



## Baseline

# Specific profiles of polybrominated diphenylethers (PBDEs) and polychlorinated biphenyls (PCBs) in fish and tucuxi dolphins from the estuary of Paraíba do Sul River, Southeastern Brazil

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## ABSTRACT

Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) are ubiquitous pollutants in the environment and subject of several studies due to their adverse effects as endocrine disruptors. Despite the concern over widespread distribution of PBDEs even in sparsely populated regions of the world, few studies have reported their occurrence in Brazil. In this study, PBDEs and PCBs levels were measured in selected fish species and dolphins from Paraíba do Sul River, Brazil. BDE 47 and 85 were the predominant congeners. Low chlorinated congeners showed the highest concentrations in fish; however dolphins presented the highest proportion of PCBs 153, followed by 138 and 180. The daily intake of PBDEs and PCBs was estimated for the population of this region. PCB daily intake through consumption of croaker was above the limits set by the Brazilian Ministry of Agriculture, raising great concern over the existence of a source of PCB contamination in Brazil.

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Polybrominated diphenyl ethers (PBDEs) are a class of synthetic halogenated organic compounds used in a wide variety of consumer products, such as electronic equipment, upholstered furniture, and polyurethane foams, as flame retardants (Staskal et al., 2008; Shaw and Kannan, 2009). As a result of their environmental persistence and widespread use in household and commercial products, PBDEs have become ubiquitous global contaminants in the environment and human tissues, even in remote areas (de Wit et al., 2006). They are structurally similar to polychlorinated biphenyls (PCBs) and DDT and, therefore, their physicochemical properties (environmental persistence, tendency to bioaccumulate and biomagnify in food webs, and potential toxicity in the environment) follow similar patterns. However, there is still little information on PBDE specific accumulation profiles in wildlife (Kajiwara et al., 2008).

Recently, increasing scientific evidence has proven the association of several PBDEs congeners with endocrine disruption, reproductive and developmental toxicity, neurotoxicity and potential carcinogens effects in laboratory animals (Hamers et al., 2006; Darnerud, 2008). Hydroxylated metabolites of PBDEs have been reported to interfere with thyroxine transport in blood (Meerts et

al., 1998) and certain hydroxylated PBDEs were shown to bind to the thyroid receptor (Marsh et al., 1998).

Many studies have shown increased PBDE concentrations over time in several fish species (Zhu and Hites, 2004; Law et al., 2006), although this trend may start to reverse due to penta- and octa-PBDE usage bans. Nevertheless, PBDEs are still present in many consumer products which were purchased before production seizure and are still in production and used in large quantities in many countries (Shaw and Kannan, 2009).

PCBs were never produced in Brazil, but most of the transformer oils already in use may contain PCBs imported from Germany and the US. Their introduction in the country was formally restricted in 1986 (de Souza et al., 2008) and nowadays PCBs are globally banned in accordance with the Stockholm Convention of 17 May 2004 ([www.pops.int](http://www.pops.int)).

Although PBDEs and PCBs studies have been previously conducted on environmental samples from North America (Schechter et al., 2003; Kannan et al., 2007; Xia et al., 2008) and Europe (Bordajandi et al., 2003; Storelli et al., 2003) among other countries, few studies have reported PBDEs levels from South America, including Brazil (Montory et al., 2010; Kalantzi et al., 2009; Dorneles et al., 2010).

The aim of this study was to determine levels of PBDEs and PCBs in scabbardfish and croaker from the Paraíba do Sul River and tucuxi dolphins from the North Coast of Rio de Janeiro, in order

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to provide baseline information on the levels and patterns of these contaminants in an estuarine ecosystem in Southeastern Brazil.

The Paraíba do Sul River, the largest river in southeastern Brazil, is 1145 km long, and flows through the most important urban and industrial centers in Brazil (Rio de Janeiro and São Paulo) (Fig. 1). Despite being the only source of drinking water for the Rio de Janeiro metropolitan area, it is heavily contaminated by agricultural and highway runoff and discharges from untreated industrial and domestic wastes (Linde-Arias et al., 2008).

Silver scabbardfish (*Lepidopus caudatus*) and whitemouth croaker (*Micropogonias furnieri*) were collected in the river near Campos dos Goytacazes by local fishermen and transported on ice to the laboratory, where dissections were performed to separate organs and tissues (liver and muscle). 10 croaker and 10 scabbardfish were collected: 14 females and 6 males. Total length ranged between 37.8 and 145 cm (mean:  $88.8 \pm 48.4$  cm) and weight ranged from 0.63 to 3.0 kg (mean:  $1.5 \pm 0.84$  kg). Ten livers, two kidneys and two muscle tissue samples were obtained from tucuxi dolphins (*Sotalia guianensis*) found stranded along the North Coast of Rio de Janeiro, represented by 5 males and 9 females and their lengths ranged from 68 to 198 cm (mean:  $163 \pm 40.8$  cm).

