183, 185, 202, 156, 157, 204, 180, 170, 198, 189, 194, 205, and 206. The following PAHs were routinely quantified: acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(*a*)anthracene, chrysene, benzo(*b*)- and benzo-(*k*)fluoranthene, benzo(*a*)pyrene, benzo(*ghi*)perylene, coronene.

Quality Control and Assurance. Approximately 20% of the samples were field blanks (FB), prepared and treated in an identical fashion to the samples. Method detection limits (MDL), defined as the mean plus three times the standard deviation of the FBs, were expressed in picograms per cubic meter by dividing the sample MDL by the average volume of air aspirated (i.e., 100 m³). FB values for individual congeners varied between 55 and 390 pg/sample (PCBs) and 0.06−3.7 ng/sample (PAHs), with MDLs of 0.5−19 pg m⁻³ and 9−67 pg m⁻³ for PCBs and PAHs. Recoveries were tested by spiking PPs and GFFs with a full range of PCBs and PAHs. The recoveries for the majority of the PCBs were >87%, although they were 71, 68, 45, and 53% for congeners 30, 18, 54, and 40, respectively. All the PAHs had recoveries of >97%, except anthracene (62%). The field spike recoveries [PCB-40 and −128; dibenz(*ah*)anthracene] were consistently >85%. Reproducibility of the method was measured with the use of an in-house homogenized air extract; six silica columns were spiked with a quantity of the extract that would give concentrations of PCBs and PAHs equivalent to the concentrations expected in an air sample of ~100 m³. The coefficient of variation (COV) for all the PCB congeners was <8%, except for congener 33, which was 8.2%. All the PAH compounds quantified had a COV of <8%, except chrysene (8.8%). The air extract was seen as the most suitable way of testing the consistency of the method.

Results and Discussion

General Comments on Concentrations. The ∑PCB (sum of the 46 congeners) concentrations varied between 156 and 1150 pg m⁻³, in line with rural concentrations measured at the site previously (*19*). The ∑PCB mixture was dominated by a range of the lower chlorinated (di- to tetra-) species, namely (concentration ranges given in brackets): PCB-18 (25−135), PCB-31 (22−139), 28 (13−152), 33 (14−133), 37 (15−87), and 66 (5.6−67). However, a full range of the heavier congeners was also routinely detected. This included relatively abundant congeners, such as PCB-153 (2.2−54), PCB-138 (2.2−24), PCB-187 (0.37−11), and PCB-180 (0.33−8.0), but also the full range of homologues up to and including several nonachlorinated congeners (i.e., PCB-189, -194, -205, and -206). In other words, rural summer air sampled in 1995 at this temperate latitude contained a full suite of PCB congeners (see Table 1).

TABLE 1. Summary of the Mean and Range of Concentrations for Selected Compounds during the Study Period[a]

compd	mean	range
PCB-18	69	25−135
PCB-28	55	13−152
PCB-52	20	8.6−35
PCB-37	34	15−87
PCB-66	23	5.6−67
PCB-101	15	4.0−68
PCB-118	2.7	0.7−7.4
PCB-153	12	2.2−54
PCB-138	7.1	2.2−24
PCB-187	2.8	0.37−11
PCB-180	2.5	0.33−8.0
PCB-170	0.77	0.25−2.1
∑PCB	471	156−1155
fluorene	3.1	0.94−6.7
phenanthrene	5.3	2.1−11
fluoranthene	1.6	0.65−3.1
pyrene	0.61	0.24−1.2
benzo(*b*)fluoranthene	0.09	0.01−0.29
benzo(*k*)fluoranthene	0.04	0.01−0.08
benzo(*a*)pyrene	0.05	0.01−0.12
benzo(*ghi*)perylene	0.07	0.02−0.15
coronene	0.03	0.01−0.08
∑PAH	12.3	4.9−25.5

[a] PCB concentrations are in picograms per cubic meter; PAH concentrations are nanograms per cubic meter.

The S−PAH (sum of compounds) concentrations varied slightly less than the PCBs, between 4.9 and 25.5 ng m⁻³ and again in line with rural concentrations measured here previously (*20*). The lighter compounds, those existing predominantly in the vapor phase during this sampling exercise, dominated the mixture. For example, phenanthrene was routinely the most abundant PAH (2.1−11.1 ng m⁻³), with fluorene (0.94−6.7) and fluoranthene (0.65−3.0) the other major contributors. The heavier PAHs were consistently present at lower concentrations than the lighter compounds. For example, benzo(*a*)pyrene, benzo(*ghi*)-perylene, and coronene concentrations ranged between 0.01 and 0.12, 0.02 and 0.15, and 0.01 and 0.08 ng m⁻³, respectively (see Table 1).

