

MERCURY CONTENT IN SHARK SPECIES FROM THE SOUTH-EASTERN BRAZILIAN COAST

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(With 1 figure)

ABSTRACT

We present here the first results of Hg concentrations in three small shark species (*Rhizoprionodon lalandei*, *R. porosus* and *Mustelus higmani*) from the SE Brazilian coast. Mercury concentrations in *R. lalandei* ranged from 21.5 to 280.0 ng.g⁻¹ dry weight (d.w.) (average 74.6 ng.g⁻¹ d.w.; 17.9 ng.g⁻¹ wet weight). In *R. porosus*, concentrations ranged from 7.6 to 90.5 ng.g⁻¹ d.w. (average 42.2 ng.g⁻¹ d.w., 9.4 ng.g⁻¹ wet weight), whereas in *M. higmani*, concentrations ranged from 13.0 to 162.8 ng.g⁻¹ d.w. (average 54.9 ng.g⁻¹ d.w., 13.4 ng.g⁻¹ wet weight). These concentration ranges are very low compared with values reported for other large shark species of the Southwestern Atlantic Ocean. There was a significant positive correlation between Hg concentrations and individual size, suggesting that biomagnification is occurring in these animals.

Key words: mercury, sharks, biomagnification, SE Brazil.

RESUMO

Conteúdo de mercúrio em espécies de tubarão da costa Sudeste do Brasil

São apresentados os primeiros resultados sobre a concentração de Hg em três espécies de pequenos tubarões da costa SE brasileira (*Rhizoprionodon lalandei*, *R. porosus* e *Mustelus higmani*). As concentrações de Hg em *R. lalandei* variaram de 21,5 a 280,0 ng.g⁻¹ em peso seco (p.s.) (média de 74,6 ng.g⁻¹ p.s.; 17,9 ng.g⁻¹ em peso úmido). In *R. porosus*, variaram de 7,6 a 90,5 ng.g⁻¹ p.s. (média de 42,2 ng.g⁻¹ p.s., 9,4 ng.g⁻¹ em peso úmido), enquanto em *M. higmani* variaram de 13,0 a 162,8 ng.g⁻¹ p.s. (média de 54,9 ng.g⁻¹ p.s., 13,4 ng.g⁻¹ em peso úmido). Estas faixas de concentração são muito baixas quando comparadas com valores encontrados em espécies de grandes tubarões da costa do Atlântico Sul-Occidental. Foi verificada uma correlação positiva, significativa entre a concentração total de Hg e o tamanho dos indivíduos. Isto sugere a ocorrência de biomagnificação do Hg nesses animais.

Palavras-chave: mercúrio, tubarões, biomagnificação, Brasil sudeste.

INTRODUCTION

A relative increase of 1.2% to 1.5% per year of the mercury concentrations in the atmosphere over the Atlantic Ocean was reported recently (Slemr & Langer, 1992), suggesting an increasing of direct Hg load to this ocean. Thompson *et al.*

(1992) suggested a similar increase in oceanic deposition of Hg based on the analysis of seabird feathers. Also, significant increases in Hg fluvial inputs to the South-western Atlantic is taking place due to industrialization of most countries in this region (Lacerda *et al.*, 1993). This increase in the anthropogenic Hg load to the oceans may reflect

in pelagic fish Hg concentrations (Rolfhus & Fitzgerald, 1995), particularly in carnivorous fishes and, in special, sharks that occupy high trophic level in food chains, therefore accumulating more Hg than low trophic level species.

The setting of maximum permissible Hg concentrations in fish for human consumption in the range of 0.5 to 1.0 $\mu\text{g}\cdot\text{g}^{-1}$ on a wet weight basis (w.w.) by many countries, has triggered a process of surveying Hg concentrations in natural fish populations, in order to protect fisheries and their market. This is particularly true for large carnivorous species, such as sharks, where Hg content is positively correlated with size, and may surpass such limits in large specimens, even under natural conditions. Also, in these predatory species over 90% of the total Hg content is the highly toxic methyl-Hg (Lasorsa & Gill, 1995). For example, large (total length in excess of 2.0 m) mako shark (*Isurus oxyrinchus* Rafinesque) caught off South Africa, contain Hg in excess of the 1.0 $\mu\text{g}\cdot\text{g}^{-1}$ w.w. permissible limit (Watling *et al.*, 1981). Similarly, the Australian school shark *Galeorhinus australis* (Macleay), with total length in excess of 1.2 m, often shows Hg concentrations in excess of the 0.5 $\mu\text{g}\cdot\text{g}^{-1}$ w.w. limit in Victoria, Australia (Walker, 1976), whereas offshore species, with diet based on pelagic fish and cephalopods, systematically show Hg concentrations higher than 1.0 $\mu\text{g}\cdot\text{g}^{-1}$ (Walker, 1988). In Florida, USA, a survey of 124 individuals from 9 species of commonly commercialized sharks, showed that 33% of the animals have a methyl-Hg concentration higher than 1.0 $\mu\text{g}\cdot\text{g}^{-1}$ (Hueter *et al.*, 1995).