PBDE and PCB standards were purchased from Accustandard (New Haven, CT, USA). Purities of all standards were  $\geq 95\%$ . All solvents used in this study were HPLC grade, and chemicals were ACS grade (J.T. Baker, Phillipsburg, NJ).

PBDEs reference standards (Bromodiphenyl Ether Lake Michigan Study,  $10 \mu\text{g mL}^{-1}$  in isooctane) consisted of a mixture of 9 compounds (BDE 28, 47, 66, 85, 99, 100, 138, 153, and 154). PCBs reference standards (PCB Congener Mix for West Coast Fish Studies, C-WCFS,  $25 \mu\text{g mL}^{-1}$  in isooctane) consisted of a mixture of 24 PCBs: PCB 31, 33, 49, 56, 60, 70, 74, 87, 95, 97, 99, 110, 132, 141, 149, 151, 156, 158, 174, 177, 183, 194, 199, and 203. A mixture of 28 PCBs (WHO/NIST/NOAA Congener List, C-WNN,  $10 \mu\text{g mL}^{-1}$  in isooctane) were also used: PCB 8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206, and 209.

PCB-209 standard solution was used as surrogate for quality control of the analytical procedure and PCB-53 standard solution was used as internal standard for chromatographic analysis.

The analytical procedure for the simultaneous determination of PBDEs and PCBs consisted basically of four steps: saponification, extraction and clean-up followed by chromatographic analysis.

The methodology was based on an UltraTurrax (model T18 basic, IKA LTDA, Brazil) extraction described elsewhere (De Boer et al., 2001) with slight modifications. 1 g (dry wt) of homogenized sample was weighed and  $10 \mu\text{L}$  of  $3.5 \text{ ng } \mu\text{L}^{-1}$  solution of PCB 209 was added as surrogate standard to evaluate inherent loss along the analytical procedure. Saponification of the fat present in the biological tissues was performed by adding 20 mL of  $1 \text{ mol L}^{-1}$  of KOH solution and allowing to rest for 30 min. The mixture was homogenized using Ultra Turrax at 14000 rpm for 1 min. The solvent employed was a mixture of hexane/acetone 1:1. Then, 20 mL acetone was added and the mixture was again run in Ultra Turrax in the same initial conditions. Followed the addition of 20 mL hexane, the Ultra Turrax was run again for 1 min and this was repeated once more (at 22000 rpm for 1 min) after adding 20 mL Milli-Q water. After decantation, the organic layer was removed and transferred via a capillary pipette filled with 1 cm sodium sulphate to a beaker. The solvent was evaporated to dryness under a controlled water bath ( $40^\circ\text{C}$ ) and under a gentle stream of high-purity nitrogen. The extract was dissolved in 1 mL of hexane/acetone 1:1 for clean-up.

The clean-up step was performed by an alumina column chromatography followed by a final treatment with sulphuric acid. The glass chromatography columns (internal diameter (id): 1.5 cm) were dry packed with 6 g of 5% deactivated alumina (Merck, 70–230 mesh, activated at  $450^\circ\text{C}$  for 6 h and allowed to rest for 24 h before use) and topped with a 1 cm layer of anhydrous sodium sulphate. The sample aliquot was placed on top of the column and eluted with n-hexane, and two fractions of 4 mL were collected. As tested previously, only the second fraction contained the target analytes, which was evaporated until 1 mL followed by sulphuric acid treatment. 2 mL of sulphuric acid was added to the 1 mL n-hexane extract and this mixture was homogenised for 30 s using a vortex. The resulting emulsion was centrifuged for 1–2 h until the separation of phases. The organic phase was transferred via a capillary pipette and washed twice with Milli-Q water (extracted 5 times with 20 mL of n-hexane to each 1 L of water). After clean-up, the final extract (in hexane) was evaporated in the same conditions as described previously. At the end of the procedure,  $10 \mu\text{L}$  of  $3.5 \text{ ng } \mu\text{L}^{-1}$  of PCB-53 solution were added as internal standard for gas chromatographic analysis to a final volume of 100  $\mu\text{L}$  isooctane.

The method employed for the total lipid determination in biological tissues was based on the classical cold solvent extraction

