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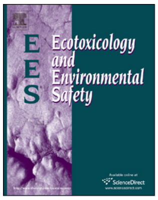

Selenium and mercury in widely consumed seafood from South Atlantic Ocean

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ABSTRACT

The growing ingestion of predatory fish by humans has increased their exposure to toxic chemicals. Mercury (Hg) is an exogenous and harmful trace-element that accumulates in all marine organisms. Selenium (Se) is nutritionally important as a micronutrient, but is potentially harmful at intakes above 1 mg per day. Se:Hg molar ratios in excess of 1:1 are thought to counteract the adverse effects of Hg, protecting against Hg toxicity. Evaluation of the health risk posed by Hg exposure from seafood consumption requires concurrent consideration of Se content in the same individuals. This study evaluated the Se and Hg concentrations in the edible tissues of 652 individual samples of commonly consumed varieties of carnivorous and planktivorous fish, squid, mussel, shrimp and crab collected from south-eastern Brazil. The Se:Hg molar ratios showed significant variation among and within tropical seafood. All organisms presented Se concentration in muscle of less than 2.0 $\mu g\ g^{-1}$, the maximum allowed selenium concentrations. Only seven individuals of a carnivorous fish species presented Hg in muscle above the maximum permissible limit of 0.5 $\mu g\ g^{-1}$ established by WHO and Brazilian legislation for human consumption of most aquatic species. These same individuals also showed Se:Hg molar ratio of less than 1:1. Se:Hg molar ratios were found to decline with increasing fish length, potentially reducing Se-dependent protection. As a result of their rich Se, low Hg contents and Se:Hg molar ratios exceeding 1:1, nearly all species included in this study provide benefits for human consumption. Two popular seafoods in the region, the carnivorous fish *Centropomus undecimalis* (common snook) and *Micropogonias furnieri* (Atlantic croaker), had the most favorable Se:Hg molar ratio values of 33 and 21, respectively. Among the invertebrates, *Xiphopenaeus kroyeri* (seabob shrimp) and *Loligo sanpaulensis* (squid) had the most favorable Se:Hg molar ratio values, higher than 20. A selenium health benefit value based on the absolute amounts and relative proportions of Se and Hg in seafood was proposed as a more comprehensive seafood safety criterion.

1. Introduction

Fish and shellfish are good dietary sources of protein, omega-3 fatty acids, and antioxidants such as selenium and vitamin E for humans (Egeland and Middaugh, 1997). Selenium (Se) is an essential trace-element for metabolic activity, because of its important roles in the brain and endocrine tissues (Ralston, 2008).

All forms of animal life containing nervous systems possess selenium-dependent enzymes that utilize selenocysteine to perform important antioxidant and redox control functions. Oxygen metabolites are essential to the brain, but can damage brain tissue via oxidation. The selenocysteine enzyme functions appear to be indispensable to protect brain tissues against oxidative damage from reactive oxygen metabolites (Ralston, 2008).

Selenium (Se) acts as a protective agent against the toxicity of exogenous metals such as mercury (Hg) (US EPA, 1997; Feroci et al., 2005). Some studies have shown that this micronutrient (Se) may reduce the availability of Hg, as methylmercury, blocking it in insoluble compounds (Sasakura and Suzuki, 1998; Feroci et al., 2005), therefore decreasing methylmercury toxicity. However, this trace-element is harmful at dietary intakes in excess of 1 mg per day (WHO, 1987).

Mercury (Hg) is a global contaminant and toxicant of major concern for both wildlife and humans (Grandjean et al., 2005). This trace-element is found in several forms in the environment mainly as: mercury vapor (elemental mercury), inorganic salts,

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and organic compounds. Hg is known to be toxic to humans in all forms but some forms are more toxic than others, depending on the chemistry of mercury containing molecule, which determines its absorption, distribution, and excretion pattern in the body (Winship, 1985). Mercury, particularly in the organic chemical form methylmercury (MeHg), is preferentially assimilated by living organisms and for that reason the dominant form found in fish consumed by humans.

Mercury has no known normal metabolic function and at high concentrations its potential hazards, include neurological damaging effects, fetal and infant growth impairment, and can contribute to cardiovascular disease (Grandjean et al., 2005; Mergler et al., 2007; Karagas et al., 2012).

Since this element has the ability to undergo biomagnification along the trophic webs, environmental exposure to methylmercury, particularly for higher trophic level consumers including humans, can be significant (Agusa et al., 2007).

As it was shown in epidemiological studies (Grandjean et al., 1992; Igata, 1993), the main pathway of mercury exposure to humans is the ingestion of contaminated seafood, which is also a source of beneficial nutrients such as selenium.

Selenium, like sulphur, readily complexes with mercury and both elements tend to be associated with sulphur in proteins. Thus, it is reasonable to expect that Se and Hg tend to be bioaccumulated together in the tissues of seafood (Ganther et al., 1972). However, Hg binds to Se with affinities a million times greater than Hg's affinity for sulfur, thus compromising selenium's biological functions and availability.

