A NOVEL APPROACH TO SOURCE APPORTIONMENT OF ATMOSPHERIC PCBs AND ORGANOCHLORINE PESTICIDES

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Introduction

Although direct human exposure *via* inhalation of outdoor air is not a significant exposure pathway, the atmosphere represents the primary vector by which PCBs and organochlorine pesticides (OCPs) enter the grass-cattle-human food chain, which is responsible for a significant proportion of human exposure. It is therefore important to monitor and improve understanding of the factors that influence atmospheric concentrations of such contaminants. This study reports concentrations of individual PCB congeners and DDT, DDE, DDD, γ-HCH, and α-HCH in samples of air collected at a background urban site on the campus of Birmingham University, UK over 62 separate 24 h periods between April 1999 and July 2000. Previous work at this site over the period July 1997 to July 1998 found that were distinct sources of (i) the tri and tetrachlorinated congeners (non-equilibrium short range transport); and (ii) the penta, hexa, and heptachlorinated congeners (equilibrium short range transport[1]. In this paper, we examine this our data for any temporal changes in source apportionment, and report a novel approach to source attribution.

Experimental

Full details of our sampling and analytical protocols for the determination of atmospheric PCBs are reported elsewhere[1]. In brief, OCPs were sampled in identical fashion to PCBs, with analysis conducted *via* similar containment-enrichment, GC/MS procedures.

Results and Discussion

Atmospheric Concentrations

Table 1 summarises the arithmetic mean concentrations (sum of both vapour and particle phases) of selected PCBs and OCPs detected during this campaign; alongside those of PCBs detected at the same location over the period 7/97-7/98[1], and those of OCPs at 2 other UK locations[2,3]. There are discernible changes in average concentrations of PCBs over the short period covered by the 2 campaigns. Continued monitoring is required to elucidate whether these are genuine temporal trends or merely a reflection of normal year-on-year variation. With respect to OCPs; concentrations in this study are reasonably consistent with those recorded in Hazelrigg, in North-West England. Our detection of DDT (not detected at Hazelrigg) is interesting, as it suggests either some continued – illicit - use of DDT within the UK, or long-range atmospheric transport. However, the 5-fold decline in the concentration of DDT compared to that recorded in 1992-93 in southern England (*ca* 150 km from our site), is – along with the decline in the DDT:DDE ratio (an indication of the "age" of the DDT) - a clear indication of the decline in DDT usage in Europe. In contrast, both γ-HCH concentrations and the γ- to α-HCH ratio are higher in this study than either of the other studies cited. While the excess of γ-HCH is to be expected, given the continuing use in the UK of "pure" γ-HCH (lindane) rather than technical HCH (a mix of largely α- and some γ-

HCH), the absence of any temporal change in both parameters suggests no decline in use over the last decade. The lower values at the Hazelrigg site are consistent with a lower rate of lindane application in that location compared to the Birmingham area.

Clausius Clapeyron Plots and the Influence of Temperature and Wind Direction on Atmospheric Concentrations
Partial pressures of individual PCBs and OCPs were calculated for each sample from gas phase concentrations (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 individual PCBs studied, the temperature-dependence of vapour-phase concentrations was significant at at least the 98 % level, with the significance level exceeding 99 % for most congeners. For ΣPCB, α- and γ-HCH, temperature dependence was significant at the 99.9% level (R^2 = 0.38, 0.28, and 0.36 for ΣPCB, α- and γ-HCH respectively), and the m_1 values (-6209 K, -4309 K, and –9337 K for ΣPCB, α- and γ-HCH respectively) were within the range reported elsewhere[4].

In addition to temperature dependence, the potential influence on atmospheric PCB levels of wind direction was investigated. Previously, we conducted multiple regression analysis of the relationship between the cosine and sine of the wind direction angle (relative to true north) and ln P of both individual homologues and ΣPCB. We now believe that rather than regressing concentration *versus* cos and sin of the wind direction *relative to true north*, one should instead calculate the angle of wind direction *relative to the direction from which maximum concentrations originate*. To illustrate, consider a situation where maximum concentration is associated with a wind direction of 150^0 and the minimum concentration associated with winds arriving from an angle of 0^0. Calculating cos WD relative to true north gives a value of –0.866 for the maximum, and 1 for the minimum. Clearly, this non-synchronisation of maximum values of concentrations and those of cos WD may lead to an incorrect conclusion that there is no significant relationship between these parameters. By comparison, if we calculate the angle of wind direction relative to the angle associated with maximum concentration, we get cos WD values of 1 and –0.866 for the wind directions associated with maximum and minimum concentrations respectively.

