PCB, DDT AND HCB IN BLUBBER OF FRANCISCANA DOLPHIN, *Pontoporia blainvillei*, FROM SOUTHEASTERN BRAZILIAN COAST.

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Introduction

Few studies have been conducted about micro-pollutant contamination in Southwest Atlantic Ocean waters. Since it is often possible to detect pollutant compounds in marine organisms when concentrations in water are too low or too variable to be determined with confidence by routine chemical analyses, the use of marine mammals to screen the neritic environment in search of micro-pollutant has an obvious attraction. Cetaceans are long-lived top marine predators, presenting large lipid reserves in proportion to their body size. This feature makes them the ideal repository for high concentrations of lipophilic chlorinated hydrocarbons. Hence, whales and dolphins are regarded as valuable indicators of organochlorine accumulation in the marine environment.

The franciscana dolphin (*Pontoporia blainvillei*) occurs exclusively in the western Atlantic coastal waters of South America, from southeastern Brazil (18°25’S) to central Argentina (~42°35’S). Due to its nearshore distribution, the franciscana may be vulnerable to the effects of human activities and high mortalities are reported due to bycatches. For these reasons *P. blainvillei* is the most endangered cetacean from South Atlantic Ocean, and it is listed as ‘vulnerable’ by IUCN – the World Conservation Union. Considering the mentioned vulnerability, it is of great interest to investigate if the accumulation of toxic environmental persistent compounds can pose an additional threat to the dolphin species concerned.

This study presents preliminary results of organochlorine bioaccumulation in franciscana dolphins from southeastern Brazilian coast, which comprises Espírito Santo, Rio de Janeiro and São Paulo States. In fact, all the dolphins analyzed in the present study were incidentally captured or stranded on the northern part of the São Paulo littoral.

Material and Methods

Blubber samples of six male franciscana dolphins were collected from specimens either incidentally captured in fishing operations or stranded on Northern São Paulo Littoral, Southeastern Brazilian Coast.

The samples were excised from the left lateral region below to the dorsal fin. After dissection, samples were wrapped in aluminum foil and kept frozen (-20°C) until analysis.

Aliquots of approximately 1.0 g of blubber were homogenized with anhydrous Na₂SO₄ and extracted by continuous Soxhlet apparatus, using a soxhlet for 8 hours with a mixture of hexane:dichloromethane (1:1). An aliquot (1mL) was mixed with sulphuric acid for the clean-up. After centrifugation and phase separation, an internal standard (octachloronaphthalene) was added for the quantification. The lipid content was measured gravimetrically.

A Shimadzu Gas Chromatographer-14B with a 63Ni electron capture detector (ECD) was used in the analyses. Organochlorine concentrations are expressed as mg.Kg⁻¹, calculated on a lipids basis.
The analytical method was validated using a standard certified material (Cod Liver Oil – SRM-1588, National Institute of Standards and Technology – NIST). The accuracy of the method was even strengthened by an intercalibration exercise carried out with Tuna muscle from International Atomic Energy Agency, since it has produced satisfactory results as well. The recovery of all compounds used in this paper ranged from 60% to 140% in both methodological tests. The analyzed organochlorines were: HCB, o,p’-DDT, p,p’-DDT, p,p’-DDD, o,p’-DDE, and p,p’-DDE, and 18 PCB isomers and congeners (08, 28, 44, 49, 52, 60, 66, 70, 87, 101, 105, 118, 128, 138, 153, 156, 169, 170, 180).

**Results and Discussion**

PCB, DDT and HCB concentrations, as well as percentages of p,p’-DDT, p,p’-DDE and p,p’-DDD in blubber of franciscana dolphins are summarized in Table 1 and Figure 1, respectively.

### Table 1. Lipid content (%), DDTs, PCBs, and HCB concentrations (mg Kg⁻¹ on a lipid basis); and DDT/PCB of blubber of franciscana dolphins from southeastern Brazilian coast.

<table>
<thead>
<tr>
<th>Individual</th>
<th>Lipid content</th>
<th>DDTs</th>
<th>PCBs</th>
<th>HCB</th>
<th>DDT/PCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb01</td>
<td>91</td>
<td>1.36</td>
<td>4.83</td>
<td>0.05</td>
<td>0.28</td>
</tr>
<tr>
<td>Pb02</td>
<td>80</td>
<td>1.09</td>
<td>4.03</td>
<td>0.04</td>
<td>0.27</td>
</tr>
<tr>
<td>Pb03</td>
<td>70</td>
<td>0.44</td>
<td>1.42</td>
<td>0.02</td>
<td>0.31</td>
</tr>
<tr>
<td>Pb04</td>
<td>66</td>
<td>1.68</td>
<td>5.85</td>
<td>0.06</td>
<td>0.29</td>
</tr>
<tr>
<td>Pb05</td>
<td>86</td>
<td>0.26</td>
<td>0.91</td>
<td>0.01</td>
<td>0.29</td>
</tr>
<tr>
<td>Pb06</td>
<td>91</td>
<td>1.55</td>
<td>3.71</td>
<td>0.05</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Regarding DDTs, p,p’-DDE predominated in all samples, which contrasts with commercial formulas, considering that there is a predominance of pp’-DDT in those products. When released in the environment, pp’-DDT degrades into pp’-DDE and pp’-DDD. Therefore, the ratio between pp’-DDE and the sum of pp’-DDT, p,p’-DDE and pp’-DDD (pp’-DDE / pp’-DDT + p,p’-DDE + pp’-DDD) was used for determination of the recentness of DDT entrance in the ecosystem. The distribution of the mean percentages was verified in the following order: p,p’-DDE (63.9%) > p,p’-DDD (19.7%) > p,p’-DDT (16.4%) (Figure 1). Since the higher the percentage of p,p’-DDE the less recent is the DDT release in the environment, the results pointed to a non-recent usage of DDT in the region, considering that the franciscana has access to a high percentage of DDE. The same pattern was also reported for other cetaceans from Brazilian Coast.\textsuperscript{1,10,12}

