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MERCURY DISTRIBUTION IN FISH COMMERCIALIZED AT THE MUCURIPE MARKET, FORTALEZA, CEARÁ STATE, BRAZIL

Distribuição de mercúrio em peixes comercializados no Mercado do Mucuripe, Fortaleza, Estado do Ceará, Brasil

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ABSTRACT

Average total Hg concentrations measured in fish muscle from species commercialized in the Fortaleza Market, CE, Brazil varied from 14 to 509 ng.g^{-1} wet weight. Lowest concentrations occurred in small omnivorous fish and the highest in large carnivorous species, in particular sharks. The largest individuals (>110 cm in length) of the piscivorous species Scomberomorus cavalla *showed Hg concentrations of up to 1,737 ng.g^{-1}, although the average concentration for this species was much lower (352 ng.g^{-1}). With the exception of the* S. cavalla *largest individuals, all species presented Hg concentrations below the Brazilian legal limits for human consumption. Hazard quotients (HQ) estimated using the local fish consumption rate and the observed Hg concentrations varied from 0.015 based on small omnivorous species to 0.551 in sharks. All species average HQ was 0.148 and the average HQ based on the most consumed species only was slightly higher (0.155). Both average HQs suggest insignificant exposure risk to consumers.*

Keywords: *fish market, mercury, human exposure.*

RESUMO

As concentrações médias de Hg total medidas no músculo de peixes de espécies comercializadas no mercado de Fortaleza, CE, Brasil variaram de 14 a 509 ng.g^{-1} em peso úmido. As menores concentrações ocorreram em pequenos peixes onívoros e as maiores em grandes espécies de carnívoros, especialmente tubarões. Os maiores indivíduos (> 110 cm de comprimento) da espécie piscívora Scomberomorus cavalla *mostraram concentrações de Hg de até 1.737 ng.g^{-1}, embora a concentração média para esta espécie tenha sido muito menor (352 ng.g^{-1}). Com exceção dos indivíduos maiores de* S. cavalla*, todas as espécies apresentaram concentrações de Hg abaixo dos limites legais para consumo humano. Quocientes de risco (HQ) estimado utilizando a taxa de consumo de peixe local e as concentrações de Hg observadas variaram entre 0,015, referente a pequenas espécies onívoras, e 0,551 a tubarões. Considerando-se todas as espécies o HQ médio foi de 0,148 enquanto que o HQ médio baseado nas espécies mais consumidas foi apenas ligeiramente superior (0,155). Ambos HQs sugerem risco insignificante de exposição ao Hg pelos consumidores.*

Palavras-chaves: *mercado de peixe, mercúrio, exposição humana.*

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INTRODUCTION

The recognition of the benefits from eating fish has increased in recent years, since a fish-rich diet is an excellent low-fat source of protein for humans. Increasing fish consumption has been the goal of many public policies. Unfortunately, however, some fish also contain contaminants, such as mercury (Hg), which may increase exposure risk to consumers. Therefore, information on Hg levels in commercial fish is mandatory since Hg poisoning may threaten human populations with high rates of fish ingestion (Burger & Gochfeld, 2006). Since the Minamata accident in Japan in 1957 and the establishment of the link between human Hg contamination and fish intake, known as the Minamata disease, increasing awareness of the risk of exposure to Hg by consuming contaminated fish resulted in many studies aiming to assess Hg levels in fish from markets, the0 most readily available fish source to humans.

In Brazil, apart from the large ingestion rate of the Amazon region population, entirely of freshwater fish (34.7 $kg.hab^{-1}.yr^{-1}$), coastal populations along the northeastern coast show the highest rates of fish consumption (12.8 $kg.hab^{-1}.yr^{-1}$) compared to 2.5 and 4.2 $kg.hab^{-1}.yr^{-1}$, observed along the south and southeast portions of the country's littoral (Sartori & Amancio, 2012). Recent studies in this region reported overall low Hg concentrations in fish, but also high Hg concentrations in fish species occupying higher trophic levels like *Rhinobatos percellens, Cephalopholis fulva* and *Scomberomorus cavalla* (Costa & Lacerda, 2009; Lacerda *et al.*, 2007 and 2013). Some of these species are also the most appreciated by consumers, but because the greater economic value, they constitute a smaller part of the local fish meals, therefore resulting in a lower exposure risk to Hg due to fish consumption by artisanal fishery communities (Costa & Lacerda, 2014). Considering the overall population however, with the recent increase in the average income, higher ingestion rates of economic valuable species are expected, in particular on the northeastern coast, with higher fish consumption rates compared to the average Brazilian littoral population.

