MERCURY SPECIATION IN FISH OF THE CABO FRIO UPWELLING REGION, SE - BRAZIL

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A B S T R A C T

Mercury distribution in the oceans is controlled by complex biogeochemical cycles, resulting in retention of trace amounts of this metal in marine biota. The impact of upwelling processes in this metal behavior has been overlooked. Data from literature are insufficient to evaluate the risks associated with the presence of mercury in the fish collected in upwelling areas and its consumers. Therefore, the aim of the present work was to perform a study of mercury speciation in four fish species belonging to different trophic levels from Cabo Frio-Brazil upwelling region. The total mercury content vary of 53 ng g-1 (*Sardinella brasiliensis* - sardine) to 1215 ng g-1 (*Cynoscion striatus* - striped weakfish) and, with exception of the planktivorous fish, methylmercury levels reaches circa 90% of total mercury concentration.

R E S U M O

A distribuição de Mercúrio nos oceanos é controlada por um complexo ciclo biogeoquímico, resultando na retenção de pequenas quantidades na biota marinha. O impacto dos processos de ressurgência costeira no comportamento desse metal tem sido negligenciado. Dados da literatura são insuficientes para elucidar o risco associado com a presença de mercúrio em peixes capturados em áreas de ressurgência e seus consumidores. Portanto o objetivo do presente trabalho foi realizar um estudo de especiação de mercúrio em quatro espécies de peixes pertencentes a diferentes níveis tróficos da região de ressurgência de Cabo Frio - Brasil. O conteúdo total de mercúrio variou de 53 ng g-1 (*Sardinella brasiliensis* - sardinha) to 1215 ng g-1 (*Cynoscion striatus* - pescada) e, com exceção da espécie planctivora, os níveis de metilmercúrio atingem cerca de 90% da concentração total de mercúrio.

Descriptors: Marine fish, Methylmercury, Food chain, SACW - South Atlantic Central Water.
Descritores: Peixes marinhos, Metilmercúrio, Cadeia trófica, ACAS - Água Central do Atlântico Sul.

INTRODUCTION

The importance of fish consumption for humans is well established, they sustain poor coastal communities and constitute their most important source of proteins and omega-3 polyunsaturated fatty acids (EGELAND and MIDDAUGHT, 1997; BURGER AND GOCHFELD, 2004). In spite of their benefits as food, fish are also well known to be a trophic link for the biomagnification of the mercury that is emitted from anthropogenic sources.

The principal dietary source of neurotoxic mercury compounds is the ingestion of species of fish in which methylmercury has accumulated (HARRIS et al, 2003). Methylmercury from fish has been linked to neurological damage (Minamata disease) (GOYER et al, 2000) and increased risk of myocardial infarction (GUALLAR et al, 2002). On the other hand, their Chronic Exposure to considerable concentrations of dietary methylmercury impairs fishes' reproductive capacity, by inducing apoptosis in steroidogenic gonadal cells (DREVNICK et al. 2006).

In the case of mercury, the main contamination path to the aquatic and terrestrial environments is through the atmosphere that is constantly being enriched by anthropic inputs that spread the inorganic form of the metal worldwide. Although the inorganic form is relatively less toxic, in the anoxic zones of aquatic ecosystems Hg may undergo methylation that enables it to enter the trophic chain, thus affecting humans and constituting a significant toxic hazard, mainly for fishing communities (ROSS, 1996).

Fishing communities are spread throughout coastal zones but are largely concentrated in the productive upwelling areas where the plentiful supply of fish is able to sustain a greater number of fishermen's families. Although the surface covered by these upwelling areas accounts for less than 0.1% of the world ocean, they are important for the world fishery catch, representing 10 % of total production (CHAVES et al., 2008). For instance, the northern Humboldt Current System off Peru produces more fish per unit surface than any other area of the oceans. On the other hand, the upwelling phenomenon is the main route by which methylmercury is transferred from the minimum oxygen zones to higher productive photic zones. Therefore, during the phytoplankton bloom in upwelling zones, the methylmercury formed in the deeper areas may be incorporated into the food chain and reach humans. That is why the mercury transfer in the upwelling environment should be observed more closely than is necessary in other coastal areas.

