ORGANOCHLORINE COMPOUNDS IN BLUBBER OF GUIANA DOLPHINS, *Sotalia guianensis*, FROM SEPETIBA BAY, RIO DE JANEIRO STATE, BRAZIL

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Introduction

Regarding environmental contamination by organochlorine compounds, the knowledge generated on Rio de Janeiro state presents importance for the entire Brazil, a newly industrialized country with a fast-growing economy. A large set of construction works is planned for the establishment of harbors, shipyards and industries on coastal bays and estuaries. Sepetiba Bay is currently a dramatic example of this process of environmental deterioration. The coastal bay seems to be on the same degradation path once followed by Guanabara Bay, a neighboring estuary that constitutes the most dramatic example of man-made degradation on the Brazilian coast[1]. Sepetiba Bay has been suffering from a large series of different types of pressure, receiving industries on its drainage basin, new harbors, a shipyard for nuclear submarines, as well as broad dredging and demolishing of underwater rocks. In addition to the industrialization process, agricultural areas are also present in Sepetiba Bay drainage basin. These features turn the area into a particularly important region for monitoring environmental contamination by pollutants of urban, industrial and agricultural origin. The present study comprises part of this monitoring, since determination of polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane and its metabolites (ΣDDT), hexachlorobenzene (HCB), hexachlorocyclohexane isomers (HCHs) and mirex was performed in blubber samples of Guiana dolphins from Sepetiba Bay.

Cetaceans have been pointed as monitor species for the health of aquatic systems and regarded as sentinel organisms for environmental and human health assessments. Therefore, the present investigation provides information of importance from the human health point of view, as well as for wildlife conservation purposes.

Guiana dolphin (*Sotalia guianensis*) is a coastal delphinid that is endemic in Western Atlantic. The species has shown to present habitat fidelity along its distribution, which ranges from Honduras in Central America, to Florianópolis in Santa Catarina State, Brazil[2]. The perspective of the Brazilian economic growth and the consequent use and degradation of the coastal zone constitutes a matter of concern for Guiana dolphin conservation. In this context, Sepetiba Bay constitutes an important area to be evaluated since it houses one of the largest Guiana dolphin populations along the Brazilian coast.

Materials and methods

Blubber samples were collected from Guiana dolphins (n=10) either incidentally captured in fishing operations or stranded on the beaches of Sepetiba Bay, between 2007 and 2010. The analytical procedure was detailed elsewhere[3]. Briefly, aliquots of approximately 1.0 g of blubber were homogenized with anhydrous sodium sulfate and extracted by *Ultra Turrax*, for 10 minutes, using a mixture of hexane:dichloromethane (1:1). Sulphuric acid was used for removing organic matter from the extracts. Samples were fortified with standard solutions of PCB-103 and PCB-198, as well as with the GC internal standard TCMX (*AccuStandard Laboratory*). Analyses were performed in a gas chromatographer Agilent GC-7890, equipped with an electron capture detector (GC-ECD). The analytical method was validated using the standard certified materials SRM 1945 and SRM 1588a (National Institute of Standards and Technology – NIST). The organochlorine pesticides determined were: HCB, mirex, *o,p'*-DDE, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, *α*-HCH, *β*-HCH, *δ*-HCH and *γ*-HCH. Concerning PCBs, the following 27 congeners (IUPAC numbers) were targeted for analysis: 08, 28, 44, 49, 52, 97, 101, 105, 118, 132, 138, 141, 151, 153, 158, 170, 174, 177, 180, 183, 187, 194, 195, 199, 203, 206 and 209. In addition to the abovementioned quality control measures, regular analyses of procedural blanks were performed (Relative Standard Deviation - RSD<20% for 8 replicates).

Depending on data normality (Shapiro-Wilk's W test), a parametric (Student's t-test) or a non-parametric test (Mann–Whitney U test) was used.

Results and discussion:
PCB, DDT, HCH, mirex and HCB concentrations ($\mu g.g^{-1}$, lipid weight) in blubber of Guiana dolphins from Sepetiba Bay, along with sex and total length of the individuals, as well as lipid content (%) of the samples, are presented in the Table 1.

Table 1. Biological data and organochlorine concentrations (mean ± SD, range, median; $\mu g.g^{-1}$ on a lipid basis) in blubber of Guiana dolphins from Sepetiba Bay, Brazil.

