



# Occurrence of legacy and emerging organic pollutants in whitemouth croakers from Southeastern Brazil

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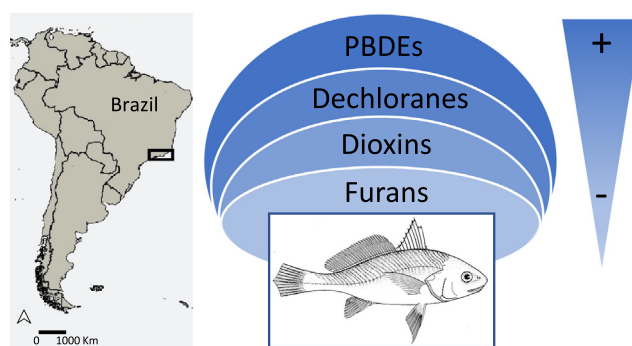
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## HIGHLIGHTS

- Analysis suggested the presence of PBDE commercial mixtures in whitemouth croakers
- First assessment of emerging flame retardants in fish from Southwest Atlantic Ocean
- Dec 603 and DP were the predominant DRCs, followed by Mirex, Dec 602 and CP

## GRAPHICAL ABSTRACT



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## ABSTRACT

The whitemouth croaker (*Micropogonias furnieri*) is one of the most commercially important species along the Atlantic coast of South America. Moreover, some of its biological traits (long life span, inshore feeding, high trophic position) make this species a suitable sentinel of coastal pollution. Here, we investigated contamination by multiple legacy and emerging organic pollutants, such as brominated and chlorinated flame retardants, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), in whitemouth croakers from two estuaries (Guanabara and Sepetiba Bays) located in industrialized and urbanized areas in Rio de Janeiro State, Southeastern Brazil. Furthermore, we assessed how biological and ecological features could explain the observed contamination patterns. Regarding brominated flame retardants, concentrations of polybrominated diphenyl ethers (PBDEs) varied from 7.6 to 879.7 pg g<sup>-1</sup> wet weight (w.w.), with high contribution of tetra-, penta-, hexa- and deca-BDEs. The sum of chlorinated flame retardants (dechlorane-related compounds, ΣDRC) ranged from <LOD to 41.1 pg g<sup>-1</sup> w.w., mostly represented by Dechlorane 603 and Dechlorane Plus (DP). Concentrations of PCDDs and PCDFs varied from <LOD to 1.7 pg g<sup>-1</sup> w.w., while the Toxic Equivalent

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(TEQ-PCDD/Fs) levels ranged from 0.1 to 0.2 pg g<sup>-1</sup> w.w. Positive correlations between  $\delta^{15}\text{N}$  and concentrations of tri-, tetra- and penta-BDEs, as well as  $\Sigma\text{DRC}$ , DP and *anti*-DP isomers suggested that ecological factors (namely biomagnification along the food web) influence contamination of whitemouth croakers in the estuaries studied. Moreover, the sum of PBDEs ( $\Sigma\text{PBDE}$ ), tri- and tetra-BDEs concentrations were negatively correlated with fish size, suggesting that depuration by fishes and/or habitat shift throughout the whitemouth croaker's life cycle might also influence concentrations. Overall, our study emphasized the need for further investigations to help understand the complex patterns of bioaccumulation and biomagnification that seem to exist in Southeastern Brazil.

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## 1. Introduction

Persistent organic pollutants (POPs) comprise a wide range of chemicals that have received considerable attention due to their persistence in the environment, long-range transport and toxic properties (Jones and De Voogt, 1999; Walker et al., 2012). Restricted or banned POPs – known as legacy POPs – are regulated by the Stockholm Convention, and include substances classified as unintentional products [i.e. polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)], pesticides, and industrial chemicals [i.e. flame retardants (FRs), such as polybrominated diphenyl ethers (PBDEs) commercial mixtures] (UNEP, 2017). On the other hand, the term emerging pollutants refers to replacement substances for the legacy chemicals, which have been recently observed in the environment. Among the emerging pollutants, the category of FRs stand out, including brominated [i.e. pentabromoethylbenzene (PBEB) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)] and chlorinated flame retardants, such as the dechlorane-related compounds (DRCs) [i.e. Dechlorane 602 (Dec 602; CAS# 31107-44-5), 603 (Dec 603, CAS# 13560-92-4), 604 (Dec 604; CAS# 34571-16-9) and Dechlorane Plus (Dec 605 or DP, CAS# 13560-89-9) that are used as substitutes to the banned Mirex. Legacy and emerging pollutants are prone to accumulate in organisms and biomagnify throughout food webs due to their persistent and hydrophobic properties (Kelly et al., 2007; Walters et al., 2016; Navarro et al., 2016, 2017, 2018). Therefore, marine organisms provide opportunities to act as monitors of their environment, as levels and profiles of these contaminants can serve as intrinsic markers, reflecting the ecosystem conditions under which biota live and feed (Alonso et al., 2012; Chauvelon et al., 2014, 2017).

In Brazil, the whitemouth croaker, *Micropogonias furnieri* (Desmarest, 1823) (Perciformes, Sciaenidae), has been recommended as a good indicator of environmental contamination (Dorneles et al., 2016) due to its distribution along the coastal waters of the western Atlantic Ocean, to its longevity (~35 years), and high trophic position in estuarine ecosystems (Bisi et al., 2012; Pizzochero et al., 2018; Vazzoler, 1991). Additionally, this species constitutes a commercially-important resource in coastal demersal fisheries along the Atlantic coast of South America (FAO, 2018; Haimovici et al., 2016). In this context, investigations on legacy and emerging pollutants in this species would not only provide information on the contaminants that are spreading through marine food webs in Brazilian coastal waters, but would also be relevant in public and human health assessment as ingestion of seafood constitutes the principal source of human exposure to POPs (Cruz et al., 2015; Sidhu, 2003).

In the present study, concentrations of legacy and emerging POPs were measured in white muscle samples of whitemouth croakers from Rio de Janeiro state, Southeastern Brazil. We aimed to investigate whitemouth croaker exposure to POPs and its relation with stable isotopes ratios of carbon ( $\delta^{13}\text{C}$ ), nitrogen ( $\delta^{15}\text{N}$ ) and sulfur ( $\delta^{34}\text{S}$ ), in order to provide a more comprehensive view of their potential use as sentinels. Combining pollutant determination with measurements of ecological tracers such as stable isotopes has been shown to be useful for better understanding sources, pathways, and the trophic flow of toxicants (Bisi et al., 2012; Chauvelon et al., 2014, 2017). To the authors'

knowledge, this is the first study to determine emerging pollutants [brominated (HBB – hexabromobenzene, BB-153 – 2,2',4,4',5,5'-hexabromobiphenyl, PBEB and BTBPE) and chlorinated (Dec 602, Dec 603, Dec 604, DP and Chlordene Plus) flame retardants] in fish from the southwest Atlantic Ocean.