Generally, the highs and lows of changing concentrations for PCBs occurred for all congeners simultaneously, i.e., individual PCB congeners correlated well with other PCB congeners. Table 2 presents the correlation coefficients between selected congeners and between selected congeners and temperature. The lighter congeners (e.g., PCB-18; PCB-28) were more strongly correlated with temperature than the heavier congeners (e.g., PCB-138; PCB-180). In contrast, PCB concentrations did not correlate significantly with the PAHs (e.g., ∑PCB versus phenanthrene, $r^2 = 0.173$; fluoranthene, $r^2 = 0.313$; benzo(*a*)pyrene, $r^2 = 0.244$). Table 3 presents the correlation coefficients between the individual PAH compounds and between the compounds and temperature. This highlights some interesting aspects of PAH behavior. Generally, individual PAHs correlated well with others of similar physicochemical properties (e.g., phenanthrene versus fluoranthene, $r^2 = 0.907$) and less well with compounds of rather different properties (e.g., phenanthrene versus benzo(*a*) pyrene, $r^2 = 0.550$). The intermediate molecular weight grouping of phenanthrene, fluoranthene, and pyrene, for example, was strongly correlated with each other, as were the higher molecular weight grouping of benzo-(*b*)- and benzo(*k*)-fluoranthene, benzo(*a*)pyrene, and benzo-(*ghi*)perylene.

It is important to note that the concentrations of these compounds varied markedly over quite short time periods, a factor that needs to be borne in mind when designing a

TABLE 2. Correlation Coefficients between Individual PCB Congeners and with Ambient Temperature

	PCB-18	PCB-28	PCB-52	PCB-118	PCB-153	PCB-138	PCB-180	T
PCB-18		0.870	0.838	0.771	0.613	0.681	0.538	0.719
PCB-28			0.682	0.657	0.647	0.652	0.499	0.613
PCB-52				0.763	0.459	0.535	0.402	0.628
PCB-118					0.817	0.905	0.727	0.653
PCB-153						0.929	0.778	0.461
PCB-138							0.849	0.547
PCB-180								0.456

TABLE 3. Correlation Coefficients between Individual PAH Compounds and with Ambient Temperature

	Ace	fluorene	Phen	Anth	Fluoranth	pyrene	B(a)anth	Chrys	B(b)Fl	B(k)Fl	B(a)P	B(ghi)P	Coro	T
Ace		0.371	0.360	0.078	0.287	0.357	0.261	0.109	0.026	0.071	0.154	0.216	0.145	0.000
fluorene			0.623	−0.025	0.565	0.482	0.300	0.145	0.288	0.448	0.525	0.404	0.173	0.006
Phen				0.000	0.905	0.841	0.401	0.442	0.385	0.541	0.551	0.551	0.353	0.157
Anth					0.000	0.032	0.222	0.154	0.003	−0.002	−0.001	0.074	0.049	−0.098
Fluoranth						0.926	0.433	0.550	0.441	0.627	0.638	0.623	0.381	0.257
Py							0.584	0.612	0.391	0.580	0.648	0.692	0.412	0.170
B(a)anth								0.674	0.291	0.506	0.649	0.786	0.413	0.013
Chrys									0.552	0.640	0.496	0.698	0.440	0.161
B(b)Fl										0.832	0.432	0.473	0.236	0.050
B(k)Fl											0.801	0.727	0.351	0.127
B(a)P												0.770	0.350	0.131
B(ghi)P													0.681	0.094
Coro														0.170

TABLE 4. Summary Meteorological Data for the Study Period[a]

date	samples	barometric pressure (mbar)	weather system	wind direction from	run of wind (km day^{-1})	min/max (°C)	rainfall (mm)	sunshine (h)
17/8/95	1, 2	1019−1025	high	70°	223	12.8−32	0	10.6
18/8/95	3−6	1020−1022	high, trough in sample 6	130°	291	17.3−29	0	2
19/8/95	7−10	1020−1021	high, high pressure dominant	60°	161	17−31	0	7.9
20/8/95	11−14	1020−1022	high; high pressure dominant	120°	13	15−29	0	12.7
21/8/95	15−18	1024	high	70°	118	16−29	0	12.1
22/8/95	19−22	1024−1016	high; low pressure trough and cold front moving in during sample 22	80°	150	16−27	6	11.9
23/8/95	23−26	1016−1014	low pressure trough; cold fronts	320°	321	14−19.5	0	10.4
24/8/95	27−28	1014	low pressure dominant	230°	441	14.2−18.8	83	0.1

[a] Soil temperatures at 10 cm varied between 17.8 and 19.5 °C during study period; grass minimum temperatures for each 24 h ranged between 9.3 and 14.5 °C.

representative air sampling strategy. Indeed, the range of six hourly concentrations measured in this 7 day study was greater than for daily (24 h) samples taken over 9 months at the same site but during a different study (*20*).