	TL (cm)	**Lipid %**	**ΣPCB**	**ΣDDT**	**ΣHCH**	**Mirex**	**HCB**
	159 ± 26	54 ± 11	7.88 ± 8.53	1.93 ± 2.06	0.22 ± 0.052	0.10 ± 0.03	0.02 ± 0.04
Male (n=6)	125 - 188	35 - 69	2.04 – 23.19	0.55 – 5.75	0.15 – 0.31	0.06 – 0.13	0.003 – 0.10
	161	55	3.40	0.91	0.22	0.11	0.01
	166 ± 21	68 ± 7	3.25 ± 1.24	2.61 ± 3.81	0.12 ± 0.03	0.05 ± 0.01	0.004 ± 0.003
Female (n=4)	135 - 183	63 - 78	1.43 – 4.20	0.35 – 8.30	0.09 – 0.15	0.05 – 0.06	0.0004 – 0.006
	172	65	3.68	0.89	0.12	0.05	0.004

The ratio between DDTs and PCBs (DDT/PCB) has been used for characterizing the magnitude of the contributions from agricultural (or insect-borne disease control) and industrial sources to marine mammal contamination[4]. The ΣDDT/ΣPCB ratio observed for Sepetiba Bay (0.35) points to a greater influence of pollution by organochlorines of industrial and urban origin. This pattern has been reported for the coastal bays of Rio de Janeiro state[3].
Considering DDT and its metabolites exclusively, there was predominance on the contribution of *p,p*'-DDE for ΣDDT (Fig. 1). In the commercial formulation, there is predominance of *pp'*-DDT. When this compound is released into the environment, it is degraded into *p,p*'-DDE and *p,p*'-DDD. Thus, the ratio between *p,p*'-DDE and the sum of *p,p*'-DDT, *p,p*'-DDE and *p,p*'-DDD [*p,p*'-DDE/(*p,p*'-DDT + *p,p*'-DDE + *p,p*'-DDD)] has been used for determining the chronology of DDT input into the ecosystem. In the present study, the average value of 0.59 was observed for the ratio. Through comparison with data from a recent study of our team[3], which dealt with Guiana dolphins from Guanabara Bay, it is possible to verify a probable more recent usage of DDT in Sepetiba Bay drainage basin. The latter observation may be explained by the DDT use for insect-borne disease control, in addition to the presence of a number of farming activities in Sepetiba Bay drainage basin[5].

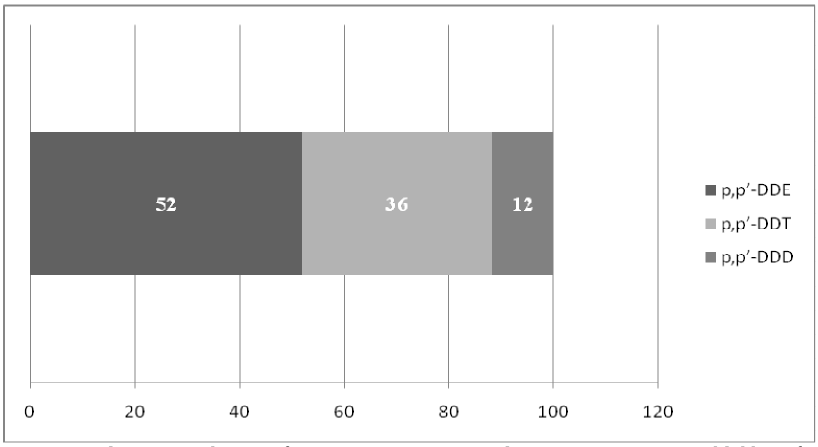

Figure 1. Relative contribution of *p,p'*-DDE, *p,p'*-DDT and *p,p'*-DDD to ΣDDT in blubber of Guiana dolphins (*Sotalia guianensis*) from Sepetiba Bay, Brazil.

Regarding ΣPCB, there was predominance of PCB-153 and PCB-138 (Fig. 2). These congeners have been reported as the most abundant PCBs in marine mammals from different parts of the globe[6]. The higher contribution of these congeners is related to their predominance in commercial mixtures, as well as to the fact that they have relatively unreactive substitution patterns, which turns them highly resistant to degradation.

