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Mercury: biogeochemical and toxicological aspects and levels found in marine fish along the Southern and Southeastern coasts of Brazil

Mercúrio: aspectos biogeoquímicos e toxicológicos e níveis encontrados em peixes marinhos ao longo das costas sul e sudeste do Brasil

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Abstract

Sources of mercury (Hg) introduced into the environment can be natural or anthropogenic. Methylmercury (MeHg) is the most toxic form of the mercury, and is responsible for detrimental effects on human health through the consumption of food, notably marine vertebrates such as carnivorous fish and sharks. This review focuses on aspects related to biogeochemistry and ecotoxicology of mercury in aquatic environments and presents 12 studies with marine fish along the southern and southeastern coasts of Brazil where 50% of the fish sampled had Hg concentrations, above the level established by national and international agencies as safe for human consumption.

Keywords: Mercury. Methylmercury. Biomagnification. Marine fish. Brazilian coast.

Resumo

Fontes de mercúrio (Hg) introduzidos no ambiente podem ser naturais ou antropogênicas. O metilmercúrio (MeHg) é a forma mais tóxica do mercúrio, e é responsável por efeitos prejudiciais sobre a saúde humana através do consumo de alimentos, principalmente por vertebrados marinhos, como peixes carnívoros e tubarões. Esta revisão aborda os aspectos referentes à biogeoquímica e ecotoxicologia do mercúrio em ambientes aquáticos e apresenta 12 estudos com peixes marinhos ao longo das costas sul e sudeste do Brasil, onde 50% dos peixes amostrados apresentaram concentrações de Hg acima do nível estabelecido por agências nacionais e internacionais, como seguros para o consumo humano.

Palavras-chave: Mercúrio. Metilmercúrio. Biomagnificação. Peixes marinhos. Costa brasileira

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1 Introduction

Mercury is a trace element distributed throughout the biosphere, whether by atmospheric transport from natural sources or anthropogenic emissions. However, land and ocean processes play an important role in the redistribution of the element in all ecosystems. It is considered a global pollutant that affects the entire freshwater and marine aquatic food web, via biomagnification process (BELTRAN-PEDREIROS et al., 2011; DIETZ et al., 2013). This work discusses various issues related to mercury, including the biogeochemistry, chemistry, and toxicology involved in the presence of this element mainly marine fish. We thus present a report that will help raise awareness of the need to monitor the presence of this metal in marine environments.

2 Classification and sources of contamination

Metals can be classified as essential and non-essential. Non-essential are those that do not have known biological functions, as is the case of lead (Pb), cadmium (Cd), and mercury (Hg). Essential metals have well-known metabolic functions and are important for the proper functioning of the organism. In this case, copper (Cu), zinc (Zn), and iron (Fe) are a few examples that show toxicity only when they reach excessive levels of incorporation (FERREIRO, 1976). However, it is noteworthy that at high concentrations and in some chemical forms essential elements also represent significant toxicological risk to human health and disruption to ecosystems.

Mercury (Hg) is usually present in low concentrations in the environment, except for places in which this element is naturally enriched. In general, when this metal reaches significant concentrations, usually originating from anthropogenic sources such as urban, industrial or mining waste, it poses a threat to ecosystems, aquatic biota, and consequently to human health. Anthropogenic sources can be classified into two types of sources: point and diffuses. In areas where point sources are absent, the natural contributions added to diffuse inputs are the main forms of Hg emission. In this context, high background levels of this element, as a consequence of lithology or pedology, also can be verified in different regions. There issues are another category of sources for Hg, which currently comprises a percentage above 50% of mercury emissions into the atmosphere. This process is amplified by global warming (UNEP, 2013). Thus the atmosphere acts as a significant diffuse source of mercury to soil, watershed drainage and ocean. The ocean, whose main input is Hg in wet and dry atmospheric deposition, plays an important role in the overall cycle of mercury, acting both as a dispersing medium and as an exposure means (BATRAKOVA et al., 2014). Deep marine sediments are considered important deposits of mercury integration, through the association of this metal with geochemical substrates such as organic matter, oxides - hydroxides of iron and Mn and carbonates. Originated from the suspended particulate matter, this substrate can be deposited to bottom sediments, and may remain there for long periods (tens to thousands of years) (AMOS et al., 2013).

Once released into an aquatic ecosystem in inorganic form, Hg may be altered by processes mediated by micro-organisms and thus join the organic matter present in the environment. During this process, it assumes its organified form of methylmercury (MeHg), which is of greater toxicity to humans (WHO, 1990).

Mercury is present in many industrial activities, such as the production of chlorine, household batteries, fluorescent light bulbs, cement, and charcoal and during mining and mineral processing (WHO, 2007). Human population growth results in an increase in mercury-related activities in order to meet the demand for various products, which leads, in turn, to increased urban and industrial discharges of Hg into aquatic systems, especially in coastal regions. In addition, it is also important to consider both dry deposition and that related to rainfall, as well as soils and sediments as potential sources through which sites far from contaminating sources may present a history of contamination (POISSANT et al., 2008).