Methylmercury is the fraction of total Hg that is most efficiently transferred to the highest levels in the aquatic food chain (WATRAS AND BLOOM, 1992). The organic form (MeHg) is absorbed faster and more efficiently than the inorganic (Hg^{2+}) species and presents a longer biological half-life. The elimination of MeHg from aquatic organisms, including fish, takes months (VAN WALLEGHEM et al., 2007). Many studies have shown increasing mercury concentrations from planktivorous fish to carnivorous species (AUGELLI et al., 2007; MAURICE-BOURGOIN, et al., 2000; STORELLI, et al., 2005a). This indicates that methylmercury can concentrate progressively up the successive links of the aquatic food chain reaching high concentrations due to biomagnification (MASON et al, 1996). Furthermore, considering that almost 100 % of the mercury in predator fish is of the organic form, it is supposed that methylmercury is strongly linked through covalent bindings to sulfidril groups of proteins (BLOOM, 1992).

In the Southern Hemisphere, several studies have reported total mercury contamination in aquatic environments and mercury accumulation in fish (MIRLEAN et al., 2005; KEHRING et al., 2002; BOISCHIO and HENSHEL, 2000). However, the vast majority of studies are devoted to freshwater or estuarine environments.

Brazil is the Latin American country with the greatest extension of territorial sea (3.6 million km^2) in the Atlantic Ocean. However, little is known about the concentration of mercury in marine fish of the South Atlantic. SILVA-FILHO et al. (2008), in a recent review of mercury accumulation in Brazilian fish, found only 9 articles dealing with these species, including data on only 39 of them , 9 being sharks.

The Brazilian coast between 22ºS (Cabo de São Tomé) and 28ºS (Cabo de Santa Marta Grande) is one of the most important sites for marine fisheries on the western coast of the South Atlantic Ocean. This area consists of approximately 1000 Km of coastline influenced by coastal upwellings, including the Cabo de São Tomé (22ºS), Cabo Frio (23ºS) and Cabo de Santa Marta Grande (28ºS) (ROSSI-WONGTSCHOWSKI and MADUREIRA, 2006; CALADO et al., 2010). Within this region, the coastal region of Cabo Frio is where this phenomenon occurs with greatest intensity. This site has great ecological and economic importance (fisheries and tourism) since it is an area for the recruitment of species like squids, sardine and anchovy (VALENTIN, 2001). This abundance of organisms during upwelling events provides a source of food for species at the top of the food chain such as carnivorous fish, seabirds and marine mammals.

In view of the fact that the consumption of fish (which may contain high levels of MeHg) is the main mercury transfer route to humans, this study seeks to characterize mercury speciation in fish of different trophic levels in the Cabo Frio upwelling region, Rio de Janeiro, Brazil.

Study Area

The coastal region of Cabo Frio is located on the southeastern coast of Brazil (23º01'S, 42º00'W, Fig. 1) and is characterized by upwelling events driven by the wind (CARBONEL, 2003) that induces a particularly dry climate (BARBIERI, 1984). The coastal upwelling and also the occurrence of hot and dry northeasterly trade winds are the main factors responsible for the low rainfall (823 mm) in this region (BARBIERI, 1984). The land use in the Cabo Frio region is dominated by summer residences and tourism. Within the region there is only one industrial plant (Álcalis National Company) that applies the Solvay process to produce sodium carbonate from shells extracted from the neighboring Araruama Lagoon.

This region is known for its elevated marine productivity, due to the seasonal upwelling phenomenon. The upwelling occurs generally after 3 or 4 days of constant 10-knot NE winds which bring cold deeper nutrient-rich water to the surface, resulting

in a phytoplankton bloom. The sea surface temperature that normally ranges from 20 to 22ºC, may decrease to 15°C, triggering an enrichment in nutrient concentration of up to 10-12 µM NO_3-N and a phytoplankton production of up to 6 mg L^{-1} (in chlorophyll a; CARBONEL and VALENTIN, 1999). The upwelling intensifies during the summer months, under the influence of prevailing E-NE winds; the surface water flows offshore due to Coriolis transport and is replaced by the South Atlantic Central Waters (SACW). The SACW rises from a depth of 300 m and reaches the surface in a coastal string extending for 5 km (RODRIGUES and LORENZZETTI, 2001). The upwelling waters are advected in a W-SW direction and affect the oceanographic conditions along the coast, reaching areas located 70 km or more to the west of Cabo Frio (GUIMARAENS et al., 2005). This pattern is reversed during the passage of frontal systems from the South, with prevailing Southwest winds and associated downwelling. During these periods, the warmer water approaches the coast. The thermocline depth fluctuates according to the intensity and duration of the winds (CARBONEL, 2003).

