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# Measurement of chlorinated dioxins, furans and PCBs in Ardea alba Great Egret, and Puffinus puffinus Manx Shearwater: Ilha Grande Bay, Rio de Janeiro, Brazil *

## *Medição dos níveis de poluentes orgânicos persistentes em Ardea alba (Linnaeus, 1758), Garça branca, e Puffinus puffinus (Brünnich, 1764), Pardela. Estudo de caso: baía da Ilha Grande, Rio de Janeiro, Brasil*

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**ABSTRACT**

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) concentrations were measured in seabirds from Rio de Janeiro, Brazil. Species, Great Egret and Manx Shearwater, were collected in 2008-2010 on Ilha Grande bay. Detectable hepatic concentrations of PCDD/Fs and PCBs were found in all samples analyzed. The concentrations were below the range of concern established by WHO. This is the first measurements of PCDD/Fs and PCBs congeners in seabirds from this area, and suggests that future studies should take note of the results in order to test for a greater range of compounds and species and to determine levels of environmental contamination.

**Keywords:** Persistent organic pollutant; risk to environment and health**;** seabird; dioxin; polychlorinated biphenyl ethers

***RESUMO***

*Concentrações de dibenzeno-p-dioxinas policloradas (PCDD), dibenzofuranos policlorados (PCDF) e bifenilas policloradas (PCBs) foram analisadas em aves marinhas do Rio de Janeiro, Brasil. Ardea alba e Puffinus puffinnus foram coletadas durante 2008-2010 na baía da Ilha Grande. Detectáveis concentrações hepáticas da PCDD/Fs e PCBs foram encontradas em todas as amostras analisadas, apesar da concentração dos poluentes pesquisados estarem dentro dos limites de segurança estabelecidos pela OMS. Estes dados representam algumas das primeiras medições de PCDD/Fs e PCBs em aves marinhas da área, e pressupõe que futuros estudos devam dar sequencia a esta iniciativa, de forma a se ter uma maior gama de testes ampliando as espécies pesquisadas, bem como uma abrangência dos níveis de contaminação ambiental.*

***Palavras-chave:*** *Poluente orgânico persistente; risco ao ambiente e saúde; ave marinha; dioxinas, éteres bifenilos policlorados.*

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## 1. INTRODUCTION

The success of modern societies is, in part, based on extensive achievements of chemistry with a systematic development of products in medicine, agriculture, and in almost all manufacturing industry sectors and materials for daily use. Chemistry, herein, contributes to the quality of life for billions of human beings (Larsson, 1985; Mackay *et al.,* 1991). However, the negative impacts to environment and health are an important issue of public concern. Social and ecological interests should not be disregarded in spite of the economic forces.

Annual world production of chemicals has increased from around 7 million tons per year in the 1950s to 400 million tons in the last few years (Allen *et al.,* 2008). The number of commercially produced substances is not precisely known, although the upper estimate is about 100,000 (Carpenter, 1998; Zarkera & Kerr, 2008). Related to the increasing production of the chemical industry, it is imperative to improve regulation of substances that have been proved or suspected to cause adverse effects to human and environmental health (Ferreira, 2007).

Persistent organic pollutants (POPs) are hazardous to the environment and human health. Due to their physical and chemical properties, particularly their high stability, POPs can accumulate in the tissues of humans and animals (Ferreira, 2008). POPs consist of intentionally produced compounds such as pesticides or industrial chemicals, and unintended by-products of industrial processes (Kumar *et al.,* 2001).

Among the POPs, PCDD/Fs and PCBs constitute three groups of relevant persistent organic pollutants with chronic toxicity to humans and biota (Moriarty, 1999). Due to their persistency, the distribution and recirculation in the environment often continues for a long period of time. Due to their hydrophobic nature and resistance towards metabolism, these chemicals have been found in fatty tissues of animals and humans. Thereby they appear virtually everywhere within the biosphere, and poses a toxic stress to living organisms (Tanabe *et al.,* 2004).

All have been widely banned or restricted for more than twenty years and yet all appear ubiquitously in the environment. With respect to bio-accumulation in organisms, more than 90% of the average human intake of PCDD/Fs and PCBs originates from food, especially food of animal origin (Walker *et al.,* 2006). There is no legislation in Brazil to establish a limit for human consumption of aquatic organisms contaminated by dioxins and furans.

