# Chlorinated pesticides and polychlorinated biphenyls in marine tucuxi dolphins (*Sotalia fluviatilis*) from the Cananéia estuary, southeastern Brazil

Gilvan Takeshi Yogui[a], Marcos César de Oliveira Santos[b], Rosalinda Carmela Montone[a],*

[a]*Laboratório de Química Orgânica Marinha, Instituto Oceanográfico, Universidade de São Paulo, Praça do Oceanográfico 191, São Paulo, SP, 05508-120, Brazil*
[b]*Projeto Atlantis; LABMAR, Departamento de Ecologia Geral, Instituto de Biociências, Universidade de São Paulo, Rua do Matão 321 travessa 14, São Paulo, SP, 05508-090, Brazil*

## Abstract

The Cananéia estuary is an important biological area on the southeast coast of Brazil. In the past, it was impacted by both chlorinated pesticides and polychlorinated biphenyls (PCBs) due to its natural location. The marine tucuxi dolphin (*Sotalia fluviatilis*) is a top predator in this ecosystem and can be found year round in Cananéia estuarine waters that represent an important nursing area for the species. This work investigated chlorinated compounds in the blubber of nine individuals from the Cananéia estuary. Residue levels of DDTs (0.541–125 µg g$^{-1}$ lipid wt.) were the highest, followed by PCBs (0.2–9.22 µg g$^{-1}$ lipid wt.), mirex (0.014–0.312 µg g$^{-1}$ lipid wt.), chlordanes (0.001–0.047 µg g$^{-1}$ lipid wt.), HCHs (<0.003–0.044 µg g$^{-1}$ lipid wt.), and HCB (n.d.−0.024 µg g$^{-1}$ lipid wt.). The mean $p,p'$-DDE/$\Sigma$ DDT ratio was approximately 0.8 and is indicative of the former DDT application in the study area. PCB contamination is suggested to be associated with atmospheric transport and relative proximity to the Cubatão industrial complex—the most important along the Brazilian coast. Low levels of HCHs and HCB can be attributed to their high volatility in tropical environments. Concentrations of organochlorines in the blubber of marine tucuxis from the Cananéia estuary were lower than levels found in small cetacean species from developed countries, where the input of these compounds was considerably greater than in Brazil. At extremes, male dolphins can present DDT burden several orders of magnitude higher than females. Despite the high levels of total DDT found in males, the major detected compound was $p,p'$-DDE which is considered to be of low toxicity.
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*Corresponding author. Tel.: +55-11-3091-6570; fax: +55-11-3091-6610.
*E-mail address:* rmontone@usp.br (R.C. Montone).

## 1. Introduction

The Cananéia estuary is located on the southeast coast of Brazil (Fig. 1). It receives waters from the Ribeira de Iguape river and its tributaries which drain important agricultural areas of two Brazilian states (São Paulo and Paraná). The Cananéia estuary is inserted into a 160-km-long estuarine system with a muddy bottom and relatively turbid waters, surrounded by a large mangrove area with high concentrations of nutrients, zooplankton, shrimps, and fishes (Besnard, 1950; Schaeffer-Novelli et al., 1990). This area has special relevance as an important biological reserve and contains federal and state Environmental Protected Areas (SMA, 1990, 1996). It is not far from the Santos estuary (23°55′S, 046°20′W), which has the largest commercial harbour in Latin America and the most important industrial region along the Brazilian coast—the Cubatão industrial complex. In 1985, chlorinated hydrocarbons were prohibited by law in Brazil, however, they were used in large scale during the 1970s and early 1980s. As a consequence, considering its geographical location, the Cananéia estuary was impacted by both chlorinated pesticides and polychlorinated biphenyls (PCBs) (Matos, 2002). Indeed, chlorinated insecticides such as DDT, HCH, aldrin, endrin, heptachlor and mirex were the most commonly used insecticides in 1975 in the Vale do Ribeira region (Ferreira et al., 1980).

