Biomagnification Potential of Polybrominated Diphenyl Ethers in a Canadian Arctic Marine Food web

Barry C. Kelly[1], Michael G. Ikonomou, Frank A.P.C. Gobas[2]

[1]Fisheries and Oceans Canada, Institute of Ocean Sciences
[2]Simon Fraser University

Introduction

Bioaccumulation potential is an important aspect for assessing the overall risk posed by organic chemicals. While "legacy" Persistent Organic Pollutants (POPs) such as PCBs, DDTs and toxaphene have consistently shown a high degree of biomagnification in food chains, "current-use"high production volume (HPV) chemicals such as polybrominateddiphenyl ethers (PBDEs) used in commercial flame retardant mixtures have not been fully evaluated for their bioaccumulation behaviour. Some field-based bioaccumulation studies have observed PBDE biomagnification comparable to PCBs,[1] while others have found minimal or no bioamagnification potential of PBDEs.[2] The degree of accumulation and recalcitrance of PBDEs in organisms and food chains is of particular concern due to observed adverse effects in laboratory animals at doses in the low mg/kg body weight.[3] To better aid PBDE risk evaluations, determination of congener specific bioaccumulation behaviour parameters such as predator/prey biomagnification factors (BMFs) and food web magnification factors (FWMFs) is necessary.

Materials and Methods

Sediment and biota samples were collected from E. Hudson Bay during July and September 1999-2002.Approximately 0.2-10 g (wet) of tissue (blubber, liver and muscle tissue samples) were spiked with a suite of ^{13}C-labeled PBDE procedural internal standards (Cambridge Isotope Laboratories, Andover, MA) and extracted with CH_2Cl_2:hexane (1:1 v/v). Clean-up involved gel permeation chromatography (GPC), followed by Silica and Alumina chromatography.[4] PBDE analysis was conducted using a GC-HRMS isotope dilution method with either a 15 m DB-5HT or a standard 30 m DB-5 column.[4] A total of 31 individual mono- to hepta- PBDE congener peaks and three co-eluting bands (each composed of two congeners) were identified and quantified. One-Way Analyses of Variance (ANOVA) tests were performed on log-transformed concentrations data. To determine food web magnification factors (FWMFs), log-linear regression between log10 analyte concentrations in biota (CB) and trophic position (TP), i.e., $\log C_B = (m \cdot TP) + b$, where m and b are the empirical slope and y-intercept, respectively. FWMFs are calculated as the antilog of the slope (m), (i.e., $FWMF = 10^m$). We determined three separate FWMFs for (i) poikilotherms, e.g., bivalves and fish, (ii) homeotherms, e.g., birds and marine mammals and (iii) the entire food web. FWMFs > 1 indicate trophic transfer and biomagnification in the food web, while FWMFs near or less than unity represent trophic dilution.

Results and Discussion

Levels of BDEs in E. Hudson Bay biota. Figure 1 illustrates concentrations ($ng.g^{-1}lw$) of BDE 47, 100 and 99 in E. Hudson Bay cod and tissues' from beluga whale females, milk, calves and males. Concentrations of BDEs in tissue of Arctic cod and beluga tissues were relatively low (ranging between 1 to 15 $ng \cdot g^{-1}lw$) when compared to other fish and marine mammal species in more southern/urbanized coastal marine locations. There was only significant ($p < 0.05$) increases from cod to male beluga for BDE 47 and 100, while no significant differences were observed between cod and beluga for BDE 99. The predator/prey biomagnification factors (i.e., C_{PRED}/C_{PREY} lw) for male beluga/cod were approximately 2.8, 2.4 and 1.1 for BDEs 47, 100 and 99, respectively. The observed BMFs of BDEs in E. Hudson Bay male beluga are very low compared to other hydrophobic organohalogens with comparable physical chemical properties such as PCB153 and 180, which exhibited male beluga/cod BMFs of ~ 50.

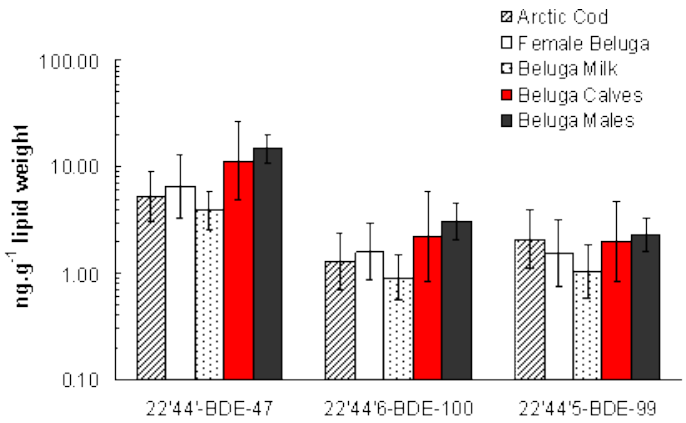

Figure 1. Concentrations (ng·g^{-1} lw) of BDEs congeners 47,100 and 99 in tissue samples of E. Hudson Bay beluga whales and Arctic cod. Error bars represent 1 SD of the geometric mean.

