GLOBAL DISTRIBUTION OF HALOGENATED DIMETHYL BIPYRROLES – EVIDENCE OF A NATURAL ORIGIN?

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Introduction

Halogenated dimethyl bipyrroles (HDBPs) are a group of mixed halogenated aromatic heterocycles with an N,N'-dimethyl-2,2'-bipyrrole structural skeleton. They have been detected in many types of organisms from the Pacific, Atlantic, and Arctic marine regions of Canada[1,2], but appear to be absent in the freshwater environment of the Great Lakes. This absence, coupled with a structural similarity to a known marine bacterial product[3], suggest a natural origin of HDBPs.

Materials and Methods

Blubber samples from a variety of cetacean and pinniped species were obtained from the locations listed in Table 1. The majority of samples underwent a column extraction procedure and clean-up similar to the one described in Tittlemier et al.[1] Samples and blanks were analyzed for CB-153 using gas chromatography electron impact ionization in the single ion monitoring mode using the method outlined by Sandau et al.[4] HDBPs were analyzed using gas chromatography electron capture negative ionization mass spectrometry in the single ion monitoring mode described in Tittlemier et al.[2]

Results and Discussion

Table 1 lists the geometric means and ranges of recovery corrected, lipid normalized ΣHDBP concentrations (ie. the sum of DBPs-Br_3Cl_3, -Br_4Cl_2, -Br_5Cl, -Br_6). Due to the lack of age and sex effects (ANCOVA, $p>0.05$), the ΣHDBP and ΣHDBP/CB-153 data from male, female, adult, and immature seals were combined and treated as one group. Data for dolphins, porpoises, and sea lions were similarly combined since the majority of samples were from males. Levels of HDBPs in male beluga samples from the St. Lawrence River and Igloolik were statistically corrected for sex since males from these areas were found to have significantly higher ΣHDBP concentrations than females.

The geographical distribution of HDBPs does not resemble patterns of distribution of organohalogens from anthropogenic sources. Dolphin/porpoise and seal samples originating from a Pacific environment contained significantly higher concentrations of HDBPs than the same or similar species from other locations. A similar difference in concentrations of anthropogenic organohalogens such as PCBs, DDT and chlordane compounds in Pacific and non-Pacific organisms has not been observed. Studies monitoring these organohalogens in seals and marine fish have found the highest levels of contaminants in samples from the Atlantic Ocean, North, and

Baltic Seas, followed by the Northwest Pacific Ocean, Arctic Ocean, and finally the Antarctic Ocean.[5]

HDBPs appeared to be distributed uniformly in beluga sampled from Arctic regions and the St. Lawrence River. In contrast to HDBPs, PCBs were approximately 15 times higher in St. Lawrence beluga than in those from western Greenland.[6,7] Likewise, total PCBs were significantly higher in polar bears from eastern locations, such as Svalbard and East Greenland, than those from North America.[8] In contrast, ΣHDBP concentrations were essentially identical in the Chesterfield Inlet, Igloolik, Pt.Lay, and St. Lawrence River beluga; the Svalbard group contained lower levels.

There was also no consistent difference between concentrations of HDBPs in biota from the Northern and Southern hemispheres. Hector's dolphin and New Zealand sea lion samples contained less HDBPs than ecologically similar species in the Northern hemisphere, but New Zealand fur seals contained significantly higher levels than northern seal species. The few studies available concerning anthropogenic organohalogens in Southern hemisphere biota conclude that levels are lower than those found in the Northern hemisphere.[9]

The difference in distribution patterns of HDBPs and anthropogenic organohalogens suggests that these two classes of contaminants have different sources. The distribution of anthropogenic organohalogens in marine mammals is governed by both long and short-range atmospheric, ice, and oceanic current transport from industrial sources.[8] The degree of transport is dependent upon basic physical properties, such as vapour pressure. [10] The extent to which an organohalogen will accumulate in a marine mammal depends upon physical properties as well.[11]

Estimates of fundamental physical properties for HDBPs are similar to those for higher chlorinated PCBs.[12] This indicates that HDBPs would likely behave in the same manner as these PCBs in terms of transport to and accumulation in marine mammals. If the potential to move and accumulate is similar between higher chlorinated PCBs and HDBPs, the difference in their distribution patterns must be attributed to different sources. This provides evidence to support the hypothesis that HDBPs are naturally-produced.

