

ENANTIOMERIC FRACTIONS OF PCBs 95, 136, AND 149 IN OUTDOOR AIR AND SOIL IN BIRMINGHAM, UK

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Introduction

In a previous paper¹, we presented initial results from a study determining enantiomeric fractions (EFs) of PCBs 95, 136, and 149 in both outdoor air and topsoil within the UK's West Midlands conurbation. These limited initial data showed that in early 2001, for one site within the city of Birmingham (population 1,000,000), EFs in outdoor air were both racemic and statistically significantly different than those found in soils taken at the same time from the same location. The policy implications of these data are significant, as they imply that the principal source of atmospheric PCBs in Birmingham is racemic in nature and is not – as previously widely thought – volatilisation from environmental surfaces (*e.g.* soil) contaminated with previously deposited PCBs².

This paper reports further data from this study, comprising EFs in outdoor air and soil over a full year (January 2001 to March 2002) at the same location in Birmingham. This location is the same as that for which PCB and PAH measurements have been reported previously^{3,4}.

Methods and Materials

Air and soil samples were taken simultaneously at the same location approximately once every 1-2 weeks over the duration of the campaign. Sampling methodology was as previously reported¹.

All samples were prepared using previously reported well-validated conventional contaminant enrichment procedures¹. For the air samples both the particulate phase and the vapour phase samples were analysed together.

Chiral GC/MS was accomplished using a 25m Chirasil Dex (25m x 0.25mm x 0.25µm) column running a temperature program of 140°C for 1min, then 30°C/min to 160°C held for 20min, 1°C/min to 170°C held for 20min, and finally 1°C/min to 180°C held for 40 min.

To ensure accurate and precise measurement peaks were only accepted if:

- 1) Signal to noise ratios were greater than 10:1
- 2) Peaks eluted within 5s of standards
- 3) There were no obvious co-elutions

In addition to the QA/QC check provided by our previously reported racemic values for EFs in various Aroclor formulations¹, we have since determined EFs in 2 reference materials for which data have been reported⁵. Our data are reported in Table 1, and confirm the accuracy and reproducibility of our methods, compared with both 1- and 2-dimensional chiral GC/MS

approaches utilised elsewhere.

Table 1: EF Values Obtained for Selected Reference Materials

Congener	EC5 ^a			SRM1588a ^b		
	1-D	2-D	This study	1-D	2-D	This study
95	0.488±0.001	0.483±0.001	0.487±0.001	0.451±0.002	0.451±0.002	0.448±0.001
136	0.496±0.002	0.508±0.007	0.501±0.002	0.121±0.013	0.143 ^c	nd ^d
149	0.511±0.003	0.520±0.004	0.489±0.001	0.622±0.008	0.625±0.005	0.623±0.004

^a sediment

^b cod liver oil

^c only 1 value obtained

^d not determinable, S:N ratio below QC criterion

Results and Discussion

EF values recorded in soil and outdoor air samples are summarised in Tables 2 and 3 respectively, with mass chromatograms showing the EF of PCB 95 in: (i) an 1:1:1 mix of Aroclors 1242, 1254, and 1260; (ii) soil, and (iii) outdoor air, also shown as Figures 1, 2, and 3 respectively. Clearly, while each of the 3 target PCBs are enantioselectively degraded in soil (markedly less so for 136), the enantiomeric signatures in air are universally racemic. This is confirmed by a t-test that shows EFs of each of PCBs 95, 136 and 149 in soil and outdoor air from this same location over the same year-long period, to be statistically significantly different ($p < 0.001$). As in our first report of data from this campaign, we only studied samples taken in winter¹, we cautioned that the contribution of volatilisation from soil could be greater in summer. The data presented here show this not to be the case, and confirm that at this urban location, volatilisation from soil makes only a negligible contribution to the atmospheric PCB burden. Instead, continuing primary emissions from PCBs associated with electrical equipment or permanently elastic sealants in buildings appear to control airborne concentrations. We are continuing at monitoring at this and a number of other locations to evaluate how representative the current site is.

Table 2: Summary of EF Values Obtained in Soil Samples (n=20)

Congener	Mean	σ_{n-1}	Min	Max
95	0.456	0.014	0.435	0.489
136	0.481	0.013	0.459	0.501
149	0.458	0.009	0.440	0.474

Table 3: Summary of EF Values Obtained in Outdoor Air Samples (n=29)

Congener	Mean	σ_{n-1}	Min	Max
95	0.498	0.004	0.488	0.506
136	0.499	0.004	0.488	0.505
149	0.499	0.003	0.491	0.505

References

1. Robson, M. and Harrad, S. (2002) Organohalogen Compounds, 57, 15-18.

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Figure 1: Mass Chromatogram showing EF of PCB 95 in a 1:1:1 Mix of Aroclors 1242, 1254, and 1260

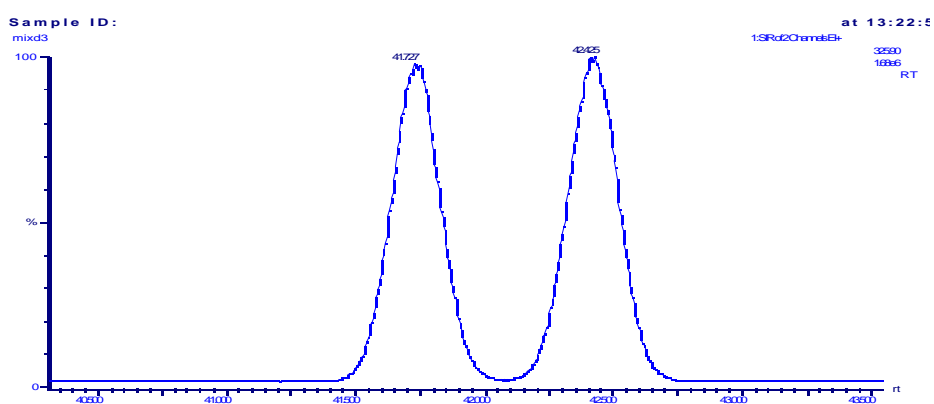


Figure 2: Mass Chromatogram showing EF of PCB 95 in a Soil Sample

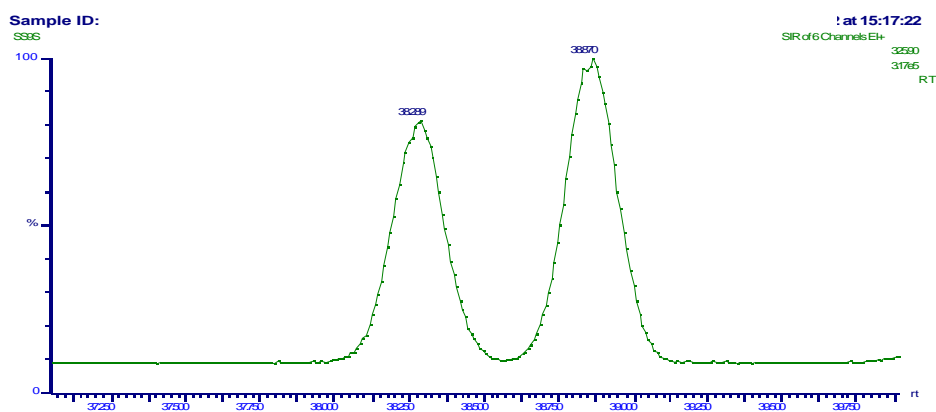


Figure 3: Mass Chromatogram showing EF of PCB 95 in an Outdoor Air Sample

