CONCENTRATIONS OF METHYL SULPHONE METABOLITES OF PCBs AND DDE IN SEALS FROM THE GULF OF ST. LAWRENCE

Nathalie Prud'homme [1], Charles Brochu [1], Serge Moore [1], Michel Lebeuf [2] and Mike Hammill[2]

1. Centre d'expertise en analyse environnementale du Québec, 850 Vanier, Laval (Québec), Canada, H7C 2M7
2. Ministère des Pêches et des Océans, Institut Maurice-Lamontagne, C.P. 1000, Mont-Joli (Québec), Canada, G5H 3Z4

Introduction

Polychlorinated biphenyls (PCBs) and chlorinated pesticides are ubiquitous in the environment and are known to accumulate in marine biota. Some of these lipophilic substances are biotransformed to methyl sulphone ($MeSO_2$-)metabolites by marine mammals (1). These metabolites are more polar than their precursor compounds, but still retain their lipophilic character and have specific protein binding properties (2). These compounds are also resistant to further metabolic degradation and may cause toxic effects, such as increased susceptibility to bacterial infections and decreased progestenic activity (3). In the present study, concentrations of specific PCB congeners and $MeSO_2$-metabolites of PCBs and DDE are reported in three seal species inhabiting the Gulf of St. Lawrence, Canada. The capacity of each seal to biotransform PCBs was assessed by calculating metabolites to precursor ratios. It was then possible to compare species differences in biotransformation of these compounds.

Experimental Methods

Blubber were sampled (0.49 to 0.52g) from 3 male grey seals (*Halichoerus grypus*) of 6, 6 and 5 years old, respectively, collected in 1997; 3 male harp seals (*Phoca groenlandica*) of 7, 6 and 7 years old, collected in 1995-96; and 3 male hooded seals (*Cystophora cristata*) of unknown age, collected in 1990. Because the hooded seals were captured on pack ice during the breeding season, it was assumed that they were all adults (4). These samples were analysed for PCBs, DDE and methyl sulphone metabolites ($MeSO_2$-PCBs and $MeSO_2$-DDE) according to the Letcher procedure (5). Briefly, samples were homogenised with sodium sulphate and Soxhlet extracted overnight with toluene. After extraction, samples were concentrated and then spiked with 3-$MeSO_2$-4-methyl-2',3',4',5,5'-pentachlorobiphenyl as surrogate standard. Extracts were then purified by GPC (Bio-bead SX-3), followed by a 33% KOH/silica gel column, a Florisil column and an alumina column. Purified extracts were reduced to a volume of 400 µl and 100 µl of internal standard was added prior to quantification. Identification and quantification of $MeSO_2$-PCBs and DDE was performed by HRGC/HRMS on an Autospec Q (Micromass, UK) at 10 000 resolution, in electron impact mode and selected ion monitoring (two masses per congener). $MeSO_2$-PCBs and DDE standards were purchased from Cambridge Isotope Laboratories (MA, USA). Surrogate recovery ranged from 74% to 107% and method detection limits varied between 5 and 50 pg/g lipid weight. Results were not corrected for surrogate recovery.

Results and Discussion

Figure 1 shows results for the total concentrations of $MeSO_2$-PCBs and $MeSO_2$-DDE for the three seal species examined. Mean concentrations of total $MeSO_2$-PCBs and $MeSO_2$-DDE range from 58 to 338 ng/g and from 2 to 38 ng/g, respectively. The highest values of $MeSO_2$-PCBs and $MeSO_2$-DDE are found in hooded seals, while harp seals have the lowest concentrations of both metabolites. Concentrations of $MeSO_2$-DDE represent about 10% of total $MeSO_2$-PCB metabolites in hooded and grey seals, whereas in harp seals the contribution of $MeSO_2$-DDE relative to total $MeSO_2$-PCB is even smaller.

In all three species, concentrations of penta were the highest, followed by hexa and tetra methyl sulphone homologue groups. The distribution pattern of PCBs is different with hexa-PCBs dominating, followed by hepta, penta and octa homologue groups. The results suggest that penta-PCBs are rapidly metabolised and hexa-PCBs are relatively slowly metabolised, in agreement with the results reported by Karlson et al (6) for porpoises. Average concentrations of total $MeSO_2$-PCBs represent between 2.0 and 5.9% of total PCBs in the three seal species examined (Figure 2). For DDE, the ratio of the $MeSO_2$ metabolite to the parent compound is 0.5% for hooded seal, 0.6% for grey seals and 0.1% for harp seals.