In the Metropolitan Region of Fortaleza (RMF), Ceará, NE Brazil, landfills, dental preparation, laboratory use, combustion of fossil fuel, medical and municipal waste disposal, petroleum refinery, wastewaters and urban runoff are among the human made sources of Hg pollution. As a result, oysters and sediments sampled in local estuaries (Cocó and Ceará Rivers) presented higher Hg concentrations when compared to rural estuaries along the coast of Ceará State (Marins *et al.*, 2002; Vaisman *et al.*, 2005; Costa & Lacerda, 2009); similarly, fish caught off the metropolitan region may also be exposed to higher Hg environmental concentrations. The Mucuripe fish market, the largest in the state, is the major source of fish to the population of Fortaleza and top carnivorous species are the preferred items. Thus, monitoring Hg levels in the marked fish is a safeguard strategy to maintain human exposure under acceptable levels. The aim of this study is to assess the Hg contamination and associated human health risk by the consumption of fish commercialized in Fortaleza coastal area.

MATERIAL AND METHODS

Fish samples taken at the Mucuripe fish market are generally caught in coastal waters by the local artisanal fisherman fleet with small sail boats 'jangadas" and therefore are under the influence of the metropolitan area of Fortaleza. Samples were constituted of fresh whole fish; avoiding fillets, eviscerated individuals or those showing signs of previous treatment for conservation. For comparison purposes, we sampled two tuna species from a different market located in Areia Branca harbor, also in NE Brazil, about 300 km east of Fortaleza. All samples were frozen and transported to the laboratory for analysis. Samples of 0.5 g of lyophilized tissue were digested in 10 ml of concentrated nitric acid (HNO_3) using heating and temperature ramp determined by MARS XPRESS - CEM microwave equipment (Bezerra *et al.*,2012). After digestion, 1 ml of hydrogen peroxide (H_2O_2) was added to the sample in order to avoid re-adsorption of Hg (Adair & Cobb, 1999). Samples extracts were taken to 100 ml flasks with distilled water for subsequent Hg quantification. Cold Vapor Atomic Absorption Spectrometry, in a Nippon Instruments Corporation (NIC) model RA3210A and in a Bacharach - Coleman, model MAS-50 D, performed the quantification of Hg. For the reduction of Hg we used a stannous chloride solution ($SnCl_2$) prepared in 10% sulfuric acid (20% H_2SO_4). Simultaneously analyzed certified standards of biological mate0rial (NIST 2976 Mussel Tissue) gave average Hg recovery of 94.9 ± 6.7%.

To assess health risk associated with ingestion of the Mucuripe Market fish we used the equation (1), reported by Newman and Unger (2002).

$$HQ=E/RfD \quad (1)$$

where, E is the level of exposure or Hg intake and RfD is the reference dose for Hg (Hg = 0.47 µg/kg body weight/day; BCS, 2007). The level of exposure (E) is calculated using the equation (2).

$$E = C \times I / W \qquad (2)$$

where, C is the concentration of Hg (µg.g^{-1} wet weight); I is the ingestion rate per capita (35.6 g day^{-1}; Sartori & Amancio, 2012) and W is the average weight of an adult (70 kg). At HQ < 1.0 exposure level is smaller than the reference dose; meaning that daily exposure to this level is unlikely to cause adverse effects to consumers.

RESULTS AND DISCUSSION

Table I summarizes total Hg concentrations (ng.g^{-1} wet weight) if fish commercialized in the Mucuripe market, Fortaleza, CE. Although most fish species analyzed were carnivorous, they feed on a variety of habitats resulting in Hg concentrations varying two orders of magnitude among them. In general, larger species and individuals presented higher Hg concentrations, in particular piscivorous species. Highest Hg concentrations occurred in large, top carnivorous species, including sharks (*S. cavalla*, *S. brasiliensis*, *G. cirratum* and *R. porosus*). Lowest concentrations (< 40 ng.g^{-1}) were found in the small benthic feeders and the planktivorous clupeid *Opisthonema oglinum*. The largest (>110 cm) individuals of *S. cavalla* were the only specimens to present Hg concentrations higher than the maximum allowed concentration for human consumption for carnivorous fish (1,000 ng.g^{-1}), reaching 1,737 ng.g^{-1}. This result, however, did not occur for any other species, including sharks, with all individuals presenting Hg concentrations below the legal limit. The tuna species (*Thunnus albacares* and *T. obesus*) from the Areia Branca harbor, notwithstanding being top carnivorous, showed average Hg concentration of 166 ± 59 ng.g^{-1} and 231 ± 43 ng.g^{-1}, respectively, probably reflecting their more diversified diet including pelagic invertebrates. Even considering individual specimens, Hg concentration never surpassed the legal limit in these two species.

