ARE PCBs REALLY "LEGACY" POPS? CHIRAL SIGNATURES OF PCBs IN MATCHED AIR AND SOIL SAMPLES FROM UK AND GLOBAL SITES

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Introduction

Considerable concern remains surrounding the toxicity of polychlorinated biphenyls (PCBs), despite long standing restrictions on their production and use[1,2]. As a result, human exposure has declined, although a substantial environmental burden still exists. Therefore the identification and control of emissions remains a research priority. We have previously 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[3] along with preliminary results from a small number of non-UK sites[4]. These studies 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 all sites arise from racemic (*i.e.* primary) sources, rather than volatilization from soil; and (ii) that appreciable enantioselective degradation of PCBs 95 and 149 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 is 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 findings depends on the extent to which they are replicated at other locations. This study evaluates how representative our earlier results 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

Air samples were collected using PUF disk samplers (each fitted with 2 PUF disks) deployed over a period of 12 weeks (10th December 2004 – 4th March 2005) at 29 UK and 11 non-UK sites. 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. For all but 11 locations (26 UK,) 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[4]. For non-UK sampling (11 sites listed in Table 1), the soil was homogenised and a 50 g aliquot extracted by the laboratory conducting the sampling and concentrated prior to overnight courier return along with the sealed air sampler to Birmingham. Each location provided information on the exact extraction procedure used (e.g. soxhlet, ASE). All samples were stored at -18° until further purification and analysis.

Sampling, Purification and Analytical Methodology

All samples were extracted (where necessary), purified, and subjected to enantioselective GC/MS for the determination of chiral signatures as previously described[3]. We have previously reported the accuracy and reproducibility of our methods for determining chiral signatures and concentrations of PCBs[3,4] but as a continuing QA/QC procedure, replicate analyses of a standard reference material were conducted and the data reported in Table

2. Low concentrations of the target congeners (particularly #136, but also #149) resulted in some samples failing our strict QA/QC criteria requiring a minimum signal:noise ratio of 10:1 for the least abundant ion. Where this was the case, these samples along with reference samples were run on a GC/HRMS system, using similar chromatographic conditions to those used previously[3]. In summary, such samples were run on an Agilent 6890 GC, coupled to a Waters Autospec operated at 10000 resolution in EI+ ionisation mode. Oven conditions were 100˚C for 2 min; 25˚C/min to 162˚ held for 20 min; 0.2˚C/min to 175˚C, no hold; 10˚C/min to 200˚C held for 5 min.

Location
Spain (Zaragoza)
Canada (Alberta)
USA (Athens)
Brunei
Australia (New South Wales)
Belgium (Antwerp)
Sri Lanka (Colombo)
Portugal (Aveiro)
China (Miyun)
Beijing
Mexico (Puebla)

Table 1: Locations of Non-UK sampling sites (*italics – no soil sample available)*

EC5 Reference Material (5 Replicate Samples)	*This Study*	Robson & Harrad (2004)	Wong *et al* (2002)
PCB #95	**0.488 ± 0.003**	**0.487 ± 0.001**	**0.488 ± 0.001**
PCB #136	**0.497 ± 0.002**	**0.501 ± 0.002**	**0.496 ± 0.002**
PCB #149	**0.509 ± 0.006**	**0.511 ± 0.001**	**0.511 ± 0.003**

Table 2: EFs of Target PCBs in Replicate Samples of a Sediment Reference Material

Results and Discussion

Table 3 summarises the EFs detected in all samples in this study, while Figure 1 illustrates the frequency distribution of data in both air and soil samples. In summary, this study confirms previous observations of appreciable enantioselective degradation in soil of PCB 95. Furthermore, paired t-test comparison of chiral signatures of PCB 95 in matched soil and air samples, reveals them to be significantly different ($p<0.001$). This – combined with the fact that EFs in air are predominantly racemic or near-racemic - suggests that the predominant source of PCB 95 in air is *not* volatilisation from soil. Interestingly, comparison of EFs of PCB 95 in a small number of matched air and soil sample pairs (specifically those for which the soil samples displayed the greatest enantioselective degradation) provide some indication of an appreciable contribution arising from volatilisation from soil at such locations. Notable examples are those samples from: Oxford, UK (EF_{soil} = 0.431, EF_{air} = 0.487), Cheshire, UK (EF_{soil} = 0.402, EF_{air} = 0.476), Bushmills, Ireland (EF_{soil} = 0.288, EF_{air} = 0.485), and Saffron Walden, UK (EF_{soil} = 0.429, EF_{air} = 0.488). This is consistent with our recent observation of EFs of PCB 95 and 149 in some grass samples that match the signature in soil more closely than that in air (Harrad et al, 2006).

For PCBs 136 and 149, interpretation is more difficult owing to the smaller number of samples for which EFs were detectable. Despite this, it is evident that edaphic enantioselective degradation of these PCBs is far less extensive than for PCB 95. Furthermore, while edaphic enantioselective degradation of PCB 95 is always in the same direction (*i.e.* EF<0.500), degradation for PCBs 136 and 149 is variable. In terms of atmospheric source apportionment, paired t-test comparison of chiral signatures in matched soil and air samples, reveals those for PCB 149 to be statistically different ($p<0.01$). In contrast, those for PCB 136 are not significantly different ($p<0.1$). Owing to the relative lack of edaphic enantioselective degradation for this congener, it is not possible to determine the significance of volatilisation from soil for PCB #136.

