

**OCCURENCE OF CHLORINATED PESTICIDES AND POLYCHLORINATED BIPHENYLS (PCBs) IN MARINE TUCUXI (*Sotalia guianensis*) FROM SÃO PAULO COAST, BRAZIL.**

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**Abstract:** Organochlorine pesticides and polychlorinated biphenyls (PCBs) were determined in the blubber of six marine tucuxi dolphin (*Sotalia guianensis*) from São Paulo coastal zone (Baixada Santista and Ubatuba). PCBs presented the highest levels on wet weight basis (5.17 to 16.44 $\mu\text{g}\cdot\text{g}^{-1}$ ), followed by DDTs (3.38-14.50 $\mu\text{g}\cdot\text{g}^{-1}$ ), mirex (0.144 – 0.374 $\mu\text{g}\cdot\text{g}^{-1}$ ), chlordanes (0.038-0.173 $\mu\text{g}\cdot\text{g}^{-1}$ ), HCB (0.019 – 0.079  $\mu\text{g}/\text{g}$ ) and HCHs (0.009 – 0.048  $\mu\text{g}/\text{g}$ ). The presence of PCB in the samples suggests the input from the Cubatão industrial complex—the biggest of Brazil. The mean *p,p*-DDE/ $\Sigma$ DDT ratio was approximately 0.8 and is indicative of the former DDT application in the study area. The occurrence of HCB and HCHs can be attributed to industrial effluents and dumps in the borders of Santos-São Vicente Estuarine Complex.

**Resumo:** Pesticidas organoclorados e bifenilas policloradas (PCBs) foram determinados no tecido adiposo de seis botos-cinza (*Sotalia guianensis*) da zona costeira do estado de São Paulo (Baixada Santista e Ubatuba). Os níveis residuais de PCBs em peso úmido (5.17 a 16.44 $\mu\text{g}\cdot\text{g}^{-1}$ ) foram os maiores, seguidos de DDTs (3.38 – 14.50 $\mu\text{g}\cdot\text{g}^{-1}$ ), mirex (0.144 – 0.374 $\mu\text{g}\cdot\text{g}^{-1}$ ), clordanas (0.038 – 0.173 $\mu\text{g}\cdot\text{g}^{-1}$ ), HCB (0.019 – 0.079  $\mu\text{g}/\text{g}$ ) e HCHs (0.009 – 0.048  $\mu\text{g}/\text{g}$ ). A presença de PCBs sugere a influência do complexo industrial de Cubatão – o maior do Brasil. A média de *p,p*-DDE/ $\Sigma$ DDT foi aproximadamente 0.8 e é um indicativo de 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:** Organochlorines, São Paulo State, southeastern Brazil, pollution, *Sotalia guianensis*.

### Introduction

The organochlorines (OCs) are enclosed in the lists of the priority pollutants of the Environmental Protection Agency of the United States, USEPA (Jones & Voogt, 1999) known world-wide as POPs (persistent organic pollutants). Chlorinated pesticides (DDTs, HCHs, chlordanes) and polychlorinated biphenyls (PCBs) are included among the OCs. They are toxic for the organisms, resistant to photochemical, biological and chemical degradation and therefore affect ecosystems (Johnston, 1976; Clark, 2001; Albaigés, 1990; Tanabe et al., 1994; Marsili & Focardi, 1996). The aquatic organisms

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can accumulate lipophilic OCs by direct absorption from the water, or through the feeding of contaminated organisms. The concentrations in marine mammals as dolphin, for example, can be ten million-fold the concentration in the water (Tanabe & Tatsukawa, 1992) because of the bioaccumulation and biomagnification along the food web.

Marine mammals present a metabolic imbalance, so that they are considered one of the most vulnerable organisms with regard to long-term toxicity of these man-made chemicals (Tanabe *et al.*, 1994; Fossi *et al.*, 1997).