The marine tucuxi dolphin (*Sotalia fluviatilis* GERVAIS, 1853) is one of the lesser-studied delphinids. It is listed as 'insufficiently known' by
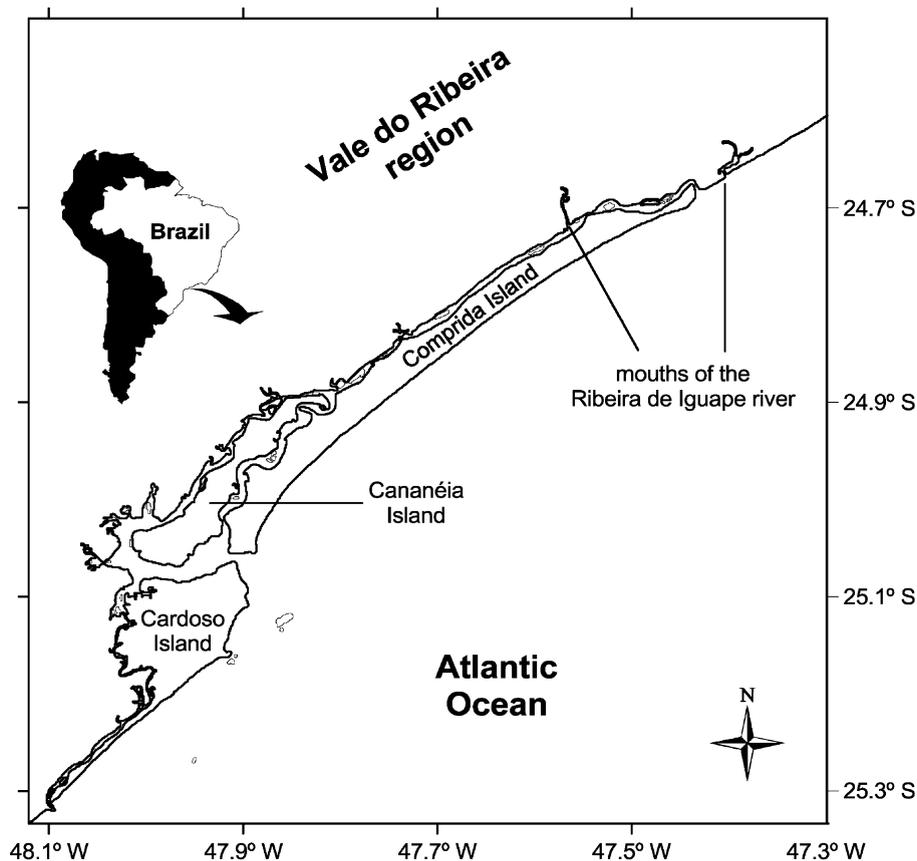


Fig. 1. Location and geography of the Cananéia estuary, southeastern Brazil.

the 1994–1998 Action Plan for the Conservation of Cetaceans (Reeves and Leatherwood, 1994). Individuals of this species have an apparently continuous distribution along most of the eastern south and central American coasts (Borobia et al., 1991; Silva and Best, 1996; Carr and Bonde, 2000; Flores, 2001). Many aspects of this species' natural history and behaviour remain unknown. The marine tucuxi's preference for coastal and estuarine brackish waters, avoidance response when approached by boats, absence of sexual dimorphism and small body size are the main features that make this species difficult to study in its natural habitat (Santos et al., 2000). Marine tucuxi female-calf pairs can be found year round in Cananéia estuarine waters that represent an important nursing area for the species (Geise, 1989; Schmiegelow, 1990; Santos, 1999). Site fidelity of 86 individuals has been observed in photo-identification studies conducted since 1997 in local waters (Santos et al., 2001), showing evidence of residency patterns.

Chlorinated hydrocarbons are persistent contaminants which biomagnify in the food chain. Marine mammals present a metabolic imbalance, i.e. high toxifying and low detoxifying potential, 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). Around the world there are many studies concerning chlorinated compounds in marine mammals, nevertheless the contamination status of these mammals along the Brazilian

coast is still poorly known. The aim of this study was to determine chlorinated pesticides and polychlorinated biphenyls in the blubber of marine tucuxi from the Cananéia estuary, southeastern Brazil. This species can provide relevant information about organochlorines contamination in the Cananéia ecosystem, since it is a top predator of local food chain (Santos et al., 2002). In addition, it contributes to the understanding of organochlorines distribution in marine mammals from tropical environments.

## 2. Material and methods

### 2.1. Sampling

Blubber samples of marine tucuxi were obtained from nine individuals which were found dead along local beaches or floating in Cananéia estuarine waters. All individuals were sampled according to international standardised procedures (see Aguilar, 1985; Borrell and Aguilar, 1990; UNEP/ICES/IOC, 1991). Based on carcass classification proposed by Geraci and Lounsbury (1993), the studied individuals were grouped in the code 2 category, which refers to fresh animals. Marine tucuxis' total lengths were measured following standardised procedures described by Norris (1961), while physical maturity of the animals was obtained from a growth curve proposed by Santos et al. (2003). Detailed information on the sampled individuals can be found in Table 1.

Table 1
Data on the nine analysed marine tucuxi dolphins (*Sotalia fluviatilis*) from the Cananéia estuary, southeastern Brazil

| Field no. | Notification date | Length (cm) | Sex | Age (years) | Growth stage | Additional information |
|---|---|---|---|---|---|---|
| PA-020 | 5 Aug 1996 | 183 | M | n.d.[a] | Adult | |
| PA-021 | 19 Aug 1996 | 187 | F | n.d. | Adult | With foetus |
| PA-080 | 11 Jun 1997 | 187 | F | 14 | Adult | |
| PA-083 | 15 Jul 1997 | 173 | F | 21 | Adult | |
| PA-095 | 11 Oct 1997 | 163 | M | 7 | Adult | |
| PA-102 | 10 Feb 1998 | 178 | M | 21 | Adult | |
| PA-131 | 31 Dec 1998 | 196 | M | 21 | Adult | |
| PA-140 | 9 Nov 2000 | 197 | F | n.d. | Adult | Lactating female |
| PA-143 | 27 Apr 2001 | 181 | F | n.d. | Adult | |

[a] n.d. = not determined.

