

POLYCHLORINATED BIPHENYLS AND DDT IN SWORDFISH (*Xiphias gladius*) AND BLUE SHARK (*Prionace glauca*) FROM BRAZILIAN COAST – PRELIMINARY RESULTS.

Claudio Eduardo Azevedo e Silva¹, Jose Lailson Brito Jr², Antonio Azeredo¹,
Rodrigo Meire¹, Joao Paulo Torres¹, Olaf Malm²

¹Laboratório de Radioisótopos E.P.F.- Inst. de Biofísica Carlos Chagas Filho, UFRJ, Rio de Janeiro, Brazil.

²Projeto Mamíferos Aquáticos – Departamento de Oceanografia, UERJ, Rio de Janeiro, Brazil

Introduction

Organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs) may bioaccumulate in the aquatic food web and have been of great concern due to their toxic effects on wildlife and human health.^{1,2}

PCBs constitute a class upon of 209 compounds with differential biological activity and toxicity as a result of differences in the number and position of chlorine atoms. The so-called dioxin-like PCBs, binding to the aryl hydrocarbon (Ah) receptor, exert a wide range of toxic responses particularly focused on the endocrine system, while the ortho-substituted congeners of PCBs, with two or more ortho-chlorines, which are not Ah receptor agonists, seems to be able to produce neurotoxic effects³.

The organochlorine *o,p*-DDT is neurotoxic and can act as an estrogen agonist, a property presumed responsible for many of its adverse effects on reproduction. More recently, anti-androgenic properties of the *pp'*-DDE have been demonstrated that may also contribute to the reproductive effects of DDT^{4,5}.

There is conclusive evidence showing that, in general, fish in meals human diet contributes with a significant proportion of the total intake of PCBs and others organochlorine compounds, particularly fish with higher fat content⁶. Thus, human exposure to PCBs is predominantly via diet, and especially from fish and seafood products⁷. Comparatively, little is know about organochlorine contaminants in elasmobranch species, although they are also top predators. Characteristically, sharks are live longer, with comparatively slow rates of growth that in conjunction with their high trophic position may contribute to the accumulation of high concentrations of pollutants⁸. Blue shark and swordfish are carnivorous fishes of great economic importance. This study investigate the concentration of polychlorinated biphenyls (PCBs) and DDTs in samples of muscle tissues of blue shark (*Prionace glauca*) and swordfish (*Xiphias gladius*) from Brazilian Coast.

Materials and Methods

Twelve specimens of the each species were caught in Brazilian Exclusive Economic Zone (EEZ) between august and setember 2001 (Fig.1). After dissection, all samples were freeze-dried and wrapped in aluminium foil, until the moment of the analysis.

About 2,5 g de muscle tissue were homogenized with anhydrous Na_2SO_4 (1:1) and extracted Soxhlet (60 ml) for 8 hours with a mixture of n-hexane:dichloromethane (1:1). An aliquot (1 ml) of each extract was treated with 2ml de concentrated sulphuric acid. After centrifugation, the organic phase was collected and the acid phase was washed with 2ml de n-hexane. The total organic portion was concentrated (1ml) and washed with 2 ml of ultrapure water. The top layer was transferred to a glass column (i.d. 7mm) filled with 1 g. of florisil (activated at 160 °C for 12 h) covered with 1g. of anhydrous Na_2SO_4 . After elution with 15 ml (15:85 dichloromethane: n-hexane), the eluate was concentrated and internal standard (octachloronaphtalene) was added for quantification.

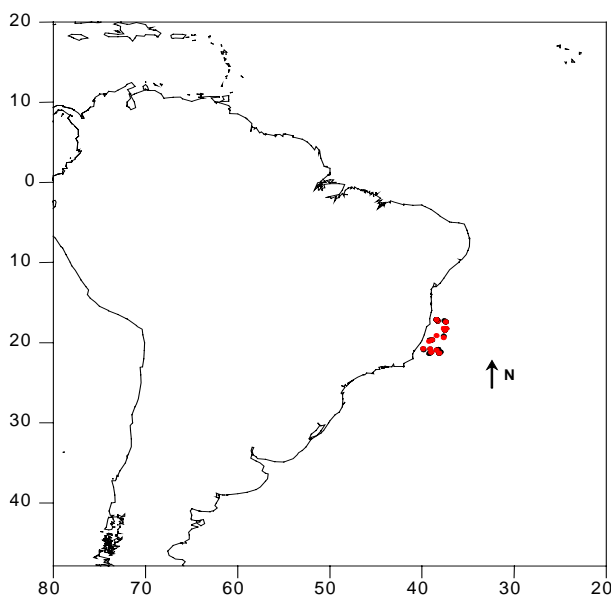


Figure 1 – Sampling locations along Brazil's Atlantic coast.

Analysis were made on a Shimadzu GC-14B with a ^{63}Ni electron capture detector (ECD). Injector and detector temperatures were maintained at 250 °C and 310 °C, respectively. The column temperature was programmed from 100 °C (4 min. hold) at a rate of 5 °C/min to 205 °C (15 min. hold) and then at a rate of 2 °C/min to 290 °C. For all the analysis a fused silica DB-5 capillary column (length = 30m, inside diameter 0,25 mm and film thickness 0,25 μm) was used. Organochlorine concentrations are expressed as ng/g wet weight.