There is growing awareness that the toxicity of MeHg is intimately linked with its high binding affinities with selenium. This corresponds remarkably well with the recognition that the target tissues of MeHg toxicity are the neuroendocrine and nervous systems. Because Hg is uniquely able to inhibit selenium-dependent enzyme activities in brain tissues (Carvalho et al., 2008; Ralston and Raymond, 2010), the risks of oxidative brain damage as a result of Hg toxicity directly correspond to Se:Hg molar ratios in tissues (Ralston et al., 2007, 2008). As a result, Hg in its more toxic form (methylmercury) becomes an increasingly potent neurotoxicant as its tissue concentrations approach tissue concentrations of Se ($\sim 1\ \mu$M) (Ralston, 2008). For this reason the issue should be studied in humans further.

Methylmercury covalently binds to Se present at selenoenzyme active sites, modifying the enzyme that result in the adverse effects associated with Hg toxicity. By biochemical definition, methylmercury is a specific inhibitor of selenoenzymes (Ralston, 2008) since it forms a highly stable organic compound, methylmercury-selenocysteine (MeHg–SeCys) in Hg stressed organisms (Ralston et al., 2008).

In Hg stressed organisms, the redistribution of Se from cells and its supplemental replacement via diet reduce the possible toxic effects caused by loss of selenium during the formation of MeHg–SeCys (Ralston and Raymond, 2010). Therefore, the levels of selenoenzymes required for brain function and protein synthesis are maintained (Kohrle, 1999). The inhibition of selenoenzymes formation critically impairs cell metabolism, because selenoenzymes are a critical component of protein synthesis and must be formed again during each cycle of cellular protein synthesis (Ralston et al., 2008).

Marine fish generally contain far more Se than Hg, and consuming marine fish has been shown to prevent, rather than contribute to, MeHg toxicity (Ralston, 2008; Burger and Gochfeld, 2012). The ability of Se compounds to decrease the toxicity of Hg has been established in all species of mammals, birds, and fish investigated (Cuvin-Aralar and Furness, 1991; Chapman and Chan, 2000; Raymond and Ralston, 2004). Se:Hg molar ratios exceeding 1:1 are thought to provide Se-dependent health benefits, but not necessarily those with Se:Hg molar ratios approaching 1:1 since that set of fish would necessarily include fish with mercury in molar excess of selenium (Ganther et al., 1972; Beijer and Jernelöv, 1978).

Although there are animal studies showing that selenite reduces inorganic Hg toxicity, there is almost no evidence for protection from MeHg toxicity by the organic forms of selenium found in the human diet. Moreover, there are no human studies showing a protective role for selenium against Hg neurotoxicity (Mergler et al. 2007).

Evaluation of the health risk posed by mercury exposure from seafood consumption requires concurrent consideration of selenium content in the same individuals. In this study, selenium and mercury concentrations, based on a wet weight basis, were evaluated in the edible tissues of 652 individuals from south-eastern Brazil, being 239 carnivorous fish, 113 planktivorous fish, 32 squids, 153 mussels, 70 shrimps and 45 crabs. These marine species are widely distributed in this region and often consumed by humans. As mercury exposure from seafood consumption has been the focus of this study, the molar ratio between selenium and mercury were investigated. In addition to better describe and integrate selenium specific nutritional benefits in relation to potential mercury exposure risks presented by these marine species a selenium health benefit (Se-HB) value was calculated.

2. Materials and methods

2.1. Rio de Janeiro coast

Rio de Janeiro coast (21–23°S) on south-eastern Brazil (15–25°S) is one of the most important areas for marine fisheries on the Western South Atlantic Ocean (Fig. 1), presenting ecological and economic importance (fisheries and oil exploration). It is the fourth largest Brazilian fish producer (MMA and IBAMA, 2008).

The Rio de Janeiro State has the third longest coastline (635 km) in Brazil. It is influenced by coastal upwelling including St. Tomé Cape (22°S) and Cabo Frio (23°S).

The region of Northern Rio de Janeiro coast (21°S) belongs to a transitional faunistic region, which presents a great biodiversity. This region is permanently influenced by the Paraíba do Sul River discharge, which is the major river run off of Rio de Janeiro. The plume of Paraíba do Sul River reaches the open ocean waters in velocities ranging from 1.6 to 2.6 km d^{-1} carrying particle and dissolved organic matter (Souza et al., 2010). The area offshore northern Rio de Janeiro is known as Campos Basin, where the shelf break is located from 40–60 nmiles from the coastline (Petrobras, 1993).

2.2. Marine organisms

The biota group, common names, scientific names, feeding habit and habitat, and the range of length of organisms are shown in Table 1. A total of 652 individuals, being 352 fish, 185 mollusks and 115 crustaceans were obtained from

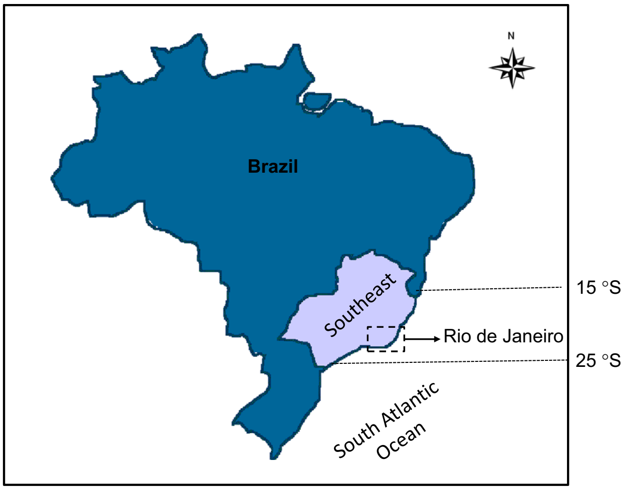

Fig. 1. Area where marine organisms were collected for Hg and Se analysis in the Rio de Janeiro coast, South-eastern Brazil.

