PERSISTENT ORGANIC POLLUTANTS IN THE DIET OF BROWN BOOBIES (*SULA LEUCOGASTER*) FROM THREE DIFFERENT ARCHIPELAGOS OF BRAZIL

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Introduction

Organochlorine pollutants, such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) form an important group of environmental contaminants. They are widespread in the environment, have a high persistency, accumulate in biological tissues and biomagnify within food chains, causing chronic adverse effects upon humans and wildlife[1].

Although forbidden in Brazil since the middle 80´s, its presence is still detected in the marine ecosystems. Atmospheric deposition and river discharges are believed to be the main entrances of organochlorine compounds, like DDT and Drins, to the sea.

Marine birds are useful bioindicators for monitoring organochlorine contamination of the environment because they are situated high on the food chain and they are sensitive to environmental changes[2]. The amount of organohalogenated pollutants accumulating within the tissues of birds is related to their diet and corresponding trophic position, but also to differences in pollutant accumulation among habitats and ecosystems (marine versus terrestrial)[4]. Brown boobies (*Sula leucogaster*) are resident birds and can reflect the background pollution of inhabiting area through the levels of contaminants in their diet. This specie has a tropical and subtropical distribution, and is by far the most abundant Sulidae species that lives along the Brazilian coastal zone, which enables the sampling of many different regions using always the same species, making it easier the comparison of data from different locations[5].

In this work, we sampled the rejected food (e.g.: fishes) that is thrown out by the animals following its capture in order to identify and quantify Persistent Organic Pollutants (POPs) in three different localities along Brazilian littoral zone. The main source of contamination was also identified. Our work aimed to depict what is the main critical bird colony in terms of POPs contamination to contribute to focus our research on conservation efforts in the near future.

Materials and methods

Sampling dates:
From January and May, 2007.

Sampling Areas:

1) Archipelago of St Peter and St Paul, situated at 00°55' N and 29°21' W and is 1,010 km away from the city of Natal in the northeastern region of Brazil.
2) Archipelago of Abrolhos, situated at 17°58' S and 38°42' W is 70 km away from the south of the BahiaState.
3) Archipelago of Cagarras is situated at 23°02' S and 43°12' W, located 4 km away from the coast of the city of Rio de Janeiro.

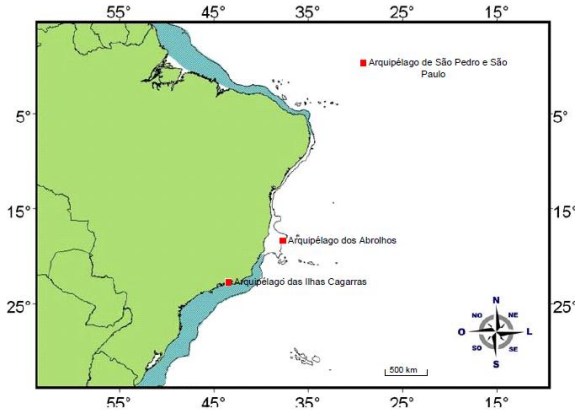

Fig.1 - Locations of the three study sites of brown booby (Sula leucogaster) breeding colonies and the largest urban center closest to each colony.

Whenever possible, we tried to identify what is the kind of food that were rejected by the animal. For the POPs analysis we made a pool of all of the fishes present. Thirteen fishes were pooled for Abrolhos, Thirteen for St. Peter and St. Paul and five for Cagarras. We followed the same method proposed by Cunha and co-workers in their paper published in 2012. We determined the concentration of p,p'-DDT and its metabolites p,p'-DDD and p,p'-DDE and several PCB congeners (PCB8,18, 28,31, 33,44,49, 52, 60,66, 70, 74, 77, 81, 87, 95, 97,99,101, 105, 110, 114, 118, 123, 126,128,132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 169, 170, 174, 177, 180, 183, 189, 194,195, 199, 203, 206 and PCB209).

Ten grams of each sample was mixed with 450 ^{o}C baked $NaSO_4$ in order to dry the sample. The extraction was done using an *Ultraturrax* homogeneizer with n-hexane and dichloromethane (1:1). Lipid contents were determined gravimetrically. For clean-up, the extracts were passed by florisil and soium sulfate glass open columns, followed by florisil SPE cartridges. For quantification, internal standard (TCMX) was added to each sample prior injection on a GC-ECD Shimadzu 2010.

Results and discussion

The diet of brown booby consisted primarily of fishes and squids.

All three locations sampled in this study were contaminated with PCBs, DDTs and it metabolites. All of the 51 PCB congeners were detected in St. Peters and St. Paul, Abrolhos and Cagarras archipelagos.

Table 1 – Concentrations in ng.g^{-1} of ∑PCBs and ∑DDTs (w.w.), found in each location studied. Numbers from top to bottom are: minimum and maximum values, mean and median.

