

The Fate of Cu, Zn and Mn in an Intensive Fish Aquaculture (Tilapia - *Oreochromis niloticus*) in an Artificial Reservoir in Northeastern Brazil

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Abstract Emissions of Cu, Zn and Mn and their fate in a typical tilapia (*Oreochromis niloticus*) cage farm in an artificial reservoir in northeastern Brazil were estimated through the analysis of their concentrations in the various compartments of the farm. Major source of Cu and Zn, but not of Mn, to the farm is from aquafeeds, with annual inputs of 3.83, 57.50 and 10.95 kg.ha⁻¹, respectively. Notwithstanding, only a small fraction of the added Mn and Zn (0.13%, 2.61%, respectively) is incorporated into fish biomass, resulting in a larger proportion of the introduced metals to be exported to reservoir environment. For Cu, a much larger fraction (47.4%) is exported within the fish biomass. Once released, metals are incorporated into bottom sediments within the farm area, resulting in higher metal contents compared to sediments far from the farm area. However, the analysis of sediment cores and the respective enrichment factors showed that a significant fraction of the net input of Zn (70%) and of Cu (30%) is exported out to the open reservoir.

Keywords Trace metals · Tilapia · Artificial reservoir · Sediments

1 Introduction

Aquaculture is seen as a sustainable option to decreasing capture fisheries worldwide. Major crops have developed technologies that allow for intensive farming practices with high and increasing productivity, which resulted in decreasing prices and a larger participation of aquaculture products in the human diet (Thomas et al. 2012). However, modern aquaculture

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depends on large additions of aquafeed, fertilizers and of other additives, such as acidity correctors and algaecide, which have raised concern on the impact of these substances on aquatic environments. Trace metals, for example, are not obvious pollutants present in aquaculture effluents, but some, in particular Cu, Zn, Cd, Mn and Hg occur as natural constituents of aquafeeds and fertilizers, or as active principles of chemical compounds of different uses (Johnston and Savage 1991; Boyd and Massaut 1999; Tacon and Forster 2003). Accumulating evidence strongly suggests that wild-caught individuals of farmed species generally present much higher concentrations of trace metals than farmed ones (Kelly et al. 2008; Lacerda et al. 2014). Notwithstanding the reported lack of contamination of the farmed fish, the continuous and direct release of effluents to the aquatic environment may eventually build up high concentrations of trace metals in water and sediments, in particular in pond and lake aquaculture, and may eventually result in the reduction of the environmental quality, and consequently, the quality of cultured fish properly.

Field evidence of metal enrichment in sediments due to fish farming is abundant, but its eventual environmental risk is still debatable. Whereas Rožič et al. (2012) for example, measured trace metals concentrations in bottom sediments below fish cages higher than the regional background concentrations in the Central Adriatic, they posed a negligible effect on local ecosystems. Sediments particularly enriched in Cu, Zn, Cd and Pb, but not of Hg, Ni, As and Mn, have been observed under fish cage aquaculture in coastal Greece, but only a number of samples presented concentrations of Cu and Zn above the Probable Effect Level (PEL) (Farmaki et al. 2014). In Baisha Bay, China, Gu et al. (2012) measured high concentrations of metals under aquaculture areas, but these could not be directly linked to the activity. Rather, other major anthropogenic metal sources in the region may threaten the sustainability of aquaculture practices. Only few among different Scottish farms studied by Russell et al. (2011) showed Zn and Cu concentrations posing potential adverse effects to the environment, but since abnormal concentrations were restricted to within 25 m of the cages, any eventual impact would be of a restricted local nature. Similarly, Kalantzi et al. (2013) reported fish farms effects to be negligible beyond 25–50 m from cages in four aquaculture areas in the Eastern Mediterranean Sea.

Most of the above results associated higher metal contents to antifouling chemicals used to protect cages and fish feed, particularly enriched in fish meal. In tilapia farming, however, evidence of environmental metal contamination due to the activities is even more debatable, since antifouling products are seldom used and fish feed is mostly from plant protein (soy) rather than fish meal. For example, Wu and Yang (2010) reported much lower enrichments of many trace metals in sediments in a tilapia farm than those in Asian seabass and shrimp farms. In experimental ponds of tilapia farming in Brazil, Marengoni et al. (2014) found concentrations of Pb and Cr in pond sediments enriched by 30% at the end, compared to the beginning of the cultivation period. Oliveira et al. (2015) reported an enrichment of Hg content in sediments under fish cages in a northeastern Brazil reservoir. On the other hand, Marengoni et al. (2013) found no differences in the concentrations of Cu, Mn, Zn, Cr, Cd and Pb in the golden mussel *Limnoperna fortunei*, sampled as biomonitors from fish cages and from a control area in the Itaipú Reservoir, south Brazil, suggesting no contamination by the aquaculture activity.

Fish aquaculture has expanded fast in Brazil, due to abundant water resources and climate conditions. In the northeastern region, in particular, the necessity of water storage due to long dry periods typical of its semiarid climate, resulted in intensive river damming and reservoir construction since the 19th century. These reservoirs became optimal sites for fish production

to a point that the northeastern region is the largest aquaculture fish producer in the country, responding for 29% of the total country's production. The most cultivated fish is tilapia (*Oreochromis niloticus*), with production increasing about 70.4% per year from 2003 to 2011 (SEBRAE 2015). The Castanhão reservoir at the Municipality of Jaguaribara in Ceará State is the largest single production area in Brazil, responding for 8.6% of the country's production. The reservoir was completely flooded in 2004, and covers an area of 325 km² and has a maximum depth of 50 m and 6.7 billion m³ of water storage capacity. Annual tilapia production between 2010 and 2014 reached 18,000 tons and farms cover about 75 ha. Presently, due to extreme drought conditions, production was reduced to 12.2 tons (DNOCS 2015) and remained around this amount in 2016. However, under optimal conditions the reservoir can produce about 40,000 tons in a total farm area of 190 ha. It is urgent therefore, to establish any eventual cause-effect relation between fish aquaculture and metal contamination of the reservoir.

