

PCB METHYL SULPHONES IN ANIMALS FROM THE BALTIC REGION

Åke Bergman<sup>A</sup>, Koichi Haraguchi<sup>B</sup>, Hiroaki Kuroki<sup>B</sup>, Yoshito Masuda<sup>B</sup>  
and Mats Olsson<sup>C</sup>

<sup>A</sup> Environmental Chemistry, Wallenberg Laboratory, Stockholm University,  
S-106 91 Stockholm, Sweden.

<sup>B</sup> Daiichi College of Pharmaceutical Sciences, 22-1 Tamagawa-cho, Minami-ku,  
Fukuoka 815, Japan.

<sup>C</sup> Swedish Museum of Natural History, Section of Vertebrate Zoology,  
Box 50007, S-104 05 Stockholm, Sweden.

PCB methyl sulphones (MeSO<sub>2</sub>-CBs) have been known as major metabolites of PCB in primarily seal blubber<sup>1,2</sup> but also in adipose tissue of other species<sup>3</sup>. Similarly, MeSO<sub>2</sub>-DDE, a DDE metabolite, has been detected in biota. These lipophilic PCB and DDE metabolites are persistent environmental contaminants in many mammals at concentrations only slightly lower than to those determined for PCB and DDT<sup>1,2,4</sup>. Some MeSO<sub>2</sub>-CBs have also been shown to bind non-covalantly to proteins in lung, kidney, uterine fluid and the intestinal tract<sup>5,6</sup>. The mechanism behind the formation of aryl methyl sulphones include mercapturic acid pathway metabolism, C-S-lyas degradation of the cystein conjugate, methylation by adenosyl-methionine and oxidation<sup>7</sup>.

In the present study the retention of PCB and DDE methyl sulphones in fish, birds and mammals from the Baltic or the vicinity to the Baltic were determined. MeSO<sub>2</sub>-CBs and MeSO<sub>2</sub>-DDE determined in herring, cod, guillemot, white tailed sea eagle, wild mink, otter and three species of seals were analyzed. Samples of both adipose tissue and/or muscle and liver have been analyzed. The samples were extracted<sup>8</sup> and the aryl methyl sulphones were isolated from PCBs by partitioning into anhydrous DMSO and, after the addition of water, reextracted with hexane<sup>4</sup>. The MeSO<sub>2</sub>-CBs and MeSO<sub>2</sub>-DDE were finally purified on a aluminum oxide column<sup>2</sup>. The samples were analyzed by GC(ECD), GC/MS (EI and/or NICI) and quantifications were performed by comparison to authentic reference compounds.

Approximately 30 MeSO<sub>2</sub>-CBs and two isomers of MeSO<sub>2</sub>-DDE were detected. Several of the compounds have been identified by comparison to the references. Both the 3- and 4-MeSO<sub>2</sub>-substituted isomers of CBs such as 2,2',4,5'-teraCB (I-49), 2,2',4,5,5'-pentaCB (I-101), 2,3,3',4',6-pentaCB (I-110), 2,2',3',4,5,6'-hexaCB (I-149) and 2,2',3,3',4,6'-hexaCB (I-132) were identified in the mammalian samples. A selectivity in the retention of MeSO<sub>2</sub>-CBs was observed to occur in liver tissue of most animals studied. Furthermore, liver samples were found to contain higher concentrations of MeSO<sub>2</sub>-CBs than adipose tissue or muscle samples on a lipid weight basis. Aryl methyl sulphones were also detected in the fish and bird samples. According to the structures of the CBs that are transformed to MeSO<sub>2</sub>-CBs mainly compounds with free 3,4-positions and chlorine atoms

in 2,5- or 2,5,6-positions in one of the phenyl rings of the biphenyl structure are transformed to PCB methyl sulphones. In PCB products containing approximately 50 - 60 % chlorine by weight ca 20 out of 80 CBs fulfill these requirements. Some of the PCB methyl sulphones that may be formed can more readily be further metabolized due to the substitution pattern of the chlorine atoms in the other phenyl ring, e.g. 2,2',5,5'-tetraCB.

#### Acknowledgment

This study has been supported by grants from the Swedish Environmental Protection Agency.

#### References

1. Jensen, S. and Jansson, B. Methyl sulfone metabolites of PCB and DDE. *Ambio*, 1976, 5, 257-260.
2. Haraguchi, K., Bergman, Å., Athanasiadou, M., Jakobsson, E., Olsson, M. and Masuda, Y.: PCB methyl sulphones in grey seal and otter from Swedish environment. *Organohalogen Compounds*, volume IV, 1990, pp 415-418, 10th International Meeting, Dioxin '90, Bayreuth, Germany.
3. Haraguchi, K., Kuroki, H. and Masuda, Y., Occurrence and distribution of chlorinated aromatic methylsulfoxides and sulfoxides in biological samples. *Chemosphere* 1989, 19, 487-492
4. Haraguchi, K., Athanasiadou, M., Bergman, Å., Hovander, L. and Jensen, S.: PCB and PCB methyl sulphones in selected groups of seals from the Swedish coastwaters. Manuscript, submitted to *Ambio*.
5. Lund, J., Brandt, I., Poellinger, L., Bergman, Å., Klasson-Wehler, E. and Gustafsson, J.-Å.: Target cells for the PCB metabolite 4,4'-bis(methylsulphonyl)-2,2',5,5'-tetrachlorobiphenyl: Characterisation of high-affinity binding in rat and mouse lung cytosol. *Molecular Pharmacol.* 1985, 27, 314-323.
6. Larsen, G.L., Bergman, Å., Klasson Wehler, E. and Bass, N.M.: A methylsulphonyl metabolite of a polychlorinated biphenyl can serve as a ligand for liver fatty acid binding protein in rat intestinal mucosa. *Chem.-Biol. Interact.*, 1991, 77, 315-323.
7. Bakke, J. & Gustafsson, J.-Å. Mercapturic acid pathway metabolites of xenobiotics: generation of potentially toxic metabolites during enterohepatic circulation. *Trends in Pharmacol.* 1984, 5, 517-521.
8. Jensen, S., Reutergårdh, L. and Jansson, B. Analytical methods for measuring organochlorines and methyl mercury by gas chromatography. *FAO/SIDA Manual of methods in aquatic environment research. Part 9. Analysis of metals and organochlorines in fish. FAO. Fish. Tech. Pap.* 1983, 212, 21-33.