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Table 1
The biota group, scientific names, common names, feeding habit and habitat, vertical trophic guilds and range of length.

Species	Group	Common name	Feeding habit and habitat	Vertical trophic guilds	Length (range—cm)
Centropomus undecimalis	Fish	Common snook	Carnivorous pelagic-demersal	CF-PD	14.0–35.5
Micropogonias furnieri	Fish	Atlantic croaker	Carnivorous demersal	CF-D	26.0–46.0
Paralonchurus brasiliensis	Fish	Banded croaker	Carnivorous demersal	CF-D	16.5–26.0
Stellifer rastrifer	Fish	Rake stardrum	Carnivorous demersal	CF-D	12.5–21.3
Isopisthus parvipinnis	Fish	Bigtooth corvina	Carnivorous demersal	CF-D	14.0–21.0
*Trichiurus lepturus**	Fish	Atlantic cutlassfish	Carnivorous pelagic-demersal	CF-PDV	45.0–150.0
Cynoscion jamaicensis	Fish	Jamaica weakfish	Carnivorous demersal	CF-D	15.4–25.0
Bagre bagre	Fish	Catfish	Carnivorous demersal	CF-D	32.5–54.0
Anchoa filifera	Fish	Longfinger anchovy	Planktivorous pelagic	PF-P	8.0–10.0
Lycengraulis grossidens	Fish	Atlantic sabretooth anchovy	Planktivorous pelagic	PF-P	10.0–29.5
Pellona harroweri	Fish	American coastal pellona	Planktivorous pelagic	PF-P	10.0–12.6
Chirocentrodon bleekerianus	Fish	Dogtooth herring	Planktivorous pelagic	PF-P	9.0–12.0
Mugil liza	Fish	Lebranche mullet	Planktivorous pelagic	PF-P	29.0–50.0
Xiphopenaeus kroyeri	Crustacean	Seabob shrimp	Omnivorous pelagic-demersal	–	7.5–13.0
Loligo sanpaulensis	Cephalopod	Squid	Carnivorous pelagic	–	4.4–7.0
Perna perna	Bivalve	Brown mussel	Suspensivorous	–	2.0–9.0
Callinectes ornatus	Crustacean	Swimming crab	Omnivorous pelagic-demersal	–	3.4–10.0

* Voracious.

the fishing community of different places along the Rio de Janeiro coastline (see Fig. 1) by fishermen, using a variety of fishing techniques. The fish species were grouped into four vertical trophic guilds according to their diet (carnivorous pelagic-demersal fish (CF-PD), carnivorous pelagic-demersal voracious fish (CF-PDV), carnivorous demersal fish (CF-D) and planktivorous pelagic fish (PF-P)), that is, in groups of fish species that feed on similar food sources and use those sources in the same manner (Townsend et al., 2000).

Following determination of the body weight, length for fish and mollusk, carapace width for crab and identification of the species (Table 1), a skinless cube of the muscle and soft tissues were removed for later analysis, according to FAO/SIDA (1983). These tissues were stored in airtight plastic bags at below −18 °C until freeze dried. All these species are characteristic from the Western South Atlantic Ocean and occur abundantly along the whole Brazilian coast (Froese and Pauly, 2011).

2.3. Mercury and selenium analyses

For mercury (Hg) analysis, wet samples (0.5 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., 2006). For selenium (Se), the samples (0.5 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 (Seixas et al., 2009).

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: $4.64 \pm 0.26\ \mu g\ g^{-1}$; Se: $1.40 \pm 0.09\ \mu g\ g^{-1}$) from the National Research Council-Canada. Our results for Hg and Se DORM-2 were $4.54 \pm 0.13\ \mu g\ g^{-1}$ ($N = 41$) and $1.47 \pm 0.27\ \mu g\ g^{-1}$ ($N = 45$), respectively. Our trace-element results of the certified reference samples analysis demonstrated the high precision and accuracy of the analytical methods, where Hg and Se quantified in the reference materials were 97 and 105 percent of the respective mean certified values.

2.4. Statistical analyses

Statistical analyses were performed using STATISTICA® 7.0 for Windows (StatSoft, Inc. 1984-2004, USA). The analysis of variance was conducted by the Kruskal–Wallis test-ANOVA followed by a post-hoc test (Mann–Whitney *U*-test) in order to define significant differences in trace-element concentrations. Spearman correlation (r) was performed to determine the relationships between length and selenium–mercury molar ratio and inter-element relationships (on a molar basis). A p value of less than 0.05 was chosen to indicate statistical significance. Values are presented as median and standard deviation of wet weights.

