THE USE OF CHIRAL CONGENERS IN THE AIRBORNE SOURCE APPORTIONMENT OF POLYCHLORINATED BIPHENYLS (PCBs)

Matthew Robson and Stuart Harrad

Division of Environmental Health and Risk Management, School of Geography, Earth and Environmental Sciences, University of Birmingham, B15 2TT, UK, S.J.Harrad@bham.ac.uk

Introduction

Although the production of PCBs has now been banned for over 20 years within the UK, it is believed that there remains a considerable amount of PCB present in use today (*e.g.* in electrical equipment and as permanently elastic sealants in buildings)[1]. The aim of this study is to determine what contribution these remaining primary sources make to the current atmospheric burden of PCBs.

This is important as if – contrary to the findings of previous source inventories which have identified the principal source to the atmosphere to be revolatilization of PCBs associated with the existing soil burden[2] – primary emissions still make a significant contribution to the contemporary atmospheric burden, there are significant implications for both future human exposure levels and control strategies.

To achieve this, we aimed to extrapolate to PCBs, chiral source apportionment techniques previously applied to organochlorine pesticides[3]. These involve measuring what is referred to as the enantiomeric fraction (EF) of the congener, as defined below.

$$EF = \frac{\text{Concn. Enantiomer 1}}{\text{Concn. Enantiomer 1} + \text{Concn. Enantiomer 2}}$$

Nineteen PCBs containing 3 or 4 chlorine atoms exist as stable atropisomers - that is, they exist in 2 forms (known as enantiomers) which are essentially physically and chemically indistinguishable, except that they rotate the plane of polarised light in opposite directions, and crucially, may biodegrade at different rates. In commercial PCB formulations, these 19 PCBs are present as racemates - *i.e.* concentrations of the 2 enantiomers are equal, EF = 0.5. By comparison, due to enantiomeric differences in resistance to biodegradative processes, the EFs of chiral organochlorines found in soils - and which are preserved upon volatilisation – deviate from 0.5, in theory varying between close to zero to *ca* 1. We therefore hypothesized that a knowledge of EFs in samples of outdoor air (EF_{OA}), commercial PCB formulations ($\mathrm{EF}_{\mathrm{COM}}$), and soil ($\mathrm{EF}_{\mathrm{SOIL}}$) could provide a useful indicator of the extent to which the contemporary ambient atmospheric burden is due to revolatilized material, and how much arises from fresh emissions from remaining PCB stocks. To illustrate, if the EF for a given chiral congener in soil (EF_{SOIL}) is known, and it is assumed that this EF would be preserved on volatilisation, the percentage contribution of primary (*i.e.* racemic) sources to outdoor air levels of that PCB (PC_{COM}) - and by inference, the contribution from volatilization from soils - may be calculated via the equation below.

$$PC_{COM} = \frac{(EF_{OA} - EF_{SOIL})}{(EF_{COM} - EF_{SOIL})} \text{x}100\%$$

Methods and materials

Air and soil samples (to 5 cm depth, with each analysed sample (75 g) a homogenised sub-sample of a number of cores) were collected simultaneously once every 2 weeks from 2 locations within the West Midlands conurbation. Air samples were taken with a HiVol sampler operated for 48 h at *ca* 0.7-0.8 m^3/min yielding a total sample volume of *ca* 2000 m^3. One location was selected to represent the background urban environment (within Birmingham city) and the other situated in a semi rural environment about 25 km southwest of the urban site. All samples were prepared for GC/MS using well-validated conventional contaminant enrichment procedures[4]. For air samples both the particulate and vapour phase were combined and analysed together. Final extract volumes were 25 ml, with 1 ml injected onto the GC/MS. Each sample was analysed in triplicate, and s_{n-1} determined for each.

Chiral GC/MS was accomplished using a Fisons MD-800 GC/MS, fitted with a Chirasil Dex column (25 m x 0.25 mm x 0.25 µm) with a temperature program of 140 °C for 1min, then 30 °C/min to 160 °C held for 20 min, 1 °C/min to 170 °C held for 20 min, and finally 1 °C/min to 180 °C held for 40 min. Mass spectrometric detection was in the EI^+ SIM mode with 2 ions monitored for each target enantiomeric pair.

Three atropisomeric PCBs (#95, 136, 149) were chosen for analysis, due to their presence at sufficiently high concentrations in air and soil for analysis and the absence of co-elution under the above temperature program.

To ensure accurate and precise measurement peaks were only accepted if the following criteria were met:

1. Signal to noise ratios of the least abundant enantiomer for the least abundant ion exceeded 10:1
2. Peaks eluted within 5 s of standards run in the same batch as the samples
3. No obvious co-elutions were observed
4. Isotope ratios for both enantiomeric peaks were within 15% of those obtained for standards run in the same batch as the samples

We also determined EFs for our target PCBs in various commercial formulations (Aroclors), as any deviation from racemic EFs for these samples would indicate our EF measurements to be inaccurate.

Results and Discussion

Table 1 lists EFs of our target atropisomers in pure Aroclors 1242, 1254, and 1260, as well as in a 1:1:1 (w/w) mix of the three. The accuracy of our data is indicated by the racemic values observed for all samples, with the reproducibility denoted by the minimal s_{n-1} values.

