may provide information on the  $^{137}\mathrm{Cs}$  bioconcentration pathway of Baikal seals.

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## Organochlorine compounds in sharks from the Brazilian coast

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Consisting of about 800 species, the elasmobranches are found worldwide, from polar oceans to tropical seas and from surface water to the abyss (Ballantyne, 1997). Sharks have a K-selected life-history strategy and most of the species are top predators, giving sharks an important role in aquatic food webs (Cortés, 1998,2002; Stevens et al., 2000). Due to their food web position, as well as physiological characteristics, sharks may accumulate high levels of organic pollutants.

Organochlorine pesticides and polychlorinated biphenyls (PCBs) are a class of pollutants that are known to bio accumulate in aquatic organisms, especially top predators (Davis, 1993). These compounds may exert different toxic effects on wildlife and human health,

mostly related to the endocrine and immune systems (ATSDR, 2000; 2002). Organochlorine pesticides (OCPs) constitute a group of compounds with different physical and chemical characteristics and environmental distribution patterns (UNEP, 1992,2002). These compounds are neurotoxic and most of them are considered endocrine disruptors (Colosio et al., 2003; LeBlanc et al., 1997). PCBs are synthetic chlorinated hydrocarbon compounds, with a large spectrum of toxic effects such as alterations in the immune and reproductive systems as well as in the thyroid (WHO, 2003).

Few data are available about levels of organochlorine compounds in sharks from the South Atlantic. In this study, we investigated concentrations of PCBs, dichlorodiphenyltrichloroethane (DDT) and its metabolites (DDE and DDD), hexachlorobenzene (HCB) and lindane (gamma-HCH) in muscle samples of smooth hammerhead (*Sphyrna zygaena*), shortfin mako (*Isurus oxyrinchus*)

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**Table 1** Biometric data and organochlorine contamination  $(ng.g^{-1})$  in the analyzed samples.

Biometry	Sphyrna zygaena			Isurus	Alopias
	C-4	C-5	C-15	oxyrinchus	superciliosus
Total length (cm)	264.0	290.1	214.0	218.0	339.0
Weight (Kg)	139.2	190.0	69.6	88.8	124.6
Sex	M	F	M	F	M
Organochlorines					
PCB-08	1.17	0.32	BDL	0.27	0.31
PCB-28	1.70	0.48	0.37	0.47	0.37
PCB-44	0.82	0.20	0.21	0.21	0.20
PCB-49	0.55	BDL	0.09	0.13	0.10
PCB-52	1.47	0.44	0.39	0.41	0.41
PCB-60	0.46	BDL	BDL	0.07	BDL
PCB-66	0.92	0.31	0.30	0.27	0.29
PCB-70	1.19	0.43	0.53	0.27	0.15
PCB-87	0.58	0.16	0.15	0.18	0.17
PCB-99	0.70	0.13	0.18	0.20	0.19
PCB-101	1.27	0.30	0.30	0.43	0.38
PCB-105	0.27	0.11	0.13	0.19	0.11
PCB-118	0.98	0.22	0.30	0.44	0.36
PCB-128	0.27	BDL	0.14	0.25	0.18
PCB-138	1.45	0.27	0.83	1.14	1.02
PCB-153	1.90	0.40	1.07	1.31	1.23
PCB-158	0.18	0.05	0.13	0.17	0.13
PCB-170	0.55	BDL	0.51	0.55	0.45
PCB-179	BDL	0.10	BDL	0.31	0.28
PCB-180	1.27	0.20	0.94	1.00	0.96
PCB-183	0.34	BDL	0.28	0.32	0.29
PCB-187	0.61	0.42	0.46	0.72	0.71
$\Sigma$ PCB	18.65	4.54	7.32	9.32	8.29
HCB	0.06	0.03	BDL	BDL	BDL
Lindane	0.10	0.11	0.11	BDL	0.12
p,p'-DDD	BDL	0.19	BDL	BDL	BDL
p,p'-DDE	2.23	1.19	1.19	1.58	1.36
p,p'-DDT	0.48	0.63	0.63	0.29	0.69
Σ DDT	2.71	2.24	1.82	1.87	2.04

BDL, below detection limit.

and bigeye thresher (*Alopias superciliosus*) sharks from the East Brazilian Coast. Cephalopods, followed by fish, are the principal prey of *S. zygaena*, while *A. superciliosus* and *I. oxyrinchus* feed mainly on fish (Cortés, 1998).

Samples of *S. zygaena* (n = 3), *I. oxyrinchus* (n = 1) and *A. superciliosus* (n = 1) were captured using a set gill net, in the Brazilian Exclusive Economic Zone ( $17^{\circ}:20^{\circ}$  lat. and  $37^{\circ}:39^{\circ}$  long.) between August and September 2001. Biometry data of the samples are shown in Table 1.

