Mercury in Indigenous, Introduced and Farmed Fish from the Semiarid Region of the Jaguaribe River Basin, NE Brazil

L. D. Lacerda · B. G. B. C. Costa · D. N. Lopes ·
K. Oliveira · M. F. Bezerra · W. R. Bastos

Abstract Indigenous, introduced and farmed fish species were collected from the Jaguaribe Basin, NE Brazil to assess total and methyl mercury concentrations in muscle tissue and to determine its relationship with fish origin. The results obtained from introduced species were compared to the Hg content of their original area of occurrence, which is located in the Amazon region. Farmed and wild individuals of *Oreochromis niloticus* (tilapia) were also compared. Introduced species presented lower Hg contents compared to their Amazonian counterparts. Wild individuals of *O. niloticus* also presented higher Hg contents than farmed individuals with similar sizes. However, methyl Hg concentrations were not significantly different between the two groups. Total Hg and methyl Hg concentrations were higher in carnivorous species, especially those from the Amazon region, and surpassed the Brazilian guidelines for fish consumption. Based on their Hg content, Jaguaribe basin fish do not pose a significant threat to human consumption.

Keywords Introduced fish · Aquaculture · Tilapia · Mercury · Contamination

The introduction of high-economic value species and intensive fish aquaculture are important uses of waterways and artificial reservoirs in the semiarid region of northeastern Brazil, where over 90 % of the region's water resources are artificially controlled by dams. The Jaguaribe River basin is strongly modified by human intervention, and water diversions and dams have been introduced to improve protein availability from aquatic ecosystems. Amazonian species have been introduced in the Jaguaribe River basin since the beginning of the 20th century, whereas exotic species such as tilapia (*Oreochromis niloticus*) have more recently been used for aquaculture.

At the Castanhão Reservoir in Ceará State, which is the largest reservoir in the Jaguaribe basin and possesses a nominal water volume of 6.7×10^9 m^3, approximately 19,000 tons per year of *O. niloticus* are produced via cage aquaculture. Moreover, annual production of *O. niloticus* is planned to expand to 66,500 tons in 2015 (Molisani et al. 2013). Because the alien species tilapia is the preferred species in local aquaculture, escaped individuals have colonized most regional sub-basins, reproducing in nature and efficiently competing with native fish species, similar to introduced Amazonian species, which were previously released in lakes and dams throughout this basin.

Intensive fish farming uses large amounts of aquafeeds, of which nearly 35 % are lost as fish excreta and excess pellets. Thus, minor constituents of aquafeeds from caged and wild individuals, including trace metals such as Hg, may contaminate fish meal (Choi and Cech 1998). Recent success in the colonization of tilapia and other introduced species, which are important items in the diet of local populations, may promote pollutant exposure via the consumption of contaminated fish by local human populations. Exposure to Hg through the contaminated fish consumption has not been investigated in the Jaguaribe basin, although present expansion plans indicate that aquafeed use in local aquaculture may reach 150,000 tons by 2015.

L. D. Lacerda (✉) · B. G. B. C. Costa ·
D. N. Lopes · K. Oliveira · M. F. Bezerra
Laboratório de Biogeoquímica Costeira, Instituto de Ciências do Mar, Av. Abolição 3207, Fortaleza, CE 60165-081, Brazil
e-mail: ldrude@pq.cnpq.br

W. R. Bastos
Laboratório de Biogeoquímica Ambiental Wolfgang Christian Pfeiffer, Universidade Federal de Rondônia, Rodovia BR-364 Km 9.5, Porto Velho, RO 78900-500, Brazil

In the present study, we compared Hg concentrations in aquafeeds, bottom sediments and the muscle tissue of farmed and wild fish collected in the Castanhão Reservoir region and captured by local fishermen downstream of the reservoir dam along the Jaguaribe River in order to compare the Hg contents of fish to Brazilian legal limits and to evaluate potential human exposure to Hg through fish consumption.

Materials and Methods

Farmed fish individuals (n = 18) were collected in a local farm and were selected to fill in the range of sizes and weights of captured wild individuals (n = 20), which were collected by local fishermen from the Jaguaribe River, downstream of the reservoir dam. Indigenous and introduced species were also collected from the same area. For comparison, individuals from both introduced and indigenous species were collected in the Madeira River basin, Amazon. River and reservoir sediments (n = 20) were collected using a Van Veen grab sampler to compare Hg concentrations. Samples (n = 6) of the five different brands of aquafeeds used in the farm were also collected for analysis.