General Comments on the Weather and Meteorology. Having made some general observations on the concentrations and temperature effect, it is now appropriate to examine the weather and meteorological conditions in greater detail. Table 4 summarizes the meteorological data for the study period. From August 17 to 22, 1995, the wind was blowing from the northeast/east/southeast and therefore passed over the northern England terrestrial surface, after crossing the North Sea. Midway through August 22 (starting in sample 22), the air mass changed and a period of lower pressure commenced, with winds coming in from the west (i.e., over the Irish Sea). It is quite unusual to have easterly winds at Lancaster; winds usually come from the west/southwest, off the Irish Sea and Atlantic Ocean. There was clear diurnal temperature cycling in the first 5 days; temperatures in a given 24 h period would reach maxima of 27−32 °C (very hot for Lancaster) and lows of 13−17 °C. In contrast, August 23/24 had a very low-temperature range (~5 °C). Rain fell on just 2 days, August 22 and 24 (Table 4). The windspeeds in the middle of the study period were quite stable from the east at ~120−160 km day^{-1} (1.4−1.8 m s^{-1}). At this rate, a given air mass would take about 24 h to pass from the northeast coast of England to the Lancaster site. More turbulent wind was noted on August 23/24—at 320 and 440 km day^{-1}.

Concentrations of SOCs recorded in air at the Lancaster site can retain something of the history of the air mass, often being affected by the origin of the air several days previously (*20*). However, the recent or short-term history is also important, as the air mass moves over the earth's surface and exchanges SOCs across the air−surface interface (*4*). Figure 1 shows a general plot of the air mass back trajectories, based on surface wind speed calculated every 6 h from the isobars/pressure readings given on synoptic charts. Figure 1 emphasizes the point made earlier, namely that early samples contained air that had reached Lancaster after passing over land from the east; some may have travelled over parts of southern Scandinavia and northern mainland Europe. Later samples had a history which presumably reflected their passage over the oceans and seas to the west of the U.K.

