

HIGH ACCUMULATION OF ORGANOCHLORINE COMPOUNDS IN SOUTHERN HEMISPHERE – THE CASE OF DELPHINIDS FROM RIO DE JANEIRO CONTINENTAL SHELF, BRAZIL.

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Introduction

Since they are long-lived predators that occupy high trophic levels and present large lipidic reserve in relation to their body size, cetaceans can be considered the ideal repositories for high concentrations of chlorinated hydrocarbons¹. As a result, these mammals can integrate spatial and temporal variations of environmental contamination by persistent organic pollutants¹. Marine mammals have been indicated as monitor species for the health of aquatic systems and regarded as sentinel organisms for environmental and human health assessments¹.

Cetacean contamination by metals and organic compounds has been reported for all over the world¹. It still constitutes a new field of study and the understanding on the processes that control accumulation and effects in aquatic mammals are still incipient¹. A reduced number of studies have dealt with the chlorinated pollutant problem in cetaceans from South-Western Atlantic, and none of them comprised animals collected in the most industrialized area of Brazilian coast, the Rio de Janeiro state¹.

The present study aimed to generate information on the current levels of PCB, DDT and HCB in the subcutaneous adipose tissue of delphinids from Rio de Janeiro Continental Shelf, Southeast Brazilian coast.

Materials and methods

Studied Area

The analyzed delphinids inhabit the continental shelf adjacent to Rio de Janeiro state. This region is strongly influenced by discharge from highly impacted coastal systems, such as Guanabara Bay. This estuary is the coastal body of water under the strongest anthropogenic pressure on the Brazilian littoral². An assessed population of 14 million people lives in the 12 cities of its drainage basin and 35 rivers flow into the bay. These cities house 12 000 industrial plants. In addition, 500 tons of “in natura” sewage and 6.9 tons of oil are released daily into the bay². Blubber samples of 11 delphinids (01 killer whale, *Orcinus orca*; 01 false killer whale, *Pseudorca crassidens*; 03 rough-toothed dolphins, *Steno bredanensis*; 02 bottle-nosed dolphins, *Tursiops truncatus*; and 04 common dolphins, *Delphinus delphis*) were collected from specimens either incidentally captured in fishing operations or stranded in Rio de Janeiro State, 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 analysis⁹. 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 ng. g⁻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 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 determined 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 (IUPAC numbers: 08, 28, 44, 49, 52, 60, 66, 70, 87, 101, 105, 118, 128, 138, 153, 156, 169, 170, 180).

Results and Discussion

General Considerations

High organochlorine concentrations were observed in delphinids from Rio de Janeiro state (Table 1). The levels are high even if compared to cetaceans from industrialized regions of the Northern Hemisphere. The accumulation pattern shown by the different studied species owns straight relationship with high exposure to organochlorine compounds, particularly DDT and PCB.

Higher concentrations were found in species that occupy the inner continental shelf (rough-toothed dolphin and bottle-nosed dolphin), as well as in cetaceans (killer whale and false killer whale) that prey on other mammals. The analyzed rough-toothed dolphins (a juvenile and two individuals with low lipid content) may not represent the normal pattern of organochlorine accumulation in the population.

For all the delphinids from Rio de Janeiro state, the higher contribution for the sum of all the measured organochlorines was from PCB, followed by DDT, and, at last, from HCB.

Using the mean values, it is possible to observe the decreasing orders for DDT: killer whale > false killer whale > rough-toothed dolphin > bottle-nosed dolphin > common dolphin; for PCB: killer whale > rough-toothed dolphin > false killer whale > bottle-nosed dolphin > common dolphin. For HCB the same order found for DDT was observed.

Table 1 – Organochlorine concentrations (Σ DDT, Σ PCB, HCB), ng.g⁻¹ lipid, in blubber of delphinids from the Continental Shelf of Rio de Janeiro State. Sex (F= female and M= male) and lipid content (%).

