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BROMINATED FLAME RETARDANTS, DECHLORANE RELATED COMPOUNDS, ΣPCDD AND ΣPCDF DETERMINATION IN WHITEMOUTH CROAKERS (MICROPOGONIAS FURNIERI) FROM SOUTHEAST BRAZILIAN REGION

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Introduction

The whitemouth croaker, Micropogonias furnieri (Desmarest, 1823) (Perciformes, Sciaenidae) is the main demersal fishery target along the Atlantic coast in South America[1]. This euryhaline and eurythermic demersal-pelagic fish has a wide geographical distribution in the Western Atlantic, from Yucatan Peninsula (25ºN), along the southern Caribbean and the Brazilian coast, to the Gulf of San Matías, Argentina (41ºS)[2]. It occurs on sandy and muddy bottom areas in coastal waters and estuaries where the nursery and feeding grounds are located. In Brazil, this species occupies the second place among coastal fishes of commercial value[3]. In this perspective, the present study attempted to investigate the levels of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), dechlorane-related compounds - DRCs [Mirex, Dechlorane 602, 603, 604, Dechlorane Plus (DP) and Chlordane Plus (CP)] and polybrominated diphenyl ethers (PBDEs) (IUPAC congener numbers 17, 28, 30, 47, 49 & 71, 66, 77, 85, 99, 100, 119, 126, 138, 139, 140, 153, 154, 156 & 169, 171, 180, 183, 184, 191, 196, 197, 201, 203, 204, 205, 206, 207, 208 and 209) in muscle samples of whitemouth croakers from Southeastern Brazilian coast.

Materials and methods

Muscle samples were obtained (in 2014) from 20 individuals caught in Guanabara (n=14) and Sepetiba (n=6) Bays, two important fishing areas in the Rio de Janeiro state (RJ), Southeast Brazilian region (Figure 1). Once collected, samples were lyophilized and stored up to the moment of the analyses.

Inserted in the metropolitan area of the city of Rio de Janeiro, Guanabara Bay (22º24' and 22º57' S / 43º33' and 43° W, 328 km^2) is under direct influence of the approximately 11 million people living in its surroundings, which comprise 80% of the RJ state population[4]. This estuary is the most anthropogenically disturbed area along the Brazilian coastline (around 8500 km), receiving sewage, industrial waste and consequently many contaminants that are transported along its drainage basin, which is composed of 45 rivers in total[5]. Sepetiba Bay is located in Rio de Janeiro state (Brazil, 22º55' and 23º 05'S/ 43º40' and 44º40'W, 450 km^2). This estuary has been severely impacted by human occupation and industrial activities in its basin, during the past 30 years. Its drainage basin is surrounded by a population of about 1.2 million people and over 400 industries, including metallurgical, petrochemical and pyrometallurgical smelters[6].

The analytical procedure was detailed elsewhere[7]. Briefly, aliquots of 1-8 g of freeze-dried muscle were fortified with ^{13}C labeled surrogate standards including $^{13}C_{12}$-PBDEs (BFR-LCS; Wellington Laboratories Inc.), $^{13}C_{12}$-PCDD/Fs (1613-LCS; Wellington Laboratories Inc.) and $^{13}C_{10}$ syn- and anti-DP (Cambridge Isotope Laboratories Inc). The extraction was performed using a Dionex ASE100 apparatus. The resulting extract was evaporated to constant weight for gravimetric lipid determination, and then redissolved in hexane. After using sulphuric acid to remove organic matter from the extracts, the organic phase was transferred to an open glass column (i.d. 7 mm) filled with acid silica, covered with 1 g anhydrous sodium sulfate and eluted with 50 mL of hexane. Fractionation step was performed in an automated purification Power Prep TM System (FMS, Inc., USA) including acidic silica gel and basic alumina columns. The final extracts were concentrated avoiding dryness, spiked with (BFR-ISS and 1613-ISS; Wellington Laboratories Inc) internal standard solutions and further analyzed by GC–HRMS. Toxic equivalent (TEQ) concentrations of PCDD/Fs were calculated using the World Health

Organization-2005 toxic equivalency factors (TEF)[8]. Recoveries for Dechlorane Plus ($^{13}C_{10}$-syn-DP and $^{13}C_{10}$-anti-DP), $^{13}C_{12}$-PCDD/Fs, and $^{13}C_{12}$-PBDEs in this study were 81 ± 10%, 79 ± 14%, 82 ± 9% (mean ± SD), respectively. A nonparametric statistical test (Mann-Whitney U test) was used since data significantly deviated from a normal distribution (Shapiro-Wilk's W test).

Results and discussion

Biological data and results for PBDE, DRC, PCDD, PCDF, and TEQ concentrations in whitemouth croaker muscle samples are summarized in Table 1. Levels of some PCDDs (2,3,7,8– Tetra CDD; 1,2,3,7,8– Penta CDD and 1,2,3,4,7,8– Hexa CDD), dechorane 604 and some PBDEs (BDE-30, -138, -171, -180, -191, -196, -197, -201, -203, -204 and -205) were below detection limit in all of the samples and thus they were considered as zero.