To assess the fraction of the total Cu, Zn and Mn loads to the reservoir due to cage fish aquaculture relative to other sources, Emission Factors (EFs) were calculated for each metal through the monitoring of the production process in a local tilapia farm and compared them with known EFs from other sources, in particular agriculture and urban activities. EFs were obtained by the quantification of the concentrations of Cu, Zn and Mn in the different compartments of the farm (fish and fish organs, aquafeeds, sediments, and suspended particles) and the transfers of the trace metals among compartments through fish production, sedimentation rates and hydrodynamics. Since the tilapia farming procedures in the studied farm is typical of all other tilapia farms, not only in the Castanhão reservoir but also worldwide, the estimated EFs could be used in upscaling trace metals emissions to the entire reservoir.

2 Materials and Methods

2.1 Environmental Setting

Emission Factors (EFs) are used to estimate contaminant loads to a given environment from anthropogenic and natural sources when actual measurements of loads are not available. EFs take into consideration the type and nature of the contaminant sources, the production processes and the magnitude of the effluents, using information on the use of primary materials, their contaminants concentrations and their fate into the environment prior to reaching the receptor body, in this case the Castanhão Reservoir. EFs for metals (Zn, Cu and Mn) from fish aquaculture were derived from the observed metal concentrations in aquafeeds and fish organs, and multiplying by the production parameters obtained from a typical net-cage fish farm installed in 2010 and located on the northern banks of the Castanhão Reservoir, 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*), the major farmed fish species in Brazil because of its fast growing and good performance under the regional climate and on intensive production conditions. Table 1 shows the major characteristics of the tilapia farm studied in the Castanhão reservoir. Production and yield, as well as aquafeed utilization rate are typically found in all other tilapia farms in Ceará state, the largest producer in Brazil (SEBRAE 2008) and are roughly the same worldwide. The results obtained from the studied farm were

Table 1 Management features of fish farming practiced in the Castanhão Reservoir in northeastern Brazil

Feature	Amount
Total area of the studied farm	4 ha
Fish production	600 t.yr ⁻¹ (150 t.ha ⁻¹ .yr ⁻¹)*
Aquafeed consumption	1032 t.yr ⁻¹ (258 t.ha ⁻¹ .yr ⁻¹)*
Food conversion rate	1.72*

Values within the range of typical tilapia farms in Northeastern Brazil (SEBRAE 2008)

extrapolated to the entire reservoir using the annual tilapia production of the Castanhão reservoir estimated by the Political Council for the Environment of Ceará State.

2.2 Trace Metals Emission Estimates and Distribution

The mass balance of Zn, Cu and Mn of the studied fish farm included only the inputs and outputs of the production processes in this typical farm. Aquafeed was considered the only source of metals to the production processes. Sedimentation and the total fish biomass produced and exported from the farm were considered the major processes removing metals from the farm. Other sources of metals, both natural and anthropogenic, located in the reservoir basin, were not considered as significant sources of metals, since the low rainfall regime of the semi-arid climate area results in the retention of over 60% of the eventual eroded soils (Medeiros et al. 2014) and over 80% of nutrients and metals from those sources emissions within the basin (Oliveira et al. 2015; Santos et al. 2016). Other typical anthropogenic Zn, Cu and Mn sources, such as industries, do not exist in the reservoir basin and were also not quantified. Also, due to the very low solubility of metals in the oxygenated waters of the reservoir (>5 mg.L⁻¹ during the study period; Santos et al. 2016), we considered that dissolved export of metals would be negligible. The magnitude and management features of the studied farm are presented in Table 1.

To estimate Zn, Cu and Mn inputs from fish farms, metal concentrations were measured in samples of the five different types of aquafeeds used in the farm and their period of utilization (as percent of the total duration of the production cycle) during a typical growth cycle: Minow (0.2%); Juvenile (3.0%); Growing (6.5%); Fattening 1 (13%) and Fattening 2 (77.3%). These different aquafeed types and their utilization proportions are roughly similar to other tilapia production farms, using fish cages, throughout the semiarid region of Brazil. Aquafeed samples ($n = 20$) were dried in an oven at 60 °C to constant weight prior to digestion. To quantify inputs, metals concentrations were estimated by the extension of the utilization period of each aquafeed class. Metals concentrations were also measured in the different tissues of commercial size tilapia (≥ 1.000 kg) obtained in the studied farm. Each animal was dissected, and muscle tissues, internal organs, gills, skin, and bones were separated. Composite samples of tissues from 5 to 10 individuals were homogenized and freeze-dried before analysis. Concentrations were multiplied by the relative contribution of each organ to the total fish biomass since only whole fish are commercialized from the farm.

