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Dioxins and polychlorinated biphenyls concentrations in *Larus dominicanus*. Case study: Marambaia island, Sepetiba bay, Rio de Janeiro State, Brazil

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ABSTRACT. Seabirds play a significant role as bioindicators: they are conspicuous, relatively easy to observe, well-established studied group of organisms, and in the focus of public interest due to pollution in aquatic ecosystem. Systematically, a significant number of man-made chemicals have been introduced in the marine environment and represent the major problem arising in the development worldwide. Many of these chemical contaminants are persistent, known to bioaccumulate and biomagnify through the aquatic food web, affecting species associated with aquatic systems. Dioxins [polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF)] and polychlorinated biphenyls (PCB) concentrations were measured in Kelp gull *Larus dominicanus* collected from 2006 to 2011 on Marambaia Island, Sepetiba Bay, Rio de Janeiro State, Brazil. Detectable liver concentrations of PCDD Fs^{-1} and PCBs were found in all samples analyzed. These represent some of the first measurements of PCDD Fs^{-1} and PCBs in seabirds from this area. Although levels of these contaminants in the tested species currently appear to fall below critical values, a continuous and systematic monitoring on these compounds becomes essential and desirable to not express toxic values in the future.

Keywords: marine pollution, environmental exposure, dioxins, polychlorinated biphenyls.

Concentrações de dioxinas e bifenilas policloradas em *Larus dominicanus*. Estudo de caso: ilha da Marambaia, baía de Sepetiba, Estado do Rio de Janeiro, Brasil

RESUMO. Aves marinhas desempenham uma função significativa como bioindicadores: elas são conspícuas, relativamente fáceis de observar, grupos de organismos de estudo bem estabelecidos e no foco de interesse público devido à poluição no ecossistema aquático. Sistematicamente, um número significativo de produtos químicos sintéticos vêm sendo introduzidos no ambiente marinho, representando um dos principais problemas que se coloca no desenvolvimento em todo o mundo. Muitos desses contaminantes químicos são persistentes, conhecidos por bioacumular e biomagnificar através de suas movimentações na cadeia alimentar, afetando espécies associadas aos sistemas aquáticos. Concentrações de dioxinas [dibenzo-p-dioxinas policloradas (PCDD), dibenzofuranos (PCDF)] e bifenilas policloradas (PCB) foram medidas em gaivotões *Larus dominicanus* coletadas de 2006 a 2011 na Ilha da Marambaia, Baía de Sepetiba, Rio de Janeiro, Brasil. Estes dados representam algumas das primeiras medições de PCDD Fs^{-1} e PCBs em aves marinhas nesta área estudada. Embora os níveis destes contaminantes na espécie testada apresentarem níveis abaixo dos valores críticos, o monitoramento contínuo, sistemático, torna-se imprescindível e desejável para que estes compostos não expressem no futuro valores tóxicos.

Palavras-chave: poluição marinha, exposição ambiental, dioxinas, bifenilas policloradas.

Introduction

Oceans cover about 70% of the earth's surface. Effects of pollution on marine ecosystems have become a matter of great concern, especially to coastal states (FLEMING et al., 2006). The oceans cannot supply an infinite sink for anthropogenic wastes but inadequate attention has been given for evaluating the limits of capacity of coastal areas for waste assimilation (KITE-POWELL et al., 2008). Thus, instances of fisheries shortage, spoiled beaches, destroyed coral reefs and wildlife habitat, toxic blooms and lost coastal ecological communities are extensive, with a corresponding determination of cost benefit (KNAP et al., 2002). Current concerns about connectivity of ocean health issues and the relationship to human disease highlight an essential area for research (FLEMING et al., 2006; KNAP et al., 2002). Awareness of the ocean role and the impact of human performance on it can expose the complexity and interdependence of all aspects of the system (STEWART et al., 2008). Enhanced 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.

Worldwide contamination by dioxins [polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF)] and polychlorinated biphenyls (PCB) is of great concern due to the persistency, bioaccumulative nature, and toxicity of these compounds (SAVINOVA et al., 2007). For several decades, these compounds have been produced and extensively used for various purposes. Numerous of these chemical contaminants are persistent polyhalogenated aromatic hydrocarbons known to bioaccumulate and biomagnify as they move through the aquatic food web, affecting species associated with aquatic systems, including humans (GIESY et al., 1994; PEREIRA, 2004).