Beluga calves exhibited comparable BDE concentrations to those observed in male beluga whales, which may be attributed to maternal transfer of BDEs during the nursing period (~ 2 year duration for beluga whales). Figure 1 shows levels of BDEs in beluga calves were greater than those concentrations in mother's milk, indicating that a small degree of BDE biomagnification may enhance the accumulation of BDEs in newborns during this early life-stage.

Chemical concentration relationships with trophic level and FWMFs. Figure 2 shows measured CB-153 concentrations (GM ± 1 SD ng·g^{-1}lw) along with CB-153-TP linear regression lines for poikilotherms, homeotherms and the overall food web. The estimated FWMFs of CB-153 were equal to approximately 11.02 for the overall food web, 11.33 for homeotherms and 6.84 for poikilotherms. CB-153 concentration data for E. Hudson Bay male walrus[5], Hudson Bay male polar bears[6] and breast milk samples of Northern Quebec Inuit women[7] are plotted in figure 2 for comparison and generally agree with the CB-153 –TP regression estimates. The higher degree of biomagnification of recalcitrant CBs such as CB-153 observed in homeotherms compared to poikilotherms is consistent with other studies of species specific bioaccumulation differences [8,9,10]and is likely the result of more efficient digestive physiology and hence dietary accumulation of organohalogens for relatively high trophic animals such as ringed seals, beluga whales and polar bears.

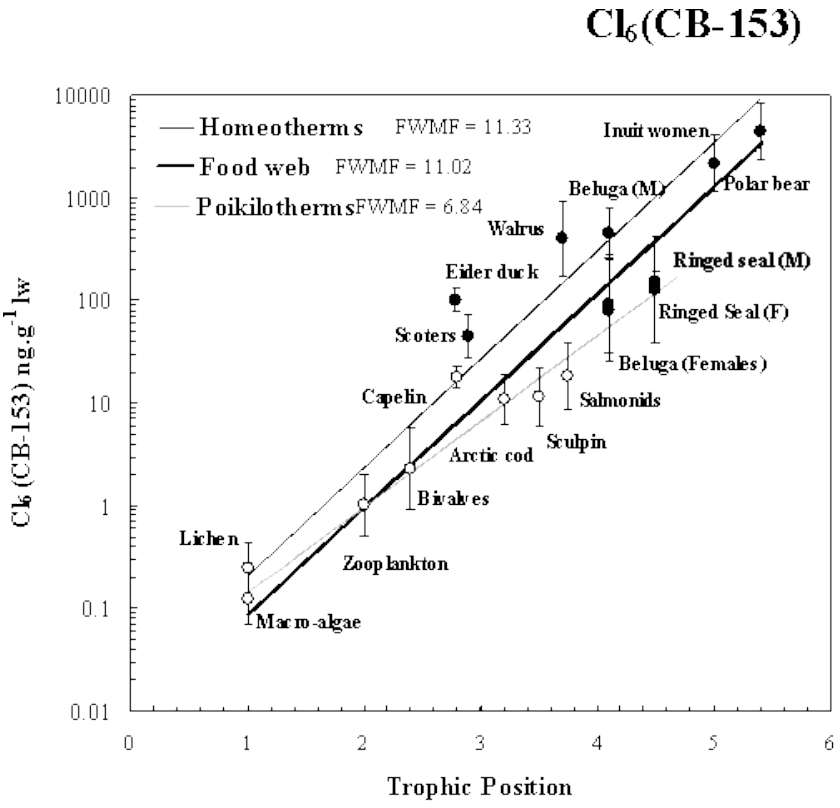

Figure 2. Relationship between CB-153 concentrations (ng g^{-1} lw) and trophic position (TP) for the various poikilotherms and homeotherms of the E. Hudson's Bay marine food web.