## 2.2. Age determination

To estimate the age of sampled cetaceans, the method based on thin and decalcified teeth sections for optical microscope analyses was used following Kasuya (1976), Perrin and Myrick (1980) and Hohn et al. (1989). All the collected teeth were preserved in a solution composed by glycerine and ethanol (1:1). Large and straight teeth were selected, fixed in 10% formalin and decalcified in a commercial bone decalcifier, in intervals between 2 and 32 h. These intervals ended when each tooth presented adequate flexibility and transparency. Teeth were sectioned in a freezing microtome. Labial-lingual sections of 40 $\mu$m were stained with Mayer's haematoxylin for 30 min and mounted in 100% glycerine. Only the mid-longitudinal sections with well-marked layers were selected for age estimation. Age was estimated by the number of Growth Layer Groups (GLGs) (see Perrin and Myrick, 1980). In this study, we considered only complete GLG counts—expressed as years old. Teeth sections were analysed with a stereoscopic microscope at magnifications of $16\times$ and $50\times$ as well as with an optic microscope at $25\times$ and $75\times$, both with transmitted light. Three readers made three distinct counts with a minimum interval of 20 days between readings. Data were then compared among readers. When necessary, photographs were taken with a Nikon SMZ-U stereoscopic microscope to investigate different readers' counts.

## 2.3. Chemical analysis

A sample of 1.0 g of blubber was ground with 15 g of anhydrous sodium sulphate and extracted in Soxhlet apparatus for 8 h using approximately 70 ml of *n*-hexane and dichloromethane (1:1) (v/ v). The extract was concentrated to 5 ml, from which a 1 ml aliquot was removed and submitted to treatment with concentrated sulfuric acid (96%). Subsequently, the lipid-free extract was analysed in a gas chromatograph equipped with a $^{63}$Ni electron capture detector (GC-ECD). Lipid content in the blubber samples was estimated gravimetrically, while confirmatory tests for each analyte followed a saponification method.

GC-ECD analyses were performed with a Hewlett Packard 5890 series II gas chromatograph using a 25 m$\times$0.32 mm i.d. capillary column coated with 5% phenyl-substituted dimethylpolysiloxane phase (0.52 $\mu$m film thickness). Splitless injections of 2 $\mu$l (purge off time = 1.25 min) were done manually and the total purge rate was adjusted to 50 ml min$^{-1}$. Hydrogen was used as carrier gas under constant pressure (40 kPa at 100 °C) into the column, while nitrogen was the make up gas at a rate of 30 ml min$^{-1}$. Injector and detector temperatures were 300 °C and 320 °C, respectively. The oven temperature was programmed as follows: 100 °C for 1 min, at 5 °C min$^{-1}$ to 140 °C (holding at this temperature for 1 min), at 1.5 °C min$^{-1}$ to 250 °C (holding for 1 min), and at 10 °C min$^{-1}$ to 300 °C with a final hold for 10 min.

Analytical methodology was validated using a standard reference material (SRM 1588a—organics in cod liver oil) purchased from the National Institute of Standards and Technology (NIST). SRM was analysed in duplicate and analyte recoveries ranged from 59% to 139% (mean = 95%). Quality assurance/quality control (QA/QC) procedures followed criteria established by Wade and Cantillo (1994), which is tailored to marine pollution programmes such as the International Mussel Watch. Recovery of analytes in spiked blanks and matrices were also performed and fitted to satisfactory results. Method detection limit ranged from < 0.001 $\mu$g g$^{-1}$ lipid wt. to 0.024 $\mu$g g$^{-1}$ lipid wt., with mean value of 0.002 $\mu$g g$^{-1}$ lipid wt. For further details on QA/QC see Yogui and Montone (in press).

## 2.4. Data interpretation

Concentrations of chlorinated hydrocarbons in the marine tucuxi are presented on a lipid weight basis. According to Aguilar (1985), residue levels expressed in relation to the fresh weight of the tissue are inadequate for establishing comparisons between different organs in the same individual, different individuals in a population, or different species, since variations in lipid content of the tissues substantially affect pollutant load. Thus, whenever possible, data in the literature expressed

as wet weight were converted to lipid weight in order to compare residue levels.