Metals concentrations in bottom sediments were determined in six sampling stations: three located among the net cages (PT1, PT2, and PT3) under direct influence of cultivation, receiving excess aquafeed and fish excreta; two stations located about 50 to 100 m from the cages but still located in the farm area (PT4 and PT5); and one station located outside the boundary of the farm area (PT6) and considered as a control station

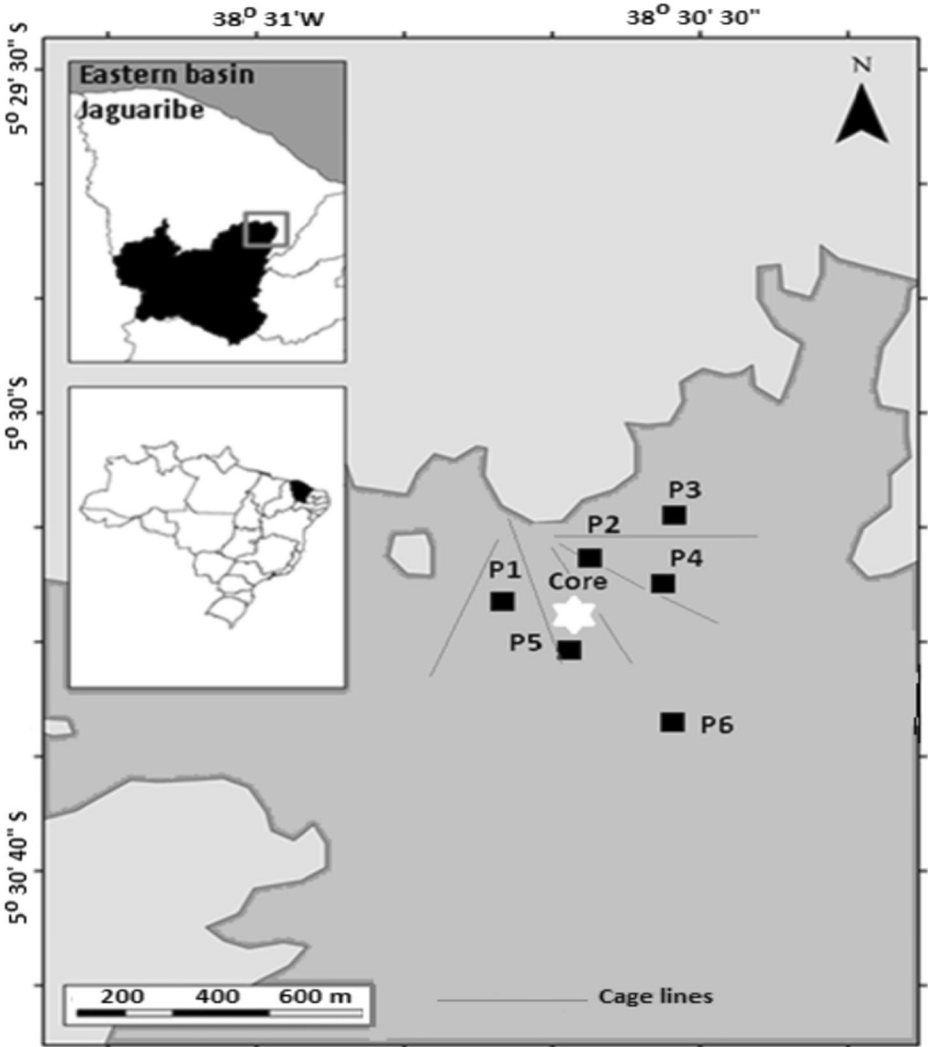


Fig. 1 Study area, sampling points, and locations of the sediment cores in the aquaculture farm studied in the Castanhão Reservoir, NE Brazil

(Fig. 1). Sediment samples were collected from these stations in 2011, 2012 and 2013, using a van Veen dredge. In laboratory, sediment samples were 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.

At a single station located just under the cages, two sediment cores were collected by divers, by inserting 50-mm diameter acrylic tubes in the sediment until reaching the hard surface of the original flooded soil. This procedure allowed a rough estimation of sedimentation rates in the farm area. The concentrations of Zn, Cu, Mn, Al and organic matter that had accumulated in the cores were measured in 1-cm sediment layers. Absolute sediment density was obtained by subtracting sediment moisture content.

2.3 Sample Preparation and Analysis

Duplicate subsamples of aquafeeds, fish and sediment were weighed (~0.5 g) and digested in 12 mL of a 50% *aqua regia* (HCL:HNO₃; 3:1) solution. The samples were taken to a microwave oven EMFS Mars Xpress and metal concentrations in the produced extracts were quantified by flame atomic absorption spectrophotometry, in a AA-6200 Shimadzu's model spectrophotometer. Metal enrichment factors (MEFs) of the different sediment layers in the cores were estimated following Salomons and Föstner (1984). Al concentrations were used as an indicator of the lithogenic source of metals because of its low mobility and reactivity. Concentrations 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 in an oven muffle furnace at 450 °C for 24 h (Loring and Rantala 1992).

The calculated net accumulation rates of metals considered the average of each metal concentration in each layer, the sediment density, and the time interval between two adjacent layers. We assumed that flooding of the reservoir began in 2002 and the sedimentation rate remained constant to present.

All samples were analyzed in duplicate, and the metals concentrations in fish and aquafeeds were expressed on a wet weight basis. To ensure the quality of the analysis, Cu, Zn and Mn concentrations in certified standards from the National Institute of Standards and Technology-NIST were simultaneously quantified by the same procedure: NIST 2976 (Mussel Tissue) for biological material and NIST 1646a (Estuarine Sediment) for sediment. The detection limits of the method were calculated according to USEPA (2000) and are presented in the specific tables. The average recoveries of certificated sediment standards were: 70% for Al; 83% for Zn; 83.9% for Cu and 101.3% for Mn. Recoveries of biological standards were: 80.8% for Mn; 91.7% for Zn and 83.6 for Cu (Table 2).