Figure 3 illustrates similar plots for BDE-47 and 99, with measured BDE concentrations (GM ± 1 SD $ng.g^{-1}$lw) along with BDE-TP linear regressions for poikilotherms, homeotherms and the overall E. Hudson Bay marine food web. In contrast to the food web plot for the relatively non-metabolizable CB-153, BDE congeners 47 and 99 do not show significant biomagnification in the food web. FWMFs for BDE-47 were near unity for poikilotherms, homeotherms and the overall food web. The slope estimates for BDE-99 were negative (i.e., FWMFs < 1) demonstrating trophic dilution of this congener in the food web. The data indicate no substantial biomagnification of BDEs occurs in these Arctic marine organisms and is likely the result of debromination and/or metabolism of BDEs. Previous studies have indicated that debromination of higher brominated (penta-hepta) to lower brominated (tetra) congeners can occur through abiotic means such as photolysis[11]or *in vivo*.[12] The identified degradation pathways include BDE-153 - BDE-99 - BDE-47 and BDE-183 - BDE-154 - BDE-100. This may ultimately result in increased tissue burdens of lower brominated BDE congeners (e.g., BDE-47) in high trophic animals such as ringed seals and beluga whale. Our findings of minimal biomagnification of BDE congeners in the E. Hudson Bay marine food web support the assertion of the debromination of higher brominatedBDEs and also indicate that BDE-47 may also under go further *in vivo* debromination and/or is biotransformed (e.g., via hydroxylation/methylation) in these Arctic marine organisms. Future studies should include investigations regarding the debromination and metabolic pathways and metabolites of PBDEs.

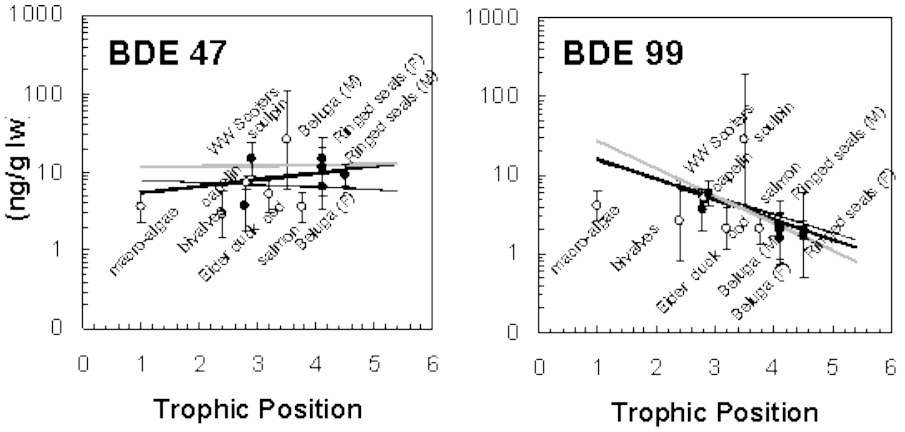

Figure 3. Relationship between chemical concentration (ng g^{-1} lw) in various organisms in the E. Hudson Bay marine food web versus organism trophic position (TP) for BDE-47 and 99.

Acknowledgements

We acknowledge DFO-ESSRF, TSRI for financial support and RDL staff for sample analysis and technical assistance.

References

1 Burreau,, S.; Broman, D.; Zebuhr, Y. Organohalogen Compd., 1999, 40:363-366.

2 Wolkers, H.;VanBavel, B.;Derocher, A.E.;Wiig, O.;Kovacs, K.M.;Lydersen, C.;Lindstrom, G. *Environ. Sci. Technol.* 2004, 38: 1667-1674.

3 Darnerud, P.O. *Environmental International*, 2003, 29: 841-853.

4 Ikonomou, M.G., S. Rayne, M. Fischer, M.P. Fernandez, W. Cretney. *Chemosphere*, 2002, 46: 649-663.

5 Muir, D.C.G., Segstro, M.D.; Hobson, K.A.; Ford, C.A.; Stewart, R.E.A.; Olpinski, S. *Environ. Poll.* 1995, 90:335-348.

6 Norstrom, R.J.; Belikov, S.E.; Born, E.W.; Garner, G.W.; Malone, B; Olpinski, S.; Ramsay, M.A.; Schliebe, S.; Stirling, I.; Stishov, M.S. *Arch. Environ. Contam. Toxicol*. 1998, 35:354-367.

7 Muckle, G.; Ayotte, P.; Dewailly, E.; Jacobson, S.W.; Jacobson, J.L. *Environ. Health Persp*., 109:1291-1299.

8 Norstrom, R.J.; Hallett, D.J.;Sonstegard, R.A. *J Fish Res Board Can.* 1978. 35: 1401-1406.

9 Fisk, A.T., Hobson, K.A.; Norstrom, R.J. *Environ. Sci. Technol*. 2001. 35:732-738.

10 Hop, H.; Borga, K.; Gabrielsen, G.W.; Kleivane, L.; Skarre, J.U. *Environ. Sci. Technol*. 2002. 36:2589-2597

11 Soderstrom, G.; Sellstrom, U.; de Wit, C. A.; Tysklind, M.; *Environ. Sci. Technol*. 2004,38:127-132.

12 Stapleton, H. M.; Letcher, R. J.; Baker, J. E. *Environ. Sci. Technol*. 2004 , 38:1054-1061.