PCB Compound Relationships with Ambient Temperatures. All the PCB congeners cycled with temperature during August 17−22, 1995. Figure 2 presents data for two congeners, PCB-52 and PCB-138. Clearly, air concentrations were higher during the warm days than the cooler nights.
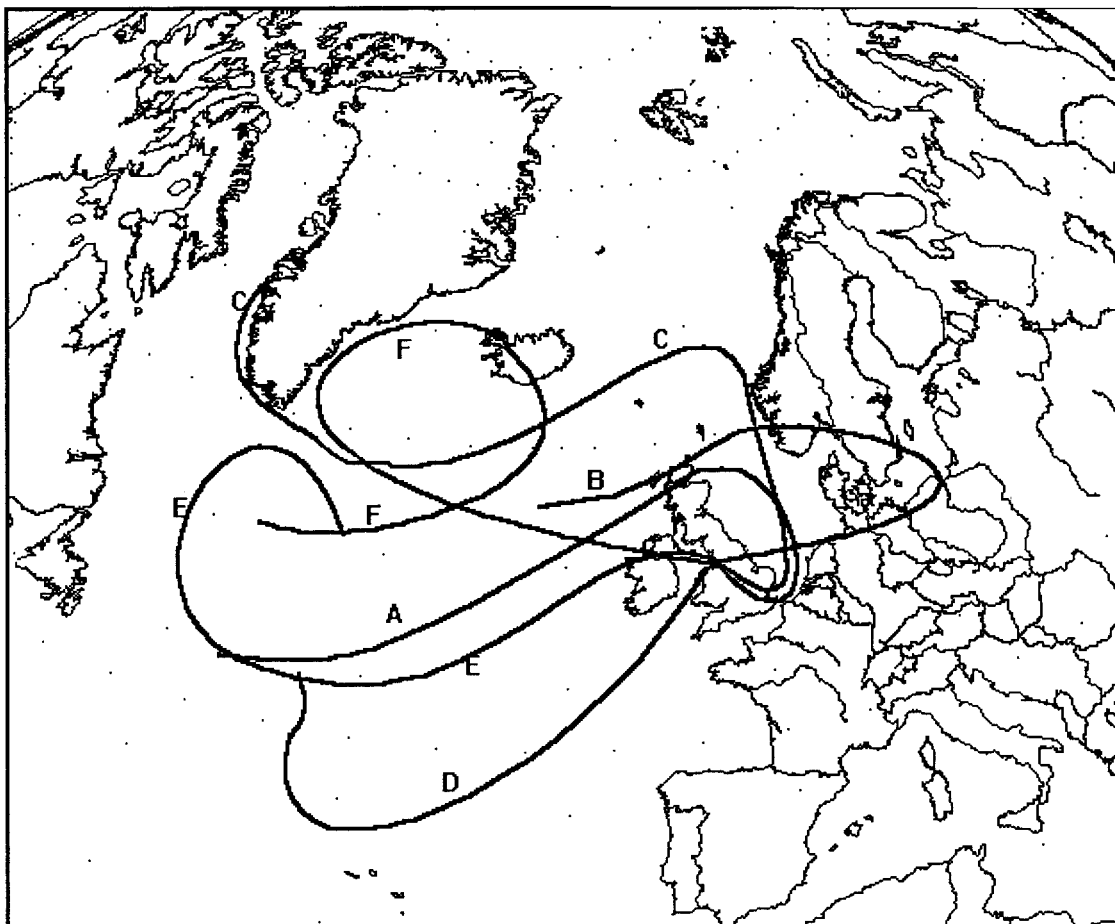
FIGURE 1. Illustrative air mass back trajectories for the study period.
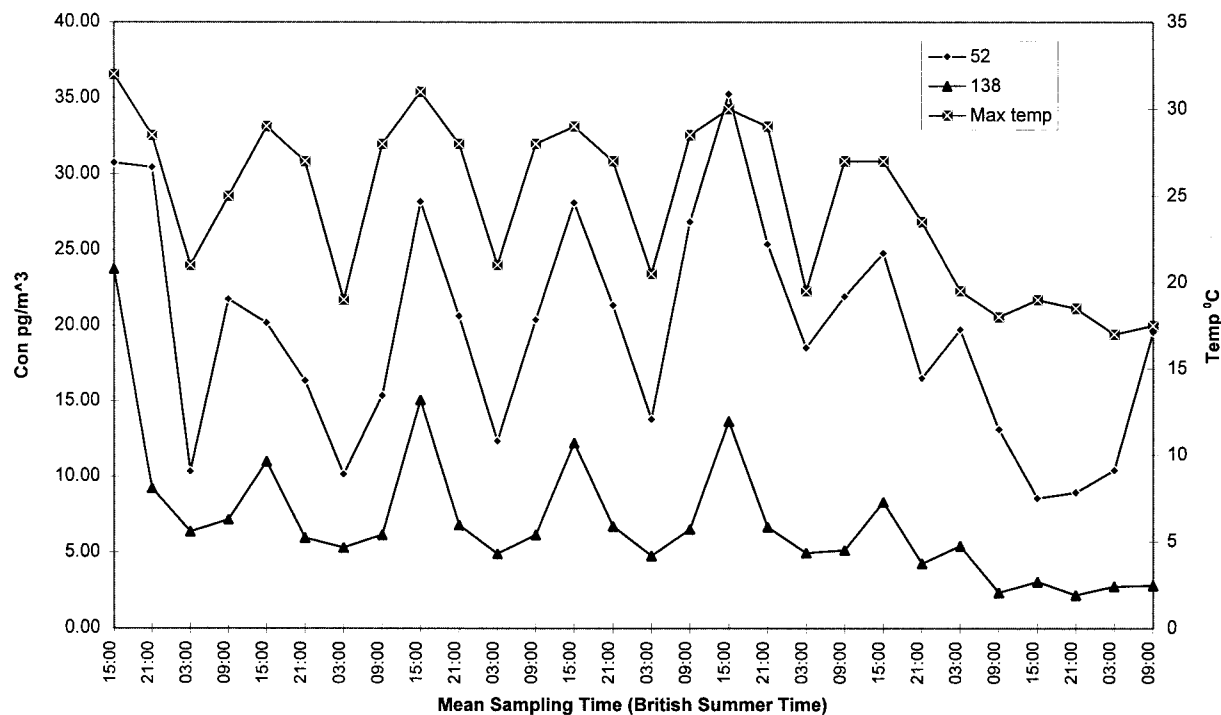
FIGURE 2. Concentrations of (a) PCB-52 and (b) PCB-138 and the ambient temperature.

