

POLYCHLORINATED DIBENZO-P-DIOXINS, DIBENZOFURANS, AND BIPHENYLS IN FREGATA MAGNIFICENS FROM ILHA GRANDE BAY, RIO DE JANEIRO STATE, SOUTH-EASTERN BRAZIL

Aldo Pacheco Ferreira

Sergio Arouca Escola Nacional de Saúde Pública da Fundação Oswaldo Cruz
(CESTEH / ENSP / FIOCRUZ)
(Rua Leopoldo Bulhões, 1480, 21041-210 Manguinhos, RJ, Brasil)

Corresponding author: aldopachecoferreira@gmail.com

<http://dx.doi.org/10.1590/S1679-87592015074906301>

ABSTRACT

The purpose of this paper is to perform analyses in a fish-eating seabird species which is recognized to be at risk of accumulating toxic contaminants due to its high position in the trophic web and to its low ability to metabolize xenobiotic compounds. *Fregata magnificens* were collected at Ilha Grande Bay, Rio de Janeiro, Brazil (23°8'26"S, 44°14'50"W) between February, 2009 and April, 2013. Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs), were analyzed in tissue composites, being subsequently identified and quantified using gas chromatography coupled with mass spectrometry. The concentrations were below the range of concern established by World Health Organization. The sum of PCB-congeners analyzed had the concentration of 968 pg/g lipid weight, and 13.9 pg TEQ/g lipid weight. The PCDD/F-congeners analyzed had the concentration of 331.04 pg/g lipid weight, and 13.4 pg TEQ/g lipid weight. This type of study aims to integrate information from analyses of seabirds with halogenated hydrocarbons and could also make contribution to the scientific support for political decisions on coastal zone management.

RESUMO

O objetivo deste trabalho é realizar análises químicas em tecidos da ave marinha *Fregata magnificens* que se alimenta de peixes. Esta ave é reconhecida por estar em risco de acumular contaminantes tóxicos, devido a sua alta posição na teia trófica e a sua baixa capacidade de metabolizar compostos xenobióticos. Exemplos de *Fregata magnificens* foram coletados na Baía da Ilha Grande, Rio de Janeiro, Brasil (23°8'26"S, 44°14'50"W) entre fevereiro de 2009 e abril de 2013. Concentrações de dibenzeno-p-dioxinas policloradas (PCDD), dibenzofuranos policlorados (PCDF) e bifenilas policloradas (PCBs) foram analisadas em compostos de tecido, sendo posteriormente identificados e quantificados por cromatografia gasosa acoplada à espectrometria de massas. Os resultados indicam que as concentrações estavam abaixo do limite de segurança estabelecido pela Organização Mundial de Saúde. A soma dos congêneres de PCBs analisados apresentou a concentração de 968 pg/g de peso lipídico e 13,9 pg TEQ/g de peso lipídico. Os congêneres de PCDD/Fs analisados tiveram a concentração de 331,04 pg/g de peso lipídico e 13,4 pg TEQ/g de peso lipídico. Este tipo de estudo tem por objetivo integrar informações de análise de aves marinhas com hidrocarbonetos halogenados e, também, pode contribuir dando apoio científico para as decisões políticas sobre gestão da zona costeira.

Descriptors: Ilha Grande Bay, Halogenated hydrocarbons, *Fregata magnificens*, Contamination, Anthropic actions, Sustainability.

Descritores: Baía da Ilha Grande, Hidrocarbonetos halogenados, *Fregata magnificens*, Contaminação, Ações antrópicas, Sustentabilidade.

INTRODUCTION

Halogenated aromatic compounds, typified by the polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs), are industrial compounds or by-products which have been

widely identified in the environment and in chemical-waste dumpsites (LAUWERYS; HOET, 1993). Halogenated aromatics are invariably present in diverse analyses as highly complex mixtures of isomers and congeners, complicating a secure detection and risk assessment of these compounds

(SAFE, 1990). They persist in the environment (XU et al., 2013) in target bioaccumulation in living organisms, often preferentially in the lipid or fatty tissues (TANABE et al., 2004; PARERA et al., 2013).