3 Biogeochemical cycle

Metallic mercury (Hg^0), inorganic mercury (in its different mercury forms - Hg^{2+} or Hg_2^{2+}) and organic mercury (methylmercury, henceforth referred to as MeHg) are possible chemical forms of mercury in the aquatic environment. The conversion of inorganic mercury form to MeHg by the action of sulphate-reducing bacteria and/ or reducing iron bacteria, or to a lesser extent by photo-oxidation, increases the bioavailability of the metal (WEBER, 1993; BOENING, 2000). After this conversion, MeHg generally enters the food chain mainly via phytoplankton and also through debris chain mediated by bacteria (WEBER, 1993; MASON et al., 2000). Microbial degradation is the dominant methylmercury via demethylation, on the other hand, as photodegradation processes and oxidative demethylation is also considered (WEBER, 1993; MARVIN-DIPASQUALE et al., 2000).

The quality of water in an ecosystem also affects the biogeochemical cycling of mercury. The suspended particulate matter, responsible for most of the migration of Hg^{2+} in the aquatic environment, usually end up settling in the sediment, where this metal can be methylated by sulfate-reducing bacteria particularly in anaerobic conditions (ALMEIDA et al., 2007).

Some physicochemical conditions of the medium encourage and amplify methylation. These include acidic characteristics, low redox potential values, and a high concentration of organic matter. In this environment MeHg, which represents on average only about 0.1 to 1.5% of the total mercury, can still undergo demethylation via reverse reaction due to bacteria present in the sediment (BISINOTI; JARDIM, 2004; LACERDA; MALM, 2008). In addition, about 85% of the total stock of mercury in biota is in the form of methylmercury (LACERDA et al., 1994) while, in the water, this value rarely exceeds 10% of total Hg stock (BISINOTI & JARDIM, 2004).

The balance from these methylation and demethylation reactions determines whether an environment will act as a source or sink of MeHg (BISINOTI; JARDIM, 2004; LACERDA; MALM, 2008).

Marine organisms directly participate in the dynamics of Hg due to bioaccumulation and biomagnifications capacity, which increases the concentrations of the metal to levels higher than water along the food chain. Therefore, because they are at the top of the food chain, predators and larger fish tend to accumulate more Hg in their tissues, and represent the group with the highest potential for human contamination (FERREIRA et al., 2012).

In the aquatic environment, dissolved organic matter interacts with mercury, changing its chemical form, solubility, mobility, viability, and toxicity (RAVICHANDRAN, 2004). When fish ingest Hg, particularly in the form of MeHg, it combines with sulfhydryl radicals of the proteins, forming a very stable chemical bond, thereby hindering its elimination. Neither the cooking process or any other type of treatment eliminates the mercury present in the fish (MARIÑO; MARTÍN, 1976; LACERDA; MENESES, 1995; GUENKA et al., 2003).

4 Ecotoxicology

Ecotoxicological studies are important on fish since these bodies promote greater toxicological risk to humans through the diet. Recently, however, it has been found that the effect on other wild organisms was underestimated. Birds and bats that feed on invertebrates are also showing high levels of methylmercury. Methylmercury is highly harmful to the reproduction of fish and birds (WIENER, 2013).

In marine vertebrates, the major route of absorption of Hg occurs through the diet, which together with the low rate of excretion of those animals leads to increased concentrations of the element along the trophic chain (LEGAT; LAILSON-BRITO, 2010).

Mercury in the environment can be absorbed by the tissues and organs of fish by way of the respiratory system (ex: gills), the integumentary system, and through feeding. The accumulation capacity and the concentration of mercury in fish depend mainly on the amount and bioavailability of the chemical form Hg takes in the environment and vary according to the species, size of the individual, feeding habits, length, weight, age, and mobility (FERREIRO, 1976).