The four fish species of this study (sardine *Sardinella brasiliensis*, skipjack tuna *Katsuwonus pelamis*, blue runner *Caranx latus*, and striped weakfish *Cynoscion striatus*) are important fishery resources exploited along the Rio de Janeiro State coast and contributed with about one third (30.2%) of the fishery production in 2006 (IBAMA, 2008). Some information regarding the classification, habitats, alimentary habits and respective fishing areas are shown in Table 1. Although the skipjack tuna is an oceanic species, during upwellings it approaches the coast to benefit from the increased production. The specimens collected in this study were caught during these periods. The other species use the upwelling area as their regular habitat.

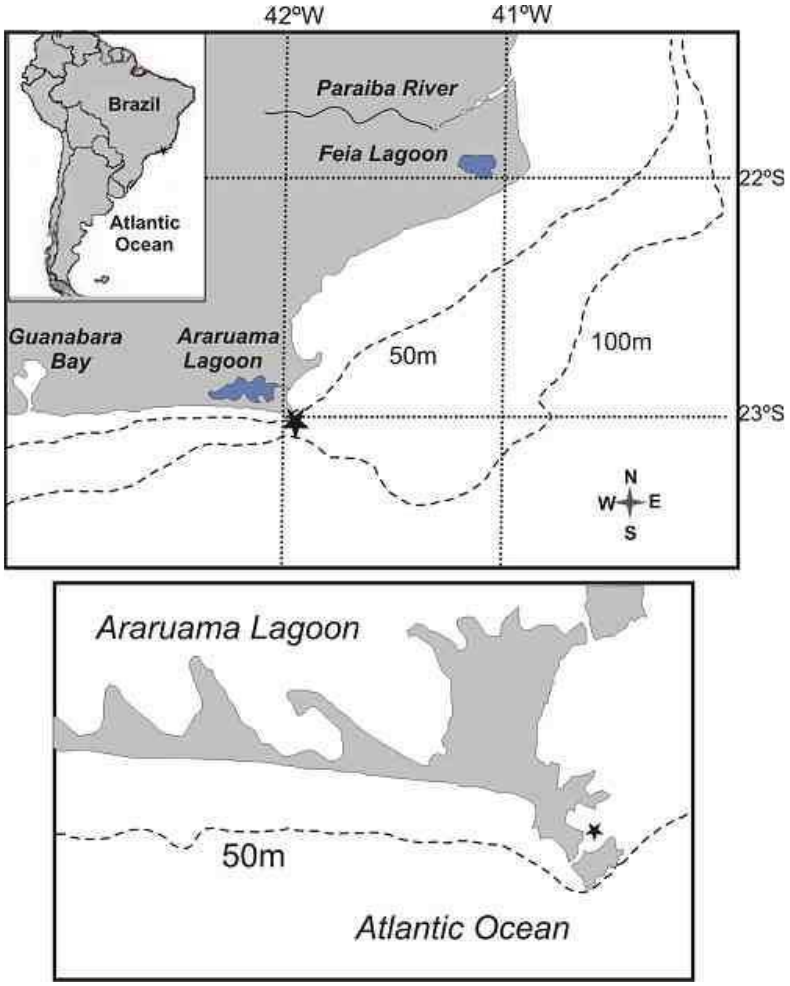

Fig. 1. Map showing the study area.

Table 1. Classification, Habitat, Food habitat and occurrence area of the fish species studied.

Common Name	*Family*	*Species*	*Habitat*	*Food habit*	*Fishing area*
Skipjack tuna	Scombridae	*Katsuwonus pelamis*	Pelagic	Piscivorous	Oceanic
Striped weakfish	Sciaenidae	*Cynoscion striatus*	Demersal	Carnivorous	Coastal Estuarine
Sardine	Clupeidade	*Sardinella brasiliensis*	Pelagic	Planktivorous	Coastal Estuarine
Blue runner	Carangidae	*Caranx latus*	Pelagic	Carnivorous	Coastal Estuarine

METHODS

Samples of fresh fish were obtained from local fishermen to assure its local origin. The samples were conditioned in plastic bags and transported under cooling to the laboratory, where composite samples were prepared. The muscle tissue was removed from the dorsal-lateral area (in filets) and stocked in polyethylene bags at a sub-zero temperature (-20ºC) until analysis.