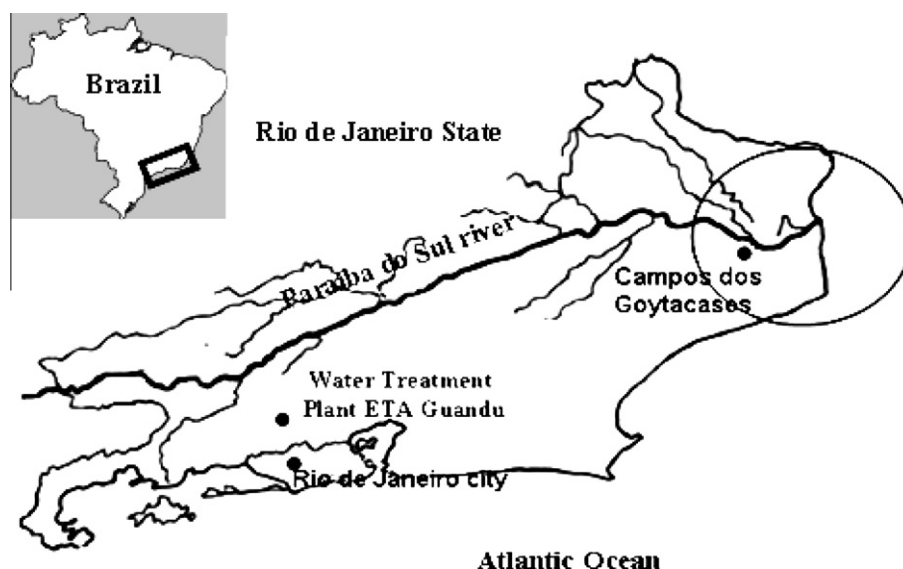


Fig. 1. Map of Brazil showing the sampling point in Paraíba do Sul River, Rio de Janeiro State.

(Bligh and Dyer, 1959) with the modifications proposed by Honeycutt (Honeycutt et al., 1995).

PBDEs and PCBs were analyzed by a gas chromatographic coupled to mass spectrometry (GC–MS) in electron capture negative ionization mode (GC/MS–ECNI) and operated in selected ion monitoring (SIM) mode. A HP-5MS capillary column (30 m × 250 µm i.d. × 0.25 µm film thickness of 5% phenyl methyl siloxane) from J&W Scientific was used for the determination of both compounds and 1 µL of sample extract was injected at splitless mode.

Conditions for PBDEs determination were the following: The column oven was programmed for an initial temperature of 70 °C for 1 min and a rate of 12 °C min<sup>−1</sup> from 70 to 154 °C, then ramped to 210 °C at a rate of 2 °C min<sup>−1</sup>, and finally increased at a rate of 3 °C min<sup>−1</sup> to 300 °C and held for 5 min; with helium as the carrier gas (at a flow rate of 1.3 mL min<sup>−1</sup>). The injector, interface and ion source temperatures were maintained at 280, 280, and 300 °C, respectively.

Conditions for PCBs determination were the following: The column oven was programmed for an initial temperature of 75 °C for 3 min and a rate of 15 °C min<sup>−1</sup> from 75 to 150 °C, then ramped to 260 °C at a rate of 2 °C min<sup>−1</sup>, and finally increased at a rate of 20 °C min<sup>−1</sup> to 300 °C and held for 1 min; with helium as the carrier gas (at a flow rate of 1.1 mL min<sup>−1</sup>). The injector, interface and ion source temperatures were maintained at 270, 280, and 300 °C, respectively.

For quality control, calibration standards were injected daily after analysis of a batch of approximately 20 samples, procedural blanks were analyzed by passing the reagents through the entire analytical procedure to monitor for possible sources of contamination and samples were spiked with a known concentration of PBDEs standards at different concentrations. Matrix spike recoveries for all target analytes ranged from 71% to 106% (90 ± 9%) for liver samples, 66–121% (92 ± 13%) for muscles samples and 65–133% (101 ± 19%) for kidney samples.

The recoveries for PCB-209 spiked into each sample were in the range, 63–136% (mean ± SD: 114 ± 22%) for liver, 119–135% (127 ± 7%) for kidney and 75–135% (105 ± 18%) for muscle tissue samples.

Calibration curves for PBDEs were prepared at different concentrations (1–100 ng mL<sup>−1</sup>) in isooctane and for PCBs (1–200 ng mL<sup>−1</sup>) in n-hexane, and surrogate (PCB-209) and internal standard (PCB-53) both at 350 ng mL<sup>−1</sup> were added. All standard calibration curves exhibited excellent linearity (correlation coefficient >0.99).

The limit of quantification (LOQ) was estimated as 10\*s/S, being s the standard deviation of the blank measures and S the sensitivity of the method. The mass of samples taken for analysis were included in the calculation of the LOQ. In PFDEs analyses, LOQ values were below 1 ng g<sup>−1</sup> wet wt, with the exception of BDE 153 (2.32 ng g<sup>−1</sup> wet wt) and BDE 138 (1.53 ng g<sup>−1</sup> wet wt). In PCBs analysis, LOQ values ranged from 1.36 to 10.6 ng g<sup>−1</sup> wet wt for all types of samples.

Statistical tests were performed using SPSS 16.0 software. Kolmogorov–Smirnov and Shapiro–Wilk tests were used to verify data normality. These tests were applied for each fish species separately. When normal distributions were observed within the data, Pearson test was applied; otherwise, non-parametric methods, such as Kendalls and Spearman tests, were performed to investigate the correlation between PBDEs and PCBs concentrations, on a lipid weight basis, and the lipid content, fish total length and weight. The level of significance was set to  $p \leq 0.05$ .

