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Fine-Scale Spatial Variation of Persistent Organic Pollutants in Bottlenose Dolphins (*Tursiops truncatus*) in Biscayne Bay, Florida

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Bottlenose dolphins (*Tursiops truncatus*) are long-term residents and apex predators in southeast U.S. estuaries and are vulnerable to bioaccumulation of persistent organic pollutants (POPs). Dart biopsy samples were collected from 45 dolphins in Biscayne Bay (Miami, FL), 34 of which were matched using fin markings to a photo identification catalogue. Blubber samples were analyzed for 73 polychlorinated biphenyl (PCB) congeners, six polybrominated diphenyl ether (PBDE) congeners, and organochlorine pesticides including dichloro-diphenyl-trichloroethane (DDT) and metabolites, chlordanes, and dieldrin. Total PCBs (Σ73PCBs) were present in the highest concentrations and were 5 times higher in males with sighting histories in the northern, metropolitan area of Biscayne Bay than males with sighting histories in the southern, more rural area [geometric mean: 43.3 (95% confidence interval: 28.0−66.9) vs 8.6 (6.3−11.9) μg/g wet mass, respectively]. All compound classes had higher concentrations in northern animals than southern. The differences in POP concentrations found on this small geographic scale demonstrate that differential habitat use can strongly influence pollutant concentrations and should be considered when interpreting bottlenose dolphin POP data. The PCB concentrations in northern Bay dolphins are high as compared to other studies of estuarine dolphins and may place these animals at risk of reproductive failure and decreased immune function.

Introduction

Bottlenose dolphins (*Tursiops truncatus*) are long-lived, upper trophic level predators with a high lipid content blubber layer. Dolphins are predisposed to the accumulation of lipophilic xenobiotics such as persistent organic pollutants (POPs) and can be good indicators of the levels of bioavailable POPs in marine habitats. Furthermore, POP profiles from dolphin tissues have been found to differ across geographical regions and may provide clues as to the source and/or timing of pollutant input as well as stock structure (*1*−*4*). Hansen et al. (*1*) found significant differences in POP concentrations between dolphins in Indian River Lagoon, FL, Charleston, SC, and Beaufort, NC. Borrell et al. (*5*) found differences in PCB congener profiles and dichloro-diphenyl-trichloroethane (DDT)/PCB ratios among bottlenose dolphins in different regions of the Iberian Peninsula.

While these studies and others have found significant differences in POP profiles on large geographic scales, little has been reported on fine-scale spatial variation. Bottlenose dolphins tend to use certain core areas within their larger home ranges (*6*, *7*). In areas such as Biscayne Bay (BB), FL, where dolphins utilize different core areas across a gradient of urban development, the patterns of contaminants measured from dolphins within a localized population may provide an indication of relatively fine-scale differences in habitat quality.

Biscayne Bay is a shallow subtropical estuary of approximately 450 km^2 located along the east coast of Miami-Dade County, FL (Figure 1). The northern portion of Biscayne Bay is centered between the City of Miami and Miami Beach. It is a narrow area that is highly developed and has relatively poor water circulation. Central Biscayne Bay opens to the Atlantic Ocean through a large area of grass flats and tidal channels called the Safety Valve. The Bay connects to Florida Bay in the south through a series of small embayments. The northern portion of the Bay is more extensively developed and more contaminated than the southern area (*8*−*10*). For example, the National Status and Trends Program found that the total PCBs in sediments in northern Biscayne Bay was around 40−50 ng/g dry weight and that the PCBs in the sediments of central Biscayne Bay were approximately half of that, from 20 to 30 ng/g dry weight (*11*). In general, southern Biscayne Bay is better flushed and has less input from urban and industrial land uses than northern Biscayne Bay (*12*). Various studies have examined contaminant levels in water, sediments, and/or oysters of Biscayne Bay; however, there is little additional information on biotic POP concentrations.

Photo identification (photo-ID) studies by the National Marine Fisheries Service Southeast Fisheries Science Center (NMFS/SEFSC) indicate that bottlenose dolphins are year-round residents within Biscayne Bay. This ongoing study uses photo-ID techniques to identify individuals based on dorsal fin markings and track these individuals over time. While there is overlap in the home ranges of individuals, many animals have a higher occurrence in either the northern/central portions of Biscayne Bay or in the central/southern portion. This photo-ID database also provides information on age classes and reproductive histories of identified animals.