Due to its position in the marine food chain and their long life cycle, seabirds congregate significant levels of trace elements. These organisms are good sentinel species because are observable, sensitive to toxicants, and live in different trophic positions (MALLORY et al., 2010; TASKER; REID, 1997). Consequently, studies assessing avian population status, reproductive success, and toxicological importance of metal exposures can be extrapolated to other wildlife and probably humans (ALLOWAY; AYRES, 1997; CARPENTER, 1998).

Pollution in the marine environment has become a subject of enormous apprehension, especially to coastal states (FERREIRA, 2011; SCHMITT-JANSEN et al., 2008). Knowledge of the ocean and of the impact of human activities on it can reveal the complexity and interdependence of all aspects of the system (PEREIRA, 2004). Improved acquaintance with these and better forecasting ability 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). Recent concerns about the connectivity of ocean health issues and their relationship to human disease highlight an important area for study.

PCDDs Fs^{-1} and PCBs Contamination

The study of PCDDs Fs^{-1} and PCBs contamination in aquatic environments has allowed to predict or identify sources of pollution and extensiveness of these pollutants, since they potentially pose a threat to ecosystem balance, being an important instrument to predict the effects to human and animal health (BREIVIK et al., 2002; KUMAR et al., 2001).

There are 75 different PCDDs and 135 PCDFs, which differ from each other in the number and positions of the chlorine atoms (BREIVIK et al., 2002; WALKER et al., 2006). From the human/biota point of view, 17 PCDD Fs^{-1} chlorine substitution in the (2,3,7,8) positions are considered to be toxicologically important (ALLOWAY; AYRES, 1997; FERREIRA, 2008; PEREIRA; EBECKEN, 2009). PCDDs have a planar aromatic tricyclic structure with 1-8 chlorine atoms as substituents. 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). The PCDD and PCDF, commonly called 'dioxins', are two classes of 'quasi-planar' tricycles aromatic ethers with 210 different compounds (congeners) in total. The PCDD F^{-1} has similar physical-chemical properties but different biological potencies (HAGENMAIER, 1987). Figure 1 shows the general structure of these classes of compounds.

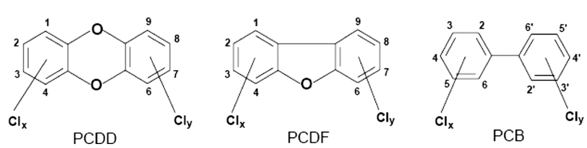

Figure 1. Generalized structures of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs).

Most industrial countries have restricted or stopped their use since 1970s, leading to decreasing concentrations in long-term environmental surveillance programs (CHOI et al., 2001; THOMPSON et al., 2007). However, compounds remained in ecosystems either due to their persistency or transport from developing countries where use in agricultural and industrial purposes is still current (FERREIRA, 2011). Due to their chemical stability and hydrophobic nature, these compounds are adsorbed onto particles, accumulated in aquatic organisms, and highly biomagnified through the aquatic food webs (LAUWERYS; HOET, 1993). Many organochlorines have been implicated in a wide range of adverse biological effects, including impaired reproduction and immunosuppression (RITTLER; CASTILLA, 2002).

Larus dominicanus (Lichtenstein, 1823, Charadriiformes: Laridae) inhabits the coast and coastal islands of the Pacific and Atlantic South America, Earth del Fuego to northern Peru, on the brazilian coast are found in Rio Grande do Sul to Espírito Santo States.

It is also found in South Africa, Australia, New Zealand and Subantarctic islands (BARBIERI, 2008). This gull is a bird of natural wetlands, fresh or salt, grass or forested. It feeds in shallow to deep water along lake shores, rivers, estuaries, and beaches. Given its high abundance in the study site, it was then chosen for this research.

