THE INFLUENCE OF CONCENTRATIONS OF PAH AND TRACE METALS ON ENANTIOMERIC FRACTIONS OF PCBs 95, 136, AND 149 IN UK LAKE SEDIMENTS

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Introduction
Nineteen individual PCBs exist as stable atropisomers and are racemic (*i.e.* enantiomeric fractions (EFs) = 0.5) in commercial formulations. In contrast, where biodegradation occurs, enantioselective differences in resistance to such degradation, means that EFs in sediments, biological tissues, and soils, can deviate from racemic (*i.e.* EFs ≠ 0.5), thus providing direct and unequivocal evidence of the existence and extent of biodegradation.

In another paper presented in this session, the evidence is summarised for the relationships between the category of location (urban, suburban, rural, agricultural, forest) and the extent of biodegradation of chlorinated aromatic pollutants[1]. Furthermore, considerable spatial variability in the extent of enantioselective degradation of a number of PCBs was reported for US lake and river sediments[2]. The purpose of this study was therefore to examine the extent of spatial variability in and the possible causes of enantioselective degradation of PCBs # 95, 136, and 149 in lake sediments from various UK locations.

Methods and Materials
Sampling Locations and Protocols
Sediment samples were taken in October and November 2002 from 10 lakes located throughout England, Scotland and Wales. The sampling locations are indicated on Figure 1. Seven sediment cores were taken from the profundal area of each selected lake using a gravity corer fitted with a perspex tube of internal diameter of 74 mm. The 0-5 cm section of each core was extruded vertically in the field, amalgamated and homogenised in a hexane washed glass container. The core tube and all utensils in contact with the sediment were hexane washed, and kept contaminant-free until use by wrapping in hexane washed aluminium foil.

Approximately 100 g of the homogenised wet sediment was transferred into hexane-washed amber jars. This sub-sample was freeze-dried before transfer for PAH and PCB analysis. A second sub-sample of ca.10 g wet sediment was stored in sealable plastic bags, freeze-dried and retained for the determination of trace metals.

Determination of PAH, achiral PCBs and EFs of PCBs 95, 136, and 149
Sediment samples were extracted, purified and subjected to GC/MS analysis using previously reported procedures[3,4,5] - EFs were determined on a 25m Chirasil Dex (25m x 0.25mm x 0.25μm) column. For the purposes of this study, ΣPAH represents the sum of the USEPA 16 species, except for naphthalene, and ΣPCB represents the sum of PCB#s 28, 52, 101, 118, 138, 153, and 180. The concentrations of PCB #s 95, 136, and 149 were also determined but were not included in the calculation of ΣPCB.

Determination of Trace Metals

Accurately weighed samples of approximately 0.2 g freeze-dried sediment were heated at 100 °C on a hotplate with 8 mL Aristar HNO_3 for 1 hour. The solutions were transferred to 20 mL volumetric flasks and made up to volume using distilled deionised water. Duplicate certified standard reference materials (Buffalo River sediment SRM2704; Stream sediment GBW07305) and reagent blanks were digested and analysed with the samples. As was analysed using ICP-MS, Cd, Pb, Cu, Zn and Ni were analysed by AAS and Hg was analysed by cold vapour-AAS.

Results and Discussion

EF values recorded in each of the sediment samples are given in Table 1. Appreciable site-specific variability in EF values is evident for each of our target chiral PCBs. Interestingly, while the enantiomeric preference is in the same direction in all samples for PCB # 136, there is reversal of the enantioselectivity between sites for both PCB #s 95 and 149, an effect similar to that observed previously for PCB # 91 in river sediments[2]. Our observed enantioselective degradation for PCB # 149 is particularly interesting, as a recent study of US lake sediments found no evidence of such behaviour for this congener[6]; findings supported by our own measurements of EFs of PCB # 149 in Ontario soils[1]. In contrast, our data on soils at a single UK location[5,7] clearly demonstrate enantioselective degradation of PCB # 149. This apparent intersite variation in enantioselective degradation of this congener merits further investigation.

We analysed our data for relationships between concentrations of various pollutants and the extent of enantioselective degradation. Given the reversal of degradation between sites for 2 of the 3 target congeners, we expressed the extent of enantioselective degradation as the modulus of the deviation from the racemic EF value of 0.500 (DFR). To illustrate, the DFR value for PCB # 95 in Lochanagar = 0.019; while that for PCB # 149 in the same sample = 0.012. We then regressed DFR values against concentrations of the following pollutants: PCB # 95, 136, and 149, ΣPCB, ΣPAH, Hg, Pb, Cu, Ni, Zn, Cd, and As.

Figure 2 shows the statistically significant ($p<0.05$) negative linear relationship between DFR for PCB #149 and ΣPAH. For PCB # 149, the extent of enantioselective degradation appears to be significantly inversely related ($p<0.05$) to the concentration of all pollutants except Ni, As, ΣPCB, PCB #s 95, 136, and 149. In contrast, the enantioselective degradation of both PCB #s 95 and 136 do not appear to be significantly related ($p>0.05$) to concentrations of any of the pollutants monitored.

These limited data suggest that the higher concentrations of PAH and some trace metals inhibit the enantioselective degradation of PCB #149 in lake sediments. This is not inconsistent with the hypothesis that the viability and diversity of the microbial population present in a given lake sediment will be reduced in more contaminated sediments. However, more detailed research is required if a fuller understanding is to be acquired.

Acknowledgements

References

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Figure 1: Lake Sediment Sampling Locations

Table 1: EFs of PCB #s 95, 136 and 149 in UK Lake Sediments

Location	EF of # 95	EF of # 136	EF of # 149
Agden Reservoir	0.505	0.504	0.506
Burnmoor Tarn	nd	nd	nd
Loch Chon	0.502	0.517	0.511
Loch Doilet	0.475	nd	0.480
Loch Coire Fionnaraich	0.463	nd	0.529
Llyn Llagi	0.532	0.556	0.505
Llyn Cwm Mynach	0.537	0.526	0.503
Lochnagar	0.519	0.564	0.488
Scoat Tarn	0.505	0.562	0.480
Tooting Common Lake	0.514	0.522	0.522

nd = not determinable; failed to meet minimum signal to noise criterion

Figure 2: Relationship Between Extent of Enantioselective Degradation of PCB # 149 and ΣPAH Concentration in Lake Sediments