Chlorinated pesticides analysed in this study were DDTs, HCHs, chlordanes, HCB, and mirex. In the DDT family, six compounds were investigated: *o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDE, and *p,p′*-DDE. Among the HCHs and chlordane-related compounds the following were determined: α-, β-, γ- and δ-HCH and α- and γ-chlordane, respectively. Besides these pesticides, polychlorinated biphenyls were also investigated, including the sum of 27 isomers and congeners as follows: 8, 18, 44, 49, 50, 52, 66, 87, 101, 105, 110, 118, 128, 138, 149, 151, 153, 157, 160, 169, 170, 173, 180, 194, 195, 206 and 209 (according to the numeration proposed by Ballschmiter and Zell, 1980).

## 3. Results and discussion

Total DDT concentrations ranged from 0.541 to 125 $\mu$g g$^{-1}$ lipid wt. (Table 2). The mean value

of 35.9 $\mu$g g$^{-1}$ lipid wt. shows that DDT contamination was the highest among organochlorine groups studied in local marine tucuxis. The $\Sigma$ DDT/$\Sigma$ PCB ratio was high (6.5), probably due to agricultural characteristics of the Cananéia region which was directly impacted by DDT in the past. The largest use of chlorinated pesticides in Brazilian agriculture occurred between the 1970s and early 1980s, after that a law was approved prohibiting its application for agricultural purposes. This explains the relatively high *p,p′*-DDE/$\Sigma$ DDT ratio which has been used to assess the chronology of DDT input into the ecosystem. In local marine tucuxis, the mean *p,p′*-DDE/$\Sigma$ DDT ratio was approximately 0.8. This may be an indicator of the former DDT application through the study area since ratios higher than 0.6 indicate old DDT input (Aguilar, 1985; Borrell and Aguilar, 1987). Similar ratios have been found in marine mammals from many countries where DDT was prohibited (see de Kock et al., 1994; Gauthier et

Table 2
Concentration of chlorinated pesticides and polychlorinated biphenyls ($\mu$g g$^{-1}$ lipid wt.) in the blubber of marine tucuxi dolphins (*Sotalia fluviatilis*) from the Cananéia estuary, southeastern Brazil

| Field no. | Sex | Lipid (%) | $\Sigma$ PCB[a] ($\mu$g g$^{-1}$ lipid wt.) | $\Sigma$DDT[b] ($\mu$g g$^{-1}$ lipid wt.) | $\Sigma$HCH[c] ($\mu$g g$^{-1}$ lipid wt.) | $\Sigma$ chlordane[d] ($\mu$g g$^{-1}$ lipid wt.) | HCB ($\mu$g g$^{-1}$ lipid wt.) | Mirex ($\mu$g g$^{-1}$ lipid wt.) |
|---|---|---|---|---|---|---|---|---|
| PA-020 | M | 62.4 | 7.6 | 57.4 | 0.044 | 0.031 | 0.023 | 0.178 |
| PA-095 | M | 64.6 | 1.61 | 7.24 | <0.003 | 0.021 | 0.009 | 0.129 |
| PA-102 | M | 78.4 | 6.39 | 100 | 0.032 | 0.033 | 0.019 | 0.147 |
| PA-131 | M | 65.2 | 7.18 | 125 | 0.034 | 0.047 | 0.022 | 0.141 |
| **Mean** | ***n*=4** | **67.7** | **5.7** | **72.3** | **0.028** | **0.033** | **0.018** | **0.149** |
| **S.D.[e]** | | | **7.3** | **2.77** | **51.5** | **0.019** | **0.011** | **0.007** |
| PA-021 | F | 65.8 | 1.97 | 9.28 | 0.01 | 0.023 | 0.01 | 0.099 |
| PA-080 | F | 77.8 | 5.95 | 9.26 | 0.005 | 0.022 | 0.024 | 0.235 |
| PA-083 | F | 73.9 | 1.37 | 5.05 | 0.005 | 0.012 | n.d.[f] | 0.106 |
| PA-140 | F | 71.7 | 0.2 | 0.541 | <0.003 | 0.001 | 0.004 | 0.014 |
| PA-143 | F | 56.8 | 9.22 | 9.9 | 0.011 | 0.02 | 0.023 | 0.312 |
| **Mean** | ***n*=5** | **69.2** | **3.74** | **6.81** | **0.006** | **0.016** | **0.013** | **0.153** |
| **S.D.** | | **8.2** | **3.75** | **4** | **0.004** | **0.009** | **0.011** | **0.119** |
| **Mean** | ***n*=9** | **68.5** | **4.61** | **35.9** | **0.016** | **0.024** | **0.015** | **0.151** |
| **S.D.** | | **7.3** | **3.31** | **46.8** | **0.017** | **0.013** | **0.009** | **0.085** |

[a] Sum of congeners 8, 18, 44, 49, 50, 52, 66, 87, 101, 105, 110, 118, 128, 138, 149, 151, 153, 157, 160, 169, 170, 173, 180, 194, 195, 206 and 209.
[b] Sum of *o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDE, and *p,p′*-DDE.
[c] α-HCH, β-HCH, γ-HCH and δ-HCH.
[d] Sum of α-chlordane and γ-chlordane.
[e] Standard deviation.
[f] n.d.=not detected.

al., 1997; Nakata et al., 1998; Metcalfe et al., 1999; Storelli and Marcotrigiano, 2000).