3. Results and discussion

3.1. Selenium and mercury

Selenium (Se) and mercury (Hg) concentrations in seafood and the number of specimens analyzed from the Rio de Janeiro coast are summarized in Table 2. All organisms presented selenium concentration in muscle of less than $2.0\ \mu g\ g^{-1}$ wet wt or $25.33\ nmol\ g^{-1}$, the maximum allowed selenium concentrations proposed by Lemly (2007).

The median Se concentration is higher for carnivorous fish (*Centropomus undecimalis*, *Micropogonias furnieri*, *Paralonchurus brasiliensis*, *Stellifer rastrifer* and *Trichiurus lepturus*) than for planktivorous fish. The muscular selenium concentrations in planktivorous fish are in the same range of those found in crustaceans and mollusks (Table 2).

The Kruskal–Wallis ANOVA test demonstrated the presence of highly significant differences ($p < 0.01$) in muscular Se concentrations among the three groups of carnivorous fish (CF-PD, CF-PDV and CF-D). The highest median selenium concentrations were found in the group of CF-PD ($10.11\ nmol\ g^{-1}$; $N = 18$) composed of *C. undecimalis*, and the lowest in the group of CF-PDV ($3.02\ nmol\ g^{-1}$; $N = 52$) composed of *T. lepturus. C. undecimalis* feed mainly on invertebrates and small fish (Froese and Pauly, 2011) whereas adult individuals of *T. lepturus* feed on squids and fishes, including co-specifics (Martins et al., 2005).

The group of CF-D composed by different species of fish, *M. furnieri*, *P. brasiliensis*, *S. rastrifer*, *Isopisthus parvipinnis*, *Cynoscion jamaicensis* and *Bagre bagre* showed an intermediary median muscular Se concentrations ($5.89\ nmol\ g^{-1}$, $N = 147$). The fish species forming group CF-D that are intermediary voracious predatory fish, feed mainly on invertebrates and small fish (Froese and Pauly, 2011).

The highest median Hg concentrations were found in the muscle of *P. brasiliensis* that is a demersal carnivorous fish (Table 2). However, the median Hg concentration for all carnivorous fish ($0.39\ nmol\ g^{-1}$, range: 0.05–4.77, $N = 216$) is higher than that found for all planktivorous fish ($0.24\ nmol\ g^{-1}$, range: 0.03–0.62, $N = 98$) (U test, $p < 0.001$). The non-carnivorous fish species *Mugil liza*, *Pellona harroweri* and *Chirocentrodon bleekerianus* that live associated with the surface of water mass, presented similar muscular median Hg concentration than that found in the muscle of *I. parvipinnis*, a demersal carnivorous fish (Table 2).

Seven out of 52 specimens of *T. lepturus* presented Hg concentration in muscle (range: $2.53–4.77\ nmol\ g^{-1}$ wet wt) above the maximum permissible limit of $0.50\ \mu g\ g^{-1}$ wet wt or $2.50\ nmol\ g^{-1}$ established by WHO and Brazilian legislation (MAPA Brasil, 2000) for human consumption of most aquatic species. These same individuals also showed the lowest median Se concentration ($0.06\ \mu g\ g^{-1}$ wet wt or $0.78\ nmol\ g^{-1}$) in muscle, i.e. presenting an excess of mercury molar concentration in relation to selenium in this tissue.

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Table 2
Number of specimens, median and range of mercury and selenium concentrations (in nmol g^{-1} wet wt), median of Se:Hg molar ratios and free selenium concentration (in nmol g^{-1}) and median and range of selenium health benefit (Se-HB) values in seafood.

Species	*N*	Mercury (nmol g^{-1}) median (range)	Selenium (nmol g^{-1}) median (range)	Se:Hg molar ratio	Free Se (Se–Hg) (nmol g^{-1})	Se-HB values median (range)
Centropomus undecimalis	18	0.31 (0.16–0.86)	10.11 (5.27–18.81)	33	9.8	336.6 (69.8–934.9)
Micropogonias furnieri	73	0.31 (0.11–0.55)	6.20 (4.48–13.10)	21	5.8	133.1 (38.9–683.9)
Paralonchurus brasiliensis	17	0.73 (0.08–3.32)	8.85 (0.43–17.55)	13	8.3	107.1 (0.1–377.3)
Stellifer rastrifer	15	0.42 (0.16–1.59)	5.30 (2.81–10.12)	13	4.9	67.6 (4.9–240.9)
Isopisthus parvipinnis	23	0.23 (0.13–0.61)	2.51 (1.99–3.59)	11	2.3	28.1 (7.4–72.1)
Trichiurus lepturus	52	0.37 (0.15–4.77)	3.02 (0.06–9.88)	8	2.4	20.1 (−1.6–80.1)
Cynoscion jamaicensis	27	0.35 (0.24–0.58)	1.98 (1.31–3.54)	5	1.4	10.0 (3.6–45.2)
Bagre bagre	14	0.33 (0.22–0.87)	0.84 (0.56–1.48)	3	0.6	2.4 (−0.1–4.4)
Anchoa filifera	10	0.32 (0.17–0.46)	2.81 (2.37–3.24)	12	2.5	37.0 (12.1–62.0)
Lycengraulis grossidens	22	0.12 (0.06–0.25)	1.69 (0.66–9.73)	16	1.6	27.1 (2.9–105.2)
Pellona harroweri	30	0.26 (0.17–0.56)	2.10 (1.54–3.05)	7	1.8	16.7 (8.4–31.4)
Chirocentrodon bleekerianus	20	0.29 (0.10–0.50)	2.14 (1.99–2.86)	6	2.0	12.2 (10.4–29.7)
Mugil liza	31	0.26 (0.03–0.47)	1.04 (0.27–2.09)	6	1.0	5.9 (0.5–18.1)
Xiphopenaeus kroyeri	70	0.10 (0.07–0.16)	2.47 (1.40–3.22)	23	2.3	55.1 (29.3–83.9)
Loligo sanpaulensis	32	0.06 (0.03–0.12)	0.95(0.30–1.70)	20	0.9	37.7 (46.6–112.6)
Perna perna	153	0.20 (0.10–0.35)	2.75 (1.24–4.48)	13	2.5	24.8 (2.0–107.3)
Callinectes ornatus	45	0.25 (0.12–0.63)	1.12 (0.58–1.98)	6	0.9	5.0 (−0.1–32.7)
	Total = 652					