About  $2.5 \, \mathrm{g}$  of muscle tissue were homogenized with anhydrous  $\mathrm{Na_2SO_4}$  and extracted by Soxhlet for 8 h, with 50 ml of n-hexane/dichloromethane (1/1:v/v). The extract was concentrated with rotary evaporation to a final volume of 3 ml, and an aliquot of the extract (1 ml) was added and mixed with 2 ml of concentrated  $\mathrm{H_2SO_4}$ . The organic phase was collected and the acid phase was re-extracted with 2 ml n-hexane. The combined organic fractions were concentrated to 1 ml using a gentle stream of pure (99.5%) nitrogen and washed once with 2 ml ultrapure water. The extract was concentrated to 0.5 ml using a stream of pure (99.5%) nitrogen and the internal standard octachloronaphthalene (OCN) was added.

Chromatographic analysis was performed in a Shimadzu GC-14B equipped with electron capture detector (ECD) and an AOC-17 auto-sampler. Injection was performed in the split - less mode, keeping the split valve closed for 30 sec. Hydrogen was the carrier gas (2 ml/min). The injector and detector temperatures were kept at 250 °C and 310 °C, respectively. The column temperature was programmed at 100 °C, held for 4 min, and then increased from 100 °C to 205 °C at a rate of 5 °C/min. The temperature was held for 15 min at 205 °C and increased at a rate of 2 °C/min to the final temperature of 290 °C. The separation was carried out in a fused

silica capillary column DB-5 purchased from J&W Scientific Inc. ( $60 \text{ m} \times 0.25 \text{ i.d.}$  mm and 0.1 m of film thickness).

In this study we analyzed 22 congeners of PCBs, lindane, HCB and  $\Sigma$ DDT (p,p'-DDE, p,p'-DDT and p,p'-DDD). The PCB standard solution (PCB congener mix #6) was purchased from the Accustandard Laboratory (USA) and the organochlorine pesticides standard solutions were purchased from Dr. S. Ehrenstorfen Laboratory (Germany).

IAEA-406 (fish homogenate) was used as a reference material. The recoveries for PCB and DDTs ranged from 70% to 130%. The detection limit of the method (calculated as three times the SD) varied from 0.12 to 3.39  $\rm ng~g^{-1}$  for PCBs and 0.06 to 1.8  $\rm ng~g^{-1}$  for the OCPs.

The Estimated Daily Intake (EDI), derived for (i) general population and for (ii) fishermen families, was used to calculate the amount of DDT and its metabolites ingested through consumption of shark, and the results were compared with the established Acceptable Daily Intake (ADI) of 20  $\mu$ g/kg b.w./day. The average Brazilian fish intake was set at 6.2 kg/inhabitant/year by FAO, a value that corresponds to 17 g/inhabitant/day (FAO, 2002). The fish intake for fishermen families was set at 200 g/inhabitant/day (Fernandez et al., 2004) and the average body weight used was 60 kg (Vieira et al., 2001).

The concentrations of individual PCBs and OCPs, in wet weight basis (w.w.), found in the shark muscle samples are shown in Table 1. All studied species presented  $\sum$ PCBs concentrations higher than DDT and other pesticides. This could be attributed to the large number of congeners contributing to the sum weight of PCBs, in comparison with the separate weights for the different organochlorine pesticides and their metabolites. Evaluating DDT and its metabolites, the highest values were observed for p,p'-DDE (ranging from 1.19 to 2.23 ng g<sup>-1</sup>) followed by p,p'-DDT (from 0.29 to 0.69 ng g<sup>-1</sup>). This finding is consistent with the DDT biotransformation in fish, which occurs through oxidative processes by dehydrochlorination, resulting in the formation of DDE (Lee et al., 1997; Strandberg et al., 1998). Additionally, p,p'-DDE is the most persistent metabolite and has considerable potential for accumulation in organisms (WHO, 1979; ATSDR, 2002), HCB and p.p'-DDD were detected only in S. zygaena, and lindane was not detected in I. oxyrin-

The PCB congeners #138, #153, and #180 were the predominant contaminants observed in all analyzed species (Fig. 2). These three congeners were found to be the primary contaminants in other studies that analyzed Prionace glauca, Alopias vulpinus, Centrophorus granulosus, S. zygaena and Squalus blainvillei captured from the Mediterranean Sea (Corsolini et al., 1995; Storelli and Marcotrigiano, 2001; Storelli et al., 2003). The congeners #138 and #153 were also found in higher levels in P. glauca captured from the South Atlantic (Azevedo-Silva et al., 2007). In terms of the relative distribution of homologue PCB congeners, the hexachlorinated and heptachlorinated congeners were found to be predominant in muscle samples collected from I. oxyrinchus and A. superciliosus, representing 61.92% and 63.29% respectively of the total sum of PCBs, while in S. zygaena species the congeners with four, six and seven chlorine atoms were the predominant homologue groups representing 74.86% of the sum of PCBs.

The concentration of total PCBs and DDT and metabolites obtained in this study (Table 2) were higher than those observed by Azevedo-Silva et al. (2007) in *Prionace glauca*, captured from the same study area. Variation in diet could explain these observed differences in contaminant concentration among species from the same area. The species evaluated in the present study had total PCB concentrations near the values observed in *Triakis semifasciata* from San Francisco Bay. On the other hand,  $\Sigma$ DDT contamination was lower than what was observed by Davis et al. (2002) and Greenfield et al. (2005). The same is true when comparing the pres-

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