In this study, we collected tissue biopsy samples from individual bottlenose dolphins throughout Biscayne Bay and assessed blubber POP concentrations. Identifiable individuals were matched to the photo-ID database to obtain data on their spatial movements and life histories. The goal of this study was to examine variations in dolphin POP concentrations as a function of geographic distribution.

Materials and Methods

Photo-ID Study. Biscayne Bay was divided into three survey areas (Figure 1): north Biscayne Bay (Haulover Inlet to Rickenbacker Causeway), central Biscayne Bay (Rickenbacker Causeway to Sands Cut), and south Biscayne Bay (Sands Cut

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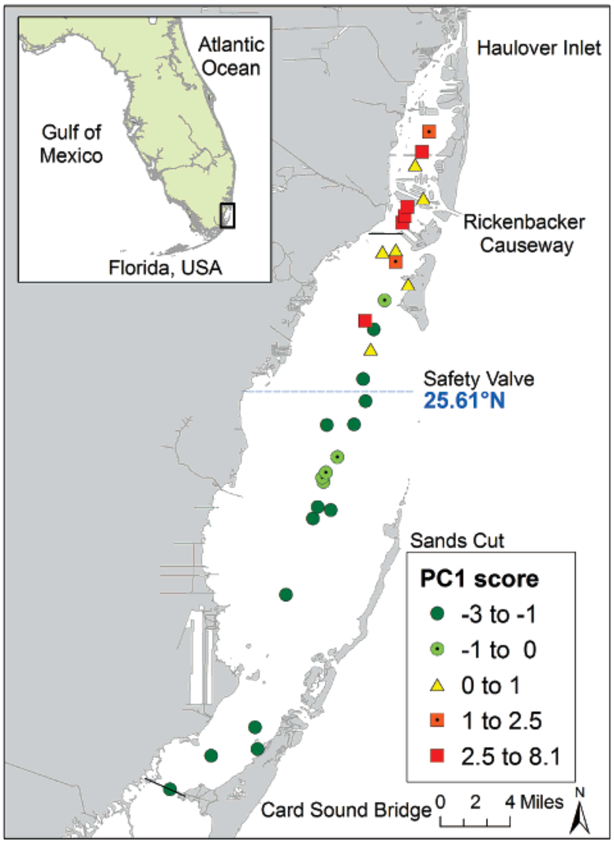

FIGURE 1. Biscayne Bay study area on the east coast of Miami, FL. Male and juvenile samples are plotted by the mean latitude of their sighting histories and coded by the PC1 score from the PCA of samples summed by compound class. Samples with high PC1 scores had high concentrations in all compound classes, and PC1 accounted for 74.4% of the variation. Samples north of 25.61 °N had higher concentrations.

to Card Sound Bridge). Since 1994, photo-ID surveys have been conducted by small boat an average of nine times per year in each of these three areas. Dolphin photo-ID was performed using established techniques (*13*, *14*). Individuals with distinct markings on their dorsal fins were identified and catalogued to provide information on spatial movements and life histories. To date, more than 200 individuals have been catalogued.

Biopsy Sample Collection. Tissue samples were obtained by remote biopsy using a dart fired from a modified 0.22 caliber pneumatic rifle (*1*). The samples obtained generally consisted of a layer of skin and a full thickness core of blubber approximately 1 cm in diameter and weighing 0.5−1 g. Samples were collected during an average of five field days per month from May 2002 through March 2003. Additional samples were collected during five field days in November of 2003 and six days in March 2004. Dorsal fin photographs were taken to identify biopsied animals. Field days were rotated in each of the three areas of the bay, and the survey effort was varied by time of day and location to minimize the chance of encountering the same dolphins. The sampling regime was designed so that the samples collected reflected the true diversity of the Biscayne Bay population and that all possible subgroups of dolphins were represented.

To prevent contamination, the biopsy darts were quickly retrieved from the water and handled with powder-free latex gloves and clean instruments. The sample was removed, and the skin was separated from the blubber using a scalpel. The blubber was placed in cryogenic Teflon vials in dry ice in the field and then transferred to a −80 °C freezer for storage prior to analysis. The darts, forceps, and scalpel handles used to process single samples were cleaned using a method similar to that described by Hansen et al. (*1*).