![Figure 1](image-url) Figure 1. Percentages of p,p’-DDT, p,p’-DDE and p,p’-DDD in blubber of franciscana dolphin (Pontoporia blainvillei) from southeastern Brazilian coast.
The highest PCB concentration verified in the present study is lower than the highest levels reported for franciscanas and marine tucuxi dolphins (another coastal species) from other regions of the Brazilian Coast (Table 2). However, it is interesting to highlight that Kajiwara et al. (2004) determined a number of PCBs (101 isomers and congeners) that was by far higher than those determined in the present study (25 isomers and congeners). Therefore, it is likely that the franciscana dolphins from the Northern São Paulo Litoral (present study) present higher PCB concentrations than individuals of the same species inhabiting Southern São Paulo and Northern Paraná, the region from which the specimens reported in Kajiwara et al. (2004) were originated. This statement is based on the fact that the Northern São Paulo Litoral finds itself under greater industrial influence than the other region concerned. It is also important to note that, concerning PCBs, there was a predomination of PCB-153, followed by PCB-138, in the present study.

Table 2. Adipose tissue PCB and DDT concentrations (mg.kg$^{-1}$ on a lipid basis) of male cetaceans, concerning coastal species (franciscana dolphins, *Pontoporia blainvillei*, and marine tucuxi dolphins, *Sotalia guianensis*) from Brazilian coast, including data generated by the present study as well as information from literature.

<table>
<thead>
<tr>
<th>Species / Reference</th>
<th>Total length (cm)</th>
<th>Number of analysed specimens</th>
<th>DDTs mg.kg$^{-1}$ on a lipid basis</th>
<th>PCBs mg.kg$^{-1}$ on a lipid basis</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pontoporia blainvillei</em></td>
<td>80 - 117</td>
<td>6</td>
<td>0.26 – 1.55</td>
<td>0.91 – 5.95</td>
</tr>
<tr>
<td><strong>Kajiwara et al. (2004)</strong></td>
<td>66 - 119</td>
<td>15</td>
<td>0.58 – 35.0</td>
<td>0.32 – 12.0</td>
</tr>
<tr>
<td><em>Sotalia guianensis</em></td>
<td>184 - 191</td>
<td>4</td>
<td>7.24 – 125.0</td>
<td>1.61 – 7.6</td>
</tr>
<tr>
<td><strong>Kajiwara et al. (2004)</strong></td>
<td>150 - 195</td>
<td>8</td>
<td>12.0 – 150.0</td>
<td>10.0 – 79.0</td>
</tr>
<tr>
<td><strong>Torres et al. (2006)</strong></td>
<td>150 - 195</td>
<td>8</td>
<td>1.11 – 21.19</td>
<td>2.17 – 44.93</td>
</tr>
</tbody>
</table>

* PCBs= (25 isomers and congeners); **PCBs= (101 isomers and congeners); ***PCBs= (27 isomers and congeners).

The ratio between DDTs and PCBs (DDT/PCB) has been used for characterizing the magnitude of the contributions from agricultural and industrial sources to marine mammal contamination. The ratio DDTs/PCBs varied between 0.27 and 0.42, which points to a greater influence of pollution by organochlorines of industrial origin. Contrastingly, analyzing marine tucuxi dolphins (*Sotalia guianensis*) from Southern São Paulo State, Yogui et al. (2003) verified a higher ΣDDT/ΣPCB ratio than the observed in the present study (6.5). Similarly, analyzing franciscana dolphins from Southern São Paulo and Northern Paraná, Kajiwara et al. (2004) also observed a DDT/PCB ratio higher than 1.0. The results generated by the quoted investigations point to a greater influence of pollution by organochlorines of agricultural origin; however, in the concerned scenario, the fight against malaria cannot be ruled out as a possible source of pollution by organochlorine compounds. The predomination of PCB over DDT in marine mammal tissues, as observed in the present study, had already been reported for waters under strong industrial influence in Rio de Janeiro, Southeastern Brazil.

In general, investigations on marine mammals in South and Central America show extremely high mean DDT/PCB ratios. Concerning South America, the mean ratios were between 72, for the spinner dolphin (*Stenella longirostris*) from Antilles, and 1610, for the Fraser’s dolphin (*Lagenodelphis hosei*) from Eastern...
Tropical Pacific.\textsuperscript{13} Regarding the South American Atlantic Coast, excluding Brazil, the mean ratios were between 64.8, for Argentinean franciscanas, and 513, for the same species in Uruguayan waters.\textsuperscript{13}

The results concerning the Brazilian Coast show the industrial characteristic of Brazil, especially the Southeast Region, with regard to São Paulo and Rio de Janeiro areas. The patterns of DDT/PCB ratio observed in franciscana dolphins from São Paulo State were similar to those reported for industrialized areas of the Northern Hemisphere.

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\textbf{References}