Along the SE coast of Brazil, there are some important nursery areas for pelagic shark species. One of these is the NE coast of Rio de Janeiro, which receives significant inputs of Hg from anthropogenic activities (Lacerda *et al.*, 1993). Due to the increasing relative importance of shark fisheries in Brazilian waters and the lack of data on the Hg content of sharks from this part of the South-western Atlantic Ocean, we carried out a survey of the Hg concentrations in Brazilian species, in order to establish background concentrations and relationships with fish size.

MATERIAL AND METHODS

Samples were collected off the coast of NE Rio de Janeiro at latitude 21°27'S and longitude 41°00'W, during the oceanographic REVIZEE pro-

gram of the Ministry of the Environment, Brazil. Shark species collected were *Rhizoprionodon lalandei* (Valenciennes, 1841) (n = 45), *Rhizoprionodon porosus* (Poey, 1861) (n = 12) and *Mustelus higmani* (Springer & Lowe, 1963) (n = 23). *Mustelus higmani* is a small shark reaching a maximum total length of about 1,000 mm. It lives in coastal waters to 100 m and feeds preferably on crustaceans, and exceptionally on squid and small fish. *Rhizoprionodon lalandei* is also a small fish reaching a maximum length of 800 mm. It inhabits very shallow coastal waters and feeds preferably on fish. *Rhizoprionodon porosus* is also a shallow water species, larger than *R. lalandei* that reaches about 1,000 mm and weights up to 4,500 g. It feeds on shrimps and squids (Figueiredo, 1977).

In general, the animals collected were very small, relative to most shark species from the Southwestern Atlantic, ranging from 230 to 500 mm in size and 300 to 1,100 g in weight. Samples were frozen after collection and transported in plastic bags to the laboratory. Sub-samples of muscle tissue (about 2.0 g) of each fish, were cut, lyophilized and Hg was analyzed through CVAAS.

The method used to prepare the samples for CVAAS was developed by Gonçalves & Paiva (1993). In summary, concentrated nitric acid (10 ml) was added to *circa* 0.5 g of lyophilized muscle tissue in a thermo kinetic reactor ("cold finger") at 70°C for one hour. After this pre-digestion, samples were cooled to ambient temperature and 50% (v/v) acid chloride (10 ml) were added and the samples, taken to the reactor and maintained at 70°C for one more hour. From these extracts, 10 ml were used to determine the Hg concentration. Mercury was reduced with 5 ml of 2% SnCl_2 and purged by a Hg-free air flow to a 2500 Bacharat Model Cold Vapor Atomic Spectrophotometer. Simultaneous determination of Hg in reference standards (NIST – USA, "Oyster tissue"; 60 $\text{ng}\cdot\text{g}^{-1}$), were also analyzed, showing good agreement with reference values ($61 \pm 4 \text{ ng}\cdot\text{g}^{-1}$). Since published surveys showed no effect of sex on Hg concentrations in sharks (Walker, 1976; Hueter *et al.*, 1995), all statistics used in this study used both sexes.

RESULTS AND DISCUSSION

Highest Hg concentrations (21.5 to 280.0 $\text{ng}\cdot\text{g}^{-1}$ d.w., average 74.6 $\text{ng}\cdot\text{g}^{-1}$ d.w.) were measured in *R. lalandei*, a piscivorous, coastal waters shark,

followed by *M. higmani* (13.0 to 162.8 ng.g⁻¹ d.w., average 54.9 ng.g⁻¹ d.w.) and *R. porosus* (7.6 to 90.5 ng.g⁻¹ d.w., average 42.2 ng.g⁻¹ d.w.), both with a more omnivorous diet based on mollusks and crustaceans (Table 1). Differences in Hg levels among species of similar lengths are probably associated with differences in growth rates (Walker, 1976). Also, food habits can contribute with such differences. In the absence of growth rates of most shark species from Brazilian waters, it is impossible to fully explain the inter-species differences found. However, a different Hg concentration in prey items of sharks has been previously reported. Juras (1988), studying the Hg concentrations in prey items of carnivorous fish from the northern Brazilian coast, found concentrations at least one order of magnitude higher in fish than in mollusks. Also, Marchovecchio *et al.* (1988a, b) reported lower concentrations in mollusks and crustacean eaten by sharks than in fish, from the northern coast of Argentina. Therefore, a piscivorous habit may explain, in part, the higher content in *R. lalandei* than in the other omnivorous species.

