

Chiral signatures and concentrations of PCBs in matched air and topsoil samples at selected global sites

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Introduction

Despite the restrictions, and subsequent ban, on the production of polychlorinated biphenyls (PCBs) in most developed countries, there is still considerable concern surrounding their toxicity. Although human exposure has declined after their ban in the 1970s^{1,2} a substantial environmental burden still exists. Therefore the identification and control of emissions remains a research priority. 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 conurbation³. 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. This study evaluates how representative our initial findings were, by comparing EFs of PCBs 95, 136, and 149 in air and - where feasible - soil from a number of locations throughout the UK and the world.

Materials and Methods

Sample Collection

Matched Air and Soil Sample Collection from International Campaign

Air samples were collected using PUF disk samplers (each fitted with 2 PUF disks) over a period of 6 weeks (1st April 2004 – 14th May 2004) in 9 locations from around the world (see Table 1). Samplers were despatched to each destination by overnight courier in airtight containers. Samplers were deployed between 1.5 and 3 metres above ground, and away from buildings. Soil samples were taken adjacent to the air sampling location at the end of the air sampling period in accordance with our previously reported protocol. After sampling, the soil was homogenised and a 50 g aliquot extracted and concentrated prior to overnight courier return along with the sealed air sampler to Birmingham for further processing. Each location provided information on the exact extraction procedure used (e.g. soxhlet, ASE) and also the soil moisture content. Although sampler calibration data (which provides air sampling rates in m³ d⁻¹ for the PUF disk samplers) is not necessary to derive EF values for the air samples, it *is* required for the estimation of concentrations. In the current absence of such calibration data for the exact configuration (*i.e.* 2 PUF disks per sampler housing) employed in this campaign; we have estimated concentrations using air sampling rates derived for similar housing using a single PUF disk in indoor air of 0.70-1.27 m³ d⁻¹, depending on the homologue group⁴.

Air Sample Collection from UK Sites

In addition to the international campaign, crude air sample extracts were provided by AEA Technology plc for analysis from 19 different locations around the UK (see Table 2). Each extract was of the combined particulate and vapour phase components collected using a HiVol air sampler operated continuously during the 3rd quarter of 2003 (1st July- 30th September).

Sampling, Purification and Analytical Methodology

All samples were extracted (where necessary), purified, and subjected to both enantioselective GC/MS for the determination of chiral signatures, and non-enantioselective GC/MS for the determination of PCB concentrations as previously described^{3,5}. We have previously reported the accuracy and reproducibility of our methods for determining chiral signatures and concentrations of PCBs^{3, 5}, but QA/QC data specific to this work are reported in Table 1.

Results and Discussion

International Campaign

The EFs of each target PCB, together with concentrations of Σ PCB in the soil and air samples at each location for which there was available data are shown in Table 1.

Table 1: EF and Σ PCB Concentration Data in Air and Soil Samples Taken at Various International Locations

Sample Location	Soil				Air			
	Concentration (pg Σ PCB g ⁻¹)	EF for PCB #			Concentration (pg Σ PCB m ⁻³)	EF for PCB #		
		95	136	149		95	136	149
Alberta, Canada	1.348	0.449	0.492	0.484	1534	0.492	0.486	0.486
Aveiro, Portugal	0.253	0.454	0.473	0.500	685	0.486	0.499	0.497
Wilrijk, Belgium	4.41	0.487	0.459	0.463	833	0.490	0.491	0.497
Brunei	0.115	0.490	n.d	n.d	288	n.d	n.d	n.d
Zaragoza, Spain	4.508	0.481	0.494	0.492	679	0.486	n.d	0.506
NSW. Australia	5.012	0.507	0.525	0.483	725	0.499	n.d	0.492
Colombo, Sri Lanka	1.908	0.480	0.522	0.530	1394	0.497	0.497	0.494
Athens, GA, USA	0.233	0.517	n.d	0.474	302	0.494	n.d	n.d
Cork, Ireland	n/a	n/a	n/a	n/a	475	0.496	n.d	n.d
EF Values in Aroclors ^a and Reference Material ^{a,b}								
Congener	Aroclor 1242	Aroclor 1254	Aroclor 1260	Aroclor mix ^c	EC5			
95	0.499 ± 0.004	0.508 ± 0.006	0.510 ± 0.005	0.508 ± 0.004	0.487 ± 0.001			
136	0.501 ± 0.001	0.496 ± 0.004	0.497 ± 0.003	0.503 ± 0.001	0.499 ± 0.000			
149	0.497 ± 0.006	0.493 ± 0.003	0.497 ± 0.001	0.488 ± 0.003	0.511 ± 0.001			

NSW New South Wales, n.d. Not detected, n/a sample not available, ^a Error estimates are $\pm 1\sigma$. σ values derived from five replicate GC/MS analyses. ^b

Sediment. ^c 1:1:1 (w/w) mix of Aroclors 1242, 1254, and 1260. *Italics* soil concentrations based on 50 g wet weight all others on dry weight as data supplied.

