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Emission factor and balance of mercury in fish farms in an artificial reservoir in NE Brazil

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Abstract This paper estimated the mercury (Hg), emission factor, and mass balance from caged fish farming in the Castanhão Reservoir, NE Brazil, based on monitoring of a typical farm of Nile tilapia (*Oreochromis niloticus*). The total Hg input to the farm reached 1.45 gHg ha^{-1} year^{-1}, from which 0.21 gHg ha^{-1} year^{-1} was exported out as fish biomass, ultimately resulting in an emission factor of 1.24 gHg ha^{-1} year^{-1} for the reservoir or approximately 8.27 mgHg ton fish^{-1} year^{-1} produced. Most of the input came from aquafeeds with concentrations varying from 1.4 to 31.1 ng g^{-1}, depending on the type of aquafeed. The Hg concentrations in fish were very low and varied from 1.0 to 2.9 ng g^{-1}. These values are two orders of magnitude lower than the legal limit for human consumption. The estimated total annual discharge of Hg from farming into the reservoir is 174 g for 18,000 tons of fish produced and may reach 387 g when the reservoir reaches its total capacity (40,000 tons), which is expected to occur in 2020. The mass balance, considering the deposition and accumulation rates, showed that approximately 40 % of the total Hg input accumulate in farm sediments (0.72 g ha^{-1} year^{-1}), which is approximately 60 % of the deposition rate estimated through the sediment traps and suggests that 0.54 gHg ha^{-1} year^{-1} could eventually be transported out of the farm to the reservoir. Notwithstanding these facts, the total annual input of Hg from fish farming to the Castanhão Reservoir is less than 1.0 % of the total input from anthropogenic sources.

Keywords *Oreochromis niloticus* · Fish farming · Mercury · Emission factor · Sedimentation · Hydrodynamics

Introduction

Mercury (Hg) is a highly toxic, persistent global that accumulates in the environment, in biota, and in humans, especially in its methylated form (MeHg) (Pourreza and Ghanem 2009). The high residence time of Hg in aquatic environments allows it to be recycled in the water column and, eventually, to be deposited in sediments, thus making it available for methylation processes, absorption, and accumulation in the trophic chain (UNEP 2013). The main route of Hg poisoning in humans is through the consumption of aquatic organisms, primarily fish that are valued for their high nutritional content but may also have high levels of Hg (Kitahara et al. 2000).

Studies on fish farms have reported the presence of metals, including Hg, in aquafeeds used commercially (Tacon and Forster 2003; Tacon and Hasan 2007). Some studies have shown that aquafeed contamination usually results from the use of ingredients that contain high concentrations of metals. For example, Choi and Cech (1998) found 66 ng g^{-1} of Hg in commercial fish pellets and noted that the excess food supply to the cages contributed to the accumulation of aquafeed residues and fish feces. This increases Hg concentrations in bottom sediments and suspended particles, directly influencing the methylation process of inorganic mercury (Hurley and Binkowski 2006). Recent studies of shrimp aquaculture in the Jaguaribe Basin showed high Hg inputs into the watershed from shrimp farms, which raised environmental concerns.

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However, no results on the relative importance of fish cage aquaculture as an Hg source to the environment exists for this basin.

In recent years, aquaculture has become a promising activity in the search for ways to meet world food demand, expanding the production of fish and evolving into an alternative to the currently stagnant fisheries industry (FAO 2007; Thomas et al. 2012). In Brazil, the availability of dammed water resources from the construction of hydropower plants and large reservoirs to supply water for urban and agricultural purposes also allows the expansion of fish farming. This promises employment and income-generating activities for locals and acts as a catalyst for social and economic development. Unfortunately, environmental impacts of fish aquaculture in reservoirs have been reported in many areas in Brazil, though these generally relate to eutrophication (Costa et al. 2014).

The Castanhão dam is the biggest public multi-use reservoir in the Brazilian northeast and is of great economic importance for the State of Ceará, where it is located. It was completely flooded in 2004 and has a total storage capacity of 6.7 billion cubic meters, covering a total flooded area of 325 km^2. The reservoir is 48 km in length and has a maximum depth of over 50 m (DNOCS 2013). The reservoir is located in the middle basin of the Jaguaribe River (Goes Filho 2013) and is the major fresh water source for approximately 40 % of human and agricultural use in the basin. In 2006, the "Castanhão Aquaculture Park" was inaugurated, and grants for the deployment of fish farming in net cages along the dam were given. There are approximately 15,000 net cages producing approximately 18,000 tons per year of Nile Tilapia (Oreochromis niloticus) in the reservoir. In total, 75 ha of net cages has been installed from 2010 to present (DNOCS 2013). This quantity represents only 40 % of the actual capacity of fish production in the reservoir, and at the end of this decade, this production may increase considerably, reaching approximately 40,000 t of fish and covering approximately 190 ha (CONPAM 2011). If the growth of fish farming production matches that of shrimp farming production, the Hg inputs to the reservoir may increase due to its ubiquitous presence in aquafeeds. The bioavailability of this toxic metal and the large annual contribution of aquafeed that is required to maintain the expected increase in productivity suggest that an evaluation of the expected Hg inputs from the activity to the reservoir needs to be performed.

