

PCBs and PCB Metabolites in Fat, Blood and Brain of Polar Bears (*Ursus maritimus*) from East Greenland

Wouter Gebbink¹, Christian Sonne², Rune Dietz², Maja Kirkegaard², Frank F. Riget², Eric W. Born³, Derek C.G. Muir⁴, Robert J. Letcher⁵

¹National Wildlife Research Centre, Environment Canada - Carleton University

²Department of Arctic Environment, National Environmental Research Institute

³Greenland Institute of Natural Resources

⁴National Water Research Institute, Environment Canada

⁵National Wildlife Research Centre, Canadian Wildlife Service, Environment Canada

Introduction

Polar bears (*Ursus maritimus*) from the East Greenland area of the Arctic are apical predators in the marine food web, and have been documented to accumulate some of the highest levels of organochlorine (OC) contaminants in their tissues relative to animals from other circumpolar populations.^{1,2} There are also a number of recent reports on novel and emerging classes of organohalogen contaminants in metabolites in polar bear tissues (mainly fat and/or blood) from Canadian, Alaskan, Greenland and Norwegian populations, such as polybrominated diphenyl ethers (PBDEs), methylsulfonyl-PCBs and -DDEs and hydroxy (OH) PCBs.^{2,3,4,5,6} However, to our knowledge, studies on the tissue distribution of many of these established and emerging organohalogens is limited or lacking for polar bears from Arctic populations. We recently reported on the established and novel organohalogens and metabolites in the brain of polar bears from East Greenland, and found that PCBs, OH-PCBs and MeSO₂-PCBs were the dominant classes of organohalogens (companion DIOXIN 2005 short paper).

There are separate reports of MeSO₂-PCBs in fat, blood and/or liver of bears from the western hemispheric Arctic.^{2,3,7} Reports on OH-PCBs in polar bear are limited to whole blood or plasma for bears from East Greenland, Svalbard and Canadian Arctic populations.^{3,4} In mammals and humans, among other species, PCBs can be biotransformed via enzyme-mediated processes (cytochrome P450) to OH-PCB and MeSO₂-PCB congener residues that can persist in tissues, this mainly occurs in the liver.^{8,9} Congeners of both OH-PCBs and MeSO₂-PCBs have been shown to be biologically active, e.g., can modulate estrogen and thyroid hormone-dependent processes, and are thus potential endocrine disruptors in exposed organisms. MeSO₂-PCBs have been known to localize mainly in the liver and lungs in mammals and humans, high levels of OH-PCBs have been found in blood as they competitively bind to transport proteins such as transthyretin (TTR).⁷ This study contrasts and compares the congener patterns, concentrations and distribution of PCBs, OH-PCBs and MeSO₂-PCBs in fat, blood and brain of polar bears from East Greenland.

Materials and Methods

Fat, blood and brain tissues from 5 male polar bears (a subset of 10 males and 10 females) were collected by local subsistence hunters in the Ittoqqortoormiit/Scoresby Sound area in central East Greenland between 69°00'N and 74°00'N in 1999–2001.¹ Procedures for the determination of PCBs, MeSO₂-PCBs and OH-PCBs in fat and blood have been described elsewhere.^{2,4,5,6,7} The methodology for the brain extraction is a modification of Chu et al¹⁰, described in more detail in a companion DIOXIN 2005 short paper titled. The recoveries for PCBs were 91% ± 5%, 96% ± 3% and 93% ± 12% for fat, blood and brain respectively. For the MeSO₂-PCBs the recoveries were 81% ± 5%, 69% ± 9% and 51% ± 30% for fat, blood and brain respectively. Recoveries for OH-PCBs were 39% ± 8% and 81% ± 26% for blood and brain. OH-PCB and MeSO₂-PCB congener levels were determined using an internal standard approach (concentrations recovery corrected). PCBs were analyzed by GC-MSD (EI), MeSO₂- and MeO-

PCBs by GC-MSD (NCI). PCBs and MeSO₂-PCBs were quantified on [M]⁺ and [M+2]⁺, OH-PCBs on [M]⁺, [M+2]⁺ and [M-15]⁺.

