Bull Environ Contam Toxicol (2012) 89:434–438
DOI 10.1007/s00128-012-0680-1

Mercury and Selenium in a Top-Predator Fish, *Trichiurus lepturus* (Linnaeus, 1758), from the Tropical Brazilian Coast, Rio de Janeiro

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Received: 19 February 2012 / Accepted: 7 May 2012 / Published online: 22 May 2012

Abstract Muscular mercury and selenium were assessed in a voracious fish from three Brazilian coastal areas with different environmental conditions. Mercury was higher in specimens from Ilha Grande Bay (0.35 ± 0.17 μg g^{-1}) than in cutlassfish from Guanabara Bay (0.30 ± 0.15 μg g^{-1}) and Buzios coast (0.13 ± 0.08 μg g^{-1}), respectively. No difference was found regarding selenium among these areas. Mercury was positively correlated with fish length and size intervals (sub-adult, small and large adult), suggesting that larger and older fish bioaccumulated more mercury. A large excess of molar selenium in relation to mercury was observed.

Keywords Trace elements · Top predator · Environmental conditions · Se:Hg molar ratio · South Atlantic Ocean

Mercury (Hg) is a pervasive pollutant that plays no biochemical function and accumulates in the tissues of organisms as they grow. Conversely, selenium (Se) is recognized as an essential element for metabolic activity of aquatic organisms, acting as a protective agent against the toxicity of Hg in the form of methylmercury (MeHg) (Peterson et al. 2009). Various hypotheses for Se protective mechanism in aquatic organisms have been proposed (Peterson et al. 2009). One of the most comprehensive involves the formation of highly stable organic MeHg-selenocysteine (MeHg-SeCys) that form in the muscle tissues of Hg stressed organisms, such as fish (Ralston et al. 2008). In the South Atlantic Ocean, several studies have reported Hg and Se concentrations in marine organisms, but information about Se in top-predator fish is still scarce. Furthermore, tropical coastal waters are less monitored than marine environments in the Temperate and Polar Regions, in particular the South Atlantic Ocean, which is often considered less contaminated then the northern ocean.

There is a need for a basin-wide and systematic approach to sampling and analysis of trace elements in fish from different tropical coastal areas. This means selecting species that are representative of the location from which they are captured. The present study makes an initial contribution to this task by presenting Hg and Se data from three different areas along the Rio de Janeiro State (Southeastern Brazilian coast). For this purpose, a predatory fish, *Trichiurus lepturus* (cutlassfish) was sampled in three coastal ecosystems with different degradation levels and environmental conditions (Ilha Grande Bay, Guanabara Bay and Buzios coast) (Fig. 1). In addition, the sampling areas were compared according to the levels of Hg, Se and Se:Hg molar ratios in fish, and consequently the Hg exposure were evaluated. This fish species are useful for this purpose because it is commonly consumed by local population, easily identified and also they may be considered good Hg bioindicator.

Materials and Methods

Among the sampling areas considered in the present study, Ilha Grande Bay—IB (total area: 3,100 Km^2; 22°50′S and

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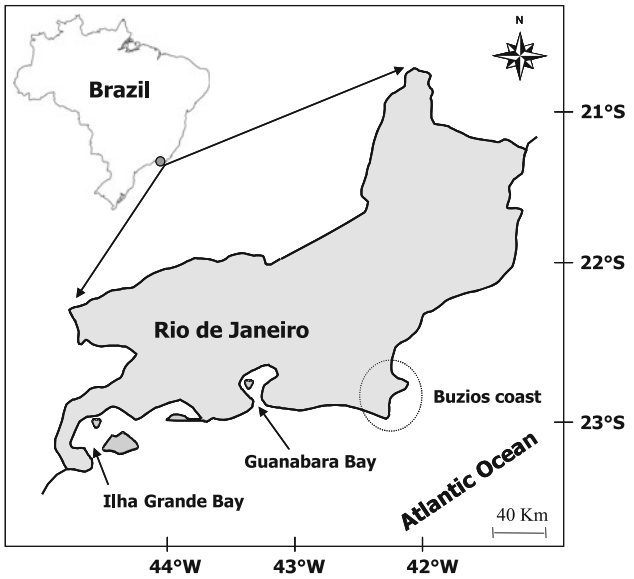

