A RBF é uma publicação da ABF

REVISTA BRASILEIRA DE FARMÁCIA (RBF)
BRAZILIAN JOURNAL OF PHARMACY (BJP)
www.rbfarma.org.br

PESQUISA/RESEARCH

Chlorinated dioxins, Furans and PCBs analysis in Brown Booby (*Sula Leucogaster*) collected from Ilha Grande Bay, Rio de Janeiro, Brazil

Análises de dioxinas cloradas, Furanos e PCBs em Atobás-Pardo (*Sula Leucogaster*) coletadas na Baía da Ilha Grande, Rio de Janeiro, Brasil

Recebido em 23/03/2012

Aceito em 05/03/2013

Aldo Pacheco Ferreira*

Centro de Estudos da Saúde do Trabalhador e Ecologia Humana (CESTEH), Escola Nacional de Saúde Pública Sérgio Arouca, Fundação Oswaldo Cruz, Rio de Janeiro, RJ, Brasil

ABSTRACT

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) concentrations were measured in seabirds from Rio de Janeiro, Brazil. Samples of *Sula Leucogaster* were collected in 2008-2011 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 type of study aims to integrate information from analysis of seabirds with chemicals, and primary results coming from these studies may allow identification of scientific evidence, helping the containment of pollution sources. Furthermore, the data 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: contamination, Ilha Grande bay, persistent organic pollutant, *Sula leucogaster*

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. Amostras de *Sula Leucogaster* foram coletadas durante 2008-2011 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. Este tipo de estudo visa integrar informações das análises das aves marinhas com compostos químicos, e os resultados procedentes destes estudos primários, podem permitir a identificação de evidências científicas, ajudando na contenção de fontes poluidoras. Além disso, estes dados representam algumas das primeiras medições de PCDD/Fs e PCBs em aves marinhas da área, e pressupõem que futuros estudos devam dar sequência 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: contaminação, Baía da Ilha Grande, poluentes orgânicos persistentes, *Sula leucogaster*

INTRODUÇÃO

Seabirds are one of the most conspicuous faunal groups of the coastal and marine environment (Corre *et al.*, 2012). 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 (Corsolini *et al.*, 2011).

* Contato: Aldo Pacheco Ferreira, Centro de Estudos da Saúde do Trabalhador e Ecologia Humana (CESTEH), Escola Nacional de Saúde Pública Sérgio Arouca, Fundação Oswaldo Cruz, Rio de Janeiro, RJ, Brasil, Rua Leopoldo Bulhões, 1480 - CEP: 21041-210, fone +55 (21) 25982814, e-mail: aldoferreira@ensp.fiocruz.br

Seabirds have been used in several environmental monitoring studies (Lauwerys & Hoet, 1993; 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). *Sula leucogaster* (Boddaert, 1783) breeds in some coastal and oceanic islands of Brazil, and uses as food a great diversity of prey, captured in flat diving, between 10 to 15 m, beyond ictiofauna discarded in shrimp's fisheries. As a type of bird with a large number in diversity at study site, it was then chosen as an indicator, corroborating other studies in the same line (Burger *et al.*, 1992; Noernberg *et al.*, 2008).

Pollution in the marine environment has become an issue of great concern, especially to coastal states (Pereira & Ebecken, 2009). The oceans cannot provide an infinite sink for anthropogenic wastes but little attention has been given to evaluating the limits of capacity of coastal areas for waste assimilation (Juresa & Blanusa, 2003). Consequently, instances of fisheries closures, spoiled beaches, destroyed coral reefs and wildlife habitat, toxic blooms and lost coastal ecological communities are widespread, with a corresponding determination of cost benefit. Recent concerns about connectivity of ocean health issues and the relationship to human disease highlight an important area for study.

The aquatic environment with its water quality is considered the main factor controlling the state of health and disease in both man and animal. Nowadays, the increasing use of the waste chemical and agricultural drainage systems represents the most dangerous chemical pollution (Lacerda & Molisani, 2006). Knowledge of the ocean and the impact of human activities on it can reveal the complexity and interdependence of all aspects of the system (Costanza & Farley, 2007). Improved acquaintance and predictive capabilities are required for more effective and sustained development of the marine environment to obtain associated economic benefits and to preserve marine resources.

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; Zarker & 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, 2012).

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**).