Sighting History Data. Digital video and still photography were used to confirm the identification of the animals sampled by matching dorsal fin markings with the SEFSC photo-ID catalogue. For each sampled animal that was matched to the catalogue, data from 1994 through 2004 photo-ID surveys were used to calculate the mean latitude and mean longitude of the animal's sighting history as the geographic reference for the sample. If an animal was sighted more than once in any photo-ID survey day, only the first sighting of that day was used. If a sample could not be matched to the catalogue, the sample collection site was used for its geographical reference, the number of sightings for that animal was one, and the age class and reproductive history were unknown. While any structure within Biscayne Bay likely runs on a gradient and does not have an exact dividing line, the selection of a point at which to geographically divide the data is necessary for some analyses. The latitude 25.61 °N was chosen for the division after exploratory analysis of the sampled animals showed a natural break in the data around that point. Animals with mean latitudes north of 25.61 °N were considered northern, and animals with mean latitudes south of 25.61 °N were considered southern.

Knowledge of the sex, age class, and reproductive history of sampled animals is critical to interpreting POP data because reproductively mature females pass a portion of their contaminant load to their offspring through the placenta and by lactation, causing the levels of POPs in the blubber of adult females to be lower than those in adult males (*15*−*17*). The sex of all sampled animals was determined using molecular techniques (*18*). The sighting histories were used to estimate the age class and reproductive histories based on known mother/calf relationships. Animals recorded as young of the year (YOY) within 5 years of being sampled were considered juveniles. Females known to have had a calf or have sighting histories longer than 10 years were considered adults. Any females that could not be confirmed as juveniles or adults were classified as unknown. POP concentrations in males increase with age (*16*). Because the specific age of sampled animals was not known, all males other than those determined to be juveniles were classified as age class unknown.

Sample Analysis. Organic pollutant analysis was performed at the National Institute of Standards and Technology Laboratory (NIST) in Charleston, SC. Individual blubber samples were minced and mixed with sodium sulfate, added to a pressurized fluid extraction cell (PFE; Dionex ASE, Salt Lake City, UT) along with an internal standard solution (containing 4,4′-DDT-d_8, 4,4′-DDT-d_8, 4,4′-DDD-d_8 (dichlorodiphenyl-dichloroethane), ^{13}C PBDE99, and ^{13}C PCB congeners 28, 52, 118, 153, 180, 194, and 206). Samples were extracted with dichloromethane using PFE. The percent lipid was determined gravimetrically by drying an aliquot of the extract. The sample extracts were reduced to between 0.5 and 1.0 mL by evaporation in a stream of purified N_2 using a Turbovap II (Caliper Life Sciences, Hopkinton, MA). High molecular mass compounds were removed by size-exclusion chromatography (*19*). Samples were further cleaned using a 5% (volume fraction) deactivated 1.8 g alumina solid phase extraction (SPE) cartridge. The sample (0.5 mL) was loaded onto the cartridge and was eluted with 9 mL of 35:65 (volume fraction) dichloromethane/hexane. Elution was conducted using an automated SPE workstation (Rapidtrace, Caliper Life Sciences).

PCBs, chlorinated pesticides, and polybrominated diphenyl ether (PBDE) congeners were quantified using gas chromatography/mass spectrometry (GC/MS; Agilent 6890/

5973, Palo Alto, CA) operated in the electron impact mode. Endosulfans and select chlordanes were determined using a GC/MS instrument operated in the negative chemical ionization mode (NCI). Compounds were separated on a 60 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5ms capillary column (Agilent Technologies). In addition, samples were screened separately for the presence of PBDE 209 using a 10 m × 0.25 mm × 0.25 μm film thickness DB-5 ms column, large-volume injection (20 μL), and GC/MS-NCI. More details on the GC/MS methods are given elsewhere (*19*). A Standard Reference Material (SRM) 1945 Organics in Whale Blubber (www.nist.gov) was analyzed with each set of 16–20 samples as an analytical control material. Values determined on this material were within less than 30% of the certified or reference values for this material. Blanks were also run with each set of samples as negative controls. A five point calibration curve was used to quantify the compounds. The limit of detection (LOD) was calculated by dividing the lowest detectible calibrant from the calibration curve by the sample mass. If a sample was below the LOD for a particular compound, the value of half of the LOD was used for analyses. If more than 90% of the samples were below the LOD for a given compound, the compound was removed from the statistical analyses. For example, a total of 14 PBDE congeners was measured; however, eight of them (including PBDE 209) were removed from the analysis because more than 90% of the samples were below the LOD for that compound.