Previous studies also reported an excess of mercury molar concentration in relation to selenium in seafood such as varieties of shark from New Jersey coast and Pacific Ocean near Hawaii (Burger and Gochfeld, 2012; Kaneko and Ralston, 2007) and pilot whale from Faroe Islands (Grandjean et al., 1992).

Some studies have been shown early signs of the neurotoxic effects in populations that were methylmercury exposure via seafood consumption, such as in the case of Faroe Islands (Weihe et al., 2005). However, no evidence was found that selenium was an important protective factor against methylmercury neurotoxicity in the Faroese study population that consumed pilot whale meat (Choi et al., 2008). This consistence may be related to the extremely high methylmercury in pilot whale meat that can exceed selenium compared with fish meat, as well as the PCBs and other possible toxins contained in whale but not typically found in fish, as Raymond and Ralston (2004) previously mentioned.

A significant and positive relationship was found between the concentration of Hg in muscle of all fish samples grouped into four vertical trophic guilds and length, presenting a not strong relationship (r=0.35; $p<0.0001$) (Fig. 2A). The highest muscular Hg concentrations were found in the largest individuals of the group CF-PDV (blue dots). However, individuals of fish from the lower vertical trophic guild, PF-P, had the lowest mercury concentrations and also, the shortest length. This fish group was composed of *Lycengraulis grossidens* and *Anchoa filifera*, ranging in fish length from about 8 to about 10 cm (see Fig. 2A).

Muscular selenium concentrations in individuals of fish might decline with increasing fish size, presenting a non-significant and negative relationship (r=−0.10; $p>0.10$) (Fig. 2B). The highest Se concentrations were found the intermediary group of CF-D (yellow dots), whereas the largest individuals of group CF-PDV (blue dots) had one of the lowest Se concentrations in muscle. However, the shorter individuals of fish from the lower vertical trophic guild, PF-P (red dots) had similar selenium concentrations to those found in the muscle of *T. lepturus* (CF-PDV) (see Fig. 2B).

As mercury exposure from seafood consumption has been the focus of this study, the free selenium and molar ratio between selenium and mercury were investigated. In general, marine fish fillets contain more selenium than fillets from freshwater fish (Ralston and Raymond, 2010).

