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Occurrence of chlorinated pesticides and polychlorinated biphenyls (PCBs) in Guiana dolphins (*Sotalia guianensis*) from Ubatuba and Baixada Santista, São Paulo, Brazil

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Abstract: Organochlorine pesticides and polychlorinated biphenyls (PCBs) were determined in the blubber of six Guiana dolphins (*Sotalia guianensis*) from the coast of the state of São Paulo, Brazil. PCBs were at the highest levels on a lipid-weight basis (25.87 to 66.03µg g^{-1}), followed by DDTs (16.91 to 55.91µg g^{-1}), mirex (0.24 to 1.87µg g^{-1}), chlordanes (0.11 to 0.49µg g^{-1}), hexachlorobenzene (HCB) (0.07 to 0.17µg g^{-1}), heptachlor epoxide (0.05 to 0.16µg g^{-1}) and hexachlorociclohexane (HCHs) (0.03 to 0.21µg g^{-1}). The presence of PCBs in Guiana dolphins suggests input from the Cubatão industrial complex – the largest in Brazil. The mean *p,p'*-DDE/ΣDDT ratio was approximately 0.8 and is indicative of previous DDT application in the study area. The occurrence of HCB and HCHs can be attributed to industrial effluents and dumping on the borders of the Santos-São Vicente estuarine complex.

Resumo: Pesticidas organoclorados e bifenilos policlorados (PCBs) foram determinados no tecido adiposo subcutâneo de seis botos-cinza (*Sotalia guianensis*) da zona costeira do estado de São Paulo. Os níveis residuais de PCBs em peso lipídico (25,87 a 66,03µg g^{-1}) foram os maiores, seguidos de DDTs (16,91 a 55,91µg g^{-1}), mirex (0,24 a 1,87µg g^{-1}), clordanas (0,11 a 0,49µg g^{-1}), hexaclorobenzeno (HCB) (0,07 a 0,17µg g^{-1}) heptacloro epóxide (0,05 a 0,16µg g^{-1}) e hexaclorociclohexano (HCHs) (0,03 a 0,21µg g^{-1}). A presença de PCBs sugere a influência do complexo industrial de Cubatão – o maior do Brasil. A média de *p,p'*-DDE/ΣDDT foi aproximadamente 0,8 indicando uma antiga aplicação de DDT na área de estudo. A ocorrência de HCB e HCHs pode ser atribuída aos efluentes e lixões industriais nas margens do complexo estuarino Santos-São Vicente.

Keywords: Cetacea, *Sotalia guianensis*, organochlorines, pesticides, polychlorinated biphenyls, Brazil.

Introduction

The American Environmental Protection Agency lists organochlorine compounds (OCs) as major pollutants. OCs include chlorinated pesticides (DDTs, HCHs, chlordanes, etc.) and polychlorinated biphenyls (PCBs) (Jones and Voogt, 1999). These compounds are toxic, bioaccumulative and resistant to photochemical, biological and chemical degradation. OCs therefore pose an adverse risk to ecosystems (Johnston, 1976; Clark, 2001). Aquatic organisms can accumulate lipophilic OCs by direct absorption through water, food or sediments. Concentrations in marine mammals can be ten million-fold the concentration in the water due to bioaccumulation and biomagnification throughout the food chain (Tanabe and Tatsukawa, 1992). Based on their metabolic imbalance and position in the food chain, marine mammals are considered among the most vulnerable organisms regarding long-term toxicity by these man-made chemicals (Tanabe *et al.*, 1994; Fossi *et al.*, 1997). Although there are many studies on chlorinated compounds in marine mammals, the contamination status of these species along the Brazilian coast remains poorly known (Yogui *et al.*, 2003; Kajiwara *et al.*, 2004; Torres *et al.*, 2006; Moura *et al.*, 2009; Dorneles *et al.*, 2008).