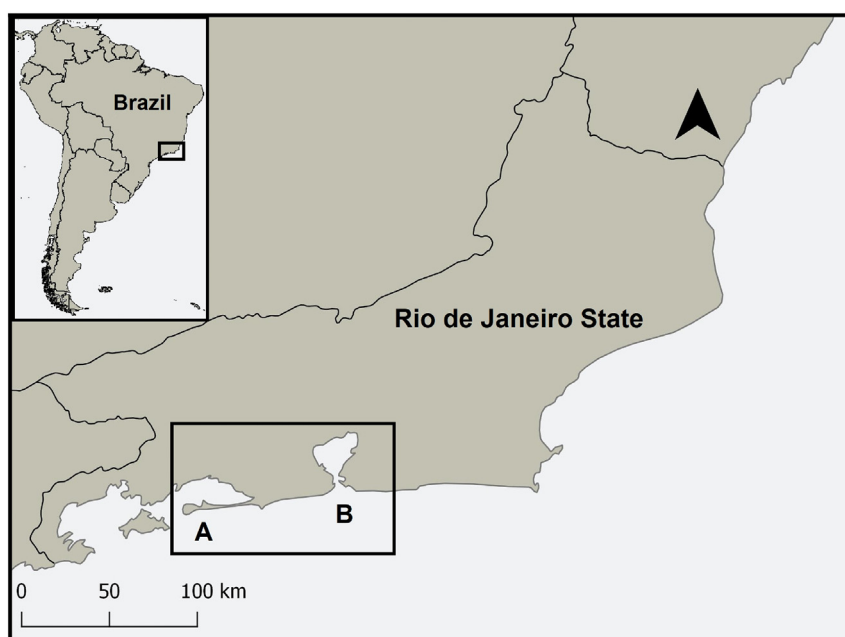
## 2. Materials and methods

### 2.1. Study area and sample collection

Guanabara Bay and Sepetiba Bay are two important fishing areas in Rio de Janeiro state (RJ), in Southeast Brazil (Fig. 1). Located in the metropolitan area of the Rio de Janeiro city, Guanabara Bay (22°24' and 22°57' S/43°33' and 43°00' W, 328 km<sup>2</sup>) is the most anthropogenically-disturbed area along the Brazilian coastline (Dorneles et al., 2008a, 2008b, 2013). This estuary is under the direct influence of approximately 11 million people living in its surroundings (IBGE, 2016), receiving sewage, industrial waste and consequently many contaminants that are transported along its drainage basin, which contains >12,000 industries (Baptista-Neto et al., 2016; Kjerfve et al., 1997). Sepetiba Bay (22°55' and 23° 05'S/43°40' and 44°40'W, 450 km<sup>2</sup>) has also been severely impacted by anthropogenic activities over the past 40 years. Its drainage basin is surrounded by a population of about 2 million people and over 400 industries, including metallurgical, petrochemical and pyrometallurgical smelters (IBGE, 2016; Molisani et al., 2004). Twenty whitemouth croaker (*Micropogonias furnieri*) specimens were obtained from commercial fishery landings in Guanabara (*n* = 14) and Sepetiba (*n* = 6) Bays in the 2014 austral winter (dry season). Each fish was weighed, measured and dissected. Dorsal white muscle samples were wrapped in individual aluminium foil and kept frozen (−20 °C) until being oven-dried at 60 °C to constant weight (>72 h) prior to analysis. Biological parameters [size, mass and lipid content (%)] of the specimens analyzed in the present study are presented in Table 1.

### 2.2. Chemicals and reagents

Complete details on the standards used are presented in Table S1 (Supplementary data). Dec 602 (95% purity), Dec 603 (98%), and Dec 604 (98%) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). Chlordene Plus (CP; CAS# 13560-91-3) and DP (*syn*-DP and *anti*-DP standards) were obtained from Wellington Laboratories Inc. (Guelph, ON, Canada). Mirex (CAS# 2385-85-5) was purchased from Cambridge Isotope Laboratories Inc. (Andover, MA). For brominated flame retardant (BFR) determinations, BFR-LCS (containing 14 <sup>13</sup>C<sub>12</sub>-PBDEs, <sup>13</sup>C<sub>6</sub>-HBB, <sup>13</sup>C<sub>12</sub>-BB-153 and <sup>13</sup>C<sub>6</sub>-BTBPE), BFR-ISS (containing 4 <sup>13</sup>C<sub>12</sub>-PBDEs) and BFR-CVS (five individual calibration solutions containing among others 35 <sup>12</sup>C<sub>12</sub>-PBDEs, 20 <sup>13</sup>C<sub>12</sub>-PBDEs, <sup>13</sup>C<sub>6</sub> and <sup>12</sup>C-HBB, <sup>13</sup>C<sub>12</sub>- and <sup>12</sup>C-BB-153, <sup>13</sup>C<sub>6</sub>- and <sup>12</sup>C-BTBPE) were obtained from Wellington laboratories Inc. (Guelph, ON, Canada). For PCDD and PCDF determinations, EPA-1613LCS (containing 15 <sup>13</sup>C<sub>12</sub>-PCDD/Fs), EPA-1613ISS (containing 2 <sup>13</sup>C<sub>12</sub>-PCDDs) and EPA-1613CVS (five individual calibration solutions containing among others 17 <sup>12</sup>C<sub>12</sub>-PCDD/Fs and 17 <sup>13</sup>C<sub>12</sub>-PCDD/Fs) were obtained from Wellington



**Fig. 1.** Map of South America showing Brazil and Rio de Janeiro state. The insert shows the locations of Sepetiba Bay (A) and Guanabara Bay (B) within Rio de Janeiro state.

**Table 1**

Biological parameters, organic pollutants concentrations (pg g<sup>-1</sup> wet weight),  $f_{anti}$  values, TEQ values, and stable isotopes ratios of carbon ( $\delta^{13}C$ ), nitrogen ( $\delta^{15}N$ ) and sulfur ( $\delta^{34}S$ ) in whitemouth croaker (*Micropogonias furnieri*) muscle samples from Southeastern Brazil.