Brominated compounds

No statistically significant difference ($p>0,05$) was found in muscle ΣPBDE levels between whitemouth croakers from the two estuaries. A high percentage of the tetra-BDE congeners was observed in the vast majority of the samples analysed, being BDE-47 the major congener (accounting from 5 to 97% to total PBDEs levels; min–max), followed by the deca-BDE (BDE-209) (0 – 78%, min–max) and by the penta-BDEs, being the BDE-100 (1 – 23%; min–max) and BDE-99 (0 – 12%; min–max) the most expressive penta-BDE congeners (Figure 2). The high contribution of BDE-47 corroborates several other studies, reflecting a worldwide trend observed in many aquatic ecosystems[9]. Ondarza et al.[10] reported a similar predominance of BDE-47 (69 ± 18%; mean ± SD) in the muscle of Patagonian silverside (Odontesthes hatcheri) from Argentina. Little is known about PBDE concentrations in fish samples from South Atlantic, but the consistently higher BDE-47 concentration implies that either BDE-47 is much more resistant to any kind of degradation processes, or that it has a much higher bioaccumulation and/or biomagnification potential. It is also important to keep in mind the high BDE-209 concentrations found in the present study. This deca-BDE is said to degrade through a variety of mechanisms, forming lighter congeners[11].

Dechlorane related compounds

Possible differences in ΣDRC concentrations were also investigated; however, the test did not indicate any significant difference between whitemouth croakers from the two areas ($p>0.05$). The DRC pattern found in this study ranked the compounds as follows: Dec 603 [n.d. – 26 (3.4) pg g^{-1} ww; min–max (mean)] > DP [n.d. – 32 (4) pg g^{-1} ww] > Dec 602 [n.d. – 7 (1.3) pg g^{-1} ww; min–max (mean)] > Mirex [n.d. – 4.2 (1.2) pg g^{-1} ww] > CP [n.d. – 0.9 (0.5) pg g^{-1} ww]. The percentual contribution from individual dechlorane-related compounds to ΣDRCs is shown in Figure 3. Caution should be exercised regarding interspecies and intersite comparisons; however, the dechlorane pattern found in whitemouth croaker was opposite to the one found in Baltic wild salmon[12]. Up to now, no specific applications for dechlorane 603 were found. Only some references to its presence as an impurity in some organochlorine pesticides such as aldrin and dieldrin were found[12, 13, 14].

The fractional abundance of the anti-DP isomer (fanti) was calculated for each sample by dividing the concentration of anti-DP with the sum of syn-DP and anti-DP concentrations. The obtained fanti value (0.7 ± 0.2; mean ± SD) closely resembled the one reported for franciscana dolphin (Pontoporia blainvillei) from the same area (southeastern and southern Brazilian regions)[7], or even those reported by other studies worlwide[12]. To the best of our knowledge, with the exception of a study on a marine mammal species[7], there are no previous investigations on dechlorane-related compounds on nektonic organisms from South Atlantic.

PCDDs and PCDFs values

The dl-PCBs were not determined in this study. Therefore, total WHO-TEQ comprised only PCDDs and PCDFs values. WHO-TEQ total levels ranged from 0.1 to 0.2 pg WHO-TEQ g^{-1} ww (Table 1). Despite the possible contamination sources of these pollutants surrounding the estuaries, the founded values are lower than the European action level (EC, 2002) and maximum permissible level (EC, 2006) of PCDDs, PCDFs and dl-PCBs for muscle meat fish and products (set at 2.3 and 3.2 pg TEQ g^{-1} ww, respectively)[8]. However, it is also important to keep in mind that these fishes were sampled in two estuaries under high

anthropogenic disturbance, as well as that a previous study from our research team has demonstrated PCBs to be the main cause for environmental concern in RJ state when compared to PCDDs, PCDFs[15].

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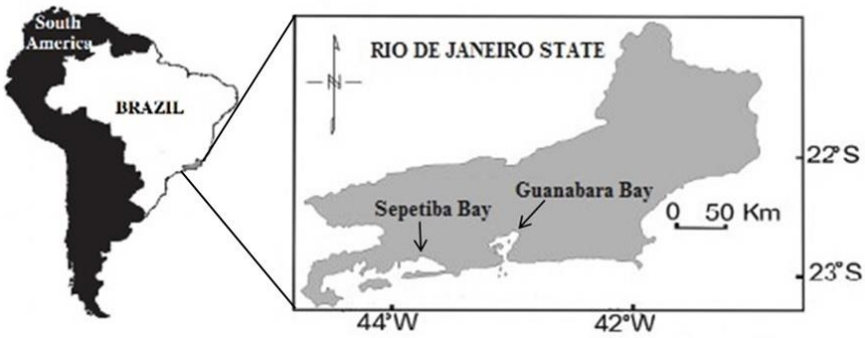

Figure 1: South America map stressing Brazil and the Brazilian state of Rio de Janeiro (gray). The map of Rio de Janeiro state is amplified and shows Guanabara and Sepetiba Bays.