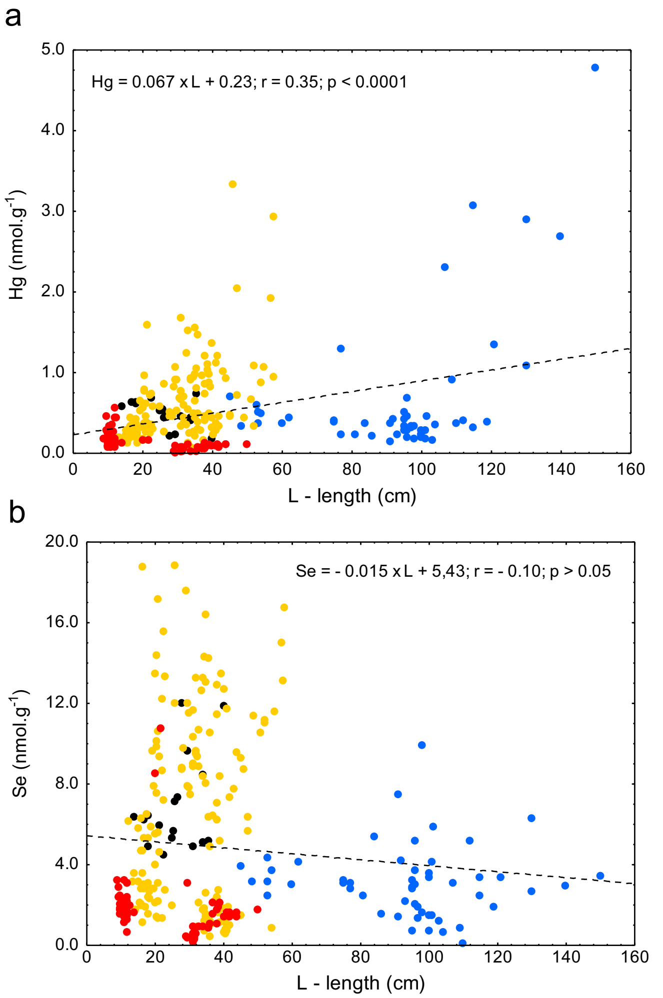

Fig. 2. (A) Relationship between muscular mercury concentrations and fish length, according to the four vertical trophic guilds. (B) Relationship between muscular selenium concentrations and fish length, according to the four vertical trophic guilds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Our data (Table 2) show that selenium was in molar excess of mercury in almost all species evaluated, indicating that substantial selenium was available to counter the mercury concentration that was also present in them.

The molar excess of selenium or free selenium in the seafood samples was calculated by subtracting the molar selenium concentration from the molar mercury concentration for each individual sample (Table 2).

Among all seafood evaluated, four carnivorous fish (*C. undecimalis*, *M. furnieri*, *P. brasiliensis*, and *S. rastrifer*) presented the highest excess of free selenium that ranged from 4.9 to 9.8 (Table 2). As a result of their rich Se and low Hg contents, these carnivorous fish species tend to be the most favorable source of dietary supplemental selenium.

The results found in this study are in agreement with previous studies that revealed that marine fish tend to be rich dietary sources of Se (Andersen and Depledge, 1997; Branco et al., 2007; Kaneko and Ralston, 2007; Kehrig et al., 2009; Burger and Gochfeld, 2012).

3.2. Relation of molar selenium and mercury concentrations

Significant and positive relationships were found between the molar concentrations of Se and Hg in muscle of carnivorous and planktivorous fish. The relationship for carnivores ($r=0.32$; $p<0.01$) is not strong significant (Fig. 3A) and the one for planktivores ($r=0.57$; $p<0.01$) is stronger (Fig. 3B). Our results are in agreement with previous studies that found that marine fish tend to show a weak but statistically significant positive regression of selenium on mercury (Kehrig et al., 2009; Burger and Gochfeld, 2012). However, Andersen and Depledge (1997) found a robust linear regression of selenium on mercury in the muscle of *Diplodus sargus cadenati* (white seabream), a carnivorous fish, from the Azorean area, demonstrating that the correlation of the molar concentrations of these two elements varied markedly between individual fish and also fish species. Normally, only bigger ocean fish and marine mammals present a robust relationship between molar concentrations of selenium and mercury (Mikac et al., 1985).

3.3. Selenium–mercury molar ratio

Selenium–mercury molar ratio (Se:Hg) showed significant variation among and within marine species. According to Table 2, all seafood evaluated exhibited Se:Hg of >3, i.e. an excess of selenium in relation to mercury. Among the marine species evaluated, *C. undecimalis* and *M. furnieri* (carnivorous fish), *L. grossidens* (planktivorous fish), *Xiphopenaeus kroyeri* (crustacean) and *Loligo sanpaulensis* (mollusk) presented the highest Se: Hg molar ratio that ranged from 16:1–33:1 (Table 2).

In some muscle samples of all species, the selenium molar concentrations were approximately 70 times higher than those of mercury. This was mainly observed in *C. undecimalis* and *P. brasiliensis*, two carnivorous fish species evaluated. However, five specimens (0.8 percent) of all seafood evaluated presented the Se:Hg molar ratio less than 1:1, ranging from 0.2:1 to 0.9:1. These five individuals are individuals of *T. lepturus* that presented one of the highest muscular mercury concentrations found in this study.

The highest muscular Se:Hg molar ratio (77:1) was found in an individual of *P. brasiliensis* that presented low mercury concentration (0.08 nmol g^{-1} wet wt), whereas the lowest Se:Hg molar ratio (0.2:1) was found in the muscle of *T. lepturus* with a mercury concentration of 0.07 $\mu g\ g^{-1}$ wet wt or 0.37 nmol g^{-1}.

Our results are in agreement with previous studies that found that marine species (Kaneko and Ralston, 2007; Kehrig et al., 2009; Burger and Gochfeld, 2012; Seixas et al., 2012) and freshwater fish (Dorea et al., 1998; Lima et al., 2005; Peterson et al., 2009) tend to have Se:Hg molar ratios above 1:1.

