PERSISTENT ORGANIC POLLUTANTS (POPs) IN TWO SPECIES OF EDIBLE FISHES (*Micropogonias furnieri* AND *Sardinella brasiliensis*) FROM GUANABARA BAY, RIO DE JANEIRO, BRAZIL

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Introduction

Persistent Organic Pollutants (POPs) are chlorinated organic chemicals which present high lipophility and chemical stability, being strongly bioaccumulative in the environment. They represent a threat to animals and humans so their production and use were restricted and/or banned in the 1970s[1]. In spite of that, they can be still found in all environmental compartments. Organochlorine pesticides (OCPs) and Polychlorinated Biphnenyls (PCBs) are examples of POPs. OCPs were produced and use for several decades - mainly for agriculture and public health purposes, while PCBs were widely used in industrial and commercial applications. In Brazil, the most frequently used commercial mixture of PCBs was Ascarel, which main composition included PCBs 28, 52, 101, 118, 138, 153 and 180, sometimes referred to ascalled indicator PCBs (ind-PCBs). The term ind-PCBs is used because they are commonly found at higher concentrations in the environment[2]. The main route of exposure to these contaminants for human is food; specially, seafood and dairy products[3].

The Guanabara Bay is an oceanic bay located in the southeastern region of Brazil, in the State of Rio de Janeiro. Every day, the Bay receives a large amount of untreated domestic sewage and industrial effluents from a densely populated area with over 10.000 factories, has intense port activity and a big petrochemical complex[4]. This results in severe degradation of the Guanabara Bay that features eutrophic conditions. For example, high density of phytoplankton and high concentrations of nutrients, which result in waters with high organic production. Eutrophication produces changes in water quality, including the reduction of dissolved oxygen and aquatic biodiversity; hence, can generate extensive fish casualties and can lead to serious consequences related to public health[5]. Moreover, the bay has a high sedimentation rate, high concentrations of toxic metals, aromatics and other persistent organic pollutants (POPs) in the sediments. Micropollutants such as heavy metals, organochlorine pesticides, and polychlorinated biphenyls flow through food chains and may experience an increase in their concentration as they reach high trophic levels, characterizing the process called biomagnification[6].

Despite its high level of pollution, fishing in Guanabara Bay is responsible for most of the fish production in the Rio de Janeiro market, reaching over 50% of fish production in the state. Two representative edible fish species found in this bay are *Sardinella brasilensis* and *Micropogonias furnieri*[7]. They belong to two different families (Clupeidae and Scianeidae, respectively) with different feeding habits, being *S. brasiliensis* a sample of planktonic fish[8] while *M. furnieri* are benthic fishes[9]. Therefore, this study aims to determine OCPs and ind-PCBs in samples of *S. brasiliensis* and *M. furnieri* collected from Guanabara Bay, Rio de Janeiro, Brazil.

Materials and methods

Twelve samples of two edible fish species (*Sardinella brasiliensis* and *Micropogonias furnieri*) were collected from Guanabara Bay, in Rio de Janeiro, Brazil. Composite samples of muscle tissues (fillets) of each species were taken from fresh fish and stored in aluminum foil at -20 °C. Two specimens were used to form 6 composite samples of each species. Before OCPs and PCBs analysis, fillets were submitted to freeze-drying for total water removal.

Extraction of pesticides and PCBs was carried out using Soxhlet and 10g of freeze dried fish composite samples. All steps of sample preparation were carried out as described previously[10]. In this study, the concentration of the following compounds were determined in samples of fish: aldrin, endrin, isodrin, dieldrin, endosulfan, heptachlor, heptachlor epoxide, methoxychlor, mirex, hexachlorobenzene (HCB), hexachlorocychlohexane (α-

HCH, β-HCH, δ-HCH, γ-HCH), α-chlordane, γ-chlordane, DDTs (o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE) and the 7 ind-PCBs (PCBs 28, 52, 101, 118, 138, 158, 180). The analytical recovery rate (using PCB-103 and PCB-198 as Standards) in the samples was of the order of 80% - 120%. OCPs and PCBs determination was carried out using a Gas Chromatograph with an automatic injector AOC-20i coupled to an Electron Capture Detector (GC-ECD) (GC-2010 from Shimadzu, Japan).

Analysis of sample extracts were preceded by the analysis of a standard solution to all OCPs and PCBs detected in this study. All chromatograms were scrutinized for chromatographic peak shape and resolution. The chromatographic conditions were: automatic injector operates in split-less mode at 180 °C; Hydrogen was used as carrier gas at a flow of 2 mL min^{-1}; Nitrogen was employed as an auxiliary gas at a flow of 45 mL min^{-1} and the ECD temperature was 310 °C. All solvents, Silica and Florisil® used in this study were of trace analysis quality and were purchased from Merck Co., Sigma Aldrich Co. or TediaBrazil. OCPs and PCBs standards were obtained from AccuStandard (New Haven, CT, USA).