Little is known about PBDEs concentrations on environmental and biological samples from Brazil (Kalantzi et al., 2009; Dorneles et al., 2010). Concentrations of 9 BDEs in livers of scabbardfish, croaker and tucuxi dolphins from Paraiba do Sul River are summa-

rized in Table 1. BDE 47 and 85 were detected in all liver samples ranging from 1.7 to 8.2 ng g<sup>−1</sup> and <0.9 to 1.5 ng g<sup>−1</sup> wet wt for scabbardfish, <0.5–2.7 ng g<sup>−1</sup> and 0.9–4.6 ng g<sup>−1</sup> wet wt for croaker, and <0.5–33 ng g<sup>−1</sup> and <0.9–52 ng g<sup>−1</sup> wet wt for dolphins, respectively. BDE 66, 99, 100, and 154 were detected in scabbardfish in 70%, 80%, 80%, and 40% of the samples, respectively, as for dolphins BDE 28, 100, 99, 154, and 153 were detected in 40%, 70%, 60%, 40%, and 30% of the samples, respectively. Others BDEs were not detected in croaker livers.

BDE patterns were shown to be similar in muscles that also present BDE 47 and 85 in all samples from scabbardfish, croaker and tucuxi dolphins (Table 2). BDE 47 ranged from 0.5 to 3.4 ng g<sup>−1</sup> wet wt for scabbardfish, <0.45–1.0 ng g<sup>−1</sup> wet wt for croaker and <0.45–0.5 ng g<sup>−1</sup> wet wt for dolphins, respectively. BDE 85 concentrations varied from <0.9 to 1.5 ng g<sup>−1</sup> wet wt for scabbardfish, <0.9–1.6 ng g<sup>−1</sup> wet wt for croaker and 0.9–6.8 ng g<sup>−1</sup> wet wt for dolphins, respectively. Others BDEs were rarely found in all studied species. The highest BDE 47 concentration (33 ng g<sup>−1</sup> wet wt or 134 ng g<sup>−1</sup> lipid wt) was found in liver of tucuxi dolphins, however BDE 85 was even higher (52 ng g<sup>−1</sup> wet wt or 453 ng g<sup>−1</sup> lipid wt).

**Table 1**

Mean concentration (ng g<sup>−1</sup> wet wt), standard deviation and range of PBDEs in liver samples of scabbardfish, croaker and dolphins from Paraiba do Sul River.

PBDEs	Scabbardfish (n = 10)	Croaker (n = 9)	Dolphins (n = 10)
BDE 28	<0.39	ND	0.77 ± 0.36 (<0.39–1.25)
BDE 47	4.05 ± 1.94 (1.67–8.23)	1.52 ± 0.70 (<0.45–2.69)	11.0 ± 12.7 (<0.45–33.4)
BDE 66	0.98 ± 0.52 (<0.42–1.87)	ND	ND
BDE 100	1.47 ± 0.43 (0.84–2.37)	ND	4.62 ± 4.39 (<0.42–10.8)
BDE 99	1.27 ± 0.50 (<0.47–2.19)	ND	7.24 ± 6.56 (<0.47–14.9)
BDE 85	1.07 ± 0.26 (<0.93–1.51)	1.93 ± 1.35 (0.93–4.55)	10.6 ± 18.7 (<0.93–52.3)
BDE 154	1.40 ± 0.37 (<0.71–1.93)	ND	8.81 ± 7.34 (<0.71–15.6)
BDE 153	ND	ND	10.0 ± 0.62 (<2.32–10.4)*
BDE 138	ND	ND	ND
Σ BDE	10.2	3.45	53.0
Lipid content (%)	17.3 ± 6.69	N.A.	4.89 ± 1.73

ND: not detected, N.A.: not available sample.

\* Only detected in two samples.

**Table 2**

Mean concentration (ng g<sup>−1</sup> wet wt), standard deviation and range of PBDEs in muscles samples of scabbardfish, croaker and dolphins from Paraiba do Sul River.

PBDEs	Scabbardfish (n = 10)	Croaker (n = 9)	Dolphins (n = 2)
BDE 28	<0.39	<0.39	<0.39
BDE 47	1.17 ± 0.93 (0.46–3.42)	0.80 ± 0.26 (<0.45–0.98)	<0.45–0.5)
BDE 66	<0.42	<0.42	<0.42
BDE 100	0.70 ± 0.27 (<0.42–0.98)*	<0.42	ND
BDE 99	0.94 ± 0.32 (<0.47–1.16)*	<0.47	ND
BDE 85	1.09 ± 0.24 (<0.93–1.45)	1.30 ± 0.44 (<0.93–1.56)*	(0.93–6.79)
BDE 154	ND	<0.71	ND
BDE 153	ND	ND	ND
BDE 138	ND	ND	ND
Σ BDE	3.9	2.1	
Lipid content (%)	3.19 ± 4.51	0.98 ± 0.29	0.27

ND: not detected.

\* Only detected in three samples.

The presence of BDE 47, 99, and 100 in the livers of estuarine dolphins suggest the possible use of the penta BDE mixture in Brazil.

The levels found in this study were similar to previous reports in fish from Chile, China, some locations in USA and Europe (Domingo et al., 2008; Staskal et al., 2008; Shen et al., 2009; Montory et al., 2010; Schecter et al., 2010). In dolphins, the results were one order of magnitude higher than in marine mammals from Australia (Losada et al., 2009) and similar to estuarine tucuxi dolphins from the Região dos Lagos in Brazil (Dorneles et al., 2010).

