

Mercury Distribution in a Mangrove Tidal Creek Affected by Intensive Shrimp Farming

B. G. B. Costa · T. M. Soares · R. F. Torres ·
L. D. Lacerda

Received: 24 September 2012 / Accepted: 27 December 2012 / Published online: 31 January 2013
© Springer Science+Business Media New York 2013

Abstract In this study, the Hg distributions in water and sediments from a mangrove creek that receives intensive shrimp farming effluents were determined. The average dissolved and particulate Hg concentrations in the water varied from 3.1 to 9.2 ng L⁻¹ and from 4.4 to 9.4 ng L⁻¹, respectively. However, the Hg concentrations in the suspended particulate matter and the bottom sediments varied from 95.4 to 115.7 ng g⁻¹ and from 1.6 to 10.3 ng g⁻¹, respectively. A Ward quadratic distance cluster analysis based on the Hg concentrations and hydro- and geochemical parameters (oxygen, salinity, temperature, pH, and organic matter and aluminum content) showed the effects of shrimp farming effluents on the Hg distribution pattern. Furthermore, these results were supported by the Hg distribution in the sediment cores. This study emphasizes the necessity of including Hg as a potential pollutant when monitoring the environmental impacts of intensive shrimp farming.

Keywords Mercury · Shrimp aquaculture · Mangrove

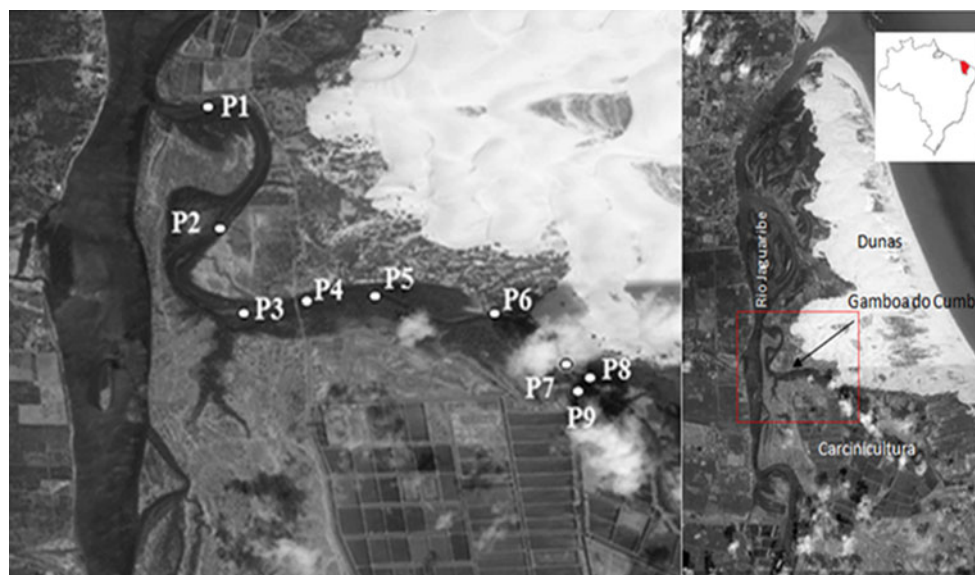
Rapid world population growth has created an urgent need for enhanced food security. Intensive shrimp aquaculture has proven to be a feasible alternative for increasing the availability of high-quality protein for human consumption (FAO 2010). However, shrimp aquaculture depends on large inputs of artificial feed, fertilizer and other chemical additives, such as algacides or chemicals that adjust the acidity. Thus, the environmental impacts of shrimp

aquaculture activities on coastal environments should be evaluated (Gräslund et al. 2003). Several authors have reported altered environmental conditions downstream of shrimp farms. Most studies reported increasing nutrient concentrations that resulted from large N and P emissions, which typically result from shrimp aquaculture (Burford et al. 2003; Lacerda et al. 2006). More recently, high emission factors for metals, such as Cu (Lacerda et al. 2006) and Hg (Lacerda et al. 2011), and changes in Zn concentrations in receiving water bodies have been reported (Silva et al. 2003).