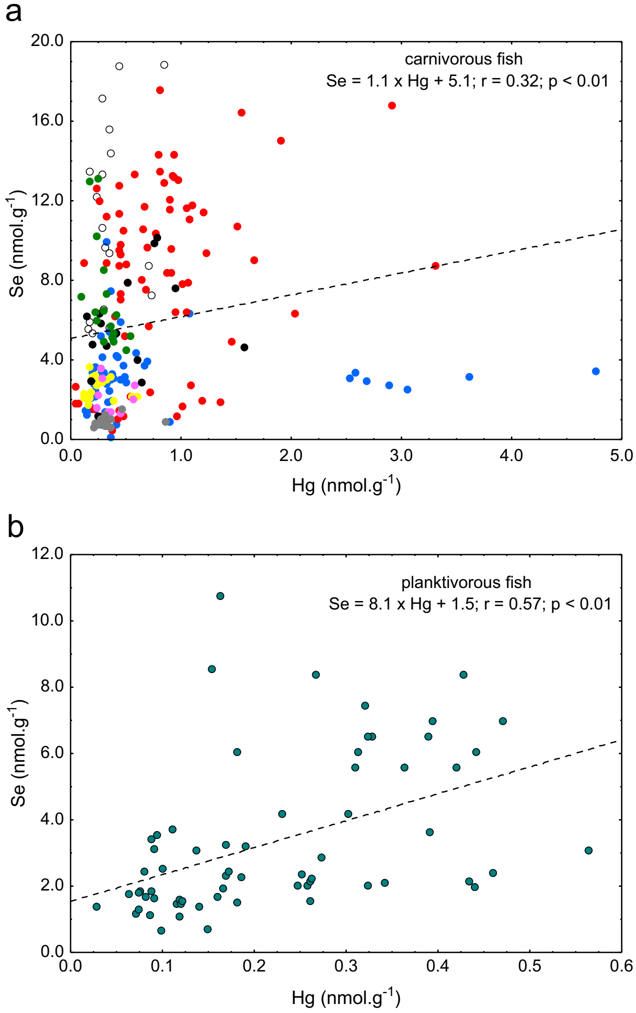

Fig. 3. (A) Relationship between muscular selenium and mercury concentrations in carnivorous fish (blue dots=*Trichiurus lepturus*; open dots=*Paralonchurus brasiliensis*; red dots=*Micropogonias furnieri*; green dots=*Centropomus undecimalis*; yellow dots=*Isopisthus parvipinnis*; rose dots=*Cynoscion jamaicensis*; black dots=*Stellifer rastrifer*; grey dots=*Bagre bagre*). (B) Relationship between muscular selenium and mercury concentrations in planktivorous fish. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Some studies have suggested that Se:Hg molar ratios above 1:1 protect against mercury toxicity (Ralston, 2008; Peterson et al., 2009). However, the practical implications of the modification of mercury toxicity by selenium are unclear (Watanabe, 2002) because of the variability in toxicokinetics.

However, according to Burger and Gochfeld (2012) it is difficult to use the Se:Hg molar ratio in risk assessment and risk management, due to more information is needed on how mercury and selenium interact and also on the relationship between the molar ratios and health outcomes.

The Kruskal–Wallis ANOVA test demonstrated significant differences ($p<0.01$) in the Se:Hg molar ratios among the four groups of fish species (CF-PDV, CF-PD, CF-D and PF-P). The lowest median muscular Se:Hg molar ratio (8:1; range: 0.2:1–30:1) was found in the top level of food chain, represented by the carnivorous pelagic-demersal voracious fish (CF-PDV), *T. lepturus* (Fig. 4). The two groups of carnivorous fish, CF-PD and CF-D, are *T. lepturus* main prey species in Rio de Janeiro coast (Bittar and Di Beneditto, 2009). The groups of CF-PD and CF-D had similar median muscular Se:Hg molar ratios (11:1, range: 1:1 –77:1). The group formed by planktivorous pelagic fish (PF-P) showed the highest median Se:

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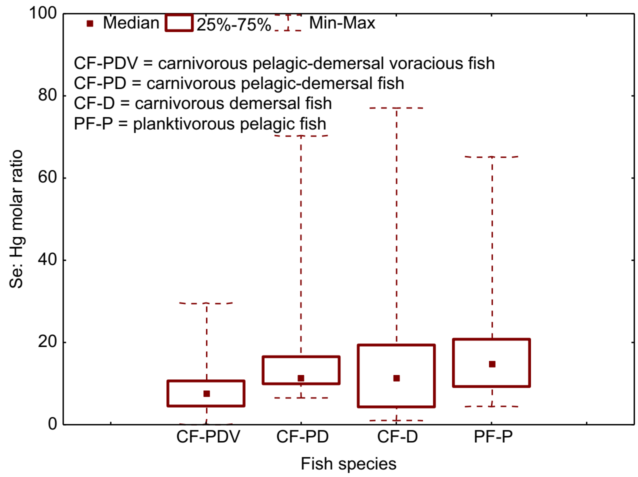

Fig. 4. Median and 25th, 75th percentiles of Se:Hg molar ratios in fish species grouped into four vertical trophic guilds according to their diet.

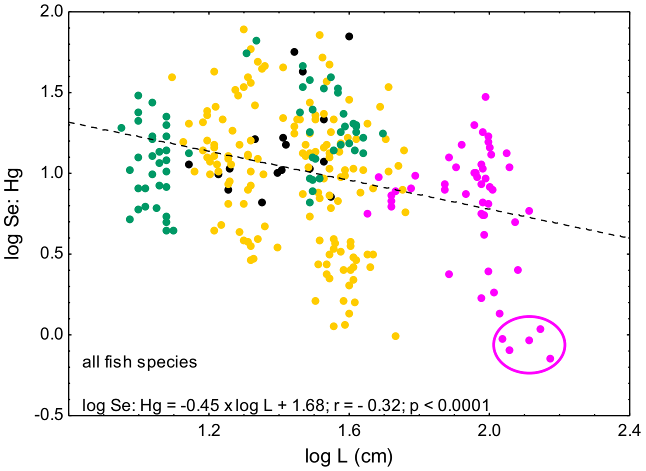

Fig. 5. Se:Hg molar ratio in relation to length (L) of all fish species.

