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Bioaccumulation of organohalogenated compounds in sharks and rays from the southeastern USA

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ABSTRACT

Organohalogenated compounds are widespread in the marine environment and can be a serious threat to organisms in all levels of aquatic food webs, including elasmobranch species. Information about the concentrations of POPs (persistent organic pollutants) and of MeO-PBDEs (methoxylated polybrominated diphenyl ethers) in elasmobranchs is scarce and potential toxic effects are poorly understood. The aims of the present study were therefore to investigate the occurrence of multiple POP classes (PCBs, PBDEs, DDXs, HCB, CHLs) and of MeO-PBDEs in various elasmobranch species from different trophic levels in estuarine and marine waters of the southeastern United States. Overall, levels and patterns of PCBs, PBDEs, DDXs, HCB, CHLs and of MeO-PBDEs varied according to the species, maturity stage, gender and habitat type. The lowest levels of POPs were found in Atlantic stingrays and the highest levels were found in bull sharks. As both species are respectively near the bottom and at top of the trophic web, with juvenile bull sharks frequently feeding on Atlantic stingrays, these findings further suggest a bioaccumulation and biomagnification process with trophic position. MeO-PBDEs were not detected in Atlantic stingrays, but were found in all shark species. HCB was not found in Atlantic stingrays, bonnetheads or lemon sharks, but was detected in the majority of bull sharks examined. Comparison with previous studies suggests that Atlantic stingrays may be experiencing toxic effects of PCBs and DDXs on their immune system. However, the effect of these compounds on the health of shark species remains unclear.

1. Introduction

Persistent organic pollutants (POPs) can bioaccumulate and biomagnify through food webs, and are of particular concern for top predators that typically contain the highest concentrations (Ross, 2000; Kelly et al., 2007). Top predators within marine environments typically include marine mammal and shark species. Numerous studies have found elevated levels of POPs in the tissues of marine mammals, as well as adverse effects that can be linked to those POP levels. Indeed, it has been shown in top predator species, such as harbor seals (*Phoca vitulina*), bottlenose dolphins (*Tursiops truncatus*) and polar bears (*Ursus maritimus*), that pollutants can reach high concentrations with negative effects on reproductive, immune and endocrine systems (Ross et al., 1996; Sonne et al., 2009; Schwacke et al., 2012). Marine mammals accumulate pollutants primarily via uptake through their diet and this may also be true for sharks. Shark species, however, may have a minor additional pathway for uptake, as there is also a substantial water flow and subsequent potential chemical uptake via gill respiration.

Toxicological studies are available for teleost fish and, to a lesser extent, also for sharks. Effect studies have been performed in several fish species like Atlantic salmon (*Salmo salar*), European flounder (*Platichthys flesus*) or Japanese medaka (*Oryzias latipes*) in the wild as well as in the lab (Nirmala et al., 1999; Vigano et al., 2001; Muirhead et al., 2006; Lerner et al., 2007; Nakayama and Oshima, 2008). Effects studies on sharks typically focus on smaller shark species, such as the spiny dogfish (*Squalus acanthias*, De Boeck et al., 2001; Eyckmans et al., 2013), since many larger shark species are difficult to maintain in captivity in adequate numbers and can be protected by conservation regulations. POP monitoring

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studies are frequently conducted on teleost fish, but are relatively scarce for sharks (Schlenk et al., 2005; Gelsleichter et al., 2005 and 2008; De Azevedo e Silva et al., 2009).

Chondrichthyan fishes (i.e. sharks, rays, skates, sawfishes and chimaeras) are an evolutionarily conservative group with diverse life histories and complex reproductive strategies. We examined one species of ray (Atlantic stingray – *Dasyatis sabina*) and three shark species (bonnethead – *Sphyrna tiburo*; lemon shark – *Negaprion brevirostris*; bull shark – *Carcharhinus leucas*).

Atlantic stingrays are a common benthic species in coastal waters of the southeastern USA, including the Gulf of Mexico, which occupies a wide range of habitats (freshwater, estuarine, or marine) and prefers depths less than 25 m (Funicelli, 1975; Johnson and Snelson, 1996). They prey upon small benthic crustaceans, polychaetes, echinoderms, and to a lesser extent, small fishes (Cook, 1994; Kajiura and Tricas, 1996). Atlantic stingrays are an aplacental viviparous species where embryos rely primarily on yolk for the first period of development, after which they survive on histotroph or uterine milk enriched with proteins and lipids (Snelson et al., 1988; Bone and Moore, 2008).

Bonnetheads are an abundant coastal shark species in estuarine and marine waters of the southeastern U.S. This hammerhead shark species is a dietary specialist that feeds principally on crustaceans, with crabs being a dominant prey, along with lesser amounts of mollusks and small fishes (Cortés et al., 1996; Lessa and Almeida, 1998; Bethea et al., 2007; Olin et al., 2013). The reproductive mode of bonnetheads is placental viviparity, and many estuarine and shallow nearshore waters of the southeastern USA serve as nursery grounds for this species (Heupel et al., 2006; Bethea et al., 2006).