The Guiana dolphin (*Sotalia guianensis*) is one of the lesser-studied Delphinidae and is listed as 'insufficiently known' by the 2004-2010 Conservation Action Plan for the World's Cetaceans/ IUCN (Reeves *et al.*, 2003). Due to its coastal distribution, *S. guianensis* is exposed to a number of threats, such as incidental catch in fishery gear (Siciliano, 1994; Di Beneditto *et al.*, 2001, Meirelles *et al.*, 2010 this volume) and the degradation of coastal environments resulting from domestic and industrial sewage (Yogui *et al.*, 2003; Lailson Brito *et al.*, 2008; Moura *et al.*, 2009; Kajiwara *et al.*, 2004). Studies have demonstrated that Guiana dolphins exhibit residence patterns with preferences for the same bays and estuaries in Brazil, such as Pipa Beach, RN (Link, 2000; de Jesus, 2004); Caravelas River Estuary, BA (Rossi-Santos *et al.*, 2007); Guanabara Bay (Pizzorno, 1999; Azevedo and Vans Sluys, 2005) and Sepetiba Bay, RJ (Flach *et al.*, 2008); Santos Estuary (Farias Junior and Alonso, 2004[6]) and

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Cananéia Estuary, SP (Santos *et al.*, 2001; Santos and Rosso, 2008); Babitonga Bay (Cremer, 2000; 2007, Hardt *et al*., 2010 this volume) and North Bay, SC (Flores, 1999; Flores and Bazzalo, 2004). Thus, this species is a good biomonitor of pollution in their habitats.

The aim of the present study was to determine concentrations of chlorinated pesticides and polychlorinated biphenyls in the blubber of *S. guianensis* from two different coastal areas in the state of São Paulo (southeastern Brazil).

Material and Methods

Study area

The coastal region of the state of São Paulo (southeastern Brazil) is divided into three large areas based on morpho-geographical and population characteristics: Baixada Santista, North Shore and South Shore (Figure 1). In the present study, only the Baixada Santista (central coast) and part of North Shore were considered due to their being areas that are impacted and non-impacted by human activities, respectively.

The Santos-São Vicente estuarine complex (23°55'S, 46°20'W), located in the metropolitan region of Baixada Santista, with a population of 1,368,511 habitants, is the most important Brazilian example of environmental degradation in the form of water and atmospheric pollution of an industrial origin in a coastal area. The largest harbor in Latin America (the Port of Santos) and the largest industrial complex in Brazil (Cubatão complex) are located in this area. Industrial activities began in the 1950s with the establishment of diverse factories (steel, oil, agribusiness) and have turned the Santos-São Vicente estuarine complex into the final destination for toxic waste and contaminated effluents (Lamparelli *et al.*, 2001[7]).