Fig. 1 *Trichiurus lepturus* sampling areas along the Rio de Janeiro state coast

23°20′S; Fig. 1) presents the most preserved ecosystem and it is considered to be a biodiversity hotspot and includes a high number of protected areas (Bisi et al. 2012). Conversely, Guanabara Bay—GB (total area: 384 Km^2; 22°40′S and 23°00′S; Fig. 1) presents the most degraded ecosystem and also, is the most studied area in the Brazilian coast (Bisi et al. 2012). Buzios coast—BC (22°44′S, 41°52′W; Fig. 1) is a region characterized by the occurrence of coastal upwelling events driven by the wind (Carbonel 1998) that induces a particularly dry climate. This region presents a totally different climatic regime when compared to GB and IB. A total of 64 specimens of cutlassfish with different total body lengths (L) were acquired from local fishermen, between 2009 and 2010. After sampling, the biological characteristics of each individual were obtained, and sub-samples of dorsolateral muscle were removed. The specimens presented total length varying from 84.4 to 130.0 cm (mean = 100.5 cm), 62.2–123.0 cm (mean = 87.5 cm) and 81.0-103.0 cm (mean = 95.5 cm) for IB, GB and BC, respectively. Fish were classified according the size intervals reported by Martins et al. (2005) for cutlassfish from the South Western Atlantic (L > 100 cm—large adult; L, 70–100 cm—small-adult; L, 30–70 cm—sub-adult). All samples taken were freeze-dried and sheltered from light until analysis. After the procedure of lyophilization the muscle samples lost around 75 % of their water content.

For Hg analysis, dried samples (0.05 g) were digested in a sulphuric-nitric acid mixture. Hg was determined by cold vapor atomic absorption spectrometry, using $NaBH_4$ as a reducing agent. A detailed description of the method used is given elsewhere (Kehrig et al. 2009a). For Se, the samples (0.05 g) were digested in nitric acid and Se content was determined by graphite furnace atomic absorption spectrometry, using palladium nitrate as chemical modifier. A detailed description of the method used is given elsewhere (Kehrig et al. 2009a). The limits of detection were 0.05 μg L^{-1} and 0.80 μg L^{-1} for Hg and Se, respectively.

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-2 (Hg: 4.60 ± 0.45 mg Kg^{-1}; Se: 1.38 ± 0.09 mg Kg^{-1}) from the National Research Council-Canada. 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 15 %.

Data was tested for normal distributions and non-parametric tests were then applied. An analysis of variance (Kruskal–Wallis ANOVA) was used to verify the differences among the sampling areas. A simple linear regression (R^2; significance at $p < 0.05$) was used to further explore the relationship between the elements concentrations as a function of L. Statistical analyses were performed using STATISTICA® 7.0 for Windows (StatSoft, Inc. 1984–2004, USA).

Results and Discussion

Mean Hg and Se concentrations (μg g^{-1} dry wt.) in muscle tissue of cutlassfish, the ratios of molar concentrations of Se to Hg in cutlassfish from this study, as well as the respective biological parameters and size intervals are summarized in Table 1. The results were of the same order of magnitude as those reported in earlier studies with the same species from some South America regions (Table 1). However, it is difficult to compare data for Hg and Se in species that live in different environments, since the prevalent environmental conditions, and also other factors, such as the level of food contamination can to influence on Hg and Se accumulation. It is known that Hg and Se in fish tissues is expected to vary in a wide range of concentration, reflecting feeding behavior and exposure to environmental levels (Reinfelder et al. 1998).

No significant difference ($p > 0.05$) in L was found between the individuals from the three sampling areas, suggesting that both groups are equally represented in the sampled groups, making it possible to directly compare inter-site differences regarding Hg and Se concentrations. However, despite the fact that fish collected at all areas presented similar L, they are not necessarily of the same size intervals. The specimens from IB and BC were presented in two different size intervals (see Table 1) while the specimens from GB were constituted by three different size intervals (see Table 1).