Due to the strength of the carbon-chlorine bond there is a tendency to be more resistant to the common degradation pathways in the environment and organisms, which causes them to have an environmental half-life of several years to even decades (DORNELES et al., 2013), increasing the concentration throughout the food chain, in such a way as to cause toxic effects, especially at the highest trophic levels (MORIARTY, 1999; KUMAR et al., 2002). This longevity enables them to be transported over long distances either through the atmosphere or by ocean currents, depending on the physical properties of the molecule (ALCOCK et al., 1998). Many of these compounds have been deliberately produced as agricultural pesticides (e.g. DDT (Dichlorodiphenyltrichloroethane), Chlordane (Hexachlorocyclopentadiene) and Lindane (gamma-hexachlorocyclohexane)) or for use in industrial applications (e.g. PCBs and Brominated Flame retardants), while others were or are still being produced as by-products of industrial synthesis or incomplete combustion (e.g. PCDDs) (ALLEN et al., 2008). Even today, some of them are still deliberately used. For instance, DDT can still be used for Malaria control in Africa (RANSON et al., 2011), and is still used as an anti-fouling agent in paints in China (LIN et al., 2009). This leads to an estimated environmental release of 250 tons per year (UNEP, 2007). The increasing use of chemical waste and agricultural drainage systems represents the most dangerous chemical pollution (GARCÍA DE LA PARRA et al., 2012). Knowledge of the oceans and the impact of human activities on them can reveal the complexity and interdependence of all the aspects of the system (FERREIRA, 2008). Improved acquaintance with the oceans and improved predictive capabilities are required for more effective and sustained development of the marine environment to obtain associated economic benefits and to preserve marine resources (COSTANZA; FARLEY, 2007; GORNI; WEBER, 2004).

The marine environment receives organochlorine compounds through wet and dry deposition at the water-surface, and by diffusive vapour exchange between air and water (WANIA et al., 1998). Transport of these compounds 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, and thereby prolong the exposure of biota, long after emissions have been stopped. The key processes that determine their transport across the sediment-water interface are: (a) the sedimentation and resuspension

of particles, (b) the diffusive movement of the organochlorine compounds and also when attached to dissolved organic matter (HOLMSTRÖM; BERGER, 2008).

In ecosystems, organisms interact through complex trophic relationships, which involve energy and nutrient flow between trophic levels. Understanding trophic relationships, as well as quantitatively assessing trophic levels is of fundamental importance for the comprehension of ecosystem structure. Seabirds are good indicators of productivity and health in the marine environment (TASKER; REID, 1997; PARRISH; ZADOR, 2003). Their patterns of distribution and abundance are strongly correlated with primary production (WHITEHOUSE et al., 1999), with the abundance of fish shoals (FREDERIKSEN et al., 2008) and nest-site availability (FASOLA; CANOVA, 1992; BOURGEOIS et al., 2008). Population fluctuations, mass mortality and other anomalies in their populations can be taken as criteria indicating the presence of contaminants in the sea (KUSHLAN, 1993) and abrupt amendments to climate change (JENOUVRIER et al., 2003; STEMPNIEWICZ et al., 2007). Worldwide, seabird research has undergone a major evolution in terms of data collection, interpretation of information and application in the field of management and policy (TASKER; REID, 1997). Seabirds have, thus, been used in several environmental monitoring studies (LAUWERYS; HOET, 1993; CHOY et al., 2010).

Magnificent Frigatebirds *Fregata magnificens* occur along the tropical and subtropical coasts of the Americas (HARRISON, 1983). Colonies of the species are widely distributed in Brazil, being found in Fernando de Noronha, Bahia, Rio de Janeiro, São Paulo, Paraná and Santa Catarina (COELHO et al., 1991; ALVES; VECCHI, 2009). The detailed knowledge of general seabird ecology and of the numbers and productivity of many populations also makes them particularly appropriate as bioindicators. This knowledge has several benefits, e.g. the large quantities of data collected from a particular site can be separated in a relatively short period of time. *F. magnificens* as a fish-eating bird is well suited for the assessment of the effects of PCDD/Fs and PCBs due to its wide distribution. Additionally, it is particularly appropriate as a biomonitor of pollutants whose concentration is increased along the food chain (ALVES; VECCHI, 2009).

The present study sought to evaluate the concentrations of PCDD/Fs and PCBs in *F. magnificens* (Ilha Grande Bay, Rio de Janeiro, Brazil) that breed on the South Atlantic Ocean, where local pollution by PCDD/Fs and PCBs is presumed to be negligible or non-existent.

MATERIAL AND METHODS

Study Site

The Ilha Grande Bay is a large area located in Rio de Janeiro state, Brazil. It is characterized by a system of estuarine and oligotrophic waters, with a significant diversity of marine ecosystems, such as rocky shores, islands, mangrove forests and sandy beaches (Fig. 1). The weather is hot, tropical and humid, with average annual temperature of 22.5°C, and water temperature varying between 18°C and 24°C. The region is relatively well preserved, still presenting vestiges of the insular Atlantic Forest, and is considered a priority area for conservation. It has great scenic beauty, a rich fauna and flora, and is therefore a natural sanctuary for biodiversity (a hot-spot), and 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 geographical peculiarities, and its being a hydrographic oceanographic region, coupled with factors such as the diversity and connectivity of coastal systems, input of organic matter from rivers, physical variation and chemical oceanographic factors (ALHO et al., 2002).