The MeHg is the compound with the highest bioaccumulation in fish due to its lipophilic characteristics (HOFFMAN et al., 2002). In addition, MeHg is more persistent in fish because it is metabolized slowly (MELA, 2004). Yet, it is through their diets that fish absorb most MeHg (above 90%), (GOCHFELD, 2003). In relation to the absorption route, MeHg concentrations in gills are very high when they occur in water, and the intestines present higher concentrations when food is the route of entry. After going through the gills or the gut membranes, MeHg binds to red blood cells and is transported to diverse organs, such as the liver, kidney, spleen, and brain, and much of the MeHg is directed to the skeletal muscle which is bound to the sulfhydryl groups of muscle protein (HOFFMAN et al., 2002). In fish, this fact may be related to the presence of a protective brain mechanism against the accumulation of MeHg (WIENER; SPRY, 1996; HOFFMAN et al., 2002). Controlled experiments have shown that MeHg profoundly affects the development of the central nervous system of *Danio rerio* (zebrafish) embryo (HASSAN et al., 2012). Fish suffering from chronic exposure to MeHg showed loss of motor function and visual acuity, as well as changes in behavior due to the action of the compound in certain regions of the brain (EVANS et al., 1975). Alterations in reproduction are another important toxic effect of mercury in fish. Studies exposing *Pimephales promelas* (fathead minnow) to 0.87 and 3.93 μg.g^{-1} dry weight of MeHg showed that testosterone levels in males and 17β estradiol in females were lower than in those of the control fish. The fall in these hormone levels reduced the gonadosomatic index, decreasing the reproductive success of fish and resulting in a progressive decline in spawning (DREVNICK; SANDHEINRICH, 2003). In another study, Drevnick et al., (2006) found that the same concentrations of MeHg used in the previous study were able to trigger apoptosis in the ovarian follicles of female *P. promelas,* causing a decrease in the production of 17β estradiol. In yet another study, concentrations of 75 ng.g^{-1} dry weight of MeHg injected intraperitoneally in *Astyanax sp.* (tetra), which were provided as prey to *Hoplias malabaricus* (wolf fish or trahira) for 70 days, caused strong toxic effects on the liver and kidney, with necrosis, leukocyte accumulation, and the formation of macrophage aggregates (MELA et al., 2007). Other histological lesions are correlated with the presence of mercury in fish. As they are caused by Hg, these lesions may be important biomarkers of effect for this metal. Safahieh et al. (2012) use histopathology as a biomarker of exposure to mercury. In this work, *Acanthopagrus latus* specimens (yellowfin seabream) were exposed at concentrations of mercury (10-80 μg.L^{-1}). After 3 weeks of exposure, many liver lesions were observed, including enlarged and lateral nuclei, nuclear degeneration and vacuolation; oncotic, apoptic, focal, massive, centrilobular and periportal necrosis; atrophy, lipidosis, hydropic and cloudy swelling, oval cell proliferation; bile stagnation, dilation of sinusoid, intracellular oedema and dark granules in both field and laboratory conditions.

Oxidative stress is also triggered during exposure of fish to methylmercury. Studies with golden grey mullet (*Liza aurata*) collected in Ria de Aveiro, Portugal, showed the occurrence high level of total mercury, as antioxidant responses and peroxidative damage in the liver, gills and kidney. Among the analyzed organs, the kidney presented more mercury accumulated. Among the oxidative answers, catalase showed an increase in all analyzed organs (liver and kidney). The glutathione S-transferase (GST), another antioxidant response, also increased in kidney, organ with mercury accumulated. There was no peroxidative damage (MIEIRO et al., 2011). The antioxidant enzymes superoxide dismutase, catalase, glutathione peroxidase, glutathione S-transferase (GST) and glutathione reductase (GR) increased in liver, muscle and heart. And were also associated increases in peroxidative damage and metallothionein. As for metallothionein, notwithstanding the foregoing result, its application as a biomarker of mercury is now questioned, because the expression of this peptide is subjected to varying tissue and specific species (MIEIRO et al., 2011b).

Jesus and Carvalho (2008) presented a review of other important biomarkers associated with ecotoxicology of mercury in fish, such as chemical, genotoxic (comet and micronucleus assay), hematological, biochemical, histopathological, reproductive and endocrine parameters showing biological changes associated with mercury in fish. An important study was carried out by Rodrigues et al., (2010) in species with different feeding habits collected in Guanabara Bay (impacted area) and Ribeira Bay (reference area). The authors determined the total mercury concentration in white muscle, erythrocytes and plasma tropical fish (*Genidens genidens*/guri sea catfish, *Aspistor luniscutis*/catfish, *Haemulon steindachneri*/chere-chere grunt and *Micropogonias furnieri*/whitemouth croaker). Several biomarkers were used (genotoxic, biochemical and hematologic), but haematocrit, global leucometry and micronucleus essays seemed to reflect the differences on mercury exposure among areas. Currently, these molecular and cellular changes may be accompanied and best known in laboratory studies to prove the cause and effect relationships (dose response curves). The biomarker can show the alterations in the organism before the deleterious effect is established. The aim of these essays is to obtain deeper knowledge of toxicological mechanism and use this information as monitoring tools. They are useful when associated to field studies, when the area impacted with Mercury is compared to supposedly mercury-free area used as reference. This is a more ecotoxicological approach. And in this case, the physical chemical characteristics of the environment that decisively influence the speciation and bioavailability of mercury is relevant to studies.

5 Methylmercury bioaccumulation and biomagnification in fish

Hg has a high absorption rate compared to its rate of elimination, a process known as bioaccumulation, thus levels become concentrated in the bodies of animals that have long life cycles and that feed on other organisms (BRAUNE et al., 2005).