A survey on total Hg concentration (wet weight) observed in several fish markets worldwide showed varying results depending on fish species and location. Swordfish, a top predator, commercialized around the USA and surveyed nationwide by the Mercury Policy Project (2005), averaged 1,110 ng.g^{-1} with a maximum of 2,330 ng.g^{-1}, whereas in tuna from the same survey average Hg concentrations reached 330 ng.g^{-1} with a

Table I - Total Hg concentrations (ng.g-1 wet weight) in fish marketed at the Mucuripe market, Fortaleza, Ceará State.

Species	N	Major Diet[a]	Size (cm)	Hg
Rhizoprionodon porosus	1	Carnivorous (fish & invertebrates)	85	509
Ginglymostoma cirratum	2	Carnivorous (benthic invertebrates)	185 (154 - 215)	500 ± 330 (266 - 733)
Scomberomorus cavalla	18	Piscivorous	82,2 ± 22,3 (59 – 127)	352 ± 468 (36 – 1,737)
Thunnus obesus	3	Carnivorous (fish & invertebrates)	82 ± 4.4 (79 - 87)	231 ± 43 (189 - 274)
Thunnus albacares	7	Carnivorous (fish & invertebrates)	115.6 + 28.8 (78 - 150)	166 ± 59 (93 - 242)
Scomberomorus brasiliensis	13	Piscivorous	66 ± 12 (53 – 88)	126 ± 108 (48 – 497)
Carangoides bartholomaei	4	Piscivorous	36.4 (30 – 40)	121 ± 21 (54 – 197)
Ocyurus chrysurus	5	Planktivorous	39.4 (33 – 60)	99 ± 33 (39 – 281)
Dasyatis guttata	1	Carnivorous (fish & shellfish)	84	83.4
Diapterus rhombeus	8	Carnivorous (benthic invertebrates)	23.8 (23 – 25)	69 ± 15 (39 – 117)
Holocentrus adscensionis	6	Carnivorous (benthic invertebrates)	28.9 (28 – 30)	66 ± 8,0 (19 – 95)
Lutjanus synagris	7	Carnivorous (fish & shellfish)	32.9 (30 – 37)	58 ± 12 (36 – 80)
Haemulon carbonarium	4	Carnivorous (benthic invertebrates)	18.4 (18 – 19)	52 ± 6.0 (27 – 95)
Cephalopholis fulva[b]	15	Carnivorous (fish & shellfish)	26 ± 4.9 (20 – 33)	50 ± 28 (23 – 94)
Opisthonema oglinum	6	Planktivorous	24.3 (23.5 – 25)	40.9 ± 3.0 (10.2 – 60.4)
Pomadasys corvinaeformis	5	Carnivorous (shellfish & small fish)	23.9 (23 – 25)	39 ± 7.6 (19 – 75)
Haemulon plumieri	5	Carnivorous (shellfish & small fish)	27.1 (24 – 29)	15 ± 8.0 (1.6 – 8.0)
Syacium micrurum	5	Carnivorous (benthic invertebrates)	32.5 (31 – 34)	14 ± 1.2 (11 – 20)

[a] www.fishbase.org; [b]100% organic Hg (Lacerda et al., 2007).

maximum of 680 $ng.g^{-1}$. In New York markets, tuna steaks averaged 600 $ng.g^{-1}$ with a maximum of 2,500 $ng.g^{-1}$ (Burger & Gochfeld, 2006). By-catch commercialized in Guerrero coast, Mexico also showed relatively higher Hg concentrations than those from the Mucuripe market. Species of *Pomadasys* and *Dipterus*, for example, showed average Hg concentrations of 100 and 230 $ng.g^{-1}$, respectively (Spanopoulos-Zarco *et al*., 2014), about 2.5 times higher than the concentrations found in the same species from Fortaleza.