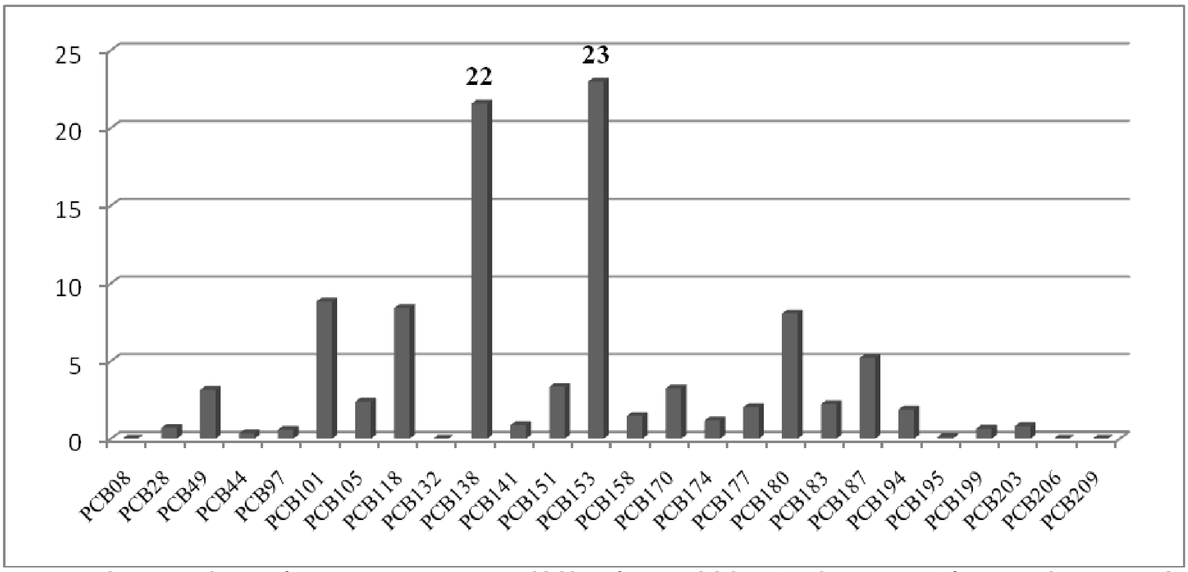

Figure 2. Relative contribution of PCB congeners to ΣPCB in blubber of Guiana dolphins (*Sotalia guianensis*) from Sepetiba Bay, Brazil.

Higher ΣHCH concentrations were found by the present study in comparison to those verified in previous investigations dealing with Guiana dolphins from São Paulo (SP) and Paraná (PR) states (Brazil)[7,8]. This can be stated due to the fact that the highest ΣHCH concentration (38 ng.g^{-1} lipid wt.) observed among Guiana dolphins from SP and PR[7,8] was lower than the lowest level (87 ng.g^{-1} lipid wt.) verified among dolphins from Sepetiba Bay. The later finding indicates a probable more intense usage of this pesticide around Sepetiba Bay than in the other regions investigated. In addition, the ΣHCH levels verified in Sepetiba Bay were in the same range as the concentrations found in coastal cetaceans from temperate regions, such as bottlenose dolphins from Spanish waters[9]. With regard to the isomeric contribution to ΣHCH, there was predominance of γ-HCH. This finding contrasts with the results of a previous investigation dealing with Guiana dolphins from SP [8], in which β-HCH was the isomer of highest contribution.

Table 2. Blubber organochlorine concentrations (mean ± SD and range; µg.g^{-1} on a lipid basis) of mature male Guiana dolphins, (*Sotalia guianensis*) from Brazilian coast, information from literature.