Sampling site	Code	Size (cm)	Lipid content (%)	Mass (kg)	$\Sigma PBDE^a$ (pg g <sup>-1</sup> )	$\Sigma DRC^b$ (pg g <sup>-1</sup> )	$f_{anti}^c$	$\Sigma PCDD/F^d$ (pg g <sup>-1</sup> )	TEQ <sup>e</sup> (pg g <sup>-1</sup> )	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
Sepetiba Bay	Sb#1	49	0.7	1.5	879.7	33.8	0.6	n.a.	–	–14	15.2	11.5
	Sb#2	48	4.9	1.4	101.6	1.1	n.c.	n.a.	–	–14.5	15.3	12.3
	Sb#3	47	3.4	1.4	111.1	5.1	0.5	n.a.	–	–14.7	15.5	12.3
	Sb#4	46	2.5	1.45	160.8	2.8	0.6	n.a.	–	–14.5	15.2	10.8
	Sb#5	49	4.3	1.4	40.7	3.8	0.7	n.a.	–	–15.4	14.4	12.2
	Sb#6	45	4.2	1.05	84.4	4.5	1	n.a.	–	–14.4	14.9	12.7
Mean $\pm$ SD		47.3 $\pm$ 1.6	3.3 $\pm$ 1.6	1.4 $\pm$ 0.2	229.7 $\pm$ 320.8	8.5 $\pm$ 12.5	0.7 $\pm$ 0.2	–	–	–14.6 $\pm$ 0.5	15.1 $\pm$ 0.4	12 $\pm$ 0.7
Min – max		45–49	0.7–4.9	1.05–1.5	40.7–879.7	1.1–33.8	0.5–1	–	–	–15.4 to –14	14.4–15.5	10.8–12.7
Median		47.5	3.8	1.4	106.4	4.2	0.6	–	–	–14.5	15.2	12.3
Guanabara Bay	Gb#1	46	1.6	0.9	221.4	n.d.	n.c.	n.a.	–	–18.5	13.3	14.7
	Gb#2	47	1.6	1.1	7.6	0.7	n.c.	n.a.	–	–18.9	13.6	12.5
	Gb#3	49	2.7	1.09	326.2	3.0	0.4	n.a.	–	–15.6	12.8	15.0
	Gb#4	50	4.9	1.3	67.3	7.0	0.4	n.a.	–	–16.6	14.4	15.0
	Gb#5	51	2.2	1.4	59.7	9.7	1.0	0.4	0.1	–16.4	15.2	16.5
	Gb#6	52	4.9	1.4	43.1	5.1	0.7	0.6	0.1	–18.3	13.5	12.3
	Gb#7	53	3.8	1.9	53.0	2.7	n.c.	0.5	0.1	–16.7	14.0	17.3
	Gb#8	56	2.8	1.8	21.0	4.1	n.c.	n.d.	0.1	–15.8	14.2	15.3
	Gb#9	61	6.5	2.2	23.4	2.1	n.c.	0.3	0.1	–16.5	13.9	15.2
	Gb#10	61	15.9	1.8	315.2	41.7	0.6	0.2	0.1	–18.1	14.7	16.6
	Gb#11	62	3.4	2.1	30.6	6.6	0.6	1.4	0.1	–16.6	14.0	17.3
	Gb#12	65	3.4	2.7	43.6	1.0	n.c.	0.01	0.1	–16.1	12.9	15.8
	Gb#13	66	2.7	3	47.9	3.2	1	1.3	0.1	–15.8	14.1	16.4
	Gb#14	75	1.6	4.4	14.2	1.1	1	1.7	0.2	–15.4	14.4	14.9
Mean $\pm$ SD		56.7 $\pm$ 8.5	4.1 $\pm$ 3.7	1.9 $\pm$ 0.9	91 $\pm$ 110.2	6.8 $\pm$ 10.8	0.7 $\pm$ 0.3	0.7 $\pm$ 0.6	0.1 $\pm$ 0.03	–16.8 $\pm$ 1.2	13.9 $\pm$ 0.7	15.3 $\pm$ 1.5
Min – max		46–75	1.6–15.9	0.9–4.4	7.6–326.2	n.d.–41.7	0.4–1	n.d.–1.7	0.1–0.2	–18.9 to –15.4	12.8–15.2	12.3–17.3
Median		54.5	3.1	1.8	45.8	3.2	0.6	0.5	0.1	–16.6	14	15.3
Total												
Mean $\pm$ SD		53 $\pm$ 8.3	3.9 $\pm$ 3.2	1.8 $\pm$ 0.8	132.6 $\pm$ 199.1	7.3 $\pm$ 11.1	0.7 $\pm$ 0.2	–	–	–16.1 $\pm$ 1.4	14.3 $\pm$ 0.8	14.3 $\pm$ 2
Min – max		45–75	0.7–15.9	0.9–4.4	7.6–879.7	n.d.–41.1	0.4–1	–	–	–18.9 to –14	12.8–15.5	10.8–17.3
Median		50.5	3.4	1.5	56.4	3.8	0.6	–	–	–16	14.3	15

n.d. = not detected.

n.c. = not calculated due *syn*-DP value below LOD.

n.a. = not analyzed.

<sup>a</sup>  $\Sigma PBDE$ : sum of PBDEs (IUPAC congener numbers: 17, 28, 47, 49 & 71, 66, 77, 85, 99, 100, 119, 126, 139, 140, 153, 154, 156 & 169, 183, 184, 206, 207, 208 and 209).

<sup>b</sup>  $\Sigma DRC$ : sum of Mirex, Decchlorane 602, Decchlorane 603, Decchlorane Plus and Chlordene Plus.

<sup>c</sup>  $f_{anti}$ : *anti*-DP divided by the sum of *syn*-DP and *anti*-DP.

<sup>d</sup>  $\Sigma PCDD/F$ : sum of 1,2,3,6,7,8-HexaCDD; 1,2,3,7,8,9-HexaCDD; 1,2,3,4,6,7,8-HeptaCDD; OctaCDD (OCDD); 1,2,7,8-TCDF; 2,3,7,8-TCDF; 1,2,3,7,8-PCDF; 2,3,4,7,8-PCDF; 1,2,3,4,7,8-HCDF; 1,2,3,6,7,8-HCDF; 1,2,3,7,8,9-HCDF; 2,3,4,6,7,8-HCDF; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF and OCDF.

<sup>e</sup> TEQ: sum of TEQ of PCDDs and PCDFs.

laboratories Inc. (Guelph, ON, Canada). The other chemicals used, i.e. anhydrous sodium sulfate, silica, sulfuric acid (95–97%) and solvents (hexane, dichloromethane, ethyl acetate and toluene) for organic trace analysis, were all obtained from Merck (Darmstadt, Germany).

### 2.3. Sample preparation and chemical analysis

The analytical methods used are described in detail elsewhere (De la Torre et al., 2011, 2012). Extractions were performed with an Accelerated Solvent Extraction system (ASE 100, Dionex, Sunnyvale, CA, USA) using a mixture of hexane:dichloromethane (1:1 v/v) as solvent, at 100 °C, 1500 psi, 90% flush volume and three static cycles (10 min time each, 70 mL total volume). Prior to the extraction step, the samples were spiked with  $^{13}\text{C}_{12}$  labeled surrogate standards (see Table S1). The oven-dried dorsal white muscle samples, ranging from 1 to 8 g, were homogenized with 15 g of anhydrous sodium sulfate and introduced into a 30 mL cell previously loaded by inserting two cellulose filters followed by 2 g of anhydrous sodium sulfate. The resulting extract of each sample was evaporated to constant weight for gravimetric lipid determination and then re-dissolved in hexane. Sample purification consisted of two steps: a liquid extraction with 100 mL of hexane and 50 mL of concentrated sulfuric acid to remove organic matter from the extracts, followed by the transfer of the organic phase to an open glass column with 15 g acid silica modified with 44% sulfuric acid, covered with 1 g anhydrous sodium sulfate and eluted with 150 mL of hexane. The cleaned extracts were concentrated to approximately 1 mL. The fractionation step was performed in an automated purification Power Prep™ System (FMS, Inc., USA) including acidic silica gel, basic alumina and carbon columns. Two fractions were obtained: Fraction A containing PCDD/Fs and Fraction B containing BFRs and DRCs. Both fractions were concentrated to approximately 1 mL under a flow of nitrogen using a Turbo Vap II evaporator (Vertex, Technics, Madrid, Spain), and spiked with the internal standard spiking solutions (see Table S1).