In kidney samples from tucuxi dolphins, BDE 47, 100, 99, and 154 were detected ranging from <0.5 to 2.8, <0.4 to 1.6, <0.5 to 2.2 and <0.7 to 4.7 ng g<sup>-1</sup> wet wt, respectively and a total concentration of BDE of 14.2 ng g<sup>-1</sup> wet wt (142 ng g<sup>-1</sup> lipid wt). To the best of our knowledge, few studies have analyzed kidney samples. Similarly to this study, PBDE levels were reported in kidney of Irrawaddy dolphins from India ranging from 0.07 to 1.2 ng g<sup>-1</sup> lipid wt (Kannan et al., 2005).

The mean residual pattern of PCBs congeners in liver and muscle from croaker, scabbardfish and dolphins are shown in Figs. 2 and 3, respectively, for concentrations above LOQ. PCBs 28, 52, and 70 were the highest concentrations in liver and muscle of fish. Nevertheless, dolphins presented a different profile; where relatively concentrations showed the highest proportion of PCBs 153, followed by 138 and 180, evidencing a different accumulation pattern in tucuxi dolphins. Similar contamination patterns have been found in several others marine mammals species all over the world

in which hexa-CB congeners 153, 138, and 189 have also been detected at higher levels (Yogui et al., 2003; Kannan et al., 2007). Elevated PCB concentrations showed to be associated with infectious diseases and frequent cause of death of marine mammals (Kannan et al., 2007).

It is normally expected that the contribution of PCB congeners 101, 153, and 138 are higher in biota samples. However, the remarkable contribution of low chlorinated congeners of PCB in croaker and scabbardfish is consistent with previous studies in marine and freshwater fish species from other locations (Bordajandi et al., 2003; Sapozhnikova et al., 2004). Scabbardfish presented high contribution of PCB 138, while no high chlorinated PCB is observed in croaker.

In this study the  $\Sigma$  PCBs in liver samples was 105, 140, and 790 ng g<sup>-1</sup> wet wt (1786, 2526, and 24312 ng g<sup>-1</sup> lipid wt), while  $\Sigma$  PCBs in muscles samples was 45, 106, and 124 ng g<sup>-1</sup> wet wt (8074, 27673, and 41539 ng g<sup>-1</sup> lipid wt) for scabbardfish, croaker and dolphins, respectively.

Recently, elevated concentrations of PCBs were detected in small cetaceans stranded along the Brazilian coast (Kajiwarara et al., 2002; Yogui et al., 2003; Fillmann et al., 2007), and also in some locations offshore Brazil (Ueno et al., 2003), suggesting the presence of a highly polluted source in the Southern Hemisphere, which may be related to the industrial growth in recent years, as well as possible impacts from northern developed nations (Kajiwarara et al., 2002). Therefore, our results corroborate the existence of a source of PCB contamination in Brazil.