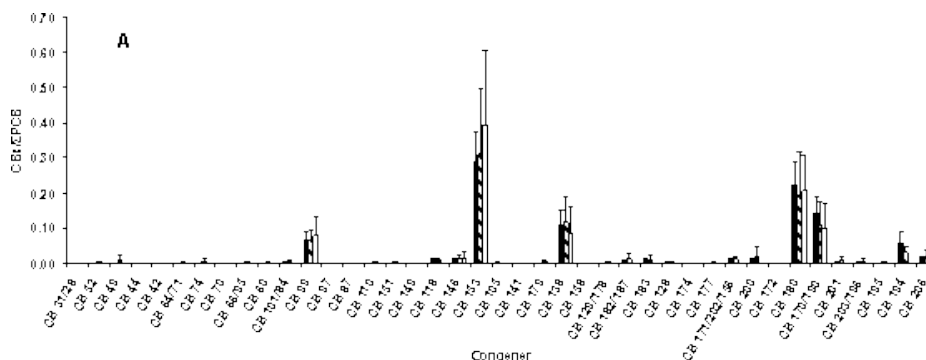
Results and Discussion

Of the 51 PCB congeners analyzed, five congeners dominate the PCB pattern for all 3 tissues, CB-99, -153, -138, -180, -170/190 (Figure 1A). Comparing the ratio of individual congener concentrations relative to the sum (Σ)PCBs showed that these 5 congeners make up a similar proportion of Σ PCBs in each tissue. The MeSO₂-PCB pattern for fat, blood and brain is similar with 3'-/4'-MeSO₂-CB101 and the co-eluting 4-MeSO₂-CB110/4'-MeSO₂-CB87 as the major congeners (Figure 1B). In the brain 3-MeSO₂-CB70 constitutes a greater proportion of the Σ MeSO₂-PCB concentration, which is not the case for the fat and blood samples, while 3-MeSO₂-CB132 is not detectable in the brain but is present in fat and blood. Σ PCBs and Σ MeSO₂-PCBs concentrations on a wet weight basis are by far the highest in fat relative to blood and brain samples. When corrected on a lipid weight basis, Σ PCBs and Σ MeSO₂-PCBs in fat and blood are in the same order, whereas concentrations in the brain are one order of magnitude lower for both compound classes (Table 1). Lower Σ PCB and Σ MeSO₂-PCB concentrations in the brain may be due to the protective affect of the blood-brain barrier (BBB), and/or is influenced by the different lipid composition in the brain (e.g., phospholipids) compared to fat and blood. The OH-PCB congener patterns in blood and brain are the same, with 4-OH-CB146, 4-OH-CB187, 4'-OH-CB172, 4-OH-CB192 and 4,4'-diOH-CB202 as the major congeners (Figure 1C). 4'-OH-CB120 was not detected in the brain while it was present in the blood. Σ OH-PCB concentration (on a wet weight as well as lipid weight basis) was much higher in blood relative to brain (Table 1), which suggests that although not congener selective, the BBB prevents a substantial portion of OH-PCB concentrations from entering the brain.

Table 1. Sum (Σ) concentrations of PCBs and PCB metabolites in tissues and blood from polar bears from East Greenland in wet weight (w.w.) and lipid weight (l.w.) (ng/g)

	Lipid	Σ PCB		Σ MeSO ₂ -PCB		Σ OH-PCB	
	%	w.w.	l.w.	w.w.	l.w.	w.w.	l.w.
Fat	78	5163 (958)	6619 (1364)	341 (66)	437 (93)	n.a.*	n.a.*
Blood	0.91	43 (16)	4725 (2801)	5 (1)	549 (276)	144 (74)	15,824 (10930)
Brain	18	70 (26)	389 (151)	14 (3)	78 (19)	9 (4)	50 (23)

* Not analyzed as yet.