Ninety-four compounds were used in statistical analyses: 73 PCB congeners, six DDT compounds, six PBDEs, six chlordanes, hexachlorobenzene (HCB), mirex, and dieldrin. A list of individual compounds measured, along with geometric means and 95% confidence intervals by compound and sex/age class, are provided in the Supporting Information (Table S1). Compounds were summed in each compound class, and concentrations were expressed as ng/g wet mass (ww).

Statistical Analyses. Organic pollutant data are difficult to interpret in reproductively active females. To remove this known variability, only the data from males and juveniles were used for geographic comparisons. To investigate differences in the concentrations of compounds within Biscayne Bay, a principal components analysis (PCA) using a correlation matrix was conducted on the data from 31 male and juvenile samples summed by compound class. To investigate differences in patterns of POPs in Biscayne Bay, a second PCA was conducted using a covariance matrix, and the variables were all of the individual compounds for each sample expressed as a fraction of total POPs. The data points in both PCAs were coded by mean latitude to examine geographic patterns.

For each major compound class (ΣPCBs, ΣDDTs, Σchlordanes, and ΣPBDEs), a backward stepwise linear regression was conducted to select significant explanatory variables including season (winter/spring vs summer/fall), sample location on body (anterior to dorsal fin, posterior to dorsal fin, and below dorsal fin), percent lipids in the sample, sample mass, sex/age class (adult female, unknown female, juvenile, unknown male), and mean latitude of the animal's sighting history. All data were log-transformed prior to regression analyses to meet assumptions of normality. Following the initial selection of significant single terms, all two-way interactions were evaluated as allowed by sample sizes. The regression coefficients and model statistics are provided in the Supporting Information (Table S2).

Comparison to Other Studies. Male data from Biscayne Bay dolphins as a whole and as subgroups (north of 25.61 °N and south of 25.61 °N) were compared to published data for Charleston, SC, Beaufort, NC, Indian River Lagoon, FL (*1*), and Florida Bay, FL (*20*). To standardize the Biscayne Bay data for comparison, the data were lipid normalized by dividing the concentration of each compound by the fraction of lipids resulting in data expressed μg/g lipid. The compounds used for comparison were limited to the same 15 PCB congeners (Σ15PCBs), six DDT group compounds, and four chlordane compounds used in Hansen et al. (*1*). Mean data from males and females for six PBDE congeners (47, 85, 99, 100, 153, and 154) expressed as lipid weight were compared with stranded bottlenose dolphin data from the east coast of Florida (2001–2004) and the west coast of Florida (2000–2001) (*21*).

Results

Biopsy Samples. Samples were obtained from 45 individual dolphins, 34 of which were matched to the SEFSC photo-ID catalogue. The remaining 11 could not be matched because the animals had non-distinct fins, they had a distinct fin not recognized in the catalogue, or a poor photo and video of the shot prevented identification. Of the 34 animals matched to the catalogue, the number of sightings between 1994 and 2004 for each animal ranged from 4 to 48 sightings with an average of 20 sightings. Seven animals were inadvertently sampled more than once with the time between duplicate samples ranging from hours to 8 months. In these cases, the values from duplicate blubber samples were averaged for the regression and PCA analyses. The percent difference of each duplicate sample as compared to the mean of that individual was calculated for the sum of each of the compound classes using lipid weight data. In general, the average percent differences from the mean for each individual were between 1 and 20% with the exception of one animal (Table S3, Supporting Information). Two samples collected from animal A had a higher percent difference (16–38% depending on compound class). The reason for the variation was unclear. This animal is known to be an adult female with at least two previous calves. It is possible that there was a change in reproductive or nutritional status within the 8 months between samples.

Sample Analysis. ΣPCBs were present in the highest concentrations followed by ΣDDTs, Σchlordanes, ΣPBDEs, and other pesticides including dieldrin, mirex, and HCB (Table 1). POP concentrations were higher in males and juveniles than in females. An initial linear regression analysis indicated that adult females were significantly different from all other sex/age classes. Juveniles, females of unknown age class, and males of unknown age class were not significantly different from each other ($p > 0.05$ for all compound classes) and therefore were combined into a single category for the remaining analyses.

