SPATIAL VARIATION IN CHIRAL SIGNATURES OF PCBs IN MATCHED AIR AND TOPSOIL SAMPLES ON AN URBAN-RURAL TRANSECT: IMPLICATIONS FOR ATMOSPHERIC SOURCE APPORTIONMENT

Stuart Harrad[1], Arslan Jamshidi[1], Matthew Robson[1]

[1]University of Birmingham, Birmingham

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]. Although the majority of non-occupational exposure to PCBs occurs *via* the diet[4] the atmosphere is an important point of entry into human food chains. As a result, identifying and controlling emissions to the atmosphere plays a pivotal role in efforts to minimise human exposure. Two principal categories of PCB emissions to the atmosphere have been identified[1,5-9]. One is emissions from environmental surfaces, the other emissions from PCB-containing materials such as transformers, capacitors, and permanently-elastic construction sealants that remain in use. Distinguishing the relative contributions of these two source categories is of considerable policy relevance, as if – as is widely believed - emissions from environmental surfaces predominate[1,5-7], then there is little that policy-makers can do to reduce airborne concentrations. In contrast, if – as recently implied[8-10] - emissions from remaining PCB stocks are significant, then their destruction offers real hope of effecting a speedy reduction in atmospheric concentrations and human exposure. Distinguishing between atmospheric PCBs arising from different source categories is thus an important research objective.

Previous attempts to elucidate the relative significance of emissions from environmental surfaces such as soil, as opposed to emissions from remaining PCB usage, have relied on indirect methods and mathematical modelling[1,8,9]. More recent work has utilised the chiral properties of organochlorines such as α-HCH, heptachlor epoxide, and chlordane to directly distinguish between such source categories[11,12]. These techniques are also applicable to PCBs, as a number of individual PCBs are both chiral and present at measurable quantities in the environment[13].

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[14]. The study revealed that while EFs in air were essentially racemic, those in topsoil indicated appreciable enantioenrichment of the 2nd eluting enantiomer for PCB 95 and the (+) enantiomer for PCBs 136 and 149. This suggests: (i) that essentially all atmospheric PCBs at both sites arise from racemic (*i.e.* primary) sources, rather than volatilization from soil; and (ii) that appreciable enantioselective degradation of the monitored PCBs in topsoil occurs. These results have potentially important implications for public health and environmental protection, as they imply that destruction of PCB stocks remaining in use are likely to result in a significant reduction in atmospheric concentrations. As the atmosphere is the principal point of entry of PCBs into the food chain, and is also the principal vector *via* which PCBs are transported from their source regions, such action is likely to reduce human exposure and limit the future spread of these compounds. Clearly however, the wider policy significance of these surprising findings depends on the extent to which they are replicated at other locations. As a result, this study evaluates how representative our initial findings were, by comparing EFs of PCBs 95, 136, and 149 in air and soil from a number of locations in the West Midlands conurbation.

Materials and Methods

Sample Collection
Air and soil samples were collected from 11 different sites within the West Midlands conurbation in the United Kingdom. Sampling locations were located on a southwest (upwind) to northeast (downwind) transect at intervals of between 3 and 15 km across the conurbation. In this way, a mix of rural, suburban, and urban sampling locations were studied.

One topsoil sample per sampling location per month was collected as previously described[14]. For the initial phase (October-November 2003), the air sampling duration was 2 months to verify that sufficient material could be sampled to provide a measurable signal at all locations. In future, one air sample per month will be collected at each location, to provide greater temporal resolution. To provide a time-integrated atmospheric signal over each sampling period, passive air samplers *i.e.* PUF disks were employed. These have been used successfully in other studies[15, 16]. While their use for determining absolute concentrations requires calibration to determine the air sampling rate of the device, this is unnecessary for the determination of EFs, as only the relative abundance of the two enantiomers is required. Once collected, all samples were stored at 4°C until extraction and analysis.

In order to evaluate the existence of any seasonal variability in the data, the study is scheduled to run for 12 months from October 2003. Data reported in this paper cover the 1st three months (October-December 2003) for soil (3 sampling periods), and the 1st two months for air (one sampling period). Unfortunately, although EFs for all three target PCBs in air samples passed QA/QC criteria, in soil, only those for PCBs 95 and 136 were acceptable, owing to an as yet unidentified interference.