Lemon sharks typically reside in shallow estuarine or nearshore coastal habitats as small juveniles (Reyier et al., 2008), but move to more open ocean waters at maturity (Morrissey and Gruber, 1993). Juvenile lemon sharks typically feed on a wide array of teleost fishes, with lesser amounts of crustaceans, elasmobranchs, and mollusks (Cortés and Gruber, 1990; Reyier et al., 2008). Lemon sharks are a placental viviparous species with direct transfer of nutrients from pregnant females to embryos through a yolk-sac placenta (Feldheim et al., 2002). This species is currently classified as 'near threatened' on the IUCN Red List, and are fully protected within Florida waters (FWC, 2014).

Bull sharks are one of the few completely euryhaline shark species, inhabiting estuarine and freshwater rivers throughout its range (Thorson, 1971; Thomerson et al., 1997). Shallow estuarine areas serve as nursery grounds for small juveniles, after which they move to coastal ocean waters as they begin to mature (Curtis et al., 2011). Adults have been found to migrate over fairly long distances (Carlson et al., 2010; Tillett et al., 2012). These sharks are opportunistic predators with a large variation in their diet spanning from teleost fishes to elasmobranchs, seabirds and marine mammals. As juveniles, they typically feed on small teleost fishes, Atlantic stingrays and lesser amounts of crustaceans (Snelson et al., 1984; Adams, unpublished data).

All species investigated in the present study were collected from estuarine waters of Indian River Lagoon (IRL) system on the Atlantic coast of Florida or adjacent nearshore waters of the Atlantic Ocean. The IRL is a shallow, estuarine system that occupies approximately one-third of Florida's central Atlantic coast and is considered one of the most diverse estuaries in North America. The IRL is a critical nursery ground for bull sharks (Curtis et al., 2011). Nearshore waters of the adjacent Atlantic Ocean in the area near Cape Canaveral, FL are critical nursery areas for many shark species including bonnetheads and lemon sharks (Adams and Paperno, 2007; Reyier et al., 2008). The IRL region has been suffering from long-term, large-scale mortality events across multiple species such as the Florida manatee (*Trichechus manatus latirostris*), bottlenose dolphin (*Tursiops truncatus*) and brown pelican (*Pelecanus occidentalis*) in recent years. Considering the known negative effects of POPs on marine mammals and teleost fish, it is important to better understand the concentrations of POPs in elasmobranch species that serve as key predators in many aquatic ecosystems. As such, the goal of the present study was to investigate the occurrence and patterns of POPs in sharks and rays from coastal waters of the southeastern USA.

2. Materials and methods

2.1. Samples

A total of 53 liver samples were analyzed for POPs and MeO-PBDEs (methoxylated polybrominated diphenyl ethers), which are organohalogenated compounds with a potentially natural origin (Haraguchi et al., 2009). These samples were from 4 different species (Atlantic stingray – *Dasyatis sabina*; bonnethead shark – *Sphyrna tiburo*; lemon shark – *Negaprion brevirostris*; bull shark – *Carcharhinus leucas*; Table 1). For two species (Atlantic stingray and bonnethead), stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) in muscle samples were also analyzed (15 samples in total; Table 1) from the same animals as included in the POP analyzes giving matched liver and muscle samples. All fish were collected from estuarine waters of Indian River Lagoon (IRL) system on the Atlantic coast of Florida or from adjacent nearshore waters of the Atlantic Ocean from north of Cape Canaveral, Florida (latitude 28° 40′N) south to Sebastian Inlet, Florida (latitude 27° 50′N) during 2009 to 2012. For the POP analysis, 38 PCB (polychlorinated biphenyls) congeners, 6 PBDEs (polybrominated diphenyl ethers), 6 DDXs (dichlorodiphenyltrichloroethane and metabolites and isomers), HCB (hexachlorobenzene), 5 chlordanes (CHLs) and 4 MeO-PBDEs were targeted in all liver samples (Table S2).

2.2. Sample preparation and POP analysis

Approximately 0.2 g of liver was spiked with internal standards BDE 77 and CB 143 and extracted by hot Soxhlet for 2 h with hexane/acetone (3/1; v/v). After lipid determination performed on an aliquot of the extract (typically 1/8th), the extract was cleaned on 8 g of acidified silica and analytes were eluted with 20 ml hexane and 15 ml dichloromethane. The cleaned extract was evaporated to dryness and reconstituted in 150 μl iso-octane. Details of the analytical methods are given in Weijs et al. (2009) and are briefly given here. PBDEs, MeO-PBDEs and CHLs were measured by GC-ECNI/MS (gas chromatography-electron capture negative ion/mass spectrometry) on a 30 m × 0.25 mm × 0.25 μm DB-5 column by monitoring ions $m/z=79$ and 81 (for PBDEs and MeO-PBDEs) and 2 specific ions for each CHL. PCBs and DDXs were measured by GC-EI/MS (gas chromatography-electron ionization/mass spectrometry) on a 25 m × 0.22 mm × 0.25 μm HT-8 column by monitoring 2 ions for each homolog group. This system was also used to confirm MeO-PBDEs.

Table 1
Overview of the number of samples of all species analyzed in this study. Gray indicates muscle tissue, white indicates liver tissue. Atlantic stingray – *Dasyatis sabina*; bonnethead – *Sphyrna tiburo*; bull shark – *Carcharhinus leucas*; lemon shark – *Negaprion brevirostris*.

	Atlantic stingray	Bonnethead	Lemon shark	Bull shark
Trophic transfer (TT)	14	19	12	8
Stable isotopes (SI)	14	1		