3 Results and Discussion

Average metals concentrations obtained in the five different types of aquafeeds ranged for Zn from 147 to 290 $\mu\text{g}\cdot\text{g}^{-1}$, for Cu from 6.5 to 19.2 $\mu\text{g}\cdot\text{g}^{-1}$ and for Mn from 34.6 to 82.7 $\mu\text{g}\cdot\text{g}^{-1}$, depending on the specific constituents of the aquafeed. Aquafeeds applied in the initial fry and juvenile stages, relatively enriched in protein from fishmeal, showed the highest average concentrations of Zn, Cu and Mn (290, 19.2 and 82.7 $\mu\text{g}\cdot\text{g}^{-1}$, respectively). Aquafeeds used

Table 2 Trace metal concentrations ($\mu\text{g}\cdot\text{g}^{-1}$ d.w.) in certified standards analyzed using the described methodologies

	Metal	Certified Value	Obtained Value	Recovery (%)
Sediment (NIST 1646a)	Al	2.297 ± 0.018	1.540 ± 0.1	70 ± 4.7
	Zn	48.9 ± 1.6	40.6 ± 0.3	83 ± 1.6
	Cu	10.01 ± 0.34	8.4 ± 1.0	83.9 ± 1.2
	Mn	234.5 ± 2.8	237.5 ± 4.1	101.3 ± 2.2
Biota (NIST 2976)	Zn	137 ± 13	46.1 ± 0.3	91.7 ± 4.6
	Cu	4.02 ± 0.33	7.8 ± 1.2	83.6 ± 3.1
	Mn	33 ± 2	192.4 ± 15.7	80.8 ± 5.2

Table 3 Aquafeed type and consumption, and the respective concentrations of Zn, Cu and Mn and inputs during the different production phases from a typical tilapia cage farm in the Castanhão Reservoir, NE Brazil

Aquafeed type	Fraction of the production cycle (%)	Zn ($\mu\text{g/g}$)	Total Zn input ($\text{kg}\cdot\text{yr}^{-1}$)	Cu ($\mu\text{g/g}$)	Total Cu input ($\text{kg}\cdot\text{yr}^{-1}$)	Mn ($\mu\text{g/g}$)	Total Mn input ($\text{kg}\cdot\text{yr}^{-1}$)
Minnow ($n=5$)	0.15	290 ± 10	0.45	19 ± 0.2	0.03	82.5 ± 4	0.13
Juvenile ($n=5$)	3.00	269 ± 12	8.3	17 ± 0.8	0.53	55.4 ± 6.5	1.71
Growing ($n=5$)	6.50	229 ± 1.7	15.4	13 ± 0.1	0.87	82.0 ± 3.8	5.55
Fattening 1 ($n=5$)	13.00	150 ± 4.0	20.1	7.9 ± 0.3	1.06	34.6 ± 2.3	4.64
Fattening 2 ($n=5$)	77.35	233 ± 26	186	13 ± 1	12.8	40.3 ± 0.7	31.8
Total farm (4 ha)	100	—	230	—	15.3	—	43.8
Total per ha.yr ⁻¹	—	—	57.50	—	3.83	—	10.95
Total per ton of fish	—	—	0.38	—	0.03	—	0.07

Detection limit: Zn = $0.9 \mu\text{g}\cdot\text{g}^{-1}$, Cu = $0.2 \mu\text{g}\cdot\text{g}^{-1}$; Mn = $0.66 \mu\text{g}\cdot\text{g}^{-1}$ wet weight

in the final fattening stages, with lower protein content and grains, particularly soy being the major content, presented the lowest average Zn, Cu and Mn concentrations (150–233; 7.9–13 and 34.6–40.3 $\mu\text{g}\cdot\text{g}^{-1}$, respectively) (Table 3).

Boyd and Massaut (1999), Tacon and Forster (2003) and Berntssen et al. (2004), evaluating the productive process in fish farms, reported the presence of contaminants in feed used commercially, indicating that the food supply may be the main route of introduction of metals in these crops. There are specific rations for each stage of the development of fish, which may have different protein composition, containing different concentrations of contaminants which may vary over the cycle of cultivation (Oliveira et al. 2015).

Our results show that the highest concentrations of Zn, Cu and Mn were found in feeds provided in the first two stages of the fish life, which last for 3.15% of a complete growth cycle, and introducing 8.8 $\text{kg}\cdot\text{yr}^{-1}$ of Zn, 0.56 $\text{kg}\cdot\text{yr}^{-1}$ of Cu and 1.84 $\text{kg}\cdot\text{yr}^{-1}$ of Mn. The food at this stage has an increased crude protein proportion (40%), being composed primarily of fishmeal from captured fish and bycatch, which are known for their relatively high Hg concentrations (Dorea 2006). During the fattening phases of cultivation, metal concentrations in aquafeed were smaller since the contained proteins are of vegetable origin typically low in trace metals (Go et al. 2007). However, since the supply of such feeds represents about 84% of a complete production cycle, these types of aquafeed introduce to the cultivation 221.4 kilograms of Zn, 14.7 kg of Cu and 42 kg of Mn. The total amount of metals added per hectare per year in the farm reached 57.5 kg for Zn, 3.8 kg for Cu and 11 kg for Mn. Given that a ton of fish contains 0.38 kg of Zn, 0.03 kg of Cu and 0.07 kg of Mn, and by extrapolating this to the entire aquaculture production in the reservoir (18,000 tons), about 6.8 t of Zn, 0.5 t of Cu and 1.3 t of Mn are introduced by aquaculture yearly. Further, when extrapolated to the planned production of 40,000 tons by 2020, the total Zn, Cu and Mn introduced by the tilapia farming within the entire Castanhão Reservoir may reach 152, 1.2 and 2.8 tons annually, respectively.