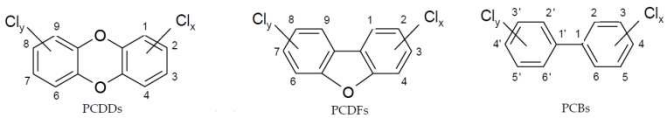

Figure 1. Generalised structures of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs).

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 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).

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.

The goal of this work was to evaluate concentrations of PCDD/Fs and PCBs in livers of *Sula leucogaster* (Boddaert, 1783) collected from Ilha Grande Bay, which is situated in the southern Atlantic Coast of Rio de Janeiro State, Brazil.

MATERIALS and METHODS

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, which 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).

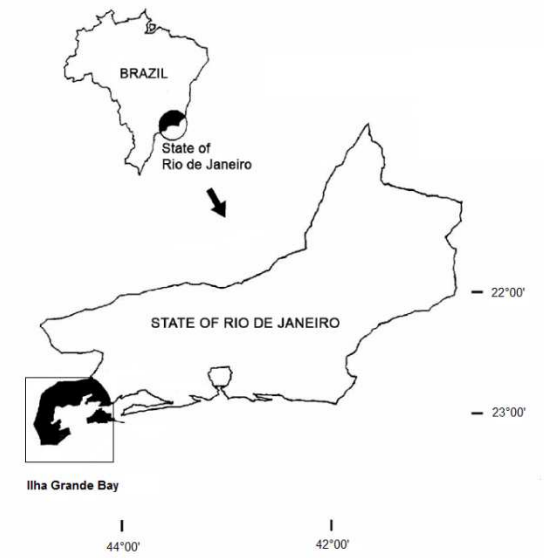

Figure 2. Study area: Ilha Grande Bay, Rio de Janeiro, Brazil

Analysis: Identification and Quantification

A total of thirty nine specimens (adults) found stranded or dead in areas related to the study site, between March 2008 and September 2011, were evaluated. All fresh carcasses were necropsied following a standardized protocol (Jauniaux *et al*., 1998). 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 (USEPA Method 1668, 2003; USEPA Method 8290 A, 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 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.) 300^{o}C. Temperature program of the oven: 110^{o}C (1 min.); 15^{o}C/min up 170^{o}C; 7.5^{o}C/min up to 290^{o}C, hold for 10 minutes. Total run time: 25 minutes. Electron Capture Detector (^{63}Ni) temperature: 310^{o}C; (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.

$$TEQ = \sum_{i=1}^{n} (Ci \times TEFi) \qquad \text{(Eq. 1)}$$

The different congeners present in the sample were then analyzed 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.

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. All statistical tests were performed using Origin software (7.5, 2004) with a significant level of $p<0.05$.

RESULTS

Concentrations of PCDD/Fs and PCB-congeners with fat percentages are presented. No significant sex-related differences in PCDD/F or PCB concentrations were found. All PCDD congeners and hexachlorinated PCDFs were found (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.

TEQs of PCDD/Fs and PCBs were calculated using TEFs for birds proposed byWHO (Van der Berg *et al.*, 2006), and compositions are shown in Figure 3.

DISCUSSION

Increased human activities such as industrialization, coupled with over-population and increased ambient temperature amongst other factors, have become major environmental issues in recent years. As a result of such actions, additional studies which include the environment and their indicators are important because they can show potential impacts that are being reflected on the public health. Thus, 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 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 behavior within ecosystems is essential, and therefore researchers develop methods to manage this issue. 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.

