

## Chiral Xenobiotics and Natural Halogenated Compounds

The session on chiral xenobiotics and natural halogenated compounds encapsulates the truly international character of the POPs symposium, with the 8 oral and 5 poster presentations generated by authors from a large number of countries.

In the first paper naturally occurring organobromine compounds are described that were detected in samples of sponges collected off King George Island, Antarctica, at water depths of about 10 m. Samples were screened with the help of GC/ECNI-MS and halogen-specific  $m/z$  values. Brominated components were identified by the bromide ion and the correct isotope ratio of  $m/z$  79 and  $m/z$  81. For example, the sample of *Halichondridae* sp. contained 47 brominated compounds, according to the correct isotope ratio, the lowest detected molecular masses of which were  $m/z$  206 and  $m/z$  210, respectively. The later was tentatively identified as a dibromobutadiene isomer. In addition, 2,4,6-tribromoanisole and dibromo homologues were identified as well.

The subsequent presentation extends this subject to mammal samples from Queensland, North-eastern Australia, and commercial shark liver oil from Lovely Health, Auckland, New Zealand. In accordance with previous estimations, the highest concentrations of 3,5-dibromo-2-(2', 4'-dibromophenoxy)anisole (in short BC-3) were found in marine samples from Australia, suggesting that a major reservoir of BC-3 should be located there. Furthermore, the authors stress that in the Australian marine mammal samples, the concentrations of BC-3 were equal or higher than those of anthropogenic halogenated compounds such as *p,p'*-DDE.

The third paper presents new evidence of natural dioxin formation generated by analysis of a ball clay core from Kentucky, USA. At Dioxin 2003, the authors had reported concentrations of 2,3,7,8-chlorinated PCDD/Fs only. The current paper reports concentrations of other non-2,3,7,8-chlorinated PCDD/Fs which could be important additional indicators of sources and/or formation processes. The key finding of this paper is that – in contrast to other studies – there is no substantial change in the contribution of 1,4,6,9-substituted congeners (in particular 1,2,3,4,6,7,9-HpCDD: 1,2,3,4,6,7,8-HpCDD) with core depth. It has been previously suggested that this preference for 1,4,6,9-chlorination arises primarily as a result of anaerobic dechlorination; the findings of this study demonstrate that this pattern is not always present in “naturally” contaminated samples, and furthermore that more than one dechlorination mechanism may be involved. By further characterisation of each core slice with respect to bulk mineralogy and elemental analysis, and subsequent principal component analysis, the paper also presents preliminary evidence that both absolute PCDD/F concentrations and patterns may be influenced by the relative abundance of certain mineral oxides and/or elements.

The chiral section of this session is opened by a study on chiral signatures of PCBs in matched air and topsoil samples on an urban-rural transect aiming at atmospheric source appointment. Air and soil samples were collected from 11 different sites within the West Midlands conurbation in the United Kingdom. The enantioselective analyses supplied provide evidence that volatilisation from soil appears to make a minimal contribution to atmospheric PCB concentrations at the experimental sites. The data obtained for soil samples clearly constituted appreciable more evidence of enantioselective transformation of PCBs at concentrations typically encountered in the UK and

other industrialised countries. The authors tentatively assume an inverse relationship between the degree of urbanisation and the extent of enantioselective transformation, where the greatest enantioselective transformation can be expected at the most rural locations.

The next presentation describes the results of a study of the enantioselective fate and distribution of both Aroclor 1254 and a soil extract contaminated with Chlorofen – a Polish PCB formulation – in male rats. Such studies are an important step towards furthering understanding of the influence of enantioselective processes such as metabolism and plasma protein binding on the developmental and neurotoxic effects of chiral PCBs. The study revealed enantioenrichment of the chiral PCBs 91, 95, and 149 in rats, which confirms findings elsewhere of enantioenrichment in human tissues. Owing to the presence of PCBs 91 and 95 in only a few tissue samples, the most significant findings deal with the behaviour of the more prevalent PCB 149. A key finding is that in the Aroclor treatment group, there was enrichment of the 2<sup>nd</sup> eluting enantiomer in the liver, with the opposite observed in whole blood. No such enrichment was observed in animals exposed to the Chlorofen soil extract. The authors hypothesise that these differences may be at least partly due to variations in the induction of CYP1A and CYP2B in the liver of rats treated with Aroclor and Chlorofen. Specifically, while CYP1A activity was nearly 30 times greater in Aroclor-treated rats, CYP2B activity was 4.5 times higher in soil extract treated animals. This suggests that the 2<sup>nd</sup> eluting enantiomer of PCB 149 may bind selectively to CYP1A that is markedly induced in the liver of Aroclor-exposed rats. The highly perfused nature of the liver subsequently results in selective removal of this enantiomer from the blood stream.