There are 75 different PCDDs and 135 PCDFs, which differ from each other in the number and positions for the chlorine atoms (Breivik *et al.,* 2002). From the human/biota point of view, 17 PCDD/Fs chlorine substitution in the (2,3,7,8-) positions are considered to be toxicologically important (Walker *et al.*, 2006; Ferreira, 2008). PCDDs have a planar aromatic tricyclic structure with 1-8 chlorine atoms as substituents (**Figure 1**).

There are 209 possible congeners of PCBs, but even the technical mixtures of PCBs have only a fraction of the total possible number. Some PCBs are called dioxin-like (co-planar/non-ortho-) PCBs. Those congeners do not have any or have only one chlorine atom (mono-ortho-PCBs) in the ortho-position to the carbon-carbon bond between the two benzene rings. Approximately 120 of PCBs are present in commercial products such as Aroclor 1254, Aroclor 1260 and Chlopen A60 (Walker *et al.,* 2006). Ballschmiter & Zell (1980) proposed a simple numbering system of the PCB congeners, giving each congener a number from one to 209. PCBs have two benzene rings attached to each other, with 1-10 chlorine atoms as substituents (**Figure 1**).

### 1.1 Persistency and toxicity

PCDD/Fs and PCBs are environmentally stable and (in particular 2,3,7,8-chlorine substituted PCDD/F congeners) biologically persistent (Giesy *et al.,* 1994). These characteristics together with high lipophilicity (log $K_{ow}$ for PCDD/Fs ranging from 6.1 to 8.2, and for PCBs from 4.9 to 8.2; Mackay et al., 1991), result in accumulation of PCDD/Fs and PCBs in food web (Shaw *et al.,* 2006).

The toxicity of PCDD/Fs involves the cytosolic aryl hydrocarbon receptor (AHR), which is a ligand-activated transcription factor. Binding of PCDD/Fs to AHR initiates the expression of several genes in a cell (Assmuth & Vartiainen, 1994). The most toxic congener of PCDD/Fs is 2,3,7,8-tetrachlorodibenzo-pdioxin (TCDD), which serves as a reference compound in terms of its affinity to AHR for the

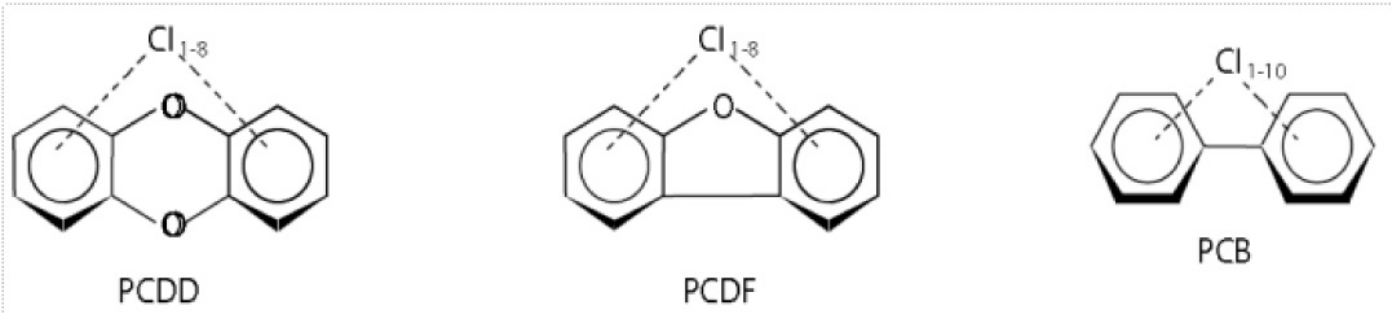


**Figure 1.** Chemical structures of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs).
***Figura 1.*** *Estruturas químicas de Dibenzo-p-dioxinas policloradas (PCDDs), dibenzo-furanos policlorados (PCFs) e bifenilas policloradas.*

other PCDD/Fs, and also for dioxin-like PCBs. The concept of TCDD toxic equivalency factor (TEF) was developed to describe the total toxic equivalent quantity (TEQ) of a mixture of PCDD/Fs and/or dioxin-like PCBs (Alcock *et al.,* 1998). Each congener of dioxins or dioxin-like PCBs exhibits a different level of toxicity. In order to be able to sum up the toxicity of these different congeners, the concept of toxic equivalency factors (TEFs) has been introduced to facilitate risk assessment and regulatory control. This means that the analytical results relating to all the individual congeners or compounds of toxicological relevance (17 dioxin and 12 dioxin-like PCB congeners) are summed and expressed as TCDD toxic equivalent concentration or TEQ (Wania *et al.,* 1998; Moriarty, 1999).