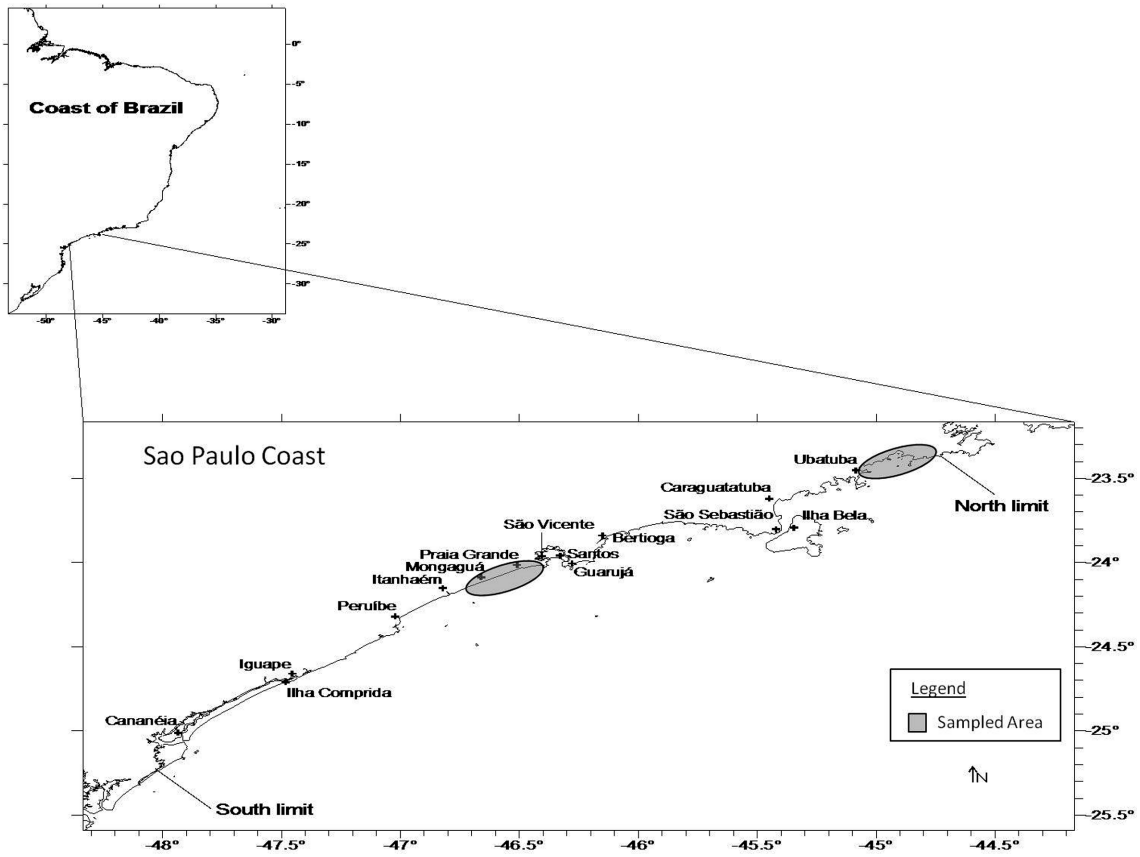

Figure 1. Map of the coast of São Paulo State showing the sampling areas.

[6] Farias Junior, S. G and Alonso, M. B. (2004) O boto-cinza (*Sotalia guianensis*) no Estuário de Santos: provável repovoamento de uma antiga área de ocorrência? Page 52 *in* Resumos, *VII Simpósio de Biologia Marinha,* July 2004, Santos, SP, Brazil.

[7] Lamparelli, M.C., Costa, M.P., Prósperi, V.A., Bevilacqua, J.E., Araújo, R.P.A., Eysink, G.G.J. and Pompéia, S. (2001) Sistema Estuarino de Santos e São Vicente. *Brasil. Secretaria do Meio Ambiente, Companhia Ambiental do Estado de São Paulo, Technical Report:* 183 pp. [Available from CETESB, São Paulo, SP, Brazil].

Ubatuba (22˚53'S, 45˚08'W) is a city located on the northern shore of the state of São Paulo, with a population of 75008 habitants, occupying an area of 712km², 83% of which lies within the Sea Mountain State Park (Parque Estadual da Serra do Mar). No large industries are found in this region and there are no reports of the use of OCs. It is not an industrial or agricultural area. The main economic activity is tourism and the main sources of pollution are domestic waste and occasional oil spills (SMA/CPLEA, 2005[8]).

SAMPLING

Blubber samples from six Guiana dolphins were collected from specimens either caught incidentally during fishing operations or stranded on the coast of the state of São Paulo between June 2004 and June 2005. Table 1 lists the collection sites and biological data on these specimens. The samples were excised from the left lateral region to the dorsal fin. After dissection, all samples were wrapped in aluminum foil and preserved at -20ºC until analysis (Geraci and Lounsbury, 1993).

CHEMICAL ANALYSIS

The analytical procedure followed the protocol described by MacLeod *et al.* (1985[9]), with minor modifications. Approximately 0.5g of wet tissue was extracted, after the addition of 10g of anhydrous Na_2SO_4, with 60mL dichloromethane and n-hexane (50% v/v), using a tissue homogenizer. Prior to extraction, 4,4'-dibromooctafluorbiphenyl (DBOFB) and 2,2',4,5',6-pentachlorobiphenyl (PCB 103) were added as surrogates to all samples, blanks and reference material (Whale Blubber - SRM 1945, National Institute of Standards and Technology – NIST). Extracts were cleaned in partially deactivated silica:alumina column chromatography eluting with a 7:3 mixture of n-hexane and methylene chloride. The tissue extract was further purified by high-performance liquid chromatography (HPLC), using two columns for chromatography by gel permeation (Phenogel 100 A, 7.8 x 50mm and 22.5 x 250mm) to remove lipids. The extract was concentrated to a volume of 0.5mL in hexane and the internal standard (tetrachlorometaxylene) was added.