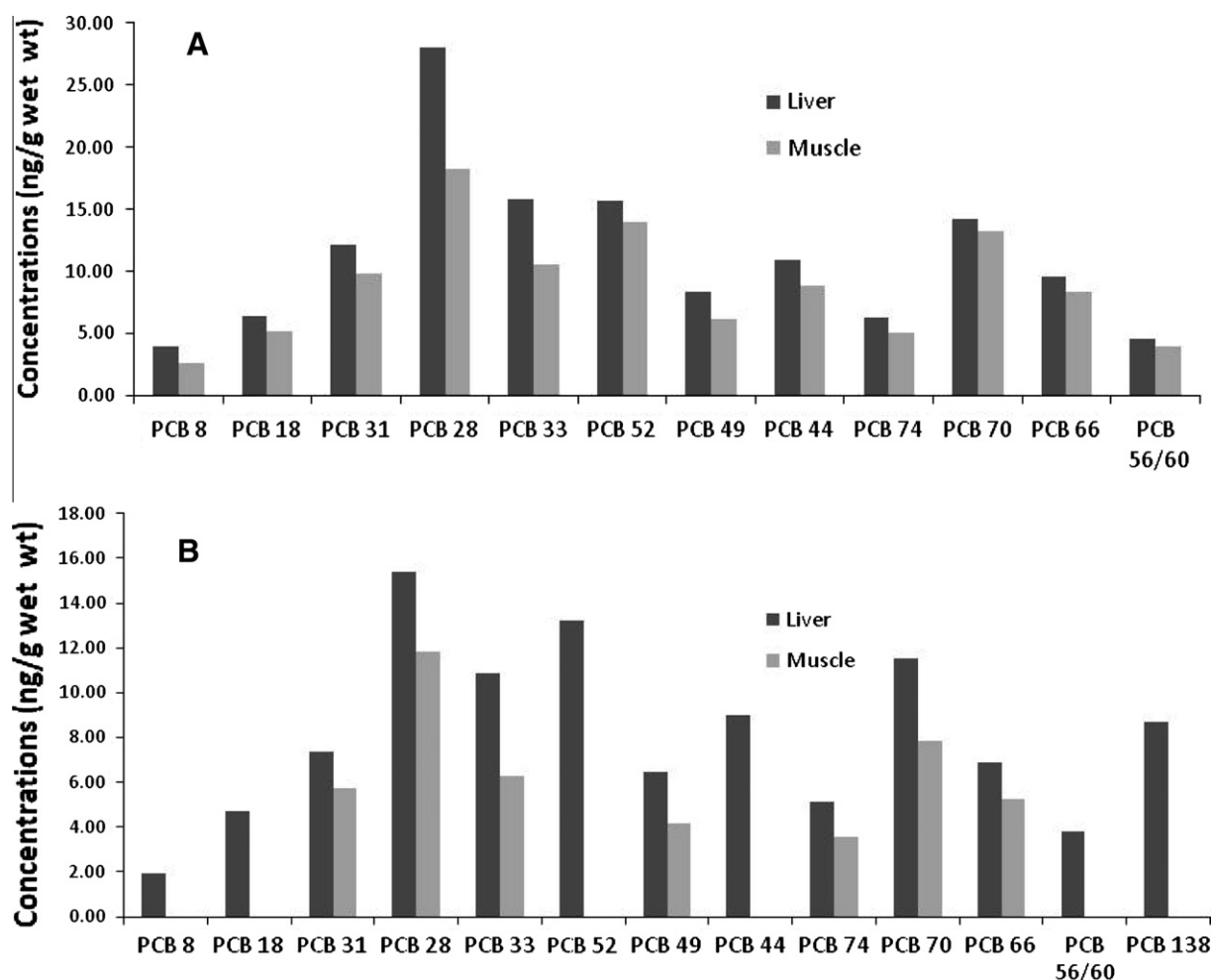


Fig. 2. Mean distribution of PCBs isomers and congeners in liver and muscle of croaker (A) and scabbardfish (B).

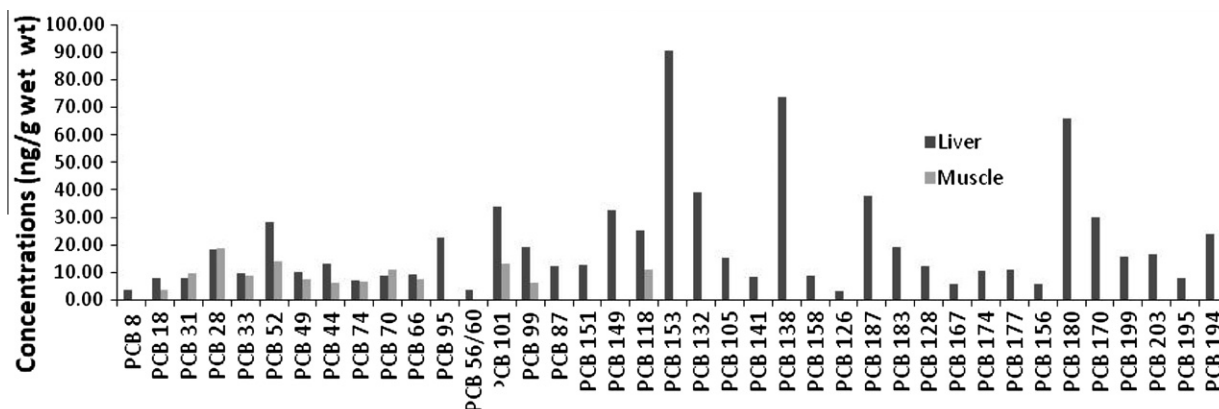


Fig. 3. Mean distribution of PCBs isomers and congeners in liver and muscle of dolphins.

In Brazil there is a lack of legislation regarding PCBs and PBDEs maximum allowed concentration specifically to fish. The daily intake of PBDEs and PCBs was estimated for the population of this region. Considering a daily intake of 20 g of fish  $\text{hab}^{-1}$  corresponding to the average value of 7 kg of fish per inhabitant per year consumed in Brazil and a standard male adult of 70 kg body weight, it was estimated that PBDE intake through fish consumption was  $42 \text{ ng day}^{-1}$  or  $0.6 \text{ ng kg bw}^{-1} \text{ day}^{-1}$  by croaker and  $78 \text{ ng day}^{-1}$  or  $1.1 \text{ ng kg bw}^{-1} \text{ day}^{-1}$  by scabbardfish. The minimal risk level (MRL) of Health and human services is  $0.007 \text{ mg PBDE kg bw}^{-1} \text{ day}^{-1}$  (Pohl and Bosch, 2003). The values obtained in this study were similar to other studies (Domingo et al., 2008; Staskal et al., 2008), and much lower by several orders of magnitude than the proposed MRL.