### *1.1.1 Environmental chemistry*

The marine environment receives POPs through wet- and dry deposition to the water-surface, and by diffusive vapour exchange between air and water (Wania *et al.,* 1998). Transport of POPs from sediment to water is of great concern since it is suspected that historically polluted sediments may act as a source to the overlying water column (Larsson 1985), thereby prolonging the exposure of biota, long after emissions are stopped. The key processes that determine the transport of POPs over the sediment-water interface are (a) the sedimentation and resuspension of particles, (b) the diffusive movement of the POPs and also POPs attached to dissolved organic matter. In systems where oxygen is present, benthic animals such as worms, bivalves, and molluscs increase the mixing of the particles with the associated pollutants.

### *1.1.2 Seabirds*

Seabirds are one of the most conspicuous faunal groups of the coastal and marine environment (Tasker & Reid, 1997). For millennia humans have followed birds at sea to locate fish and mammals (Montevecchi, 1993). Worldwide, seabird research has undergone a major evolution in terms of data collection, interpretation of the information and application in the field of management and policy (Tasker & Reid, 1997). Seabirds have been used in several environmental monitoring studies (Walker *et al.,* 2006). Fish-eating birds may be well suited for the assessment of effects of PCDD/Fs and PCBs due to their wide distribution (Basler, 1994). They also bioaccumulate relatively high levels of PCDD/Fs and PCBs due to their higher trophic levels and due to their limited abilities to metabolize anthropogenic compounds (Becher *et al.,* 1995).

The goal of this work was to evaluate concentrations of PCDD/Fs and PCBs in livers of *Ardea alba* (Linnaeus, 1758), Great Egret, and *Puffinus puffinus* (Brünnich, 1764), Manx Shearwater, collected from Ilha Grande Bay, which is situated in the southern Atlantic Coast of Rio de Janeiro State, Brazil.

## 2. MATERIALS AND METHODS

### 2.1 Study site

Ilha Grande Bay is located in the southern state of Rio de Janeiro (22° 50'- 23° 20'S, 44° 00' - 44° 45'W), and has an area of about 65.258 ha and 350 km perimeter on the waterline (**Figure 2**). The region has great scenic beauty a rich fauna and flora, and therefore a natural sanctuary for biodiversity (hot-spot), which lies between the two largest cities in South America - the cities of Rio de Janeiro and São Paulo. This richness and diversity of species, still little known, are due to geographic peculiarities, and hydrographic oceanographic region, coupled with factors such as diversity and connectivity of coastal systems, input of organic matter from rivers, physical variation and chemical oceanographic factors (Lailson-Brito *et al.,* 2010).

The region of Ilha Grande Bay is home to the territories of the cities of Parati and Angra dos Reis, who had 145,000 inhabitants in 2010. In view of the beautiful landscape of the region, its main vocation naturally focuses on tourism and nautical leisure. Consequently, along the coast there is a green series of developments that, through the occupation of hillsides, riverbanks or islands and the landfill of mangrove areas, cause deforestation and polluted coastal waters. This growth as tourist hub promoted a disorderly development and causes severe damage to coastal systems. In the region there are still other large projects, such as a commercial port, a petroleum terminal, an ore terminal, two nuclear power plants and a shipyard (Ferreira, 2010).

### 2.2 Analysis: Identification and Quantification

A total of 21 male seabirds (*Ardea alba*, n=9; *Puffinus puffinus*, n=12) were collected as dead stranded animals from 2008 to 2010. All fresh carcasses were necropsied following a standardised protocol (Jauniaux *et al.,* 1996). Livers were collected, weighed and kept frozen (-18°C) prior to chemical analyses.