The instrumental analysis was conducted using high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC–HRMS; Agilent GC 6890N connected to a Waters Micromass AutoSpec Ultima NT) at 10,000 resolving power (10% valley) and working in selected ion monitoring (SIM) mode. The GC column used for PCDD/F determination was 60 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$  film thickness (DB-5MS, J&W Scientific), while a short and narrow column [15 m  $\times$  0.25 mm  $\times$  0.10  $\mu\text{m}$  film thickness; DB-5MS (J&W Scientific)] was used for BFR and DRC determinations. Instrument operating conditions were as described in De la Torre et al. (2011, 2012).

Quantification was carried out using the isotopic dilution method (US EPA, 1994). Three criteria were used to ensure the correct identification and quantification of analytes: i)  $\pm 2$  s retention time between the analyte and the standard, ii) the ratio of quantifier and qualifier ions had to be within  $\pm 15\%$  of the theoretical values and iii) a signal to noise ratio greater than three. Recoveries for DP ( $^{13}\text{C}_{10}$ -syn-DP and  $^{13}\text{C}_{10}$ -anti-DP),  $^{13}\text{C}_{12}$ -PCDD/Fs, and  $^{13}\text{C}_{12}$ -PBDEs in this study were  $81 \pm 10\%$ ,  $79 \pm 14\%$ ,  $82 \pm 9\%$  (mean  $\pm$  SD), respectively. The limits of detection (LODs) and quantification (LOQs) of the method were calculated as the concentration corresponding to a signal-to-noise ratio of 3 and 10 respectively (see Table S2). Procedural blanks were processed and analyzed with every batch of samples under the same conditions. In addition, instrumental blanks consisting of nonane were run before each sample injection to check for memory effects and contamination from the gas chromatograph system. Concentrations in instrumental and procedural blanks were below LOD. For statistical descriptive calculations, samples with concentrations below LODs were considered as zero. However, for PCDD/F World Health Organization 2005 Toxic Equivalent (TEQ; Van den Berg et al., 2006) calculations, not detected values were replaced by LODs.

### 2.4. Stable isotope measurements

The data on stable isotope ratios of carbon ( $\delta^{13}\text{C}$ ), nitrogen ( $\delta^{15}\text{N}$ ) and sulfur ( $\delta^{34}\text{S}$ ) in muscle samples of whitemouth croakers from Guanabara Bay were extracted from Pizzochero et al. (2018). This dataset was supplemented with specimens from Sepetiba Bay. Oven-dried dorsal white muscle samples were ground into powder using mortar and pestle. Approximately 4 mg of dry powdered material were analyzed. Measurements of stable isotope ratios were performed via continuous flow – elemental analysis – isotope ratio mass spectrometry (CF-EA-IRMS) at the Laboratory for Oceanology, University of Liege (Belgium), using a vario MICRO cube C-N-S elemental analyzer (Elementar Analysensysteme GMBH, Hanau, Germany) coupled to an IsoPrime100 isotope ratio mass spectrometer (Isoprime, Cheadle, United Kingdom). Isotopic ratios were expressed using the widespread  $\delta$  notation (Coplen, 2011), in ‰ and relative to the international references [Vienna Pee Dee Belemnite (for carbon), Atmospheric Air (for nitrogen) and Vienna Canyon Diablo Troilite (for sulfur)]. IAEA (International Atomic Energy Agency, Vienna, Austria) certified reference materials sucrose (IAEA-C-6;  $\delta^{13}\text{C} = -10.8 \pm 0.5\%$ ; mean  $\pm$  SD), ammonium sulfate (IAEA-N-2;  $\delta^{15}\text{N} = 20.3 \pm 0.2\%$ ) and silver sulfide (IAEA-S-1;  $\delta^{34}\text{S} = -0.3\%$ ) were used as primary analytical standards. Sulfanilic acid (Sigma-Aldrich;  $\delta^{13}\text{C} = -25.6 \pm 0.4\%$ ;  $\delta^{15}\text{N} = -0.1 \pm 0.4\%$ ;  $\delta^{34}\text{S} = 5.9 \pm 0.5\%$ ) was used as secondary analytical standard. Standard deviations on multi-batch replicate measurements of secondary and internal lab standards (animal muscle tissue) analyzed interspersed with samples (one replicate of each standard every 15 analyses) were 0.2‰ for both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  and 0.4‰ for  $\delta^{34}\text{S}$  respectively.

### 2.5. Data analysis

Each dataset (i.e., each pollutant concentration, stable isotope ratio or biological parameter) was tested for normality using the Shapiro–Wilk's W test, and non-parametric tests were applied since most datasets did not follow a Gaussian distribution. All data are presented as mean  $\pm$  standard deviation.

To test whether fishes from Sepetiba and Guanabara bays presented differences in their contamination pattern, we used one-way ANOSIM (ANalysis Of SIMilarity) to compare pollutant concentrations in fishes from the two sites. ANOSIM is a non-parametric, multivariate procedure that uses ranked dissimilarities between samples (here, fishes) to investigate the presence of significant differences between several groups. ANOSIM is permutation-based and assumption-free, which makes it a generally applicable way to test the hypothesis that one response variable (here, the sampling site) is linked with significant differences in a multivariate dataset (here, the pollutant concentrations; Clarke and Warwick, 2001). All compounds found in at least one individual fish were used as input variables. The resemblance matrix was built using Bray–Curtis similarity coefficients, and the number of permutations was set to 9999. The ANOSIM analyses were conducted using PAST 3.20 (Hammer et al., 2001).