Table 1 Mean Hg and Se concentrations (μg g^{-1} dry wt.) in muscle tissue of *Trichiurus lepturus* collected from some regions of South America, the ratios of molar concentrations of Se to Hg in *T. lepturus* from this study, as well as the respective biological parameters and size intervals

Total length (L in cm)	N	Size intervals	Hg	Se	Se:Hg molar ratios	Location	Ref
(70.0–100.0)	13	Small adult	0.30 ± 0.08	0.79 ± 0.49	6.78 ± 4.32	IB	a
(101.5–130.0)	8	Large adult	**0.44 ± 0.23***	1.25 ± 1.09	9.82 ± 8.73		
		Mean	0.35 ± 0.17	0.96 ± 0.78	7.52 ± 6.78		
(62.0–69.0)	4	Sub-adult	0.20 ± 0.03	1.10 ± 0.20	13.97 ± 2.37	GB	a
(71.0–100.0)	18	Small adult	0.25 ± 0.06	0.94 ± 0.05	9.55 ± 6.10		
(104.5–138.0)	6	Large adult	**0.50 ± 0.21***	0.94 ± 0.12	4.78 ± 3.66		
		Mean	0.30 ± 0.15	1.01 ± 0.17	9.43 ± 4.60		
(81.0–100.0)	12	Small adult	0.12 ± 0.09	0.93 ± 0.57	24.05 ± 16.25	BC	a
(101.0–103.0)	3	Large adult	0.13 ± 0.09	0.71 ± 0.51	16.25 ± 9.56		
		Mean	0.13 ± 0.08	0.88 ± 0.55	22.49 ± 3.74		
63.1 ± 10.1	104		0.50 ± 0.25	–	–	Northeastern Brazil	b
(45.0–150.0)	17		1.07 ± 1.06	1.02 ± 0.17	–	North Rio de Janeiro	c
141.0 ± 6.2	12		1.30 ± 0.90	–	–	North Rio de Janeiro	d
(62.0–120.0)	18		0.77 ± 0.37	–	–	GB	e
–	5		0.09 ± 0.68	–	–	IB	f
–	6		0.15 ± 0.04	–	–	South Rio de Janeiro	f

* Significant higher ($p < 0.05$) than others size intervals—in bold

a, This study; b, Costa et al. (2009); c,Kehrig et al. (2009b); d, Di Beneditto et al. (2012); e, Kehrig et al. (2010); f, Bisi et al. (2012)

Data analysis showed that the size intervals and/or L seem to influence muscular Hg accumulation in fish specimens collected at IB ($R^2 = 0.38$; $p < 0.05$) and GB ($R^2 = 0.37$; $p << 0.05$), since the large adult specimens presented the highest Hg concentrations in both areas. *T. lepturus* from these areas presented similar Se concentrations. The size intervals and/or L presented no significant influence on Se accumulation by the specimens from IB and GB (see Table 1). The positive correlation found between muscular Hg concentrations and the L of cutlassfish is in accordance to others studies conducted with this fish species (Costa et al. 2009). The ongoing accumulation can be explained by the fact that MeHg, that constitutes the major fraction of Hg in the muscle of predatory fish, binds strongly to thiol groups of proteins whose content increases with L (Sfezer et al. 2003). In general, the adult specimens of top-predators fish present the highest muscular Hg concentrations as a consequence of the MeHg biomagnification process along the aquatic food web (Kehrig et al. 2010), since the trophic transfer of trace elements from prey to predator has been recognized as an important route for the incorporation and bioaccumulation of Hg and Se by aquatic animals (Kehrig et al. 2010). A weak and positive correlation was found between Se concentrations in muscle tissue and L of cutlassfish from IB ($R^2 = 0.16$; $p > 0.05$). More weak and negative correlations were found between Se concentrations in muscle tissue and L of cutlassfish from GB ($R^2 = 0.10$; $p > 0.05$) and BC ($R^2 = 0.004$; $p > 0.05$), indicating that the accumulation of Se in this fish species did not necessarily take place with the increase in L, as in the case of Hg. A similar pattern was observed by Branco et al. (2007) in a study with two predatory fish species (swordfish and blue shark) from two areas in the North Atlantic Ocean close to the line of Equator. These fish species presented negative correlations between muscular Se and L.