Chemical analysis of PCDDs, PCDFs (PCDD/Fs) and coplanar PCBs followed the method described in a previous report (EPA, 2003; EPA, 2007). Five grams of liver samples were weighed and lyophilised. Dry tissues were inserted in a steel extraction cell and placed in the Accelerated Solvent Extractor (ASE 200, Dionex). This machine using organic solvents operates under high pressure and temperature conditions (10 minutes at 125°C and 1500psi) and allows the extraction of the different organic compounds present from the biological matrix. After being extracted, the samples were concentrated using Kuderna-Danish, the extract evaporated down to 1 ml, and the solvent was transferred to 10 ml of n-hexane. Fat content was determined gravimetrically from an aliquot of the extract (Kiviranta *et al.,* 1999).

Seventeen 2,3,7,8-substituted $^{13}$C-labeled tetra- through octa-CDD and CDF congeners and 12 dioxin-like PCBs (IUPAC Nos. 81, 77, 126, 169, 105, 114, 118, 123, 156, 157, 167, and 189) were spiked. Furthermore, aliquots were treated with sulfuric acid (approximately 7-10 times) in a separation funnel. Then the hexane layer with PCDDs/DFs and PCBs was rinsed with hexane-washed water and dried by passing through anhydrous sodium sulfate in a glass funnel. The solution was concentrated to 2 ml and sequentially subjected to silica gel, alumina, and silica gel-impregnated activated carbon column chromatography. Extracts were passed through a silica gel-packed glass column (Wakogel, silica gel 60; 2g) and eluted with 130 ml of hexane. The

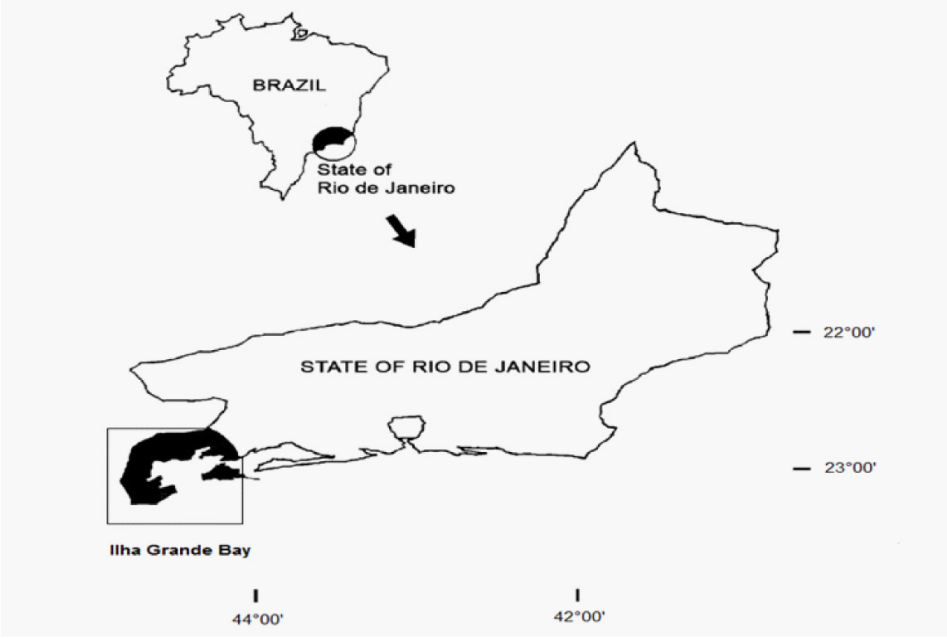


**Figure 2.** Study area: Ilha Grande Bay, Rio de Janeiro, Brazil
***Figura 2.*** *Área de estudo: Baía da Ilha Grande, Rio de Janeiro, Brasil*

hexane extract was Kuderna-Danish concentrated and passed through alumina column (Merck-Alumina oxide, activity grade 1; 5g) and eluted with 30 ml of 2% dichloromethane in hexane as a first fraction, which contained multi-ortho-substituted PCBs. The second fraction eluted with 30 ml of 50% dichloromethane in hexane, containing non- and mono-ortho-PCBs and PCDDs/DFs, was Kuderna-Danish concentrated and passed through silica gel-impregnated activated carbon column (0.5g). The first fraction eluted with 25% dichloromethane in hexane contained mono- and di-ortho-PCBs. The second fraction eluted with 250 ml of toluene containing PCDDs/DFs was concentrated and analyzed using a high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC/HRMS).