Under the turbulent conditions with little day/night temperature difference (August 23/24), the cyclicity disappeared. Maximum:minimum concentration (amplitude) data averaged for the first 5 days were calculated by dividing the afternoon concentrations (mean sampling time 3:00 p.m.) by the early morning sample concentrations (3:00 a.m.) for selected compounds. These are given in Table 5. For the PCBs, this varied between 2.1 and 3.7, with seemingly no

TABLE 5. Average Ratios of the 15:00 h/03:00 h Samples for the First 5 days of the Study Period

PCB-18	2.28	acenaphthene	0.69
PCB-28	3.73	fluorene	0.47
PCB-52	2.22	phenanthrene	0.90
PCB-118	2.96	anthracene	1.24
PCB-153	3.16	fluoranthene	1.00
PCB-138	2.88	pyrene	0.99
PCB-180	2.14	benzanthracene	1.01
		chrysene	1.32
		benzo(*b*)fluoranthene	0.78
		benzo(*k*)fluoranthene	0.90
		benzo(*a*)pyrene	0.92
		benzo(*ghi*)perylene	1.06
		coronene	1.44

systematic difference with compound volatility. It is possible, of course, that the cycling of the PCB congeners does vary with molecular weight, but that the 6 h sampling is too long to detect any differences in their synchronicity.

The data showed an interesting phenomenon which can be discerned in Figure 2; lighter congeners (e.g., PCB-52) appear to show a sharper, quicker response to temperature changes, while heavier congeners (e.g., PCB-138) display a more spiky profile in which the samples taken at 6:00 a.m. to 12:00 p.m. and 6:00 p.m. to 12:00 a.m. contain concentrations which is low relative to that in the 12:00 to 6:00 p.m. sample. This may indicate that higher temperatures are required before heavier congeners partition off the terrestrial surface to the air; this would have important implications for recycling processes affecting the global distribution of SOCs (*1*).

The diurnal cycling of PCBs and other OCs is noted here and previously by others (*17, 18*) and could be interpreted as evidence for the influence of recycling (i.e., volatilization/deposition) as a major controlling factor on the contemporary ambient concentrations of PCBs.

Comments on PAH Trends. As noted above, despite some PAHs having physicochemical properties similar to those of PCBs, there is no evidence of diurnal cycling correlated with temperature (see Table 3). It is known that some PAHs are quite reactive in the atmosphere (e.g., ref *21*), much more so than for PCBs (*22*). Indeed, anthracene is particularly photoreactive and it is interesting to note that it gives a negative (though not statistically significant) r^2 when plotted against temperature (analogous to sunlight). PAHs are also different from PCBs in that there are important ongoing primary atmospheric sources (*10*). It is therefore hypothesized that short-term PAH air concentrations are controlled by recent local/regional source inputs, atmospheric reactions, and deposition processes.

Brief Comment on Potential Confounding Factors. (a) Sea Breezes. The correlation between PCB concentrations and ambient temperature is very clear (Table 2 and Figure 2). However, it is important to bear in mind that other factors which may operate diurnally could act as confounders to the concentration/temperature relationship. One of these is the local scale influence of sea breezes at sites such as the Lancaster one, within a few kilometers of the coast. These can result in winds moving on to the land during the day and onto the sea at night, driven by different rates of heating/cooling of land and water masses. This was not an important factor during this sampling period, because air movements were consistent and controlled by larger scale air mass movements. No short-term shifts in air movement coming from the west (i.e., off the Irish Sea) and east (i.e., over the U.K. landmass) were noted during the sampling period.

(b) Atmospheric Mixing Height. Another extremely important factor which can influence air concentrations near the surface is the atmospheric mixing height. For substances exchanging with the earth's surface, the height of air which is impacted and effectively dilutes emissions from the surface is obviously critical in controlling concentrations near the surface. The air sampler operated at 1.5 m above the surface. The atmospheric mixing height often varies markedly on a day/night cycle, with a greater mixing height during summer days than summer nights (e.g., refs *23* and *24*).

The height of the atmosphere impacted by exchanges of SOCs across the air−surface interface is critical when trying to derive estimates of the mass transfers mixing height. For modeling of longer term exchange processes, workers have used atmospheric mixing heights of 1 to a few kilometers (e.g., ref *10*). However, over a diurnal cycle, it may well be considerably less than this.

The atmospheric boundary layer (ABL) height can be measured/estimated (*24*), but this was not done at the Lancaster site during sampling. However, typically in this part of northwest England in late summer, the ABL height would be ∼1000 m during the day and ∼100−500 m at night. This does not necessarily imply, of course, that SOCs are mixed evenly to correspond with these heights.

It is interesting to note that the high molecular weight PAHs which are present in the ambient air almost exclusively on fine aerosols show no diurnal cycle (see Figure 3). It may be reasonable to assume that they behave conservatively in the atmosphere (at least over time scales of a few days), and it is tentatively suggested that the fact that they do not *increase* in concentration at night *may* be implying that there was a relatively minor diurnal fluctuation in the mixed/boundary layer height.