Significant regional differences ($p < 0.05$) were observed regarding Hg accumulation in cutlassfish. In general, specimens collected in IB presented the highest Hg concentrations (0.35 ± 0.17 μg g^{-1} d.w.), followed by GB (0.30 ± 0.15 μg g^{-1} d.w.) and BC (0.13 ± 0.08 μg g^{-1} d.w.). However, the mean Se concentrations found in the muscle tissue of cutlassfish from these areas can be considered similar (Kruskal–Wallis ANOVA; $p > 0.05$), since no significant difference was observed among them: IB (0.96 ± 0.78 μg g^{-1} d.w.), GB (1.01 ± 0.17 μg g^{-1} d.w.) and BC (0.88 ± 0.55 μg g^{-1} d.w.). The lowest Hg concentrations found in cutlassfish from BC could be related to the upwelling events that occur in this area. According to Bargagli et al. (1998), the low temperature of the marine coastal water affects the metabolic rate of organisms and could reduce inorganic mercury (Hg^{2+}) methylation rates by heterotrophic microorganisms. Methylation rates appear to be correlated with primary productivity (Mason and Fitzgerald 1996). Consequently less Hg, in the form of MeHg, can be incorporated into this food chain. Furthermore, in the upwelling zones, MeHg is converted into elemental Hg, leading to a supersaturation of the elemental

species in surface waters (Poissant et al. 2002). The highest Hg concentrations found in cutlassfish from IB and GB can be explained by the fact that, in these areas, Hg methylation can take place both in the water column near the oxycline and in the sediment (Rolfus and Fitzgerald 1995). The MeHg formed in these places is transported to the mixed layer where it can be accumulated in the food chain. This accumulation can be observed in communities that live in sediments and in the water column, such as phytoplankton and zooplankton (Poissant et al. 2002). Between the bay regions, cutlassfish from GB presented lower Hg concentrations than fish from IB. It was observed that the eutrophication conditions of GB influences the bioavailability of Hg to organisms, promoting a decrease in its trophic transfer efficiency through the food web of that estuarine system (Kehrig et al. 2009a).

In this study, all fish Se:Hg molar ratios were higher than 1 (surplus Se). The mean molar Se:Hg ratios in cutlassfish from BC were higher (22.49 ± 3.74) than in cutlassfish from IB (7.52 ± 6.78) and GB (9.43 ± 4.60) (see Table 1). Generally, marine fish species present the Se:Hg > 1 in muscle tissue (Kehrig et al. 2009a). The muscle tissue of two carnivorous fish species, *Centropomus undecimalis* (snook) and *Micropogonias furnieri* (croaker), from GB, presented Se:Hg molar ratio of 8.0 and 8.0, respectively (Kehrig et al. 2009a). In our study, cutlassfish muscle samples also presented a considerable Se excess in relation to Hg, demonstrating that the ratio between Se:Hg levels was of the same order of magnitude as those reported by Kehrig et al. (2009a). If we consider that a molar ratio surplus of Se:Hg > 1 in fish might be sufficient to prevent Hg toxicity in the fish and the fish consumers, all samples would be considered suitable for consumption (Peterson et al. 2009). Data from Table 1 suggests that Se:Hg molar ratios might decline with increasing of L, possibly reducing Se protection in large fish. We tested this by applying a linear regression of surplus Se against total fish length for IB, GB and BC. The reduction in Se protection in large fish was only observed in GB, where a significant relationship was found ($R^2 = 0.60$; $p < 0.05$). The relationship observed for cutlassfish from IB was weak and non-significant ($R^2 = 0.004$; $p > 0.05$) and for BC fish was stronger and non-significant ($R^2 = 0.22$; $p > 0.05$), indicating that in these areas Se protection against Hg toxicity in large fish probably does not decline with increasing L.

Differences found among the concentrations of Hg and Se in cutlassfish from IB, GB and BC were probably related to the food supplies and bioavailability of elements in the marine environment due to these coastal areas present different environmental condition and degradation level. However, more data and analysis are needed to affirm this proposition. In addition, the Se:Hg > 1 indicates that this fish species could be considered suitable for consumption.

Acknowledgments The authors would like to thank the financial support of the Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ Proc 101976/2009), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior and Conselho Nacional de Desenvolvimento Científico e Tecnológico.

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