Chlorinated pesticides and PCBs were analyzed by a 6890N gas chromatograph (Agilent Technologies), using a ^{63}Ni electron capture detector (GC-ECD). The following organochlorines were analyzed in the present study: DDTs (*o,p'*-DDD; *p,p'*-DDD; *o,p'*-DDE; *p,p'*-DDE; *o,p'*-DDT; *p,p'*-DDT), HCHs (α-HCH; β-HCH; γ-HCH (lindane); δ-HCH); chlordanes (*cis*-chlordane; *trans*-chlordane; heptachlor; heptachlor epoxi), mirex, HCB (hexachlorobenzene) and 31 PCB isomers and congeners (08, 18, 26, 28, 44, 49, 50, 52, 66, 87, 101, 105, 110, 118, 128, 138, 149, 151, 153, 157, 160, 169, 170, 173, 180, 183, 187, 195, 194, 206, 209).

STATISTICS

The Statistica software program (Statsoft, 1999) was used to analyze the data, using non-parametric tests. Analysis of variance (ANOVA) and Kruskal-Wallis Median tests ($p < 0.05$) were employed to determine significant differences comparing two groups of multiple independent samples.

Results

Several OC contaminants were detected in all *S. guianensis* blubber samples from Baixada Santista and Ubatuba, state of São Paulo (Brazil) (Table 2). PCB concentrations ranged from 25.87 to 66.03μg g^{-1} on a lipid-weight basis, followed by DDTs (16.91 to 55.91μg g^{-1}), mirex (0.24 to 1.87μg g^{-1}), chlordanes (0.11 to 0.49μg g^{-1}), HCB (0.07 to 0.17μg g^{-1}), HP epoxide (0.05 to 0.16μg g^{-1}) and HCHs (0.03 to 0.21μg g^{-1}).

Table 1. Biological data from six *Sotalia guianensis* from the state of São Paulo (southeastern Brazil) used in this study.

FIELD NO.	ORIGIN	DATE	BL* (cm)	SEX	LOCATION	SEXUAL MATURITY
BP 69	Capture	Jun-04	122	F	Praia Grande, Baixada Santista	immature
BP 76	Capture	Aug-04	147	M	Praia Grande, Baixada Santista	immature
BP 81	Stranding	Aug-04	163	M	Ubatuba, North Coast	immature
BP 96	Capture	Feb-05	186	M	Ubatuba, North Coast	mature
BP 97	Capture	Feb-05	172	M	Ubatuba, North Coast	mature
BP 105	Capture	Jun-05	173	M	Mongaguá, Baixada Santista	mature

* BL - Body length

[8] SMA/CPLEA (2005) Zoneamento Ecológico-Econômico - Litoral Norte São Paulo. Brazil. Governo do Estado de Sao Paulo. *Secretaria de Estado de Meio Ambiente. Coordenadoria de Planejamento Ambiental Estratégico e Educação Ambiental.* São Paulo, SP. 56pp. Unpublished. [PDF available from <http://www.ambiente.sp.gov.br/litoral_norte/07_economia_zoneamento.pdf>].

[9] MACLEOD, W. D., BROWN, D. W., FRIEDMAN, A. J., BURROWS, D. G., MAYNES, O., PEARCE, R. W., PEARCE, R. W., WIGREN, C. A., BOGAR, R. G. (1985) Extractable Toxic Organic Components. Standard Analytical Procedures of the NOAA National Analytical Facility, 1985-1986. U.S. Department of Commerce, *Northeast Fisheries Science Center Reference Document* 92: 121 pp. [Available from NMFS, F/NWC, USA].

Among the organochlorine pesticides, *p-p'*-DDE was detected at the highest concentrations, ranging from 13.30 to 46.63µg g^{-1} lipid weight and the *p,p*-DDE/ΣDDT ratio was 0.8 in all samples. Mirex, CHLs (chlordanes), HCBs, HCHs and heptachlor epoxide were detected at levels one to four orders of magnitude lower than those of PCBs and DDTs. The predominant PCB congeners were hexachlorinated biphenyls (53 to 58%), followed by heptachlorinated biphenyls (23 to 29%) in all samples. Organochlorine concentrations were similar ($p < 0.05$) in both regions, but the DDT/PCB ratios were significantly different ($p < 0.014$) between the two shores, reaching values of 0.9 to 1.0 in Baixada Santista and 0.7 in Ubatuba (Figure 2).