To highlight potential relationships (or the absence thereof) between pollutant concentrations and stable isotope ratios and biological parameters [length, mass and lipid content (%)], we performed correlation analyses. 10 pollutants or pollutant classes were retained for correlation analysis: tri-, tetra, penta, hexa and hepta-BDEs (summed concentrations of all PBDE congeners with 3, 4, 5, 6 and 7 bromine atoms, respectively),  $\Sigma$ PBDE (summed concentrations of all polybrominated compounds),  $\Sigma$ DRC (summed concentrations of all dechlorane-related compounds), Dechlorane 603, anti-Dechlorane Plus, and total Dechlorane Plus (sum of anti- and syn-Dechlorane Plus concentrations). Correlation analyses between all these pollutants or pollutant categories (that could be quantified in >50% of the fishes) and each stable isotope ratio ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $\delta^{34}\text{S}$ ) and biological parameter (mass, size and relative lipid content) were performed. Since data



did not follow a Gaussian distribution, Spearman's rank correlation coefficients ( $r_s$ ) were used. Since the ANOSIM test did not reveal significant inter-site difference in fish contamination patterns (see below), correlations were performed grouping all fishes from both estuaries. Analyses were conducted using Prism 6.07 (GraphPad Software, La Jolla, U.S.A.), and the level of significance ( $\alpha$ ) was set to 0.05. To make visualization of these numerous correlations easier, results were synthesized in a correlation matrix (Fig. 3). This correlation matrix was generated using R 3.5.1 (R Core Team, 2018) and the corrrplot package v. 0.84 (Wei and Simko, 2017).

### 3. Results

#### 3.1. Organic pollutant levels

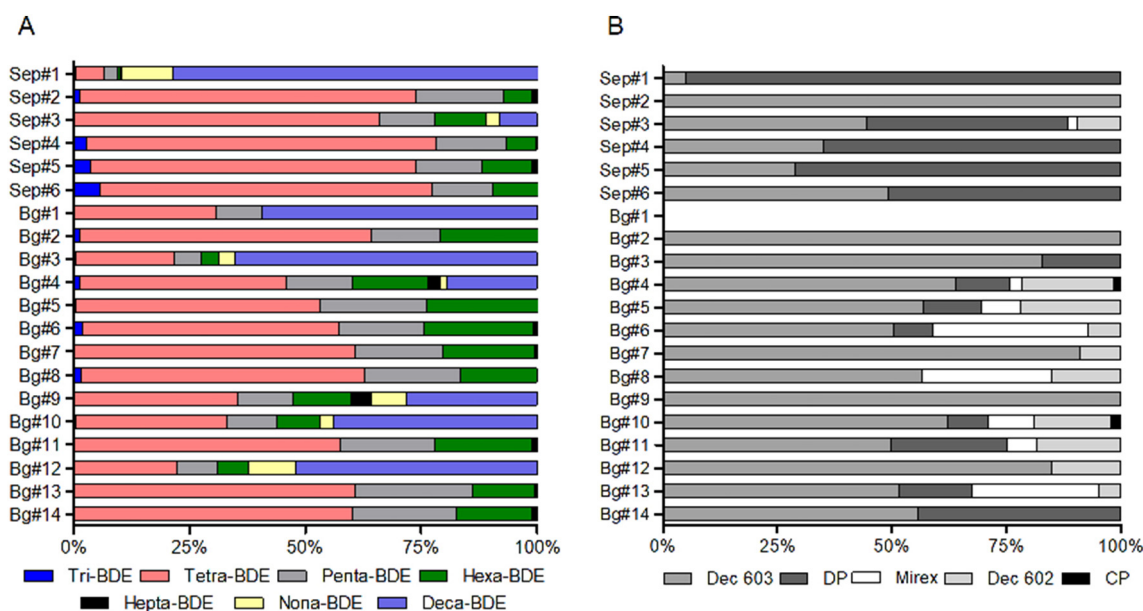
The sums of PCDD/Fs ( $\Sigma$ PCDD/F), PBDEs ( $\Sigma$ PBDE) and DRCs ( $\Sigma$ DRC) in each individual sample are listed in Table 1. Additionally, detailed concentrations in wet weight (w.w.) and lipid weight (l.w.) for all target analytes are reported in the Supplementary data (Tables S3–S9). Research budget only allowed PCDD/F investigations in 10 specimens from Guanabara Bay (Tables S3 and S4). Compounds 2,3,7,8-Tetra-CDD, 1,2,3,7,8-Penta-CDD and 1,2,3,4,7,8-Hexa-CDD could not be detected in any sample. Concentrations of PCDDs were greater than those of PCDFs in 90% of the individuals, being OCDD predominant PCDD/F in 80% of the samples, with concentrations ranging from <LOD to 1.25 pg g<sup>-1</sup> w.w. (Table S3). Calculated TEQ values ranged from 0.1 to 0.2 pg TEQ g<sup>-1</sup> w.w. (Tables 1 and S5). For PBDEs, from 35 congeners evaluated only ten presented quantification frequencies >50%: BDE-47 and BDE-100 (100% of samples; Tables S6 and S7); BDE-154, BDE-49 & 71 and BDE-153 (95%); BDE-66 (85%); BDE-99 (75%); BDE-28 (65%); and BDE-183 (60%). The PBDE profiles observed in whitemouth croaker (Fig. 2A) indicated a high contribution of tetra-BDE (51 ± 20%), penta-BDE (15 ± 6%), and hexa-BDE (12 ± 7%). The most common compounds represented were the tetra congener BDE-47 (predominant congener in 15 samples), the penta congeners BDE-100 and BDE-99 and the hexa congeners BDE-153 and BDE-154. Although BDE-209 (decaBDE) was only quantified in 40% of the fish samples (Tables S6 and S7), its contribution to total PBDE content achieved levels up to 78% (Fig. 2A). Quantification frequencies decreased for emerging brominated pollutants. PBEB, BB-153, and BTBPE levels were below

LOD in all samples, while HBB was only found in one sample from Guanabara Bay (Gb#3) with a value of 0.1 pg g<sup>-1</sup> w.w. (Table S6).

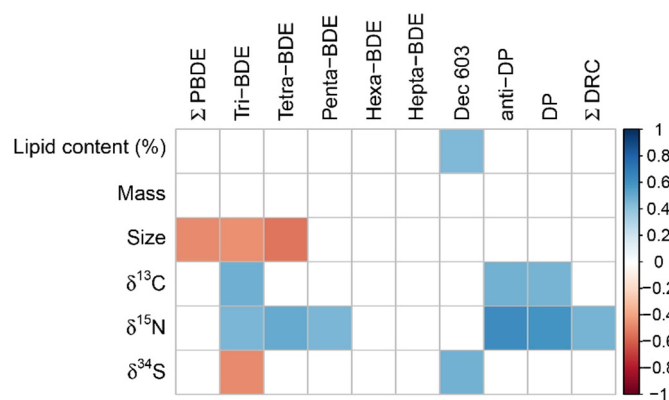
Among the dechlorane-related compounds (DRCs), Dec 604 could not be detected in any sample (Table S8). Detection frequencies of each DRC ranked as follows: Dec 603 (95% of samples), DP [65% (anti-DP: 65% and syn-DP: 45%)], Dec 602 (55%), mirex (40%) and CP (10%). Percentage contributions from individual dechlorane compounds to  $\Sigma$ DRC followed the same order as seen in their frequency of detection, ranking as follows: Dec 603 (61 ± 26%), DP (25 ± 29%), Dec 602 (7 ± 8%), mirex (6 ± 11%) and CP (0.2 ± 0.6%) (Fig. 2B). Considering the samples in which any DP isomer was quantified ( $n = 13$ ), anti-DP was predominant in 85% of them. The relative concentrations of the DP isomers in whitemouth croaker was explored using the values of the anti-DP fractions ( $f_{anti}$ ), calculated as the concentration of the anti-DP divided by the sum of syn- and anti-DP concentrations. The  $f_{anti}$  values obtained ranged from 0.4 to 1 (0.7 ± 0.2; mean ± SD) (Table 1).