This study evaluates the relative importance of fish farming as a significant source of Hg to the Jaguaribe basin, similar to that reported for shrimp farming, by presenting the first estimate of an emission factor and calculated the Hg mass balance associated with intensive fish farming. These values are derived from a typical farm in the semi-arid region of NE Brazil. The emission factor (EF) was calculated by monitoring all stages of the farm's production process, and the mass balance

was quantified by measuring Hg concentrations in different elements of the farm (fish, aquafeed, sediment, water, and suspended material) and by measuring the flows between these elements (fish production; sedimentation rate, and hydrodynamics). Given these representative features and production processes, the data were then extrapolated to the entire Castanhão Reservoir.

Materials and methods

The emission factor (EF) is a tool primarily used to quantify contaminant loads when systematic measures to do so are nonexistent in situ, and it is applicable globally (Nriagu and Pacyna 1988; Lacerda 2003), regionally (Vaisman and Lacerda 2003; Lacerda and Marins 1997), and locally (Marins et al. 1998; Lacerda et al. 2011). This estimate accounts for the sources of Hg and aims to identify relationships between the productive activity and the Hg load released into the environment; it does so by using production data, inputs of Hg containing substances to the activity, volumes and Hg concentrations available for effluents, and retention rates of Hg before it reaches the receiving body of interest (Lacerda et al. 2011).

The emission factor of fish aquaculture was generated by determining Hg concentrations present in aquafeeds and fish and calculating the production parameters for a net-cage fish farm installed in 2010 and located on the northern banks of the Castanhão Reservoir in the Jaguaribe River, NE Brazil (latitude, 5.50° 30′ S; longitude 38.46° 99′ W). The primary species grown in local fish farms is the Nile tilapia (O. niloticus). This fish is widely farmed in Brazil and around the world because it is fast growing and performs well in intensive production systems. Table 1 shows the main parameters of the production farm studied, which are typical of intensive, net-cage Nile Tilapia farms both in Brazil and around the world. To extrapolate the results obtained from the farm, we used data on the annual production of the reservoir available from the Political Council for the Environment of Ceará State (SEDETA 2013).

To quantify the Hg mass balance of net-cage fish farming, we considered only the inputs and outputs of production. Aquafeed was considered the sole source of Hg to the farm,

Table 1 Management features of the studied fish farm representative of the net-cage aquaculture practiced in the Castanhão Reservoir and in northeastern Brazil

Feature	Amount
Total area of the studied farm	4 ha
Fish production	600 ton year^{-1}
Aquafeed consumption	1032 ton year^{-1}
Food conversion rate	1.72

and sedimentation and commercialized fish biomass were the major outputs. Inputs from atmospheric deposition and soil denudation were not accounted for because of the very low rainfall in this semi-arid region. Other typical anthropogenic Hg sources have not been observed in the reservoir basin and were thus not quantified. The magnitude and management features of the studied farm are presented in Table 1.

To estimate Hg inputs from the fish farm, the Hg concentrations were measured in samples of the five different aquafeeds used in the region; their length of utilization during a typical growth cycle was also noted. Aquafeed samples ($n=$ 20) were dried in an oven at 60 °C to a constant weight prior to digestion. Total inputs were obtained by estimating Hg concentrations based on the utilization period of each aquafeed class. To estimate Hg outputs as exported fish biomass, 60 commercial-size (≥1.000 g) individuals of *O. niloticus* were collected from the farm. Each animal was dissected, and muscle tissues, internal organs, gills, skin, and bones were isolated. Samples from approximately 10 individuals were homogenized and freeze-dried before analysis. Concentrations were multiplied by the relative contribution of the sample type to the total fish biomass because only whole fish are commercialized from the farm.

The Hg concentrations were also obtained from six sampling stations. Three stations were located among the net cages (PT1, PT2, and PT3) to obtain concentrations of Hg in the area under the direct influence of cultivation; two stations were set at a distance from the cages but were still in the farm area (PT4 and PT5); and one point was set outside the boundary of the farm area (PT6) and considered as a control station. Duplicate samples of water, suspended matter, and bottom sediments were collected from each station.

Water samples were collected in acid washed 1500 ml polyethylene terephthalate (PET) bottles. Samples were filtered for suspended matter analysis in glass microfiber filters (Whatman GF/F) with a pore diameter of approximately 0.7 μm, after being ashed to 450 °C for 12 h. Sampling stations are depicted in Fig. 1. After filtration, a subsample of the filtrate was stored in 500 ml PET bottles (Copeland et al. 1996) and frozen until they were analyzed for dissolved Hg (Hg-D). Filters were dried at 40 °C to constant weight to quantify total suspended solids (TSS) and were used to determine the particulate Hg (Hg-P). Sediment samples were collected from the same sampling stations (Fig. 1) with the help of a Van Veen dredge and dried in an oven at 60 °C to a constant weight. Because all sediment samples were composed of fine clays, no separation of grain size was performed. Two sediment traps were deployed inside the farm to obtain deposition rates (Fig. 1). At a single station, two sediment cores were collected by divers, who inserted 50-mm-diameter acrylic tubes in the reservoir bed until they reached the hard surface of the flooded soil, thus allowing a rough estimation of sedimentation rates within the farm area. The concentrations of Hg, organic matter, and Al that had