Part of the introduced metals is exported out of the reservoir through fish commercialization. Therefore, to estimate the Zn, Cu and Mn emission factor to the reservoir, the amount exported outside the reservoir as fish biomass must be subtracted from the total amount of

Table 4 Average concentrations of Cu, Zn and Mn ($\mu\text{g}\cdot\text{g}^{-1}$ wet weight) in the muscle, skin, internal organs, and bone of Nile tilapia (*O. niloticus*) and their relative contribution to total fish biomass and export through commercialized fish ($\text{g ton fish}^{-1} \text{ year}^{-1}$)

Organs	Fish biomass (%)	Zn	Cu	Mn
Muscle	42	4.3 ± 0.01	0.3 ± 0.4	0.3 ± 0.02
Bone	35	11.8 ± 0.8	32.0 ± 2.3	1.3 ± 0.01
Organ				
Intestine	11	6.8 ± 0.3	1.6 ± 0.1	1.6 ± 0.1
Kidney		10.9 ± 0.5	0.5 ± 0.01	1.5 ± 0.2
Liver		7.5 ± 0.3	6.9 ± 0.1	0.5 ± 0.03
Heart		10.9 ± 1.5	12.7 ± 1.5	0.3 ± 0.01
Skin	7.5	28.1 ± 1.2	0.6 ± 0.01	1.3 ± 0.01
Gills	5	13.7 ± 1.0	0.6 ± 0.03	1.2 ± 0.03
Total	100			
Export through biomass ($\text{g}\cdot\text{t}^{-1}$ of fish)		9.7	12.0	0.9
Export through biomass ($\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$)		1.5	1.8	0.14

metals introduced. Table 4 shows the Zn, Cu and Mn concentrations in the different organs of tilapia produced in the Castanhão Reservoir.

Average Zn concentrations (wet weight) in the muscle ($4.2 \pm 0.4 \mu\text{g g}^{-1}$) are lower compared to other internal organs ($6.8 \mu\text{g g}^{-1}$, in intestines to $28.1 \mu\text{g g}^{-1}$ in skin). Also for Cu, average concentrations in muscle were the smallest ($0.3 \pm 0.4 \mu\text{g g}^{-1}$) whereas the highest occurred in bones ($32.2 \pm 2.3 \mu\text{g g}^{-1}$) and heart ($12.7 \pm 1.5 \mu\text{g g}^{-1}$). Similarly, Mn concentrations were also lowest in muscle ($0.3 \pm 0.02 \mu\text{g g}^{-1}$) and highest in intestines ($1.6 \pm 0.2 \mu\text{g g}^{-1}$). Considering the relative biomass of each organ and that fish from the Castanhão farms are commercialized whole, the total Zn, Cu and Mn exported out of the reservoir as fish biomass are: $9.7 \text{ gZn ton fish}^{-1} \text{ year}^{-1}$ or $1.8 \text{ kgZn ha}^{-1} \text{ year}^{-1}$; $12.0 \text{ gCu ton fish}^{-1} \text{ year}^{-1}$ or $1.5 \text{ kg Cu ha}^{-1} \text{ year}^{-1}$; and $0.9 \text{ g Mn ton fish}^{-1} \text{ year}^{-1}$ or $0.14 \text{ Mn kg ha}^{-1} \text{ year}^{-1}$.

The amount of Mn and Zn exported as commercialized fish is only a small fraction of the amount added with aquafeeds: for Mn 0.14 out of $11 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ (0.13%); and for Zn 1.5 out of $57.5 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ (2.61%). These suggest low incorporation of these trace metals in the fish biomass. For Cu, however, nearly half of the added Cu in aquafeed is incorporated into fish biomass (1.8 out of $3.8 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$; 47.4%).

Concentrations of the three metals found in muscle tissues are within the range of values reported for tilapia from other important tropical producers in Asia (Malaysia, Taiwan and India; Low et al. 2015); in China (Kwok et al. 2014); in Africa (El-Sadaawy et al. 2013); and in South America (Tajiri et al. 2011). Highest concentrations in viscera relative to muscle have also been reported for Zn, Cu and Mn in these studies. Lower muscle concentrations in muscles relative to internal organs have been frequently associated with the fast growth of tilapia and, therefore, short period of exposure to metals present in aquafeed under intensive fish cage aquaculture (Ikem and Egilla 2008).

Taking into account the figures in Table 3, approximately 2.6% of the total introduced Zn, 47% of the total introduced Cu and 0.13% of the total introduced Mn to the system via aquafeed, are exported as fish biomass. Therefore, the remaining amounts of metals (56 kgZn, 2.0 kgCu and 10.8 kgMn per hectare and per year) end into the reservoir annually in the studied farm. A fraction of these metal loads may accumulate in bottom sediments within the farm area, whereas another fraction can be exported to the open reservoir through hydrodynamics, mostly associated with suspended particles, since under the prevailing physical-