Table 2 compares the Hg concentrations in shark species from other areas of the Southwestern Atlantic Ocean, with the results obtained from SE

Brazil. The results obtained with the SE Brazilian species are much lower than most reported for other areas in the southwestern Atlantic Ocean. Apart from differences in Hg load, since the Argentinean fish were collected in more coastal areas (bays and estuaries), the small size of the species analyzed is probably the major reason for the differences observed. The sharks collected in Brazilian waters are much smaller than those from Argentinean waters. The Brazilian species, however, presented Hg concentrations similar to the lower end of the concentration range found in oceanic species from Australia (Walker, 1976, 1977).

Geographical variability has been reported as the major source of differences in Hg concentrations observed in sharks of similar size. Walker (1988) reported higher Hg concentrations in sharks from offshore compared to inshore waters, Hueter *et al.* (1995) found significant differences in Florida shark catches from the NE relative to the SE coast. These observed differences were probably associated with differences in food habit, different catch composition, both in species and in size of individuals, since the Hg loads to a given oceanic area, do not differ from another at least in the scale of hundreds of kilometers.

TABLE 1

Mercury concentrations (ng.g⁻¹), on a dry weight basis, in three shark species from the SE Brazilian coast.
n = number of individuals analyzed.

| Species | Size (mm) | n | Hg (range) | Hg (average) |
|--------------------------------|-----------|----|------------|--------------|
| <i>Rhizoprionodon lalandei</i> | 230-490 | 45 | 21.5-280.0 | 74.6 |
| <i>Mustelus higmani</i> | 250-490 | 23 | 13.0-162.8 | 54.9 |
| <i>Rhizoprionodon porosus</i> | 260-500 | 12 | 7.6-90.5 | 42.2 |

Positive relationships between Hg concentrations and fish size has been reported for most shark species. Notwithstanding the small size of the studied animals, significant, positive correlations were also found for the three species sampled (Fig. 1). The relationship found support the occurrence of biomagnification of Hg in these species and the dominance of methyl-Hg as the major Hg form present in the fishes. In *R. porosus*, size explained almost all of the differences found among individuals ($r^2 = 0.9512$, $P < 0.01$). The-

refore, it is possible, by using the equation in Fig. 1, to estimate the total Hg content in larger individuals, at least from this species, with total size similar to the animals analyzed in Argentinean waters, of about 1,000 mm. The result of such exercise gives about 400 ng.g⁻¹ w.w. which is in fairly agreement with the values found in Argentinean species of similar size (Marchovecchio *et al.*, 1988a, b; 1991; Scapini *et al.*, 1993). This suggests that maximum concentration limits can be reached by large animals of the species studied

in SE Brazil and support the launching of monitoring programs on the Hg concentration in this important fishery item. The data presented here

however, have to be viewed with care, since they are only preliminary and obtained on very small animals.