The stepwise linear regression retained three significant factors for inclusion in the model: mean latitude, sex/age class (adult female vs all others), and sample mass. POP concentrations were positively correlated with mean latitude for all compound classes ($p < 0.0001$) (Figure 2 and Table S2 in the Supporting Information). Adult females had significantly lower POP concentrations for all compound classes ($p < 0.0001$) than the other age/sex classes (Table 1). A generally weaker but significantly positive correlation between sample mass and POP concentration was observed for ΣDDTs, ΣPBDEs, ΣPCBs, and Σchlordanes ($p = 0.0225$, 0.0168, 0.0042, and 0.0002, respectively). It is unclear as to why the sample mass was significantly correlated with compound class concentrations. The regression parameter for this effect was small relative to those of age class and mean latitude (Table S2, Supporting Information). Examination of residuals and two-way interaction effects indicated that correlations between POP concentration and latitude or sex/age class were not confounded by sample mass. Sample location, percent lipid, and season were not significantly correlated to any compound class nor were any two-way interaction effects. Comparison of the regression models

TABLE 1. Geometric Means and 95% Confidence Intervals [GM (CIs)] in ng/g Wet Mass for Blubber Biopsies from Males and Juveniles Versus Adult Females for All Biscayne Bay Samples (All BB) and Samples from Animals with a Sighting History of Mean Latitudes North of 25.61 °N and South of 25.61 °N (NBB and SBB, Respectively)[a]

Males and Juveniles	∑PCBs	∑DDTs	∑Chlordanes	∑PBDEs	∑Other Pesticides
All BB (*n* = 31)	19900 (13400 - 29400)	2980 (2370 - 3750)	1070 (777 - 1470)	394 (300 - 520)	124 (91 - 168)
NBB (*n* = 16)	43300 (28000 - 66900)	4260 (3290 - 5520)	1940 (1340 - 2830)	663 (484 - 520)	214 (142 - 322)
SBB (*n* = 15)	8640 (6270 - 11900)	2040 (1540 - 2700)	565 (431 - 740)	226 (177 - 290)	69 (57 - 84)
Adult Females	∑PCBs	∑DDTs	∑Chlordanes	∑PBDEs	∑Other Pesticides
All BB (*n* = 6)	891 (574 - 1380)	97 (66 - 143)	39 (31- 51)	21 (14 - 31)	14 (12 - 17)
NBB (*n* = 3)	1460 (1230 - 1720)	140 (90 - 218)	49 (34 - 71)	30 (29 - 30)	17 (16 - 18)
SBB (*n* = 3)	545 (495 - 599)	68 (56 - 82)	32 (28 - 36)	15 (9 - 24)	12 (10 - 14)

[a] ΣOther pesticides include Dieldrin, HCB, and Mirex. Eight females of unknown age are not included in this table.

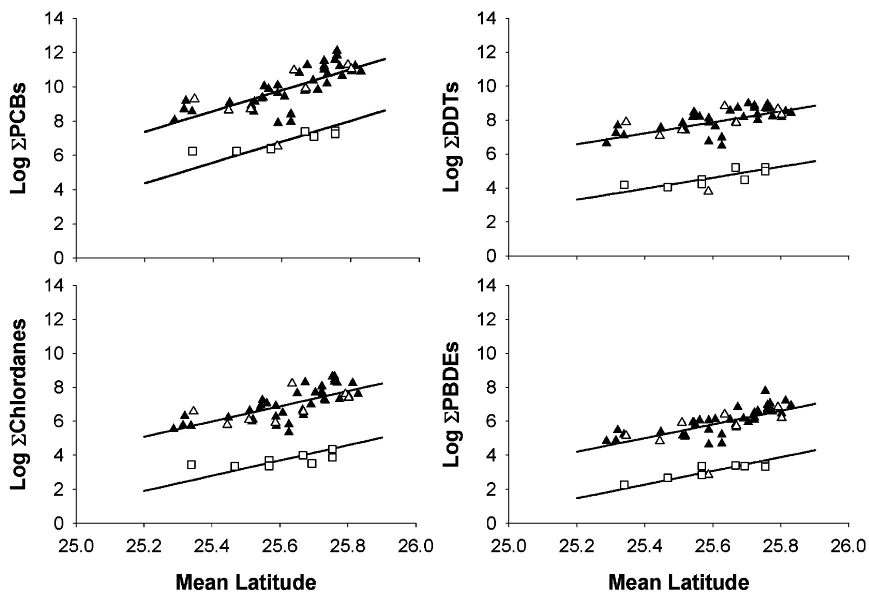

FIGURE 2. Observed and predicted values from a stepwise linear regression model. Open squares (□) represent the observed values for adult females, open triangles (△) represent the observed values for females of unknown age class, and black triangles (▲) represent the observed values for all males and juveniles. Solid lines represent the predicted values based on the linear regression model for adult females and for all other sex/age classes combined.

to observed data indicated a very strong fit and consistent relationship between mean latitude and POP concentrations for all compound classes (Figure 2).