For PCBs, the daily ingestion calculated was  $2120 \text{ ng day}^{-1}$  or  $30.3 \text{ ng kg bw}^{-1} \text{ day}^{-1}$  by croaker fish and  $900 \text{ ng day}^{-1}$  or  $12.9 \text{ ng kg bw}^{-1} \text{ day}^{-1}$  by scabbardfish. According to the Brazilian recommendation of a maximum level of  $3000 \text{ ng of } \sum \text{ PCB/g of lipid}$  for animal food products (Brazil, 1999), the average value

found for PCB was  $2250 \text{ ng}$  for scabbardfish and  $10,600 \text{ ng}$  for croaker, which surpass the proposed limit. Compared to available literature, the maximum level for PCB was set at  $2 \mu\text{g g}^{-1}$  by FDA/EPA (FDA/EPA, 2001) and a maximum limit of  $100 \text{ ng g}^{-1}$  lipid wt was stated by the Italian Government for food of animal origins (Storelli et al., 2003). Our results are below FDA/EPA limits; however they are higher for both species than the limit set by the Italian Government. These values are of great concern due to the high consumption of these fish species by the local population.

Meanwhile, the dietary threshold concentration of total PCBs in marine mammals ranged from  $10$  to  $150 \text{ ng g}^{-1}$  wet wt, which has been shown to exhibit toxic effects in aquatic mammals (Kannan et al., 2000). The present results obtained for dolphins ( $790 \text{ ng g}^{-1}$  wet wt) were much higher than the proposed threshold, suggesting a contamination exposure risk to marine mammals from the studied area.

PBDEs and PCBs tissue distributions follow the order liver > kidney > muscles for dolphins and in fish liver concentrations were higher than in muscles. This study clearly demonstrates that many

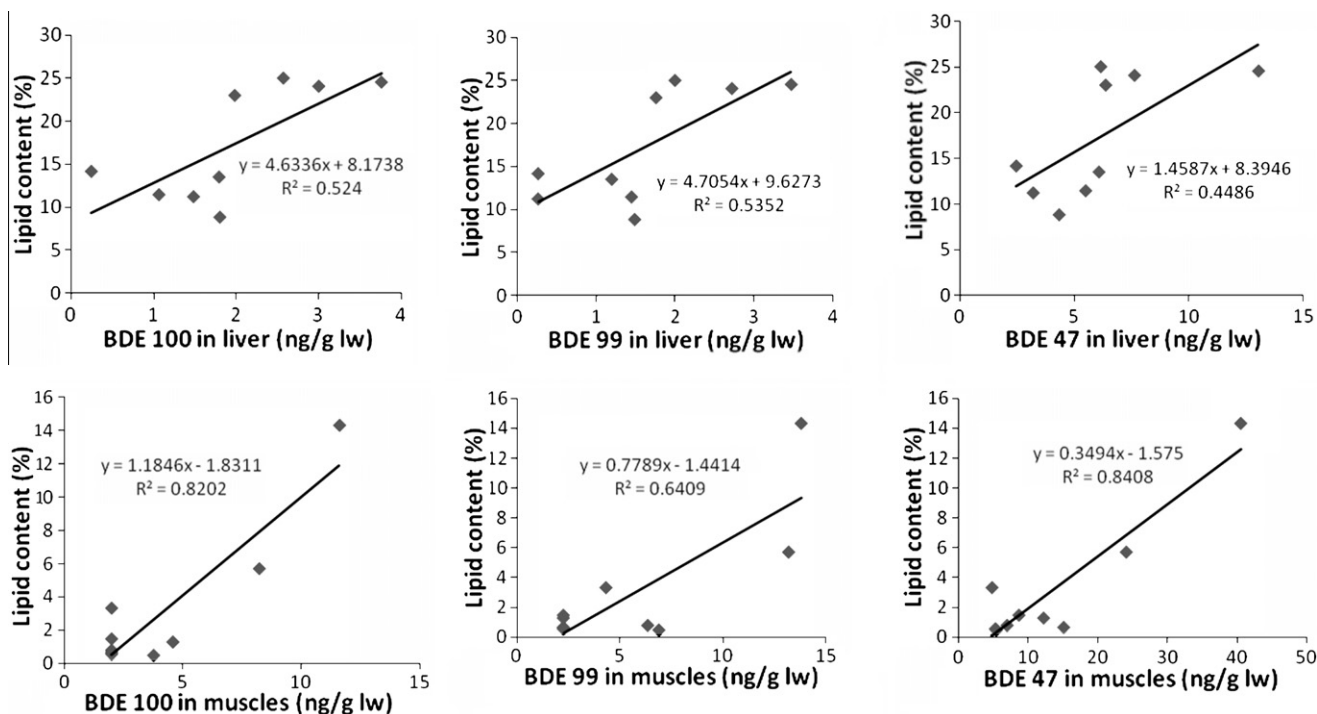


Fig. 4. Pair-wise correlations of BDE 100, 99 and 47 in liver and muscles with the lipid content in liver and muscles of scabbardfish from Paraíba do Sul River.