Sample Purification and Analytical method
Samples were extracted, purified, and subjected to enantioselective GC/MS as previously described[14].

As part of our on-going quality control measures, we determined EFs of the target PCBs in five separate aliquots of a reference material (EC5 - sediment) for which data have been previously reported[14,17]. Our data are reported in Table 1, and confirm the accuracy and reproducibility of the data produced by our methods, compared with that generated using both 1-and 2-dimensional enantioselective GC/MS approaches utilised elsewhere[17].

Table 1: EF Values Obtained for EC5 Reference Material

Congener	1-Dimensional[17]	2-Dimensional[17]	This study
95	0.488±0.001	0.483±0.001	0.489±0.001
136	0.496±0.002	0.508±0.007	0.498±0.001
149	0.511±0.003	0.520±0.004	0.505±0.003

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. Table 2 reveals that there appears minimal variation in EFs of PCBs 95 and 136 between these soil samples, indicating that any spatial or temporal differences in EFs observed, do not appear to be attributable to sampling and/or analytical variability.

Table 2: EF Values Obtained in Five Replicate Soil Samples from the Same Location

Soil #	EF for PCB 95	EF for PCB 136
1	0.470	0.493
2	0.468	0.499
3	0.478	0.508
4	0.467	0.515
5	0.467	0.509
Average	0.470	0.505
RSD[a] (%)	1.0	1.7

[a]relative standard deviation

Results and Discussion

The EFs of each measurable target PCB in soil and air samples at each location for the periods for which data are available are presented in Tables 3 and 4 respectively. The sampling locations are classified broadly according to whether they are rural (R), suburban (S), or urban (U).

Atmospheric Source Apportionment One striking feature of these initial data is that EFs in air for PCBs 136 and 149 are essentially racemic at all of the 7 locations for which data are available. The EFs for PCB 95 in air are less obviously racemic, but display appreciable divergence from the EFs found in the corresponding soil samples. As a result, while far more data are required to confirm these tentative findings, it appears that our earlier obervations at EROS[14] are broadly replicated at other locations within the West Midlands conurbation, and that volatilisation from soil appears to make a minimal contribution to atmospheric PCB concentrations at each location.

EFs in Soil Our data on EFs in soil are more difficult to interpret, although they clearly constitute appreciable further evidence of enantioselective degradation of PCBs at concentrations typically encountered in the UK and other industrialised countries. One interesting observation is that EFs of PCBs 95 and 136 are

essentially racemic in all 3 samples taken at the most urban location (Centenary Square, located in the centre of Birmingham). This is not inconsistent with previous observations for soils from the Greater Toronto Area that the extent of enantioselective degradation was inversely related to the concentration of both PAH and PCBs (and by inference the degree of urbanisation), which we tentatively hypothesised impaired microbial activity[18]. These racemic EFs at Centenary Square may also reflect the fact that that at this highly urbanised location, the supply of atmospheric PCB inputs (for which EFs are essentially racemic) may exceed the rate at which enantioselective degradation occurs. Further tentative support for this inverse relationship between degree of urbanisation and extent of enantioselective degradation comes from the fact that the greatest enantioselective degradation is observed at the most rural locations (Whitbourne and Newton Regis).

As with our previous study[14], there are congener-specific variations in the extent of enantioselective degradation, with 95 being degraded > 136. The direction of this enantioselective degradation is also broadly in line with our previous findings, although there appears to be less enantioselective degradation of 136 than previously observed.

Also of interest is the variations in EF values in soil for a given PCB from month-to-month, although one should not infer too much at this early stage of the study. We had observed previously similar month-to-month variability at EROS[14], which we could not attribute to seasonal variations in microbial activity as there was no statistically significant difference between EFs in summer and winter. Furthermore, the extremely high sampling and analytical precision of our measurements of EFs in soil (see Table 1), indicates that these variable EFs are not an artefact resulting from sampling and analytical uncertainty. At the present time therefore, we are unable to satsifactorily explain this apparent month-to-month variability.