The area of Ilha Grande Bay is home to the territories of the cities of Parati and Angra dos Reis,

which together 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 activities. Consequently, along the coast there is a series of developments that, through the occupation of hillsides, riverbanks or islands and the landfilling of mangrove areas, cause deforestation and polluted coastal waters. This growth as a tourist hub has promoted haphazard development and caused severe damage to the coastal systems. There are still other large projects planned for the region, such as a commercial port, a petroleum terminal, an iron-ore terminal, two nuclear power plants and a shipyard. This area was selected for this study because of the large number of the birds harbour that inhabit it (NUNES; SANTOS, 2012).

Sample Collection and Handling

Dead or injured *F. magnificens* adults were collected from the Ilha Grande Bay (23°8'26"S, 44°14'50"W). Samples were collected between February, 2009 and April, 2013. After collection the birds were examined externally and necropsied in accordance with a standardized protocol (JAUNIAUX et al., 1998). Livers were collected, weighed and kept frozen until analysis.

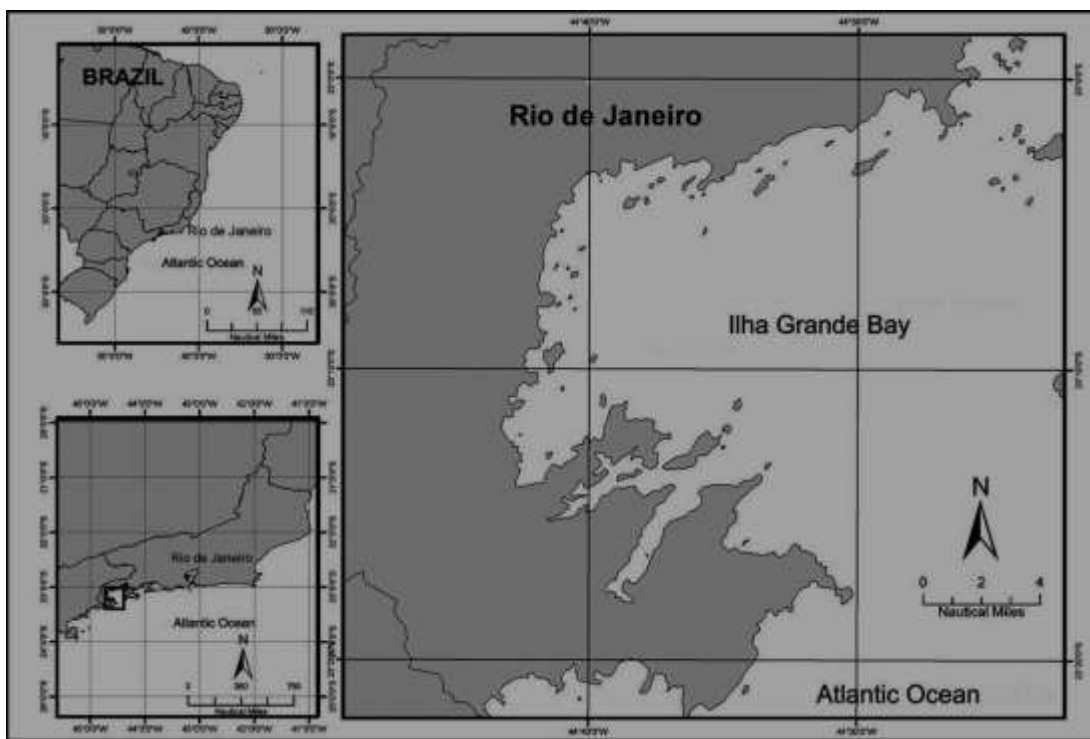


Fig. 1. Map of the study area: Ilha Grande Bay, Rio de Janeiro State, South-eastern Brazil.