Table 2. Total length (cm), lipid content (%) and range/mean of organochlorine concentrations in blubber (µg g^{-1} lipid weight) of *Sotalia guianensis* from Baixada Santista and Ubatuba, São Paulo State (southeastern Brazil).

	BAIXADA SANTISTA	UBATUBA
TL (cm) [a]	122 - 173	163 - 186
Lip. (%) [b]	20 - 59	20 - 33
PCBs	27.86 - 61.34	25.87 - 66.03
	39.69	47.78
DDTs	24.57 - 55.91	16.91 - 48.04
	36.98	34.03
HCHs	0.03 - 0.21	0.06 - 0.07
	0.09	0.07
HCB	0.07 - 0.17	0.08 - 0.14
	0.12	0.11
Mirex	0.24 - 1.04	0.57 - 1.87
	0.76	1.26
CHL	0.11 - 0.49	0.3 - 0.39
	0.30	0.33
HP epox.	0.06 - 0.16	0.05 - 0.13
	0.11	0.08

[a] Total length, [b] Lipid content.

Discussion

For comparison purposes, mean concentrations of organochlorine residues in the blubber of *S. guianensis* are listed in Table 3 separately for different sites along the Brazilian coast. The mean concentration of PCBs was higher in both sexes than for animals from the southern portion of the state of São Paulo/northern portion of the state of Paraná as well as from two studies carried out in the state of Rio de Janeiro State, with exception of one study carried out on Guanabara Bay, RJ, is one of the most anthropogenically impacted areas along the Brazilian coastline and the estuary is bordered by 12,000 industries and a total population of approximately 11 million people (Dorneles *et al.*, 2008). There are many sources of PCBs in Baixada Santista that could be contributing the levels found in Guiana dolphins on the coast of the state of São Paulo, such as the steel industry (Lamparelli *et al.*, 2001; Freitas-Guimarães, 2005[10]).

DDT concentrations in males were similar to those found on the southern coast of São Paulo/ northern Paraná (Kajiwara *et al.*, 2004) and higher than those described for the state of Rio de Janeiro (Torres *et al.*, 2006), but lower than those described for the Cananéia estuary, which is an agricultural area in southern São Paulo that has been directly impacted by DDTs in the past (Yogui *et al.*, 2003).

The HCH concentrations encountered suggest that Guiana dolphins, like a number of other marine species, may have the capacity to regulate HCH levels in their metabolic system (McHugh *et al.*, 2007). Moisey *et al.* (2001) suggests that the ability of an organism to degrade/ eliminate a-HCH increases with the trophic level. Mean concentrations of HCHs and HCBs in Guiana dolphins were one to two magnitude orders higher in the present

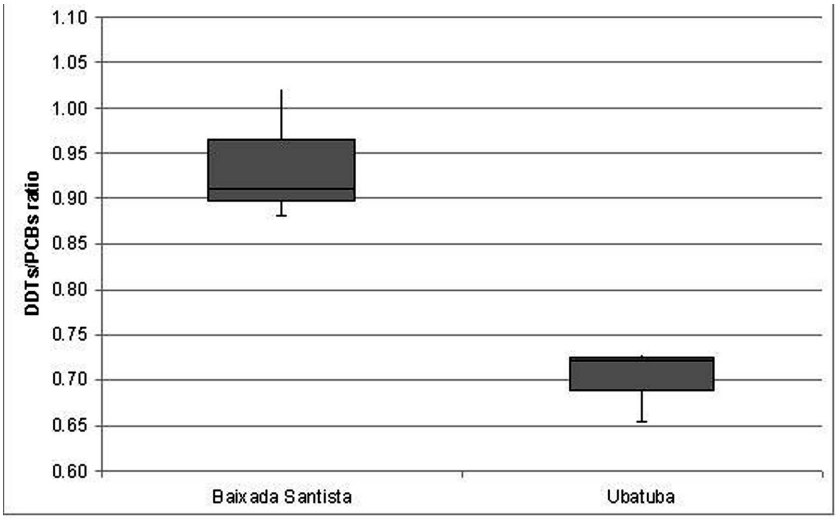

Figure 2. Significant differences ($p < 0.143$) in DDT/PCB ratios in Guiana dolphins from Baixada Santista and Ubatuba, state of São Paulo (southeastern Brazil).