PCB parent molecules with 2,5- or 2,5,6- substitution patterns are transformed to form 3- and 4-$MeSO_2$ PCBs. To date, a total of 14 metabolites pairs have been reported in the biota (7). In this study, we measured 13 pairs of $MeSO_2$-PCB metabolites in the seals examined. PCB congeners 31, 52, 49, 70 et 101, were metabolised to produce mainly the 3-$MeSO_2$ isomers, while congeners 87, 110 et 149, were metabolised to 4-$MeSO_2$ isomers (Figure 3). This is in agreement with another study on grey seals (8). For congeners 31, 49, 70, 87 and 149, biotransformation of the parent molecules to $MeSO_2$ metabolites appears to be an important process for all seal species. It is important to note that the concentrations of methyl sulphone metabolites in these animals are, in some cases, higher than those of the PCB precursors. However, the methyl sulphone route does not seem to be a favorable process for PCB congener 52.

Acknowledgements.

The authors gratefully acknowledge the assistance of Michelle Noël, Steve Trottier, Hélène Lemaire and Louis Vromet. This study was supported in part by the Toxic Chemicals Program of the Department of Fisheries and Oceans.

References.

1. Letcher, R.J., Muir, D.C.G., Norstrom, R.J., Michaud, R., Béland, P., *Organohalogen Compounds*, 33, 290, **1997**
2. Weistrand, C., Noren, K., Grimelius, L., *Organohalogen Compounds*, 28, 522, **1996**
3. Troisi, G.M., Haraguchi, Simmonds, M.P., Mason, C.F., *Arch. Environ. Contam.* Toxicol., 35, 121, **1998**
4. Hammill, M.O., Lydersen, C., Kovacs, K.M. and Sjare, B.; *J. Northw. Atl. Fish. Sci*., **1997**, 22, 249
5. Letcher, R.J., Norstrom, R.J., Bergman, A., *Anal. Chem,* **1995**, vol. 67, p.4155-4163.
6. Karlson, K., Ishaq, R., Zebühr, Y., Berggren, P., Broman, D., *Organohalogen Compounds*, 39, 277, **1998**
7. Letcher, R.J., Norstrom, R.J , Muir, D.C.G., *Environ. Sci. Technol*., **1998**, 32, 1656-1661
8. Janak, K., Becker, G., Colmsjö, Östman, C., *Organohalogen Compounds*, 39, 35, **1998**

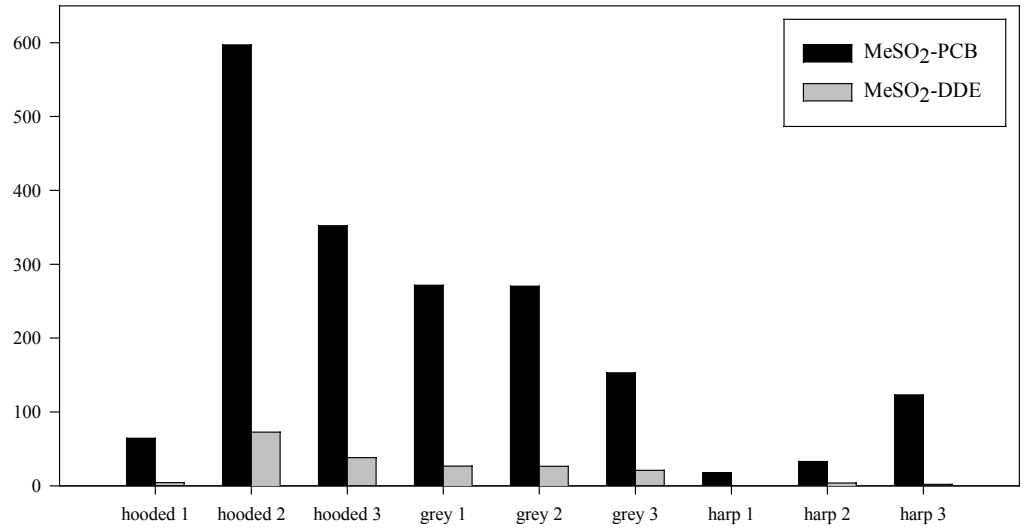

Figure 1. Concentrations of total methyl sulphone-PCBs and methyl sulphone-DDE in the three seal species from the Gulf of St. Lawrence (ng/g lipid weight).