Table 3: EF Values for PCBs 95 and 136 Obtained in Soil Samples from Each Location

Sampling Site	EF for PCB 95			EF for PCB 136		
	10/03	11/03	12/03	10/03	11/03	12/03
Whitbourne (R)	0.449	0.452	0.458	ND	ND	ND
Bishops Wood (R)	0.479	0.480	0.478	ND	ND	ND
Chaddesley Wood (R)	0.480	0.534	0.474	0.496	0.503	0.510
West Heath (S)	0.493	0.437	0.476	0.519	0.502	0.501
Weoley Castle (S)	0.453	0.485	0.421	0.509	0.508	0.525
EROS (U)	0.463	0.471	0.488	0.503	0.489	0.515
Centenary Square (U)	0.498	0.491	0.498	0.496	0.490	0.500
Hodge Hill (U)	0.456	0.447	0.458	0.505	0.506	ND
Kingsbury Water Park (R)	ND	0.474	0.449	0.581	ND	ND
Tamworth (S)	0.485	ND	0.499	ND	ND	0.500
Newton Regis (R)	0.447	0.489	0.398	0.556	0.516	ND

ND = no data, failed QA/QC criterion

Table 4: EF Values Obtained In Air Samples from Each Location

Sampling Site	EF for PCB 95	EF for PCB 136	EF for PCB 149
	10+11/03	10+11/03	10+11/03
Whitbourne (R)	0.490	NA	NA
Bishops Wood (R)	NA	NA	NA
Chaddesley Wood (R)	NA	NA	NA
West Heath (S)	0.477	0.509	0.497
Weoley Castle (S)	0.480	0.501	0.496
EROS (U)	0.487	0.508	0.501
Centenary Square (U)	0.497	0.504	0.498
Hodge Hill (U)	0.483	0.509	0.498
Kingsbury Water Park (R)	0.480	0.497	0.503
Tamworth (S)	NA	NA	NA
Newton Regis (R)	0.491	0.500	0.485

NA = not analysed

References
1. Harrad S. J., Sewart A. P., Alcock R., Boumphrey R., Burnett V., Duarte-Davidson R. Halsall C., Sanders G., Waterhouse K., Wild S. R., Jones K. C. (1994) Environ. Pollut. 85, 131.
2. Food Standards Agency (2000) Food Standards Agency UK - Dioxins and PCBs in the UK Diet: 1997 Total Diet Study (Food Survey Information Sheet Number 04/00).
3. Food Standards Agency. (2003) Food Standards Agency UK – Dioxins and Dioxin-Like PCBs in the UK Diet: 2001 Total Diet Study Samples, (Food Survey Information Sheet 38/03).
4. Duarte-Davidson R., Jones K. C. (1994) Sci. Tot. Environ. 151, 131.
5. Harner T., Mackay D., Jones K. C. (1995) Environ. Sci. Technol. 29, 1200.
6. Alcock R. E., Johnston A. E., McGrath S. P., Berrow M. L., Jones K. C. (1993) Environ. Sci. Technol. 27, 1918.
7. Jeremiason J. D., Hornbuckle K. C., and Eisenreich S. J. (1994) Environ. Sci. Technol. 28, 903.
8. Currado, G. M., Harrad, S. (2000) Environ. Sci. Technol. 34, 78.
9. Halsall C. J., Lee R. G. M., Coleman P. J., Burnett V., Harding-Jones P., Jones K. C. (1995) Environ. Sci. Technol. 29, 2368.
10. Meijer S. N., Ockenden W. A., Steinnes E., Corrigan B. P., Jones K. C. (2003) Environ. Sci. Technol. 37, 454.
11. Bidleman T. F., Falconer R. L. (1999) Environ. Sci. Technol. 33, 206A.
12. Bidleman T. F., Jantunen L. M. M., Wiberg K., Harner T., Brice K. A., Su K., Falconer R. L., Leone A. D., Aigner E. J., Parkhurst W. J. (1998) Environ. Sci. Technol. 32, 1546.
13. Wong C. W., Garrison A.W. (2000) J. Chromatgr. A 866, 213.
14. Robson M. E., Harrad S. (2004) Environ. Sci. Technol. 38, 1662.
15. Shoeib M., Harner T. (2002) Environ. Sci. Technol. 36, 4142.
16. Jaward F. M., Farrar N. J., Harner T., Sweetman A. J., Jones K. C. (2004) Environ. Sci. Technol. 38, 34.
17. Wong C. S., Hoekstra P. F., Karlsson H., Backus S. M., Mabury S. A., Muir D. C. G. (2002) Chemosphere 49, 1339.
18. Wong, F., Diamond M., Truong J., Robson M., Harrad, S. (2003) Organohalogen Compds 62, 301.