[10] FREITAS-GUIMARÃES, J.R.P. (2005) Resíduos Industriais na Baixada Santista: Classificação e Riscos. 9 pp. Unpublished. [Available from the Associação de Combate aos Poluentes <http://www.acpo.org.br>].

study than those described by Yogui *et al.* (2003) and Kajiwara *et al.* (2004) in southern São Paulo/northern Paraná. In Baixada Santista, HCHs have been known to be present in water and sediment since 1974 and hexachlorobenzene (HCB) was detected in the marine environment in 1989, presumably due to industrial effluents and dumping in the Santos Estuary (Tommasi, 1979; Lamparelli *et al.*, 2001). HCB was manufactured as a fungicide, but was mainly a by-product of a large number of chlorinated compounds (UNEP, 2002). Among the OCs manufactured in Cubatão industrial complex, HCB was produced in high concentrations in the past (Lamparelli *et al.*, 2001). The present study reveals that OCs are still found in the region and have accumulated in the top predators of coastal marine biota.

Only one study was found with mirex measures in Guiana dolphins and the concentrations in males in both areas of the present study was one order of magnitude higher than that found in the Cananéia Estuary (Yogui *et al.*, 2003). This compound was mainly used for controlling ants in Brazil, Argentina and Uruguay (UNEP, 2002).

Chlordane concentrations in the present study were one order of magnitude higher in both sexes than those described for the Cananéia Estuary (Yogui *et al.*, 2003), but similar to those found in southern São Paulo/ northern Paraná (Kajiwara *et al.*, 2004). This is not a conclusive result in comparison to the findings described by Kajiwara *et al.* (2004), as the metabolite oxychlordane (the predominant compound in the total) was not analyzed in the present study. According to the UNEP (2002) report, 162 ton of heptachlor are available in Brazil for preserving wood, which indicates a continual source of this compound released into the environment.

Based on PCB concentrations found in cetaceans around the world, the values found in the present study are comparable with most impacted, industrialized coastal regions, such as *Tursiops truncatus* and *Phocoena phocoena* on the Atlantic and Mediterranean coasts of Europe (Clausen and Andersen, 1988; Borrell *et al.*, 2006; Marsili and Focardi, 1997), US Pacific and Atlantic coasts, Mexico (Kuehl *et al.*, 1991; Salata *et al.*, 1995) Japan and Hong Kong (Ramu *et al.*, 2005; Kajiwara *et al.*, 2002; 2006).

In the present survey, absolute OC concentrations proved of little use in distinguishing groups, whereas the DDT/ PCB ratio efficiently discriminated these populations. This is consistent with previous studies in which it has been shown that, unless dissimilarities are very apparent, pollutant concentrations are unable to distinguish populations due to the high individual variability. In contrast, ratios, which are usually less variable, more sensitively reflect population structuring (Aguilar, 1984).

As previously noted, the ratios of certain POPs in marine biota can provide insight into regional patterns of pollutants, as has been seen in the bottlenose dolphin (*Tursiops truncatus*) subpopulation structure around the Iberian Peninsula (Borrel *et al.*, 2006) and from the two 'pods' of Southern Resident killer whales (*Orcinus orca*) from Puget Sound (WA, USA) and the coast of California (Krahn *et al.*, 2007). One interesting observation to emerge from studying DDT/PCB ratios in Guiana dolphins from the coast of São Paulo was the significant difference ($p < 0.014$) between the animals from Baixada Santista (BS) and those from Ubatuba (UBT). This difference in ratios suggests either that they are

Table 3. Concentrations of organochlorine residues (μg g^{-1} lipid weight) in the blubber of *S. guianensis* from southeastern and southern Brazil.