	St. Peter and St. Paul	*Abrolhos*	*Cagarras*
∑DDTs	0,04-1,07 0,51 0,45	0,31-1,87 0,91 0,65	0,78-1,87 1,27 1,03
∑PCBs	2,39 -22,79 13,35 13,25	10,32- 43,86 24,74 22,00	9,02-75,72 31,79 29,99

The rejected food itemns collected had their pollutant concentrations inversely related to their distance to the continent. St. Peter and St. Paul presented the lower concentrations both for DDTs and PCBs, with average rage of 0.51 ng/g and 13.35 ng/g, respectively. The Archipelago of Abrolhos had intermediate concentrations, with 0.91 ng/g for total DDTs and 24.74 ng;g of total PCBs. Both localities presented PCB 52, 101 and 95 as the most abudant congeners, representing 17% in SP&SP and 14% at Abrolhos. The Cagarras Archipelago had the higher concentrations, with total DDT average of 1.27 ng/g and 31.79 ng/g for PCBs, with hexachlorinated congeners 138, 149 and 153 as the most abundant..

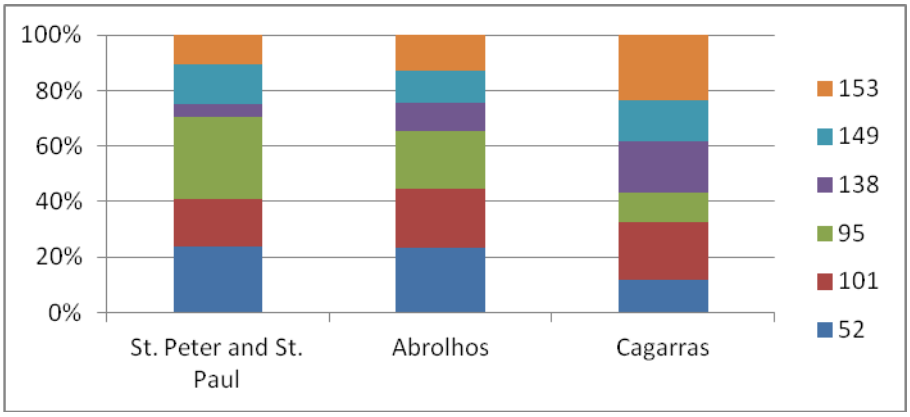

Fig 2- Percentages of main congeners of PCB in the diet from each study site.

None of the three sampled locations had a normal distribution for the pollutant concentrations (Shapiro-Wilk, P < 0.05). A significant difference was found for the PCBs and DDTs concentrations among the locations sampled (Kruskal-Wallis, $p < 0,02$; $p < 0,03$). Wilcoxon Rank-Sun Test indicates that the concentration of both ∑DDTs and ∑PCBs in Cagarras archipelago were significantly different only from those in the St. Peter and St. Paul ($p<0,05$).

The ratio DDT/PCB may depict the main source of contamination at each location. We found rations of 0.05, 0.04 and 0.05 to SP&SP, Abrolhos and Cagarras respectively. Taking this in account we believe that 90% of the PCB contamination is mainly derived from urban and industrial sources. The ratio DDE/∑DDT obtained was 0.8 for SP&SP, 0.8 in Abrolhos and 0.5 for Cagarras. At all localities DDE were higher than DDT. Although at Abrolhos, the ratio of 0.4 is low, the contribution of DDD plus DDE (metabolites) responded to 69.2% of the total.

Differences in gender, foraging habits and fish availability throughout the year as well as external influences of foraging behaviors (fisheries activities) may represent bias in the study results[4]. However, a comparison among individuals from a same species, but from different localities permits to observe how differently the populations are exposed.

The increase in the concentrations for the PCBs and DDTs showed up to be related to the distance from the coast between the islands and the continent. This gradient of concentrations showed the influence of the continent as the source of the contamination. Cunha and co-workers (2012), showed the same pattern of contamination upon eggs of the same species. Zimmermann et al. (1997) have suggested for PCBs that patterns are influenced principally by individual dietary factors.

The birds in SP&SP and Abrolhos have basically the same diet of flying-fish (*Exocoetus volitans*) and present a pattern very similar regarding the main congeners group. At both localities the 4 and 5 chlorine compound

predomine, since they are more volatile and may have a broader atmospheric dispersion. Heavier congeners, being less volatile and with a lower atmospheric dispersion rate are shown more frequently near the sea shore.

The higher proportion of 90% of PCBs in relation to DDT in the three localities may be explained by the remaining use of this kind of equipments in Brazil, which will be permitted until 2025 by the Stockholm convention protocol. Taking in account the poor law enforcement in Brazil, we believe that hot spots of contamination like unsafe deposits may exist and contaminate soil, animals and even human beings.

Traditionally, the ratio of p,p'-DDE/∑DDT has been used to discriminate between recent and past usages of DDT, since DDT degrades to DDE and DDD in non-oxic environments. Low p,p '-DDE/∑DDT ratios indicate the recent use of DDT, slow degradation or exceptional degradation scenarios[6]. This information suggests that the brown booby colony located close to the Rio de Janeiro coast (i.e., Cagarras) has been more recently exposed to this pesticide in comparison with the other two colonies. The same results were found for eggs in these locations, according to the work of Cunha in 2012.

The brown-booby population along Brazilian coast is exposed to POPs basically due to their fish based diet. The colonies of the Cagarras Archipelago, located near Rio de Janeiro are the most exposed ones, and more detailed studies are recommended to determine the effects of these industrial pollutants on the Cagarras breeding colony. Furthermore, the ratios of DDE/∑ DDT suggest recent use of DDT and new studies upon these colony may help to clarify this issue.

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