The marine tucuxi dolphin (*Sotalia guianensis*) is one of the lesser-studied delphinids and is listed as ‘insufficiently known’ by the 1994–1998 Action Plan for the Conservation of Cetaceans (Reeves and Leatherwood, 1994). Due to its coastal distribution, the estuarine dolphin is submitted to several kinds of threats, like incidental catch in fishery gear mainly by artisanal fleet (Siciliano, 1994; Di Benedito *et al.*, 2001), degradation of coastal environment resultant of domestic and industrial sewage (Yogui *et al.*, 2003). Therefore this species is highly vulnerable and threatened by disordered human action.

There are many studies concerning chlorinated compounds in marine mammals around the world, nevertheless the contamination status of these mammals along the Brazilian coast is still poorly known (Yogui *et al.*, 2003).

The aim of this study was to determine chlorinated pesticides and polychlorinated biphenyls in the blubber of marine tucuxi from two different areas at central and northern Coast of São Paulo State, Southeastern Brazil, respectively: Baixada Santista, an industrialized area impacted also by human action and Ubatuba, a non-industrialized place.

## Material and Method

### *Study area*

The Santos - São Vicente Estuarine Complex (23° 55’S, 46° 20’W) (Fig. 01), inserted in the Metropolitan Region of Baixada Santista, represents the most important Brazilian example of environmental degradation by hydric and atmospheric pollution from industrial origin in coastal areas. The biggest Port of Latin America, the Port of Santos and the biggest industrial Pole of the country, in Cubatão city are located in this area. The industrial activity had beginning in 50’s, with the implantation of diverse factories (metallurgical, petrochemical and fertilizing), that leads the Santos-São Vicente Estuarine Complex a great receptor of toxic residues and contaminated effluents (CETESB, 2001).

Ubatuba city (~22° 53’S, 45° 08’W) (Fig. 01) is located in the north shore of São Paulo, with 100 km of coast with 74 beaches. Different from the central coast, it does not hold a big population, because is an extremely indented area inserted between the range (Serra do Mar) and the Atlantic Ocean. In addition to intense tourism, Ubatuba is one of the biggest fishery producers of the state (Ab’Saber, 1965).

The blubber samples were obtained from six individuals of marine tucuxi (*S. guianensis*). Three animals from Baixada Santista region and two from Ubatuba were bycaught in gillnets. One dolphin was found dead at a beach of Ubatuba (Table 01). The major part of the captures was occurred near important fishery points of those regions, as Santos Bay and Praia Grande, central coast of São Paulo state (Bertozzi & Zerbini, 2002; Alonso *et al.*, 2005). The samples have been collected through the monitoring of fishery communities of São Paulo coast since 1998 (Bertozzi & Zerbini, 2002; Bertozzi *et al.*, 2003; Alonso *et al.*, 2004; 2005) and were deposited in The Marine Mammals Tissues Bank of the Laboratório de Patologia Comparada de Animais Silvestres (LAPCOM) of Pathology Department (VPT) in Faculdade de Medicina Veterinária da Universidade de São Paulo (FMVZ-USP), tumbled by BioPesca Project.

### Chemical analysis

The analytical procedure followed that described in MacLeod *et al.* (1986) with minor modifications. Briefly, approximately 0.5 g of wet tissue was extracted, after the addition of anhydrous Na<sub>2</sub>SO<sub>4</sub>, with methylene chloride and n-hexane (50% v/v) using a tissumizer. Before extraction, dibromooctafluorobiphenyl (DBOBF) and PCB 103 were added to all samples, blanks and reference material as surrogates. Extracts were eluted in partially deactivated silica:alumina column chromatography by eluting with a 7:3 mixture of n-hexane and methylene chloride. The tissue fraction is further purified by high-performance liquid chromatography (HPLC) to remove lipids and finally concentrated to a volume of 0.5 mL in hexane and internal standard (tetrachlorometaxylene - TCMX) was added before gas chromatographic analysis. Chlorinated pesticides and PCBs were analyzed by gas chromatography using an electron capture detector (GC-ECD).

### Results

Preliminary results showed that OCs contaminants were detected in all the blubber samples of marine tucuxi dolphin from São Paulo coastal waters (Table 02). The mean concentrations of organochlorine residues in Baixada Santista were similar to Ubatuba region, São Paulo State.