This study aimed to provide metal concentrations data of *L. dominicanus* collected from Marambaia Island, which is an important natural breeding ground for many seabird species. Marambaia Island is located in the Sepetiba bay, on the southern coast of Rio de Janeiro State (23°04' S and 43°53' W). The island is 42 km^2 and has a sand zone of around 40 km in extension (Marambaia Coastal Restinga), which is connected to the continent and to the municipality of Rio de Janeiro. The regional climate is classified as tropical wet; July is the coldest month (average of 16.8°C), whereas February is the warmest (average of 32.3°C). From November to March the average rainfall exceeds 100 mm. Nearly 37% of the average annual rainfall (1,240 mm) occurs during summer; March is the wettest month and July is the driest (LOURENÇO et al., 2010). It is situated in the southern Atlantic Coast of Rio de Janeiro State, Brazil (Figure 2).

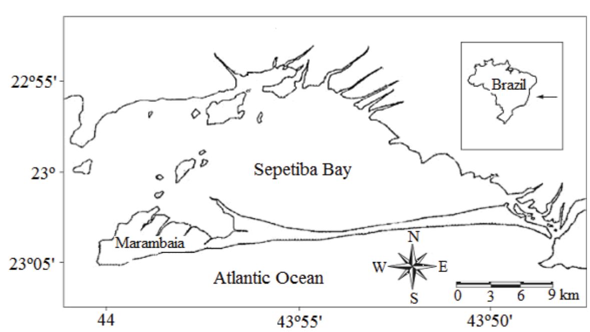

Figure 2. Study area: Marambaia island, Sepetiba bay, Rio de Janeiro State, Brazil.

Material and methods

Analysis: Identification and Quantification

For this study, we used a total of thirty one adult specimens found stranded or dead in areas related to the study site, between March 2006 and December 2011. All fresh carcasses were necropsied following a standardized protocol (JAUNIAUX et al., 1998), while putrescent specimens were discarded. Livers were collected, weighed, and maintained at - 20°C for later analysis.

Chemical analysis of dioxins and polyclrorinated biphenyls followed the USEPA Method 1668 (2003), and USEPA Method 8290 A (USEPA, 2007). Five grams of liver samples were weighed and lyophilized. 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 min. at 125°C and 1500 psi) and allows the extraction of the different organic compounds present from the biological matrix. After being extracted, 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 (BECHER et al., 1995; 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^{-1} and PCBs was rinsed 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 passed through a silica gel-packed glass column (Wakogel, silica gel 60; 2 g) 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; 5 g) 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^{-1}, was Kuderna-Danish concentrated and passed through silica gel impregnated activated carbon column (0.5 g). 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^{-1} 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^{-1} and dioxin-like PCBs (non- and mono-ortho-substituted congeners) was performed by using 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 seg.) 300°C. Temperature program of the oven: 110°C (1 min.); 15°C min.$^{-1}$ up 170°C; 7.5°C min.$^{-1}$ up to 290°C, hold for 10 minutes. Total run time: 25 min. Electron Capture Detector (^{63}Ni) temperature: 310°C; (ii) HPLC: Shimadzu LC-10AS; Mobile phase: acetonitrile: water 80%, isocratic run. Column: Shimadzu STR-ODS-II (C-18 reverse phase) 25 cm, L: 4 mm 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^{-1} 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 'ith' 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.

$$TEQ = \sum_{i=1}^{n}(Ci \times TEFi) \quad (1)$$

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 (GURUGE et al., 2000; HOLMSTRÖM; BERGER, 2008). Results are expressed either as pg g^{-1} of lipid mass or in terms of toxicity, using WHO TEF for birds (VAN DEN BERG et al., 2006) as pg TEQ g^{-1}, lipid weight.

Statistical analysis was undertaken using the Origin 7.5 software package (Origin Lab Corporation). The average distribution of PCDDs FS^{-1} and PCBs was assessed using analysis of variance (ANOVA). For all the tests, p-values of < 0.05 were used to determine significant differences.

Results

No significant species-related differences in PCB and PCDD Fs^{-1} concentrations were found. Concentrations of PCB-congeners with fat percentages are presented in Table 1, and Concentrations of PCDD Fs^{-1} -congeners with fat percentages are presented in Table 2.