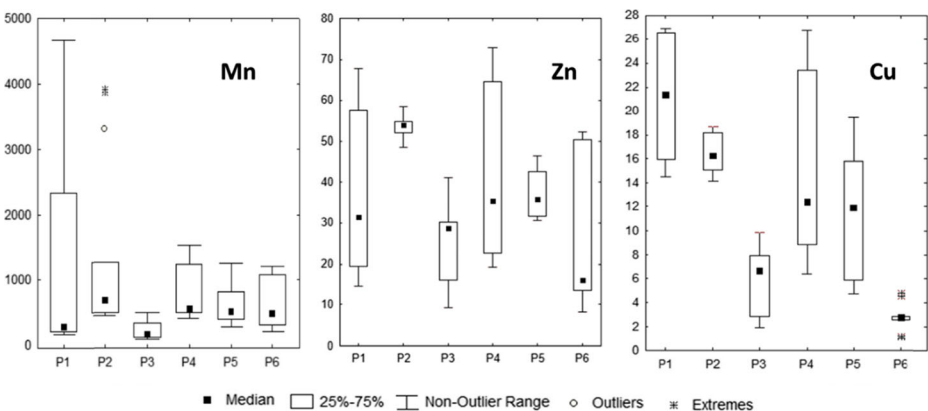


Fig. 2 Concentrations of Mn, Zn and Cu in sediments in the six sampling stations of the studied farm

chemical conditions of the reservoir surface waters (high pH and oxygen levels) only a very small portion may remain as dissolved metals.

Surface bottom sediments are enriched in organic matter, with a higher content inside the farm area ($9.5 \pm 7.7\%$) compared to the control stations ($7.9 \pm 6.9\%$). Figure 2 shows the concentrations of Mn, Zn and Cu in bottom sediments from the six stations sampled. Among the 5 stations within the farm area, Mn and Zn concentrations varied widely from and 227 to 1279 $\mu\text{g.g}^{-1}$ (median of 847 $\mu\text{g.g}^{-1}$) for Mn and from 25.3 to 53.8 $\mu\text{g.g}^{-1}$ (median of 39.0 $\mu\text{g.g}^{-1}$) for Zn ($n = 15$). In the control station, concentrations also varied from 211 to 1207 $\mu\text{g.g}^{-1}$ (median of 608 $\mu\text{g.g}^{-1}$) for Mn and from 8.1 to 52.3 $\mu\text{g.g}^{-1}$ (median of 25.3 $\mu\text{g.g}^{-1}$) for Zn. Highest concentrations occurred in stations just below the cages (P1 and P2). However, the large variability renders similar Mn and Zn concentrations and no clear trend of decreasing concentrations from the stations closer to cages to those farther is evident (Fig. 2).

Concentrations of Cu presented a different pattern; although also variable, there is a clear decrease from the stations located under cages to the farther and control stations. Stations in the farm area showed Cu concentrations varying from 5.8 to 21.1 $\mu\text{g.g}^{-1}$ (median of 13.9 $\mu\text{g.g}^{-1}$). Also, highest Cu concentrations occurred in stations just below the cages (P1 and P2). In the control station, Cu concentrations were much lower and did not vary particularly from 1.1 to 4.8 $\mu\text{g.g}^{-1}$ (median of 2.8 $\mu\text{g.g}^{-1}$).

After deposition in bottom sediments, metals can accumulate through diverse physical-chemical processes including adsorption, cation exchange, precipitation and co-precipitation of discrete minerals, and forming complexes with organic matter (Mountouris et al. 2002). However, a variable fraction of the accumulated metals is remobilized by sediment resuspension or dissolution of metal compounds due to the physical-chemical conditions of the pore water-sediment interface, and may pass through consecutive cycles of deposition and mobilization before buried definitively in bottom sediments (Barcellos et al. 1997). In the studied farm, hydrodynamics of the region exports most of the particles introduced by the farming activities prior to sedimentation, resulting in a small fraction of the net input being deposited in

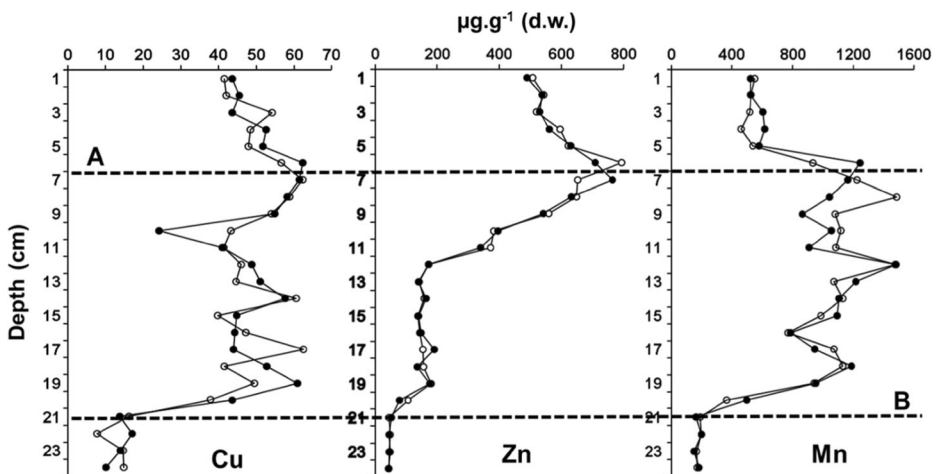


Fig. 3 Distribution of Cu, Zn and Mn in the cores collected inside the studied farm in the Castanhão Reservoir, NE Brazil. Dashed lines A and B represent, respectively, the period of the starting of the fish farming activities (year 2010) and the beginning of the reservoir flooding period (year 2003)

the farm's bottom sediments (Molisani et al. 2015; Oliveira et al. 2015). Thus, in order to estimate the actual retention rate of metals in bottom sediments within the farm, an analysis of the sedimentation rates derived from sediment cores are needed.

Figure 3 shows the distribution of Mn, Zn, Cu in the cores collected inside the studied farm. The dashed horizontal lines represent inflection points of the curves associated with the establishment of the fish farm in 2010 (A) and with the end of the flooding period in 2003 (B). Metal concentrations below 21 cm (line B) are relatively constant and considered those typical of the flooded soil, before 2003, prior to flooding.

