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Guiana Dolphins (*Sotalia guianensis*, Van Benédén 1864) as Indicators of the Bioaccumulation of Total Mercury along the Coast of Rio de Janeiro State, Southeastern Brazil

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Abstract Total mercury (Hg) was determined in muscle tissue of 20 Guiana dolphins stranded along the coast of Rio de Janeiro state, Brazil, with a mean of 1.07 µg/g wet weight. Mercury concentrations were positively related to body length, possibly related to the capacity of the dolphins to bioaccumulate this element throughout life. The Hg concentrations were not significantly different between males and females, although females (1.08 µg/g) showed slightly higher levels than males (1.04 µg/g). Concentrations were low when compared to results of studies carried out with small cetaceans in the Northern Hemisphere, and with previous studies in the Southeastern Brazil.

Keywords Guiana dolphin · *Sotalia guianensis* · Mercury · Brazil

In the last several decades, a huge increase in the number of chemical industries has occurred. This has resulted in the presence of increased amounts of many chemical pollutants, including Hg, in the marine environment. This trend has impacted environmental integrity, biodiversity and human health (Fleming et al. 2006; Moura et al. 2011). There is considerable evidence that background levels of mercury in the environment have been increasing in the past century. This evidence comes from studies of lakes and ocean sediment profiles and ice cores, in remote and industrialized regions of the planet (Outridge et al. 2007). Most wildlife is exposed to Hg primarily as MeHg through diet, rather than to other chemical forms of Hg. Due to its lengthy persistence and high mobility in the ocean, mercury shows a high level of biomagnification in the upper levels of the food web (O'Shea 1999).

Cetaceans have been considered bioindicators for the health of the marine environment, mainly due to their biological characteristics and feeding habits (Aguilar et al. 1999). These marine mammals are top predators in the marine trophic web, and have long life-spans. Therefore, they are highly exposed to persistent contaminants, like Hg, through bioaccumulation and biomagnification processes (O' Shea 1999). Due to its nearshore distribution (<50 m deep), the Guiana dolphin (*Sotalia guianensis*) is especially vulnerable to the effects of the pollution in coastal waters along its distribution from Santa Catarina, Brazil, to Nicaragua in the Caribbean coast (Fig. 1). Therefore some concerns regarding possible adverse effects of toxic chemicals on this coastal dolphin have been noted, mainly related to the emerging infectious diseases that have been detected in some populations along the Brazilian coast (Van Bressem et al. 2009). The aim of this study was to evaluate the concentrations of total mercury in muscle tissues of Guiana dolphins found stranded along the north-central coast of the Rio de Janeiro State, Brazil.

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Materials and Methods

The study area comprised about 300 km of coastline, from São Francisco de Itabapoana (north, 21°25′10″S; 41°00′36″W) to Saquarema (south, 22°55′12″S; 42°30′37″W) in Rio de Janeiro State, South-eastern Brazil (Fig. 1). The coastline of the study area was regularly patrolled once a month to search for stranded marine mammals. In addition, during these surveys, awareness campaigns were implemented in the communities along the coast in order to promote a collaboration network and improve stranding reports. Muscle samples of 20 dead Guiana dolphins stranded from 2002 to 2008 were collected and stored frozen in plastic bags at −20°C prior to laboratory analysis. Necropsies of each dolphin were performed for the collection of biological material, biometric measurements and sex determination according to the protocol of Geraci and Lounsbury (2005). The muscle samples were collected in the dorsal region of the dolphins. Only fresh or initially decomposed dolphins were included in this study. The body length of the animals was measured along the longitudinal axis of the body, from the tip of the upper jaw to the caudal notch.

Approximately 0.5 g of tissue were weighed and digested with a 1:1 mixture of sulfuric and nitric acid, in the presence of 0.01% vanadium pentoxide (Vega et al. 2009). The digestion temperature was 80°C, and oxidation was completed by the addition of sufficient volume of 5% m/v potassium permanganate solution. Immediately before the instrumental analysis the oxidant excess was reduced with a 20% m/v solution of hydroxylammonium chloride and diluted to 50 mL. Mercury levels were determined using cold vapor atomic absorption spectrometry with a model AA5 Varian atomic absorption spectrometer, the detection limit being 0.05 μg/L. Calibration was performed with external calibration curves prepared using adequate dilutions of 1,000 μg mL^{-1} standard solutions prepared from Titrisol (Merck, Darmstadt, Germany) ampoules diluted with 0.2% v/v nitric acid. Analyte addition tests demonstrated the adequacy of this calibration procedure, as well as the lack of any multiplicative matrix effect.

Quality control was performed by a strict blank control, the analysis of replicates and certified reference materials. Accuracy was assessed through the analysis of certified material DORM-1 (Hg: 798 ± 74 $\eta g\ g^{-1}$) from NIST (National Institute of Standards and Technology; http://www.nist.gov). Average recovery values were always ≥90% of the certified values. Reproducibility was evaluated using the coefficient of variation of the replicates, which was always less than 25%.