The medians of concentrations in *L. dominicanus* ranged from 13 to 211 pg g^{-1} lipid weight of PCBs (mean 76.33333, median 61.5, SD = 64.86116) and toxic equivalents of PCBs (pg TEQ g^{-1} lipid weight) from 1.5E-4 to 7.0 pg g^{-1} lipid weight of PCBs (mean 1.48428, median 0.00945, SD = 2.70384); and ranged from 0.41 to 192 pg g^{-1} lipid weight of PCDD Fs^{-1} (mean 19.71118, median 7.0, SD = 41.98975) and toxic equivalents of PCDD Fs^{-1} (pg TEQ g^{-1} lipid weight) from 9E-4 to 5.0 pg g^{-1} lipid weight of PCDD Fs^{-1} (mean 0.94304, median 0.5, SD = 1.35553).

Table 1. Medians (range) of concentrations as pg g^{-1} lipid weight of PCBs and toxic equivalents of PCBs (pg TEQ g^{-1} lipid weight) in *Larus dominicanus*.

Elements	*Larus dominicanus*	
	Concentration	WHO TEF (birds)
	Non-ortho PCBs	
3,3',4,4'-TCB (77)	128 (60 – 416)	6.9
3,4,4',5-TCB (81)	45 (20 – 397)	4.5
3,3',4,4',5-PeCB (126)	79 (39 – 171)	7.9
3,3',4,4',5,5'-HxCB (169)	55 (31 – 197)	0.055
	Mono-ortho PCBs	
2,3,3',4,4'-PeCB (105)	211 (51 – 308)	0.0211
2,3,4,4',5-PeCB (114)	179 (42 – 278)	0.0179
2,3',4,4',5-PeCB (118)	166 (40 – 244)	0.00166
2',3,4,4',5-PeCB (123)	58 (22 – 133)	0.00058
2,3,3',4,4',5-HxCB (156)	16 (9 – 44)	0.0016
2,3,3',4,4',5'-HxCB (157)	15 (7 – 39)	0.0015
2,3',4,4',5,5'-HxCB (167)	25 (8 – 50)	0.00025
2,3,3',4,4',5,5'-HeCB (189)	13 (8 – 46)	0.00013
	∑= 990	∑= 19.38

Table 2. Medians (range) of concentrations (pg g^{-1}, lipid weight) of PCDD Fs^{-1} and toxic equivalents of PCDD Fs^{-1} (pg TEQ g^{-1}, lipid weight) in *Larus dominicanus*.

Elements	*Larus dominicanus*	
	Concentration	WHO TEF (birds)
	Dibenzo-p-dioxins (PCDD)	
2378-TCDD	1.3 (ND – 6.5)	1.3
12378-PeCDD	7 (1.4 – 12.6)	7.0
123478-HxCDD	17 (7 - 39)	0.85
123678-HxCDD	5 (ND - 12)	0.05
123789-HxCDD	11 (5 - 33)	1.1
1234678-HpCDD	48 (11 - 82)	0.048
OCDD	192 (22 - 301)	0.0192
2378-TCDF	0.41 (ND - 5)	0.41
12378-PeCDF	28 (12 - 35)	2.8
23478-PeCDF	2.2 (2 - 13)	2.2
123478-HxCDF	9.6 (5 - 24)	0.96
123678-HxCDF	6 (ND - 14)	0.6
1234789-HxCDF	5 (4– 18)	0.5
234678-HxCDF	7 (0.7 - 12)	0.7
1234678-HpCDF	13 (4 - 33)	0.13
1234789-HpCDF	11 (8 - 22)	0.11
OCDF	12 (3 - 28)	0.0012
	∑= 375.51	∑= 18.78

Fat-based log-transformed concentrations were used to detect significant differences between group geometric means (Tukey's test). Null hypothesis (equality of means) was rejected at the 95% significance level ($p < 0.05$). There was no statistically significant difference between mean PCDD F^{-1} and PCB-congeners concentrations. PCB 105 congener accounted for 22.16% of ΣPCB, PCB 114 congener accounted for 19.32% of ΣPCB, and PCB congeners 118 and 77 accounted for 12.88% of ΣPCB, respectively. PCDD OCDD congener accounted for 53.12% of ΣPCDD/Fs. Data in Figure 3 shows the distribution of PCB and PCDD Fs^{-1} congeners.