Total DDT found in local marine tucuxis was much lower than concentrations detected by Morris et al. (1989), Corsolini et al. (1995) and Minh et al. (1999), which stressed the negative impact of DDTs on the health of some cetacean populations (see Table 3). On the other hand, total DDT in the blubber of dolphins from the Cananéia estuary was close to that found in the spinner dolphin (*Stenella longirostris*) from Bay of Bengal, India (Tanabe et al., 1993). Interestingly, DDT loads in the marine tucuxi were higher than some small cetacean species studied in Indian waters, such as humpback dolphin (*Sousa chinensis*), bottlenose dolphin (*Tursiops truncatus*), and Ganges river dolphin (*Platanista gangetica*) (Tanabe et al., 1993; Kannan et al., 1994).

Levels of total HCH detected in local marine tucuxis were low and ranged from < 0.003 to 0.044 $\mu$g g$^{-1}$ lipid wt. (mean = 0.016 $\mu$g g$^{-1}$ lipid wt.) (Table 2). $\beta$-HCH was present in the highest proportion among analysed isomers, whereas $\alpha$-HCH was not detected in the blubber of marine tucuxi. The higher proportion of $\beta$-HCH may arise as a consequence of its bioaccumulative nature and persistence in terms of enzymatic degradation in cetacean bodies among HCH isomers (Tanabe et al., 1997). Low concentrations of total HCH can be attributed to the geographical position of the Cananéia estuary, which is located in a tropical region. The relatively high vapour pressure of HCHs (compared to other organochlorines) favours their volatilisation, and consequently decreases their deposition into the marine ecosystem. Indeed, Iwata et al. (1993) suggested the atmospheric transport of HCHs from low- to mid- and high-latitudes where deposition takes place over the cold ocean surface.

Residues of HCH have been detected at low levels in other marine mammal species from tropical coastal waters of the Southern hemisphere (Cockcroft et al., 1991; Kemper et al., 1994). Comparing HCH data in Table 3, the contamination levels found in local marine tucuxis are at least one order of magnitude lower than other marine mammal species, including individuals from tropical regions such as India. This may be

a consequence of the prohibition of HCH usage in Brazil (1985), which avoided new inputs into the environment.

Concentrations of HCB in local marine tucuxis ranged from not detected to 0.024 $\mu$g g$^{-1}$ lipid wt. (mean = 0.015 $\mu$g g$^{-1}$ lipid wt.) (Table 2). As pointed out for HCHs, these levels can be considered low and attributed to the high volatility of HCB, supporting the hypothesis that the extent of its pollution is not severe in tropical marine environments (Tanabe et al., 1993). According to Table 3, HCB was detected at similar levels in both cetacean species from Brazil (marine tucuxi) and India (Ganges River dolphin). On the other hand, these values were much lower than the ones that were found in individuals from temperate regions, especially European countries (Morris et al., 1989; Kannan et al., 1993; Tanabe et al., 1997).

Measured chlordane concentrations ranged from 0.001 to 0.047 $\mu$g g$^{-1}$ lipid wt. (mean = 0.024 $\mu$g g$^{-1}$ lipid wt.) (Table 2). Low concentrations are to be expected since chlordane-related compounds were not extensively used in Brazil. However, total chlordane contamination in marine tucuxis from the Cananéia estuary is probably higher than the presented levels because only $\alpha$- and $\gamma$-chlordane were analysed. According to Kawano et al. (1988), *trans*-nonachlor is the constituent most retained by marine mammals. In addition, in the environment $\alpha$- and $\gamma$-chlordane are converted into *oxy*-chlordane which is more persistent than their precursor compounds (Wells et al., 1994). As a consequence, total measured chlordane in the blubber of marine tucuxi was the lowest among cetacean species presented in Table 3.

Mirex concentrations ranged from 0.014 to 0.312 $\mu$g g$^{-1}$ lipid wt. (mean = 0.151 $\mu$g g$^{-1}$ lipid wt.) (Table 2). In the past, mirex was used by farmers of the Cananéia region in order to combat ants. Thus, its occurrence in local marine tucuxis is probably linked to that practice. In this study, mirex was detected at higher concentrations than other compounds like HCHs, chlordanes, and HCB. A possible explanation for such persistence might be the number of chlorine atoms bonded to its molecule (12). HCH isomers and HCB have six chlorine atoms each, while chlordane isomers have eight chlorines (all are less chlorinated than