An independent T-test was used to verify the differences between the mean metal concentrations of males and females. A simple linear regression (R^2; significance at $p < 0.05$) was used to further explore the relationship between the metal concentrations as a function of total length (TL) of individuals. Statistical analyses were performed using the software Windows SPSS (http://www-01.ibm.com/software/analytics/spss/).

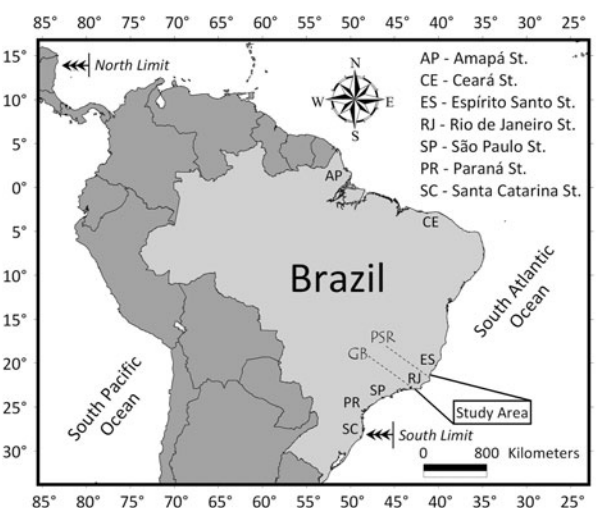

Fig. 1 Study area, from São Francisco de Itabapoana to Saquarema, Rio de Janeiro State. *Arrows* showing the northern (Nicaragua, Caribbean Sea) and southern (Santa Catarina, Southern Brazil) limits of the distribution of Guiana dolphins (*Sotalia guianensis*). The abbreviations refer to the states mentioned in the text and other sites cited, such as Guanabara Bay (GB) and the Paraíba do Sul River (PSR)

Results and Discussion

The presence of Hg was detected in all samples. Concentrations are expressed on a wet weight basis (ww). Dry weight (dw) basis concentration in literature was converted to wet weight (ww) basis concentrations, assuming a moisture content of 70% based on the results of Yang and Miyazaki (2003). The mean concentration of total Hg was 1.07 ± 0.35 μg g^{-1} ww, ranging from 0.2 to 1.66 μg g^{-1} ww (Table 1).

Mercury concentrations in muscle tissue remained within the range of observed values for other studies carried out with *S. guianensis*. Carvalho et al. (2008) found similar Hg levels in muscle tissue of this species from the northern coast of the Rio de Janeiro state, which is probably the same population of the dolphins as those in the present study. These authors found relatively high concentrations of Hg in cutlassfish (*Trichiurus lepturus*) muscle tissue, increasing with weight and body length. Kehrig et al. (2009) analyzed the trophic transfer of Total Hg in muscle from this main prey species to *S. guianensis* in northern Rio de Janeiro state. The Guiana dolphin contained the highest Hg level (3.28 ± 1.69 μg g^{-1} dw)

Table 1 Biological data and total mercury concentration (μg g^{-1} wet weight) of Guiana dolphins (*Sotalia guianensis*) stranded in the central-north coast of the Rio de Janeiro State, Brazil

GEMM number	Date	Latitude[a]	Longitude[a]	Sex	Body length (cm)	Hg
GEMM 034	23 August 2002	−23.01099	−43.35789	♀	153	0.20
GEMM 137	04 October 2007	−22.51762	−41.91754	♂	170	0.73
GEMM 153	10 August 2008	−22.10337	−41.14559	♀	–	0.74
GEMM 111	13 September 2006	−22.73284	−41.96547	♂	165	0.78
GEMM 104	21 June 2006	−22.71121	−41.98802	♂	183	0.84
GEMM 108	11 July 2006	−22.11558	−41.16797	♂	194	0.86
GEMM 125	13 July 2007	−21.62777	−41.0136	♂	187	0.89
GEMM 126	13 July 2007	−21.62567	−41.01343	♀	168	0.93
GEMM 123	22 May 2007	−21.55096	−41.06550	♀	179	0.97
GEMM 040	11 September 2002	−22.590038	−41.987867	–	70	1.00
GEMM 129	01 August 2007	−21.63227	−41.0141	♂	183	1.13
GEMM 041	23 November 2002	−22.55906	−41.97800	–	–	1.23
GEMM 073	18 November 2004	−22.72726	−41.97816	♀	180	1.25
GEMM 096	13 February 2006	−22.20045	−41.44670	♂	196	1.26
GEMM 128	31 July 2007	−21.40073	−40.9987	♂	183	1.26
GEMM 089	24 September 2005	−22.94508	−42.17465	♀	177	1.36
GEMM 105	28 June 2006	−22.9347	−42.49793	♀	174	1.37
GEMM 114	14 October 2006	−22.21029	−41.48050	♀	182	1.42
GEMM 050	05 November 2003	−22.09690	−41.13579	♀	186.5	1.52
GEMM 131	22 August 2007	−21.90109	−40.98497	♂	198	1.66