The phenomenon of the bioaccumulation of substances, especially Hg, allows them to be transferred from one trophic level to another when they are present in water, and complexed to dissolved organic matter, reaching levels in fish that exceed limits established for human consumption, notably in carnivorous species (EYSINK, 1991). The higher the position in the food chain, the higher the concentration of Hg and MeHg (WASSERMAN et al., 2001). Bioaccumulation has been reported in many studies describing the relationship between Hg concentrations and the age and length of fish (MONTEIRO; LOPES, 1990; RENZONI, et al., 1998; KASPER et al., 2007; DIAS et al., 2008; KEHRIG et al., 2011; LOPEZ et al., 2013). Kehrig et al., (2002) found that carnivorous fish (*Micropogonias furnieri*/whitemouth croaker) captured in Guanabara Bay accumulated more mercury than planktivorous fish (*Mugil liza*/lebranche mullet) and bivalve molluscs (*Perna perna*/mussel). The use of carnivorous fish is well established as biomonitor of mercury, but some species can be used for the specific purpose of evaluating a particular environmental matrix, such as sediment. In this case, it uses a benthic species. The catfish *Cathorops spixii* (madamango sea catfish) was used to monitor the sediment of two estuaries in the state of São Paulo, Brazil, the estuary of Santos/São Vicente (impacted area) and the Cananeia estuary (reference area). The results of determination of total mercury in *C. spixii* confirmed that the estuary of Santos/São Vicente was impacted with mercury (AZEVEDO et al., 2011). Another relevant aspect is the tissue analyzed in fish. Lacerda et al., (2007) showed greater accumulation of total mercury in *Cephalopholis fulva* (coney) liver than in white muscle in two populations of this species. However, the accumulation of organic mercury, methylmercury, the most toxic form of the metal, occurred more intensely in the muscle.

Similarly, concentrations of MeHg tend to increase as it is transferred through the food web; absorption occurring through its ingestion by large marine organisms (BOWLES, 1999; SHOHAM-FRIDER et al., 2002). Thus, organisms with high trophic levels tend to have higher metal concentrations as a result of this process - called biomagnification (GRAY, 2002). Animals with greater size and longevity therefore tend to present higher MeHg concentrations in their tissues (ATSDR, 1999).

The biomagnification process occurs via feeding when algae and plants are ingested by smaller herbivorous fish (of the lower level of the food chain) and these, in turn, are eaten by carnivorous fish (at the top of the food chain), (KEHRIG et al., 2011).

Because of biomagnification, there is a predictable Hg distribution pattern in the aquatic food chain. In general, for example, omnivorous and piscivorous fish have higher concentrations of mercury than herbivorous fish and scavengers (BOISCHIO; HENSHEL, 2000). Likewise, large predatory species with long life cycles tend to accumulate high concentrations of Hg (RENZONI et al., 1998). Currently, we use the isotopic stability of C and N ($\delta^{13}C$ and $\delta^{15}N$) to determine the mercury flow through the food chain. The $\delta^{13}C$ indicates the feeding behavior of the species and the $\delta^{15}N$ indicates the position (trophic level) of the species in the food chain. Study including crustaceans, cephalopods, fish and dolphins was carried out in three bays of the state of Rio de Janeiro, Guanabara, Sepetiba and Ilha Grande - biomagnification being present in Guanabara and Sepetiba bays. The trophic magnification factor (TMF) values were all above 1 indicating mercury accumulation through the food chain in the three bays studied (BISI et al., 2012). In another study, Kehrig et al., (2013) evaluated the dispersion of mercury from the Paraíba do Sul River plume in the northern state of Rio de Janeiro, in various trophic levels. And the value of the magnification factor for the food chain (FWMF) of 5.4 indicates mercury biomagnification in the study area.

6 Legislation to protect public health

International agencies regulate food consumption by the world population, such as WHO (World Health Organization), FAO (Food and Agriculture Organization - United Nations Organization Food and Agriculture), FDA (Food and Drug Administration - the government agency of the United States responsible for the control of food, food supplements, drugs, cosmetics, medical equipment, biological materials, and products derived from human blood), and the European Union. According to these organs, the maximum values of Hg allowed for human consumption in carnivorous fish is 1 $\mu g.g^{-1}$ wet weight of tissue (W.W.), while for non-carnivorous fish and fishery products the maximum permitted level is 0.5 $\mu g.g^{-1}$. In Brazil, these same values are applied in accordance with the following relevant laws: Decree No. 55871, of 03/26/65 of the Ministry of Health (BRASIL, 1965), Ordinance No. 11 of 5/15/87 of the National Surveillance Secretariat Health - MS (BRASIL, 1987), Ordinance No. 685 of 08/27/98 of the National Surveillance Secretariat Health - MS (BRASIL, 1998), and Normative Ruling No. 42 of 12/20/99 of the Ministry of Agriculture, Livestock, and Supply (BRASIL, 1999).