Table 3
Comparison of organochlorine residues (μg g$^{-1}$ lipid wt.) in the blubber of small cetacean species from several areas of the world

| Species | Location | Survey years | Sex | $N$ | Σ PCB (μg g$^{-1}$ lipid wt.) | Σ DDT (μg g$^{-1}$ lipid wt.) | Σ HCH (μg g$^{-1}$ lipid wt.) | HCB (μg g$^{-1}$ lipid wt.) | Σ CHL (μg g$^{-1}$ lipid wt.) | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Ganges river dolphin (*Platanista gangetica*) | Ganges River, India | 1988–1992 | M | 2 | 1.19 | 21.6 | 1.04 | 0.016 | 0.104 | Kannan et al. (1994)[a] |
|  |  |  | F | 2 | 1.04 | 23.4 | 0.937 | 0.012 | 0.087 |  |
| Marine tucuxi dolphin (*Sotalia fluviatilis*) | South Atlantic, Brazil | 1996–2001 | M | 4 | 5.7 | 72.3 | 0.027 | 0.018 | 0.033 | This study[b] |
|  |  |  | F | 5 | 3.74 | 6.81 | 0.006 | 0.013 | 0.016 |  |
| Humpback dolphin (*Sousa chinensis*) | South China Sea, Hong Kong | 1993–1997 | M | 7 | 72.1 | 138 | 2.85 | 0.197 | 1.01 | Minh et al. (1999)[c] |
|  |  |  | F | 4 | 24.7 | 61 | 0.573 | 0.08 | 0.513 |  |
| Humpback dolphin (*Sousa chinensis*) | Bay of Bengal, India | 1990–1991 | M | 3 | 1.6 | 16.4 | 0.61 | 0.004 | n.a.[j] | Tanabe et al. (1993)[d] |
| Harbour porpoise (*Phocoena phocoena*) | Baltic Sea, Poland | 1989–1990 | F | 3 | 34 | 12.6 | 1.1 | 0.627 | 1.17 | Kannan et al. (1993)[e] |
| Harbour porpoise (*Phocoena phocoena*) | Black Sea, Turkey |  | M | 25 | 18.6 | 80 | 11.8 | 0.493 | 0.968 | Tanabe et al. (1997)[f] |
|  |  |  | F | 24 | 14 | 60.4 | 8.93 | 0.459 | 0.744 |  |
| Harbour porpoise (*Phocoena phocoena*) | North Pacific, Japan |  | M | 6 | 7.52 | 5.36 | 1.04 | 0.428 | 1.1 | Tanabe et al. (1997)[f] |
| Burmeister's porpoise (*Phocoena spinipinnis*) | South Atlantic, Argentina | 1989–1990 | M | 4 | 3.9 | 5.64 | n.a. | n.a. | n.a. | Corcuera et al. (1995)[g] |
|  |  |  | F | 4 | 2.29 | 2.21 | n.a. | n.a. | n.a. |  |
| Finless porpoise (*Neophocaena phocaenoides*) | South China Sea, Hong Kong | 1993–1997 | M | 3 | 31.3 | 115 | 0.62 | 0.112 | 0.474 | Minh et al. (1999)[c] |
|  |  |  | F | 4 | 9.92 | 32.1 | 0.216 | 0.096 | 0.225 |  |
| Bottlenose dolphin (*Tursiops truncatus*) | Mediterranean Sea, Italy |  | M | 5 | 1192 | 394 | n.a. | n.a. | n.a. | Corsolini et al. (1995)[h] |
|  |  |  | F | 2 | 587 | 138 | n.a. | n.a. | n.a. |  |
| Bottlenose dolphin (*Tursiops truncatus*) | Cardigan Bay, Wales |  | F | 1 | 760 | 391 | 2.07 | 1.69 | n.a. | Morris et al. (1989)[i] |
| Bottlenose dolphin (*Tursiops truncatus*) | Bay of Bengal, India | 1990–1991 | M | 2 | 1.19 | 9.28 | 0.213 | 0.028 | n.a. | Tanabe et al. (1993)[d] |
|  |  |  | F | 2 | 0.753 | 14.9 | 0.238 | 0.6 | n.a. |  |
| Spinner dolphin (*Stenella longirostris*) | Bay of Bengal, India | 1990–1991 | M | 3 | 1.31 | 37.3 | 0.744 | 0.03 | n.a. | Tanabe et al. (1993)[d] |
|  |  |  | F | 2 | 1.27 | 42.1 | 0.966 | 0.015 | n.a. |  |
| Risso's dolphin (*Grampus griseus*) | Mediterranean Sea, Italy |  | M | 1 | 1017 | 667 | n.a. | n.a. | n.a. | Corsolini et al. (1995)[h] |
|  |  |  | F | 1 | 41.7 | 12.5 | n.a. | n.a. | n.a. |  |

[a] Σ PCB=sum of 95 congeners; Σ DDT=sum of *o,p*′-DDT, and *p,p*′-DDT, DDD and DDE; Σ HCH=sum of α-, β-, γ- and δ-HCH; Σ CHL=sum of α-, γ-, and *oxy*-chlordane, and *cis*-, and *trans*-nonachlor.

