Novel Organohalogens and Metabolites in the Brain of Polar Bears (Ursus maritimus) from East Greenland

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Introduction

Polar bears (*Ursusmaritimus*) 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.[1,2,3,4]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 polybrominateddiphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), total-hexabromocyclododecane (HBCD), methoxy (MeO)-PBDEs, methylsulfonyl ($MeSO_2$) -PCBs and -DDEs, hydroxy (OH) PCBs, pentachlorophenol (PCP) and 4-OH-hepatchlorostyrene (4-OH-HpCS).[4,5,6,7,8] However, to our knowledge there are currently no reports on organhalogen contaminants of any kind in the brain of polar bears.

The brain is protected by the blood-brain barrier (BBB). Despite the fact that the BBB should protect the brain from exogenous compounds, in a few human and rat studies it has been shown that some organohalogens (e.g., PBDEs) and metabolites (e.g., OH-PCBs) can migrate though the BBB and into the brain, and may perturb, e.g., thyroid hormone dependent brain function and development.[9,10]Phenolic organohalogens such as OH-PCBs, PCP and 4-OH-HpCS, which have been identified and found at very high concentrations in the blood of Norwegian, Canadian and Svalbard bears, have been shown to be potent competitors for the thyroid hormone transport protein, transthyretin (TTR) in competitive binding studies with human TTR. Determining the complexity of organohalogens and metabolites in polar bear brain is therefore of interest since these contaminants have the potential of a wide range of toxicities (e.g., endocrine and neurotoxicological) that my be unique to the brain. The objectives of this study are to identify, quantify and compare novel and emerging persistent organic pollutants (POPs) in the brain of polar bears from East Greenland.

Materials and Methods

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.[2]Procedures for the determination of PCBs, OCs, PBDEs, total-HBCD, PBBs, MeO-PBDEs, OH-PCBs, PCP, 4-OH-HpCS, and MeSO2-PCBs/-DDE have been described elsewhere.[2,4,5,6,7] For brain tissue, modification to the analytical methodology was based on Chu et al.[11] Briefly, samples of 1 gram of brain tissue were extracted by Soxhlet, and 10% of the extract was taken for gravimetric lipid determination. Liquid-liquid partitioning with H_2SO_4 was used to separated aryl sulfones from contaminants that are not protonated (neutrals), subsequently cleaned up by 33% KOH/silica column. Phenolics were separated from neutrals by KOH partitioning. The neutral fraction was cleaned up by 1.2% deactivated Florisil column chromatography as follows; fraction 1 contains PCBs, and fraction 2 contains $MeSO_2$-PCBs. For the $MeSO_2$-PCBs a final 2.3% deactivated basic alumina column clean up is preformed. In the phenolic fraction, phenolic contaminants were methylated to MeO-derivatives, and were further cleaned up using a 22% H_2SO_4/silica column. PCBs/OCs were determined by GC-MSD(EI), and MeO-PCBs/$MeSO_2$-PCBs and all brominated compounds by GC-MSD(NCI).

Results and Discussion

Relative to the sum (S) concentrations of other classes of POPs, SPCBs were the highest in the brain (Table 1). Of the 51 PCB congeners analyzed, only 7 congeners were detectable: CB-99, -146, -153, -138, -180, -170/190. These congeners are also the main congeners found in other polar bear tissues (fat and blood).[3,4,5,7] A similar PCB pattern has been reported in brain tissue from humans and other mammalian wildlife.[11,12,13] Twelve $MeSO_2$-PCB congeners were detected at a sum concentration of 14 ± 3 ng/g (wet weight) (Tables 1 and 2). The major congeners, 3-$MeSO_2$-CB70, 3'-$MeSO_2$-CB101, 4'-$MeSO_2$-CB101, 4-$MeSO_2$-CB110/4'-$MeSO_2$-CB87 were also detected in the fat and blood of East Greenland polar bears.[5] The congeners 4-$MeSO_2$-CB87 and 4-$MeSO_2$-CB101 were also detected in human brain.[11] Of the 33 OH-PCBs analyzed, 18 congeners were detectable (Table 3).The OH-PCB pattern was dominated by 4'-OH-CB101, 4-OH-CB146, 4-OH-CB187, 4'-OH-CB199, 4-OH-CB193 and 4'-OH-CB202 (Table 3).The OH-PCB congener pattern in the brain was similar to that found in blood of East Greenland polar bears.[5] Two other phenolic compounds, PCP and 4OH-HpCS were also detected in the brain at levels much lower than other classes, e.g., SOH-PCBs, SPCBs and S$MeSO_2$-PCBs (Table 1).