Region	n	TL (cm)	ΣPCB	ΣDDT	ΣHCH	Mirex	HCB	References
Cananéia, S São Paulo, Brazil	4	180±14	5.70±2.77	72.30±51.50	0.03±0.02	0.15±0.02	0.02±0.01	Yogui *et al.* (2003)[11]
		163-196	1.61–7.60	7.24–125.0	<0.003–0.04	0.13–0.18	0.01–0.02	
N Paraná and S São Paulo, Brazil	8	187	34.00	52.00	0.02	ND	0.07	Kajiwara *et al.* (2004)[7]
		180-198	10.00–79.00	12.00–150.00	0.01–0.04		0.01–0.4	
Guanabara Bay, Rio de Janeiro, Brazil	7	185±7	39.35±31.41	10.40±8.16	ND	ND	0.05±0.04	Lailson-Brito *et al.* (2010)[3]
		170-191	6.66–99.18	2.08–21.50			0.02–0.11	

Apparently, mirex concentrations in Guiana dolphins from Sepetiba Bay were lower than those found in Cananéia estuary (São Paulo state)[8] (Table 2). This is probably related to a less intense usage of this organochlorine compound in Sepetiba Bay drainage basin, since mirex is not easily transported via the atmosphere[10]. In this context, it is important to bear in mind that this chlorinated compound was not only used as pesticide but also as flame retardant in SP state[11].

HCB was the pollutant that rendered the lowest levels among the organochlorine compounds considered herewith. In fact, HCB concentrations in Guiana dolphins from Sepetiba Bay were apparently lower than those found in previous studies[3,7,8]. However, comparisons like these should be done with caution, since the animals lived in different periods of time. Besides, the age of the dolphins has to be taken into account.

Differences in organohalogen compound profiles and concentrations between males and females constitute a common finding in aquatic mammals, as a consequence of transplacental and lactational transfer of lipophilic organic compounds to the offspring[12]. In the present study, significant higher concentrations of β-HCH (p=0.038), γ-HCH (p=0.01), ΣHCH (p=0.01) and Mirex (p=0.019) were found in males. Regarding previous investigations on organochlorine compound accumulation by Guiana dolphins, Yogui et al.[8] did not find significant differences between sexes, while Kajiwara et al.[7] verified lower levels in females. The former authors attributed the absence of significant difference to the low sampling number of females.

Our results demonstrate the high exposure of Guiana dolphins from Sepetiba Bay to organochlorine compounds, especially DDTs and PCBs. This generates concerns about the conservation of this cetacean population, considering the toxicity of these pollutants. However, additional studies should be carried out for a better comprehension on the consequences of Guiana dolphin exposure to these persistent bioaccumulative toxicants.

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References:

1. Dorneles PR, Lailson-Brito J, Fernandez MAS, Vidal LG, Barbosa LA, Azevedo AF, Fragoso ABL, Torres JPM and Malm O. (2008); *Environ Pollut*. 156: 1268–76.
2. Flores PAC, da Silva VMF.(2009); *Encyclopedia of Marine Mammals*. 1188 - 92
3. Lailson-Brito J, Dorneles PR, Azevedo-Silva CE, Azevedo AF, Vidal LG, Lozinski CPC, Azeredo A, Fragoso ABL, Cunha HA, Torres JPM, Malm O. (2010); *Environ Pollut.* 158(5): 1800–8
4. Aguilar A, Borrel A, Pastor T. (1999); *J Cetacean Res Man*. Special Issue 1:83-116
5. Ministério do Meio Ambiente (MMA). (2007); Biodiversidade marinha da Baía de Ilha Grande.
6. Reijnders PJH, Aguilar A. (2002); *Encyclopedia of marine mammals*. 948.
7. Kajiwara N, Matsuoka S, Iwata H, Tanabe S, Rosas FCW, Fillmann G, Readman JW. (2004); *Arch Env Contam Toxicol.* 46(1): 124-34
8. Yogui GT, Santos MCO, Montone RC. (2003); *Sci Total Environ.* 3121: 67-78
9. Borrel A, Aguilar A, Tornero V, Sequeira M, Fernandez G, Alis S. (2006); *Environ Int.* 32(4): 516-23
10. O’Hara TM, Becker PR. (2003). In: *Toxicology of Marine Mammals*, Vos JG, Bossart GD, Fournier M, O’Shea TJ. (eds.), Taylor and Francis Group, London, 135-67
11. Yogui GT, Santos MCO, Bertozzi CP, Montone RC. (2010) *Mar Pollut Bull*. 60: 1862–7
12. Dorneles PR, Lailson-Brito J, Dirtu AC, Weijs L, Azevedo AF, Torres JPM, Malm O, Neels H, Blust R, Das K, Covaci A. (2010); *Environ Int*. 36(1): 60-7