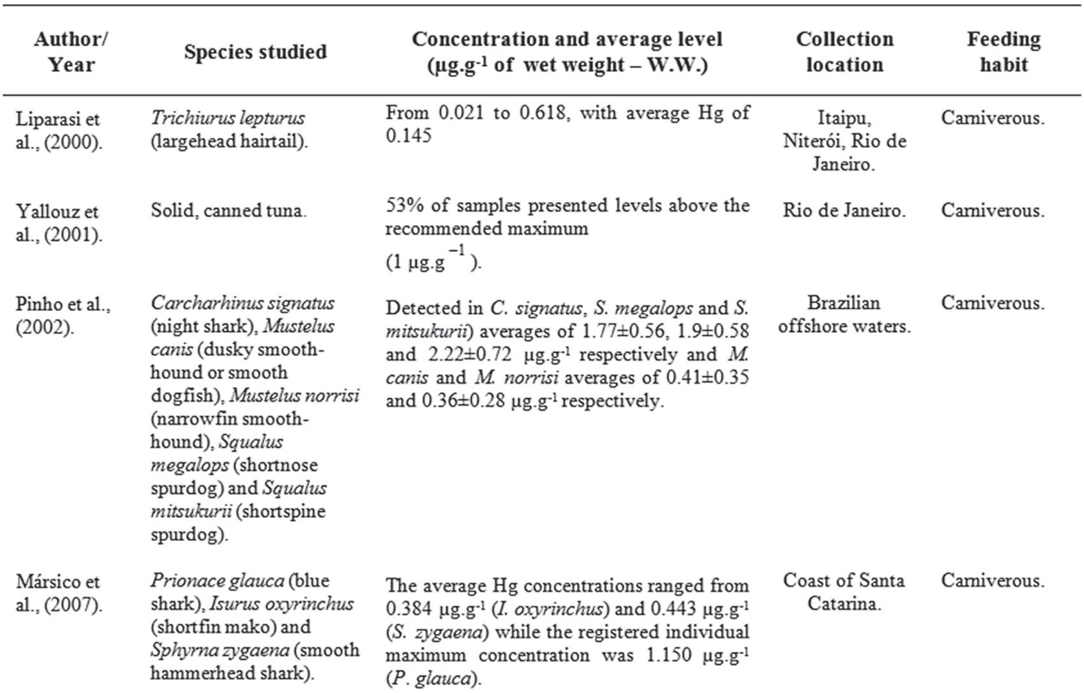
The World Health Organization (WHO, 1990) also established limits for the daily consumption of Hg in food (TDI- Tolerable Daily Intake), which is 0.3 $\mu g.Kg^{-1}.day^{-1}$ of Hg.

7 Studies with marine fish along the Brazilian coast

The first studies aimed at describing the presence of Hg in fish, carried out in Stockholm, Sweden, found high percentages (above 90%) of MeHg corresponding to the total Hg present in muscle tissue and viscera of the salmon and trout analyzed (WESTÖÖ, 1973).

All data discussed in the text refer to the survey carried out between 2000 and 2014, arranged in sequence in Table 1.

Table 1*: Data results on Hg in the muscles of fish collected in Brazil*



Author/ Year	Species studied	Concentration and average level ($\mu g.g^{-1}$ of wet weight – W.W.)	Collection location	Feeding habit
Liparasi et al., (2000).	*Trichiurus lepturus* (largehead hairtail).	From 0.021 to 0.618, with average Hg of 0.145	Itaipu, Niterói, Rio de Janeiro.	Carniverous.
Yallouz et al., (2001).	Solid, canned tuna.	53% of samples presented levels above the recommended maximum (1 $\mu g.g^{-1}$).	Rio de Janeiro.	Carniverous.
Pinho et al., (2002).	*Carcharhinus signatus* (night shark), *Mustelus canis* (dusky smooth-hound or smooth dogfish), *Mustelus norrisi* (narrowfin smooth-hound), *Squalus megalops* (shortnose spurdog) and *Squalus mitsukurii* (shortspine spurdog).	Detected in *C. signatus*, *S. megalops* and *S. mitsukurii*) averages of 1.77±0.56, 1.9±0.58 and 2.22±0.72 $\mu g.g^{-1}$ respectively and *M. canis* and *M. norrisi* averages of 0.41±0.35 and 0.36±0.28 $\mu g.g^{-1}$ respectively.	Brazilian offshore waters.	Carniverous.
Mársico et al., (2007).	*Prionace glauca* (blue shark), *Isurus oxyrinchus* (shortfin mako) and *Sphyrna zygaena* (smooth hammerhead shark).	The average Hg concentrations ranged from 0.384 $\mu g.g^{-1}$ (*I. oxyrinchus*) and 0.443 $\mu g.g^{-1}$ (*S. zygaena*) while the registered individual maximum concentration was 1.150 $\mu g.g^{-1}$ (*P. glauca*).	Coast of Santa Catarina.	Carniverous.