Fig. 1 Study area, sampling points, and deployment locations of the sediment traps in the aquaculture farm studied are highlighted
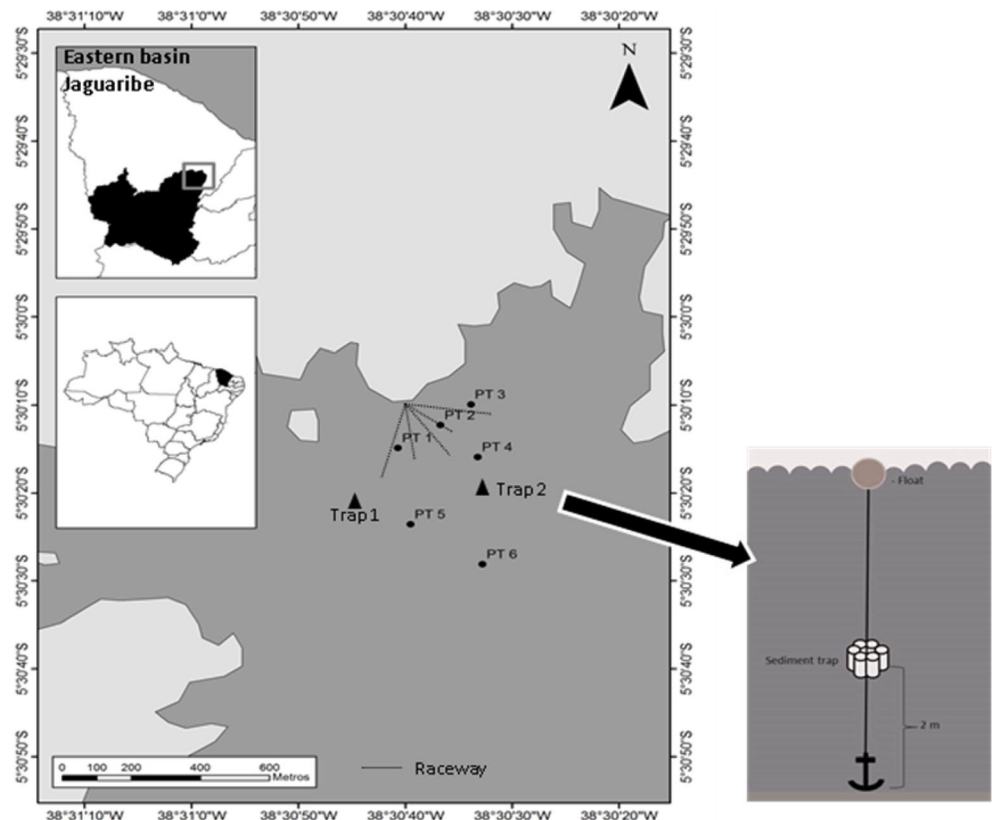
accumulated throughout the cores were measured in 2-cm layers along the cores. Absolute sediment density was obtained by subtracting sediment moisture content.

To analyze Hg in water, the filtrate was analyzed for the dissolved Hg (Hg-D) by placing 40 ml of the sample in Boeco glass jars. First, 7 ml of previously distilled by diffusion HCl (4 N) and 1 ml of a $KBrO_3/KBr$ (0.1 N) solution were then added and left to stand for 30 min. Subsequently, 25 μl of hydroxylamine (12 %) was added to reduce residual potassium bromate/bromide and avoid the detection signal suppression appliance. The particulate fraction (Hg-P) was analyzed directly in the filters after being weighted. Then, 20 ml of aqua regia 50 % ($HCl:HNO_3$; 3:1) was added to the 125-ml Erlenmeyer flasks, which were then closed with cold fingers, heated in a water bath (70 °C) for an hour, and subsequently quantified by cold vapor atomic fluorescence spectrophotometry (CN-AFS) in a PSA equipment Millennium Merlin 10.025 (Marins et al. 2002).

To determine the Hg concentrations in the aquafeed, fish and sediment samples were analyzed. Duplicate subsamples were weighed (~0.5 g), digested in 10 ml of HNO_3 and 1 ml of H_2O_2, and taken into a microwave oven following the equipment methodology (Limaverde Filho and Campos 1999; Francioni et al. 2004). The Hg concentrations were obtained using a cold vapor generation atomic absorption spectrophotometer (CVAAS), particularly a NIC model RA-3 of NIPON spectrophotometer (Bezerra et al. 2012).

Aluminum (Al) content was used to calculate enrichment factors in this study. To determine the Al content in the core sediment samples, approximately 0.5 g of dry sediment was weighed and digested using 12 ml of aqua regia 50 % ($HCL:HNO_3$; 3:1). The samples were taken to a microwave oven EMFS Mars Xpress, and the Al in the extracts produced was further quantified by flame atomic absorption spectrophotometry in a AA-6200 Schimadzu's model spectrophotometer (Pereira et al. 2007). To calculate the enrichment factors (EF) of the different sediment layers in the cores, we used the methodology proposed by Salomons and Föstner (1984). We used Al as an indicator of the lithogenic influence because of its low mobility and reactivity. The levels obtained from the base of the core were considered background concentrations that existed prior to the filling of the reservoir. The organic matter content in the sediment samples was determined using the gravimetric method, calculated as the difference in the weight of the samples after ignition on an oven muffle furnace at 450 °C for 24 h (Loring and Rantala 1992).