Identification and quantification of 2,3,7,8-substituted congeners of PCDDs/DFs and dioxin-like PCBs (non- and mono-ortho-substituted congeners) was performed by use of a (i) Shimadzu GC-14B gas chromatograph with AOC-1400 auto-sampler. Columns: CBP-1 (SE-30) and CBP-5 (SE-52/54 confirmatory column). Injection: Splitless (30seg.) 300ºC. Temperature program of the oven: 110ºC (1 min.); 15ºC/min up 170ºC; 7.5ºC/min up to 290ºC, hold for 10 minutes. Total run time: 25 minutes. Electron Capture Detector ($^{63}$Ni) temperature: 310oC; (ii) HPLC: Shimadzu LC-10AS; Mobile phase: acetonitrile: water 80%, isocratic run. Column: Shimadzu STR-ODS-II (C-18 reverse phase) 25cm, L: 4mm ID. UV/VIS detector model: Shimadzu SPD-10A.

A procedural blank including extraction of blank Kimwipe and whole purification procedure was run with every batch (normally seven samples). The limit of quantification (LOQ) was set at 2 times the detected amount in the procedural blank. Reproducibility and recovery were confirmed through four replicate analyses of an abdominal adipose tissue sample with and without standard spiking. The relative standard deviations of concentrations of individual PCDD/F and PCB-congeners were less than 5.8%, and the recoveries were more than 96%. The lipid contents were determined gravimetrically after aliquots of the sample extracts were evaporated to complete dryness.

TEQ is the product of the concentration of an individual dioxin-like compound (DLC) in an environmental mixture and the corresponding TCDD TEF for that compound. **Equation 1** is the formula for calculating exposure concentration for *n* DLCs in a mixture in TCDD toxic equivalence (TEQ). Exposure to the $i^{th}$ individual PCDD, PCDF, or PCB compound is expressed in terms of an equivalent exposure of TCDD by computing the product of the concentration of the individual compound (*Ci*) and its assigned *TEFi*. TEQ is then calculated by summing these products across the *n* DLCs compounds present in the mixture. The TEQ may be compared to the dose-response slope for TCDD and used to assess the risk posed by exposures to mixtures of DLCs.

$$TEQ = \sum_{i=1}^{n} (C_i \times TEF_i) \qquad 1$$

The different congeners present in the sample were then analysed using a Gas Chromatography equipped with a capillary column of 40 µm coupled to a High Resolution Mass Spectrometer (GCHRMS). They can be quantified and their concentration calculated when compared to the added internal $13^{C}$ standard (Windal, 2001). Results are expressed either as pg/g of lipid mass or in terms of toxicity, using WHO TEF for birds (Van den Berg *et al.,* 2006) as pg TEQ/g, lipid weight.

All statistical tests were performed using Origin software (7.5, 2004) with a significant level of $p<0.05$. Data were checked for adherence to the standard assumptions of parametric tests using the Kolmogorov-Smirnov test for normality and the Levene's test for homogeneity of variances.

## 3. RESULTS

No significant sex-related differences in PCDD/F or PCB concentrations were found in Great Egret and Manx Shearwater.

Concentrations of PCDD/Fs and PCB-congeners with fat percentages are presented. All PCDD congeners and hexachlorinated PCDFs were found in Great Egret and Manx Shearwater (**Table 1**). All PCB congeners showed detectable levels, although to a lesser extent than dioxins (**Table 2**).

Fat-based log-transformed concentrations were used to determine whether there were significant differences between group geometric means (Tukey test). Null hypothesis (equality of means) was rejected at the 95% significance level ($p<0.05$). There were no statistically significant differences between mean PCDD/F and PCB-congeners concentrations between the two species.

For comparison purposes is shown in **figure 3** the concentrations of congeners researched, PCDD/FS and PCBs, respectively.

TEQs of PCDD/Fs and PCBs were calculated using TEFs for birds proposed byWHO (Van der Berg et al., 2006), and compositions in the two avian species are shown in **figure 4**.