Oliveira and Marins (2011) reported concentrations of metals in the reservoir basin soils varying from 0.4 to 12.5 $\mu\text{g}\cdot\text{g}^{-1}$ for Cu, from 3.3 to 40.5 $\mu\text{g}\cdot\text{g}^{-1}$ for Zn, and from 12.8 to 240 $\mu\text{g}\cdot\text{g}^{-1}$ for Mn, which are compatible to the concentrations observed below 21 cm of core depth. There is an increase in metal concentrations after the flooding of the reservoir (line B, corresponding to the year 2003 in Fig. 4), probably associated with washing of surface soils and associated litter, and the accumulation of finer sediments due to the recently established lake conditions. The organic matter and aluminum profiles (Fig. 4) confirm the enrichment of sediments with fine particles and organic debris after 2003.

After the initiation of the farming activities (line A, corresponding to the year 2010), metal content decreased progressively by a factor of 2.6 for Mn, 1.6 for Zn and 1.4 for Cu. Organic matter contents of the sediment, however, continued to increase, by a factor of 1.4 after the farm establishment, reaching about 35% in weight of the dry sediment. Aluminum concentrations, similarly to the trace metals, also showed a decrease in concentrations by a factor of 1.7 relative to concentrations found before the initiation of the farming activities (Fig. 4). Enrichment factors started to increase just after flooding, keeping this trend until the initiation of the farm's activity and remained relative constant (≈ 2 , for Mn and Cu; and ≈ 4 for Zn). The maintenance of high enrichment factors along the top 6 cm of the core suggests a continuous contribution of metals by farming activities and that the large input of organic matter ends up diluting the metal concentrations, including Al, in sediments.

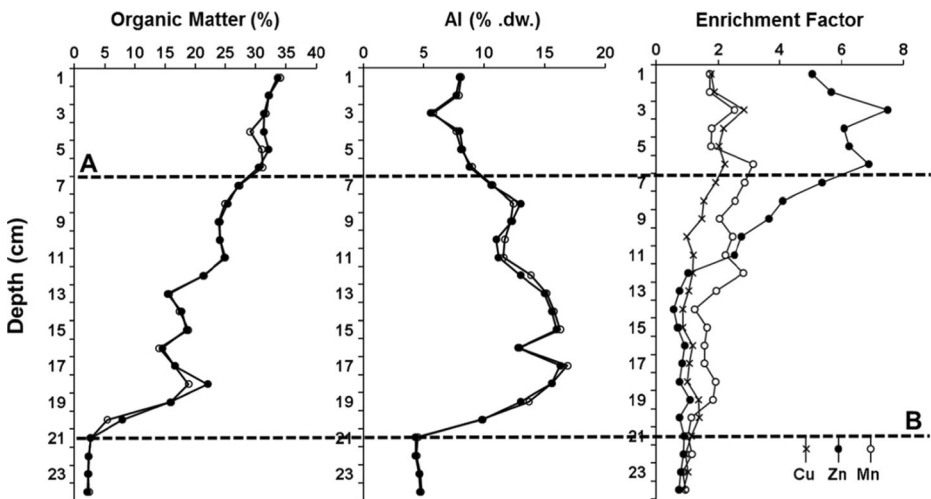


Fig. 4 Distribution of organic matter, Al and enrichment factors in the cores collected inside the studied farm in the Castanhão Reservoir, NE Brazil. Dashed lines A and B represent, respectively, the period of the starting of the fish farming activities (corresponding to the year 2010) and the beginning of the reservoir flooding period (corresponding to the year 2003)

Considering the flooding of the reservoir in 2003, sedimentation rates averaged about 1.75 cm.yr^{-1} until the establishment of the farm in 2010. Afterwards, observed sedimentation rates increased to about 2.0 cm.yr^{-1} , probably as a result of the addition of farming activity effluents. At the top 3 cm of the core samples, concentrations and accumulation rates decreased relative to the maximum peaks from 3 to 7 cm of depth. The presence of abundant fish schools below cages has been frequently observed by divers; this fish can both consume excess aquafeed and also increase bioturbidity, allowing for a certain remobilization and export of sediments, and the associated metals, to the open reservoir area.

The general trend of accumulation rates after the flooding of the reservoir in 2003 were similar for the three metals, increasing sharply after flooding due to sediment transport from flood marginal areas and higher suspended particles deposition due to lake condition. After the initiation of farming activities, however, trends of accumulation were different for the three metals. Average Cu and Mn accumulation rates were lower in the top 6 cm of depth ($12.4 \text{ }\mu\text{g.cm}^{-2}.\text{yr}^{-1}$ for Cu, and $134 \text{ }\mu\text{g.cm}^{-2}.\text{yr}^{-1}$ for Mn), compared to pre-farm rates of $16.4 \text{ }\mu\text{g.cm}^{-2}.\text{yr}^{-1}$ for Cu, and $342 \text{ }\mu\text{g.cm}^{-2}.\text{yr}^{-1}$ for Mn. Average Zn accumulation rate, however, increased in the top 6 cm ($149 \text{ }\mu\text{g.cm}^{-2}.\text{yr}^{-1}$) relative to pre-farm average rate ($87.1 \text{ }\mu\text{g.cm}^{-2}.\text{yr}^{-1}$) (Fig. 5). Assuming these average sedimentation rates, present metal accumulation in the farm sediments would reach $16.4 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ for Zn, $1.38 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ for Cu and $15.2 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ of Mn. Compared with the net input of these metals (the amount added with aquafeeds minus the amount exported as fish biomass), Mn, Cu and Zn accumulation corresponds to 140%, 70% and 30% of the net inputs of these metals, respectively, highlighting the contribution of aquaculture effluents to Zn and Cu, but not of Mn. Thus, a significant portion of Cu, and in particular of Zn, derived from the fish farm effluents is eventually exported to the reservoir.

