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TOXAPHENE AND PBDEs IN ATLANTIC WHITE-SIDED AND ROUGH-TOOTHED DOLPHINS

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Introduction

Due to their persistence and highly lipophilic nature, many persistent organic pollutants [POPs] bioaccumulate and biomagnify in the food chain [*e.g.*, 1,2]. POP residues have been detected in all levels of aquatic biota ranging from phytoplankton to marine mammals [3]. Biological effects of these compounds on mammals include hepatocellular carcinoma, reproductive, endocrine, and developmental toxicity, immunotoxicity, and wasting syndrome [4]. Toothed whales (odontocetes) are particularly susceptible to bioaccumulation and the effects of POPs due to many factors including their relatively high trophic position, long life spans, limited metabolic capability to degrade chemical contaminants, and reproductive strategies [5].

There have been few measurements of Toxaphene or polybrominated diphenylether congeners (PBDEs) in dolphins from the US East Coast [6, 7]. Given the high concentrations of other POPs, such as PCBs and organochlorine pesticides observed in some coastal and offshore dolphins (approaching 100 mg/kg), it is anticipated that levels of toxaphene and PBDEs may be of similar magnitude [6, 7]. The goal of this investigation was to determine levels of POPs including toxaphene and PBDEs in the Atlantic white-sided dolphin (*Lagenorhynchus acutus*) and the rough-toothed dolphin (*Steno bredadensis*) especially as a function of age and gender.

Materials and Methods

Samples of blubber from 47 Atlantic white-sided dolphins (23 females and 24 males) were collected from 1993-2000 from animals that mass stranded on Cape Cod. Samples of blubber from 15 rough-toothed dolphins (9 females and 6 males) were collected in 1997 from a mass stranding of these animals on the north shore of the Gulf of Mexico. All samples were collected using methods established for the collection of marine mammals for long term archiving in the National Marine Mammal Tissue Bank [8]. Discreet ages were obtained for 20 white-sided dolphins and 13 rough-toothed dolphins by enumerating growth layers from sectioned, stained teeth.

Methods for the analysis of PCBs and organochlorine pesticides have been detailed elsewhere [9], but are summarized here. One gram samples of cryohomogenized blubber were mixed with sodium sulfate and added to pressurized fluid extraction (PFE) cells. A mixed internal standard was added and the samples were extracted with dichloromethane. High-molecular weight compounds were removed by size exclusion chromatography and the cleaned-up extracts were fractionated by LC using an aminopropyl silane column. Samples were analyzed using GC-MS (Agilent 6890-5973, Palo Alto, CA) for approximately 50 PCB congeners and 20 organochlorine pesticides. The compounds were separated

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using a 60 m DB-5 column (J&W Scientific, Folsom, CA) and the signal from selected ions were acquired with the instrument operated in the electron impact mode.

Toxaphene and PBDEs were determined in recombined sample fractions. Total toxaphene was determined using the instrument above operated in the negative chemical ionization mode using a method modified from [10] to include rigorous peak matching and ion ration checking. In addition, four toxaphene congeners, congeners 26, 32, 50, 62 were also quantified. PBDEs were determined in the recombined samples using the instrument above equipped with a 30 m DB-5 column. PBDE congeners 47, 99, 100, 153, and 183 were determined from the response of selected ions with the instrument operated in the electron impact mode.

Results and Discussion

The concentrations of POPs determined in the Atlantic white-sided and rough-toothed dolphin are shown in Table 1. Mean Σ PBDE concentrations were comparable in the two species, with male concentrations higher than female. Toxaphene concentrations (Table 1) were higher in male and female white-sided dolphins (10990 ng/g wet wt. (4210 ng/g wet wt.) versus 5410 ng/g wet wt. (7420 ng/g wet wt)) than in rough-toothed dolphin males and females (3420 ng/g wet wt. (1530 ng/g wet wt.) versus 1990 ng/g wet wt. (1520 ng/g wet wt.)). In general, POP concentrations were greater in the white-sided dolphin than in the rough-toothed dolphin, with the exception of mirex and Σ PCBs, which were higher in the rough-toothed dolphin. Mirex was at one time heavily used in the Southeast US to control fire ants. The reason for the higher PCB levels is being investigated.

Of the four toxaphene congeners measured, congeners 26 and 50 were found in the highest concentration. In white-sided dolphins, toxaphene congener 26 was 4.6 % (1.2 %) and 4.9 % (1.8 %) of total toxaphene and congener 50 was 6.1 % (1.5 %) and 6.5 % (1.5 %) of total toxaphene in males and females, respectively. In the rough-toothed dolphin, congener 26 was 3.2 % (0.8 %) and 4.2 % (2.1 %) of total toxaphene and congener 50 was 7.8 % (1.1 %) and 8.6 % (2.1 %) of total toxaphene in males and females, respectively. Total toxaphene concentrations were lower than previously observed in the white beaked dolphin (*L. albirostris*) by Muir *et al.* [6]. Toxaphene concentrations were 46000 ng/g wet wt. (22000 ng/g wet wt.) and 38200 ng/g wet wt. (10700 ng/g wet wt.) in males and females, respectively.

Persistent organic contaminants concentrations were influenced by age and gender. For instance, adult female white-sided dolphins had significantly lower concentrations of Σ PCBs, Σ Chlordanes, toxaphene and Σ DDTs. The same was true for rough-toothed dolphins. There was no relationship between discreet age and POP concentration for male white-sided dolphins, but a significant negative relationship for females was observed.

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Table 1. Concentrations of POPs in rough-toothed and white-sided dolphins. Values are the mean and 1 SD (in parentheses).

| Compound | Rough-toothed Dolphin (ng/g wet wt.) | | White-sided Dolphin (ng/g wet wt) | |
|---------------------|---|----------------|--------------------------------------|---------------|
| | Female $(n = 9)$ | Male $(n = 6)$ | Female $(n = 23)$ | Male (n = 24) |
| ΣPBDE | 1100 (935) | 1820 (820) | 1530 (1400) | 2530 (990) |
| toxaphene | 1990 (1520) | 3420 (1530) | 5410 (7420) | 10990 (4210) |
| ΣΡĊΒ | 25900 (16900) | 46900 (20400) | 20390 (16500) | 30300 (10300) |
| Σ Chlordanes | 3670 (4010) | 4060 (2460) | 6344 (6250) | 8030 (2900) |
| ΣDDT | 14100 (12200) | 22100 (12200) | 11400 (10800) | 15400 (4736) |
| mirex | 376 (131) | 710 (373) | 49.2 (25) | 71.0 (22) |
| dieldrin | 306 (11) | 467 (578) | 1190 (1050) | 1580 (542) |
| ΣΗCH | 23.0(11) | 59.5 (85) | 199 (128) | 253 (161) |