**Table 1.** Medians (range) of concentrations (pg/g, lipid weight) of PCDD/Fs and toxic equivalents of PCDD/Fs (pg TEQ/g, lipid weight) in Great Egret and Manx Shearwater.
***Tabela 1.*** *Médias (faixa) de concentrações (pg/g, peso lipídico) de PCDD/Fs e tóxico equivalentes de PCDD/Fs (pg/g, peso lipídico) em Great Egret e Manx Shearwater.*

| Elements | Great Egret | | Manx Shearwater | |
|---|---|---|---|---|
| | Concentration | WHO TEF (birds) | Concentration | WHO TEF (birds) |
| *Dibenzo-p-dioxins (PCDD)* | | | | |
| 2378-TCDD | 3 (0.1 - 12) | 3 | 1 (0.5 - 6) | 1 |
| 12378-PeCDD | 2 (0.2 - 17) | 2 | 3 (0.3 - 17) | 3 |
| 123478-HxCDD | 73 (2 - 128) | 3.65 | 23 (7 - 52) | 1.15 |
| 123678-HxCDD | 21 (6 - 125) | 0.21 | 17 (4 - 47) | 0.17 |
| 123789-HxCDD | 12 (6 - 29) | 1.2 | 5 (2 - 28) | 0.5 |
| 1234678-HpCDD | 17 (4 - 54) | 0.017 | 24 (3 - 58) | 0.024 |
| OCDD | 241 (18 - 464) | 0.0241 | 162 (12 - 299) | 0.0162 |
| *Dibenzofurans (PCDF)* | | | | |
| 2378-TCDF | 0.15 (0.1 - 7) | 0.15 | 0.23 (ND - 4) | 0.23 |
| 12378-PeCDF | 19 (5 - 41) | 1.9 | 16 (9 - 31) | 1.6 |
| 23478-PeCDF | 2.8 (0.73 - 18) | 2.8 | 2.2 (1.2 - 35) | 2.2 |
| 123478-HxCDF | 1.8 (0.7 - 28) | 0.18 | 8.7 (2 - 34) | 0.87 |
| 123678-HxCDF | 0.5 (0.2 - 16) | 0.05 | 4 (2 - 17) | 0.4 |
| 1234789-HxCDF | 5 (2 – 31) | 0.5 | 2 (ND – 30) | 0.2 |
| 234678-HxCDF | 4 (2.1 - 8) | 0.4 | 1 (ND - 12) | 0.1 |
| 1234678-HpCDF | 9 (5 - 47) | 0.09 | 5 (3 - 26) | 0.05 |
| 1234789-HpCDF | 3 (ND - 19) | 0.03 | 5 (2 - 29) | 0.05 |
| OCDF | 4 (2.9 - 23) | 0.0004 | 6 (1.5 - 16) | 0.0006 |
| | Σ= 407.15 | Σ= 16.2 | Σ= 285.13 | Σ= 11.7 |

**Table 2.** Medians (range) of concentrations as pg/g lipid weight of PCBs and toxic equivalents of PCBs (pg TEQ/g lipid weight) in Great Egret and Manx Shearwater.
***Tabela 2.*** *Médias (faixa) de concentrações (pg/g, peso lipídico) de PCBs e tóxico equivalentes de PCBs (pg TEQ/g, peso lipídico) em Great Egret e Manx Shearwater.*

| Elements | Great Egret | | Manx Shearwater | |
|---|---|---|---|---|
| | Concentration | WHO TEF (birds) | Concentration | WHO TEF (birds) |
| *Non-ortho PCBs* | | | | |
| 3,3',4,4'-TCB (77) | 110 (54 - 670) | 5.5 | 103 (76 - 140) | 5.15 |
| 3,4,4',5-TCB (81) | 64 (18 - 740) | 6.4 | 28 (11- 93) | 2.8 |
| 3,3',4,4',5-PeCB (126) | 94 (81 - 130) | 9.4 | 58 (34 - 150) | 5.8 |
| 3,3',4,4',5,5'-HxCB (169) | 58 (35 - 100) | 0.058 | 16 (9 - 57) | 0.016 |
| *Mono-ortho PCBs* | | | | |
| 2,3,3',4,4'-PeCB (105) | 187 (58 - 220) | 0.0187 | 156 (18 - 210) | 0.0156 |
| 2,3,4,4',5-PeCB (114) | 213 (67 - 349) | 0.0213 | 437 (216 - 511) | 0.0437 |
| 2,3',4,4',5-PeCB (118) | 169 (12 - 258) | 0.00169 | 138 (19 - 231) | 0.00138 |
| 2',3,4,4',5-PeCB (123) | 64 (33 - 122) | 0.00064 | 31 (13 - 55) | 0.00031 |
| 2,3,3',4,4',5-HxCB (156) | 17 (5 -78) | 0.0017 | 23 (7 - 112) | 0.0023 |
| 2,3,3',4,4',5'-HxCB (157) | 13 (11 - 18) | 0.0013 | 17 (8 - 54) | 0.0017 |
| 2,3',4,4',5,5'-HxCB (167) | 22 (18 - 30) | 0.00022 | 21 (12 - 70) | 0.00021 |
| 2,3,3',4,4',5,5'-HeCB (189) | 12 (7 - 18) | 0.00012 | 9 (4 - 16) | 0.00009 |
| | Σ= 1023 | Σ= 21.4 | Σ= 1034 | Σ= 13.8 |