#### 3.2. Relationships between pollutant levels, stable isotopes and biological parameters

The stable isotope ratios of carbon ( $\delta^{13}C$ ), nitrogen ( $\delta^{15}N$ ) and sulfur ( $\delta^{34}S$ ) measured in the whitemouth croaker muscle samples in the present study are summarized in Table 1. Considering that the ANOSIM test did not reveal significant inter-site difference in fish contamination patterns ( $p = 0.17$ ,  $R = 0.11$ ), correlations were performed after grouping individuals from both estuaries. Regarding correlations between pollutant levels (or grouped pollutants) and stable isotope ratios,  $\Sigma$ PBDE values were not correlated to any stable isotope ratios; however, using the PBDE congener groups according to the number of bromine atoms, tri-BDE was positively correlated with  $\delta^{13}C$  ( $r_s = 0.48$ ,  $p = 0.03$ ) and  $\delta^{15}N$  ( $r_s = 0.45$ ,  $p = 0.04$ ), while negatively correlated with  $\delta^{34}S$  ( $r_s = -0.48$ ,  $p = 0.03$ ) values (Fig. 3; Table S10). Tetra- and penta-BDE levels increased with higher  $\delta^{15}N$  values ( $r_s = 0.50$ ,  $p = 0.02$  and  $r_s = 0.45$ ,  $p = 0.045$ , respectively). On the other hand,  $\Sigma$ DRC was positively correlated with  $\delta^{15}N$  ( $r_s = 0.46$ ,  $p = 0.04$ ); DP and anti-DP were both positively correlated with  $\delta^{13}C$  ( $r_s = 0.47$ ,  $p = 0.04$  and  $r_s = 0.48$ ,  $p = 0.03$ , respectively) and  $\delta^{15}N$  values ( $r_s = 0.59$ ,  $p = 0.006$  and  $r_s = 0.62$ ,  $p = 0.003$ , respectively), while a positive correlation was found between Dec 603 and with  $\delta^{34}S$  ( $r_s = 0.47$ ,  $p = 0.04$ ) values. Regarding biological parameters, a positive correlation was



**Fig. 2.** (A) Relative contribution of PBDEs grouped by the number of bromine atoms in the molecule to  $\Sigma$ PBDE, and (B) relative contribution of individual dechlorane-related compounds to  $\Sigma$ DRC in muscle samples of whitemouth croakers from Southeastern Brazil. The figure presents the individual code of each fish, which includes the sampling area (Sep: Sepetiba Bay; Gb: Guanabara Bay) and the specimen number (#1, #2...).



**Fig. 3.** Spearman rank correlation matrix between organic pollutants and biological parameters [length, mass and lipid content (%)] and stable isotope ratios of carbon ( $\delta^{13}\text{C}$ ), nitrogen ( $\delta^{15}\text{N}$ ) and sulfur ( $\delta^{34}\text{S}$ ) in muscle samples of whitemouth croakers from Southeastern Brazil. Statistically-significant spearman rank correlations ( $r_s$ ,  $p < 0.05$ ) are shown in blue (positive correlation) and red (negative correlation) color scale (color intensity related to  $r_s$  value), while non-significant correlations are left blank. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

found between Dec 603 and lipid content ( $r_s = 0.45$ ,  $p = 0.048$ ), while size was negatively correlated with  $\Sigma\text{PBDE}$ , tri- and tetra-BDEs ( $r_s = -0.48$ ,  $p = 0.03$ ;  $r_s = -0.45$ ,  $p = 0.046$ ; and  $r_s = -0.54$ ,  $p = 0.01$ , respectively). No significant correlations ( $p > 0.05$ ) were found between  $\Sigma\text{PCDD/F}$  or TEQ values and biological parameters or stable isotope ratios ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $\delta^{34}\text{S}$ ) (Table S10).

## 4. Discussion

### 4.1. Pollutant exposure of whitemouth croakers from Southeastern Brazil

The PCDD/Fs levels in whitemouth croakers from Guanabara Bay (from  $<\text{LOD}$  to  $512.7 \text{ pg g}^{-1} \text{ l.w.}$ ; Table S4) were apparently higher compared to those found in skipjack tuna (*Katsuwonus pelamis*) from Brazilian offshore waters (mean:  $4.2 \text{ pg g}^{-1} \text{ l.w.}$ ) (Ueno et al., 2005). This is not surprising, given that Guanabara Bay is the most anthropogenically-disturbed area along the Brazilian coast (Dorneles et al., 2008a, 2008b, 2013). Additionally, the predominance of OCDD in whitemouth croaker samples agrees with the results observed in blubber samples of Guiana dolphin (Dorneles et al., 2013), as well as in sewage sludge samples from wastewater treatment facilities in the Rio de Janeiro metropolitan area (Pereira and Kuch, 2005). Such predominance suggests that combustion processes, i.e. mass combustion, unleaded gasoline and diesel fuel combustion, and urban wastewater treatment plants, might be important sources of PCDD/F contamination in Guanabara Bay (Guerzoni et al., 2007). Regarding TEQ values, the levels reported in this study were lower than the European action level (Recommendation 2006/88/EC) and maximum permissible level (Regulation 1881/2006) for PCDD/Fs in fish muscle meat and products (set at  $2.3$  and  $3.2 \text{ pg TEQ g}^{-1} \text{ w.w.}$ , respectively) (EFSA, 2010). However, these results should be taken with caution, since previous research has demonstrated that PCDD/Fs accounted for  $<1.2\%$  of the total TEQ in all Guiana dolphins, indicating that polychlorinated biphenyls (PCBs) are the main cause for environmental concern in Rio de Janeiro state when compared to PCDD/Fs (Dorneles et al., 2013).