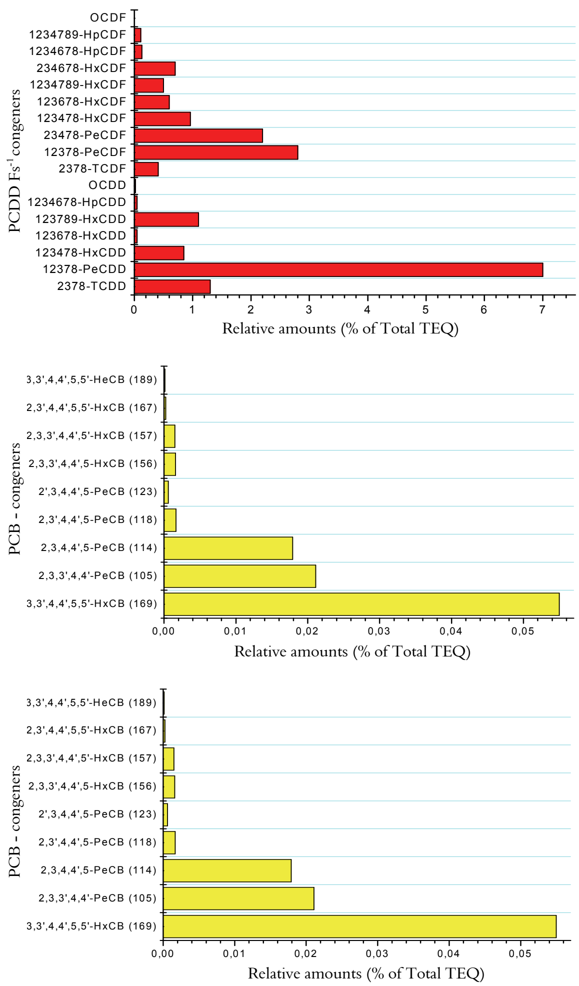

Figure 3. Contributions of PCDDs, PCDFs and dioxin-like PCBs to Total TEQ (pg g^{-1} lipid).

Discussion

The use of seabirds for analysis of pollutants, rather than the analysis of pollutants in the abiotic environment, it becomes more attractive and promising because these indicators can provide precise information on the bioavailability of pollutants, their bio-magnification and transfer. Thus, the magnitude of the observed data reinforces that there are startling signs regarding the potential risks to public health and these indicators are important to environmental monitoring by being at top the food chain, are sensitive to toxic products, respond to subtle changes in the environment, and also because of its high metabolic rate (CHOI et al., 2001; KANNAN et al., 2002; KRUUK; CONROY, 1996; KUMAR et al., 2002).

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. The presence of anthropogenic pollutants, such as PCDD F^{-1} and PCB-congeners, throughout all compartments of the marine environment has been of international concern for a number of decades (LAILSON-BRITO et al., 2010; MORIARTY, 1999; OLSSON et al., 2000). 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, increased incidence of 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).

In previous studies, the monitoring of POPs in seabirds has been limited by the availability of organs (MACKAY et al. 1991, MONTEVECCHI, 1993; MORLEY, 2010; PEAKALL et al., 1990). 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. Recently, electronic tracking tags have revolutionized our understanding of the large-scale movements and habitat use of mobile marine animals (SHAFFER et al., 2006).

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 can show potential impacts that are being reflected, and extended to public health.

It was presented a scientific approach for assessing the ecological condition of the Sepetiba Bay and the impacts caused by PCBs and PCDD FS^{-1} to a particular species of bird used as indicator, which has weights throughout Latin America. The key assumptions underlying the approach are: (a) the importance of putting analysis on ecosystems attributes of public importance, (b) the consistency with scientific understanding of what is important to sustain ecosystems structure and function, (c) measurements in environmental indicators must be scientifically defensible, and (d) are there implications on health risk to man and along marine trophic chains?

The presence of tissue levels of POPs has been associated with biological and physiological effects in marine organisms, especially seabirds. The animals sampled in the current study had PCDD F^{-1} and PCB congeners that exceeded the values found in some studies (LAILSON-BRITO et al., 2010; MACKAY et al., 1991; MONTEVECCHI, 1993; MORIARTY, 1999; MORLEY, 2010; OLSSON et al., 2000; PEAKALL et al., 1990). 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.