Fish samples for Hg determination were collected using pre-cleaned materials according to accepted protocols for Hg analysis (Marins et al. 2002). All glass and plastic ware were washed with a 5 % Extran solution and deionized water and were immersed in 10 % HNO_3 for at least 24 h. Prior to analysis, glass and plastic ware were washed with deionized, ultrapure water, dried in an oven at 40°C and protected from dust and contact with metallic surfaces. Approximately 0.5 g of aquafeed, fish muscle and dried sediment were digested with 10 mL of concentrated HNO_3 in Teflon vials and a MARS-Plus microwave furnace and were analyzed by cold vapor atomic absorption spectrophotometer (CVAAS). The detection and quantification limits were 0.03 and 1.7 ng g^{-1}, respectively. The total Hg (Hg-T) determination was validated using a standard reference material (NIST 2976 – Mussel tissue and NIST 1646a – Estuarine Sediment). The analytical results were precise and were accurate at 94 ± 3 % and 102 ± 3 %, respectively. Concentration values were not corrected for the recoveries found in certified material. Samples for methyl Hg determinations comprising aliquots of approximately 100 mg of lyophilized fish muscle tissue were placed in an oven at 68°C for 3–4 h with 3.0 mL of 25 % KOH/methanol (degree HPLC) (Liang et al. 1994; Bloom and Fitzgerald 1988; EPA 2001). The samples were placed in the dark to avoid possible degradation of MeHg. Subsequently, the ethylation process was performed using 200 mL of 2 mol/L acetate buffer (pH 4.5) followed by

30 μL of sample and 50 μL of tetra ethyl sodium borate (1 %). MeHg was quantified on a GC–AFS (MERX^{TM} Automated Methyl Mercury Analytical System, Brooks Rand, USA) (Taylor et al. 2011). Certified material (DOLT-2) was run with each batch of samples, and a mean recovery of 104 % ± 6 % was obtained for MeHg. The detection limit of the method was 0.50 ng g^{-1}.

Results and Discussion

The Hg-T concentration in aquafeed and bottom sediment is presented in Table 1. Different aquafeeds presented significantly different Hg concentrations. Specifically, aquafeeds used for juveniles showed higher Hg concentrations (11.5–30.1 ng g^{-1}) than those used for adults (1.4–6.3 ng g^{-1}) due to the higher content of fish meal in juvenile formulations than those for adult fish, which is primarily composed of plant protein (soya). Sediment Hg concentrations were nearly four times higher in the reservoir than areas downstream of the dam, likely due to the accumulation of debris from fish cages and the high organic matter content and small particle size of reservoir sediments compared to fluvial sediment.

Table 2 presents Hg-T and methyl Hg concentrations in fish species sampled from the Jaguaribe River basin, NE Brazil and the Madeira River basin in the western Amazon, with the exception of tilapia, which is not present in the Madeira River basin. For all of the species, concentrations in the Amazon site were higher than in the Jaguaribe basin, even for species that were originally introduced from the Amazon region (*S. rhombeus* and *C. pleiozonas*). The Madeira River basin is known for its relatively higher Hg content due to small scale gold mining (Bastos et al. 2006) and naturally Hg-enriched soils (Lechler et al. 2000), as confirmed by the higher concentrations found in bottom

Table 1 Total Hg concentration in the different types of aquafeed used in Castanhão Reservoir aquaculture and the average concentration of bottom sediments obtained from the reservoir and areas downstream of the dam

Sample type	n	Hg-Tot. (ng g^{-1} dry weight)
R1 – small juveniles	6	30.1 ± 6.3
R2 – juveniles	6	11.5 ± 2.1
R3 – growth period	6	2.7 ± 2.1
R4 – growth period	6	1.4 ± 0.5
R5 – final fattening	6	6.3 ± 3.5
Reservoir sediment	20	26.5 ± 1.5
Fluvial sediments downstream of the dam	20	7.5 ± 4.1
Madeira River bottom sediments[a]	14	46.2 ± 4.9

[a] Data from Bastos et al. (2006)

Table 2 Size (cm), weight (g), total Hg (Hg-Tot) concentration (ng g^{-1}) and percent of methyl Hg (MeHg) in indigenous and introduced fish species in the Jaguaribe River Basin, NE Brazil and in the same species residing in the Madeira River Basin, Western Amazon

Fish species	Origin/diet	Location (Basin)	Length (cm)	Weight (g)	Hg-Tot (ng g^{-1})	MeHg (%)	n
Prochilodus nigricans	Indigenous	Jaguaribe	(237)	(271)	(6.9)	(60.9)	10
	Detritivorous		190–310	128–578	5.8–8.4	19–100	
		Madeira	(251)	(393)	(95)	n.a.	53
			192–308	163–682	12–409		
Leporinus friderici	Omnivorous	Jaguaribe	(209)	(160)	(18.4)	n.a.	14
	Indigenous		185–230	140–180	12.6–23.2		
		Madeira	(210)	(240)	(79)	n.a.	8
			192–230	181–308	23–272		
Serrasalmus rhombeus	Carnivorous	Jaguaribe	(174)	(130)	(40.9)	67	40
	Introduced		133–210	40–204	7.6–68.5	35–93	
		Madeira	(167)	80–324	(568)	100	13
			135–201	(178)	226–1,703	–	
Hoplias malabaricus	Carnivorous	Jaguaribe	(353)	620–717	(21.3)	86	4
	Indigenous		330–375	(668)	14.9–27.7	61–100	
		Madeira	(297)	412–824	(319)	n.a.	7
			282–322	(540)	192–567		
Cichla pleiozonas	Carnivorous	Jaguaribe	(253)	(243)	(30.4)	n.a.	10
	Introduced		215–290	130–362	13.3–59.5		
		Madeira	(245)	(402)	(379)	100	13
			211–299	211–777	110–1,143	–	

sediments compared to the Jaguaribe River basin and the Castanhão reservoir.