Species/Code	Sex	Lipids (%)	Σ DDT	Σ PCB	HCB
Sbr#1	F	43	1 566	789	80
Sbr#2	M	6	27 439	119 268	488
Sbr#3	F	7	50 041	139 035	292
Tt#1	M	31	4 551	13 517	72
Tt#2	M	36	5 475	10 095	38
Dd#1	F	57	755	2 734	14
Dd#2	F	22	147	1 774	<4.4*
Dd#3	M	6	7 557	25 496	76
Dd#4	M	82	1 307	3 790	25
Oo#1	F	44	125 575	257 182	2 910
Pc#1	F	18	17 904	63 669	284

Sbr, *Steno bredanensis*; Tt, *tursiops truncatus*; Dd, *Delphinus delphis*; Oo, *Orcinus orca*; Pc, *Pseudorca crassidens*. *Detection limit

There was predominance of p,p'-DDE for the Σ DDT in all analyzed samples. The ratio between pp'-DDE and the sum of pp'-DDT, p,p'-DDE and pp'-DDD [$\text{pp}'\text{-DDE}/(\text{pp}'\text{-DDT} + \text{p,p}'\text{-DDE} + \text{pp}'\text{-DDD})$] was used for determining the chronology of DDT input into the ecosystem. The mean values exceed 70% in all species, indicating a not recent usage of DDT in Rio de Janeiro state.

Among the analyzed PCB congeners and isomers, there was predominance of PCB-153, followed by PCB-138 and by PCB-180.

The ratio between Σ DDT and Σ PCB were also used for characterizing the magnitude of the contributions from agricultural (or from insect borne disease control) and industrial sources to marine mammal contamination in Rio de Janeiro State coast. The mean values of the Σ DDT/ Σ PCB ratios were: 0.86 for the rough-toothed dolphins; 0.44 for the bottle-nosed dolphins; 0.25 for the common dolphins; 0.28 for the false killer whale; and 0.49 for the killer whale.

The rough-toothed dolphin

High organochlorine compound concentrations were found in subcutaneous adipose tissue of rough-toothed dolphins (Table 1). In the two adult individuals the Σ PCB concentrations were higher than the Σ DDT; however, a

higher Σ DDT level than Σ PCB was found in the juvenile specimen. Information on rough-toothed dolphin contamination is scarce. Yogui (2002)³ reported organochlorine concentrations in adult male rough-toothed dolphin from southern São Paulo state (83 180 ng.g⁻¹lip, for Σ DDT; 18 802 ng.g⁻¹lip, for Σ PCB; and 13 ng.g⁻¹lip, for HCB)³. Comparing these data to the concentrations reported for the adult male (Sbr#2) analyzed in the present study, a higher Σ DDT was found in the animal from southern São Paulo state, but higher Σ PCB and HCB concentrations were found in the dolphin from Rio de Janeiro state. Struntz *et al.* (2004)⁴ measured high organochlorine compound concentrations in rough-toothed dolphins sampled during a massive stranding in Florida, USA. In this case, as well as in the present study, the mean Σ PCB concentrations exceeded those of Σ DDT, which demonstrates that the exposure to compounds of industrial origin is predominant in both areas (Florida-USA and Rio de Janeiro state-Brazil).

The bottle-nosed dolphin

The concentrations were not high in bottle-nosed dolphins when compared to other species from the region. In average, they were lower than the levels observed in the mammal-eating cetaceans (killer whale and false killer whale), as well as in rough-toothed dolphins. The concentrations found in the present study are higher than those reported by Yogui (2002)³, who determined 2 424 ng.g⁻¹lip, for Σ DDT; 5 905 ng.g⁻¹lip, for Σ PCB; and 80 ng.g⁻¹lip, for HCB, in a male bottle-nosed dolphin. The author highlighted that the higher Σ PCB than Σ DDT concentration was due to the fact that the animal was collected in an area close to Santos city, a region strongly influenced by pollutant discharge from the industrial district of Cubatão city. In this same investigation³, predominance of PCB was observed in a franciscana dolphin (*Pontoporia blainvillei*) from Praia Grande region, an area also influenced by Cubatão industrial park³. Regarding the present study, in bottle-nosed dolphins, as well as in the other analyzed species, higher Σ PCB than Σ DDT concentrations were found. Other investigations reported higher DDT and PCB concentrations in bottle-nosed dolphins from Mediterranean Sea⁵, Norte Sea⁶ and east coast of USA⁷ than those found in the present study.

The common dolphin

The lowest concentrations were found in this species. Kajiwara *et al.* (2004)⁸ reported DDT (11 000 ng.g⁻¹lip), PCB (17 000 ng.g⁻¹lip) and HCB (32 ng.g⁻¹lip) concentrations in tissues of a common dolphin from an area between São Paulo and Paraná states. Similarly than in the present study, the authors observed a higher contribution of PCBs than DDTs, which suggest that the species feeds more to the north, in an area under stronger industrial influence. De Kock *et al.* (1994)⁹ reported lower DDT, PCB and HCB concentrations in a common dolphin from South Africa than the levels found in the present study. This latter study⁹ reported a higher DDT contribution, which demonstrates a greater influence from compounds of agricultural origin in local contamination. Borrel *et al.*¹⁰ reported high DDT and PCB concentrations in common dolphins from Iberian Peninsula, with predominance of PCBs.