For the determination of mercury the samples were lyophilized for 48 h to ensure the complete removal of moisture. Immediately afterwards, they were ground in an agate mortar to obtain homogeneous samples. Between each pulverization, the mortar was thoroughly washed with a nitric acid 10% v/v solution and then with ultrapure water Milli-Q (<18 μΩ) to avoid cross-contamination. 0.50 g of the powdered muscle tissue samples was placed in an extraction vessel together with 5 mL of ultrapure tetramethyl ammonium hydroxide (TMAH, 25% w/w). This mixture was then placed in an open microwave system and submitted to an irradiation of 40W, for 3 min. The extracts obtained were stored in ultra-clean glass tubes for later mercury speciation analysis. Detailed information on this procedure may be found in MONPERRUS et al. (2005).

The extract obtained (2 mL) was transferred to a glass tube and the solution then buffered to pH 4 with 5 mL acetic acid-sodium acetate solution (0.1 M). One mL of iso-octane and 1 mL of tetrapropylborate (1% w/w) were added for derivatization reactions. The glass tube was then closed, shaken by hand for 5 minutes and centrifuged at 2500 rpm for 15 minutes. The concentrated mercurial species in the iso-octane phase were separated with pipettes and stored in an injection vial at -18ºC until measurement.

The mercury species determination was undertaken in the Laboratoires de Chimie Analytique, Bio-Inorganique et Environnement of the Université de Pau et des Pays de l'Adour, France, using the hyphenated techniques of Gas Chromatography and Microwave Induced Plasma Atomic Emission Spectrometry (GC-MIP-AES).

The chromatographic separation of mercury species was performed using a GC HP 6890, with an injection volume of 2 μL, each analysis taking about 10 minutes. Gas chromatography is an efficient and effective technique, currently used in environmental evaluations (URÍA and SANZ-MEDEL, 1998). The detection system MIP-AES used was an HP G2350A, a plasma detector which has been frequently used in mercury speciation studies (Uría and Sanz-Medel, 1998). The coupling between GC and MIP-AES was undertaken with a heated tubular transfer line of silicon reaching a higher temperature than that of the GC oven.

The validation of the analytical methodology was assessed by using two certified reference material (DORM-2 dogfish muscle tissue, NRCC and CRM 710 oyster tissue, IRMM). Excellent recoveries (varying from 88 to 98%, inorganic mercury and methylmercury, respectively) were obtained with a similar repeatability to that reported by NRCC and IRMM, thus validating the methodology employed. Blanks were run with every batch of 10 samples and the results are reported in ng g^{-1} on a dry weight basis, the detection limit being estimated at 0.2 ng g^{-1} for both mercury species (Hg^{2+} and MeHg).

External standards were used daily for the correction of possible mercury losses during the extraction and derivatization steps of the biological samples and also for the detection of eventual matrix effects. The total mercury (HgT) concentrations were not measured. However, due to the analytical methodology employed the value of HgT can be considered as being the sum of Hg^{2+} plus MeHg concentrations.

RESULTS AND DISCUSSION

Table 2 shows concentrations of each mercury species present in the sample extracts. In general, the total Hg concentrations in the fish of this region are lower than the data given in the literature. For *Sardinella brasiliensis* species (pelagic fish inhabiting coastal waters) the total mercury concentration is around 1.7 to 10 times lower than those observed in the Mediterranean Sea and on the Tunisian coast for *Sardina pilchardus* (JOIRIS et al., 1999). Moreover, the species *Katsuwonus pelamis* also presented lower total mercury concentrations than those reported in studies of the tuna species of the Western Indian Ocean (KOJADINOVIC et al., 2006) and Mediterranean Sea (CABÃNERO et al., 2004; STORELLI et al., 2005a). The higher mercury concentrations observed in fish in the Mediterranean Sea can be attributed to the fact that their waters are 5 times richer than those of the Atlantic (BALDI, 1984).

Table 2. Total, organic (methylmercury) and inorganic (Hg^{2+}) mercury concentration in four marine fishes from Cabo frio region. All concentration values are expressed in ng g^{-1} (dry weight).