PCBs were the predominant contaminants with concentrations ranging from 5.17 to 16.44  $\mu\text{g}\cdot\text{g}^{-1}$  on a wet weight basis, followed by DDTs (3.38 – 14.50  $\mu\text{g}\cdot\text{g}^{-1}$ ), mirex (0.144 – 0.374  $\mu\text{g}\cdot\text{g}^{-1}$ ), chlordanes (0.038 – 0.173  $\mu\text{g}\cdot\text{g}^{-1}$ ), HCB (0.019 – 0.079  $\mu\text{g}/\text{g}$ ) and HCHs (0.009 – 0.048  $\mu\text{g}/\text{g}$ ).

The compound that presented the major concentrations in all samples was *p-p'*-DDE. Mirex, CHLs (chlordanes), HCB, HCHs and heptachlor epoxide were detected at levels one to three orders of magnitude lower than those of PCBs and DDTs.

The predominant PCBs congeners were the hexachlorinated biphenyls (53-58%), followed by heptachlorinated biphenyls (23-29%) in all samples analyzed.

### Discussion

All individuals presented ratios DDT/PCB near 0.8, indicating a greater contribution by industrial activities in the region, in comparison to agricultural input. The occurrence of PCBs and DDTs suggests contamination on the southeastern Brazilian coast, as well as Kajiwara *et al.* (2004) found in the same species on the southern coast of Brazil. PCBs levels probably proceed from the industrial effluents from Santos estuary and according to CETESB (2001), their presence can be associated with the preterit use of “Ascarel” in energy transformers in the Cubatão industrial complex.

The average concentration of *p,p'*-DDE in six blubber samples of *S. guianensis* was 8.15  $\mu\text{g}\cdot\text{g}^{-1}$  wet wt while *p,p'*-DDT was 0.49  $\mu\text{g}\cdot\text{g}^{-1}$ . The mean *p,p'*-DDE/ $\Sigma$ DDT ratio was approximately 0.8 and is indicative of the former DDT application in the study area. In Brazil, DDT and other persistent chlorinated pesticides were forbidden for agricultural use in 1985, but they remained allowed for use in public health campaigns until 1998 (Brazil, 1985; 1998). They had been used in a large scale during the decade of the 70 and beginning of 80's (Paumgarten *et al.* 2000; Yogui *et al.*, 2003).

The comparisons of mean concentrations of organochlorine residues in the blubber of *S. guianensis* from southeastern and southern off Brazil were in Table 03. The mean concentration of DDTs in tucuxi males presented in this study was one order of magnitude lower than the males reported by Yogui *et al.* (2003) and Kajiwara *et al.* (2004) in animals from southern of São Paulo and Paraná state between 1996 and 2001. In spite of the few samples, this preliminary study suggests a reduction in concentrations of DDTs during the last decade in southeastern off Brazil.

The mean levels of HCHs, HCB and CHLs in this study presented average concentrations similar to those from Yogui *et al.* (2003) and Kajiwara *et al.* (2004). In Baixada Santista, the compounds

HCHs have been found since 1974 in the water and sediments from Santos-São Vicente Estuarine Complex and Santos Bay and HCB has been detected since 1989 in the marine environment due to the industrial effluents and dumps in Santos estuary (Tommasi, 1979; CETESB, 2001). This study showed that OCs are still being found in the region and accumulated in the top predators of coastal marine biota.

HCB was produced as fungicide, but it was mainly a by-product of large number of chlorinated compounds (UNEP, 2002). Among the OCs manufactured in Cubatão industrial complex, the HCB was produced in high volume in the past (CETESB, 2001).

The two regions analyzed in this study, showed similar concentrations of organochlorine compounds in the marine tucuxi dolphins from Baixada Santista and from Ubatuba. It may suggest that the animals from northern and central coast of São Paulo state may feed in the same region.

The preliminary results of OCs identified in the two regions, even in low concentrations are indicative of their use, or their presence (even if its input has been interrupted), in the proximities. Their detection shows the necessity of a monitoring study to verify the conditions of the region regarding to the occurred contamination.

Data on OCs in small cetaceans as *Sotalia guianensis* are limited. This study will contribute with OCs data related to global distribution of these organic contaminants in South Atlantic.