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Table 1. Geometric means of recovery corrected, lipid normalized ΣHDBP concentrations, ng/g.

Species	Location	Valid N	ΣHDBP, geomean (range), ng/g
Beluga			
beluga (*Delphinapterus leucas*)	Chesterfield Inlet, Nunavut	3	17.8 (9.5-27.1)
beluga (*Delphinapterus leucas*)	Igloolik, Nunavut	9	16.6 (0.5-54.4)
beluga (*Delphinapterus leucas*)	Svalbard, Norway	2	2.0 (0.6-6.1)
beluga (*Delphinapterus leucas*)	Pt. Lay, Alaska	5	14.4 (2.04-99.2)
beluga (*Delphinapterus leucas*)	St. Lawrence River	12	14.8 (2.4-52.7)
Dolphins and porpoises			
bottlenose dolphin (*Tursiops truncatus*)	Georgia / South Carolina	5	102 (24.9-235)
Dall's porpoise (*Phocoenoides dalli*)	NW North Pacific Ocean	5	2540 (1430-4710)
harbour porpoise (*Phocoena phocoena*)	Vancouver I., British Columbia	4	176 (6.2-977)
Hector's dolphin (*Cephalorynchus hectori*)	New Zealand	5	59.0 (15.4-841)
hump-backed dolphin (*Sousa chinensis*)	Bay of Bengal	1	1890
killer whale (*Orcinus orca*)	Vancouver I., British Columbia	1	584
Risso's dolphin (*Grampus griseus*)	Taiji, Japan	1	210
Fraser's dolphin (*Lagenodelphis hosei*) Spinner dolphin (*Stenella*	Minanao Sea, Phillipines	5	432 (49.3-2300)

longirostris)			
striped dolphin (*Stenella coeruleoalba*)	Catalonia, Spain	7	516 (306-1480)
Sea lions			
California sea lion (*Zalophus californicus*)	California	5	479 (92.5-9800)
New Zealand sea lion (*Phocarctos hookeri*)	New Zealand	5	48.2 (27.5-84.4)
Steller sea lion (*Eumetopias jubatus*)	Hokkaido coast, Japan	1	331
Steller sea lion (*Eumetopias jubatus*)	California	1	177
Steller sea lion (*Eumetopias jubatus*)	S Alaska	3	234 (82.7-1040)
Seals			
harbour seal (*Phoca vitulina*)	Washington	6	16.2 (6.9-44.5)
harbour seal (*Phoca vitulina*)	Bering Sea	18	8.3 (1.0-526)
harbour seal (*Phoca vitulina*)	Sweden	8	2.4 (0.4-22.4)
harbour seal (*Phoca vitulina*)	St. Lawrence River	4	0.8 (0.3-2.5)
harbour seal (*Phoca vitulina*)	Svalbard, Norway	3	4.3 (0.4-37.2)
harbour seal (*Phoca vitulina*)	SW Scotland	5	9.7 (0.5-29.6)
harbour seal (*Phoca vitulina*)	Wadden Sea	9	1.4 (0.2-15.8)
Baikal seal (*Phoca siberica*)	Lake Baikal, Russia	3	2.4 (0.1-32.4)
Largha seal (*Phoca largha*)	Japan	3	14.3 (11.2-18.0)
New Zealand fur seal (*Arctocephalus forsteri*)	New Zealand	5	126 (27.6-402)
ringed seal (*Phoca hispida*)	Eureka, Nunavut	6	1.2 (0.1-46.4)
ringed seal (*Phoca hispida*)	western Greenland	9	0.8 (0.3-1.5)
ringed seal (*Phoca hispida*)	Kara Sea	5	1.6 (0.6-11.5)
ringed seal (*Phoca hispida*)	Pangnirtang, Nunavut	9	1.4 (0.4-17.2)
ringed seal (*Phoca hispida*)	White Sea	9	0.4 (0.1-6.0)