In Brazil, Hg distribution in fish commercialized in local markets was the subject of some studies in the southern coast. The concentration of total Hg found in several fish species sampled from commercial selling shops in São Paulo ranged from 166 to 878 $ng.g^{-1}$. The majority of fish samples presented total Hg concentration lower than the maximum permitted value according to Brazilian legislation (500 $ng.g^{-1}$ for non-predatory and 1,000 $ng.g^{-1}$ for predatory fish species, respectively) (Morgano *et al*., 2007). Concentrations were, in general, higher than those reported for our samples from Fortaleza.

In southern Brazil, Kutter *et al*. (2009) reported average Hg concentrations in 12 commercialized fish, mostly from herbivorous and omnivorous species, varying for 30 to 125 $ng.g^{-1}$, values somewhat higher than many of the species from the Mucuripe market with amore omnivorous diet. In Cabo Frio, SE coast, Silva *et al*. (2011) reported average Hg concentrations in one planktivorous (13 - 57 $ng.g^{-1}$) and three carnivorous (22 - 303 $ng.g^{-1}$) commercialized fish species; similar or slightly lower than the values found in the Mucuripe market fish, of similar diet. Ferreira *et al*., (2012) in an extensive survey of Hg concentrations in fish markets from southern Brazil reported much higher values than those from the Mucuripe market. For example, oceanic top predators, such as *T. albacares* (varying from 10 to 620 $ng.g^{-1}$) and *Xiphias gladius* (varying from 100 to 5,100 $ng.g^{-1}$), showed concentrations up to one order of magnitude higher. Similar results have been reported for top predators commercialized in Uruguay with values varying from 40 to 2,210 $ng.g^{-1}$ (Mendez *et al*., 2001). In general, Hg concentrations increases with fish size in top predators, however, most studies carried on in fish markets frequently included flitches and fillets, which hamper direct comparisons between Hg levels on a regional level. Overall, the levels of Hg found in fish species commercialized in Southern Brazil are generally higher as those reported here for the Mucuripe market, at least for off shore pelagic species mostly of a piscivorous diet.

Table II shows the estimated hazard quotients (HQ) for all the fish species analyzed from the Mucuripe Marked, assuming equal consumption of all species, which is an overestimation for most species. The HQs varied from 0.015 in small omnivorous to 0.551 in sharks, the mean HQ value was 0.148, but the hazard quotients based only on the most consumed species was somewhat larger (0.155). No individual HQ value exceeded the limit of 1.0 considered as the level of actual risk (Spanopoulos-Zarco *et al*., 2014), meaning that daily exposure to levels and rate of fish consumption from the Mucuripe market are not likely to cause adverse effects during the lifetime of the consumers. Even considering critical groups of the larger population, such as artisanal fishers, whose fish consumption rate is generally 2-4 times higher; the low HQ obtained for the Mucuripe fish would not represent any significant exposure risk.

The results show low Hg concentrations in fish marketed at the Mucuripe market, as compared to other markets in Brazil and abroad. Large piscivorous species, however, can show Hg concentrations highest than the acceptable limits for human consumption. Consumers' exposure levels, either considering all analyzed species or only the most consumed top carnivorous species, are much lower than those considered a risk to humans.

Table II - Health risk, expressed as HQ (hazard quotient) associate with fish consumption from the Mucuripe market, Fortaleza, Ceará State.

Fish species	HQ= E/RfD
Rhizoprionodon porosus	0.551
Ginglymostoma cirratum	0.541
*Scomberomorus cavalla**	0.381
Thunnus obesus	0.250
Thunnus albacares	0.180
*Scomberomorus brasiliensis**	0.136
Carangoides bartholomaei	0.131
*Ocyurus chrysurus**	0.107
*Dasyatis guttata**	0.090
Diapterus rhombeus	0.075
Holocentrus adscensionis	0.071
*Lutjanus synagris**	0.063
Haemulon carbonarieum	0.056
Cephalopholis fulva	0.054
Opisthonema oglinum	0.044
Pomadasys corvinaeformis	0.042
Acanthostracion polygonius	0.025
Haemulon plumieri	0.016
Syacium micrurum	0.015
Total Average	0.148
Average of most consumed species	0.155

* Most consumed species based on local observation.

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