### Acknowledgments

Organochlorine analyses were financially supported by Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP), Brazil. Field work was supported by Project AWARE Foundation – PADI, USA; Cetacean Society International, USA and Society for Marine Mammalogy, USA.

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Table 01. Biological data from six marine tucuxi dolphins (*Sotalia guianensis*) from São Paulo State, southeastern Brazil.

Field no.	Origin	Date	Length (cm)	Sex	Site	Sexual Maturity
BP 69	Capture	28-Jun-2004	122	F	Praia Grande, Baixada Santista	immature
BP 76	Capture	10-Aug-2004	147	M	Praia Grande, Baixada Santista	immature
BP 81	Strand	30-Aug-2004	163	M	Ubatuba, North Coast	immature
BP 96	Capture	15-Feb-2005	186	M	Ubatuba, North Coast	mature
BP 97	Capture	15-Feb-2005	172	M	Ubatuba, North Coast	mature
BP 105	Capture	11-Jun-2005	173	M	Mongaguá, Baixada Santista	mature

Table 02. Concentration of chlorinated pesticides and polychlorinated biphenyls ( $\mu\text{g.g}^{-1}$  wet weight) in the blubber of marine tucuxi dolphins (*Sotalia guianensis*) from Baixada Santista and Ubatuba region, São Paulo State, southeastern Brazil.

Field no. <sup>a</sup>	Sex	$\Sigma$ PCBs	$\Sigma$ DDTs	$\Sigma$ HCHs	HCB	Mirex	$\Sigma$ CHL	HP epox.
BP69 (BS)	F	16.44	14.50	0.023	0.079	0.144	0.173	0.065
BP76 (BS)	M	14.11	12.86	0.048	0.039	0.240	0.113	0.037
BP105 (BS)	M	9.86	10.06	0.009	0.023	0.323	0.038	0.020
BP81 (UBT)	M	5.17	3.38	0.013	0.022	0.113	0.060	0.011
BP96 (UBT)	M	13.21	9.61	0.014	0.029	0.374	0.078	0.026
BP97 (UBT)	M	11.83	8.54	0.016	0.019	0.311	0.069	0.015
mean		11.77	9.82	0.02	0.04	0.25	0.09	0.03
S.D.		3.91	3.85	0.01	0.02	0.10	0.05	0.02

<sup>a</sup>(BS) = Baixada Santista

(UBT) = Ubatuba

Table 03. Comparison of mean concentrations of organochlorine residues ( $\mu\text{g.g}^{-1}$  wet weight) in the blubber of *S. guianensis* from southeastern and southern off Brazil.