[b] Σ PCB=sum of 27 congeners; Σ DDT=sum of *o,p*′-DDT, DDD, and DDE, and *p,p*′-DDT, DDD and DDE; Σ HCH=sum of α-, β-, γ- and δ-HCH; Σ CHL=sum of α- and γ-chlordane.

[c] Σ PCB=sum of 78 congeners; Σ DDT=sum of *p,p*′-DDT, DDD and DDE; Σ HCH=sum of α-, β- and γ-HCH; Σ CHL=sum of α-, γ- and *oxy*-chlordane, and *cis*-, and *trans*-nonachlor.

[d] Σ DDT=sum of *o,p*′-DDT, and *p,p*′-DDT, DDD and DDE; Σ HCH=sum of α-, β-, γ- and δ-HCH.

[e] Σ PCB=an equivalent KC-300, 400, 500 and 600 mixture; Σ DDT=sum of *o,p*′-DDT, and *p,p*′-DDT, DDD and DDE; Σ HCH=sum of α-, β-, γ- and δ-HCH; Σ CHL=sum of α-, γ- and *oxy*-chlordane, and *cis*-, and *trans*-nonachlor.

[f] Σ PCB=an equivalent KC-300, 400, 500 and 600 mixture; Σ DDT=sum of *o,p*′-DDT, and *p,p*′-DDT, DDD and DDE; Σ HCH=sum of α-, β-, and γ-HCH; Σ CHL=sum of α-, γ- and *oxy*-chlordane, and *cis*-, and *trans*-nonachlor.

[g] Total PCB not defined by the authors; Σ DDT=sum of *o,p*′-DDT, and *p,p*′-DDT, DDD and DDE.

[h] Σ PCB=sum of 55 congeners; Σ DDT=sum of *p,p*′-DDT and DDE.

[i] Σ PCB=sum of seven congeners; Σ DDT=sum of *p,p*′-DDT, DDD and DDE; Σ HCH=sum of α-, β- and γ-HCH.

[j] n.a.=not analysed.

mirex). Similarly, Wells et al. (1994) associated the higher persistence of *trans*-nonachlor in the environment to its higher chlorination degree when compared to other chlordane-related compounds.

Concentrations of total PCB (sum of 27 isomers and congeners) ranged from 0.2 to 9.22 $\mu$g g$^{-1}$ lipid wt. (Table 2). The mean value of 4.61 $\mu$g g$^{-1}$ lipid wt. places PCBs as the second highest organochlorine group in local marine tucuxis. Considering the agricultural characteristics of the Cananéia region these levels are unlikely to derive from a local input. They are probably associated with atmospheric transport and relative proximity to the Cubatão industrial complex (approx. 200 km northeast from the Cananéia estuary), where several chemical industries occupy a large area in the vicinities of the Santos estuary. Indeed, predominant winds on the region blow from the northeast quadrant, especially during Summer (Castro and Miranda, 1998). Another hypothesis would consider that dolphins could be feeding on contaminated fish in migration from polluted areas (e.g. Santos estuary). Such possibility can be rejected since the main prey item of local marine tucuxis is the rake stardrum (*Stellifer rastrifer*)—a non-migratory fish of the Cananéia estuary (see Rios, 2000; Santos et al., 2002).

The mean residual pattern of PCBs in local marine tucuxis is shown in Fig. 2. Relative concentrations show the highest proportion of IUPAC no. 153 followed by 138/160, 180 and 149. Hexachlorobiphenyls represented approximately 66% of PCBs distribution, while penta-, hexa- and heptachlorobiphenyls totalled more than 90% of the analysed isomers and congeners. Similar contamination patterns have been found in several other marine mammal species all over the world in which IUPAC nos. 153, 138 and 180 have also been detected at higher levels (see Corsolini et al., 1995; Minh et al., 1999; Storelli and Marcotrigiano, 2000).