Analysis of Dioxin, Furan, and PCB Congeners

The analytical procedures were undertaken in accordance with previous reports (KUMAR et al., 2001; SHAW et al., 2006; PARVEZ et al., 2013). Moisture content was determined and samples were extracted using a Soxhlet apparatus for 10-15 hours in dichloromethane. Briefly, after the extraction, samples were concentrated to 10 ml using a Kuderna-Danish (K-D) concentrator and the solvent transferred to n-hexane. Lipid content was determined gravimetrically from an aliquot of the extract. Seventeen ¹³C-labeled 2,3,7,8-substituted tetra-, penta-, hexa-, hepta-, and octa-CDD and CDF congeners and twelve dioxin-like PCBs (IUPAC Nos. 77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167, and 189) were spiked into hexane extracts prior to sulphuric acid treatment. The hexane layer was rinsed twice with hexane-washed water, and dried by passing through anhydrous sodium sulphate 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 activated silica gel packed in a glass column (Wakogel, silica gel 60; 2 g) and eluted with 130 ml of hexane, which contained PCDD/DFs and dioxin-like PCBs. The hexane extract was K-D concentrated and passed through activated alumina column (Merck-Alumina oxide, activity grade 1; 5g) and eluted with 30 ml of 2% dichloromethane in hexane as the first fraction, which contained several *ortho*-substituted PCBs. The second fraction eluted with 30 ml of 50% dichloromethane in hexane contained PCDD/DFs and dioxin-like PCBs, which was purged under a gentle stream of nitrogen to 0.5 ml and passed through a silica gel impregnated activated carbon column (0.5 g) to further separate mono- and di-*ortho* PCBs from non-*ortho* PCBs and PCDD/DFs. The first fraction eluted with 25 ml of 25% dichloromethane in hexane contained mono and di-*ortho* PCBs. The second fraction eluted with 250 ml toluene contained non-*ortho* PCBs and PCDD/DFs. Sample extracts were analyzed by a high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC-HRMS). Procedural blanks (n=3) were analyzed to check for interferences. PhD and HpCDF were detected in blanks at concentrations approximately <0.01 pg/g, and OCDD at approximately 0.1 pg/g. The values obtained for HpCDD, OCDD and HpCDF were not corrected for the blank concentrations.

Identification and Quantification

Identification and quantification of 2378-substituted congeners of PCDD/DFs and dioxin-like PCBs were 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 (30 seconds) 300°C. Temperature program of the oven: 110°C (1 minute); 15°C/min up to 170°C; 7.5°C/min up to 290°C, hold for 10 minutes. Total run time: 25 minutes. Electron Capture Detector (⁶³Ni) temperature: 310°C; (ii) HPLC: Shimadzu LC-10AS; Mobile phase: acetonitrile: water 80%, isocratic run. Column: Shimadzu STR-ODS-II (C18 reverse phase) 25cm, L: 4mm ID. UV/VIS detector model: Shimadzu SPD-10A. Prior to injection, ¹³C-labeled 1234-TeCDD and 123789-HxCDD were added as injection recovery standard. Mean recovery of spiked internal standard through the whole analytical procedure was 74% (range: 60–95%) and the reported concentrations were not corrected for the surrogate recoveries. PCDD/DFs, dioxin-like PCBs and TEQ concentrations are reported on a lipid weight basis using WHO TEQ for birds (VAN DEN BERG et al., 2006) as pg TEQ/g, lipid weight.

Statistical Tests

The hypothesis of normal distribution (Shapiro-Wilk's W test) was not rejected for log-transformed data. Lipid base log-transformed concentrations were used to determine the significant differences between group geometric means (Tukey test). Null hypothesis (equality of means) was rejected at the 95% significance level (p<0.05).

RESULTS

PCDD, PCDF, and PCB Congeners

Results for the congener-specific analysis of PCDD, PCDF, and PCB congeners are given in Table 1 and 2. 2,3,7,8-Substituted PCDD and PCDF congeners were detected in all samples analyzed (n=17). No significant sex-related differences in PCDD/F or PCB concentrations were found. Fat-based log-transformed concentrations were used to determine whether there were significant differences between group geometric means. 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. The five most abundant congeners were 2,3,4,7,8-pentachlorodibenzofuran (PeCDF) > 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (PeCDD) > 1,2,3,7,8-pentachlorodibenzofuran (PeCDF) > 1,2,3,7,8,9 hexachlorodibenzo-*p*-dioxin (HxCDD) > 2,3,4,6,7,8-hexachlorodibenzofuran (HxCDF). Polychlorinated biphenyl congeners were detected in all samples analyzed. The sum of the 12

congeners analyzed had the concentration of 968 pg/g lipid weight, and 13.9 pg TEQ/g lipid weight. The sum of 17 congeners analyzed of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans had the concentration of 331.04 pg/g lipid weight, and 13.4 pg TEQ/g lipid weight.

Toxic equivalents, calculated using TEFs for birds proposed by WHO (VAN DEN BERG et al., 2006), and compositions are shown in Figure 2. Correspondingly, from a toxicological point of view, even if the TEF values for these minor contaminants were as high as those of PCBs, or even of PCDDs, the contribution to TEQs would be small compared to those of PCDDs, PCDFs, and PCBs.