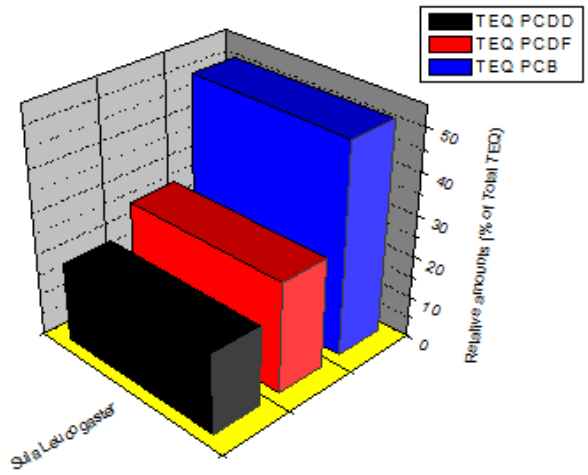

Figure 3. Contributions of PCDDs, PCDFs and dioxin-like PCBs to Total TEQ

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 *Sula Leucogaster*

Elements	*Sula Leucogaster*	
	Concentration	WHO TEF (birds)
Dibenzo-p-dioxins (PCDD)		
2378-TCDD	0.6 (0.2 - 4)	0.6
12378-PeCDD	3 (0.5 - 8)	3
123478-HxCDD	14 (6 - 44)	0.7
123678-HxCDD	5 (1 - 9)	0.05
123789-HxCDD	9 (5 - 31)	0.9
1234678-HpCDD	35 (6 - 66)	0.035
OCDD	199 (33 - 291)	0.0199
2378-TCDF	0.34 (1 - 4)	0.34
12378-PeCDF	16 (9 - 31)	1.6
23478-PeCDF	4.9 (ND - 32)	4.9
123478-HxCDF	8.2 (2 - 32)	0.82
123678-HxCDF	3 (ND - 12)	0.3
1234789-HxCDF	7 (1– 30)	0.7
234678-HxCDF	3 (2 - 12)	0.3
1234678-HpCDF	9 (3 - 23)	0.09
1234789-HpCDF	5 (2 - 22)	0.05
OCDF	9 (2 - 19)	0.0009
	Σ= 331.04	Σ= 13.4

ND = concentration below LOD

Table 2. Medians (range) of concentrations as pg/g lipid weight of PCBs and toxic equivalents of PCBs (pg TEQ/g lipid weight) in *Sula Leucogaster*

Elements	*Sula Leucogaster*	
	Concentration	WHO TEF (birds)
Non-ortho PCBs		
3,3',4,4'-TCB (77)	86 (33 - 543)	4.3
3,4,4',5-TCB (81)	47 (18 - 550)	4.7
3,3',4,4',5-PeCB (126)	48 (32 - 111)	4.8
3,3',4,4',5,5'-HxCB (169)	67 (26 - 104)	0.067
Mono-ortho PCBs		
2,3,3',4,4'-PeCB (105)	244 (37 - 289)	0.0244
2,3,4,4',5-PeCB (114)	185 (55 - 312)	0.0185
2,3',4,4',5-PeCB (118)	134 (49 - 244)	0.00134
2',3,4,4',5-PeCB (123)	61 (22 - 114)	0.00061
2,3,3',4,4',5-HxCB (156)	18 (7 -72)	0.0018
2,3,3',4,4',5'-HxCB (157)	24 (4 - 33)	0.0024
2,3',4,4',5,5'-HxCB (167)	35 (13 - 53)	0.00035
2,3,3',4,4',5,5'-HeCB (189)	19 (7 - 29)	0.00019
	Σ= 968	Σ= 13.9

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 the birds researched 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.

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.

Some oceanic islands, such as São Pedro e São Paulo Archipelago, is a group of small rocky islands that lies in the central equatorial Atlantic Ocean, lying 627 km from the archipelago of Fernando de Noronha, 986 km from the nearest point on the mainland and 1010 km from Natal, in Rio Grande do Norte, Brazil; may be considered remote areas and preserved due to its distance from the mainland. However, these areas are not exempt from the influence of anthropogenic agents from coastal regions, such as persistent organic pollutants (POPs).

The predominant compounds were PCBs that presented 98.15 ng/g to *Sula leucogaster* (Brown Booby) (Dias, 2010). Contrasting also with data obtained from significant concentrations of PCBs which were detected in all oil samples, with a concentration ranging between 9 – 4,834 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). The low levels of contaminants suggest a relative degree of isolation and preservation, but the occurrence and distribution profiles of PCBs supports the hypothesis that the main source of contamination in remote areas is long range atmospheric transport, and demonstrates the ubiquity of those pollutants in the marine environment.

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).

CONCLUSION

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 *Sula Leucogaster*, belonging to the marine environment of Ilha Grande Bay, Rio de Janeiro, Brazil. Biomagnification process may be the cause of the observed levels in the specimens evaluated. 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.

ACKNOWLEDGEMENTS

The author is grateful for financial support received from the Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq (302946/2011-0).

REFERENCES

Alcock RE, Behnisch PA, Jones KC, Hagenmaier H. Dioxin-Like PCBS in the environment. Human exposure and the significance of sources. *Chemosphere,* 37: 1457-1472, 1998.

