

Brominated Flame Retardants in Blubber Collected from Gulf of Mexico and Western North Atlantic Bottlenose Dolphins (*Tursiops truncatus*)

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Introduction

Bottlenose dolphins (*Tursiops truncatus*) are common toothed whales present in most estuarine and near shore areas of the US Southeast and Mid Atlantic regions. Bottlenose dolphins are near the top of the aquatic food web making them susceptible to the bioaccumulation of persistent and lipophilic compounds. Bottlenose dolphins inhabiting inshore areas generally show a high degree of site fidelity and because of this may be indicators of ambient environmental conditions¹. This, along with the occurrence of several bottlenose dolphin unusual mortality events (UMEs) along the US coast has catalyzed several multi-investigator studies assessing the health of this species in selected geographical areas. This study presents the results from the analysis of blubber for brominated diphenyl ether congeners (BDE) collected from dolphin health assessment live captures (surgical biopsies), remote dart biopsies, and from an UME. BDEs are of interest in bottlenose dolphins as they likely have similar toxicological properties to the polychlorinated biphenyls and BDE concentrations are increasing in some marine mammal populations. BDEs have also been detected in cetaceans from several other populations³⁻⁷ although little is known regarding how concentrations differ within a species on a spatial scale.

Materials and Methods

Samples for this project were obtained from several locations from juvenile or adult male bottlenose dolphins. The study was limited to this gender and age class as it has been shown that these two classes are generally not statistically different with respect to other persistent organic pollutants and BDE concentrations³. Dolphins sampled from Florida included animals from Sarasota Bay (n = 23, surgical biopsies), Tampa Bay (n = 5, dart biopsies), Biscayne Bay near Miami (n = 35, dart biopsies), St. Joe Bay (n = 8, post mortem samples from animals involved in an UME). Dolphins from US East Coast locations included Charleston Harbor, South Carolina (n = 12 dart biopsies), Holden Beach, North Carolina (n = 4, surgical biopsies), and Cape May, New Jersey (n = 3, surgical biopsies). Samples were minced, dried with sodium sulfate, then added to a pressurized fluid extraction (PFE) cell along with a solution of isotopically labeled BDE 99 and 209 and other labeled organochlorine pesticides and polychlorinated biphenyls. Samples were extracted with the PFE with dichloromethane and cleaned up using size exclusion chromatography followed by an alumina solid phase extraction cartridge. Samples were analyzed using gas chromatography/mass spectrometry in the electron impact mode. The instrument was equipped with a 60 m x 0.25 mm x 0.25 mm DB-5ms column (Agilent Technologies, Folsom, California). Samples were analyzed for BDE congeners 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 185, and 190 using ¹³C BDE 99 was used as the internal standard. Selected samples were analyzed for an additional 15 BDE congeners.

Results and Discussion

While 13 BDE congeners were examined, BDE 47, 99, 100, 153, and 154 were detected in all the samples and BDE 85 was also frequently detected. The sum BDE 47, 99, 100, 153, and 154 (SBDE) concentrations (wet basis) in the dolphin blubber samples were 710 ng/g (340 ng/g) (geometric mean (1 SD)), 650 ng/g (250 ng/g), 410 ng/g (440 ng/g), 200 ng/g (100 ng/g) for males and juveniles sampled from Sarasota Bay, St. Joe Bay, Biscayne Bay and Tampa Bay, FL, respectively. SBDE concentrations were approximately 5% of SPCB concentrations. It is interesting that of these four estuaries, Sarasota Bay and St. Joe Bay have smaller human populations but have the highest BDE

concentrations in dolphins. This suggests that ecological factors may be important in determining BDE concentrations. The contribution of the five BDE congeners to the total BDEs in blubber are shown in Figure 1. The samples from Biscayne Bay and Tampa Bay had a higher proportion of more highly brominated congeners. This may be due to a closer proximity to BDE sources, such as sewage outfalls or industrial sources⁸.

Work is in progress determining concentrations of BDEs from bottlenose dolphin blubber collected from other locations including Charleston, South Carolina, Holden Beach, North Carolina, and coastal New Jersey as well as in blood from animals collected during the course of dolphin health assessments. In addition, hexabromocyclododecane isomers and enantiomers are also being determined in bottlenose dolphin and white sided dolphin blubber.