Dias et al., (2008).	*Xiphias gladius* (swordfish) and *Prionace glauca* (blue shark).	Total Hg: 0.13 to 2.26.	Southern coast and Southeastern Brazil.	Carniverous.
Kehrig et al., (2009).*	*Trichiurus lepturus* (largehead hairtail), *Anchoa filifera* (longfinger anchovy), *Paralonchurus brasiliensis* (banded croaker), *Pellona harroweri* (American coastal pellona), *Isopisthus parvipinnis* (bigtooth corvina), and *Cynoscion jamaicensis* (Jamaica weakfish).	Dry weight (D.W.) - *T. lepturus* (1.07±1.06 µg.g^{-1}), *A. filifera* (0.26±0.13 µg.g^{-1}), *P. brasiliensis* (1.07±1.06 µg.g^{-1}), *P. harroweri* (0.25±0.17 µg.g^{-1}), *I parvipinnis* (0.25±0.11 µg.g^{-1}), *C. jamaicensis* (0.30±0.11 µg.g^{-1}).	Northern coast of Rio de Janeiro.	Carniverous, pisciverous, planktiverous and benthic.
Rodrigues et al., (2010).	*Genidens genidens* (marine catfish), *Aspistor luniscutis* (sea catfish), *Haemulon steindachneri* (chere-chere grunt or grunt) and *Micropogonias furnieri* (whitemouth croaker).	Guanabara Bay: *G. genidens* (0.102±0.043 µg.g^{-1}), *M. furnieri* (0.057±0.013 µg.g^{-1}). Ribeira Bay: *H. steindachneri* (0.310±0.206 µg.g^{-1}), *A. luniscutis* (0.178±0.078 µg.g^{-1}).	Ribeira Bay and Guanabara Bay, both located in Rio de Janeiro State.	Carniverous and omniverous.
Silva et al., (2011).	*Sardinella brasiliensis* (Brazilian sardinella), *Katsuwonus pelamis* (skipjack tuna), *Caranx latus* (horse-eye jack) and *Cynoscion striatus* (striped weakfish).	*S. brasiliensis*: 0.128±0.045 µg.g^{-1} *K. pelamis:* 0.209±0.036 µg.g^{-1} *C. latus:* 0.210±0.113 µg.g^{-1} *C. striatus:* 0.466±0.389 µg.g^{-1}	Cabo Frio, Rio de Janeiro State.	Carniverous and planktiverous.
Ferreira et al., (2012).	*Micropogonias furnieri* (whitemouth croaker), *Trichiurus lepturus* (largehead hairtail), *Thunnus sp.* (canned tuna), *Thunnus albacares* (yellowfin tuna), *Xiphias gladius* (swordfish) and *Pteroplatytrygon violacea* (pelagic stingray).	Average Hg: *M. furnieri* (0.124±0.054 µg.g^{-1}), *T. lepturus* (0.078±0.034 µg.g^{-1}), *Thunnus sp.* (0.169±0.122 µg.g^{-1}), *T. albacores* (0.187±0.112 µg.g^{-1}), *X. gladius* (0.393±0.637 µg.g^{-1}), *P. violacea* (0.224±0.074 µg.g^{-1}).	Brazil.	Carniverous.
Seixas et al., (2012). *	*Trichiurus lepturus* (largehead hairtail).	0.44 to 0.87 µg.g^{-1}.	Guanabara Bay, Ilha Grande Bay and Búzios, Rio de Janeiro.	Carniverous.
Beneditto et al., (2013).	*Trichiurus lepturus* (largehead hairtail).	Non-adult samples: (48.5±8.9 cm) - 0.309±0.120 µg.g^{-1}. Adult samples: (143.0±11.0 cm) - 1.290±0.908 µg.g^{-1}	Northern Rio de Janeiro State.	Planktiverous and carniverous.
Seixas et al., (2014).	*Mugil liza* (lebranche mullet), *Citharichthys spilopterus* (bay whiff); *Micropogonias furnieri* (whitemouth croaker), *Trichiurus lepturus* (largehead hairtail).	*M. liza*: 0.032±0.018 (inorganic Hg) and 0.035 ±0.02 (MeHg); *C. spilopterus*: 0.003 ± 0.003 (inorganic Hg) and 0.127±0.070 (MeHg); *M. furnieri*: 0.002±0.001 (inorganic Hg) and 0.271±0.100 (MeHg); *T. lepturus*: 0.009±0.005 (inorganic Hg) and 0.349±0.094 (MeHg).	Ilha Grande Bay, Rio de Janeiro State.	Planktiverous, benthic, and carniverous

** Dry weight (D.W.); # liver analyzed in addition to muscle.*

In a study of *Trichiurus lepturus* (largehead hairtail) specimens, caught at Itaipu Beach in Niterói, State of Rio de Janeiro, although the total Hg levels did not exceed 1 $\mu g.g^{-1}$ of W.W., the authors point out that *T. lepturus*' carnivorous status fosters the accumulation of small or large amounts of Hg in its tissues and organs, posing risk to human health due to high rates of human consumption of the specie (LIPARASI et al., 2000).

Yallouz et al., (2001) studied Hg levels of solid canned tuna sold in the city of Rio de Janeiro. Thirty nine samples from 5 different brands and lots were analyzed. According to these findings, 53% of the samples had Hg levels that exceeded the recommended maximum. In only one of the five brands tested all Hg levels were within the limits permitted by the World Health Organization.

Pinho et al., (2002) conducted an analysis of the Hg levels in muscle tissue of species of sharks collected in southern Brazilian offshore waters. Sharks usually have relatively high Hg levels also affected by diet, age, length, and sex. Five species of sharks with different habits were analyzed: *Carcharhinus signatus* (night shark), *Mustelus canis* (dusky smooth-hound or smooth dogfish), *Mustelus norrisi* (narrowfin smooth-hound), *Squalus megalops* (shortnose spurdog) and *Squalus mitsukurii* (shortspine spurdog). The highest Hg concentrations were all above the limit established by the Brazilian legislation. Lied piscivorous species (*C. signatus, S. megalops* and *S. mitsukurii*) and species that feed mainly on invertebrates (*M. canis* and *M. norrisi*) in the stomach contents. The authors concluded that the results indicate that feeding habits influence the total Hg level in sharks, and that concentrations of methylmercury (MeHg) analyzed in *S. mitsukurii* and *M. canis* are also influenced by feeding habits.