LOCATION	SURVEY YEARS	SEX	N	PCBS	DDTS	HCHS	HCB	MIREX	CHL	REFERENCE
Baixada Santista, SP	2004 - 2005	M	2	45.61	43.19	0.12	0.12	1.01	0.30	This study
		F	1	27.86	24.57	0.04	0.13	0.24	0.29	
Ubatuba, SP	2004 - 2005	M	3	47.78	34.03	0.07	0.11	1.26	0.33	
Cananéia estuary, SP	1996–2001	M	4	5.7	72.3	0.03	0.018	0.15	0.033	Yogui et al, 2003
		F	5	3.74	6.81	0.006	0.013	0.15	0.016	
Sao Paulo and Paraná States	1997 and 1999	(i) M	9	9.7	22	0.015	0.016	N.A	0.15	Kajiwara et al, 2004
		(m) M	8	34	52	0.019	0.068	N.A	0.42	
		(i) F	4	12	14	0.012	0.019	N.A	0.15	
		(m) F	5	11	7.6	0.002	0.025	N.A	0.18	
Guanabara Bay, RJ	1996	M	1	8.99	N.A	N.A	N.A	N.A	N.A	Silva et al, 2003
		F	1	2.62	N.A	N.A	N.A	N.A	N.A	
Guanabara Bay, RJ		M		28.49	11.87	N.A	N.A	N.A	N.A	Torres *et al.*, 2003
Sepetiba / Ilha Grande Bay, RJ		M		14.75	4.86	N.A	N.A	N.A	N.A	
Guanabara Bay, RJ	2000 - 2006	M	7	78.00	N.A	N.A	N.A	N.A	N.A	Dorneles *et al.*, 2008
		F	3	41.00	N.A	N.A	N.A	N.A	N.A	

[a](i) = Immature, (m) = Mature, [b]N.A. = Not analyzed.

feeding on different prey or that the areas in which BS dolphins feed are, at times, spatially distinct from those of UBT dolphins. Flores and da Silva (2009) suggest that different stocks or significant evolutionary units of *Sotalia* are evident from residency, site fidelity, genetic and acoustical data.

The origin of PCBs found in *S. guianensis* on the coast of São Paulo was probably the industrial effluents in the Santos Estuary, where PCBs are still being used and bound to soils and sediments. The presence of the compounds may be associated with the previous use of the most common commercial PCB mixtures (mainly Aroclor 1254) in energy transformers in the Cubatão industrial complex in the Baixada Santista region (Lamparelli *et al.*, 2001).

A number of studies on contaminants in marine mammals have determined the *p,p'*-DDE/DDT ratio in order to assess the chronology of DDT inputs (Aguilar *et al.*, 2002; Yogui *et al.*, 2003; McHugh *et al.*, 2007). Aguilar (1984) and Tanabe *et al.* (1997) state that a ratio > 0.6 is indicative of a stable system with no new DDT inputs. In the current study, the *p,p*-DDE/ΣDDT ratio determined in Guiana dolphin blubber samples was 0.8, suggesting that Guiana dolphin DDT residues are derived from historic contamination. In Brazil, DDT and other persistent chlorinated pesticides were banned from agricultural use in 1985, but their use remained permitted in public health campaigns until 1998 (Brazil, 1985; 1998). These compounds were used on a large scale during the 1970s and beginning of the 1980s (Paumgartten *et al.*, 2000; Yogui *et al.*, 2003). The log K_{ow} values for DDT, *p,p'*-DDE and PCB congeners in combination with their relatively low water solubility can render these contaminant groups difficult to eliminate from an organism, ultimately leading to bioaccumulation in lipid rich tissues such as blubber (McHugh *et al.*, 2007).

A high relative percentage of hexa- and heptachlorinated-biphenyls in PCBs has been found in many studies on marine mammals around the world (*e.g.* Corsolini *et al.*, 1995; Minh *et al.*, 2000). Mackay and Shiu (1992) report log K_{ow} values for PCB congeners of between 5 and 8 chlorine molecules, with the log K_{ow} value increasing with an increase in the degree of chlorination. This is corroborated in the present study, in which trophic transfer/bioaccumulation was less pronounced for lower chlorinated congeners with lower log K_{ow} values. These results suggest that bioconcentration through the food chain of higher log K_{ow} compounds is the primary exposure pathway for cetaceans and marine mammals with regard to a number of organochlorine compounds (McHugh *et al.*, 2007).

The results of the OCs evaluated are indicative of their use and persistence in the environment. The detection of these compounds in marine mammals, such as the Guiana dolphin, demonstrates the need for continual monitoring in order to determine the tendency of their presence in the habitat over the upcoming decades.

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