FACTORS INFLUENCING ATMOSPHERIC CONCENTRATIONS OF PCBs

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Introduction. This study reports levels of individual PCBs in air collected at a background urban site over 41 separate 24 h periods between 13/7/97 and 27/7/98 and places them in context with those reported elsewhere (1-13). The influence on atmospheric PCB concentrations of rainfall, air temperature and humidity, wind speed and direction is examined, and heats of vapourisation calculated.

Sampling and Analysis. Samples were taken on the campus of Birmingham University, about 3 km southwest of the city centre of Birmingham, U.K.. Birmingham is the major city within the West Midlands conurbation, a major urban centre with a population of ca 2.5 million. Sampling equipment was located at ground level ca 20 m from the nearest building, well clear of any building air outfalls. Our sampling procedures for determining PCBs in air have been reported previously (14). In summary, samples were taken using a Graseby-Andersen Hi-Vol sampler modified to hold a glass-fibre filter (GFF, 0.6 µm pore size) and a pre-cleaned polyurethane foam (PUF) plug. Sampling was conducted for 24 h at a flow-rate of 0.7 m^3 min^{-1} yielding sample volumes of ca 1000 m^3. Analyses were conducted using well-validated, containment enrichment, GC/MS procedures reported elsewhere (14, 15). Mean recoveries of quantitation standards added to check analyte losses during both sampling (PCB congeners 19 and 147) and analysis (PCB congeners 34, 62, 119, 131, and 173) ranged between 67 and 92 % for all samples. Note that ΣPCB refers to the sum of all trichlorinated through heptachlorinated PCB congeners detected in a sample. Automatic monitoring of air temperature (T), relative humidity (RH), rainfall (RF), wind direction (WD), and wind speed (WS), was conducted during all sampling events.

Results and Discussion

Comparison of levels with other studies. While ΣPCB levels in Birmingham (arithmetic mean for ΣPCB = 290 pg m^{-3}) exceed the majority of data reported for rural locations in the U.K. and North America, they are at the lower end of those reported for urban areas. This may be due to the non-city centre location of our sampling site, away from high densities of buildings, outgassing of contaminated air from which may influence outdoor air levels.

Seasonal variation Figure 1 plots the variation of ΣPCB with mean air temperature for each individual sampling event. PCB levels over the warmer months (April to September inclusive; mean concentration = 384 pg ΣPCB m^{-3}; mean temperature = 13.9°C) clearly exceed those in colder months (October to March inclusive; mean concentration = 209 pg ΣPCB m^{-3}; mean temperature = 7.6°C). This "summer peak" in PCB concentrations is consistent with other studies (1, 2, 5-7, 16), and with the hypothesis that PCB volatilisation from soil makes an important contribution to atmospheric levels (17).

Figure 1: Variation of ΣPCB with Air Temperature
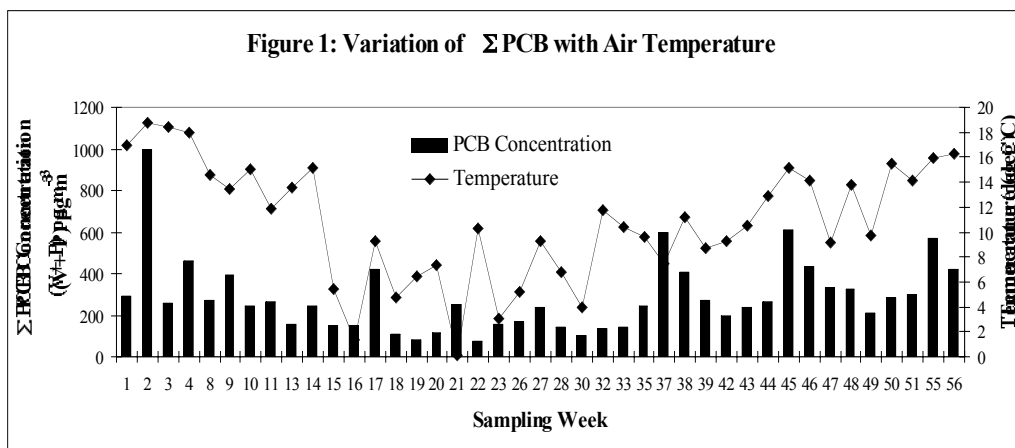
Influence of temperature on atmospheric PCB concentrations. Partial pressures of individual PCBs were calculated for each sample from gas phase concentrations using the ideal gas law (for ΣPCB, an average molecular mass of 326.4 was assumed). Natural logarithms of these partial pressures were plotted against reciprocal mean temperature for each sampling event. For all PCBs studied, the temperature-dependence of vapour-phase concentrations was significant at at least the 90 % level, with the significance level exceeding 99 % for 45 out of 47 chromatographic peaks. For ΣPCB, the temperature dependence is highly significant (R^2 = 0.37; 99.9 % significance), and the m_1 value (-6323 ± 1328 K) is within the range typically reported elsewhere (-4500 to -7500 K) (16) – see Figure 2. A recent review (16), reported that m_1 values increased with increasing