Allen VG, Brown CP, Segarra E, Green CJ, Wheeler TA, Acosta-Martinez V, Zobeck TM. In search of sustainable agricultural systems. *Agriculture, Ecosystems & Environment*, 124(1-2): 3-12, 2008.

Assmuth T, Vartiainen T. Concentrations of 2,3,7,8-chlorinated dibenzo-p-dioxins and dibenzofurans at landfills and disposal sites for chlorophenolic wood preservative wastes. *Chemosphere,* 25: 971-979, 1994.

Ballschmiter K, Zell M. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius' Journal of Analytical Chemistry*, 302: 20-31, 1980.

Basler A. Regulatory measures in the Federal Republic of Germany to reduce the exposure of man and the environment to dioxins. *Organohalogen Compounds,* 20: 567-570, 1994.

Breivik K, Sweetman A, Pacyna JM, Jones KC. Towards a global historical emission inventory for selected PCB congeners - a mass balance approach 2. Global production and consumption. *Science of Total Environment*, 290: 181-198, 2002.

Carpenter DO. Polychlorinated Biphenyls and Human Health. *International Journal of Occupational Medicine and Environmental Health,* 11: 291-303, 1998.

Corre ML, Jaeger A, Pinet P, Kappes MA, Weimerskirch H, Catry T, Ramos JA, Russell JC, Shah N, Jaquemet S. Tracking seabirds to identify potential Marine Protected Areas in the tropical western Indian Ocean. *Biological Conservation*, 156: 83-93, 2012.

Corsolini S, Borghesi N, Ademollo N, Focardi S. Chlorinated biphenyls and pesticides in migrating and resident seabirds from East and West Antarctica. *Environment International*, 37(8): 1329-1335, 2011.

Costanza R, Farley J. Ecological economics of coastal disasters: Introduction to the special issue. *Ecology & Economics*, 63(2-3): 249-253, 2007.

Dias OS. *Poluentes orgânicos persistentes na biota marinha do arquipélago de São Pedro e São Paulo*. Dissertação de Mestrado. Instituto Oceanográfico. Universidade de São Paulo, 79p., 2010.

Ferreira AP. *Integrated environmental and health risk assessment: A case study of persistent organic pollutants in humans and wildlife*. In: Carolina Biblio; Jeferson Francisco Selbach; Oliver Hensel. (Org.). Sustainable water management in the tropics and subtopics: Case studys in Brazil. 1ed.Jaguarão/RS: Fundação Universidade Federal do Pampa, UNIKASSEL VERSITAT (University of Kassel, Germany), UFMA, 1:11-26, 2012.

Ferreira AP. Environmental fate of bioaccumulative and persistent substances. A synopsis of existing and future actions. *Gerencia y Politicas de Salud,* 7(15):14-23, 2008.

Ferreira AP. Trace metals analysis in Brown Booby (*Sula Leocogaster*) collected from Ilha Grande Bay, Rio de Janeiro, Brazil. *Uniandrade,* 11(2): 41-53, 2010.

Giesy JP, Ludwig JP, Tillitt DE. *Dioxins, Dibenzofurans, Pcbs and colonial, fish-eating water birds*. In: Dioxins and Health. A. Schecter (Ed.). Plenum Publishers, New York, NY. 307p., 1994.

Holmström K, Berger U. Tissue distribution of perfluorinated surfactants in common Guillemot (*Uria*

Aalge) from the Baltic sea. *Environmental Science & Technology*, 42: 5879–5884, 2008.

Jauniaux T, Brosens L, Meire P, Offringa H, Coignoul F. Pathological investigations on Guillemots (*Uria Aalge*) stranded at the Belgian coast during the winter 1993-1994. *Veterinary Records*, 143(14): 387–390, 1998.

Kiviranta H, Purkunen R, Vartiainen T. Levels and trends of PCDD/FS and PCBS in human milk in Finland. *Chemosphere*, 38(2): 311-323, 1999.

Kumar KS, Kannan K, Paramasivan ON, Sundaram VPS, Nakanishi J, Masunaga S. Polychlorinated Dibenzo-p-Dioxins, Dibenzofurans, and Polychlorinated Biphenyls in human tissues, meat, fish, and wildlife samples from India. *Environmental Science & Technology*, 35(17): 3448-3455, 2001.

Larsson P. Contaminated sediments of lakes and oceans act as sources of chlorinated hydrocarbons for release to water and atmosphere. *Nature*, 317: 247-349, 1985.