The calculated net accumulation rates of Hg considered the average Hg concentrations, the sediment density, and the time interval between two layers. We assumed that flooding of the reservoir began in 2002 and the sedimentation rate remained stable. Layers used to calculate background Hg deposition rates were those deeper layers in the cores where the variations in the Hg, organic matter, and Al concentrations were comparatively at their lowest.

All samples were analyzed in duplicate, and the Hg concentrations in fish and aquafeed were expressed in nanogram per gram on a wet weight basis. To ensure the quality of the analysis, certificated standards from the National Institute of Standards and Technology-NIST were used; NIST 2976 was used for biological material, and NIST 1646a was used for sediment. The detection limit of the method was calculated according to USEPA (2000), and the recoveries of certificated standards ranged from 82 to 103 %.

The hydrodynamic values of the water masses between the farm and the reservoir were obtained along five sampling profiles using a 1500-MHz Doppler Current Profiler-ADCP (Sontek/Ysi). The interval of data acquisition ("Burst Interval") was 5 s, with three profiles recorded at each interval ("Profile per Burst"). To remove inconsistent data stored in the equipment, we deleted records that exceeded or were less than the average by three times the value of the standard deviation; to do so, we applied a mobile window (box-car window) containing the mean and standard deviation of the 5-min records (Emery and Thomsom 1998). The gaps in the original series of data that were generated during the removal of the spurious data were filled using a linear interpolation. In the present study, the percent of gaps filled ranged between 0.5 and 0.8 % of the total original dataset, indicating that the data series was very consistent.

Results and discussion

The total Hg concentrations for the five types of aquafeeds analyzed ranged from 1.4±0.5 to 30.1±6.3 ng g^{-1}, depending on the specifications of the aquafeed and its use during different stages of the captive fish's development. Aquafeeds applied in the initial fry and juvenile stages more protein-enriched from fishmeal, and these showed the highest average concentrations of Hg (30.1 and 11.5 ng g^{-1}, respectively). Aquafeeds applied in the final fattening stages, when protein content is lower and grains, particularly soya, make up the majority of content, had much lower average Hg concentrations (1.4–6.3.5 ng g^{-1}) (Table 2).

Studies on fish farms have reported the presence of contaminants in commercial feed. The contamination of aquafeed is related to ingredients that contain high concentrations of contaminants (Choi and Cech 1998). Concentrations of Hg varying from 20 to 60 ng g^{-1} have been observed in fishmeal used in freshwater fish aquaculture (Johnston and Savage 1991), which is the major source of protein in the early stages of the production cycle. This finding indicates that diet is a major source of contamination in the fish produced (Fisher 1995). In the fattening stage, vegetable-based flours used for the manufacture of feed generally present lower concentrations of metals, which reduce the presence of Hg in aquafeed. The higher Hg concentrations in aquafeed used for fry and juvenile

Table 2 Aquafeed type and consumption, and the respective Hg concentrations and inputs during the different production phases from a typical tilapia cage farm in the Castanhão Reservoir, NE Brazil

Aquafeed type (protein content %)	Fraction of the production cycle (%)	Hg (ng g^{-1})	Aquafeed annual consumption (ton)	Annual total Hg input (mg)
1—fry (45)	0.15	30.1±6.3	1.55	47
2—juvenile (40)	3.00	11.5±2.1	30.9	356
3—growing (32)	6.50	2.7±2.1	67.1	181
4—fattening 1 (28)	13.00	1.4±0.5	134.2	187
5—fattening 2 (28)	77.35	6.3±0.5	798.2	5029
Total farm area (4 ha)	100	–	1032	5800
Total per hectare	–	–	258	1450
Hg per ton of fish	–	–	1.72	9.68

(Detection limit=1.6 ng g^{-1})

feeding result in an Hg input to the farm of 403 mgHg year^{-1} (101 mgHg ha^{-1} year^{-1}). Nevertheless, the increased amount of low-Hg, fattening aquafeed in the fish's diet, which is composed of less than 40 % protein content (types 3, 4, and 5), is still the major source of Hg on the fish farm, inputting approximately 5400 mg (1.35 mgHg ha^{-1} year^{-1}) of Hg per year.

In comparison, aquafeeds used in shrimp farming in the lower Jaguaribe Basin have higher Hg concentrations, which vary from 10.8 to 48.1 ng g^{-1}. This results in a much higher Hg load in shrimp farms, equivalent to 374 mgHg ha^{-1} year^{-1} (Lacerda et al. 2011). Shrimp aquafeeds with Hg concentrations similar to those used in the first stage of fish farming are used throughout the growing cycle.