Table 1. Enantiomeric Fractions of PCBs 95, 136 and 149 in Aroclors.

	EF			
PCB#	Aroclor 1242	Aroclor 1254	Aroclor 1260	Aroclor mix
95	0.51±0.001	0.50±0.001	0.50±0.001	0.50±0.001
136	i	0.50±0.001	0.50±0.001	0.50±0.001
149	0.50±0.001	0.51±0.001	0.50±0.001	0.50±0.001

i = interference prevented EF determination

As this is an ongoing project, Tables 2 and 3 present EFs in 6 air and 6 soil samples taken simultaneously at the urban background site in February and March 2001. Note that soil sample 1 was taken simultaneously to air sample 1 *etc.*

Table 2. Enantiomeric Fractions of PCBs 95, 136 and 149 in Air samples from the urban background Site

	EF in air sample #					
PCB#	1	2	3	4	5	6
95	0.50±0.001	0.51±0.001	0.50±0.001	0.50±0.001	0.50±0.001	0.50±0.001
136	0.50±0.001	0.50±0.001	0.50±0.001	0.50±0.001	0.50±0.001	0.50±0.001
149	0.50±0.001	0.50±0.001	0.50±0.001	0.50±0.001	0.50±0.001	0.50±0.001

Table 3. Enantiomeric Fractions of PCBs 95, 136 and 149 in soil samples from the urban background Site

	EF in soil sample #					
PCB#	1	2	3	4	5	6
95	0.46±0.001	0.45±0.001	0.45±0.001	i	0.44±0.001	0.44±0.001
136	nd	nd	nd	i	nd	0.50±0.001
149	0.46±0.001	0.45±0.001	0.47±0.001	i	0.45±0.001	0.45±0.001

nd =Not detected - did not meet minimum signal to noise criterion
i = interference prevented EF determination

Congener-Specific Differences in Resistance to Enantioselective Degradation

While EFs of PCBs 95 and 149 in soil are consistently non-racemic, that of PCB 136 in the one soil sample where it was quantifiable is racemic (N.B. although EFs of PCB 136 were not quantifiable in other samples due to the S:N <10:1, the weak signals obtained all indicated racemic EFs). Racemic EFs of PCB 136 have been previously reported in freshwater sediments[5], and our data provides limited evidence of congener-specific differences in resistance to enantioselective degradation in soils. If correct, it is possible that such congener-specific variation may be attributable to:

(a) structural differences; specifically, while 136 contains chlorines at the 2, 3, and 6 positions on *both* rings of the biphenyl nucleus, congeners 95 and 149 have the 2, 3, 6-chlorination pattern on one ring only, and…

(b) differences in concentrations - reductive dechlorination is more effective at higher concentrations, and PCB 136 is the least prevalent in soils of the 3 congeners studied.

Atmospheric Source Apportionment Implications

A paired t-test reveals a statistically significant difference ($p<0.001$) between EFs of PCBs 95 and 149 in air and soil samples, with those in air essentially racemic in nature and those in soil, non-racemic. This indicates that the atmospheric burden of these congeners at this site derives wholly from racemic *i.e. primary sources.* This is in stark contrast to previous indications that the contemporary atmospheric burden of PCBs derives almost solely *via* revolatilisation from soil and has significant policy implications. We and other authors have previously speculated on the potential significance of the ventilation of PCB-contaminated indoor air[6,7] - which is appreciably more contaminated than outdoor air in Birmingham[8] - as a source of PCBs in outdoor air, and the preliminary data presented here is not inconsistent with this hypothesis. We are continuing our monitoring programme, with a particular focus on whether there is an increased contribution from volatilization from soil in warmer summer months, and at the semi-rural location; and also on any additional evidence of congener-specific differences in resistance to enantioselective degradation in soils.

Acknowledgements

The authors gratefully acknowledge the provision of a studentship to MR by the UK Natural Environment Research Council.

References

1. Dyke, P.H. and Stratford, J. (1998) *Organohalogen Compds.*, 36, 365
2. Harrad, S. J., Sewart, A., Alcock, R., Boumphrey, R., Burnett, V., Duarte-Davidson, R., Halsall, C., Sanders, G., Waterhouse, K., Wild, S.R., and Jones, K. C. (1994) *Environ Poll.*, 85, 131
3. Bidleman, T. F., Falconer, R. L. (1999) *Environ Sci Technol.*, 33, 206A
4. Ayris, S., Currado, G.M., Smith, D. and Harrad, S.J. (1997) *Chemosphere*, 35, 905
5. Wong, C. S., Garrison, A. W., and Foreman, W.T. (2001) *Environ Sci Technol.*, 35, 33
6. Halsall, C. J., Lee, R. G., Coleman, P. J., Burnett, V., Harding-Jones, P., Jones, K. C. (1995) *Environ Sci Technol.*, 29, 2368
7. Currado, G. M. and Harrad, S. (1998) *Environ Sci Technol.*, 32, 3043
8. Currado, G. M. and Harrad, S. (2000) *Environ Sci Technol.*, 34, 78