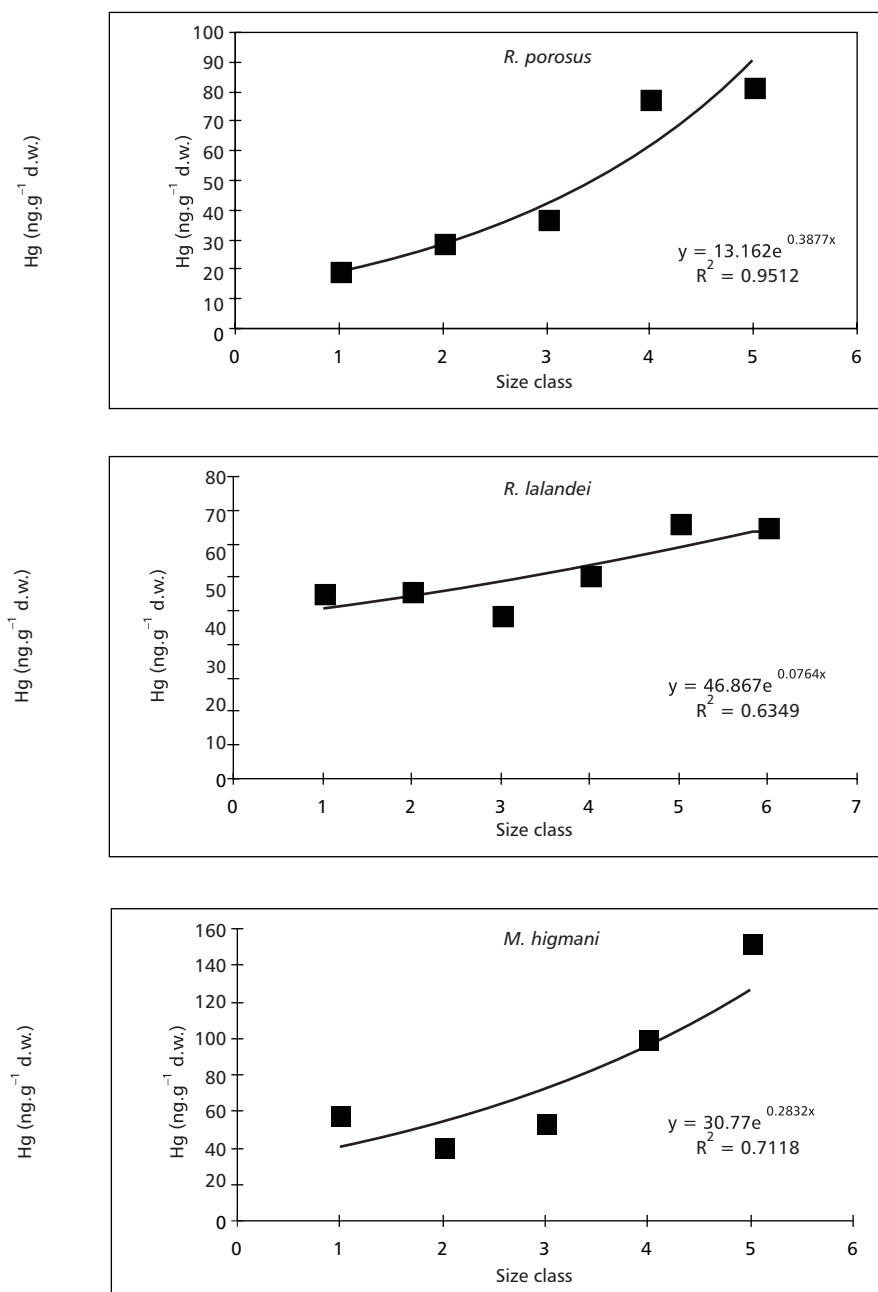


Fig. 1 — Relationship between Hg concentrations on a dry weight basis and size in three shark species from SE Brazil. (Class 1: 200 to 250 mm; Class 2: 250 to 300 mm; Class 3: 300 to 350 mm; Class 4: 350 to 400 mm; Class 5: 400 to 450 mm; Class 6: 450 to 500 mm).

TABLE 2
Mercury concentrations on a wet weight basis, in shark species from the South-western Atlantic coast compared to the concentrations found in Brazilian species.

| Species | Location | Size (mm) | Hg (ng.g ⁻¹ w.w.) | Author |
|--------------------------------|---------------------------------|-------------|------------------------------|------------------------------------|
| <i>Sympterygia bonapartei</i> | Bahia Blanca, Argentina | 290-505 | 180 ± 60 | Marcovecchio <i>et al.</i> (1988a) |
| <i>Myliobatis goodei</i> | " | 200-950 | 430 ± 140 | " |
| <i>Squalina argentina</i> | " | 185-470 | 480 ± 230 | " |
| <i>Mustelus schimitti</i> | " | 245-740 | 890 ± 290 | Marcovecchio <i>et al.</i> (1991) |
| <i>Halaeulurus bivius</i> | " | 960-1,350 | 2,510 ± 300 | " |
| <i>Notorhynchus</i> sp. | " | 1,180-1,300 | 2,990 ± 180 | " |
| <i>Mustelus schimitti</i> | Buenos Aires, Argentina | 600-1,150 | 450 ± 300 | Scapini <i>et al.</i> (1993) |
| <i>Galeorhinus viaminicus</i> | " | 550-850 | 340 ± 170 | " |
| <i>Sympterygia bonapartei</i> | Bahia Blanca estuary, Argentina | 310-490 | 100 ± 50 | Marcovecchio <i>et al.</i> (1988b) |
| <i>Squalina argentina</i> | " | 280-430 | 410 ± 260 | " |
| <i>Rhizoprionodon lalandei</i> | SE Brazil | 230-490 | 17.9 | This study |
| <i>Mustelus higmani</i> | " | 250-490 | 9.4 | " |
| <i>Rhizoprionodon porosus</i> | " | 260-500 | 13.4 | " |

