Seasonal Variation in Concentrations of PCBs in Topsoil in a Major Conurbation

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Introduction

Polychlorinated biphenyls (PCBs) are organochlorine chemicals that found widespread use in a diverse range of applications, with around 1.2 million tonnes produced worldwide[1]. Owing to their toxicity, their production - but not their use - ceased throughout most of the industrialised world in the late 1970s. Although UK human exposure to PCBs has fallen in recent years in response to the cessation of their production in the late 1970s[2,3], human health concerns remain - currently a substantial proportion of UK schoolchildren and toddlers are exposed at levels that exceed the UK government's recommended tolerable daily intake to dioxins and dioxin-like PCBs[3]. Understanding the environmental fate and behaviour of PCBs thus remains a research priority.

There is a well-documented and near universal seasonal variation in atmospheric concentrations of PCBs, whereby concentrations in summer exceed those in winter embodied in a statistically significant relationship between atmospheric concentrations and temperature. Such a relationship has been observed previously in our previous studies at the Elms Road Observatory Site (EROS), an urban „background“ location on the University of Birmingham campus ca. 3 km southwest of Birmingham city centre[4,5].

In contrast, there is to our knowledge no evidence regarding the seasonal (*i.e.* temperature-related) variation in concentrations of PCBs in soil. Recently, we reported results from a year-long study determining enantiomeric fractions (EFs) of PCBs 95, 136, and 149 in both outdoor air samples collected using a high volume sampler, and topsoil from one urban and one rural location within the UK’s West Midlands conurbation[6]. During this study, samples of topsoil and air

were taken at regular intervals over the course of ca. 1 year at both locations. This study reports the concentrations of PCBs in these samples from the EROS location and in particular, examines seasonal variations in PCB concentrations in topsoil. In addition, as the chiral analyses revealed the contribution of volatilisation from soil to make only a negligible contribution to atmospheric concentrations[6] – a conclusion that was in stark contrast to soil:air fugacity ratios for the three chiral PCBs, we examine soil:air fugacity ratios to elucidate the apparent soil:air equilibrium status for other PCBs.

Materials and Methods

Sample Collection

Twenty-six air and soil samples were collected every 2 weeks from the EROS location within the West Midlands conurbation in the United Kingdom over the period between January 2001 and March 2002. Further details of this sampling location and methods are given elsewhere[6].

Sample Purification and Analytical method

Samples were extracted and purified prior to GC/MS as previously described[6]. Achiral GC/MS and quantification were conducted as detailed elsewhere[4,5].

Results and Discussion

PCB concentrations at EROS compared with those elsewhere.

Average ΣPCB concentrations in air and topsoil at EROS are 256 pg m^{-3} (σ_{n-1} = 140 pg m^{-3}) and 2.1 μg kg^{-1} dry weight (dw) ((σ_{n-1} = 1.2 μg kg^{-1}) respectively. The concentrations in air compare closely with those previously detected at EROS, specifically: 290 pg m^{-3} in 1997-1998[4], and 252 pg m^{-3} in 1999-2000[5], but are at the lower end of the range reported previously for other urban locations[4]. Similarly, concentrations in topsoil are comparatively low for a major conurbation like Birmingham (population ca. 1,000,000)[7].

Figure 1 shows the expected statistically significant positive relationship between temperature and atmospheric concentrations of ΣPCB at EROS over the 14 months of sampling. Similar plots were obtained for all individual PCBs measured.

Figure 2 illustrates the relationship between temperature (i.e. the air temperature on the day of sampling) and ΣPCB concentrations in topsoil samples at EROS. Surprisingly, there is a statistically significant ($p<0.001$) increase in concentrations with temperature.

One possible explanation for this seasonal variation is simply that it is a chance observation that reflects the inhomogeneity of PCB concentrations in soils within even a relatively small area – note that in this study each sample consisted of 3 pooled sub-samples of soil taken using a corer to 5 cm depth from the same 10 m x 10 m area immediately adjacent to the air sampler. To evaluate the combined effect of soil sampling and analysis on the precision of our measurements; on one occasion we sampled soil at the EROS location according to our standard procedure, but replicated it so that we had a total of 5 soil samples, which were then extracted and analysed as usual. These data revealed the relative standard deviation of concentrations for individual congeners to vary between 5 and 38% (average for all congeners = 17%), with the value for ΣPCB = 16%. This indicates that any seasonal variation in PCB concentrations observed, do not appear to be attributable to sampling and/or analytical variability.

Another possible explanation is that soil fugacities increase in proportion to those in air in order to maintain soil:air equilibrium. We therefore explored this explanation further.

Soil:Air Fugacity Ratios

In order to evaluate the equilibrium status between soil and air at EROS during this study, we converted average concentrations of both individual PCB congeners and ΣPCB in air and soil into values of soil (f_{soil}) and air (f_{air}) fugacities. To do so, we followed previously reported procedures[8] utilising equations 1 and 2

$f_{air} = C_{air}/Z_{air}$ (equation 1)
and $f_{soil} = C_{soil}/Z_{soil}$ (equation 2)

Where C_{air} = concentration of a given PCB congener in air (mol m^{-3})
C_{soil} = concentration of a given PCB congener in soil (mol m^{-3}) (converted from pg g^{-1} assuming a soil density of 1,174 kg m^{-3})
$Z_{air} = 5.5 \times 10^{-4}$ mol m^{-3} Pa^{-1}
$Z_{soil} = 451$ mol m^{-3} Pa^{-1}

Values of soil density, Z_{air} and Z_{soil} are all taken from Harner et al, 1995[8].