AIR	PCB #95	PCB #136	PCB # 149
AVERAGE	0.497	0.492	0.502
MIN	0.476	0.462	0.483
MAX	0.519	0.523	0.533
TOTAL SAMPLES	40	40	40
TOTAL DETECTABLE	40	32	35
PERCENT DETECTED	100	80	88
STANDARD DEVIATION	0.009	0.013	0.010

SOIL	PCB #95	PCB #136	PCB # 149
AVERAGE	0.443	0.502	0.491
MIN	0.288	0.465	0.430
MAX	0.495	0.545	0.521
TOTAL SAMPLES	33	33	33
TOTAL DETECTABLE	29	20	29
PERCENT DETECTED	88	61	88
STANDARD DEVIATION	0.04	0.02	0.02

Table 3: Summary of EFs of Target PCBs in Soil and Air Samples in this Study

Conclusion

Chiral signatures of 3 PCBs in outdoor air from a geographically diverse range of locations are consistently racemic or near-racemic. This, coupled with the fact that paired t-test comparison with chiral signatures in co-located soil samples demonstrate signatures of PCBs 95 and 149 in air and soil to be significantly different, confirms that our previous observations that soil is not an important contributor to the contemporary burden of PCBs in outdoor air, applies at many more locations. Intriguingly however, there are indications that at some locations, volatilisation from soil may be making an appreciable contribution. Our previous detection of racemic PCB signatures in indoor air samples[5] where concentrations far exceed those in outdoor air, implies that ventilation of such indoor air (along with other on-going sources of non-weathered PCBs – *e.g.* waste dumps) are important sources of PCBs to the contemporary environment. In conclusion, PCBs are not solely the "legacy" POPs they are widely considered to be, and urgent action is required if we are to control their continuing emissions and reduce human exposure.

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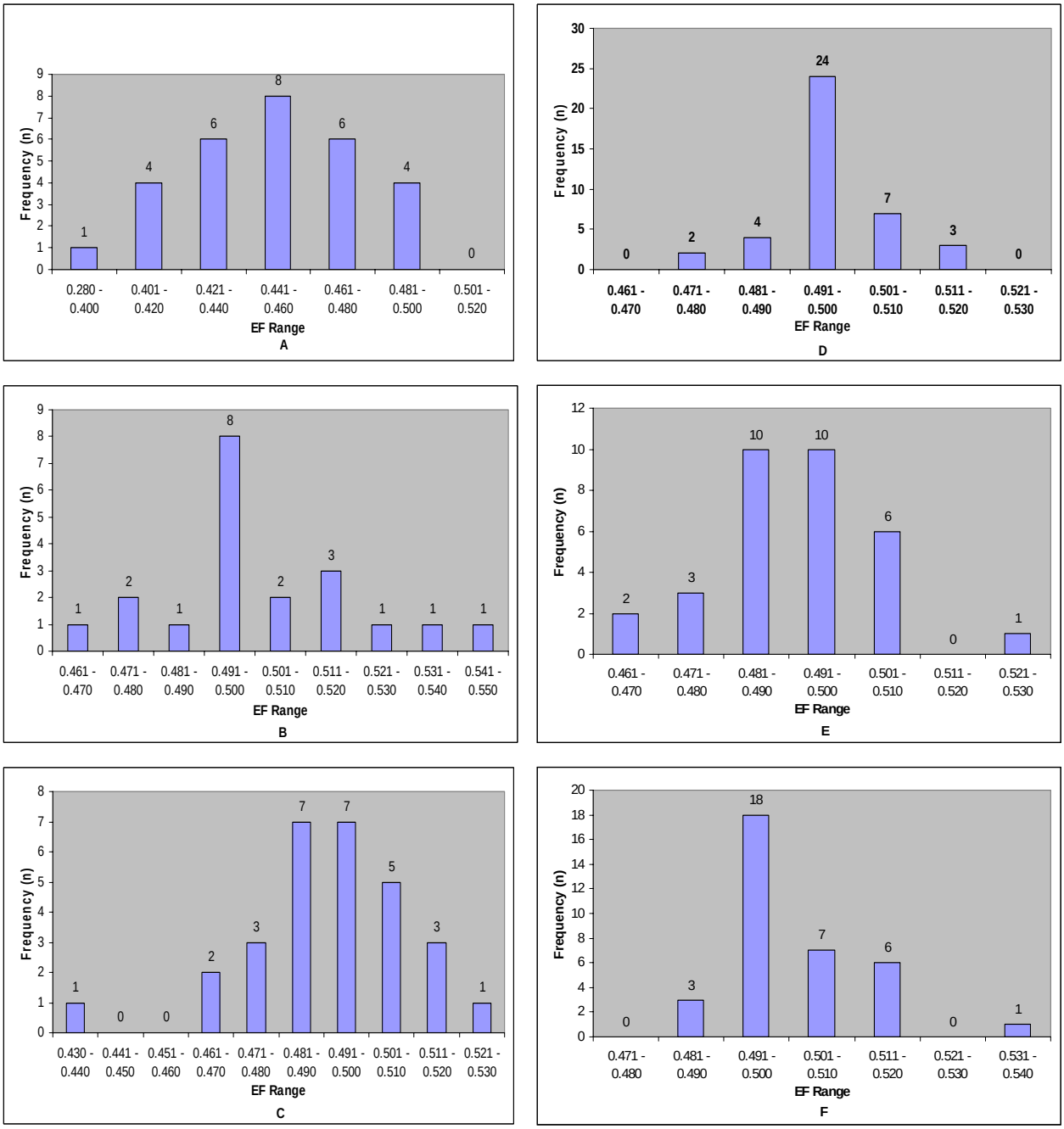

Figure 1

Figure 1: Frequency Distributions of EFs in: (A) PCB 95 in Soil, (B) PCB 136 in Soil, (C) PCB 149 in Soil, (D) PCB 95 in Air, (E) PCB 136 in Air, (F) PCB 149 in Air