Comments on the Surface−Air Exchange and Considerations for Model Development. For a full understanding of surface−air exchange processes and, hence, model development, it is pertinent to consider what is driving the PCB air concentrations above the terrestrial surface−release/exchange from soil, the overlying vegetation, or both? These exchange processes operate at different rates and time scales, i.e., hourly, diurnally, seasonally, and over many years. However, in this study, over the daily cycles, there was a rapid response of the air concentrations to temperature. This presumably resulted in a temperature-driven change in the surface−air partition coefficients (often modeled with the octanol:air partition coefficient, K_{OA}). Leaf surfaces change temperature rapidly in response to changes in ambient temperature and show a similar amplitude to ambient temperature changes (*23*). Bulk soil temperatures at depths of a few centimeters or more change much more slowly and dampen out the wider fluctuations in ambient temperatures. However, the surface skin of soil (e.g., the surface few mm or cm) shows a rapid response to air temperature changes (*23*). The surface skin of soil will contain a much greater mass of SOC than the overlying vegetation (*11, 13*), and critical issues are the extent to which the soil-bound component of SOCs is able (free) to participate in active, rapid exchange with the atmosphere and the buffering influence of the overlying vegetative sward on the micrometeorological conditions which will influence flux rates. On the basis of controlled studies in a fugacity chamber, the response time of the vegetation (i.e., desorption) may be too slow to account for the changes in ambient PCB concentrations noted here (*25*).

Simple Modeling of the Surface−Air Exchange of PCBs. An accurate model of diurnal fluctuations in air concentrations would require extensive meteorological information, including the dependence of eddy diffusivity, velocity, and temperature as a function of height and time. The height of the atmosphere impacted by exchange of SOCs across the air−surface interface is critical when attempting to derive estimates of changing air concentrations. In the absence of
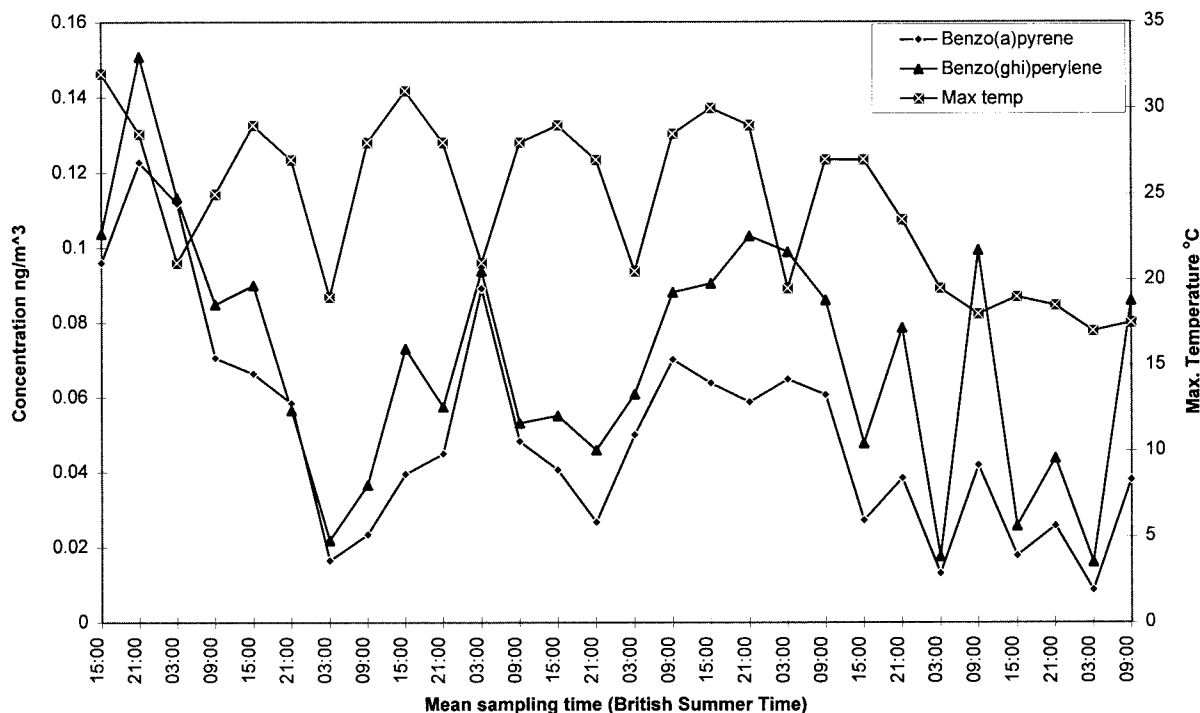
FIGURE 3. Concentrations of benzo(*a*)pyrene and benzo(*ghi*)perylene and the ambient temperature.

detailed data, here, we develop a simple one-dimensional model to assist data interpretation.