Table 1. Medians (range) of PCDD/Fs (pg/g, lipid weight) and toxic equivalents of PCDD/Fs (pg TEQ/g, lipid weight) concentrations in *Fregata magnificens*.

Elements	<i>Fregata magnificens</i>	
	Concentration	WHO TEF (birds)
<i>Dibenzo-p-dioxins (PCDD)</i>		
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
<i>PCDFs</i>		
2378-TCDF	0.34 (1 - 4)	0.34
12378-PeCDF	16 (9 - 31)	1.6
23478-PeCDF	4.9 (2 - 32)	4.9
123478-HxCDF	8.2 (2 - 32)	0.82
123678-HxCDF	3 (1 - 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
	$\Sigma = 331.04$	$\Sigma = 13.4$

Table 2. Medians (range) of PCBs (pg/g, lipid weight) and toxic equivalents of PCBs (pg TEQ/g lipid weight) concentrations in *Fregata magnificens*.

Elements	<i>Fregata magnificens</i>	
	Concentration	WHO TEF (birds)
<i>Non-ortho PCBs</i>		
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
<i>Mono-ortho PCBs</i>		
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
	$\Sigma = 968$	$\Sigma = 13.9$



Fig. 2. Contributions of PCDDs, PCDFs and dioxin-like PCBs to total TEQ.

DISCUSSION

The success of modern societies is, in part, based on extensive achievements in chemistry with a systematic, resulting development of products in medicine, agriculture, and in almost all manufacturing industry sectors and materials for daily use. Chemistry, thus, contributes to the quality of life of billions of human beings. However, its negative impacts on the environment and on health are an important issue of public concern. Social and ecological concerns should not be disregarded in spite of the economic interests affected.

Increased human activities such as industrialization, coupled with over-population and increased atmospheric temperatures, among other factors, have become major environmental issues in recent years. As a result of such circumstances, additional studies which include these environmental factors and their indicators are important because they can show the potential impacts that result from them and their effects on public health. Thus the study of ecotoxicology, a very broad field of science in which issues such as uptake by and effects on organisms, as well as distribution and residence time of the pollutants in the trophic level are studied in many different ways, is of growing importance.

Data on contaminant levels in Brazilian seabirds are limited, and no information exists regarding levels of new or emerging contaminants. High concentrations of PCDD/F and PCB congeners have been shown to adversely affect the reproductive capacity of birds (CUSTER et al., 2010). The adverse effects observed range from direct toxic and teratogenic effects on developing embryos (YAMASHITA et al., 1993; HARRIS et al., 2005) to subtle changes in parental behaviour (HARRIS et al., 2005). A comprehensive example of these effects has been the study of reproductive effects in fish-eating waterbirds in the northern Baltic (HARIO et al., 2004).

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., 2002). 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.

The predominant compounds have been PCBs that have presented 98.15 ng/g in *F. magnificens*. Contrasting also with data obtained from significant concentrations of PCBs which have been detected in all oil samples, with a concentration ranging from 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), the low levels of contaminants suggest a relative degree of isolation and preservation, but the occurrence and distribution profiles of PCBs support the hypothesis that the main source of contamination in remote areas is long range atmospheric transport, and demonstrate the ubiquity of those pollutants in the marine environment.

In previous studies, the monitoring of POPs in seabirds has been limited by the availability of organs (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 of 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). LAILSON-BRITO et al. (2010), studying organochlorine accumulation in Guiana dolphin (*Sotalia guianensis*), at the same study site found concentration levels from 765 to 99 175 for Σ PCB.

Although the data presented in this study are not a cause for concern, subsequent analyses involving more environmental and faunal aspects are necessary. The current study is the first to report seabirds' concentrations of PCDD/Fs and PCBs at this study site, and the first for any free-ranging birds from the Ilha Grande Bay. Due to the small size of the population studied, continued monitoring of these pollutants is essential for the assessment of the health and viability of these animals. Biomagnification may be the cause of the levels in the species collected and analyzed. Further assessments are recommended of organisms at higher trophic levels to assess ecotoxicological impacts. The ubiquity of these pollutants in the marine environment of Ilha Grande Bay supports the need for a greater awareness of bioaccumulation processes, particularly for organisms cultivated (shellfish) or fished locally and destined for human consumption.

ACKNOWLEDGEMENTS

I am grateful for the financial support received from the Conselho Nacional de

Desenvolvimento Científico e Tecnológico – CNPq – through the grant 302946/2011-0.

