DISTRIBUTION OF HALOGENATED DIMETHYL BIPYRROLES IN MARINE MAMMALS OF THE NORTHERN HEMISPHERE

Sheryl A. Tittlemier[1], Jennifer L. Pranschke[2], Shinsuke Tanabe[3], Peter S. Ross[4] and Ross J. Norstrom[1,2]

[1]Centre for Analytical and Environmental Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, K1S 5B6, Canada
[2]National Wildlife Research Centre, Environment Canada, 100 Gamelin Blvd., Hull, Quebec, J8Y 1V9, Canada
[3]Center for Marine Environmental Studies, Ehime University, Tarumi 3-5-7, Matsuyama 790-8566, Japan
[4]Institute of Ocean Sciences, P.O. Box 6000, Sidney, British Columbia, V8L 4B2, Canada

Introduction

Halogenated dimethyl bipyrroles (HDBPs) constitute a class of mixed halogenated heterocyclic compounds. Little is known about their geographical distribution in the environment, but they are hypothesized to be biogenic in origin, since their occurrence appears to be confined to marine environments[1], and their structure is similar to a known marine natural product[2]. HDBPs were first observed in seabird eggs from British Columbia[3]. Subsequent work showed that they were present in bird eggs from both the Pacific and Atlantic coasts of Canada but were absent in those from the Great Lakes[1]. The most abundant HDBP congener, $C_{10}H_6N_2Br_4Cl_2$, was found at levels as high as twice the concentration of CB-153 in samples from the Pacific coast.

In this study, the distribution of HDBPs in the northern Pacific Ocean was examined using blubber samples from various cetacean and pinniped species. The four most abundant HDBP congeners previously observed in birds – $C_{10}H_6N_2Br_3Cl_3$, $C_{10}H_6N_2Br_4Cl_2$ (1,1'-dimethyl-5.5'-dichloro-3,3',4,4'-tetrabromo-2,2'-bipyrrole), $C_{10}H_6N_2Br_5Cl$, and $C_{10}H_6N_2Br_6$ (1,1'-dimethyl-3,3',4,4',5,5'-hexabromo-2,2'-bipyrrole) were quantitated in the marine mammal samples.

Materials and Methods

Cetacean and pinniped species used in this study are listed in Table 1. The majority of individuals used were adult males to try to reduce any possible effects of age and sex on HDBP accumulation. All samples were worked up according to a similar method described in Tittlemier *et. al.*[2] Briefly, approximately 2 g of blubber were ground with Na_2SO_4 and extracted with 1:1 dichloromethane/hexane (v/v). Lipids were measured gravimetrically, and removed using gel permeation chromatography. Organohalogen contaminants were fractionated on a Florisil column. Carbon-13 labeled PCBs were used as recovery standards. PCB and OC analysis was performed by GC-EI-SIM-MS. HDBPs were analyzed using GC-ECNI-SIM-MS.

Results and Discussion

ΣHDBP concentrations. Individual congener and ΣHDBP (sum of the four measured HDBP congeners) concentrations are listed in Table 1. All concentrations are corrected for recovery of internal standards and lipid content of blubber.

HDBPs were detected in all of the sample groups analyzed. ΣHDBP concentrations differed significantly (1-way ANOVA, $p<0.003$) among the dolphins and porpoises from the various sampling locations, even though ΣHDBP varied considerably among individuals of the same species. Dall's porpoise samples from the northwestern north Pacific Ocean contained the highest amount of HDBPs. They comprised up to 11% of the total quantitated organohalogens (80 PCB congeners, p,p'-DDT/DDD/DDE, t/c-nonachlor, t/c-chlordane, oxychlordane, heptachlor epoxide, tetra/penta/hexachlorinated benzenes, α,β,γ-HCH, octachlorostyrene, mirex, and photomirex).

Differences in ΣHDBP concentrations between the sample groups may be driven by species differences – such as metabolic capabililty, feeding preferences, location, or a combination of these factors. The importance of each factor cannot be distinguished at this point since only one species has been analyzed from each location.

As opposed to the dolphins and porpoises, ΣHDBP concentrations did not differ significantly between the two groups of seals. The Largha seals contained larger amounts of HDBPs than the Baikal seals. The total amount of HDBPs was also much less than other quantitated organohalogens, ranging from less than 0.01% to 1.3%.

The presence of HDBPs in the freshwater environment of Lake Baikal contradicts what was reported in our previous study[1]. In this study HDBPs were not found in herring gull egg samples from the Great Lakes. It was concluded that HDBPs were a marine phenomenon and that atmospheric transport did not play a significant role in their movement. The presence of HDBPs in Lake Baikal suggests that HDBPs are either produced in freshwater environments, or more likely, that they move via atmospheric transport to freshwater environments.

ΣHDBP was also normalized to CB-153, a recalcitrant hexachlorinated PCB congener, to take into account the overall level of organohalogen contamination of the samples (Figure 1). This normalization step would also diminish any variation in HDBP concentrations caused by food chain factors, such as length. Since HDBPs are estimated to have similar log K_{ow}s to CB-153, they are expected to biomagnify through a food chain similar to CB-153 if they are not metabolized. Values of ΣHDBP/CB-153 ranged from 2.27 in Dall's porpoise from the northwestern Pacific, to 0.05 in the Risso's dolphin sample. Similarly high ratios (2.1, 0.96) were found in egg samples from Leach's storm-petrels, a pelagic species which also feeds in the northwestern Pacific[1]. The ratios for the seal samples were much lower, at 0.07 and 0.01 for the Largha and Baikal seals respectively. The fact that normalization of ΣHDBP to CB-153 did not equalize concentrations among all of the sample groups indicates that food chain factors play only a limited role in the variation of ΣHDBP concentrations. These results suggest that the sample groups have different exposures, and/or different metabolic capabilities towards HDBPs.