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REFERENCES

- FIGUEIREDO, J. L., 1977, Manual de Peixes Marinhos do Sudeste do Brasil. Museu de Zoologia da Universidade de São Paulo, São Paulo, 103p.
- GONÇALVES, G. O. & PAIVA, E. C., 1993, *Determinação de Mercúrio Total em Amostras Sólidas*. IT 003, nº 6, CETEM, Rio de Janeiro, 23p.
- HUETER, R. E., FONG, W. G., HENDERSON, G., FRENCH, M. F. & MANIRE, C. A., 1995, Methylmercury concentrations in shark muscle by species, size and distribution in Florida coastal waters. *Water Air & Soil Pollut.*, 80: 893-899.
- JURAS, A. A., 1988, A preliminary survey of heavy metals concentrations in some estuarine organisms in the littoral zone of São Luís Island, Maranhão, Brazil, pp. 16-20. In: U. Seeliger, L. D., Lacerda & S. R. Patchineelam (eds.), *Metals in coastal Environments of Latin America*. Springer Verlag, Berlin, 297p.
- LACERDA, L. D., 1997, Atmospheric mercury and fish contamination in the Amazon. *Ciência & Cultura*, 49: 54-57.
- LACERDA, L. D., CARVALHO, C. E. V., REZENDE, C. E. & PFEIFFER, W. C., 1993, Mercury in sediments from the Paraíba do Sul River continental shelf, SE-Brazil. *Mar. Pollut. Bull.*, 26: 220-222.
- LASORSA, B. & GILL, S. A., 1995, The methylmercury to total mercury ratio in selected marine, freshwater, and terrestrial organisms. *Water Air & Soil Pollut.*, 80: 905-913.
- MARCOVECCHIO, J. E., MORENO, V. J. & PÉREZ, A., 1988a, Determination of heavy metal concentrations in biota of Bahia Blanca, Argentina. *Sci. Tot. Environm.*, 75: 181-190.
- MARCOVECCHIO, J. E., MORENO, V. J. & PÉREZ, A., 1988b, Total mercury levels in marine organisms of the Bahia Blanca estuary food web, Argentina, pp. 122-129. In: U. Seeliger, L. D. Lacerda & S. R. Patchineelam (eds.), *Metals in Coastal Environments of Latin America*. Springer Verlag, Berlin.
- MARCOVECCHIO, J. E., MORENO, V. J. & PÉREZ, A., 1991, Metal accumulation in tissues of sharks from Bahia Blanca estuary, Argentina. *Mar. Environm. Res.*, 31: 263-274.
- ROLFHUS, K. R. & FITZGERALD, W. F., 1995, Linkage between atmospheric mercury deposition and the methylmercury content of marine fish. *Water Air & Soil Pollut.*, 80: 291-297.

- SCAPINI, E. M., ANDRADE, S. & MARCOVECCHIO, J. E., 1993, Total mercury distribution in two shark species from Buenos Aires province coastal waters, in Argentina. *Proc. Intern. Conf. Heavy Metals in the Environment, Toronto, 1*: 82-85.
- SLEMR, F. & LANGER, E., 1992, Increase in global atmospheric concentrations of mercury inferred from measurements over the Atlantic Ocean. *Nature*, 355: 434-437.
- THOMPSON, D. R., FURNES, R. W. & WALSH, P. M., 1992, Historical changes in mercury concentrations in the marine ecosystems of the north and north-east Atlantic Ocean as indicated by seabird feathers. *J. Appl. Ecol.*, 29: 79-84.
- WALKER, T. I., 1976, Effects of species, sex, length and locality on the mercury content of school shark *Galeorhinus australis* (Macleay) and gummy shark *Mustelus antarcticus* Guenther from south-eastern Australian waters. *Austr. J. Mar. Freshwater Res.*, 27: 603-616.
- WALKER, T. I., 1977, Statistical comparison of the results from six analytical chemistry laboratories of the mercury content of muscle tissue of two species of sharks. *Inter. J. Environm. Anal. Chem.*, 5: 25-33.
- WALKER, T. I., 1988, Mercury concentrations in edible tissues of elasmobranchs, teleosts, crustaceans and mollusks from south-eastern Australian waters. *Austr. J. Mar. Freshwater Res.*, 39: 39-49.
- WATLING, R. J., MCCLUNG, T. P. & STANTON, R. C., 1981, Relation between mercury concentration and size in the Mako shark. *Bull. Environm. Cont. Toxicol.*, 26: 352-358.