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Baseline

Persistent organic pollutants in liver of Brazilian sharpnose shark (*Rhizoprionodon lalandii*) from southeastern coast of Brazil

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ABSTRACT

In the present study, persistent organic pollutants (POPs) were determined in 14 livers from specimens of the Brazilian sharpnose shark (*Rhizoprionodon lalandii*), which is an important economic resource for small-scale fisheries on the southeastern coast of Brazil. The following concentrations (lipid weight) of POPs were found: ∑PCBs: 1019 ± 267 ng g^{-1}; ∑DDTs: 111 ± 40 ng g^{-1} and ∑PBDEs: 10.4 ± 4.78. PCB 153 made the greatest contribution to ∑PCB (21.4%), followed by PCB 138 (14.6%) and PCB 180 (9.94%). Among chlorinated pesticides, only the *p,p′*-DDE and *p,p′*-DDD isomers had concentrations above the detection limit. Moreover, levels above the detection limit were found only for PBDE congeners 47 and 100 (BDEs 47 > 99). On average, BDE 47 accounted for 88% of the total PBDE load. The feeding habits of the Brazilian sharpnose shark close to the Brazilian coastline are likely the most important difference regarding the accumulation of POPs in comparison to oceanic species that feed in deeper waters. Thus, this species may be used to evaluate the pollution of coastal areas as well as human exposure to contaminants, as the Brazilian sharpnose shark is a frequently used for human consumption. Further studies in other areas of Brazil and involving other species are needed to clarify the mechanisms and potential impact of POPs, which can affect the biology of different organisms and cause population declines.

Persistent organic pollutants (POPs), such as chlorinated pesticides, polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), are widely distributed compounds that biomagnify throughout the food chain (Ritter et al., 1995; UNEP, 2002). Thus, top predators, such as sharks, have higher concentrations of these compounds than primary consumers and are particularly vulnerable to contamination.

The Brazilian sharpnose shark [*Rhizoprionodon lalandii* (Müller and Henle, 1838)] is a small demersal placental viviparous species that has been recorded from Panama to Uruguay. This species inhabits shallow coastal waters (3–70 m in depth) of the western Atlantic over sandy and muddy bottoms (Compagno, 1984; Gadig et al., 2002; Motta et al., 2007; Menni and Lucifora, 2007) and plays an important role as a predator in the coastal ecosystem, feeding on small teleost fish, shrimps and squids (Compagno, 1984). Populations are known to be in decline due to overfishing in northern Brazil. The Brazilian sharpnose shark was once one of the most abundant elasmobranches in coastal fisheries in the state of Maranhão, but is currently rarely found in this area. Increased mortality of all age classes in coastal fisheries, as occurs off the state of São Paulo (southeastern Brazil), threatens heavily exploited populations of this species (IUCN, 2012), which remains an important economic resource for small-scale fisheries, representing 60% of total shark landings in the state (Mendonça et al., 2009).

Despite the large number of studies on POP contamination in sharks worldwide (Storelli and Marcotrigiano, 2001; Storelli et al., 2005; Cornish et al., 2007), few investigations have been carried out in Brazilian waters (Azevedo-Silva et al., 2007, 2009) and none have involved the Brazilian sharpnose shark. Thus, the aim of the present study was to investigate the occurrence of organochlorine pesticides, PCB and PBDE congeners in the liver of specimens of the Brazilian sharpnose shark on the southeastern coast of Brazil.

Juvenile Brazilian sharpnose sharks ($n = 14$; 4 males and 10 females) were captured by trawling operations in 2008 on the continental shelf off the state of São Paulo, Brazil. No adult was captured in that occasion. Total length ranged from 48 to 62 cm.

Liver samples were analyzed based on procedures described by MacLeod et al. (1985). Initially, all liver samples were macerated and homogenized using an Ultra Turrax® IKA® T18 Basic. Approximately 0.25 g of tissue were then dried with Na_2SO_4 and

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extracted with 80 mL hexane:dichloromethane (1:1 v/v) for 8 h using a Soxhlet extractor. Prior to extraction, PCB 103 and PCB 198 were added to all samples, blanks and reference material as surrogates. The extracts were purified using partially deactivated (5%) silica:alumina column chromatography with a 1:1 mixture of n-hexane and dichloromethane. The tissue fraction was further purified using high-performance liquid chromatography with gel permeation columns to remove lipids that was gravimetrically determined, and finally concentrated to a volume of 0.5 mL in hexane. Tetrachlorometaxylene was added prior to the gas chromatographic analysis as the internal standard.