Conclusion

The present study confirms the ubiquity of POPs in *L. dominicanus* belonging to the marine environment of Sepetiba bay, Rio de Janeiro, Brazil. Biomagnification may be the cause of the levels in the species collected and analyzed. Further assessments are recommended on organisms at higher trophic levels for ecotoxicological impacts. The ubiquity of these pollutants in Sepetiba 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.

This research gives reasonable alerts in marine pollution with relevant information that can support the decision-making process and provides a baseline to evaluate future clean up and restoration activities at Sepetiba bay. There are clear management decisions that must be made concerning what to clean up, and to what extent.

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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, n. 8, p. 1457-1472, 1998.

ALLOWAY, B. J.; AYRES, D. C. **Chemical principles of environmental pollution**, 2nd ed. New York: Chapman and Hall, 1997.

BARBIERI, E. Variação sazonal do gaivotão (*Larus dominicanus*) durante o ano de 2005 no estuário de Cananéia-Iguape-Ilha Comprida, São Paulo, Brasil. **Biota Neotropica**, v. 8, n. 2, p. 97-103, 2008.

BECHER, G.; SKAARE, J. U.; POLDER, A.; SLETTEN, B.; ROSSLAND, O. J.; HANSEN, H. K. PCDDS, PCDFS, and PCBS in human milk from different parts of Norway and Lithuania. **Journal of Toxicology and Environmental Health**, v. 46, n. 2, p. 133-148, 1995.

BREIVIK, K.; SWEETMAN, A.; PACYNA, J. M.; JONES, K. C. Towards a global historical emission inventory for selected PCB congeners - a mass balance approach 2. global production and consumption. **Science of Total Environment**, v. 290, n. 1-3, p. 181-198, 2002.

CARPENTER, D. O. Polychlorinated biphenyls and human health. **International Journal of Occupational Medicine and Environmental Health**, v. 11, n. 4, p. 291-303, 1998.

CHOI, J. W.; MATSUDA, M.; KAWANO, M.; MIN, B. Y.; WAKIMOTO, T. Accumulation profiles of persistent organochlorines in waterbirds from an estuary in Korea. **Archives of Environmental Contamination and Toxicology**, v. 41, n. 3, p. 353-363, 2001.

COSTANZA, R.; FARLEY, J. Ecological economics of coastal disasters: introduction to the special issue. **Ecology Economics**, v. 63, n. 2-3, p. 249-253, 2007.

FERREIRA, A. P. Environmental fate of bioaccumulative and persistent substances. a synopsis of existing and future actions. **Gerencia y Politicas de Salud**, v. 7, n. 15, p. 14-23, 2008.

FERREIRA, A. P. Assessment of heavy metals in *Egretta thula*. Case study: Coroa Grande mangrove, Sepetiba bay, Rio de Janeiro, Brazil. **Brazilian Journal of Biology**, v. 71, n. 1, p. 1- 7, 2011.

FLEMING, L. E.; BROAD, K.; CLEMENT, A.; DEWAILLY, E.; ELMIR, S.; KNAP, A.; POMPONI, S. A.; SMITH, S.; SOLO-GABRIELE, H.; WALSH, P.; SMITH, S.; GABRIELE, H.; WALSH, P. Oceans and human health: emerging public health risks in the marine environment. **Marine pollution bulletin**, v. 53, n. 10-12, p. 545-560, 2006.

GIESY, J. P.; LUDWIG, J. P.; TILLITT, D. E. Dioxins, dibenzofurans, PCBs and colonial, fish-eating water birds. In: SCHECTER, A. (Ed.). **Dioxins and health**. New York: Plenum Publishers, 1994. p. 254-307.

GURUGE, K. S.; TANABE, S.; FUKUDA, M. Toxic assessment of PCBs by the 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalent in common cormorant (*Phalacrocorax carbo*) from Japan. **Archives of Environmental Contamination and Toxicology**, v. 38, n. 4, p. 509-521, 2000.

HAGENMAIER, H. **Abschlussbericht zum forschungs- und untersuchungsvorhaben - belastung der umwelt mit dioxinen**. Tübingen: Umweltministerium Baden-Württemberg, 1987.