Results and discussion:

All samples contained all OCPs and ind-PCBs determined in this work. The concentration of organochlorine pesticides in dried fish samples of two different species (*Sardinella brasiliensis* and *Micropogonias furnieri*) collected in Guanabara Bay is exposed in table 1. Values of concentrations (mean, median, and range) are expressed in ng $g^{-}1$ fat weight.

Table 1. Mean, median, and range (minimum – maximum) of the concentration of Organochlorine Pesticides (OCPs) in muscle of *Sardinella brasiliensis* and *Micropogonias furnieri* collected from Guanabara Bay, Rio de Janeiro, Brazil. Concentrations are expressed as ng g^{-1} fat weight (n=6 composite samples, being 2 specimens for each sample).

	Sardinella brasiliensis		*Micropogonias furnieri*	
COMPOUND	**MEAN**	**MEDIAN (min-max)**	**MEAN**	**MEDIAN (min-max)**
∑'DRINs[a]	106.9	125.7 (19.3 – 175.9)	755.9	102.4 (54.6 – 2110.7)
ENDOSULFAN	13.3	13.950 (6.2 – 25.7)	34.2	32.3 (5.4 – 54.5)
∑HEPTACHLOR[b]	42.3	43.1 (36.3 – 47.7)	109.2	91.9 (90.1 – 145.8)
METHOXYCHLOR	25.5	22.73 (20.7 – 28.7)	68.3	57.5 (15.83 – 109.14)
MIREX	0.9	1.01 (0.3 – 1.4)	49.2	28.6 (26.3 – 92.4)
HEXACHLOROBENZENE (HCB)	3.0	3.15 (1.8 – 4.2)	135.9	162.0 (17.9 – 228.1)
∑α,β,δ,γ-HCH	10.7	10.63 (7.3 – 14.2)	139.1	144.1 (84.9 – 188.3)
∑CHLORDANE[c]	8.6	7.62 (2.8 – 17.4)	102.6	82.9 (58.1 – 136.8)
∑DDTs and METABOLITES[d]	126.8	141.39 (44.8 – 194.2)	520.0	455.2 (384.8 – 720.0)
TOTAL	**321.2**	**372.1 (136.2 – 506.1)**	**1903.6**	**1156.9 (728.2 – 3785.7)**

[a] Sum of aldrin, endrin, isodrin and dieldrin; [b] Sum of Hehptachlor and its epoxide; [c] Sum of α and γ chlordane; [d] Sum of o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE and p,p'-DDE.

Results displayed in Table 1 show the total OCPs levels in fishes collected from Guanabara Bay ranging from 136.22 ng g^{-1} to 506.1 ng g^{-1}, with a mean of 321.2 ng g^{-1} and a median value of 372.1 ng g^{-1} in *Sardinella brasiliensis*, while the values in *Micropogonias furnieri* ranged from 728.2 ng g^{-1} to 3785.7 ng g^{-1} with a mean of 1903.6 ng g^{-1} and median of 1156.9 ng g^{-1}. The mean concentration of total OCPs measured is almost 6 times higher in *M. furnieri* (1903.6 ng g^{-1}) than in *S. brasiliensis* (321.2 ng g^{-1}). Among OCPs, the most abundant was the sum of DDTs and its metabolites in *S. brasiliensis*, representing 39% of the total OCPs in this species. In the *M. furnieri* species, the sum of 'Drins was most abundant, representing 40% of total OCPs in this species.

Figure 1 presents that all organochlorine pesticides concentrations were higher in *M. furnieri* than in *S. brasiliensis*. Unexpectedly, aldrin presented higher levels than its metabolite dieldrin. The same was revealed with DDTs and other related compounds. Reductive conditions inside the highly polluted Guanabara Bay may have contributed to this result.