Hg molar ratio (15:1, range: 4:1–65:1) in muscle (Fig. 4). Data found in this study suggest that muscular Se:Hg molar ratio changed with vertical trophic guilds according to fish species diet.

In our study, the Se:Hg molar ratio decline with increasing fish length, possibly reducing selenium protection in larger fish (Fig. 5). The relationship between Se:Hg molar ratio and all fish length was not strong ($r = -0.32$); however it was significant ($p < 0.0001$) as previous reported for marine fish (Burger and Gochfeld, 2012) and freshwater fish (Peterson et al., 2009). According to Peterson et al. (2009), selenium protection against mercury toxicity in larger fish probably remains intact.

In Fig. 5, all carnivorous fish that have Se:Hg molar ratios < 1:1 were individuals of *T. lepturus* (CF-PDV), ranging in fish length from about 115 to about 150 cm. These were the greatest individuals in length of this study.

3.4. Selenium health benefit value

In the present study, selenium health benefit (Se-HB) value that was first proposed by Kaneko and Ralston (2007) was used to better describe and integrate selenium nutritional benefits in relation to potential mercury exposure risks presented by marine organisms. Se-HB value reflects not only the total mercury that is present in the seafood, but also its selenium content. This approach incorporates consideration of both the absolute and relative amounts of selenium and mercury ingested via food to provide an index that is easily interpreted (Ralston, 2008). Se-HB value was calculated as Kaneko and Ralston (2007), using the following equation:

$$\mathrm{Se-HB\ value} = (\mathrm{Se:Hg} \times [\mathrm{Se}]_{\mathrm{in\ nmol/g}}) - (\mathrm{Hg:Se} \times [\mathrm{Hg}]_{\mathrm{in\ nmol/g}})$$

The sign of the calculated value indicates the expected health benefits (if positive values are obtained) or health risks (if negative values result) and the magnitude of the obtained values are proportional to the expected benefits or risks (Ralston, 2008).

As a result of their rich selenium and low mercury contents, all studied species presented a positive median Se-HB value, i.e. favorable value, and it is higher or equal to two (Table 2), suggesting that they showed selenium to potentially protect them and their consumers against mercury toxicity.

The carnivorous fish (*C. undecimalis*, *M. furnieri*, *P. brasiliensis* and *S. rastrifer*) and planktivorous fish (*A. filifera*) are the ones with the best health benefits; showing the highest favorable Se-HB values (Table 2). Among the invertebrates, *X. kroyeri* (crustacean) and *L. sanpaulensis* (mollusk) had the most favorable Se-HB values (Table 2). *C. undecimalis*, *M. furnieri* and *X. kroyeri* are species of high commercial value caught in south-eastern Brazil and often consumed by humans.

The carnivorous fish *C. undecimalis*, widely consumed by humans, presented the highest Se-HB values. However, the carnivorous fish *Bagre bagre*, which is a popular seafood in the region, had the lowest Se-HB value (Table 2).

Although the carnivorous fish, *T. lepturus* had a high median Se-HB value, 20.1 (Table 2), seven specimens of this species (14 percent) presented negative Se-HB values, indicating potential health risk. These specimens presented mercury concentration higher than 0.50 $\mu g\ g^{-1}$ wet wt and Se:Hg molar ratio below 1:1.

In a previous study with fifteen species of saltwater fish from central North Pacific, near Hawaii, only one fish species, mako shark, presented a Se:Hg molar ratio lower than 1:1 (0.46), containing a net molar excess of Hg. This fish species showed a negative Se-HB value (−11.1), indicating that mako shark would not be consumed by humans, especially during pregnancy (Kaneko and Ralston, 2007). According to these authors, pilot whale meat from the Faroe Islands contains a substantial molar excess of Hg over Se content, resulting in a net delivery of Hg and a highly negative Se-HB value. The Health Ministry of the Faroe Islands recognizes that the consumption of pilot whale meat during pregnancy is contraindicated (Weihe et al., 2005).

In conclusion, as a result of their rich selenium, low mercury contents and Se:Hg molar ratios exceeding 1:1, nearly all (98.9 percent) of the seafood in our study have sufficient Se to potentially protect them and their consumers against mercury toxicity, suggesting that consideration of Se–Hg interactions might improve the understanding of risks associated with seafood Hg toxicity. The carnivorous fish *C. undecimalis* (common snook) and *M. furnieri* (Atlantic croaker), which are popular seafood in the region, had the most favorable Se:Hg molar ratio values and probably the ones with the best health benefits. This research adds new insight to tropical seafood and complements the existing studies regarding potential protective effects of selenium against mercury toxicity.

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