REFERENCES

- ALCOCK, R. E.; BEHNISCH, P. A.; JONES, K. C.; HAGENMAIER, H. Dioxin-Like PCBS in the environment. Human exposure and the significance of sources. **Chemosphere**, v. 37, p. 1457-1472, 1998.
- ALHO, C. J. R.; SCHNEIDER, M.; VASCONCELOS, L. A. Degree of threat to biological diversity in the Ilha Grande State Park (RJ) and guidelines for conservation. **Braz. J. Biol.**, v. 62, n. 3, p. 375-385, 2002.
- ALLEN, V. G.; BROWN, C. P.; SEGARRA, E.; GREEN, C. J.; WHEELER, T. A.; ACOSTA-MARTINEZ, V.; ZOBECK, T. M. In search of sustainable agricultural systems. **Agric. Ecosyst. Environ.**, v. 124, n. 1-2, p. 3-12, 2008.
- ALVES, M. A. S.; VECCHI, M. B. Birds, Ilha Grande, state of Rio de Janeiro, South-eastern Brazil. **Check List**, v. 5, n. 2, p. 300-313, 2009.
- BOURGEOIS, K.; VIDAI, E.; COMOR, V.; LEGRAND, J.; DROMZEE, S. Colony-site selection drives management priorities for *Yelkouan Shearwater* populations. **J. Wildl. Manage.**, v. 72, p. 1188-1193, 2008.
- CHOY, E. S.; KIMPE, L. E.; MALLORY, M. L.; SMOL, J. P.; BLAIS, J. M. Contamination of an arctic terrestrial food web with marine-derived persistent organic pollutants transported by breeding seabirds. **Environ. Poll.**, v. 158, n. 11, p. 3431-3438, 2010.
- COELHO, E. P.; ALVES, V. S.; FERNANDEZ, F. A. Z.; SONEGHET, M. L. L. On the bird faunas of coastal islands of Rio de Janeiro state, Brazil. **Ararajuba**, v. 2, n. 1, p. 31-40, 1991.
- COSTANZA, R.; FARLEY, J. Ecological economics of coastal disasters: Introduction to the special issue. **Ecol. Econ.**, v. 63, n. 2-3, p. 249-253, 2007.
- CUSTER, T. W.; CUSTER, C. M.; GRAY, B. R. Polychlorinated biphenyls, dioxins, furans, and organochlorine pesticides in belted kingfisher eggs from the upper Hudson River basin, New York, USA. **Environ. Toxicol. Chem.**, 29, n. 1, p. 99-110, 2010.
- DORNELES, P. R.; SANZ, P.; EPPE, G.; AZEVEDO, A. F.; BERTOZZI, C. P.; MARTÍNEZ, M. A.; SECCHI, E. R.; BARBOSA, L. A.; CREMER, M.; ALONSO, M. B.; TORRES, J. P.; LAILSON-BRITO, J.; MALM, O.; ELJARRAT, E.; BARCELÓ, D.; DAS, K. High accumulation of PCDD, PCDF, and PCB congeners in marine mammals from Brazil: a serious PCB problem. **Sci. Tot. Environ.**, v. 463-464, p. 309-318, 2013.
- FASOLA, M.; CANOVA, L. Nest habitat selection by eight syntopic species of Mediterranean Gulls and Terns. **Colon. Waterbirds**, v. 15, p. 169-178, 1992.
- FERREIRA, A. P. Environmental fate of bioaccumulative and persistent substances. A synopsis of existing and future actions. **Gerencia y Políticas de Salud**, v. 7, n. 15, p. 14-23, 2008.
- FREDERIKSEN, M.; JENSEN, H.; DAUNT, F.; MAVOR, R. A.; WANLESS, S. Differential effects of a local industrial Sand Lance fishery on seabird breeding performance. **Ecol. Appl.**, v. 18, p. 701-710, 2008.