PBDE levels in marine biota along the Brazilian coast are usually related to sampling areas close to industrial and urbanized regions (Alonso et al., 2012, 2017; Dorneles et al., 2010; Magalhães et al., 2017; Quinete et al., 2011; Rosenfelder et al., 2012). For example, Lavandier et al. (2013) have found PBDE values below LOD in muscle of whitemouth croakers from Ilha Grande Bay, a less impacted estuary classified as a biodiversity hotspot in the south of Rio de Janeiro state (Creed et al., 2007). Conversely, fish from the Paraíba do Sul river

(north of Rio de Janeiro state) have shown apparently higher PBDE muscle concentrations than the ones reported here (i.e., with a mean of  $2.1 \text{ ng g}^{-1} \text{ w.w.}$ ; Quinete et al., 2011). While Guanabara and Sepetiba bays are among the most impacted areas along the Brazilian coastline (Baptista-Neto et al., 2016; Dorneles et al., 2008a, 2008b, 2013; Kjerfve et al., 1997; Molisani et al., 2004), the presence of urban (Rio de Janeiro and São Paulo cities) and industrial centres (chemicals, textiles, sugar-alcohol) along the course of Paraíba do Sul river might play a role in the presence of POPs contamination in its estuary (Linde-Arias et al., 2008).

The high detection frequency and abundance of tetra- (BDE-47) and penta- (BDE-99 and -100) PBDE congeners in whitemouth croakers (Fig. 2A; Table S6), could reflect the use of commercial pentaBDE (C-pentaBDE) mixtures in Southeastern Brazil (La Guardia et al., 2006). Additionally, the high contribution of BDE-47 in whitemouth croakers reflects a worldwide trend observed in aquatic biota (Houde et al., 2014; Mizukawa et al., 2009; Shao et al., 2016), including Brazilian environments (Alonso et al., 2012; Dorneles et al., 2010; Magalhães et al., 2017; Quinete et al., 2011). However, these results probably originate from the combination of several factors, such as (1) higher release of BDE-47 and, consequently, higher bioavailability for uptake by biota, (2) higher assimilation efficiency and resistance to metabolism, and (3) metabolic transformation via debromination from higher to lower brominated congeners (Munschy et al., 2011; Roberts et al., 2011; Stapleton et al., 2006).

Unlike BDE-47, BDE-209 has been less reported in biota. This could be linked to its physicochemical properties that cause low availability for, and low uptake by, biota, and by debromination into lower brominated congeners (Tomy et al., 2004; Stapleton et al., 2006; Munschy et al., 2011; Roberts et al., 2011). To the authors' knowledge, this is the first study reporting BDE-209 in fish from the southwest Atlantic Ocean, as previous studies have not targeted this congener (Lavandier et al., 2013; Magalhães et al., 2017; Quinete et al., 2011). The presence of BDE-209 in muscle of whitemouth croaker (Tables S6 and S7), as well as in the blubber of Guiana dolphin (*Sotalia guianensis*) from Guanabara Bay (Vidal, 2015), indicates the use of the commercial decaBDE (C-decaBDE) mixture ( $>92\%$  of BDE-209; La Guardia et al., 2006) in Southeastern Brazil. Additionally, the presence of BDE-183 in whitemouth croaker samples also suggests the recent use of commercial octaBDE (C-octaBDE) mixtures in Southeastern Brazil, since this congener has not been quantified in previous studies using mussels (sampled in 1996; Zhu and Hites, 2003), Guiana dolphin (from 1994 to 2006; Dorneles et al., 2010) and rays (Rosenfelder et al., 2012) from Guanabara Bay.

Among emerging BFRs evaluated in the present study, only HBB was quantified in whitemouth croaker samples. To the best of our knowledge, only two studies have previously reported levels of emerging BFRs in aquatic biota from the southwest Atlantic Ocean (Alonso et al., 2012; De la Torre et al., 2012). According to Alonso et al. (2012), HBB was detected in 13 (25% of individuals sampled) Franciscana dolphins (*Pontoporia blainvillei*) from the Southeastern and Southern coasts of Brazil, while PBEB was detected in four individuals (8% of the total). The low detection frequency of these compounds in aquatic biota could indicate their low use in Brazil. While HBB can be used directly as flame retardant in manufactured products (Covaci et al., 2011; De Wit et al., 2011), its presence in the environment can also result from thermal degradation of commercial mixtures of PBDEs, and volatilization of polymeric brominated flame retardants, such as pentabromobenzyl acrylate oligomer (De Wit et al., 2011; Gouteux et al., 2008). These aspects, combined with the low frequency of HBB detection in our samples, reinforce the hypothesis of low use of this compound in Brazil.

The dechlorane-related contamination pattern observed in whitemouth croakers (Dec 603  $>$  DP  $>$  mirex  $\approx$  Dec 602  $>$  CP) in the present study suggest, for the first time, Dec 603 as the most abundant DRC in environmental samples. This pattern is notable since Dec 603 is usually reported as low or non-detected values in biota (Houde et al., 2014;

Mekni et al., 2019; Rjabova et al., 2016). Patented by Hooker Chemicals (now Occidental Chemical Company, OxyChem, United States), Dec 603 is identified as a flame retardant, and also as an impurity in technical products of aldrin and dieldrin (legacy pesticides) (Shen et al., 2011). Brazil allowed the production of aldrin until 1990 and its use as wood preservative until 2000, while dieldrin has no register of use in Brazil but its production for export occurred until 1998 (MMA, 2015; Almeida et al., 2007). However, since aldrin and dieldrin have been reported in crabs (Souza et al., 2008) and in mussels (Galvão et al., 2015) from Southeastern Brazil, the occurrence of the emerging pollutant Dec 603 in whitemouth croaker in this region could be associated to the production and use of these pesticides.

DP showed the second highest contribution to  $\Sigma$ DRC in whitemouth croaker, as well as being reported in Franciscana dolphins (*Pontoporia blainvillei*) (Mirex > DP > Dec 603 > Dec 602 > CP) from the Southeastern and Southern Brazilian coasts (De la Torre et al., 2012). Since the major applications of DP are industrial polymers used for coating electrical wires and cables, connectors used in computers, and plastic roofing material (Hoh et al., 2006), this suggests that DP in Southeastern Brazil could be linked to high anthropogenic influence and industrial activity. The predominance of *anti*-DP isomer in whitemouth croakers ( $f_{anti} = 0.7 \pm 0.2$ ; Table 1) is consistent with commercial DP products (0.6–0.8; from Sverko et al., 2011 and Wang et al., 2010).

Mirex and Dec 602 showed similar contributions to  $\Sigma$ DRC in whitemouth croaker, but this is not in agreement with previous studies in aquatic biota worldwide that report higher levels of Mirex compared to Dec 602 (De la Torre et al., 2012; Peng et al., 2014; Rjabova et al., 2016). Mirex was widely used as a pesticide for ant control in Brazil (MMA, 2015) and, although banned in the 1990s (MMA, 2015), Mirex persistence remains an important factor to consider for understanding its detection in representatives of the Brazilian marine biota that have been recently sampled (Alonso et al., 2017; De la Torre et al., 2012; Santos-Neto et al., 2014). In contrast to Mirex, there is no information on Dec 602 use in Brazil, however, its presence in the environment appears to be related to its use as flame retardant in manufactured products (Sverko et al., 2011). The presence of Dec 602 in whitemouth croaker, as well as in marine mammals off the coast of Brazil (De la Torre et al., 2012; Alonso et al., 2017) reinforces the need for further research to investigate its ecotoxicological relevance.