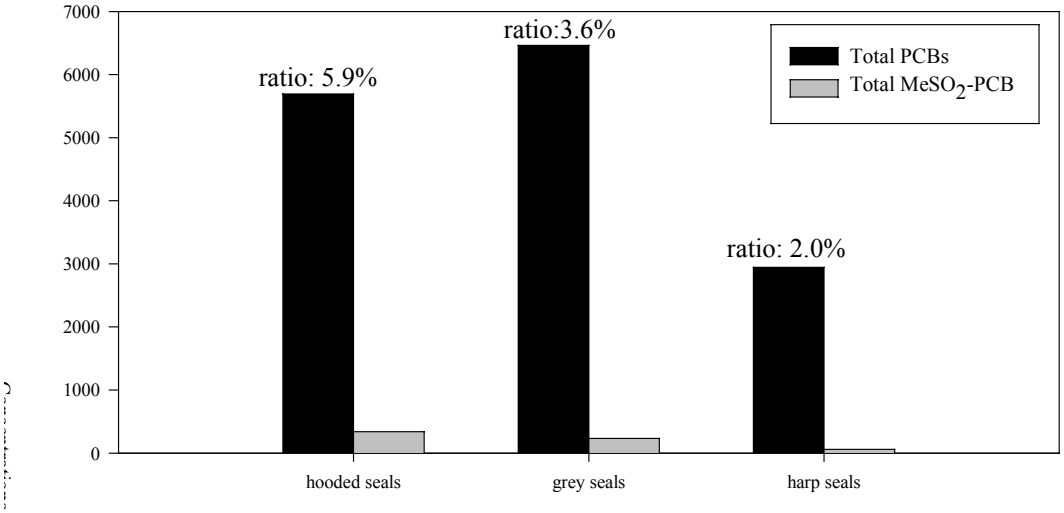

Figure 2. Concentrations of total $MeSO_2$-PCBs and total PCBs in the three seal species studied (ng/g lipid weight).

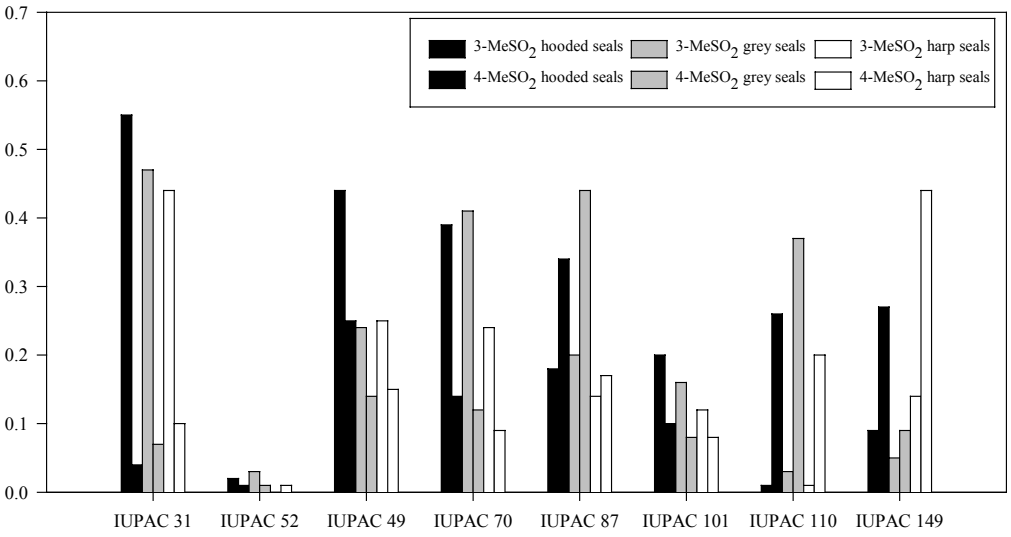

Figure 3. Relative ratio of the concentration of 3-$MeSO_2$ or 4-$MeSO_2$ to the concentration of total $MeSO_2$ metabolites and their PCB precursor compound.