ND = concentration below LOD

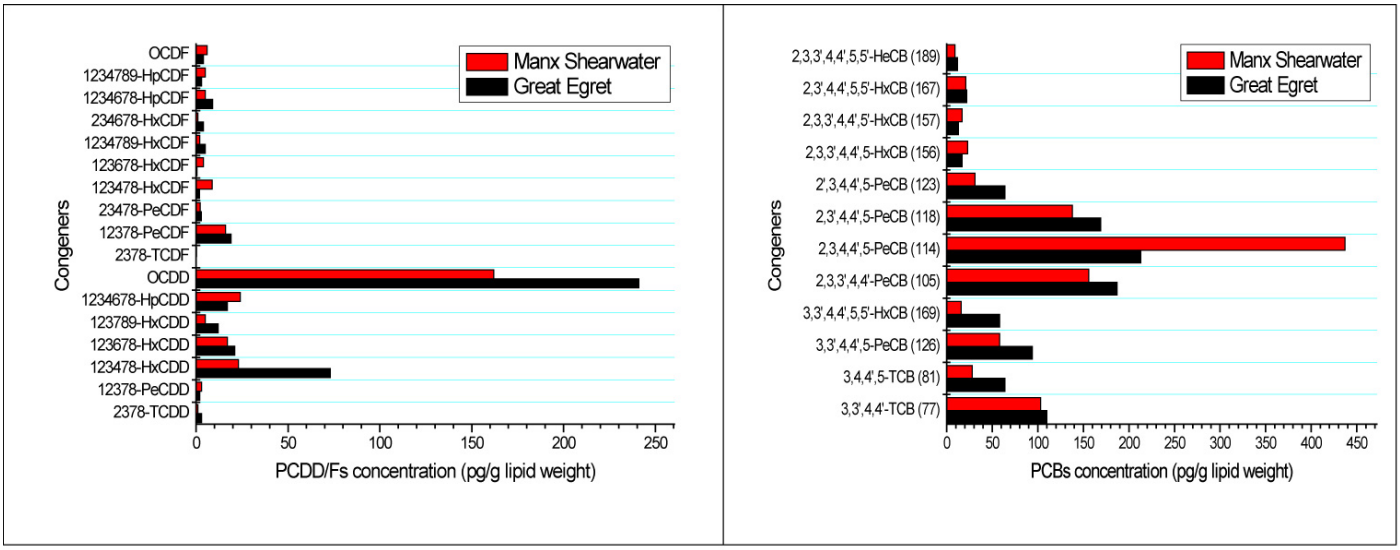


**Figure 3.** Distribution of PCDD/FS and PCBs congeners (pg/g lipid) in the organisms studied.
***Figura 3.*** *Distribuição de congêneros de PCDD/Fs e PCBs (pg/g, peso lipídico nos organismos estudados).*

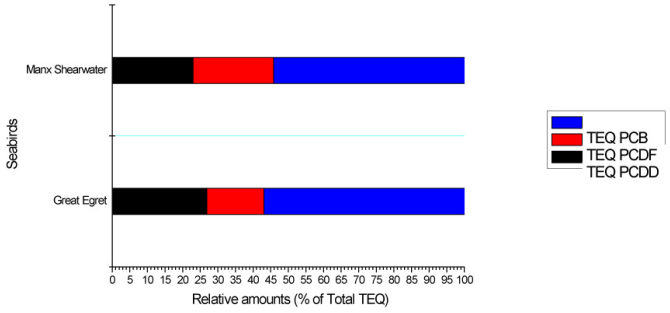


**Figure 4.** Contributions of PCDDs, PCDFs and dioxin-like PCBs to Total TEQ
***Figura 4.*** *Contribuições de PCDDs, PCDfs e PCbs no TEQ Total*