Regardless of the sampling site, carnivorous species presented higher concentrations than fish with other diets, which is a well-documented relationship that is independent of the sampling location. Compared to the Brazilian consumption guidelines of 1,000 and 500 ng g^{-1} for carnivorous and non-carnivorous fish, respectively (ANVISA 1998), only carnivorous *S. rhombeus* and *C. pleiozonas* from the Madeira River basin presented concentrations surpassing the guidelines. In the Jaguaribe basin, all species presented lower Hg concentrations than the guidelines. The percentage of methyl Hg was also higher in carnivorous species but showed no difference among sampling sites, although fewer determinations were performed, which hampered appropriate comparisons between the two sites.

Morphological parameters and total and methyl Hg concentrations in farmed and wild tilapia from the Castanhão reservoir and the Jaguaribe River, respectively, are shown in Table 3. Wild fish were heavier compared to farmed fish, and the Hg-T concentration of wild animals (29.8 ± 10.1 ng g^{-1}) was significantly higher ($p < 0.01$) than that of farmed ones (17.0 ± 9.0 ng g^{-1}). In contrast, the percentage of methyl Hg relative to the Hg-T burden was not significantly different among the two groups ($p > 0.05$). Compared to the nektonic habitat and use of aquafeed as the major diet of farmed fish, the higher Hg

concentrations of wild animals was attributed to the more diversified diet of wild individuals and access to bottom sediment. However, organic mercury accumulation in the two groups was not influenced by either variable and was similar among the two groups.

In most studies on *O. niloticus*, Hg-T concentrations are typically very low. In many African lakes, tilapia showed concentrations less than 25 ng g^{-1}, regardless of their size (Tadiso et al. 2011). Even in lakes moderately contaminated by mining effluents, the Hg content of tilapia seldom surpassed this concentration (Ouédraogo and Amyot 2013). In general, Hg concentrations are slightly higher in younger individuals, possibly due to the zooplankton-based diet of juveniles, which shifts to a more herbivorous diet in adults, causing a reduction in their Hg body burden (Desta et al. 2006). In areas where there are direct releases of Hg containing effluents, such as in several Nicaraguan lakes, tilapia presents Hg concentrations that may exceed the recommended marketing limits (McCrary et al. 2006). In a comprehensive survey of the Hg contents of cultured tilapia from 39 farms in southeastern Brazil, Morgano et al. (2005) showed detectable Hg concentrations in 32 farms and an average concentration of 19.8 ng g^{-1} (n = 108), which is not significantly different from the values obtained in tilapia from the Castanhão reservoir.

A lower Hg content is often observed in farmed fish from different species compared to their wild counterparts

Table 3 Size (cm), weight (g), total Hg concentration (ng g^{-1}) and percent of methyl Hg in wild and farmed tilapia from the Jaguaribe River Basin, NE Brazil

Species	Origin	Size (cm)	Weight	Hg-Tot. (ng g^{-1})	MeHg (%)	n
O. niloticus	Farmed	19.9 ± 2.0 (18–25)	181 ± 58 (125–316)	17.0 ± 9.0 (2.7–38.1)	84.5 (52.4–100)	18
O. niloticus	Wild, exotic	20.6 ± 1.1 (19.0–23.5)	238 ± 49 (152–300)	29.8 ± 10.1 (17.1–57.3)	70.8 (49.7–95.2)	20

(Ikem and Egilla 2008; Nakao et al. 2009). The lower Hg content of farmed fish is frequently associated with their rapid growth, which results in the dilution of Hg concentrations in fish muscle, and is also related to higher lipid accumulation in farmed individuals (Jardine et al. 2009). Differences in the diets of aquafeed of farmed fish are also responsible for lower Hg concentrations relative to wild populations (Nakao et al. 2009). Farmed tilapia at our research site feed on aquafeeds with a greater content of plant protein, in particular soya, which generally presents very low Hg concentrations (Table 1). At the studied farm, even aquafeeds used to feed juveniles during the first 30 days of rearing presented relatively low Hg concentrations ranging from 11.5 to 30.1 ng g^{-1}. During the rest of the growing period, which is approximately 1 year, aquafeeds showed even lower Hg contents (1.4–6.3 ng g^{-1}).

Carnivorous species from both river basins presented a significant positive correlation ($p < 0.01$) between size and Hg-T concentration. Therefore, the final Hg content of carnivorous fish can be predicted if they reach the largest size attained for their species. In carnivorous species from the Amazon, large animals frequently surpass the maximum limit for consumption imposed by Brazilian legislation (Bastos et al. 2006; Maurice-Bourgoin et al. 2000). However, when considering the observed size-mercury content relationship, even the largest fish sampled from the Jaguaribe basin would not reach the maximum limit for human consumption and do not pose significant risk for human consumption.

The low Hg concentrations found in farmed and wild tilapia and the lack of any correlation between size and Hg content in this species, which is the most consumed fish in the basin, strongly reduces the risk of contamination to the local human population.

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