The total amount of Hg per hectare introduced annually in the studied farm reached 1.45 g. Given that 9.68 mg of Hg (as calculated from Table 2) is contained in a ton of fish, and by extrapolating for the total magnitude of all aquaculture activities in the reservoir (18,000 tons), approximately 174 g of Hg is introduced by this production processes yearly. Further, extrapolating these data to the expected production of 40,000 tons by the end of the decade, the total Hg introduced into the tilapia production process within the Castanhão Reservoir may reach 387 g of Hg annually. However, part of the introduced Hg is exported out of the reservoir through fish commercialization. Therefore, to estimate the Hg emission factor to the reservoir, the amount exported outside the reservoir as fish biomass must be subtracted from the total amount of Hg introduced. Table 3 shows the Hg concentrations in the different organs of tilapia produced in the Castanhão Reservoir. All of the animals analyzed contained Hg concentrations that were much lower than the maximum legal limit for human consumption (500 ng g^{-1}) (ANVISA 1998) and therefore poses no threat associated with this fish consumption. Average Hg concentrations (wet weight) in the muscle (1.4±0.1 ng g^{-1}) are lower compared with other internal organs (intestines, 1.7±0.1 ng g^{-1}; heart, 2.5±0.1 ng g^{-1}; kidneys, 2.5±0.1 ng g^{-1}; bladder, 2.9±0.9 ng g^{-1}; and liver, 2.9±0.5 ng g^{-1}) but similar to those observed in the skin (1.1±0.1 ng g^{-1}), bones (1.0±0.7 ng g^{-1}), and gills (1.4±0.1 ng g^{-1}). Considering the relative biomass of each organ and the fact that all fish are commercialized whole, total Hg exported from the reservoir as fish biomass reaches 1.37 mgHg ton fish^{-1} year^{-1} or 206 mgHg ha^{-1} year^{-1}.

The amount of Hg exported as fish biomass is approximately 14.5 % of the total Hg added to the system via production. Therefore, 8.27 mgHg ton^{-1} fish year^{-1} is inputted into the reservoir, which is equivalent to approximately 1.24 gHg ha^{-1} year^{-1} or approximately 5.0 g annually for the total studied farm area. Assuming the present annual production of 18,000 tons, the expected maximum of 40,000 tons by 2020, and the emission factors calculated above, the total Hg input to the reservoir would increase from 150 g kg in the present to 330 g annually. In addition to tilapia cultivation, the Jaguaribe River basin harbors large areas of intensive shrimp farming, for which Lacerda et al. (2011) estimated an emission

Table 3 Concentrations of Hg (wet weight) in the muscle, skin, internal organs, and bone of Nile tilapia (*O. niloticus*) and their relative contribution to total fish biomass

Organs	ng g^{-1}±sd	Percent (%)	mgHg ton^{-1} of tilapia
Muscle	1.4±0.1	42	0.59
Organ			
Intestine	1.7±0.1	11	0.28
Blader	2.9±0.9		
Kidney	2.5±0.1		
Liver	2.9±0.5		
Heart	2.5±0.1		
Skin	1.1±0.1	7.5	0.08
Gills	1.4±0.1	5	0.07
Bone	1.0±0.7	35	0.35
Total	–	100	1.37

(Detection limit=0.2 ng g^{-1} wet weight)

factor of 0.37 gHg ha^{-1} year^{-1}, which results in an annual input to the basin of 0.35 kgHg year^{-1}. In comparison, the emission factor for tilapia production is nearly 3.4 times greater. Although there are lower concentrations of Hg in the majority of tilapia aquafeed, the absolute amount of aquafeed per hectare is two orders of magnitude greater than that of shrimp production, which sufficiently explains the higher emission factor of tilapia production. In contrast, the total annual contribution to the basin from shrimp farming is much greater because of the much larger extent (approximately 2800 ha) of shrimp farms in the basin. Therefore, the relative contribution of Hg to the basin from tilapia farming compared with other aquaculture products is very small.

The net 5.0 gHg year^{-1} (total introduced through aquafeed minus total exported as fish biomass) discharged in the study site was derived by estimating the accumulation in bottom sediments to determine the amount retained within the farm area and the fraction exported to the larger reservoir through the system's hydrology.

Table 4 shows the concentrations of Hg in the abiotic elements of the farm measured at the six sampling stations. The concentrations of dissolved Hg (Hg-D) in farm waters ranged from 0.2 to 28.6 ng l^{-1}. Although a clear pattern in Hg-D's spatial variation was not observed, the highest concentrations (11.5 to 28.6 ng l^{-1}) were found in the fish cage stations (PT1, PT2, PT3) and at PT4, whereas stations PT5 (0.2 ng l^{-1}), still in the area of influence of cages and PT6 (0.8 ng l^{-1}), which is beyond the farmed area, had the lowest concentrations. The particulate Hg concentrations were very low and similar across stations; values varied from 0.02 to 0.06 ng l^{-1} due to the extremely low TSS content of the reservoir waters. The relatively high Hg concentrations found in the suspended solids (17.5 to 54.2 ng g^{-1}) and the concomitant low and similar concentrations of particulate Hg suggest the importance of suspended matter removal as a major transfer process that moves Hg from the water column to bottom sediments (Andren and Harris 1975; Maurice-Bourgoin et al. 2000). The spatial variation of Hg concentrations in the sediment roughly

followed the variation observed for Hg-D, with two of the three cage stations (PT1 and PT2) showing the highest concentrations, followed by stations PT4 and PT5, which are located within the farm boundary, and station PT6, which is located at the furthest point from the area of cultivation. The spatial distribution observed suggests the impact of fish cages on Hg distribution. However, the high concentrations found at PT4, not followed by the concentration in bottom sediments at this station, suggest that other factors may also affect Hg distribution; these factors are likely associated with water circulation and some resuspension of deposited sediments. Unfortunately, a much more detailed and prolonged study would be necessary to fully explain the Hg distribution within the farm-influenced area.