- GARCÍA DE LA PARRA, L.M.; CERVANTES-MOJICA, L. J.; GONZÁLEZ-VALDIVIA, C.; MARTÍNEZ-CORDERO, F. J.; AGUILAR-ZÁRATE, G.; BASTIDAS-BASTIDAS, P.; BETANCOURT-LOZANO, M. Distribution of pesticides and PCBs in sediments of agricultural drains in the Culiacan Valley, Sinaloa, Mexico. **Arch. Environ. Contam. Toxicol.**, v. 63, n. 3, p. 323-336, 2012.
- GORNI, R.; WEBER, R. R. Organochlorine pesticides residues and PCBs in benthic organisms of the inner shelf of the São Sebastião Channel, São Paulo. Brazil. **Braz. J. Ocean.**, v. 52, n. 2, p. 141-151, 2004.
- HARIO, M.; HIRVI, J. P.; HOLLMÉN, T.; RUDBÄCK, E. Organochlorine concentrations in diseased vs. healthy gull chicks from the northern Baltic. **Environ. Poll.**, v. 127, n. 3, p. 411-423, 2004.
- HARRIS, M. L.; WILSON, L. K.; ELLIOTT, J. E. An assessment of PCBs and OC pesticides in eggs of double-crested (*Phalacrocorax auritus*) and Pelagic (*P. pelagicus*) cormorants from the west coast of Canada, 1970 to 2002. **Ecotoxicol.**, v. 14, n. 6, p. 607-625, 2005.
- HARRISON, P. **Seabirds, an identification guide**. Boston: Houghton Mifflin Co., 1983.
- HOLMSTRÖM, K.; BERGER, U. Tissue distribution of perfluorinated surfactants in common Guillemot (*Uria Aalge*) from the Baltic sea. **Environ. Sci. Technol.**, v. 42, p. 5879-5884, 2008.
- JAUNIAUX, T.; BROSENS, L.; MEIRE, P.; OFFRINGA, H.; COIGNOUL, F. Pathological investigations on Guillemots (*Uria Aalge*) stranded at (on?) the Belgian coast during the winter 1993-1994. **Veterin. Rec.**, v. 143, n. 14, p. 387-390, 1998.
- JENOUVRIER, S.; BARBRAUD, C.; WEIMERSKIRCH, H. Effects of climate variability on the temporal population dynamics of Southern Fulmars. **J. Anim. Ecol.**, v. 72, p. 576-587, 2003.
- KUMAR, K.S.; KANNAN, K.; PARAMASIVAN, O.N.; SUNDARAM, V.P.S.; NAKANISHI, J.; MASUNAGA, S. Polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and polychlorinated biphenyls in human tissues, meat, fish, and wildlife samples from India. **Environ. Sci. Technol.**, v. 35, n. 17, p. 3448-3455, 2001.
- KUMAR, K. S.; KANNAN, K.; CORSOLINI, S.; EVANS, T.; GIESY, J. P.; NAKANISHI, J.; MASUNAGA, S. Polychlorinated dibenzo-*p*-dioxins, dibenzofurans and polychlorinated biphenyls in polar bear, penguin and south polar skua. **Environ. Poll.**, v. 119, p. 151-161, 2002.
- KUSHLAN, J. A. Colonial waterbirds as bioindicators of environmental change. **Colon. Waterbirds**, v. 16, p. 223-251, 1993.
- LAILSON-BRITO, J.; DORNELES, P.R.B.; AZEVEDO-SILVA, C.E.; AZEVEDO, A.F.; VIDAL, L.G.; ZANELATTO, R.C.; LOZINSKI, C.P.; AZEREDO, A.; FRAGOSO, A.B.; CUNHA, H.A.; TORRES, J.P.; MALM, O. High organochlorine accumulation in blubber of Guiana dolphin, *Sotalia guianensis*, from Brazilian coast and its use to establish geographical differences among populations. **Environ. Poll.**, v. 158, n. 5, p. 1800-1808, 2010.
- LAUWERYS, R.; HOET, P. **Industrial Chemical Exposure**. Guidelines for biological monitoring, 2nd ed., Lewis Publishers: Boca Raton, FL, USA, 1993.