Mársico et al., (2007) analyzed samples from 39 sharks of three species (*Prionace glauca*/blue shark, *Isurus oxyrinchus*/shortfin mako and *Sphyrna zygaena*/smooth hammerhead shark), captured and collected at a depth of about 50 m and 190 miles off the coast of Santa Catarina State (27°08'S-28°38'S and 45°30'W-46°53'W) by professional fishermen of a tuna fishing boat. The species and total length of each shark were recorded. The primary purpose of the study was to collect information on the accumulation of Hg in the specimens, considering the variation of Hg concentration between individuals and the relationship between the Hg content and the size of the fish. The average Hg concentrations ranged from 0.384 (*I. oxyrinchus*) and 0.443 $\mu g.g^{-1}$ (*S. zygaena*) while the registered individual maximum concentration was 1.150 $\mu g.g^{-1}$ (*P. glauca*). The Hg concentrations measured in the muscle tissues of the analyzed sharks showed great variation. Such variability reflects the cumulative process of Hg uptake in fish and the interactions of biotic parameters such sex, age, size, and growth rate, according to Hornung et al., (1993).

Dias et al., (2008) analyzed the total Hg in the muscle tissue of *Xiphias gladius* (swordfish) and *Prionace glauca* (blue shark) specimens collected along the southern and southeastern coasts of Brazil. Samples were obtained through the Programa de Avaliação do Potencial Sustentável de Recursos Vivos na Zona Econômica Exclusiva (REVIZEE Program) and from commercial fishing sources in Itajaí, Santa Catarina State. A total of 95 specimens (48 *X. gladius* and 47 *P. glauca*) were analyzed and correlations were made between the total Hg, length, and weight of fish. The total Hg ranged from 0.13 to 2.26 $\mu g.g^{-1}$ of W.W., and in 62% of the samples it was above the limits established by the World Health Organization (WHO). The authors observed that the specimens with higher biomass showed the greatest concentrations of mercury, and that the concentrations of this element were directly related to the time of exposure of the organism to the environment and to their weight.

A study conducted by Kehrig et al., (2009) along the northern coast of Rio de Janeiro, analyzed the total Hg concentrations and Se (selenium) in muscle tissue of individuals of *Sotalia guianensis* (Guiana dolphin), accidentally caught in fishing nets and some species of fish, such as: *Trichiurus lepturus* (largehead hairtail), *Anchoa filifera* (longfinger anchovy) and *Paralonchurus brasiliensis* (banded croaker), and also the mantle of cephalopod *Loligo sanpaulensis* (Sao Paulo squid) which is part of the diet of *S. guianensis*. The total Hg concentrations and Se were also determined in the muscle tissue of fish *Pellona harroweri* (American coastal pellona), *Isopisthus parvipinnis* (bigtooth corvina), and *Cynoscion jamaicensis* (Jamaica weakfish), which are part of the diet of *T. lepturus*. The average of total Hg concentration (wet weight – W.W.) in the muscle tissue of *T. lepturus* individuals was lower than the allowed limit for human consumption by Brazilian law to predatory fish and recommended by the World Health Organization. It was also found that the total Hg concentration in muscle tissue of *S. guianensis* was approximately 12.6 times higher than the same tissue of *P. brasiliensis*, and 16.4 times higher than the mantle of *L. sanpaulensis*.

Rodrigues et al., (2010) studied mercury bioaccumulation in four fish species: *Genidens genidens* (marine catfish), *Aspistor luniscutis* (sea catfish), *Haemulon steindachneri* (chere-chere grunt or grunt), and *Micropogonias furnieri* (whitemouth croaker), collected from the Ribeira and Guanabara Bays, both located in the state of Rio de Janeiro. 198 and 83 samples of fish muscles were obtained from Ribeira Bay and Guanabara Bay, respectively. Average Hg levels of *G. genidens* were higher levels in Guanabara Bay than in Ribeira Bay. Among the species studied in Ribeira Bay, the highest mercury concentrations were found in the *H. steindachneri* species, which had an average concentration closer to the limit set by the World Health Organization (WHO) for the human consumption of fish. The carnivorous species *H. steindachneri* and *M. furnieri*, however, had significantly different concentrations of mercury. This difference may be associated with the age of the specimens collected, differences in the metabolism of each species, and migratory behavior. The authors concluded that although the release of Hg in Ribeira Bay is not significant, mercury seems to be more available to fish compared to the Guanabara Bay, where sediments act as reservoir environmental of metal. The high load of organic matter carried by sewage generates anoxic conditions in the sediment, where Hg tends to be accumulated in an unavailable form, that of HgS. The authors also point out that any change in the physicochemical conditions in Guanabara Bay may cause the Hg stored in surface sediments to become bioavailable.