In an attempt to determine the distribution of Hg in creek waters receiving effluents from shrimp farms in the lower Jaguaribe River, Costa et al. (2013) found lower Hg-D concentrations (3.1–9.2 ng l^{-1}) but higher Hg-P (4.4–9.4 ng l^{-1}) levels than were found in the present study, likely due to the much higher TSS content in the creek waters compared with the Castanhão Reservoir. Lacerda et al. (2013) also found lower concentrations of Hg-D in the Jaguaribe River proper (0.3–3.8 ng l^{-1}) and noted slightly higher Hg concentrations in the TSS (13.1–129.8 ng g^{-1}). The Hg concentrations in bottom sediments varied from 2.9 to 38.3 ng g^{-1}, with the highest concentrations also measured at the cage stations and the lowest concentrations measured farthest from the farm. Vaisman et al. (2005) found that the Hg concentrations in the bottom sediments of depositional areas of the Jaguaribe River varied from 6 to 13 ng g^{-1}, which is similar to the range found in the sampling stations far from the cage stations sampled in this study.

The average daily sediment deposition rates in the farm area were obtained using sediment traps and reached 6.21 g sediment m^{-2}, which corresponds to an Hg deposition rate of approximately 0.34 μgHg m^{-2} day^{-1} (1.26 gHg ha^{-1} year^{-1}) to the bottom sediments. These results suggest that all Hg that enters the farm area via fish farming practices may accumulate in the farm's sediments. Lacerda et al. (2009) and Costa et al. (2013) also reported that the majority of Cu emitted in the lower Jaguaribe River as a result of aquafeed used in shrimp farming does so in the bottom sediments.

Once deposited in sediment, Hg can be retained and accumulated through different chemical processes, including adsorption, cation exchange, precipitation and co-precipitation of discrete minerals, and complexation with organic matter, making sediments a primary actor in the accumulation of metals in aquatic environments (Mountouris et al. 2002). However, part of the deposited sediment and its Hg content does not immediately settle. In fact, a variable fraction can be remobilized and passes through consecutive cycles of deposition and remobilization before permanently settling in bottom

Table 4 Concentrations of Hg in sediments (Hg-Sed), suspended particulate matter (Hg-TSS), dissolved (Hg-D), and particulate Hg concentrations (Hg-P) in water, for the six sampling stations at the studied farm

| Stations	TSS (mg l^{-1})	Hg-Sed (ng g^{-1})	Hg-TSS (ng g^{-1})	Hg-D (ng l^{-1})	Hg-P (ng l^{-1})
PT1	1.92	38.3±1.4	17.8±1.3	11.5±2.7	0.04±0.01
PT2	1.00	36.6±2.8	30.2±15.5	21.0±4.8	0.03±0.01
PT3	1.10	12.9±6.6	21.3±3.3	18.7±3.4	0.02±0.01
PT4	1.06	15.0±3.1	54.2±17.9	28.6±12.0	0.06±0.02
PT5	2.00	29.7±1.7	17.5±2.3	0.2±0.01	0.04±0.01
PT6	1.00	2.9±1.0	22.7±1.7	0.8±0.3	0.02±0.01

Fig. 2 **a** Hg (ng g^{-1}). **b** Organic matter (%). **c** Enrichment factor (EF) based on Al concentrations in a sediment core collected from the study site
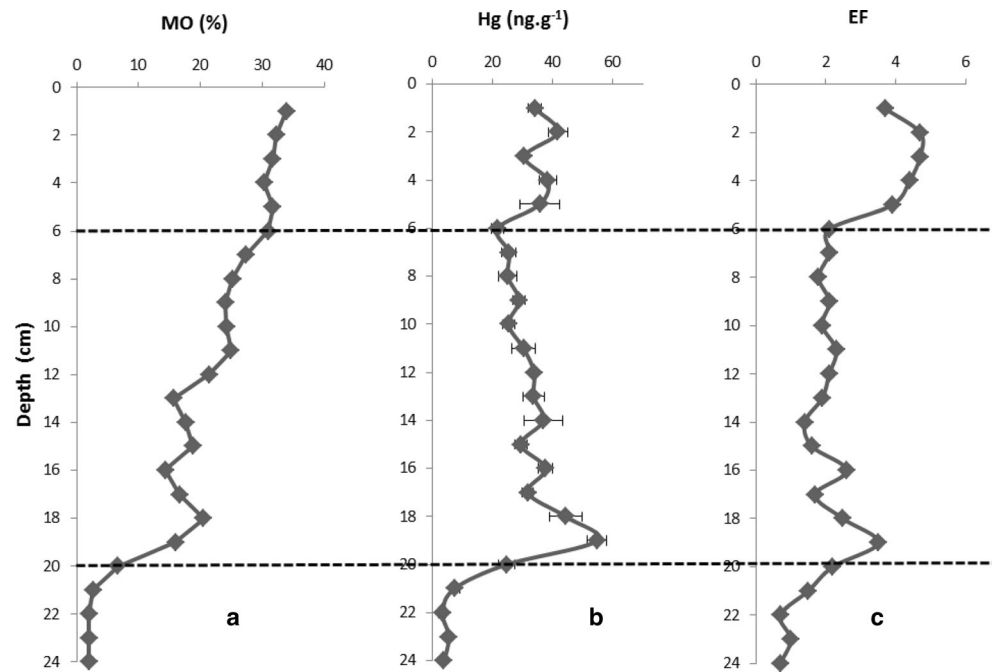
sediments (Barcellos et al. 1997). Therefore, to evaluate the actual rate of retention of Hg in the farm's sediments, an analysis of the Hg distribution in the sediment cores and sedimentation rates is needed. Figure 2 shows the distribution of Hg and organic matter, as well as the enrichment factor (Hg/Al ratio in a given sediment layer divided by the Hg/Al ratio in the deepest layer, considered the background) in the cores collected from the study site.