Hoff et al. (*26*) found that the Lorentzian function gave the best fit to their annual seasonal cycles of PCB and organochlorine air concentrations. Attempts were made to fit the diurnal temperature data in this study to the Lorentzian function. Although it gave extremely good fits for individual days (r^2 from 0.945 to 0.998), it is inappropriate for describing continuous cyclical functions (e.g., seasonal/diurnal temperature or air concentration cycles) because it is not a continuous mathematical function. Thus, the air temperature was fitted to a sine wave for the first 4 days as a function of time of day *t* hours (24 h basis), namely

$$T \, (°C) = 23.1 - 4.9 \sin[2\pi(t - 3)/24] \quad (1)$$

The fit had an r^2 of 0.966, the implication is that the amplitude is 4.9 °C with minima and maxima at 3:00 a.m. and 3:00 p.m., respectively.

As noted above, during the first 5 days of the study period, the air mass reaching Lancaster will have spent ~24 h over the U.K. terrestrial surface, which can be assumed to have essentially the same soil and vegetation PCB concentrations/loadings as those measured in the Lancaster area (*19, 27, 28*).

The air−terrestrial surface equilibrium partition coefficient (K_{TA}) is assumed to be proportional to the octanol−air partition coefficient (K_{OA}) expressed as a function of temperature (K)

$$\log K_{TA} = \log(vK_{OA}) = \log v + A + B/T \quad (2)$$

The proportionality constant *v* can be regarded as an effective lipid or octanol content of the terrestrial surface (grass/soil) and was assigned a value of 0.004, derived from the measured lipid content (*19*). It transpires that the value of *v* selected is unimportant because the surface concentration was calculated, not measured. Values of *A* and *B* were estimated from data of Harner and Bidleman (*29*) for two congeners, PCB-138 and PCB-52. For PCB-138, *A* is −5.57 and *B* is 4584, the corresponding values for PCB-52 being

−4.96 and 3981. Since K_{OA} is large, typically 10^8−10^{10} for PCBs, the quantity of PCB in the terrestrial surface is much greater than that in the air boundary layer; thus, it can be assumed that the concentrations in the surface do not change measurably diurnally. An effective surface concentration was calculated by multiplying the concentration in air by K_{TA} at a number of times and averaging the results. For example, for PCB-138 at a typical low temperature of 18 °C the air concentration is approximately 6 pg m^{-3}. Since K_{OA} is 1.5 × 10^{10}, K_{TA} is estimated to be 5.5 × 10^7 and the surface concentration is calculated as 23 × 10^7 pg m^{-3} or approximately 0.23 μg kg^{-1} wet weight. This is similar in magnitude to the reported measured values of 0.28 μg kg^{-1} dry weight for soil (of organic matter content approximately 2%) and 0.07 μg kg^{-1} wet weight for grass in the same area (*26, 27*). It appears that the measured air concentrations are consistent, in an order of magnitude sense, with measured grass and soil concentrations, and the concept that the equilibrium partition coefficient is controlled by K_{OA} and lipid and organic matter contents of grass and soil.

The simplest model is based on the assumption that the concentrations in air (C_A) and in the terrestrial surface (C_T) are in equilibrium at all times, i.e., C_A is C_T/K_{TA}. The PCB-52 and -138 air concentrations deduced using this assumption are shown in Figure 4 and fit the data fairly well. A test of this assumption is to compare the ratio of the average daily maximum and minimum concentrations in air with the ratio expected from the equilibrium expression for K_{OA}. The average maximum and minimum temperatures were 28 and 19 °C. Now K_{TA} will vary with a ratio of $10^B(1/T_1 - 1/T_2)$ where T_1 is 291 K and T_2 is 301 K. For PCB-138, for example, a value of 3.34 is calculated, with a measured ratio of 2.88 (Table 5). It thus appears that the concentration swings are consistent with a close-to-equilibrium assumption, it being recognized that it is difficult to assign maximum and minimum air concentrations because of finite sampling times. There may be differences in temperature between air and the terrestrial surface, and the temperature dependence of K_{TA} may not be exactly that of K_{OA}.