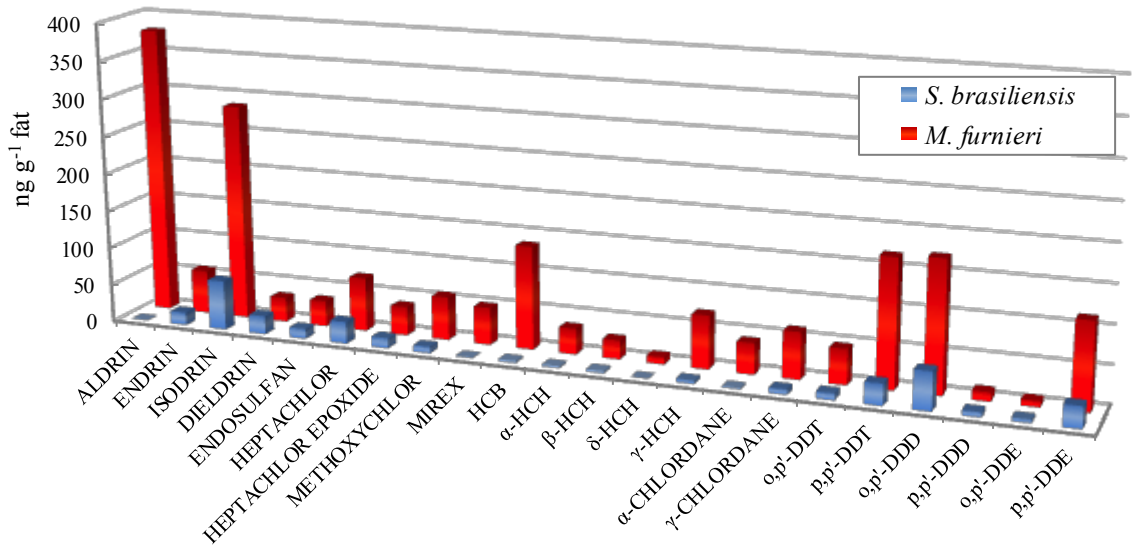

Figure 1. Level and Profile of Organochlorine Pesticides in muscle of edible fish (*Micropogonias furnieri* and *Sardinella brasiliensis*) collected from Guanabara Bay, Rio de Janeiro, Brazil. Values represent the mean concentration of ind-PCBs and are expressed as ng g^{-1} fat weight (n=6 composite samples being 2 specimens for each sample).

Levels and profile of indicator-PCBs in edible fish collected in Guanabara Bay are showed in figure 2 (fat weight basis). All seven ind-PCBs were found in both fish species. As observed within pesticides, samples of *M. furnieri* presented higher concentrations of ind-PCBs than samples of *S. brasiliensis*. The levels of ind-PCBs ranged from 390.8 ng g^{-1} to 630.3 ng g^{-1} with a mean value of 532.2 ng g^{-1} and a median value of 575.1 ng g^{-1} in *S. brasiliensis* samples, while in the *M. furnieri* samples the levels of ind-PCBs ranged from 1707.6 ng g^{-1} to 2923.0 ng g^{-1} with a mean value of 2153.7 ng g^{-1} and a median value of 1830.5 ng g^{-1}.

Since *M. furnieri* is a bentonic fish and even eat other fishes, it was expected that levels of contamination in this type of fish would be higher than contamination levels in *S. brasiliensis*. The high concentration of OCPs and PCBs observed in this study confirms that Guanabara Bay presents an elevated level of contamination which represents an inestimable risk to human health.

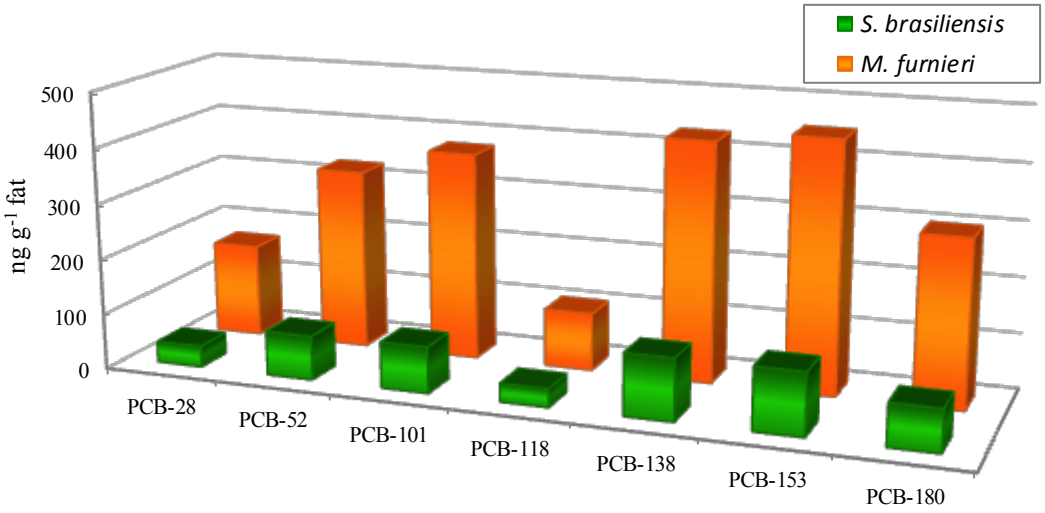

Figure 2. Level and Profile of indicator Polychlorinated Biphneyls (ind-PCBs) in muscle of edible fishes (*Micropogonias furnieri* and *Sardinella brasiliensis*) collected from Guanabara Bay, Rio de Janeiro, Brazil. Values represent the mean concentration of ind-PCBs and are expressed as ng g^{-1} fat (n=6 composite samples being 2 specimens for each species).

Acknowledgements

The authors are indebted to CNPq, CAPES and FAPERJ for scholarships and funding.

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