## 4. DISCUSSION

The study of ecotoxicology is a very broad field of science where issues such as uptake and effects in organisms, as well as distribution and residence time of the pollutants in the trophic level are studied in many different ways. The fundamental question to answer is whether the trophic level is harmfully disturbed when polluted by toxicants. To answer this important question, quantitative understanding of the pollutants behaviour within ecosystems is essential, and therefore researchers develop methods to manage this. The presence of anthropogenic pollutants, such as PCDD/F and PCB-congeners, throughout all compartments of the marine environment has been of international concern for a number of decades (Kumar et al., 2001). While a great number of datasets documenting absolute concentrations of persistent organic pollutants in a variety of marine biota are available, the bioaccumulative nature, toxicity, biomagnification, and the fate of these compounds in the marine ecosystem is still poorly understood. Data on contaminant levels in Brazilian seabirds are limited, and no information exists regarding levels of new or emerging contaminants.

Reported adverse effects of POPs in wildlife include population declines, increases in cancers, reduced reproductive function, disrupted development of immune and nervous systems, and also elicit toxic responses which could result in the disruption of the endocrine system (Alcock *et al.,* 1998; Rittler & Castilla, 2002).

Lailson-Brito *et al.* (2010) studying organochlorine accumulation in Guiana dolphin (*Sotalia guianensis)*, at the same study site found concentrations levels from 765 to 99 175 for ΣPCB. The results for the Great Egret ranged between 0.005 - 0.74, and for Manx Shearwater between 0.004 - 0.511 (pg/g lipid) for ΣPCB, denoting below levels of concern. Contrasting also with data obtained from significant concentrations of PCBs which were detected in all oil samples, with a concentration ranging between 9 – 4834 ng/g lipid and a geometric mean of 404 ng/g lipid (Yamashita *et al.,* 2007), and by higher concentrations of PCBs which had been reported in tissues of seabirds that feed near industrialized areas (e.g., near North America) than in those that feed in remote areas (e.g., Bering Sea; Tanabe *et al.,* 2004).

Possible heavier exposure to some of PCDD/F and PCB congeners in Manx Shearwater and/or differences in feeding habits of Great Egret might explain their higher concentrations also in fat. Manx Shearwater feed mainly on zooplankton, but Great Egret has a diet which also contains crustaceans and small fish, living in the upper trophic level.

In previous studies, the monitoring of POPs in seabirds has been limited by the availability in organs (Peakall *et al.,* 1990; Shaffer *et al.,* 2006). This approach can easily be combined with ecological investigations of seabirds, and so this could dramatically increase the availability of seabird samples, including repeated sampling on identical birds (Holmström & Berger, 2008). Recently, electronic tracking tags have revolutionized our understanding of the large-scale movements and habitat use of mobile marine animals (Shaffer *et al.,* 2006).

## 5. CONCLUSION

The presence of tissue levels of POPs has been associated with biological and physiological effects in marine organisms, in specially seabirds (Montevecchi, 1993; Holmström & Berger, 2008). The animals sampled in the current study had PCDD/F and PCB congeners that exceeded the values found in these studies. Wide ranges of POP concentrations were measured in these animals, and our findings indicate that these animals are exposed to POPs levels that may affect their health, and in some classes of toxic POPs that may increase their risk to adverse effects.

The current study is the first to report seabirds' concentrations of POPs at this study site, and the first for any free-ranging birds from the Ilha Grande Bay. Due to the small size of this population studied, continued monitoring of POPs is essential in assessing the health and viability of these animals.

The present study confirms the ubiquity of POPs in *Ardea alba* (Linnaeus, 1758), Great Egret, and *Puffinus puffinus* (Brünnich, 1764), Manx Shearwater, belonging the marine environment of Ilha Grande Bay, Rio de janeiro, Brazil. Biomagnification may be the cause of the levels in the species collected and analysed. Further assessments are recommended on organisms at higher trophic levels for ecotoxicological impacts. The ubiquity of these pollutants in Ilha Grande Bay's marine environment supports the need for a greater awareness of bioaccumulation processes, particularly for organisms cultivated (shellfish) or fished locally and destined for human consumption.

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