Comparison of soil and air fugacities reveal that for all PCBs soil fugacities exceed air fugacities by a considerable margin – typically around 20 for ΣPCB. The

implication of this is that soil:air equilibrium has not been attained, and that one would anticipate volatilisation from soil to occur.

This is however in direct contrast to the results of our chiral study using the same samples[6], indicating that the absolute values of soil and air fugacity ratios calculated here may not be accurate due to variety of factors[6], the most obvious being the use in this paper of a value of Z_{soil} that has been cited elsewhere as a general representation of UK soils[8], but that may be an underestimate of the true Z_{soil} value at our sites, with a concomitant overestimation of f_{soil}, and thus the likelihood of volatilization. However, this does not prevent study of seasonal trends in soil:air fugacity ratios, with Figure 3 showing the variation of soil:air fugacity ratios for ΣPCB with air temperature at EROS. Clearly, there is no seasonal variation, which is supportive of the idea that a constant soil:air fugacity ratio is being maintained.

However, if the observed seasonal variation in concentrations in topsoil are replicated at other locations, then a simple mass balance calculation reveals that a substantial proportion (ca. 50% as ΣPCB concentrations in summer are ca. twice those in winter) of the mass of PCB associated with topsoil must „disappear“ or become somehow temporarily unavailable for extraction during winter. The former concept is an unconvincing explanation as a seasonal loss of this magnitude, would rapidly reduce concentrations in topsoil when repeated over a number of years. Furthermore, such loss could only occur via biodegradation, leaching, or biotic uptake; a possibility that seems unlikely given the evidence from chiral studies that volatilisation from topsoil is negligible at EROS[6]. At present, we are unable to proffer an entirely satisfactory rationale for this apparent seasonal variation, but continue to investigate its existence and origins both at EROS and at other locations within the West Midlands conurbation.

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Figure 1: Relationship between Atmospheric Concentration ΣPCB and Air Temperature

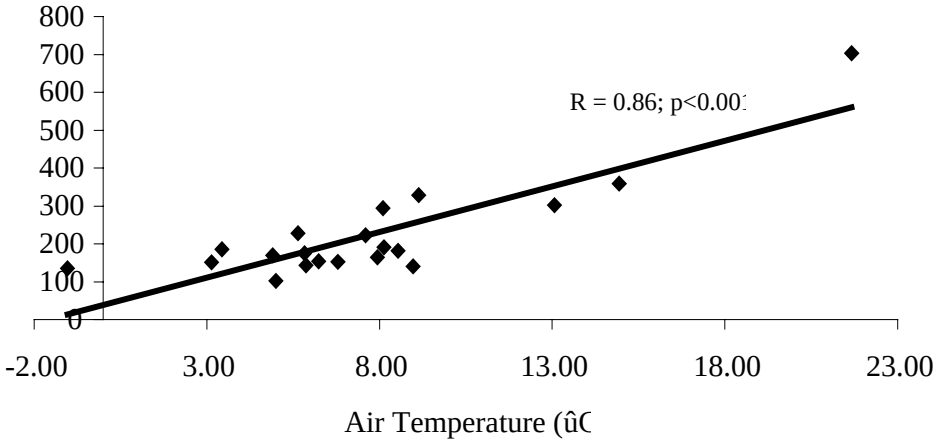

Figure 2: Relationship between ΣPCB Concentrations in Topsoil and Air Temperature

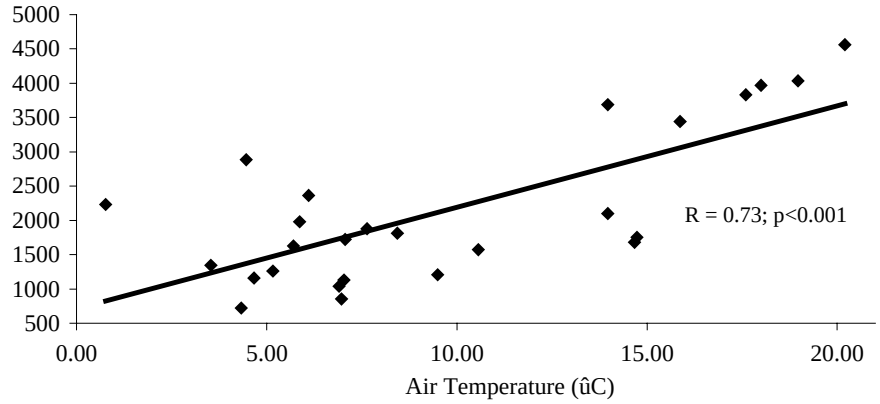

Figure 3: Relationship between Soil:Air Fugacity Ratios for ΣPCB and Air Temperature