HDBP congener fractions. The concentration of each HDBP congener relative to ΣHDBP was calculated for each sample group. As with the seabird samples in our previous study, HDBP-Br_4Cl_2 was found to be the most abundant congener. The fraction of HDBP-Br_4Cl_2 was greater in the Risso's dolphin than the porpoise samples, however HDBP-Br_3Cl_3 and HDBP-Br_5Cl were not detected in this sample. There were no differences in congener fractions between the two seal sample groups.

Conclusions. HDBPs have a widespread occurrence in marine mammals of the northern Pacific Ocean. In certain instances, HDBPs constitute the third largest fraction of organohalogens found in blubber after PCBs, chlordanes, and DDT compounds. The variation in ΣHDBP/CB-153 suggests that HDBPs have sources different from anthropogenic organohalogens, and that the sample species may metabolize HDBPs to different extents. A widespread occurrence and evidence from the presence of HDBPs in a freshwater environment also suggest that HDBPs undergo atmospheric transport.

Acknowledgements
The authors thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for the postgraduate scholarship to S.A.T. All analyses were performed at the National Wildlife Research Centre, Quebec.

References

1. Tittlemier,S.A.; Simon,M.; Jarman,W.M.; Elliott,J.E.; Norstrom,R.J. (1999) Environ.Sci.Technol. 33, 26-33.
2. Andersen,R.J.; Wolfe,M.S.; Faulkner,D.J. (1974) Mar.Biol. 27, 281-285.
3. Elliott,J.E.; Noble,D.G.; Norstrom,R.J.; Whitehead,P.E.; Simon,M.; Pearce,P.A.; Peakall,D.B. (1992). In: Persistant Polluants in Marine Ecosystems; Walker,C.H.; Livingstone,D.R. Eds. Pergamon Press, pp 181-194.

Figure 1. Ratio of ΣHDBP to CB-153.

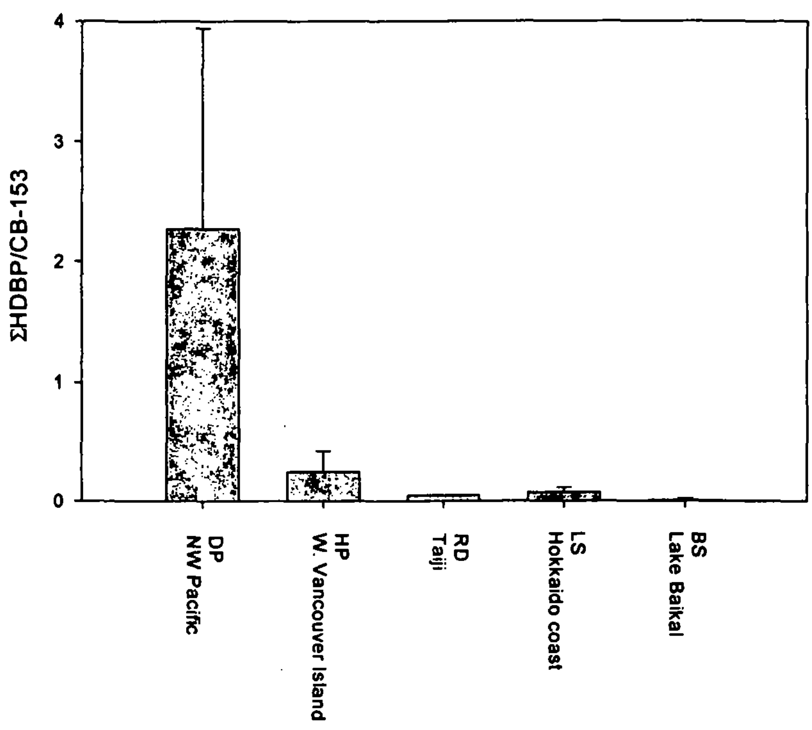

Table 1. Arithmetic means (range) of HDBP concentrations.

Species [abbreviaton]	Location	n	HDBP-Br_3Cl_3 (ng/g, lw)	HDBP-Br_4Cl_2 (ng/g, lw)	HDBP-Br_5Cl (ng/g, lw)	HDBP-Br_6 (ng/g, lw)	ΣHDBPs (ng/g, lw)
Dall's porpoise [DP] (*Phocoenoides dalli*)	NW North Pacific Ocean	5	1120 (42-2415)	1260 (30-3011)	116 (nd[a]-375)	391 (nd-1831)	2888 (1909-5863)
harbour porpoise [HP] (*Phocoena phocoena*)	west Vancouver Island, Canada	4	110 (2.6-246)	315 (4-656)	19 (0.44-45)	63 (nd-148)	507 (7.4-1095)
Risso's dolphin [RD] (*Grampus griseus*)	near Taiji, Japan	1	nd	201	0.84	8.5	210
Larga seal [LS] (*Phoca larga*)	Hokkaido coast, Japan	3	3.4 (2.4-5.1)	12 (9.9-15)	0.19 (nd-0.54)	0.22 (nd-0.65)	16 (12-20)
Baikal seal [BS] (*Phoca sibirica*)	Lake Baikal, Russia	5	2.3 (nd-10)	5.9 (nd-26)	0.16 (nd-0.71)	nd	8.4 (nd-37)

[a]not detected