The PCA analysis of the major compound classes indicated that all were positively correlated with each other. Samples that had high PC1 values for one compound class had high values for all compound classes. A high PC1 score was correlated with higher concentrations, while a low PC1 score indicated lower concentrations. The first principal component (PC1) accounted for 74.4% of the variation, while PC2 accounted for an additional 17.4%. The PCA biplot is provided in the Supporting Information (Figure S1). Animals with sighting histories in the northern portion of the bay had higher PC1 scores, indicating higher POP concentrations, than those in the southern portion of the Bay (Figure 1).

The PCA analysis of individual compounds as a fraction of the total indicated similar geographic patterns (Figure 3). PC1 accounted for 83.6% of the variation, and PC2 accounted for an additional 9.6%. A positive PC1 score was correlated with higher percentages of 4,4′-DDE, while a negative PC1 score was correlated with higher percentages of PCB 153 + 132. Dolphins with mean latitudes above 25.61 °N generally had negative PC1 scores, indicating a higher proportion of PCB 153 + 132 relative to 4,4′-DDE. This indicates that the north/south gradient for PCBs in Biscayne Bay is stronger than the DDT gradient. Specifically, the ΣPCBs were 5 times higher in northern Biscayne Bay, whereas ΣDDTs were only twice as high in northern Biscayne Bay.

No clear north/south differences were found for PCB, PBDE, or chlordane congener patterns. A weak trend was found in DDT metabolites with northern animals having a higher fraction of 2′,4′-DDT and 4′,4′-DDD and southern dolphins having a higher fraction of 4′,4′-DDE perhaps resulting from past use of DDT for agriculture in South Miami.

Comparison to Other Studies. Mean Σ15PCB concentrations from all Biscayne Bay (BB) samples, and particularly from the northern Biscayne Bay subgroup (NBB), were higher than those reported for other U.S. east coast estuaries (Figure 4). Σ15PCBs in southern Biscayne Bay (SBB) were lower than Beaufort and Charleston and comparable to Indian River Lagoon (IRL). ΣDDTs and dieldrin were lower in BB than in Beaufort and Charleston and were comparable to IRL and Florida Bay (FB). ΣChlordanes were highest in NBB, while the average for BB was comparable to Beaufort and Charles-

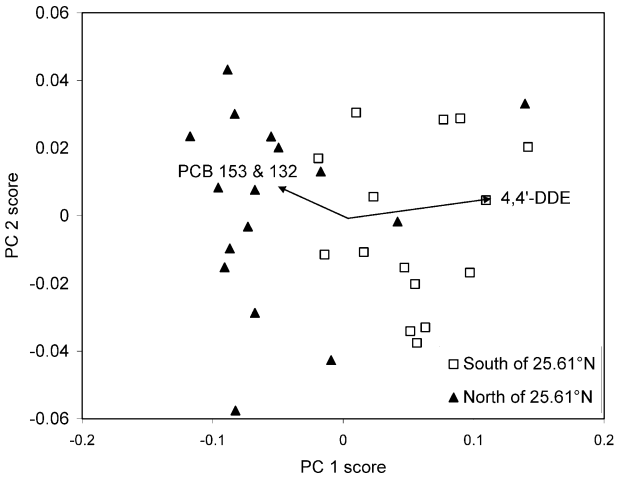

FIGURE 3. PCA, covariance matrix biplot of all compounds expressed as a fraction of total for each sample. PC1 accounted for 83.6% of the variation. Samples are plotted by the mean latitude of sighting histories. Animals from north of 25.61 °N had a higher proportion of PCBs as compared to DDTs.