To identify the wind direction from which maximum SOC concentrations originate, we have plotted the correlation coefficient (R) between concentration of SOCs and cos (WD-α), where WD is the wind direction relative to true north, and α is an angle – typically incremented at 30^0 intervals or less - against α. As illustrated in Figure 1 for ΣPCB, this process reveals the angle (relative to true north) at which maximum correlation between wind direction and SOC concentrations occurs (120^0 for ΣPCB). We refer to this angle as the "downwind angle" (α_{da}). In summary, higher concentrations of individual and ΣPCBs are associated with winds arriving at our site from the east (α_{da} = 90-120^0), while concentrations of OCPs are at a maximum when α_{da} = 90-150^0 (*i.e.* east to south east).

Having identified the "downwind angle", we conducted multiple linear regression of SOC concentration (expressed as the natural logarithm of the partial pressure of the vapour phase) against reciprocal air temperature (1/T) and cos (WD-α_{da}). By doing so, we obtained Beta weights for the regression coefficients for the 2 independent variables examined. The greater the Beta weight, the greater the influence of the independent variable. Consequently, the relative magnitude

of Beta weights for the temperature and wind direction variables provides an indication of the relative significance of the 2 parameters on SOC concentrations. Figure 2 plots $[\beta(1/T)/\beta(\cos WD-\alpha_{da})]$ (*i.e.* the modulus of the ratio of the Beta weight for 1/T to that for cos (WD-α_{da})) against the number of chlorines for individual PCBs. There is a statistically significant (p<0.01) increase in this ratio with increasing chlorine number, indicating that the relative influence of temperature on concentrations is greater for the higher congeners, with concentrations of lower PCBs more strongly influenced by wind direction. This is consistent with our previous observation of different *source attributions for different PCB homologues.* In summary, we believe that the tri and tetrachlorinated PCBs originate from a spatially-restricted temperature-dependent source – either volatilisation from surfaces contaminated in a spatially non-uniform manner (*e.g.* a landfill), or ventilation of indoor air from a specific location (*e.g.* a densely urbanised area). In contrast, the penta through heptachlorinated congeners arise from a temperature-dependent source that is not spatially-restricted, such as volatilisation from surfaces contaminated in a spatially uniform fashion. In essence, the lower chlorinated congeners at our site are supplied largely from a specific location, while the other congeners arise as a result of general background contamination.

References

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Table 1: Comparison of Mean Atmospheric Concentrations of Selected PCBs and OCPs

Compound	Birmingham '97-'98[1]	Birmingham '99-2000 (this study)	Hazelrigg, UK '97-'98[2]	Southern England '92-'93[3]
PCB 28	30	19	-	-
52	27	22	-	-
101	15	16	-	-
118	6.9	11	-	-
138	5.4	3.7	-	-
153	5.8	3.7	-	-
180	2.0	1.3	-	-
α-HCH	-	29	30	39
γ-HCH	-	450	220	408
DDD	-	1.3	-	-
DDE	-	8.4	4.0	14
DDT	-	3.1	<1.0	17

Figure 1: Relationship between the "Downwind Angle" α and the Correlation Coefficient between ΣPCB partial pressure and Cos (WD-α)
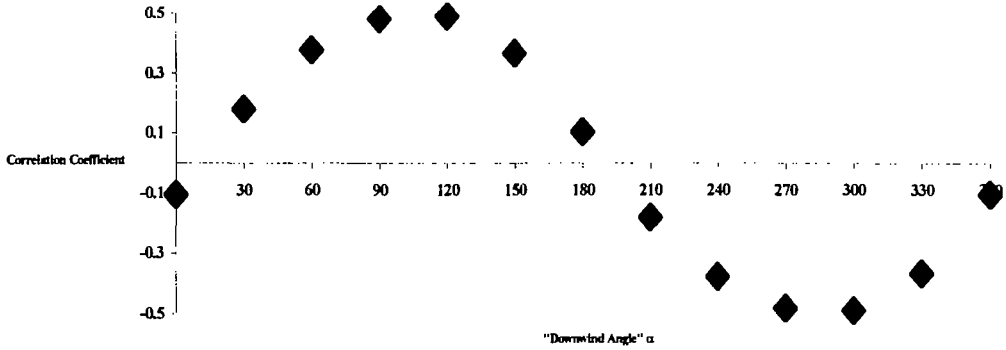

Figure 2: Relationship between $[\beta(1/T)/\beta(\cos(WD-\alpha_{da})]$ and Chlorine Number