Table 1: Biological data and muscular concentrations (Mean ± SD; Min–Max) of PBDEs, dechloranes, PCDDs, PCDFs and TEQs (pg g^{-1}wet weight) in whitemouth croakers (*Micropogonias furnieri*) from southeast Brazilian region.

Sampling	Weight (Kg)	Size (cm)	∑PBDEs[a] (pg g^{-1})	∑DRCs[b] (pg g^{-1})	∑PCDDs[c] (pg g^{-1})	∑PCDFs[d] (pg g^{-1})	TEQ[e] (pg g^{-1})
Sepetiba	1.4 ± 0.2	47 ± 1.6	230 ± 293	8.5 ± 11	-	-	-
(n = 6)	1.1 - 1.5	45 - 49	41 - 880	1 - 34	-	-	-
Guanabara Bay	1.9 ± 0.9	57 ± 8.5	91 ± 106	6.8 ± 10.4	0.5 ± 0. 4	0.3 ± 0.3	0.1 ± 0.03
(total n = 14) PCDD/Fs (n=10)	0.9 - 4.4	46 - 75	7.6 - 326	n.d. - 42	n.d. - 1.3	n.d. - 0.9	0.1 - 0.2
TOTAL	1.8 ± 0.8	54 ± 8.3	133 ± 194	7.3 ± 10.8	-	-	-
	0.9 - 4.4	45 - 75	7.6 - 880	n.d. - 42	-	-	-

n.d. = not detected.
[a] ∑PBDEs: sum of BDE-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.
[b] ∑DRCs: sum of mirex, declorane 602, 603, DP and CP.
[c] ∑PCDDs: sum of 1,2,3,6,7,8– Hexa CDD; 1,2,3,7,8,9– HexaCDD; 1,2,3,4,6,7,8– Hepta CDD; Octa CDD (OCDD).
[d] ∑PCDFs: sum of 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.
[e] TEQ: sum of TEQ of PCDDs and PCDFs.

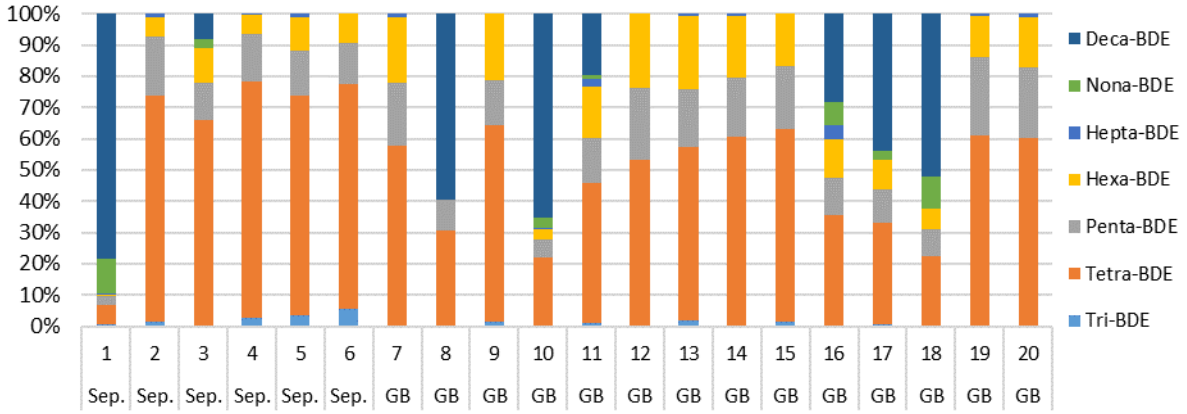

Figure 2: Relative contribution of the PBDEs, grouped by bromination degree. The figure exposes the individual codes of each whitemouth croaker (e.g 1, 2, 3, ... 20) and the sampling area (Sep. = Sepetiba Bay; GB = Guanabara Bay).

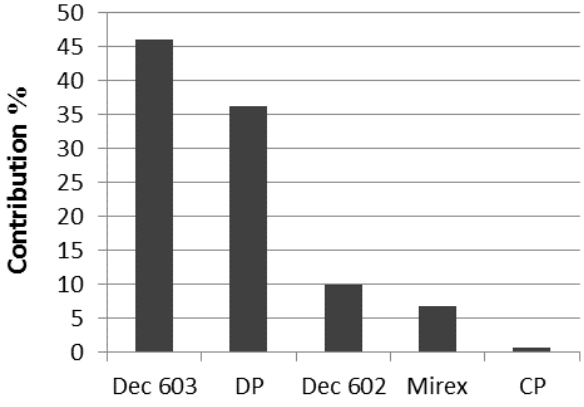

Figure 3: Contribution (%) from individual dechlorane related compounds to ΣDRC contamination in whitemouth croakers from southeast Brazilian region.