EFs in Air

Of the data reported here, essentially all sites showed racemic values for PCB 95 according to the criteria of 0.500 ± 0.005 cited previously⁶, with the exception of the samples from Canada, Portugal, Belgium and Spain, where the EF deviated slightly away from racemic. Similarly, while the samples from Canada and Belgium showed slightly non-racemic signatures for PCB 136, the 2 others that provided data for this congener showed racemic values. In the case of PCB 149, the samples from Australia, Canada and Sri Lanka showed slightly non-racemic signatures for PCB 149, while the other sites showed racemic values. On the whole, chiral signatures of each target PCB in air samples were racemic or near-racemic.

EFs in Soil

Chiral signatures in soil samples reveal that, as with our previous report³, there are congener-specific variations in the extent of enantioselective degradation (Table 1). The greatest enantioselective degradation is observed for PCB 95 indicating that this congener is degraded more extensively than 136 and 149. In contrast, however, the direction of this enantioselective degradation is different to our earlier work at 2 locations in the West Midlands of the UK³. While it is largely similar for PCB 95, the direction is highly variable in this study for PCBs 136 and 149, whereas our earlier study reported edaphic EFs for these congeners to exceed 0.5. Clearly, these initial data suggest there to be site-specific influences on both the extent and direction of enantioselective degradation of PCBs in soils.

Comparison of EFs in Co-located Air and Soil Samples

The results revealed that in most cases, chiral signatures in air samples from each site display appreciable divergence from the chiral signatures found in the corresponding soil samples. While information from a wider range of locations is required, these data are not inconsistent with our earlier observations³, that volatilisation from soil appears to make a minimal contribution to atmospheric PCB concentrations at each location.

Soil and Air Concentrations

While in the absence of data on the soil characteristics that can greatly influence PCB contamination (e.g. organic carbon content), it is difficult to draw too many conclusions; the concentrations reported here are within the range reported elsewhere⁷. Concentrations in air are slightly easier to interpret, and it is interesting to note that the concentrations at each site exceeds the average value recently reported for the University of Birmingham campus⁸, and the concentrations reported in both the Canadian and Sri Lankan samples are outside the range normally observed in Birmingham.

UK Campaign

Table 2 shows the EFs for each target PCB in the air samples collected in the UK, together with the site name and an indication of the site type (industrial, urban etc.). The majority of EF values in samples are racemic⁶. Without EF values in corresponding soil samples, it is not possible to draw any firm conclusions as to the sources of the PCBs detected in these air samples. However, the racemic or near-racemic values obtained are consistent with those previously detected in air at both an urban and a rural location in the West Midlands⁴. This indicates either that the principal source of atmospheric PCBs in these samples is from "fresh" releases from on-going PCB usage, or that volatilization from soil may contribute, but that little or no edaphic enantioselective degradation occurs at the locations sampled.

Table 2: EFs for Target PCBs in All UK Air Samples

Sample Location (Classification)	EF for PCB #		
	95	136	149
Newport, Wales (industrial – historical))	0.495	0.505	0.497
Bolsover (industrial)	0.494	0.503	0.496
Cardiff (urban)	0.511	0.501	0.495
Leeds (urban)	0.496	0.506	0.497
Port Talbot (industrial)	0.495	0.503	0.497
Birmingham (urban)	0.492	0.502	0.498

EMV - Chiral Xenobiotics and Natural Halogenated Compounds

Scunthorpe (industrial)	0.495	0.501	0.498
Kinlochleven (industrial – historical)	0.494	0.501	0.499
Brent, London (urban)	0.496	0.503	0.499
Lisburn, Northern Ireland (domestic coal burning)	0.496	0.504	0.499
Belfast (urban)	0.496	0.515	0.506
Newcastle (urban)	0.497	0.506	0.499
Bromley (roadside)	0.496	0.504	0.497
Ashington (upwind of industrial)	0.494	0.502	0.497
Glasgow (urban)	0.499	0.503	0.499
Edinburgh (urban)	0.497	0.506	0.496
Hove (urban)	0.496	0.500	0.499
Speke (urban/industrial)	0.495	0.501	0.495
Holyhead (industrial)	0.496	0.499	0.498

Acknowledgements

The authors gratefully acknowledge the provision of a studentship (NER/S/A/2003/11193) to Timothy Evans by the UK Natural Environment Research Council. We are also grateful to the participants in the international campaign.

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