Fish species	length (cm)	Mercury species (ng g^{-1} dry weight)			Site	Reference
		Methylmercury CH_3Hg^+	Inorganic mercury Hg^{2+}		Total mercury	
	range (mean±SD)					
Sardinella brasiliensis (n=25)	13-21	18.0 - 126.9 (49.9 ± 21.9)	30.3 - 152.7 (77.9 ± 31.4)	53.0 - 229.7 (127.8 ± 45.0)	Atlantic Ocean: Southeast Brazil	**This study**
Sardinella aurita (n=4)	-	-	-	(90)	Atlantic Ocean Mauritania	Romeo *et al* (1999)
Sardinella aurita (n=115)	(18.7)	-	-	(320)	Mediterranean Sea: north/east Tunisia	Joiris *et al* (1999)
Sardinella aurita (n=32)	(18.5)	-	-	(190)	Mediterranean Sea: south Tunisia	Joiris *et al* (1999)
Sardina pilchardus (n=5)	-	(280)	-	(300)	Spain	Cabañero *et al* (2004)
Sardina pilchardus (n=49)	(17.2)	-	-	270 - 750 (415)	Mediterranean Sea: north/east Tunisia	Joiris *et al* (1999)
Sardina pilchardus (n=38)	(17.4)	-	-	190 - 400 (260)	Mediterranean Sea: south Tunisia	Joiris *et al* (1999)
Sardina pilchardus (n=36)	14 - 23 (18)	-	-	*(55)	North Atlantic	Thibaud (1992)
Sardina pilchardus (n=53)	-	-	-	550-2050	Thyrrhenian Sea	Bernhard (1985)
Caranx latus (n=3)	27-36	67.0 - 309.6 (198.1 ± 22.7)	4.7 - 23.6 (11.6 ± 10.4)	90.6 - 314.3 (210.5 ± 112.7)	Atlantic Ocean: Southeast Brazil	**This study**
Caranx caninus (n=6)	-	-	-	332	Pacific Ocean Mexico:	Ruelas-Inzunza *et al* (2008)
Caranx hippos (n=4)	67 - 68			*880-1540 (1170)	Atlantic Ocean Suriname	Mol *et al* (2001)
Cynoscion striatus (n=6)	22-55	117.1 - 1126 (435.4 ± 61.7)	3.1 - 89.2 (30.9 ± 32.7)	142.6 - 1215.2 (466.4 ± 389.2)	Atlantic Ocean: Southeast Brazil	**This study**
Cynoscion guatucupa (n=4)	35 - 50	-	-	*65.3-126.9 (88.8)	Atlantic Ocean: Southern Brazil	Kütter *et al*, (2009)
Cynoscion guatucupa (n=11)	(43.2)	-	-	<150-810 (350)	Atlantic Ocean: Uruguayan Coast	Viana *et al* (2005)
Cynoscion acoupa (n=8)	39.1 - 90.0	-	-	*90 -340 (180)	Estuaries: Suriname	Mol *et al* (2001)
Cynoscion virescens (n=38)	38.5 - 78	-	-	*70-630 (290)	Estuaries: Suriname	Mol *et al* (2001)
Cynoscion arenarius (n=2)	-	1600 - 2470 (2040)	-	2210 - 2610 (2410)	Atlantic Ocean: Southern Florida (USA)	Kannan *et al* (1998)
Katsuwonus pelamis (n=4)	21-33	154.2 - 227.9 (199.1 ± 32.6)	3.0 - 21.2 (10.4 ± 8.6)	158.2 - 238.7 (209.5 ± 36.2)	Atlantic Ocean: Southeast Brazil	**This study**
Katsuwonus pelamis (n=39)	41 - 85 (68)	-	-	(670)	Western Indian Ocean	Kojadinovic *et al* (2006)
Katsuwonus pelamis (n=5)	-	-	-	(340)	Western Indian Ocean	Matthews (1983)