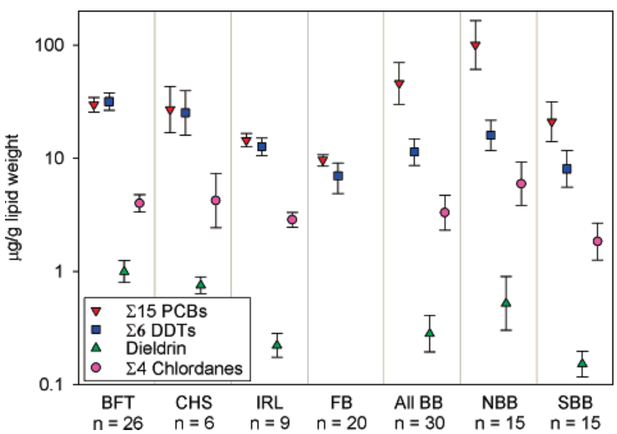

FIGURE 4. Concentrations in µg/g lipid in male dolphins by location plotted on a log scale. Data from all Biscayne Bay male samples (All BB) and the subgroups of Biscayne Bay samples (NBB: north of 25.61 °N and SBB: south of 25.61 °N) were compared to published values for Beaufort, NC (BFT), Charleston, SC (CHS), Indian River Lagoon, FL (IRL) (*1*), and Florida Bay, FL (FB) (*20*). The compounds used for comparison were limited to the same 15 PCB congeners, six DDT group compounds, and four chlordane compounds used in Hansen et al. (*1*).

ton. Σ15PCBs were very similar to ΣDDTs in each of Charleston, Beaufort, and IRL; however, BB had considerably higher levels of PCBs than DDTs (Figure 4). While caution should be used in comparing samples from live dolphins to that of stranded dolphins, Σ6PBDEs were higher in NBB and BB (2.4 and 1.6 µg/g lipid, respectively) as compared to samples from bottlenose dolphins stranded on the central west coast of Florida and the IRL (1.3 and 1.1 µg/g lipid, respectively) (*21*).

Discussion

The geographic ranging patterns of bottlenose dolphins in Biscayne Bay have a strong and consistent effect on levels of POPs in their blubber for all major compound classes, including both past-use compounds and currently produced compounds such as PBDEs. The result was consistent for both adult females and other age/sex classes, and the geographic effect was strongest for PCBs, followed by chlordanes, PBDEs, and finally DDTs (Table 1). For example, the geometric mean of Σ73PCBs in dolphins that spent the majority of time in NBB was 5 times higher than that in the southern portions of the bay [geometric mean (GM): 43.3 (95% confidence interval (CI): 28.0−66.9) vs 8.6 (6.3−11.9) µg/g wet mass, respectively], whereas the geometric mean of ΣPBDEs in northern dolphins was 3 times higher than southern dolphins [GM: 663 (95% CI: 484−520) vs 226 (117−290) ng/g wet mass, respectively] (Table 1). The higher POP concentrations for all compound classes in northern dolphins are likely due to the high levels of urban and industrial development in and around the city of Miami. Stormwater runoff from the heavily urbanized area (both directly into Biscayne Bay and into the Miami River tributary) is considered to be the primary source of contaminants to northern and central Biscayne Bay (*12*). The differences in the magnitude of the geographic effects for different compound classes can be visualized by the slope of the line in Figure 2. The higher slope for PCBs implies more localized point sources in northern Biscayne Bay, whereas the shallower slopes for PBDEs, DDTs, and chlordanes imply a more regional source, perhaps from residential and agricultural uses.

The mean latitude of the sighting histories provides a continuous variable for geographic reference of the samples without requiring an a priori division of the data. However, the use of the mean latitude has limitations in that it does not account for the area of the dolphin's home range. The dolphins sampled had an average minimum convex polygon home range area of 169 km^2 with a minimum area of 34 km^2 and a maximum area of 420 km^2. Dolphins with either a very large or a small home range could share the same mean latitude. There was also variation in the numbers of sightings for different animals that were used to calculate the mean. Some mean latitudes were based on a single sighting (non-catalogue specimens), while others were calculated from >40 sightings. It is possible that some of the animals not matched to the catalogue were migrants or recent immigrants to Biscayne Bay. Each of these potential sources of error would result in reduced precision in inferred spatial ranging patterns. Despite this lack of precision, the regressions were highly significant and had strong explanatory power. Both greater intensity of photo-ID effort and directed studies of animal movements within Biscayne Bay will be necessary to better describe animal ranges and characterize their exposure to POPs as a function of habitat use.