- LIN, T.; HU, Z.; ZHANG, G.; LI, X.; XU, W.; TANG, J.; LI, J. Levels and mass burden of DDTs in sediments from fishing harbours: the importance of DDT-containing antifouling paint to the coastal environment of China. **Environ. Sci. Technol.**, v. 43, n. 21, p. 8033-8038, 2009.
- MORIARTY, F. **Ecotoxicology**. The study of pollutants in ecosystems, 3rd ed., Academic Press, California, USA, 1999.
- NUNES, G. K.; SANTOS, S. B. Environmental factors affecting the distribution of land snails in the Atlantic Rain Forest of Ilha Grande, Angra dos Reis, RJ, Brazil. **Braz. J. Biol.**, v. 72, n. 1, p. 79-86, 2012.
- PARERA, J.; ABALOS, M.; SANTOS, F. J.; GALCERAN, M.T.; ABAD, E. Polychlorinated dibenzo-*p*-dioxins, dibenzofurans, biphenyls, paraffins and polybrominated diphenyl ethers in marine fish species from Ebro River Delta (Spain). **Chemosphere**, v. 93, n. 3, p. 499-505, 2013.
- PARRISH, J. K.; ZADOR, S. G. Seabirds as indicators: an exploratory analysis of physical forcing in the Pacific Northwest coastal environment. **Estuaries**, v. 26, p. 1044-1057, 2003.
- PARVEZ, S.; EVANS, A. M.; LORBER, M.; HAWKINS, B. S.; SWARTOUT, J. C.; TEUSCHLER, L.K.; RICE, G. E. A sensitivity analysis using alternative toxic equivalency factors to estimate U.S. dietary exposures to dioxin-like compounds. **Regulatory Toxicol. Pharmacol.**, v. 67, n. 2, p. 278-284, 2013
- RANSON, H.; N'GUESSAN, R.; LINES, J.; MOIROUX, N.; NKUNI, Z.; CORBEL, V. Pyrethroid resistance in African anopheline mosquitoes: what are the implications for malaria control? **Trends Parasitol.**, v. 2, p. 91-98, 2011.
- SAFE, S. Polychlorinated Biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). **Crit. Rev. Toxicol.**, v. 21, n. 1, p. 51-88, 1990.
- SHAFFER, S. A.; TREMBLAY, Y.; WEIMERSKIRCH, H.; SCOTT, D.; THOMPSON, D. R.; SAGAR, P. M.; MOLLER, H.; TAYLOR, G. A.; FOLEY, D. G.; BLOCK, B. A.; COSTA, D. P. Migratory shearwaters integrate oceanic resources across the Pacific ocean in an endless summer. **Proc. Nat. Acad. Sci. U.S.A.**, v. 103, p. 12799-12802, 2006.
- SHAW, S. D.; BERGER, M. L.; BRENNER, D.; CHU, M. D.; MATHERLY, C. K.; CHU, A. C.; CLARK, G. C. Application of the calux bioassay for the determination of PCDD/FS and dioxin-like PCBs in tissues of harbor seals. **Organohal. Compd.**, v. 68, p. 587-591, 2006.
- STEMPNIEWICZ, L.; BLACHOWIAK-SAMOLYK, K.; WESLAWSKI, J. M. Impact of climate change on zooplankton communities, seabird populations and arctic terrestrial ecosystem - A scenario. **Deep-Sea Res. II**, v. 54, p. 2934-2945, 2007.
- TANABE, S.; WATANABE, M.; MINH, T. B.; 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. **Environ. Sci. Technol.**, v. 38, p. 403-413, 2004.
- TASKER, M. L.; REID, J. B. Seabirds in the marine environment: Introduction. **Ices J Mar. Sci**, v. 54, p. 505-506, 1997.
- UNITED NATIONS ENVIRONMENT PROGRAM (UNEP). **Guidance for Analysis of Persistent Organic Pollutants (POPs)**, Chemicals Branch. UNEP/DTIE, Geneva, Switzerland, 2007.
- VAN DEN BERG, M.; BIRNBAUM, L. S.; DENISON, M. The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. **Toxicol. Sci.**, v. 93, n. 2, p. 223-241, 2006.
- WANIA, F.; AXELMAN, J.; BROMAN, D. A review of processes involved in the exchange of persistent organic pollutants across the air-sea interface. **Environ. Poll.**, v. 102, p. 3-23, 1998.
- WHITEHOUSE, M. J.; PRIDDLE, J.; BRANDON, M. A.; SWANSON, C. A comparison of chlorophyll/nutrient dynamics at two survey sites near South Georgia, and the potential role of planktonic nitrogen recycled by land-based predators. **Limnol. Ocean. Methods**, v. 44, p. 1498-1508, 1999.
- XU, W.; WANG, X.; CAI, Z. Analytical chemistry of the persistent organic pollutants identified in the Stockholm Convention: A review. **Anal. Chim. Acta**, v. 790, p. 1-13, 2013.
- YAMASHITA, N.; TANABE, S.; LUDWIG, J.P.; KURITA, H.; LUDWIG, M.E.; TATSUKAWA R. Embryonic abnormalities and organochlorine contamination in Double-crested Cormorants (*Phalacrocorax auritus*) and Caspian Terns (*Hydroprogne caspia*) from the upper Great Lakes in 1988. **Environ. Poll.**, v. 79, p. 163-173, 1993.
- YAMASHITA, R.; TAKADA, H.; MURAKAMI, M.; FUKUWAKA, M. A.; WATANUKI, Y. Evaluation of non-invasive approach for monitoring PCB pollution of seabirds using preen gland oil. **Environ. Sci. Technol.**, v. 41, n. 14, p. 4901-4906, 2007.

(Manuscript received 08 January 2014; revised 28 September 2014; accepted 29 September 2014)