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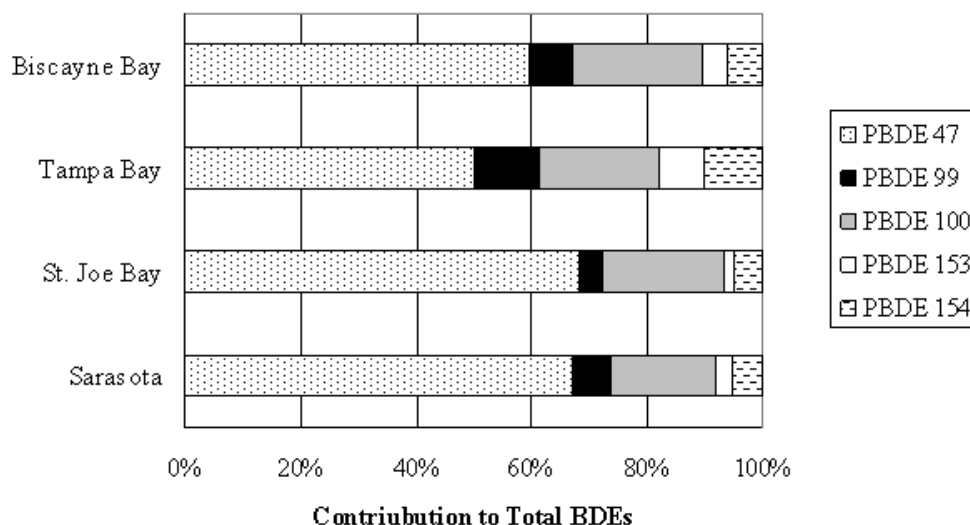


Figure 1. The contribution of individual BDEs to the total BDE in dolphins from selected areas in Florida

References

1. Wells, R.S., H.L. Rhinehart, L.J. Hansen, J.C. Sweeney, F.I. Townsend, R. Stone, D. Casper, M.D. Scott, A.A. Hohn, and T.K. Rowles. 2004. Bottlenose dolphins as marine ecosystem sentinels: Developing a health monitoring system. *EcoHealth* 1:246-254.
2. Hansen, LJ, Schwacke, LH, Mitchum, GB, Hohn, AA, Wells, RS, Zolman, ES & Fair, PA. Geographic variation in polychlorinated biphenyl and organochlorine pesticide concentrations in the blubber of bottlenose dolphins from the US Atlantic coast. *Sci Total Environ* 319, 147-72 (2004).
3. Tuerk, KJ, Kucklick, JR, Becker, PR, Stapleton, HM & Baker, JE. Persistent organic pollutants in two dolphin species with focus on toxaphene and polybrominated diphenyl ethers. *Environ Sci Technol* 39, 692-8 (2005).
4. Covaci, A, Voorspoels, S & de Boer, J. Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples--a review. *Environ Int* 29, 735-56 (2003).

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5. Boon, JP, Lewis, WE, Tjoen-A-Choy, MR, Allchin, CR, Law, RJ, de Boer, J, Ten Hallers-Tjabbes, CC & Zegers, BN. Levels of Polybrominated Diphenyl Ether (PBDE) Flame Retardants in Animals Representing Different Trophic Levels of the North Sea Food Web. *Environ Sci Technol* **36**, 4025-4032 (2002).
6. Lebeuf, M, Gouteux, B, Measures, L & Trottier, S. Levels and Temporal Trends (1988-1999) of Polybrominated Diphenyl Ethers in Beluga Whales (*Delphinapterus leucas*) from the St. Lawrence Estuary, Canada. *Environ Sci Technol* **38**, 2971-2977 (2004).
7. Rayne, S, Ikonou, MG, Ross, PS, Ellis, GM & Barrett-Lennard, LG. PBDEs, PBBs, and PCNs in three communities of free-ranging killer whales (*Orcinus orca*) from the northeastern Pacific Ocean. *Environ Sci Technol* **38**, 4293-9 (2004).
8. Hale, RC, Alae, M, Manchester-Neesvig, JB, Stapleton, HM & Ikonou, MG. Polybrominated diphenyl ether flame retardants in the North American environment. *Environ Int* **29**, 771-9 (2003).