EMV - Levels and Trends of POPs in the Arctic

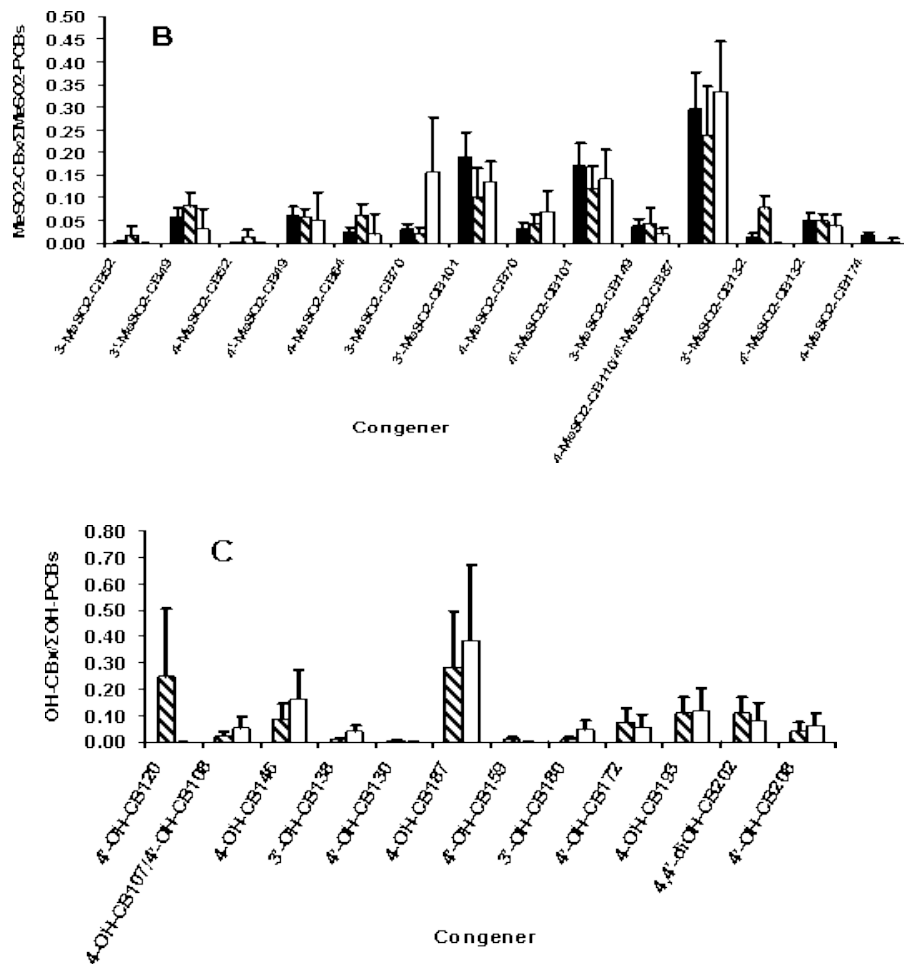


Figure 1. Pattern of the ratio of individual congener to the total (Σ) for PCBs (A), MeSO₂-PCBs (B) and OH-PCB (C) in fat (black bars), blood (stripped bars) and brain (white bars) from Greenland polar bears. OH-PCBs were not determined in fat.

Comparable ratios of the sum of the PCB metabolite to precursor SPCB concentrations demonstrate that the proportion of MeSO₂-PCBs is similar in the 3 tissues (Table 2). The SOH-PCB to SPCB concentration ratio illustrates that OH-PCBs are considerably more important in blood relative to brain. OH-PCB congeners identified in blood resemble the circulating thyroid hormone thyroxine (T₄), and can competitively displace T₄ from TTR.⁷ The present findings would suggest that possibly TTR and thus OH-PCB residues are also reduced in concentration in the brain, and/or that a proportion of the OH-PCBs are depleted as the TTR-OH-PCB complex passes through the BBB.

Table 2. Ratios of Σ MeSO₂-PCB to Σ PCB and Σ OH-PCB to Σ PCB concentrations in tissues of polar bears from East Greenland.

	Σ MeSO ₂ -PCB/ Σ PCB	Σ OH-PCB/ Σ PCB
Fat	0.07 (0.02)	n.a.*
Blood	0.12 (0.05)	2.65 (2.13)
Brain	0.20 (0.09)	0.13 (0.07)

*Not analyzed as yet.

Acknowledgements

Funding for this project is provided by the Natural Sciences and Engineering Research Council of Canada and Canada Research Chairs Program (to R.J.L.). Danish Cooperation for Environment in the Arctic and The Commission for Scientific Research in Greenland are thanked for facilitating the collection of polar bear tissue samples.

References

1. Dietz R., Riget F.F., Sonne-Hansen C., Letcher R.J., Born E.W. and Muir D.C.G. (2004) *Sci. Total Environ.* 331: 107-124.
2. Verreault J., Muir D.C.G., Norstrom R.J., Stirling I., Fisk A.T., Gabrielsen G.W., Derocher A.E., Evans T.J., Dietz R., Sonne C., Sandala G.M., Gebbink W., Born E.W., Riget F.F., Taylor M.K., Nagy J. and Letcher R.J. (2005) *Sci. Total Environ.* In press.
3. Sandala G.M., Sonne-Hansen C., Dietz R., Muir D.C.G., Valters K., Bennett E.R., Born E.W. and Letcher R.J. (2004) *Sci. Total Environ.* 331: 125-141.
4. Sandau C.D., McAlees A.J., Letcher R.J., Meerts I.A.T.M., Chittim B., Brouwer A. and Norstrom R.J. (2000) *Environ. Sci. Technol.* 34(18): 3871-3877.
5. Verreault J., Gabrielsen G.W., Chu S.-G., Muir D.C.G., Andersen M., Hamaed A. and Letcher R.J. (2005) *Environ. Sci. Technol.* Submitted.
6. Wolkers H., van Bavel B., Derocher A.E., Wiig Ø., Kovacs K.M., Lydersen C. and Lindstrøm G. (2004) *Environ. Sci. Technol.* 38: 1667-1674.
7. Letcher R.J., Klasson -Wehler E. and Bergman, Å. (2000) in: New types of persistent halogenated compounds, Berlin:Springer-Verlag, 315-359.
8. Bergman Å, Norstrom R.J., Haraguchi K., Kuroki H. and Béland P. (1994) *Environ Toxicol Chem.* 13(1): 121-128.
9. Sandau C.D., Ayotte P., Dewailly E., Duffe J. and Norstrom R.J. (2000) *Environ Health Persp.* 108: 611-616.
10. Chu S., Covaci A., Jacobs W., Haraguchi K. and Schepens P. (2003) *Environ. Health Perspect.* 111(9): 1222-1227.