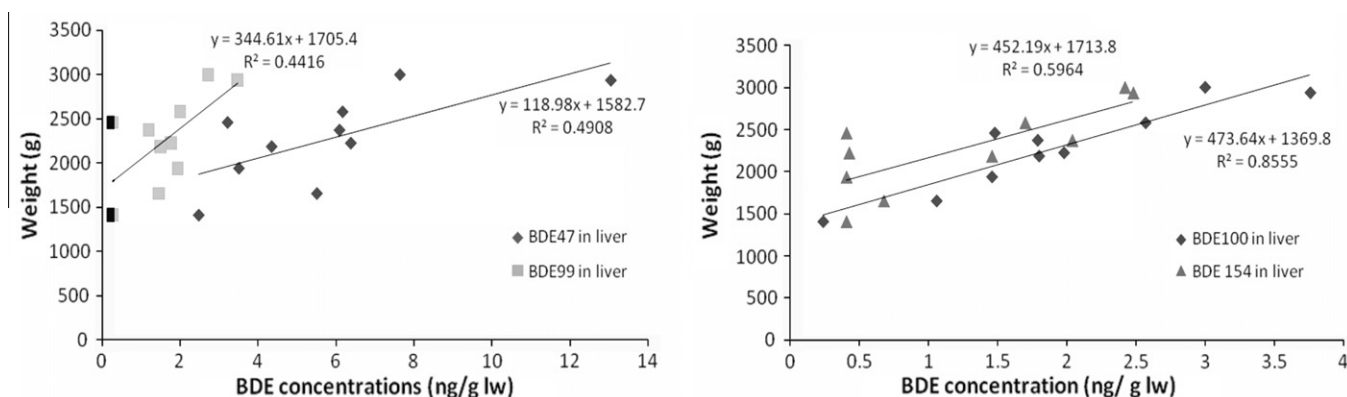


Fig. 5. Correlations between BDE 99, 100, 47 and 154 in liver and the weight in scabbardfish from the Paraíba do Sul River.

PBDEs and PCBs are able to bioaccumulate and biomagnify in this food web, since concentrations in dolphin liver were at least one order of magnitude higher than those in fish.

To estimate biomagnification factors (BMFs), we compared lipid-normalized concentrations of PBDEs and PCBs in the scabbardfish and croaker to tucuxi dolphins.

The estimated BMF of BDE 47 in tucuxi dolphin ranged from 0.73 to 20.3, and for BDE 85 ranged from 1.9 to 88.2 (compared with hepatic concentrations in croaker and scabbardfish from the Paraíba do Sul River). The BMF for BDE 100, 99 and 154 ranged from 1.5 to 9.5, 2.0 to 17.2 and 9.1 to 20.3, respectively, in scabbardfish to dolphins. BMF for  $\Sigma$ PBDEs in dolphin liver were 11.2 and 21.2 in relation to scabbardfish and croaker, respectively. Comparable BMFs for  $\Sigma$ PBDEs were reported between predatory fishes and harbor seals in the North Sea and northwest Atlantic marine food web (Boon et al., 2002; Shaw et al., 2009) and teleost fishes and bottlenose dolphins from Florida (Johnson-Restrepo et al., 2005).

The estimated BMF of PCB 153 and 138 in tucuxi dolphin ranged from 3.4 to 39 and 3.4 to 45, respectively, compared with hepatic concentrations in scabbardfish. BMF for  $\Sigma$ PCBs in tucuxi dolphin liver were 14 and 8.7 in relation to scabbardfish and croaker, respectively. Similar findings were reported for predation–prey relationship *O. jennynsi*–grass shrimp from Argentina (Sagrario et al., 2002) and BMFs between predators (whiting) and their prey (sole) from Southern North Sea (Weijjs et al., 2009).

Significant correlations were observed between BDE concentration ( $\text{ng g}^{-1}$  lipid wt) and lipid content (%) and weight (g) in dolphins (Spearman's coefficient =  $-0.857$ ,  $p < 0.01$ ,  $n = 10$  between BDE 85 and length and Spearman's coefficient =  $0.721$ ,  $p < 0.05$ ,  $n = 10$  between BDE 85 and lipid content), in croaker (Pearson's coefficient =  $0.957$ ,  $p < 0.01$ ,  $n = 9$  between weight and length and Kendall's coefficient =  $-0.571$  and  $-0.618$ ,  $p < 0.05$ ,  $n = 9$  between length/weight and lipid content) and in scabbardfish from Paraíba do Sul River (Figs. 4 and 5), confirming the lipophilic properties of these compounds. Concentrations of BDE 85 in croaker liver had a negative correlation with the concentration in muscles (Spearman's coefficient =  $-0.782$ ,  $p < 0.05$ ,  $n = 9$ ), but a positive relationship with the BDE 47 concentration in liver (Pearson's coefficient =  $0.865$ ,  $p < 0.01$ ,  $n = 9$ ).

Statistical analysis for PCBs revealed relationships between PCBs congeners in liver, muscles and kidney from dolphins, croaker and scabbardfish and some PCBs showed correlation with the total length; however no correlations were found between PCB concentrations and lipid content.

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