The Hg and organic matter concentrations peaked at depths of approximately 19–20 cm along the core. Below 20 cm, Hg and organic matter concentrations decline and are similar to regional soil concentrations of approximately 10 ng g^{-1} and 6 % (Oliveira and Marins 2011) for Hg and organic matter, respectively. This finding suggests the depth within the sediment attained in the major flooding years, the 2002–2003 water year, when up to 90 % of the reservoir's volume was achieved, although the total volume was archived only in 2004. Between 6 and 19 cm of depth, the organic matter concentrations increased. This increase in organic matter concentrations suggests a response to the reservoir's inundation. After its peak at 20–19 cm, there is a continuous increase in organic matter flux, but not Hg, through the sediment, which reflects the new slack conditions typical of a lake environment. However, no significant flux of Hg to the reservoir occurred during this period. Sharp increases in nutrients and contaminants are frequently observed following inundation due to increased runoff from surrounding soils (Junk et al. 1989). In the case of Hg, a rapid increase in concentrations also occurs immediately after flooding, but the concentrations generally decrease after a few months in the absence of additional sources (Li et al. 2013). From 6 cm to the surface of the core, the concentrations of the

two variables increased sharply to maximum values at the surface of the core. This interpretation is supported by the
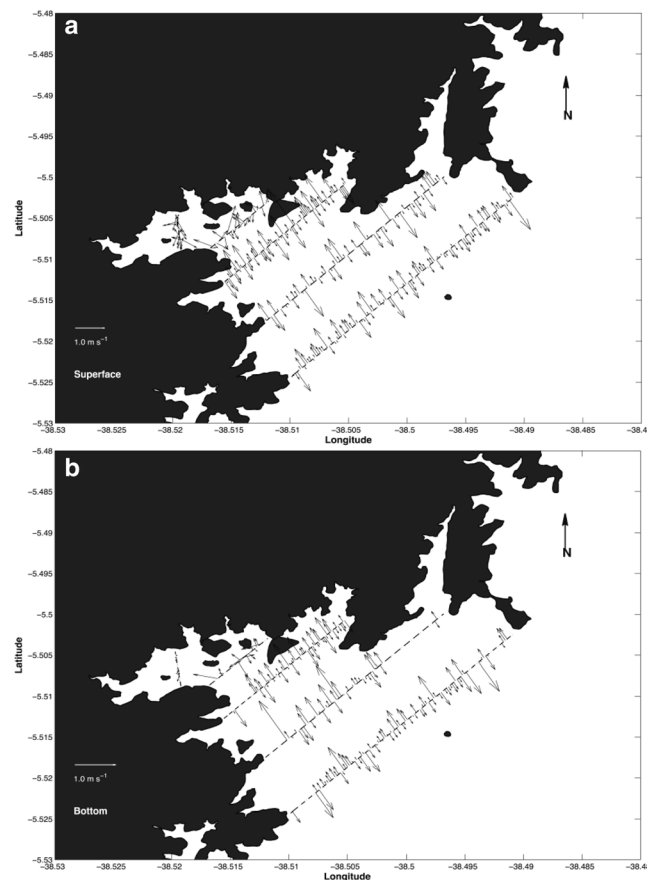
Fig. 3 Direction and intensity of water currents at the farm site. **a** Surface water currents. **b** Bottom water currents

Fig. 4 Mercury mass balance in a tilapia cage fish farm in the Castanhão Reservoir, NE Brazil (g ha^{-1} year^{-1})
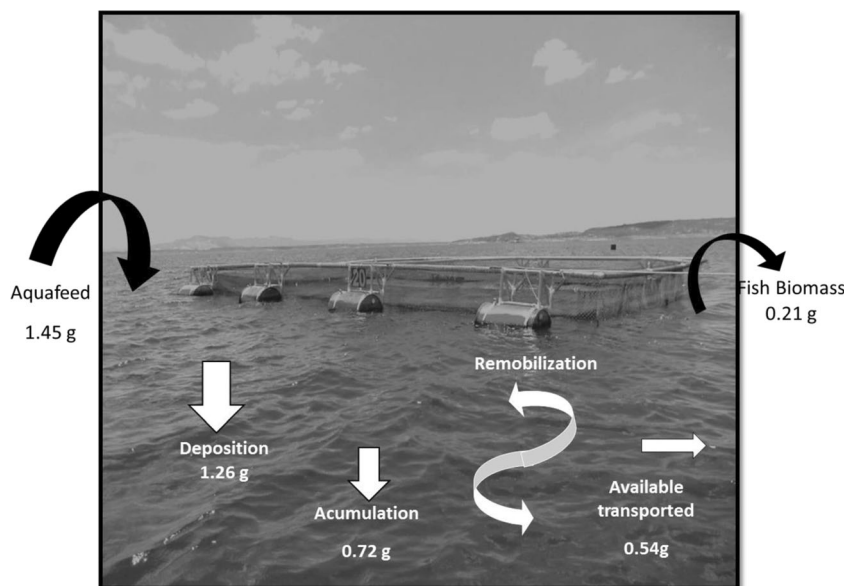
enrichment factors for Hg observed along the profile, which also increased during the flooding of the reservoir and remained relatively constant to 6 cm of depth before increasing again, likely as a result of the installation of the fish farm in 2010.