Figure 2: Clausius-Clapeyron Plot for ΣPCB

$$m_1 = -6323\pm1328$$
$$b_1 = 9.5$$
$$R^2 = 0.37$$
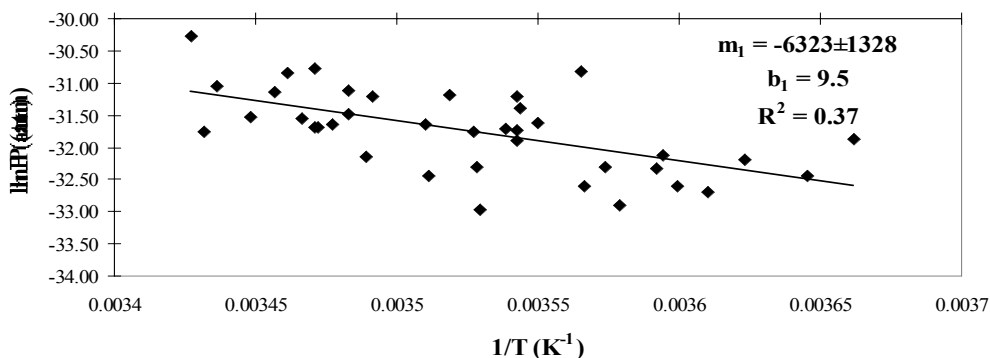
chlorine number for some studies, but did not detect such a relationship for urban locations, including one in the U.K.. It is therefore interesting that a highly significant relationship (R^2 =0.72; 99.9 % significance) was observed between m_1 and chlorine number (nCl) for this study. The slope of this regression (-1669) is within the range of -1244 to -1968 previously reported (16).

 The presence of homologue-specific temperature dependence in this study, may well reflect the "urban background" location of our sampling site. Wania et al (16) suggested that the absence of homologue-specific temperature dependence at urban locations was associated with a relatively minor influence from advection of air from outside the urban environment - i.e. levels would be essentially controlled by local sources. As discussed later, this appears not to be so at this site, as we observed a significant increase in PCB levels associated with northerly winds that had passed over the highly urbanised city centre.

The magnitude of m_1 is an indication of the extent of temperature dependence; the more negative the slope, the greater the influence of temperature. The temperature dependence is anticipated to be high if elevated surface volatilisation occurs when: (i) surface concentrations are high, and/or (ii) when surface temperatures are high. This behaviour would be expected for a soil surface, and - to a lesser degree - could be associated with contaminated building "surfaces". Whilst - as mentioned by Halsall et al (13) - outgassing of building air (significantly more contaminated than outdoor air in the West Midlands (14)) will not be wholly temperature dependent; higher indoor temperatures with concomitant increases in ventilation rates due to opening windows (air conditioned buildings are not common in the U.K.), means that a higher degree of temperature dependence would be expected for locations and homologues/congeners for which outgassing from nearby buildings makes a significant contribution. Conversely, a less negative (shallower) slope indicates an important input from the advection of background air. Hence, the observed increase in the modulus of m_1 with increasing nCl, suggests that at this site, outgassing from *nearby* buildings does not significantly influence PCB levels, otherwise m_1 values for the tri-, tetra-, and penta- homologues (the major homologues in indoor air (14)) would be higher.

Influence of atmospheric turbulence on temperature dependence of atmospheric PCB concentrations. For ΣPCB, the R^2 value indicates 37 % of the variation in vapour-phase levels to be due to temperature variation. A previously noted effect is the influence on this temperature dependence of wind speed, whereby periods of atmospheric turbulence lead to a collapse of the relationship between air concentration and temperature (16). We therefore examined our data for evidence of such an effect, by dividing them into 3 groups: (i) those where the mean wind speed for the sampling period <2.2 m s^{-1} (n=11); (ii) those where 2.2 > WS <4.4 m s^{-1} (n=16); and (iii) those where WS >4.4 m s^{-1} (n=14). Clausius-Clapeyron plots were recalculated for samples in each category for ΣPCB and individual homologue groups.

A clear decrease in the magnitude of m_1 with increased wind speed was observed for ΣPCB and all homologue groups, confirming the observations of other workers (18). When WS >4.4 m s^{-1}, temperature dependence was lost for ΣPCB and all homologue groups bar the heptachlorinated group. Furthermore, for samples where WS<2.2 m s^{-1}, 78% of the variation in PCB vapour-phase levels was attributable to temperature variation. Evidently, wind speed is an important factor in determining the temperature dependence of atmospheric PCB levels at this site.

Influence of other meteorological parameters on atmospheric PCB concentrations. In addition to temperature dependence, the potential influence on atmospheric PCB levels of wind speed and direction, air humidity, and rainfall has also been indicated (7). To assess the influence of these parameters on PCB levels at our sampling site, we conducted multiple regression analysis

of the relationship between each of these parameters and ln P of both individual homologues and ΣPCB. No significant relationships exist between ln P and any of the variables studied, except the cosine of the wind direction. Whilst there was no significant relationship between ln P and the cosine of the wind direction for hexa and heptachlorinated PCBs; significant positive relationships exist for ΣPCB (96% significance) and the tri- (98%), tetra- (96%), and pentachlorinated (92%) homologues. Positive cosine values are associated with wind directions of 270°-0°-90°, implying a statistically significant increase in atmospheric PCB levels at our sampling site when winds come from the north, passing over the centre of Birmingham. The absence of significant correlation with the hexa- and heptachlorinated homologues is probably because - unlike the lesser chlorinated PCBs - they are not the predominant species in the principal source reservoirs in the city centre (i.e. surface soil (12, 15) and building air (14)).

Heats of vapourisation Heats of vapourisation (ΔH_v) were calculated for 60 individual PCBs. The range of 27-112 kJ mol^{-1} (arithmetic mean = 61 $\pm$ 20 kJ mol^{-1}) is comparable to those derived from other field observations (2, 4, 7, 13, 19) and - in line with these studies - is lower than estimates derived from laboratory-based determinations (20). It has been suggested (2) that the lower ΔH_v values derived from field measurements are due to other atmospheric processes which reduce the temperature dependence of PCB levels. This hypothesis is supported by the fact that the calculated ΔH_v value for ΣPCB for samples from this study where WS <2.2 m s^{-1}, is - at 88 kJ mol^{-1} - much closer to the mean calculated from laboratory studies of 86 $\pm$ 7 kJ mol^{-1} (20).

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