Although the pollutant exposure of whitemouth croakers in Southeastern Brazil can be inferred through the POPs concentrations found in this study, to the best of our knowledge, no studies have focused on the mechanisms for accumulation and depuration, or on risk assessment for this species. Overall, the most likely routes of POPs uptake in fishes are dietary and respiratory via the gills and body surface area, whereas elimination is primarily via the respiratory surface, kidneys, and feces, and often involves metabolic transformation (Arnot and Gobas, 2004; Munschy et al., 2011; Tierney et al., 2013). Regarding risk assessment for POPs concentrations in fishes, studies on experimental exposure have demonstrated alterations in the immune and endocrine systems, as well as in their life-history traits such as reproductive success, growth and survival (Horri et al., 2018; Johnson et al., 2013). For example, McCarthy et al. (2003) have shown that parental exposure to a commercial PCB mixture (Aroclor 1254) through the diet, during gonadal recrudescence, affected growth and survival skills of Atlantic croaker (*Micropogonias undulatus*) larvae, reducing their growth rates and impairing their startle responses. In this context, POPs exposure could not only affect the physiological responses, but also recruitment and population dynamics and, to some extent, the effects could also affect fisheries productivity for commercial species.

#### 4.2. Linking pollutant exposure of whitemouth croakers to their ecological habits and biological features

Isotopic ratios of carbon and sulfur are usually used to establish the sources of organic matter that support food webs (Connolly et al.,

2004; McCutchan et al., 2003). Nitrogen stable isotope ratios can also be used to trace organic matter sources, but are more commonly applied to provide information on the position occupied by a species in a trophic web, as nitrogen isotopes show predictable stepwise increases in values from prey to consumer (DeNiro and Epstein, 1981). In this context, our three-isotope approach showed that  $\delta^{15}\text{N}$  was the isotopic ratio that was the most commonly correlated with pollutant concentrations in whitemouth croaker. Specimens with high  $\delta^{15}\text{N}$  showed higher levels of tri-, tetra- and penta-BDEs, as well as higher concentrations of DP, *anti*-DP isomer and  $\Sigma$ DRC. These findings suggest the occurrence of bioaccumulation and, to some extent, the biomagnification of some target pollutants through the coastal food web.

Bioaccumulation and biomagnification of organic pollutants can be influenced by many factors, such as their molecular size and octanol-water partition coefficients ( $K_{OW}$ ) (Kelly et al., 2007; Walters et al., 2016). In aquatic food webs, chemicals with  $K_{OW}$  values between  $10^5$  and  $10^8$  would have higher bioaccumulation and biomagnification potentials, while the opposite would occur for chemicals with  $K_{OW} > 10^8$  (Kelly et al., 2007; Stapleton et al., 2006; Walters et al., 2016). Therefore, low brominated PBDEs, such as tri-, tetra- and penta-PBDEs ( $K_{OW}$  between  $\sim 10^5$  and  $\sim 10^7$ ) are prone to bioaccumulate and biomagnify in aquatic food webs, as reported previously (Mizukawa et al., 2009; Shao et al., 2016), while bioaccumulation and biomagnification potentials of DP would be reduced ( $K_{OW} \sim 10^9$ ) (Hoh et al., 2006; Peng et al., 2014). Due to its high hydrophobicity, DP is mainly adsorbed to organic materials, and exhibits persistence in sediment (Sverko et al., 2011; Shen et al., 2010). From this perspective, the use of benthic species or benthivorous demersal species, such as the whitemouth croaker, might help to demonstrate bioaccumulation and biomagnification of DP through aquatic food webs (Carlsson et al., 2018; Na et al., 2017; Sühling et al., 2016). However, for DP isomers, aspects of stereoselective bioaccumulation potential and trophic transfer remain unclear. For instance, higher *anti*-DP concentrations upon organisms with  $^{15}\text{N}$ -enriched values were found in aquatic biota from Lake Winnipeg (Canada) (Tomy et al., 2007), as well as in the marine food webs of the Fildes Peninsula (Antarctica) (Na et al., 2017); while an opposite behaviour was found in the freshwater food web from Longtang Town (China) (Wu et al., 2010).

Negative correlations between fish size and  $\Sigma$ PBDE, tri- and tetra-BDEs were also found in the present study. This could be caused by depuration in fish, as reported in previous studies (Munschy et al., 2011; Tomy et al., 2004). However, it could also be linked with ontogenic habitat shifts, as older whitemouth croaker move into continental shelf waters outside of the bays, i.e. out of estuaries that are hotspots for contaminant exposure. This hypothesis is in accordance with the higher  $\delta^{34}\text{S}$  values found in larger whitemouth croaker from Guanabara Bay (Pizzochero et al., 2018), as these large fish probably mostly feed in continental shelf waters, which are  $^{34}\text{S}$ -enriched compared to coastal zones (Connolly et al., 2004; Thode, 1991).

## 5. Conclusion

This study provides new data on the contamination of Brazilian marine coastal environments by selected organic pollutants. It reveals the presence of non-PBDE brominated flame retardants and DRCs (Dec 602, 603, DP and CP) in fish from southwest Atlantic Ocean for the first time, albeit at low levels. PBDEs were detected in all samples analyzed, with the predominance of BDE-47, -99, -100, -153, 154, -183 and -209, which might reflect the use of C-pentaBDE, C-octaBDE and C-decaBDE commercial mixtures in the coastal regions of Rio de Janeiro state. Dec 603 and DP were the predominant DRCs in whitemouth croakers and their presence in fish raises concern and strengthens the need for further research not only on their toxicity and bioaccumulation potentials, but also on their occurrence and distribution in the environment. TEQ total levels for dioxins and furans ranged from 0.1 to  $0.2 \text{ pg g}^{-1} \text{ w.w.}$ , which is lower than the European action and maximum



permissible levels for PCDDs and PCDFs for fish muscle meat and products (set at 2.3 and 3.2 pg TEQ g<sup>-1</sup> w.w., respectively). Concentrations of tri-, tetra- and penta-BDEs, as well as ΣDRC, DP and anti-DP isomer were positively correlated with δ<sup>15</sup>N, suggesting biomagnification along the food web resulting in the contamination levels reported for whitemouth croaker. On the other hand, ΣPBDE, tri- and tetra-BDEs were negatively correlated with fish size, which could be linked with depuration by fishes and/or habitat shift throughout the whitemouth croaker life cycle. Overall, our study confirms that whitemouth croaker might be a suitable sentinel species of coastal pollution. Moreover, it emphasizes the need for further investigations focusing on multiple species, as well as in water and sediment samples, to help understand the complex patterns of bioaccumulation and biomagnification. These processes seem to occur in Southeastern Brazil, and they could impact not only the marine biota, but also the human population dependent on this biota for food.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.05.213>.

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