The session then moves on to a study reporting the application of a combined vibrational circular dichroism (VCD)/*ab initio* approach as an alternative improved method for determining the absolute configuration of chiral molecules. The paper studies a variety of pure enantiomers (obtained via semi-preparative HPLC) of methylsulfonyl, methylthionyl, methoxy, and hydroxy metabolites of the chiral PCB 149. The relative advantages of the method compared with the UV-CD approach are demonstrated.

The next presentation focuses on bromocyclen that has been utilised against ectoparasites in sheep farming and in pet care. Though it was banned in Germany as early as 1995, considerable amounts of this chiral xenobiotic was found in sewage sludge samples collected in sewage treatment plants from Northrhine-Westphalia, Germany, in the year 2002. The author concludes that the enantioselective transformation of this compound very much depends on the respective sewage treatment process, including different sludge retention, different dominant carbon sources, different temperatures etc., however, the transformation process within the plant remains incomplete. As a consequence, increased concentrations in soils cannot be excluded, because 30 % of the sewage is currently added to agricultural land in that country.

The oral session concludes with a study that reports on the preparation of artificial model mixtures of Polychloropinene – a Soviet analogue of Toxaphene - with the goal of evaluating the differences between the Soviet formulation and Toxaphene. In addition, the study reports the preparation and conformational characterisation of pure enantiomers of key Toxaphene congeners. The study concludes that the Soviet formulation had a composition significantly different from that of Toxaphene, and may have contained enantiomerically enriched polychlorobornanes. Both factors

are of considerable importance if observed deviations in congener pattern and chiral signature in environmental samples from those observed in industrial formulations are to be understood.

The poster session consists of 5 papers. The first reports the findings of a study examining the enantioselective distribution of a variety of chiral PCB metabolites in tissues from seals, pelicans, and humans. Although low concentrations prevented chiral signature determination in humans, significant enantioenrichment occurred in both seal blubber and pelican muscle tissue.

This is followed by a poster that determines enantiomeric fractions of 11 chiral PCBs in both milk and cheese produced by Spanish sheep, cows, and goats. The results reveal appreciable species- and congener-specific variations in enantioselective metabolism and/or uptake. A key finding is that while cows appear incapable of enantioselective metabolism and/or uptake of PCBs 171 and 183, enantiomeric fractions of these congeners are non-racemic in both milk and cheese derived from sheep and goats. Of particular interest is the fact that PCB 183 has been previously considered hard to metabolise owing to its lack of vicinal hydrogen atoms in *meta/para* and *ortho/meta* positions.

The next poster reports a comprehensive study on the variability of enantiomeric fractions (EF) for **a**-hexachlorocyclohexane in placenta samples from Finland. The exposure of the placenta might either result from the pollutant release of the body storage in adipose tissue or the continuing exposure especially from the diet. Stable EFs of about 0.5 support the hypothesis that humans are exposed to racemic or nearly racemic **a**-HCH sources, i.e., preferentially by uptake of racemic compounds. Only a few samples supplied evidence of lower EF-values which suggest that in these latter cases the uptake rate becomes less dominant in the exposure process.

Two posters complement the oral presentations on natural bromoorganic compounds. Some of the halogenated natural substances, e.g., bromoindoles, contain N-heterocyclic backbones. Since nitrogen is scarcely found in anthropogenic halogenated compounds, the authors evaluated the suitability of a nitrogen phosphorus detector (NPD) for the detection and quantification of N-containing compounds in extracts of marine biota. Another poster summarises batch tests such as AOBr analyses, in order to detect and locate sources of naturally produced organobromine compounds in surface waters.