[a] Latitude and longitude presented in decimal degrees

followed by *T. lepturus* (1.07 ± 1.06), which is situated below this dolphin in the trophic scale. Mercury levels for other prey species were 0.26 ± 0.13 (*Paralonchurus brasiliensis*), 0.25 ± 0.17 (*Anchoa filifera*), 0.25 ± 0.11 (*Pellona harroweri*), 0.22 ± 0.13 (*Isopisthus parvipinis*), 0.30 ± 0.11 (*Cynoscion jamaicensis*) and 0.20 ± 0.09 (*Loligo sanpaulensis*). Guiana dolphins contained about 3.1 times the Hg levels compared to the *T. lepturus*, and more than 10 times the other prey species analyzed.

The diet of this small cetacean is comprised of demersal fishes, squid and crustaceans, but fishes seem to provide the principal biomagnification route of Hg (Di Beneditto and Siciliano 2007; Seixas et al. 2009).

Mercury concentrations in dolphin muscle in the present study indicate that the levels are not high compared to concentrations observed in small dolphins from other regions around the world (Table 2). Nevertheless, hepatic Hg concentrations in small cetaceans from the Brazilian coast, including *S. guianensis*, have indicated similar values from those observed in cetaceans from highly polluted areas in the northern hemisphere, such as the Mediterranean Sea and Asia (Kunito et al. 2004).

Previous studies of Hg concentrations in sediment and lagoons carried out in the northern coast of Rio de Janeiro state have attributed the Hg levels in these areas to the former gold mining activity in the Paraiba do Sul River basin, and the high past use of Hg-containing fungicides. In addition, according to Knoppers and Pollehne (1991) the coast of the Rio de Janeiro state receives metals, nutrients and inorganic particles mainly from the Guanabara Bay, an area highly polluted by municipal sewage and industries, and from the Paraiba do Sul River, which exports suspended materials and metals released by chemical industries.

No statistical differences ($p > 0.05$) were observed in Hg levels regarding gender. Mean Hg concentrations were 1.08 ± 0.42 and 1.04 ± 0.30 μg g^{-1} (ww) for females and males, respectively. In general, no significant differences in Hg concentrations have been observed in tissues of females and males of marine mammals (O'Shea 1999). This same lack of variation in Hg concentrations by gender in Guiana dolphins has been observed in other studies (Monteiro-Neto et al. 2003; Kunito et al. 2004; Seixas et al. 2009).

It is widely accepted that Hg levels are positively related to the size and age of dolphins. Confirming this trend, a positive relationship between Hg concentration and body length was also observed in the *S. guianensis* specimens from this study (Fig. 2). However, while in females the relationship was strong and statistically significant ($R^2 = 0.829$; $p = 0.002$), in males the observed relationship ($R^2 = 0.441$) was not ($p = 0.051$). The lack of statistical significance in males may be related to the small sample size (n = 09). In addition, no calves or juveniles were present in our samples, which could minimize the

Table 2 Means, standard deviations and ranges of total mercury concentrations (μg g^{-1} wet weight) in muscle tissues of several small cetaceans from areas around the world

Species	Hg	Localities	n	Ref
Tursiops truncatus	2.85 (0.63–5.1)	Portugal, Atlantic Ocean	2	(a), *
Tursiops truncatus	8.9 ± 12 (0.37–39)	Israel, Mediterranean	17	(b)
Tursiops truncatus	12.78 (1.59–25.5)	France, Atlantic Ocean	5	(c), *
Tursiops truncatus	(0.22–0.77)	Australia	–	(d)
Tursiops truncatus	100	Corsica, Mediterranean	1	(e), *
Tursiops truncatus	9.55 ± 6.01 (2.36–22.5)	Japan	9	(f)
Tursiops truncatus	2	South Africa	3	(g), *
Tursiops gephyreus	5.5 ± 0.8	Argentina	2	(h)
Stenella longirostris	1.39 ± 0.30 (0.84–1.76)	Taiwan	9	(i)
Stenella longirostris	0.47 (0.4–0.57)	Gulf of California, Mexico	9	(J), *
Stenella longirostris	1.1 (0.87–1.33)	Sta Lucia, Caribbean	2	(k)
Stenella coeruleoalba	15.9	Italy, Mediterranean	39–51	(l), *
Stenella coeruleoalba	15 ± 27.1 (1.04–63.4)	Japan	5	(f)
Phocoena phocoena	3.5 ± 14.4 (0.2–108)	Germany—Baltic and North Sea	57	(m)
Stenella attenuata	3.64 ± 2.21 (1.05–12)	Taiwan	53	(i)
Globicephala macrorhynchus	9 (8.19–9.84)	New Caledonia	2	(n), *
Sotalia guianensis	0.7 (0.2–2.5)	Guanabara Bay, RJ, Brazil	15	(o)
Sotalia guianensis	1.8 ± 0.46	Espírito Santo state, Brazil	5	(p)
Sotalia guianensis	0.73 (0.34–1.42)	Northern Rio de Janeiro state	6	(q)
Sotalia guianensis	0.98	Northern Rio de Janeiro state	21	(r), *
Sotalia guianensis	1.07 ± 0.35 (0.2–1.66)	Rio de Janeiro state, Brazil	20	(s)