A study conducted in Cabo Frio, in the state of Rio de Janeiro determined the concentrations of Hg in four upwelling region fish species of different trophic levels. The species studied were *Sardinella brasiliensis* (Brazilian sardinella), *Katsuwonus pelamis* (skipjack tuna), *Caranx latus* (horse-eye jack), and *Cynoscion striatus* (striped weakfish). The Hg concentrations ranged from 0.053 $\mu g.g^{-1}$ in *S. brasiliensis* to 1.215 $\mu g.g^{-1}$ in *C. striatus* and, with the exception of planktivorous fish, MeHg levels reached about 90% of the total Hg concentrations. The average values, however, did not exceed the recommended limits for the species studied (Table 1). The authors point out that the data available in the literature are insufficient to elucidate the risk associated with the presence of Hg in fish caught in upwelling areas for its consumers (SILVA et al., 2011).

Ferreira et al., (2012) conducted a study to determine the extent of mercury contamination in *Litopenaeus vannamei* (shrimp), *Micropogonias furnieri* (whitemouth croaker), *Trichiurus lepturus* (largehead hairtail), *Thunnus sp*. (canned tuna), *Thunnus albacares* (yellowfin tuna), *Xiphias gladius* (swordfish), and *Pteroplatytrygon violacea* (pelagic stingray). In terms of the number of swordfish analyzed (n = 83), 2.4% exceeded the maximum limit of Hg recommended for carnivorous fish by national legislation. The authors concluded that, with the exception of shrimp, depending on the frequency of consumption, these species may constitute a risk to human health.

That same year, Seixas et al., (2012) conducted a study which analyzed the concentrations of Hg and Se (selenium) in muscle tissue of *Trichiurus lepturus* (largehead hairtail) caught in three different areas of Brazil: Guanabara Bay, Ilha Grande Bay, and on the coast of Buzios, all in the state of Rio de Janeiro. Significant differences were observed in the concentration of Hg between the areas. The total length and the individual size ranges also influence the accumulation of Hg. However, these biological parameters did not influence the accumulation of Se. Regional differences can probably be attributed to differences in environmental conditions such as water temperature and primary production, in addition to other factors such as the choice of prey and the availability of these elements in the environment.

Di Beneditto et al., (2013) determined the total concentrations of Hg and the isotopic signature of N and C (δ^{15}N and δ^{13}C) in *Trichiurus lepturus* (largehead hairtail) collected in northern Rio de Janeiro State. The authors concluded that adults of the species *T. lepturus* accumulate mercury through bioaccumulation caused by dietary changes at different ontogenetic stages. These changes are reflected in the δ^{15}N level, which identifies its trophic level, and the δ^{13}C level, which establishes the feeding type, of the species.

Seixas et al., (2014) conducted a study analyzing differences in inorganic Hg and MeHg biomagnification in the tropical marine food web in Ilha Grande Bay, on the southern coast of Rio de Janeiro State, Brazil, which is considered a hotspot (natural area of high biodiversity vulnerable to extinction) with a large number of protected areas. The species collected included grouped species of phytoplankton (microplankton), *Farfantepenaeus brasiliensis* (redspotted shrimp; n=90), *Mugil liza* (lebranche mullet; n=30), *Citharichthys spilopterus* (bay whiff; n=16), *Micropogonias furnieri* (whitemouth croaker; n=40), *Trichiurus lepturus* (largehead hairtail; n=21), and *Sotalia guianensis* (Guiana dolphin; n=6). The authors observed that while MeHg increased with rising trophic positions, inorganic Hg did not show the same pattern. They concluded that although the study area possesses some potential sources of pollution, it can be considered a non-contaminated area due to the low levels of metals such as nickel (Ni), copper (Cu), chromium (Cr), manganese (Mn), zinc (Zn), and Hg (mercury) found in its sediments and fish in recent decades.

8 Conclusion

Fish constitute one of the most important food items of human diet. However, their tissues and organs can absorb and accumulate large concentrations of mercury from the environment, not only through the gills via breathing, but also from integument and feeding, by way of bioaccumulation or biomagnification mechanisms.

Due to its high toxicity, high levels of absorption, low excretion rates, and its ability to bioaccumulate in the food chain, mercury absorbed by humans through the consumption of fish represents a real risk to public health.

Because of the high mercury levels found in many commercial fish species, particularly carnivores, the ingestion of such species contaminated with mercury (Hg) and methylmercury (MeHg), the most toxic and cumulative form of the element, can cause severe damage to the human body. The high mercury levels measured in fifty percent of the works with ocean fish captured in southern Brazil are in fact surprising considering the distance from the continent (i.e., the main producer of anthropogenic contamination) of the regions they occupy. The existence of these concentrations, however, may be explained by the accumulation of this element along the food chain. Therefore, high mercury levels in ocean fish should be considered a red flag signaling a possible increase in the base level of Hg in the oceans resulting from anthropogenic activities. Studies applying stable isotopes of nitrogen and carbon, as well as total mercury have contributed to elucidate the origin of this contamination.

In light of these facts, information presented in this paper may help institutions linked to fishery and public health activities, while pointing out the need for more effective actions with regard to the regulation of the consumption of certain species of fish. Programs that monitor mercury in fish are valuable tools to reduce risks associated with the consumption of fish contaminated with mercury.

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