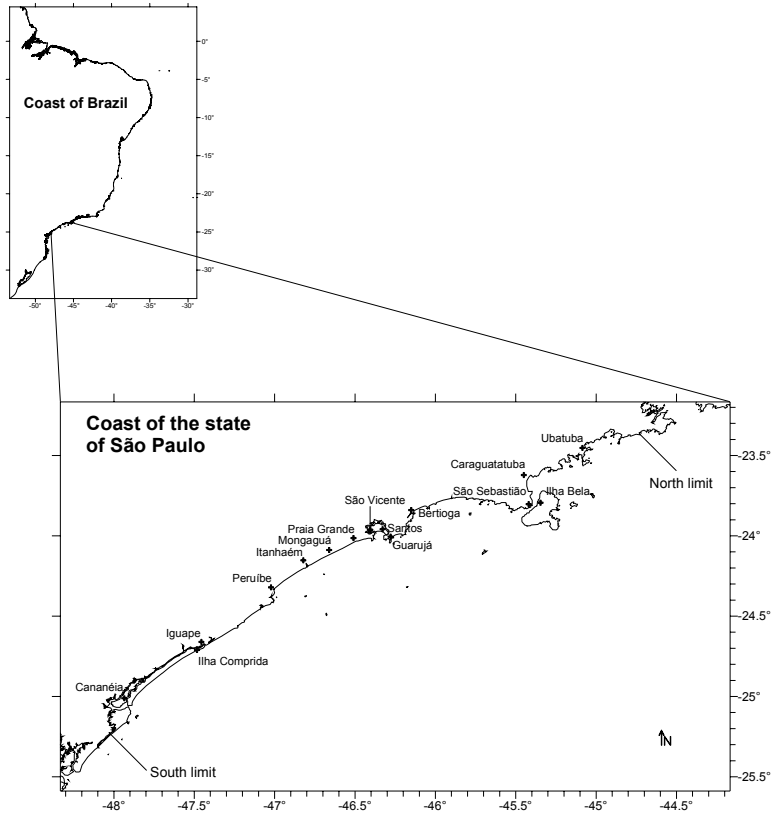
Species	Location	Survey years	Sex <sup>a</sup>	n	$\Sigma$ PCBs	$\Sigma$ DDTs	$\Sigma$ HCHs	HCB	Mirex	$\Sigma$ CHL	Reference
<i>S. guianensis</i>	Ubatuba and Baixada Santista, SP, Brazil	2004 - 2005	M	5	10.84	8.89	0.020	0.026	0.272	0.072	This study
			F	1	16.44	14.50	0.023	0.079	0.144	0.173	
	Cananéia estuary, SP, Brazil	1996-2001	M	4	3.88	49.16	0.018	0.012	0.101	0.022	Yogui et al, 2003
			F	5	2.58	4.70	0.004	0.01	0.106	0.011	
	Guanabara Bay, RJ, Brazil	1996	M	1	8.99	N.A. <sup>b</sup>	N.A.	N.A.	N.A.	N.A.	da Silva et al, 2003
			F	1	2.62	N.A.	N.A.	N.A.	N.A.	N.A.	
	São Paulo and Paraná states, Brazil	1997 and 1999	(i) M	9	7.37	16.72	0.011	0.012	N.A.	0.114	Kajiwara et al, 2003
			(m) M	8	24.48	37.44	0.014	0.049	N.A.	0.302	
			(i) F	4	9.72	11.34	0.010	0.015	N.A.	0.122	
			(m) F	5	6.05	4.18	0.001	0.014	N.A.	0.099	

<sup>a</sup>(i) = Immature

(m) = Mature

<sup>b</sup>N.A. = Not analyzed

Figure 1 – Map of the coast of São Paulo State.



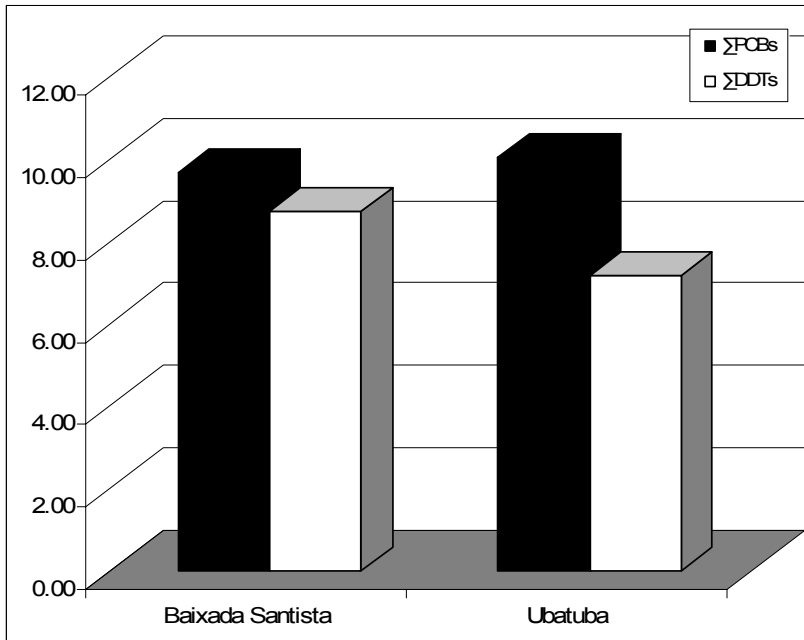


Figure 02. Mean concentrations of PCBs and DDTs ( $\mu\text{g}\cdot\text{g}^{-1}$  wet wt) in the blubber of the marine tucuxi dolphins (*Sotalia guianensis*) from Baixada Santista and Ubatuba region, São Paulo state, Brazil.