Ref references

* Converted from dry weights assuming 70% moisture content (Yang and Miyazaki, 2003)

(a) Carvalho et al. (2002); (b) Roditi-Elasar et al. (2003); (c) Holsbeek et al. (1998); (d) Kemper et al. (1994); (e) Frodello et al. (2000); (f) Endo et al. (2003); (g) Henry and Best (1999); (h) Marcovecchio et al. (1990); (i) Chen et al. (2002); (j) Ruelas et al. (2000); (k) Gaskin et al. (1974); (l) Monaci et al. (1998); (m) Siebert et al. (1999); (n) Bustamante et al. (2003); (o) Kehrig et al. (2004); (p) Lopes et al. (2008); (q) Carvalho et al. (2008); (r) Kehrig et al. (2009); (s) This study

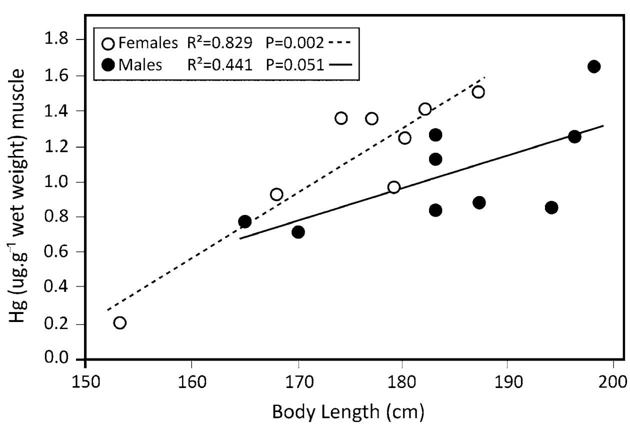

Fig. 2 Relationship between body length and Hg concentrations in muscle tissue of male and female Guiana dolphins (*Sotalia guianensis*) from the northeast coast of the Rio de Janeiro state, southeastern Brazil

power of the relationship (Di Beneditto and Ramos 2004). A similar pattern of Hg accumulation with body length was observed in Guiana dolphins from the coast of Ceará state (Monteiro-Neto et al. 2003), from the northern coast of the Rio de Janeiro state (Carvalho et al. 2008) and with age in *S. guianensis* from São Paulo and Paraná states (Kunito et al. 2004). The relationship between metal accumulation and cetacean size may be a consequence of a higher capability to bioacumulate elements throughout their life span than to eliminate them. The strong positive relationship of Hg and length in females suggest that the transference and elimination of body concentration to calves through milk and placenta is not significant in *S. guianensis*, as already observed in other species of dolphins. According to Itano et al. (1984) the proportion of the gestational transference of Hg levels to the fetus is only 0.4%–1% of the maternal burden in striped dolphins (*Stenella coeruleoalba*). These authors also found very low levels being transferred through milk to the newborns.

The positive relationship between Hg and size in muscle of males is due to the bioaccumulative capability of this tissue throughout the lives of the dolphins. In addition, as the size of the prey and the quantities of food ingested tend to increase in proportion to the growth of the dolphins, trophic supplies of the metal may also progressively increase (Monteiro-Neto et al. 2003).

The present work adds new information on Hg concentrations in muscle tissue of a small coastal dolphin from southwestern Atlantic. This coastal dolphin has been extensively impacted by fishery activities, habitat loss and skin lesion, but the conservation policies of this cetacean also have to consider its vulnerability to environmental contaminants such as metals that have been detected in the tissues analyzed. Relatively low concentrations of total Hg were found in muscle tissue of Guiana dolphins when compared with other small cetaceans worldwide, particularly from the northern hemisphere. As observed in several other cetacean species, Hg concentrations presented positive relationships to body length, likely related to the capacity to bioaccumulate this element throughout life. Mercury concentrations were not significantly different between males and females, although females showed slightly higher levels than males. Further epidemiological studies should test the relationship of metal concentration with pathologic findings in this dolphin.

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