Lailson-Brito J, Dorneles PRB, Azevedo-Silva CE, Azevedo AF, Vidal LG, Zanelatto RC, Lozinski CPC, Azeredo A, Fragoso ABL, Cunha HA, Torres JPM, Malm O. High organochlorine accumulation in blubber of guiana dolphin, *Sotalia Guianensis*, from Brazilian coast and its use to establish geographical differences among populations. *Environmental Pollution*, 158(5): 1800-1808, 2010.

Lauwerys R, Hoet P. *Industrial Chemical Exposure. Guidelines for biological monitoring*. Lewis Publishers: Boca Raton, Fl. 199p., 1993.

Mackay D, Shiu WY, Ma KC. Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Volume I. *Monoaromatic Hydrocarbons, Chlorobenzenes and PCBS*. Lewis Publishers, Boca Raton, Fl. 697 p., 1991.

Montevecchi WA. *Birds as indicators of change in marine prey stocks*. In: Furness RW and Greenwood JJD (Eds). Birds as monitors of environmental change. Chapman & Hall, London, 223p., 1993.

Moriarty F. *Ecotoxicology. The study of polluants in ecosistems*. Third Edition, Academic Press, California, USA, 109p., 1999.

Peakall DB, Noble DG, Elliott JE, Somers JD, Erickson G (1990) Environmental Contaminants in Canadian peregrine falcons, *Falco Peregrinus*: A toxicological assessment. *Canadian Field Naturalist*, 104: 244–254, 1990.

Pereira MS. Polychlorinated Dibenzo-p-Dioxins (PCDD), Dibenzofurans (PCDF) and Polychlorinated Biphenyls (PCB): Main sources, environmental behaviour and risk to man and biota. *Quím. Nova*, 27(6)*:* 934-943, 2004.

Rittler M, Castilla EE. Desreguladores endócrinos e anomalias congênitas. *Cadernos de Saúde Pública 18(2)*: 421-428, 2002.

Shaffer SA, TremblayY, Weimerskirch H, Scott D, Thompson DR, Sagar PM, Moller H, Taylor GA, Foley DG, Block BA, Costa DP. Migratory shearwaters integrate oceanic resources across the Pacific ocean in an endless summer. *Proceedings of the National Academy of Sciences of the United States of America*, 103: 12799−12802, 2006.

Shaw SD, Berger ML, Brenner D, Chu MD, Matherly CK, Chu AC, Clark GC. Application of the calux bioassay for the determination of PCDD/FS and dioxin-like PCBS in tissues of harbor seals. *Organohalogen Compounds*, 68: 587-591, 2006.

Tanabe S, Watanabe M, Minh TB, Kunisue T, Nakanishi S, Ono H, Tanaka H. PCDDS, PCDFS, and coplanar PCBS in albatross from the north pacific and southern oceans: levels, patterns, and toxicological implications. *Environmental Science & Technology*, 38: 403−413, 2004.

United States Environmental Protection Agency (USEPA). *Method 1668*: Revision A. Chlorinated Biphenyl congeners in water, soil, sediment, biosolids, and tissue by HRGC/HRMS, 2003.

United States Environmental Protection Agency (USEPA). *Method 8290 A*: Revision 1. Polychlorinated Dibenzodioxins (PCDDS) and Polychlorinated Dibenzofurans (PCDFS) by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS), 2007.

Van Den Berg M, Birnbaum LS, Denison M. The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicological Sciences*, 93(2): 223-241, 2006.

Yamashita R, Takada H, Murakami M, Fukuwaka MA, Watanuki Y. Evaluation of noninvasive approach for monitoring PCB pollution of seabirds using preen gland oil. *Environmental Science & Technology*, 41(14): 4901–4906, 2007.

Wania F, Axelman J, Broman D. A review of processes involved in the exchange of persistent organic pollutants across the air-sea interface. *Environmental Pollution*, 102: 3-23, 1998.

Windal I. *Développement de méthodes rapides d'analyse des dioxines dans lês poussières d'incinérateurs et destruction des dioxines par eaux subcritique.* Thesis. University f Liège, 135p., 2001.

Zarkera KA, Kerr. RL. Pollution prevention through performance-based initiatives and regulation in the United States. *Journal of Cleaner Production*, 16(6)*:* 673-685, 2008.