According to Table 3, the marine tucuxi from the Cananéia estuary is less contaminated by PCBs than cetaceans studied in Europe, Japan and Hong Kong (highly industrialised regions) (Morris et al., 1989; Kannan et al., 1993; Corsolini et al.,
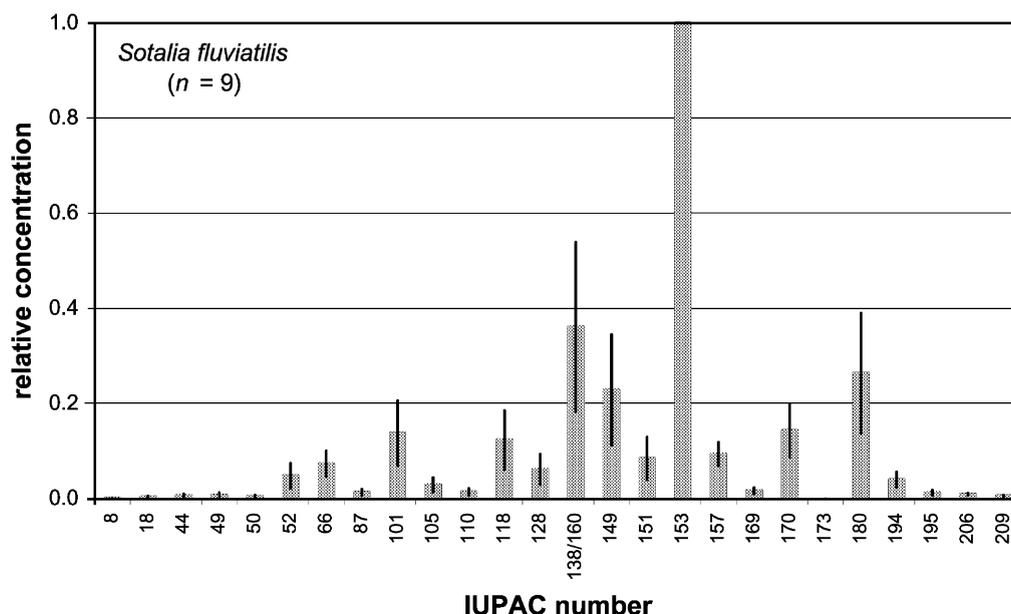


Fig. 2. Mean distribution of PCB isomers and congeners in the blubber of marine tucuxi dolphins (*Sotalia fluviatilis*) from the Cananéia estuary, southeastern Brazil. Vertical bars represent concentration of individual PCB congeners relative to the most abundant congener (IUPAC no. 153), the latter being assigned a relative concentration of 1. Error bars represent standard deviation.

1995; Tanabe et al., 1997; Minh et al., 1999). On the other hand, PCB concentrations were higher than some marine mammals from Argentinean and Indian waters (Tanabe et al., 1993; Kannan et al., 1994; Corcuera et al., 1995).

Total DDT concentrations were as low as 0.541 $\mu$g g$^{-1}$ lipid wt. in a female (PA-140) and as high as 125 $\mu$g g$^{-1}$ lipid wt. in a male (PA-131). It indicates that local marine tucuxi males are able to support a DDT burden several orders of magnitude higher than females. On the other hand, according to the Kruskal–Wallis test, mean concentrations of chlorinated hydrocarbons were not statistically different between males and females from the Cananéia estuary ($P < 0.01$). These results can be masked by the limited number of individuals under investigation, and we suggest further studies to find a conclusion on this respect. Differences between male and female loads have been found by several authors and attributed to the reproductive transfer from females to offspring during both gestation and lactation (Tanabe et al., 1987; Aguilar and Borrell, 1994; Borrell et al., 1995). While males increase their organochlorine load with age, females present this trend up to their first parturition, after which the pollutant burden decreases. In this study, the individuals PA-095 (male) and PA-143 (female) showed the lowest and the highest organochlorine concentration among their sexes, respectively. Although it cannot be fully proved because there is no available data on ageing of all studied animals, the individual PA-095 may be the youngest male, while PA-143 a young female that possibly did not have a calf before its death.

A lactating female (PA-140) presented the lowest contaminant load among all analysed individuals. Comparable low concentrations were not observed in female PA-021, which was found with a foetus inside her uterus. Similar findings have been described for other marine mammal species. In a population of long-finned pilot whales (*Globicephala melas*) from the Faroe Islands, organochlorine transfer to offspring during lactation was found to represent approximately 60–100% of the mother's body load, while that occurring during gestation was estimated to be much lower, in the range 4–10% of the mother's body load (Borrell

et al., 1995). Tanabe et al. (1982) also observed similar transfer rates for a pregnant striped dolphin (*Stenella coeruleoalba*) and suggested that the more lipophilic chemicals, such as higher chlorinated biphenyls and DDT compounds, are less transferable from mother to foetus. The transfer characteristics of chlorinated hydrocarbons can be explained by their equilibrium partitionings between blood and blubber, resulting from the differences of lipid compositions in each.

## 4. Conclusions

In general, concentrations of organochlorines in the blubber of marine tucuxis from the Cananéia estuary were lower than levels found in small cetacean species from developed countries, where the input of these compounds was considerably greater than in Brazil. DDTs and PCBs constituted the two main contaminant groups, probably as a consequence of the historical agricultural characteristics of the Cananéia region and relative proximity to the Cubatão industrial complex—the most important along the Brazilian coast. At extremes, male dolphins can present a DDT burden several orders of magnitude higher than females. Despite the high levels of total DDT observed in males, the major detected compound was $p,p'$-DDE, which is considered to be of low toxicity.

Further studies on organochlorines contamination of local marine tucuxis should be conducted to observe a temporal trend in the future. It would be useful to analyse the contamination status of local marine tucuxis main prey items (see Santos et al., 2002) in order to determine the concentration of these compounds in lower food chain levels. Concentration of contaminants in this species should also be studied in adjacent areas to gather some possible insights on population discreteness as noticed by Calambokidis and Barlow (1991).

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