Organochlorine pesticides and PCBs were analyzed using an Agilent 6890N Network gas chromatograph (GC) with a Ni-63 electron capture detector. The GC system was equipped with a 5% phenyl methyl siloxane HP-5MS capillary column measuring 30 m in length, 0.25 mm in inner diameter and 0.25 μm in thickness. The column temperature was programmed at 70 °C for 1 min, increasing at 40 °C min^{-1} to 170 °C, then increasing at 1.5 °C min^{-1} to 240 °C, held for 2 min and increasing at 15 °C min^{-1} to 300 °C, with a final hold of 5 min. The injector and detector temperatures were set to 280 °C and 320 °C, respectively. Hydrogen and nitrogen were used as the carrier and make-up gases, respectively.

PBDEs were analyzed using an Agilent 6890 Series gas chromatograph coupled with an Agilent 5973 Network Mass Selective Detector with electron impact at 70 eV. The chromatograph was equipped with a similar column as that used for organochlorine analysis, with helium as the carrier gas. The column temperature was programmed at 70 °C for 1 min, increasing at 12 °C min^{-1} to 154 °C, then increasing at 2 °C min^{-1} to 210 °C and increasing at 3 °C min^{-1} to 300 °C, with a final hold of 5 min. The injector and interface temperatures were set to 270 °C and 300 °C, respectively. Acquisition was performed in selected ion mode.

Quality assurance and quality control were based on Wade and Cantillo (1994) and included the analysis of the procedural blank, blank spike, matrix spike, matrix duplicate and standard reference material (SRM 1945 – Organics in Whale Blubber from the National Institute of Standards and Technology), which were processed with the samples.

Table 1 displays the mean concentrations, standard deviations and ranges of PCBs, PBDEs and organochlorine pesticides investigated in the Brazilian sharpnose shark. Analysis involved 51 individual PCB congeners (8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 77, 87, 95, 97, 99, 101, 105, 110, 114, 118, 123, 126, 128, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 169, 170, 174, 177, 180, 183, 187, 189, 194, 195, 199, 201, 203, 206 and 209.), 7 PBDE congeners (28, 47, 99, 100, 153, 154 and 183), DDTs (o,*p*′-DDT, *p*,*p*′-DDT, o,*p*′-DDD, *p*,*p*′-DDD, o,*p*′-DDE and *p*,*p*′-DDE), chlordanes (α- and γ- chlordane, oxychlordane, heptachlor and heptachlor epoxide), HCB, HCHs (α-, β-, γ-HCH), drins (aldrin, dieldrin,isodrin and endrin) and mirex.

Table 1
Mean concentrations, standard deviations (SD) and ranges (ng g^{-1} lipid weight) of PCBs, PBDEs and organochlorine pesticides in livers from the Brazilian sharpnose shark on the southeastern coast of Brazil.

Compounds	Mean	SD	Range
ΣPCBs	1019	267	691–1454
ΣPBDEs	10.4	4.78	<4.00–18.1
ΣDDTs	111	40	44.3–176
ΣHCHs	<1.96	–	–
ΣDRINs	<1.92	–	–
ΣChlordanes	<1.08	–	–
HCB	<3.48	–	–
Metoxichlor	<1.12	–	–
Mirex	<2.72	–	–
%Lipid	28	6	22–34

Among the POPs studied, PCBs had the highest concentrations in the livers of the Brazilian sharpnose shark, followed by DDTs > PBDEs (Table 1). The other chlorinated pesticides analyzed did not occur above the detection limit. No significant differences were found between male and female individuals, as all specimens were juveniles. PCB levels ranged from 691 to 1454 ng g^{-1} lipid weight (lw), which are only slightly lower than those reported in livers from the blue shark (*Prionace glauca*) (953–3040 ng g^{-1} lw) and kitefin shark (*Dalatias licha*) (1522–2357 ng g^{-1} lw) from a highly urbanized, industrialized region in the Mediterranean Sea (Storelli et al., 2005). PCB concentrations in the Brazilian sharpnose shark were one to two orders of magnitude higher than those reported in livers of the blue shark from other sites along the Brazilian coast (12.9–34.8 ng g^{-1} lw) (Cascaes, 2009) and higher than levels detected in muscle tissue of the smooth hammerhead (*Sphyrna zygaena*), shortfin mako (*Isurus oxyrinchus*) and bigeye thresher (*Alopias superciliosus*) reported by Azevedo-Silva et al. (2009). However, caution should be exercised in these comparisons, as the liver has much higher percentages of lipids and is the therefore the largest reservoir of organochlorines in the shark body.

The higher values found in the Brazilian sharpnose shark may be related to the behavior, as this species lives associated to the seafloor and the environmental cycling of sediments is one of major routes of PCBs to aquatic environments (Borja et al., 2005). Moreover, the Brazilian sharpnose shark is a coastal species and POP contamination is greater near the coast than in the open ocean. This is particularly true on the southeastern coast of Brazil, which has two of the most economically important metropolitan regions in South America (São Paulo and Rio de Janeiro) as well as the Port of Santos, which is the most important harbor in Latin America and a significant source of contamination (Lamparelli et al., 2001; De Souza et al., 2008).