The muscle tissues from the sardine species presented the highest inorganic mercury contents of the fish species studied, probably due to their low capacity to methylate the mercury obtained from the water. Data from the literature (MOREL et al., 1998) show that inorganic mercury corresponds to 70 - 90% of mercury levels found in surface marine waters. Furthermore, due to their feeding habits, sardines incorporate mercury from phytoplancton which do not methylate mercury, thus presenting low concentrations of the organic form (SILVA, 2006). Accordingly to SILVA (2006), inorganic mercury is the predominant form (above 70%) found in the phytoplankton and zooplankton of the study region. The results of the other three fish species show that organic mercury is the predominant form, reaching *c*. 90% of the total mercury concentrations. This behavior can be attributed to the fact that all the other fishes are carnivorous, feeding on other species that concentrate methylmercury and thus engender biomagnification. Furthermore, the selective enrichment of the organic species is also due to the low excretion rate, engendering a higher turn-over time in the fishes' tissues (BLOOM, 1992). Some authors also report that higher trophic chain level fishes are capable of converting inorganic mercury into methylmercury (GANTHER and SUNDE, 2007; MASON et al., 2000)

It may be noted in Table 2 that the lowest methylmercury values were found in sardine (planktivorous species) and the highest ones in striped weakfish (a carnivorous one). KANNAN et al. (1998) found high values of methylmercury in striped weakfish off southern Florida, four times higher than those occurring on the Cabo Frio Coast, demonstrating the important role of this species in the mercury transfer studies of Atlantic Ocean fish. CHOY et al. (2009) observed that demersal carnivorous species present a greater tendency to incorporate mercury than do the pelagic ones. This is attributed to the greater mercury availability at the water-sediment interface due to the methylation processes that occur in this system. MONTEIRO et al. (1996) verified an increase in mercury levels in fish from greater depths, with higher mercury content in species from mesopelagic than from epipelagic habitats.

The increase in methylmercury concentration along the trophic chain has been observed in previous studies (AL-MAJED and PRESTON, 2000; STORELLI et al., 2005b), which indicates that this organic mercury concentration can increase progressively toward the more elevated trophic levels, due to biomagnification (MASON et al., 1996; SCHAANNING et al., 1996).

The other two species (blue runner and skipjack tuna, both from the pelagic zone) presented similar average methylmercury concentrations. However, the largest concentration range observed for the blue runner (a carnivorous species) is probably due to its more diverse feeding habits than those of the other piscivorous species (skipjack tuna).

Brazilian quality criteria legislation for mercury in commercialized fish establishes maximum values of 500 ng g^{-1} and 1,000 ng g^{-1} for omnivorous and carnivorous species, respectively (ANVISA, 1998). Of all the fish studied, the striped weakfish was the only species that showed a mercury concentration (1215 ng g^{-1}) above those limits, in the largest fish - in total length (TL) - of this species. Significant positive correlations between the total length (TL) and total mercury concentration (THg) as well as between TL and organic mercury concentration were observed for all the species studied.

According to ROLFHUS and FITZGERALD (1995), in upwelling waters the amount of methylated mercury and its transference to the trophic web is four times greater than in typical coastal waters. However, the low methylmercury concentrations found in this study suggest that there may be some processes that regulate its availability in surface waters. One of the processes that might be advanced is photocatalytic organic mercury decomposition in surface waters that have been exposed to intensive sunlight (SELLER et al., 1996). Moreover, inorganic mercury can also be photoreduced by other biotic and abiotic mechanisms (NRIAGU, 1994; ANDERSON et al., 2007).

CONCLUSION

Mercury speciation in the tissues of fish of upwelling areas seems to be determined by their feeding habits and environmental concentrations. As observed elsewhere, the concentrations of mercury in the waters of the Atlantic are lower than those found in the Mediterranean, engendering lower concentrations throughout the trophic chain. Due to the consistent biomagnifications of methylmercury through the trophic chain, carnivourous fishes present higher concentrations of the organic form. Nonetheless, the planktivorous species seem to accumulate significant amounts of inorganic mercury, the concentrations of which are higher than those in carnivorous fish. Despite a lack of clarity regarding the methylation mechanism within a fish's body, this is also a factor that must be involved in the control of methylmercury concentrations in planktivorous fishes.

The total mercury levels presented in this study are below the maxima permitted by Brazilian legislation for fishery products, with the exception of the *Cynoscion striatus*. These results point to the need for a broad evaluation of methylmercury levels in fish that live below the thermocline, in view of the fact that this anoxic zone favors the methylation of mercury

that will enter the trophic chain, causing significant biomagnification throughout the food chain.

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