More complex models could be developed to include a resistance for transport between the surface and air using an
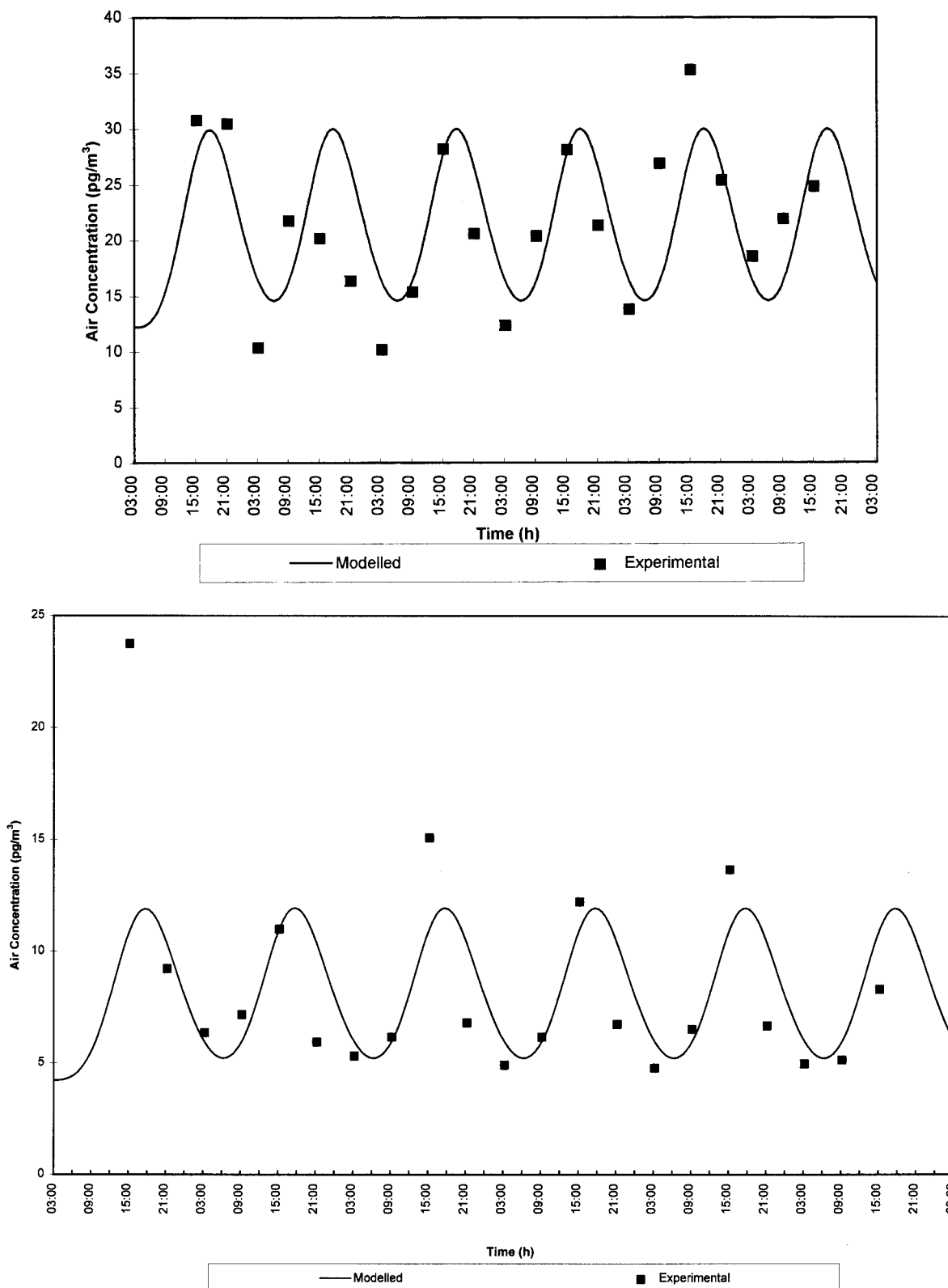
FIGURE 4. Modeled air concentrations for PCB-52 (above) and PCB-138 (below) (see text for details).

area, mass transfer coefficient approach and allowing for vertical diffusion in the air. This would have the expected effect of reducing the amplitude of the concentration swing, i.e., the air concentration would be damped, and the fit would therefore be less satisfactory. Undoubtedly, there is an exchange resistance and there is vertical eddy diffusion to heights greater than the sampling height of ~2 m, but the present data and model suggest that during the first 5 days

the boundary layer to ~2 m above ground conditions are close to equilibrium. It would be interesting to measure the diurnal fluctuations at various heights. The onset of turbulent unstable conditions after day 5 corresponds to a situation in which there was more rapid eddy transport, resulting in a damping of concentrations and temperature with PCB levels being controlled by transport rates rather than equilibrium. We conclude that, in future studies of this type, the most

valuable data are the maximum and minimum concentrations and temperatures which occur at about 3:00 a.m. and 3:00 p.m. An alternative and equivalent approach is to plot log concentration versus $1/T$, obtain a slope, and compare it with the enthalpy term B for K_{OA}. This has the benefit of using all the data (30), but is more complex than the simple approach used here.

Acknowledgments

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