HOLMSTRÖM, K. E.; BERGER, U. Tissue distribution of perfluorinated surfactants in common Guillemot (*Uria Aalge*) from the Baltic sea. **Environmental Science and Technology**, v. 42, n. 16, p. 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 Record**, v. 143, n. 14, p. 387-390, 1998.

KANNAN, K.; CORSOLINI, S.; IMAGAWA, T.; FOCARDI, S.; GIESY, J. P. Polychlorinated -naphthalenes, -biphenyls, -dibenzo-p-dioxins, dibenzofurans and p,p-DDE in bluefin tuna, swordfish, cormorants and barn swallows from Italy. **Ambio**, v. 31, n. 3, p. 207-211, 2002.

KITE-POWELL, H. L.; FLEMING, L. E.; BACKER, L. C.; FAUSTMAN, E. M.; HOAGLAND, P.; TSUCHIYA, A.; YOUNGLOVE, L. R.; WILCOX, B. A.; GAST, R. J. Linking the oceans to public health: current efforts and future directions. **Environmental Health**, v. 7, supl. 2, p. 1-15, 2008.

KIVIRANTA, H.; PURKUNEN, R.; VARTIAINEN, T. Levels and trends of PCDD/FS and PCBS in human milk in Finland. **Chemosphere**, v. 38, n. 2, p. 311-323, 1999.

KNAP, A.; DEWAILLY, É.; FURGAL, C.; GALVIN, J.; BADEN, D.; BOWEN, R. E.; DEPLEDGE, M.; DUGUAY, L.; FLEMING, L. E.; FORD, T.; MOSER, F.; OWEN, R.; SUK, W. A.; UNLUATA, U. Indicators of ocean health and human health: developing a research and monitoring framework. **Environmental Health Perspectives**, v. 110, n. 2, p. 839-845, 2002.

KRUUK, H.; CONROY, J. W. H. Concentrations of some organochlorines in otters (*Lutra lutra* L.) in Scotland: implications for populations. **Environmental Pollution**, v. 92, n. 2, p. 165-171, 1996.

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. **Environmental Science and Technology**, 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, dibenzo- furans and polychlorinated biphenyls in polar bear, penguin and south polar skua. **Environmental Pollution**, v. 119, n. 2, p. 151-161, 2002.

LAILSON-BRITO, J.; DORNELESA, P. R. B.; AZEVEDO-SILVA, C. E.; AZEVEDO, A. F.; VIDAL, L. G.; ZANELATTO, R. E.; LOZINSKI, C. P. C.; AZEREDO, A.; FRAGOSO, A. B. L.; CUNHA, H. A.; TORRES, J. P. M.; 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**, v. 158, n. 5, p. 1800-1808, 2010.

LAUWERYS, R.; HOET, P. **Industrial chemical exposure**. Guidelines for biological monitoring. Boca Raton: Lewis Publishers, 1993.

LOURENÇO, E. C.; COSTA, L. M.; SILVA, R. M.; ESBERARD, C. E. L. Bat diversity of Ilha da Marambaia, Southern Rio de Janeiro State, Brazil (Chiroptera, Mammalia). **Brazilian Journal of Biology**, v. 70, n. 3, p. 511-519, 2010.

MACKAY, D.; SHIU, W. Y.; MA, K. C. **Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals**: Monoaromatic hydrocarbons, chlorobenzenes and PCBS. Boca Raton: Lewis Publishers, 1991. v. I.

MALLORY, M. L.; ROBINSON, S. A.; HEBERT, C. E.; FORBES, M. R. Seabirds as indicators of aquatic ecosystem conditions: a case for gathering multiple proxies of seabird health. **Marine Pollution Bulletin**, v. 60, n. 1, p. 7-12, 2010.

MONTEVECCHI, W. A. Birds as indicators of change in marine prey stocks. In: FURNESS, R. W.; GREENWOOD, J. J. D. (Ed.). **Birds as monitors of environmental change**. London: Chapman and Hall, 1993. p. 270-312.

MORIARTY, F. **Ecotoxicology. The study of polluants in ecosystems**. 3rd ed. California: Academic Press, 1999.