Table 1. Sum (Σ) concentrations of classes of novel and emerging POPs in the brain of polar bears from East Greenland

Class/Compound	ng/g wet weight (SD)	Class/Compound	ng/g wet weight (SD)
ΣPCB	70 (26)	ΣOC	0.11 (0.16)
Σ$MeSO_2$-PCB	14 (3)	ΣPBDE/ ΣPBB	2.3 (2.9)
ΣOH-PCB	9 (4)	ΣOH-PBDE	n.d.*
PCP	0.20 (0.19)	ΣMeO-PBDE	n.d.*
4-OH-HpCS	1.0 (0.2)	Total-HBCD	n.d.*

* Not detectable

Table 2. Congener specific concentrations of PCBs and $MeSO_2$-PCBs in the brain of polar bears from East Greenland.

PCB congener	Concng/g w.w. (SD)	$MeSO_2$-PCBs congener	Concng/g w.w. (SD)	$MeSO_2$-PCBs congener	Concng/g w.w. (SD)
CB99	5.6 (3.3)	3'-$MeSO_2$-CB49	0.43 (0.62)	4'-$MeSO_2$-CB101	2.0 (0.8)
CB146	0.9 (1.4)	4'-$MeSO_2$-CB49	0.72 (0.81)	3-$MeSO_2$-CB149	0.26 (0.18)
CB153	27.6 (11.0)	4-$MeSO_2$-CB64	0.28 (0.62)	4-$MeSO_2$-CB110/	4.6 (1.0)
CB138	6.0 (4.8)	3-$MeSO_2$-CB70	2.2 (1.6)	4'-$MeSO_2$-CB87	
CB180	14.6 (4.7)	3'-$MeSO_2$-CB101	1.9 (0.4)	4'-$MeSO_2$-CB132	0.54 (0.31)
CB170/190	7.1 (4.2)	4-$MeSO_2$-CB70	0.95 (0.62)	4-$MeSO_2$-CB174	0.05 (0.10)

Table 3. Congener specific concentrations of OH-PCBs in the brain of polar bears from East Greenland.

OH-PCB congener	Concng/g w.w. (SD)	OH-PCB congener	Concng/g w.w. (SD)	OH-PCB congener	Concng/g w.w. (SD)
4-OH-CB107/ 4'-OH-CB108	0.46 (0.31)	4-OH-CB163	0.64 (0.29)	4-OH-CB193	1.0 (0.6)
		4-OH-CB178	0.24 (0.18)	3'-OH-CB203	0.08 (0.05)
4'-OH-CB101	0.98 (0.43)	4-OH-CB187	3.3 (1.9)	4'-OH-CB198	0.08 (0.08)
4-OH-CB134	0.20 (0.15)	4'-OH-CB202	0.96 (0.62)	4'-OH-CB199	2.3 (1.5)
4-OH-CB146	1.4 (0.8)	3'-OH-CB180	0.42 (0.21)	4,4'di-OH-CB202	0.72 (0.45)
3'-OH-CB138	0.33 (0.14)	4'-OH-CB172	0.50 (0.33)	4'-OH-CB208	0.52 (0.34)

BDE 47 was the only detectable BDE congener in brain of the fifteen congeners analyzed, which is consistent with BDE congener patterns found in the fat of the same East Greenland bears (Muir et al., unpublished data). Of the fifteen OH-PBDE and fifteen MeO-PBDE congeners, as well as the flame retardant HBCD, that were analyzed, the levels were not detectable. Very low concentrations of tetrabrominated OH-PBDE and MeO-PBDE congeners were recently found in the plasma of female polar bear plasma from the Norwegian Arctic.[7]

In summary, despite the protective ability of the BBB to prevent exogenous compounds entering the brain, our findings suggest that this barrier is not completely protective in polar bear as a complexity of organohalogen and metabolite contaminants were found. PCBs, OH-PCBs, $MeSO_2$-PCBs and PBDEs are generally to most concentrated contaminants in brain from Greenland polar bears. In a companion short paper, we compare patterns and concentrations of PCB and PCB metabolites in brain relative to other tissues and body compartments.

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