IAEA-406 (fish homogenate) was used as a reference material. The recoveries for each PCB and DDTs quantified in the certified material (101,138,153,170,180, op'DDE, pp'DDE) ranged from 70% to 130%.

Results and Discussion

The results are summarised in Table. 1. Low PCBs and DDTs concentrations were found in both species. Concentrations of Σ PCBs and Σ DDTs in *Xiphias gladius* were higher than those in *Prionace glauca*. Among DDT and metabolites, p,p-DDE was dominant in muscle of Swordfish and Blue shark.

Low level Σ PCBs were observed in Gulper shark (*Centrophorus granulosus*) and longnose spurdog (*Squalus blainvillei*) from Mediterranean sea, with value of $28,3 \pm 11,3$ e $10,8 \pm 6,6$ (ng/g wet weight), respectively⁸. Storelli (2003) also observed low concentrations of Σ PCBs (20 ± 8 ng/g wet weight) in muscle of hammerhead shark (*Sphyrna zygaena*) captured from Ionam Sea³.

The low concentrations observed in this study, can be due the fact of this animals live in open sea, without any pontual pollution sources.

Table 1. Mean \pm S.D. of Polychlorinated biphenyls and DDTs (ng/g wet weight).

| PCB / pesticides | <i>Xiphias gladius</i> | <i>Prionace glauca</i> |
|------------------|------------------------------|------------------------------|
| PCB - 49 | $0,85 \pm 0,21$ (0,7 – 1) | n.d |
| PCB - 60 | $0,83 \pm 0,31$ (0,5 – 1,1) | $0,53 \pm 0,06$ (0,5 – 0,6) |
| PCB - 66 | $2,18 \pm 0,52$ (1,4 – 2,9) | $1,53 \pm 0,42$ (1,2 – 2) |
| PCB - 82 | $0,91 \pm 0,37$ (0,5 – 1,4) | 0,9 |
| PCB - 87 | 0,7 | n.d |
| PCB - 99 | $0,6 \pm 0,46$ (0,2 – 1,3) | $0,31 \pm 0,13$ (0,1 – 0,5) |
| PCB - 105 | $0,4 \pm 0,27$ (0,1 – 0,8) | 0,2 |
| PCB - 118 | $0,76 \pm 0,61$ (0,2 – 1,9) | $0,63 \pm 0,21$ (0,4 – 1) |
| PCB - 138 | $1,4 \pm 1,6$ (0,4 – 5) | $0,6 \pm 0,14$ (0,5 – 0,8) |
| PCB - 153 | $1,26 \pm 1,20$ (0,5 – 4,5) | $0,57 \pm 0,34$ (0,3 – 1,2) |
| PCB - 170 | $0,45 \pm 0,26$ (0,2 – 0,9) | 0,1 |
| PCB - 180 | $0,67 \pm 0,6$ (0,2 – 2,2) | 0,2 |
| P,P-DDT | $0,81 \pm 0,71$ (0,1 - 2,6) | $0,45 \pm 0,11$ (0,3 – 0,7) |
| O,P-DDT | $0,2 \pm 0,08$ (0,1 – 0,3) | $0,14 \pm 0,05$ (0,1 – 0,2) |
| P,P-DDE | $2,5 \pm 2,33$ (1,1 – 7,6) | 1,5 |
| Σ PCB | $6,31 \pm 6,88$ (0,6 – 26,2) | $3,14 \pm 3,10$ (0,5 – 10,1) |
| Σ DDT | $2,53 \pm 3$ (0,1 – 10,5) | $0,73 \pm 0,44$ (0,5 – 1,9) |

Acknowledgements

We thank Andreia M. A. Gomes, Sérgio Coelho, Marcio Miranda. CNPq-PRONEX 0877 supported this work. Claudio EA Silva, M.Sc. received a M.Sc. Fellowship from CAPES/MEC. Dr. Torres is Selikoff Fellow at Mount Sinai/Queens College International Training Program of Environmental and Occupational Health and is partly funded by the Fogarty - NIH Grant 1 D43 TW00640.

References

1. In Monirith, Haruhiko Nakata, Shinsuke Tanabe and Touch Seang Tana (1999) Marine Pollution Bulletin Vol. **38**, No. 7, 604-612 pp.
2. Ralf Riedel, Daniel Schlenk, Donnell Frank, Barry Costa-Pierce, (2002) Marine Pollution Bulletin **44** 403–411pp.
3. M.M. Storelli, E. Ceci, A. Storelli, G.O. Marcotrigiano (2003) Marine Pollution Bulletin **46** 1035–1048pp.
4. Le Blanc, G.A., Bain, L.J., Wilson, V.S. (1997) Molec. And Cell. Endocrinology **126** 1-5pp
5. ENVIRONMENTAL HEALTH CRITERIA 9, (1979) DDT and its Derivatives 192 pp.
6. Smith, A. G., Gangoli, S.D. (2002) Food and Chemical Toxicology **40** 767–779pp.
7. EPA (1999) Polychlorinated Biphenyls (PCBs) Update: Impact on Fish advisores.
8. Storelli, M.M., Marcotrigiano, G.O. (2001) Marine Pollution Bulletin Vol. **42**, No. 12, 1323-1329 pp.