The false killer whale

The high concentrations determined in the individual of the species could still be consequence of a high organochlorine burden acquired from transplacental and lactational transfer, since the analyzed false killer whale was a neonate. Jarman *et al.* (1996)¹¹ reported high DDT and PCB concentrations in the adipose tissue of two false killer whales (DDT= 84 360 ng.g⁻¹lip and 2 033 000 ng.g⁻¹lip; PCB= 51 060 ng.g⁻¹lip and 36 380 ng.g⁻¹lip) from British Columbia, Canada. Data from the present study as well from literature suggest that false killer whales regularly prey on marine mammals, as the organochlorine concentrations are similar to those reported for killer whale populations that rely more on mammals than on fish¹².

The killer whale

The highest organochlorine concentrations were determined in the species. The levels observed in the present study are comparable to those found in killer whales that feed on marine mammals in other regions of the globe. Ross *et al.*¹² reported organochlorine concentrations in three killer whale aggregations from Canadian coast. The authors reported a mean (\pm S.D.) PCB concentration of 37 400 (\pm 6.100) ng.g⁻¹lip in mature males, as well as 9 300 (\pm 3.8) ng.g⁻¹lip in mature females of the resident population that inhabits an area more to the north and rely on fish¹². Regarding the resident population from the southern part of the study area of this latter investigation¹², which also preys on fish, the mean (\pm S.D.) PCB level in mature males was 146 300 (\pm 32 700) ng.g⁻¹lip, and in

mature females it was 55 400 (\pm 19 300) ng.g⁻¹lip¹². The highest PCB concentrations were observed in transient killer whales, which rely on marine mammals. In this whale population, the mean (\pm S.D.) PCB levels were: 251 200 ng.g⁻¹lip (\pm 54 700), in mature males; and , 58 800 ng.g⁻¹lip (\pm 20 600) in females¹². Ono *et al.*¹³ reported a variation of PCB concentrations from 360 to 410 ng.g⁻¹lip, in oceanic killer whales. Jarman *et al.*¹¹ determined PCB concentrations between 9 100 and 6 150 ng.g⁻¹lip in killer whales from British Columbia (Canada) and Northern Washington State (USA). Kajiwara *et al.*¹⁴ measured DDT levels between 28 000 and 220 000 ng.g⁻¹lip, as well as PCB concentrations between 18 000 and 64 000 ng.g⁻¹lip, in killer whales from Shiretoko, Japan. In the latter study¹⁴, the authors determined DDT concentrations in mature females that varied from 28 000 to 120 000 ng.g⁻¹lip, as well as PCB levels that varied from 18 000 to 44 000 ng.g⁻¹lip.

Higher concentrations were observed in the mature female killer whale analyzed in the present study than in those determined in females from Canadian coast. Indeed, the concentrations measured in the female killer whale from Rio de Janeiro State are comparable to those determined in males of the aforementioned transient population¹². Remains of a franciscana dolphin were identified in the stomach of the ~26-year-old female analyzed in the present study. The killer whale predation on franciscanas had already been described for other areas of the Brazilian coast¹⁵. Considering that sexually mature female cetaceans in general present lower organochlorine concentrations than males, our results draw attention to the possibility of occurrence of even higher levels in male killer whales from Rio de Janeiro State.

Conclusions

Cetaceans from Southeast Brazilian waters are highly exposed to organochlorines. DDT and PCB concentrations in the subcutaneous adipose tissue of killer whales, false killer whales and rough-toothed dolphins reached elevated values. The detrimental effects that occur due to organochlorine accumulation are well-known for many species, including man. In addition, a series of investigations has suggested that massive mortality and/or strandings of diseased marine mammals would be associated to immunosuppressive effects of organochlorine compounds¹⁶. Although additional studies especially dedicated to the investigation of pollutant-pathology relationships should be carried out for a better comprehension on the consequences of cetacean exposure to pollutants in Rio de Janeiro State, the extreme high concentrations exposed in the present study elicit apprehension regarding the conservation of the delphinid species.

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