Three different sedimentation periods are identified in the profile. The sedimentation rates were zero prior to inundation and were immediately followed by a large influx of materials during filing. Assuming that 18 cm depth denotes the final filing of the reservoir and the beginning of typical lake sedimentation, which occurred in 2003, a constant sedimentation rate, and a sediment density of 0.14 g cm^{-3}, one can estimate a sedimentation rate of 1.57 cm year^{-1} in the farm area. From this data, an Hg accumulation rate of 66.8 (55.2–82.9) µgHg m^{-2} year^{-1} (0.67 gHg ha^{-1} year^{-1}) can be extrapolated. The concentrations and accumulation rates of Hg remained constant or slightly decreased along the profile to 6 cm of depth, which is in accordance with a constant sediment accumulation rate during this period.

Farming in the reservoir began in 2010, and approximately 6 cm of sediment has accumulated since that time. This is equivalent to 1.5 cm year^{-1}, assuming a constant sedimentation rate, and infers an average Hg accumulation rate of 70.9 (45.6–87.8) µgHg m^{-2} year^{-1}, 0.72 gHg ha^{-1} ano^{-1}. That Hg accumulation rate is approximately 60 % of the deposition rate of 1.26 gHg ha^{-1} year^{-1} estimated through the sediment traps,

which suggests that 0.54 gHg ha^{-1} year^{-1} is remobilized and may eventually be transported out of the farm to the reservoir.

Energy transfer from winds to the water surface triggers currents in the studied area, generating a water circulation pattern that likely explains the differences in Hg-D and Hg-P found in the farm. The current velocities and directions obtained through the deployment of an ADCP showed that the highest current velocities occur at the surface and decrease to the reservoir bed (Fig. 3). This pattern supports the relatively small remobilization of sediment suggested by the high proportion of deposited Hg that has permanently accumulated in the reservoir bed beneath the farm. However, the observed water circulation pattern in the farm facilitates the renewal and dilution of farm waters, which results in the export of non-accumulated Hg to the reservoir. However, the total Hg exported annually from cage aquaculture, approximately 0.54 gHg ha^{-1}, represents a small source of Hg to the Castanhão Reservoir.

Figure 4 illustrates the Hg balance of the studied farm. The annual inputs from feeding activities are 1.41 gHg ha^{-1}, whereas the Hg exported as fish biomass based on a typical production chain in the region reaches 0.21 gHg ha^{-1}. The remaining Hg load passes through deposition cycles that result in the accumulation of 0.72 gHg ha^{-1} in bottom sediments and the eventual export of 0.54 gHg ha^{-1} to the reservoir.

Table 5 Comparison of Hg emission factors (Lacerda et al. 2011) and average total annual Hg output (kg year^{-1}) from different anthropogenic activities (Santos et al, results not released) occurring in the Jaguaribe River Basin and Castanhão Reservoir fish farm, NE Brazil (this study)

Activity	Hg emission factor g ha^{-1} year^{-1}	Hg annual input to the Castanhão Reservoir (kg year^{-1})
Agriculture and husbandry	<0.0025	<0.001
Wastewaters discharge	0.20	10
Solid wastes disposal	0.40	9
Fish farm	*1.24*	*0.15*

Comparing the emission factors and total inputs of Hg from other anthropogenic sources to the reservoir (Table 5), it is clear that intensive caged fish farming is a minor contributor to total Hg inputs. Notwithstanding the particularly high emission factor deduced for fish farming, the small extent of these farms results in a total annual Hg input from this activity of approximately 0.8 % of total input from urban sources. This situation is similar to that of shrimp farms in the lower Jaguaribe basin, for which the small pond area also results in lower Hg output than other anthropogenic sources overall, notwithstanding their high emission factor (Lacerda et al. 2011).

Conclusion

The Hg emission factor for caged fish farming in the Castanhão Reservoir reaches 1.24 gHg ha^{-1} year^{-1} or approximately 8.27 mgHg ton fish^{-1} year^{-1}. The Hg associated with fish farming originates from excess aquafeed and fish excreta. The emission factor relative to the area occupied by the activity is three to six times greater than that for urban and agriculture sources present in the Castanhão basin in general. The calculated mass balance shows that a major fraction (nearly 60 %) of the Hg output is deposited and accumulated in farm sediments. Given the relatively small size of the area occupied by fish cages, the total load to the reservoir, 0.15 kg year^{-1}, remains low and is less than 1 % of the total Hg load from all other anthropogenic sources. However, most other Hg sources to the reservoir release the metal throughout the basin because no direct effluents of industrial or urban origin exist in the region. Therefore, loads from urban and agriculture sources are the result of weathering and transport to the reservoir waters, processes that are hampered by the semiarid conditions that dominate the region. Notwithstanding this environmental setting and the expected tripling of fish production in the next few years, tilapia farming will remain a minor source of Hg to the aquatic ecosystem of the Castanhão Reservoir compared with other anthropogenic sources.

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