Baseline levels of POPs in Biscayne Bay dolphins were high as compared to published studies in other estuaries of the U.S. and the world. The Σ15PCBs in Biscayne Bay dolphins were higher than in Charleston, SC and Indian River Lagoon, FL (*1*). However, results from a more recent study (*22*) suggest that blubber PCB concentrations in Charleston and IRL dolphins are higher than those stated in Hansen et al. (*1*). This is possibly due to the expansion of sampling area or temporal variation. A recent review article listed the POP concentrations in male bottlenose dolphins in 15 published studies from around the world (*23*). The ΣPCBs, ΣDDTs, and Σchlordanes from BB dolphins were higher than the majority of studies listed. PBDEs are a growing concern in the scientific community because of their ongoing production, similar properties to PCBs, and their presence in the oceanic and coastal food chains (*24*). There are few published studies on PBDEs in bottlenose dolphins from the U.S. east coast. ΣPBDEs were higher than those listed for Florida from 2000 to 2004 (*21*) and lower than some of those found in the Gulf of Mexico in 1990 (*23*). The PBDE congener profiles were similar between north and south Biscayne Bay dolphins, and these profiles were also comparable to those seen in other studies of delphinids in the Gulf of Mexico, western North Atlantic Ocean, and Mediterranean Sea (*21*, *25*, *26*). Caution should be used in interpreting these comparisons because the same congeners may not have been used between studies and the majority of samples in these studies were from dead, stranded animals.

Kannan et al. (*27*) estimated a threshold PCB concentration of 17 μg/g lipid for adverse effects in marine mammals. If this level is accurate, then the majority of dolphins sampled in Biscayne Bay is at risk, especially dolphins north of 25.61 °N, which have a geometric mean of PCB concentrations more than 5 times higher than this threshold level. A recent risk-assessment study estimated the risk of reproductive failure for primiparous females in the Beaufort, NC population at 60% higher than the background incidence of reproductive failure (*28*). Given that the geometric mean of PCBs in Biscayne Bay dolphins was very similar to Beaufort dolphins, and the levels in northern Biscayne Bay dolphins were higher than Beaufort dolphins, we would expect to see a similar or greater risk of reproductive failure for primiparous females in Biscayne Bay. In a case-control study of stranded harbor porpoises, those that died of infectious disease had higher levels of PCBs than the control group that died of physical trauma. The risk of dying from an infectious disease doubled at a total PCB concentration of 45 μg/g lipid (*29*). While caution should be used in comparing across species because immune function effects of PCBs may vary among species, the levels of PCBs in northern Biscayne Bay dolphins were more than double this value, indicating the potential for significant immunological effects of PCB exposure.

PCB and DDT concentrations in dolphin tissues were generally similar within each of the comparison estuaries along the U.S. east coast (Figure 4). However, Biscayne Bay dolphins had much higher levels of PCBs as compared to DDTs. This was supported by the PCA of compounds expressed as a fraction of total, which indicated that dolphins in northern Biscayne Bay have a higher proportion of PCBs to DDTs than dolphins in southern Biscayne Bay. PCBs were used primarily in industrial applications, and historical sources for PCBs were concentrated in and around the city. In contrast, DDTs were used primarily in agriculture. Much of southern Dade County was farmland, and DDTs likely entered Biscayne Bay through runoff from these agricultural areas. It also appears that DDT inputs in south Florida may not have been as high as other areas in the U.S. such as Beaufort and Charleston. The results from this study suggest that geographic variation in sources for different compound classes is propagated through the food chain and is reflected in bottlenose dolphin tissue concentrations.

While other studies have examined geographic differences in POPs in cetaceans, these have generally compared locations several hundred to thousands of kilometers apart (*1*, *3*, *5*, *30*). This is the first time that large POP differences have been demonstrated within a localized population of dolphins on such a small geographic scale, and it highlights the importance of fine-scale sampling throughout the estuary to adequately represent the overall POP profile in resident dolphin populations. It also indicates that movement and home range patterns can influence POP patterns within a population. Therefore, understanding the movement patterns and foraging ecology of the dolphins studied is important for interpreting POP data.

Investigating baseline concentrations and patterns of POPs in dolphin populations is critical for future risk assessment studies and for monitoring changes in anthropogenic impacts over time. Differences in POP profiles can exist within a population and may result in differential health impacts to different segments of the same population. Live capture and release health studies of bottlenose dolphins are being conducted along the U.S. Atlantic coast to assess the potential health effects of various environmental stressors including POPs (*31*). The Biscayne Bay population is an ideal candidate for such a study to quantify the health and physiological effects of the observed exposure to POPs.

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Supporting Information Available

Geometric mean (GM) and 95% confidence intervals for males and juveniles followed by adult females for each compound in ng/g wet mass, regression coefficients and analysis of variance tables for linear regressions of major compound classes, average percent difference for each compound class listed for each animal sampled in duplicate, and PCA correlation matrix biplot using data from male and juvenile samples summed by compound class. This material is available free of charge via the Internet at http://pubs.acs.org.

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