The results from the Castanhão reservoir are similar to some other studies on the impact of cage fish farming on sediment metal content. Farmaki et al. (2014) also reported Cu and Zn enrichment associated with aquafeed and fish excreta in a marine farm in Greece, but also

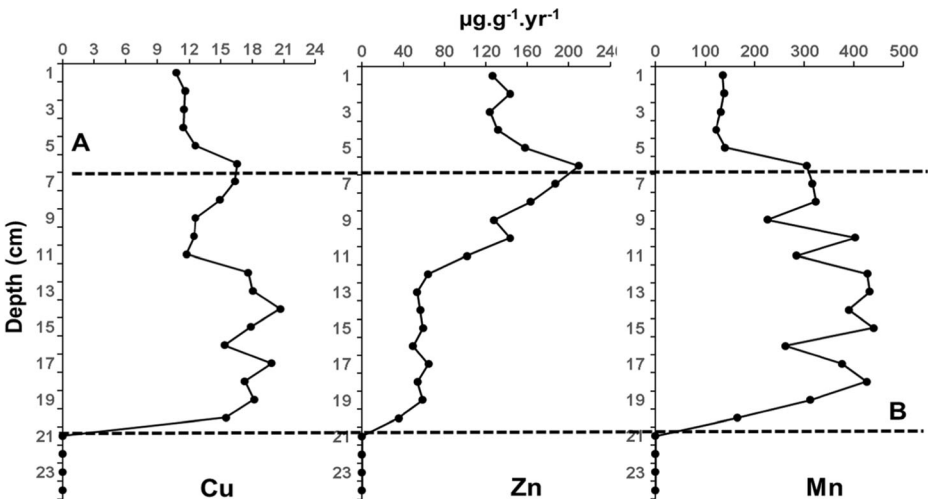


Fig. 5 Accumulation rates of Cu, Zn and Mn in the core samples collected inside the studied farm in the Castanhão Reservoir, NE Brazil. Dashed lines A and B represent, respectively, the period of the starting of the fish farming activities (corresponding to the year 2010) and the beginning of the reservoir flooding period (corresponding to the year 2003)

found Mn enrichment negligible. Mendiguchía et al. (2006) also reported enrichment of Cu and Zn in sediments under fish cages associated with increase in organic matter content of effluents in a fish farm in the Bay of Cadiz, Spain. Gu et al. (2012) reported very similar concentrations of Cu and Zn in sediments of Baisha Bay, China under fish cages. Also, they observed a progressive increase in the metals concentrations from bottom to the surface of sediment cores. Unfortunately, they did not report on metal accumulation rates. Kalantzi et al. (2013) observed that enrichment of Cu in sediments under fish cages are influenced by the redox state, amount of organic matter and grain size. Increased Cu concentrations occurred in anoxic, organic rich, fine grained sediments, whereas oxic, coarse grained sediments from impacted sites did not differ from control sites. Most studies also reported that metal-containing particles transported to aquaculture may contribute to a varying degree to the amount of metal accumulated ions in sediments (Dean et al. 2007; Voigt et al. 2016).

There is no study to our knowledge reporting the dilution effect of the farm effluents on metals concentrations in sediments as seems to be the case here. The organic matter content measured in the Castanhão farm is one of the highest ever reported reaching up to 35% d.w., and is due to the dumping of fish wastes back to the reservoir, after fillet separation in the farm. However, one has to take this hypothesis as very preliminary. Alternatively, the decrease of water flow velocity due to the presence of hundreds of fish cages, may enhance the deposition of fine particles brought in from the open reservoir and from surrounding soils, as suggested by the large contribution of Mn not derived from farm effluents. These particles, with typical low concentrations of metals, could also represent an additional dilution factor in the top layers of the sediment core.

4 Conclusions

The results presented confirm most studies that human exposure to metal pollutants through aquaculture fish is very small, if any. Fish metal concentrations are well below the maximum limits for human consumption and are also much lower than those found in wild specimens. An evaluation of the temporal buildup of metal concentrations in the farm environment shows that the studied trace metals are not a significant contamination issue suggesting fish-cage aquaculture as a less important source of trace metals to fish. In the Castanhão reservoir, flooding of soils resulted in a higher increase in metal concentrations, relative to fish farming practices; however, at least for Zn and to a lesser extent for Cu, aquaculture seems to have a significant effect on environmental concentrations. Interesting to note is the excess Zn quantity in aquafeeds when considering Zn content in fish. It seems that most of the metals are not incorporated in fish biomass; thus, in this case, reducing Zn content in aquafeed would not result in a deleterious impact on fish production, but would significantly reduce Zn emissions to the reservoir. Although accumulation in bottom sediments within the farm immobilizes a significant proportion of metals contained in the farm effluents, export to the reservoir can be significant in the case of Cu and Zn, in particular. Natural inputs of Mn seem much more significant than that from aquaculture. On the other hand, since metal accumulation is strongly associated with organic matter, at least part of the accumulated metals may eventually be released to the water column under changing physical-chemical conditions, such as increasing oxidation due to exposing the sediments to oxygenated waters during drought periods followed by reduction in water depth, for example.

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