The main sources of PCBs to the marine environment are industrial or urban effluents discharged into rivers and lakes and the fumes arising from the incineration of products containing those compounds. PCBs with lower degree of chlorination are more susceptible to biodegradation – as well as absorption and excretion in organisms (WHO, 1992). In the present study, penta to octa PCB congeners were the major contributors in the shark liver samples. In the relative distribution of PCB homologues, hexachlorobiphenyls were the predominant class (48.3%), followed by hepta- (21.2%), penta- (16.1%), tetra- (7.7%), octa- (4.3%), di- (2.26%) and trichlorobiphenyls (0.11%), whereas nona- and decachlorobiphenyls were at concentrations below the detection limit in all samples. Individually, PCB 153 made the greatest contribution to ∑PCB (21.4%), followed by PCB 138 (14.6%) and PCB 180 (9.94%).

Among organochlorine pesticides, only the *p*,*p*′-DDE and *p*,*p*′-DDD isomers were at concentrations above the detection limit. ∑DDT levels ranged from 44.3 to 176 ng g^{-1} lw (mean: 110 ± 40 ng g^{-1} lw), which are lower than the values detected in the longnose spurdog (*Squalus blainvillei*) from the Mediterranean Sea (1257–2443 ng g^{-1} wet weight) (Storelli and Marcotrigiano, 2001).

The technical formulation of DDT is a mixture of isomers, mainly *p*,*p*′-DDT and lesser amounts of *o*,*p*′-DDT. Other compounds, such as DDD and DDE, also are found in small amounts. However, these two metabolites are found in environmental analyses, since they are degradation products of DDT. The environmental or biological degradation of an HCl molecule of *p*,*p*′-DDT leads to the formation of DDE, which is more resistant than both DDT and DDD (WHO, 1979). The application of DDT in Brazil, in agriculture and against vector that causes malaria is not allowed since 1985 and 1998, respectively. However, just through the Law 11.936/2009 the manufacture, import, export, stock keeping, marketing and use of DDT were definitely forbidden (Brazil, 2009).

Although *p,p′*-DDE only accounts for 5% of the technical formulation of DDT, this compound was predominant in the liver samples of the Brazilian sharpnose shark, averaging 93%. This pattern has also been observed in the blue shark on the Brazilian coast, but with a lower percentage of *p,p′*-DDE among the total DDTs (52.2%) (Azevedo-Silva et al., 2007). Storelli et al. (2005) report a rate of approximately 81.5% of this metabolite in the blue shark from the Mediterranean Sea. These results confirm the greater persistence and considerable potential for accumulation in organisms (WHO, 1979).

Among PBDEs, only BDE 47 and BDE 100 were found at concentrations above the detection limit. In the Brazilian sharpnose shark, BDE 47 accounted for an average of 88% of the total PBDE load, with a mean concentration of 9.86 ng g^{-1} (range: not detected to 18.1 ng g^{-1} lw). PBDE flame retardant formulas available in the Americas. (e.g. technical Bromkal 70-5DE) contains approximately 37%, 35% and 6.8% of the congeners 47, 99, and 100, respectively (Sjödin et al., 1998). However, since the concentrations are too low it is difficult to evaluate the distribution of the PBDE congeners in the shark liver samples.

PBDEs analyzed in other species on the Brazilian coast exhibit the pattern BDE 47 > BDE 99 > BDE 100, which suggests the use of the commercial mixture pentaBDE (De Wit, 2002). Although this formulation contains smaller proportions of BDE 47 in comparison to other congeners, its predominance in environmental samples is related to debromination from BDE 99. However, debromination varies among species. According to Stapleton et al. (2004), carp readily debrominate BDE 99 to BDE 47, whereas the rainbow trout debrominates certain PBDEs with comparatively lesser efficiency (Stapleton et al., 2006). The absence of BDE 99 in the Brazilian sharpnose shark may suggest a high capacity for the debromination of certain PBDEs.

The Brazilian sharpnose shark proved to be a good indicator of the occurrence of POPs in marine waters along Brazil and may be used to evaluate pollution in coastal areas as well as human exposure to contaminants, as this species is frequently used for human consumption.

Feeding habits and different habitats are probably the most important reasons for the higher contamination levels found in the Brazilian sharpnose shark in comparison to other oceanic sharks. Further studies in other areas of Brazil and involving other species are needed to clarify the mechanisms and potential impact of POPs, which can affect the biology of different organisms and cause population declines.

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