MORLEY, N. J. Interactive effects of infectious diseases and pollution in aquatic molluscs. **Aquatic Toxicology**, v. 96, n. 1, p. 27-36, 2010.

OLSSON, A.; VALTERS, K.; BURREAU, S. Concentrations of organochlorine substances in relation to fish size and trophic position: a study on perch (*Perca fluvialis*). **Environmental Science and Technology**, v. 34, n. 23, p. 4878-4886, 2000.

PEAKALL, D. B.; NOBLE, D. G.; ELLIOTT, J. E.; SOMERS, J. D.; ERICKSON, G. Environmental contaminants in canadian Peregrine falcons, *Falco peregrinus*: a toxicological assessment. **Canadian Field Naturalist**, v. 104, n. 2, p. 244-254, 1990.

PEREIRA, M. S. Polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF) and polychlorinated biphenyls (PCB): main sources, environmental behaviour and risk to man and biota. **Química Nova**, v. 27, n. 6, p. 934-943, 2004.

PEREIRA, G. C.; EBECKEN, N. F. F. Knowledge discovering for coastal waters classification. **Expert Systems with Applications**, v. 36, n. 4, p. 8604-8609, 2009.

RITTLER, M.; CASTILLA, E. E. Desreguladores endócrinos e anomalias congênitas. **Cadernos de Saúde Pública**, v. 18, n. 2, p. 421-428, 2002.

SAVINOVA, T.; BATTERMAN, S.; KONOPLEV, S.; SAVINOV, V.; GABRIELSEN, G. W.; ALEKSEEVA, L.; KOCHETKOV, A.; PASYNKOVA, E.; SAMSONOV, D.; KORYAKIN, A.; CHERNYAK, S. New environmental contaminants in seabirds from the seven islands archipelago (Barents sea, Russia). **Organohalogen Compounds**, v. 69, p. 1681-1684, 2007.

SCHMITT-JANSEN, M.; VEIT, U.; DUDEL, G.; ALTENBURGER, R. An ecological perspective in aquatic ecotoxicology: approaches and challenges. **Basic and Applied Ecology**, v. 9, n. 4, p. 337-345, 2008.

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. **Proceedings of the National Academy of Sciences of**

the United States of America, v. 103, p. 12799-12802, 2006.

STEWART, J. R.; GAST, R. J.; FUJIOKA, R. S.; SOLO-GABRIELE, H. M.; MESCHKE, J. S.; AMARAL-ZETTLER, L. A.; DEL CASTILLO, E.; POLZ, M. F.; COLLIER, T. K.; STROM, M. S.; SINIGALLIANO, C. D.; MOELLER, P. D. R.; HOLLAND, A. F. The coastal environment and human health: microbial indicators, pathogens, sentinels and reservoirs. **Environmental Health**, v. 7, suppl. 2, p. S3, 2008.

TASKER, M. L.; REID, J. B. Seabirds in the marine environment: Introduction. **Ices Journal of Marine Science**, v. 54, p. 505-506, 1997.

THOMPSON, B.; ADELSBACH, T.; BROWN, C.; HUNT, J.; KUWABARA, J.; NEALE, J.; OHLENDORF, H.; SCHWARZBACH, S.; SPIES, R.; TABERSKI, K. Biological effects of anthropogenic contaminants in the San Francisco estuary. **Environmental Research**, v. 105, n. 1, p. 156-174, 2007.

USEPA-United States Environmental Protection Agency. **Method 1668**: revision A. Chlorinated biphenyl congeners in water, soil, sediment, biosolids, and tissue by HRGC/HRMS. Washington, D.C., 2003.

USEPA-United States Environmental Protection Agency. **Method 8290 A**: revision 1. Polychlorinated dibenzodioxins (PCDDS) and polychlorinated dibenzofurans (PCDFS) by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). Washington, D.C., 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. **The Journal of Toxicology Science**, v. 93, n. 2, p. 223-241, 2006.

WALKER, C. H.; HOPKIN, S. P.; SIBLY, R. M.; PEAKALL, D. B. **Principles of Ecotoxicology**. 3rd ed. Boca Raton: CRC Press, 2006.

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