In Northeastern Brazil, shrimp farming has increased exponentially in the past 10 years from an annual production of approximately 7,000 tons with less than 1,000 ha of pond area in 1998 to more than 90,000 tons and approximately 15,000 ha of pond area in 2003. Approximately 60 % of this activity is located in Ceará State, where the Jaguaribe River Estuary [latitude 4°23'S longitude and 37°36'W (Fig. 1)] is the largest production region with nearly 2,100 ha of shrimp pond area. In this estuary, Vaisman et al. (2005) reported Hg concentrations in sediments and oysters (*Crassostrea rhizophorae*) that were higher than those found in an adjacent estuary with no shrimp farming. Soares et al. (2011) suggested that abnormal Hg concentrations occurred in the Jaguaribe estuary and could be associated with the presence of Hg in aquafeeds that are used in local shrimp farms. However, a direct link between shrimp farm effluents and abnormally high environmental Hg concentrations was not found. Here, we present the Hg concentrations in water, suspended particles, bottom sediments, and in *Sphoeroides testudineos* carnivorous fish in a tidal channel that receives effluents from the largest (1,640 ha) shrimp farm located in the estuary (Fig. 1). In addition, sediment cores were collected from a selected depositional area of the creek and analyzed for Hg and other major geochemical parameters.

B. G. B. Costa · T. M. Soares · R. F. Torres · L. D. Lacerda (✉)
Instituto de Ciências do Mar, Universidade Federal do Ceará,
Av. Abolição 3207, Fortaleza, CE 60.165-081, Brazil
e-mail: ldrude@pq.cnpq.br

Fig. 1 Location of the sampling stations on the tidal creek in the Jaguaribe River estuary, NE Brazil. The depositional area (P3) and effluent releases (P8 and P9) are shown



Materials and Methods

Nine stations were sampled along the entire creek length from the effluent releasing point to the Jaguaribe River main channel during low tide. At each station, triplicate water, suspended particle and sediment samples were collected for chemical analysis. At station 3 (Fig. 1), samples were collected from a depositional area in the creek and sediment cores and *S. testudineos* specimens were collected. During sampling, dissolved oxygen, salinity, and temperature readings were obtained in triplicate with a previously calibrated YSI-85 probe. In addition, pH was measured with an Orion model 250A potentiometer, which was calibrated with standard solutions at pH 7.0 and 9.0. Samples for Hg determinations were collected with pre-cleaned 1.5 L PET bottles from the front of the boat and against the current. These samples were collected according to accepted Hg analysis protocols (Marins et al. 2002). All glass- and plasticware that was used for sampling or sample preparation was decontaminated by immersion in a 10 % (v/v) Extran solution (MERCK) for 2 days, followed by immersion in a diluted HNO₃ (10 % v/v) solution for 3 days and rinsing with Milli-Q water. Glass fiber filters with a pore diameter of 0.45 μ were used to separate suspended particles. Samples for particulate Hg determinations were heated to 450°C for 12 h before transporting in enclosed petri dishes. All chemical reagents in this study were analytical grade or purer.

Surface sediments were collected with a Van Veen grab sampler. The sediment cores were collected manually by inserting acrylic tubes (1.5 m long and 9 cm in diameter) in the sediment bank at station 3 (Fig. 1). Samples were transferred to pre-washed plastic bottles and stored at 4°C until analysis. In the laboratory, surface sediment samples

and 0.5 cm thick slices of the cores were dried overnight (60°C). Then, the shells and other oversized materials were removed by sieving through a 2 mm mesh sieve. These samples were used to determine the total Hg, Al and organic matter concentrations.

Dissolved Hg (Hg-D) was determined in the filtered samples after oxidation with BrCl at room temperature. After oxidation, a 1 N hydroxylamine solution was added to the sample to reduce the excess BrCl. Next, the sample was reduced with a 10 % SnCl₂ solution (Marins et al. 2002). Particulate Hg (Hg-P) was determined after partial digestion of the material that was retained on the filters with 50 % v/v aqua-regia at 80°C prior to reduction with SnCl₂. For each batch, blank membrane samples were analyzed simultaneously. The extracts were analyzed in a PSA Millennium Merlin 10.025 Model cold vapor atomic fluorescence spectrophotometer (CVAFS). The analytical detection limit of this method was 0.24 ng L⁻¹ for dissolved Hg and 1.0 ng g⁻¹ for particulate Hg, based on the ratio between three blank reagent standard deviations. In all cases, the blank signals were less than 0.5 % of the sample signals. All samples were analyzed in duplicate. The differences between duplicate samples were consistently below 20 %. For quality assurance of particulate Hg, a certified reference material (NRC PACS-2, Canada) was analyzed simultaneously, which showed a precision of 96 % according to the relative standard deviation of the three replicates. In addition, the average Hg recovery rate was 103 ± 4 %. The reported concentrations were not corrected for the recoveries of the certified materials.

Mercury was quantified in the sediment and biological matrices with Cold Vapor Atomic Absorption Spectrometry (CV-AAS) from Nippon Instrumentation Corp. (NIC RA-3). Approximately 0.5 g of fish muscle and dried

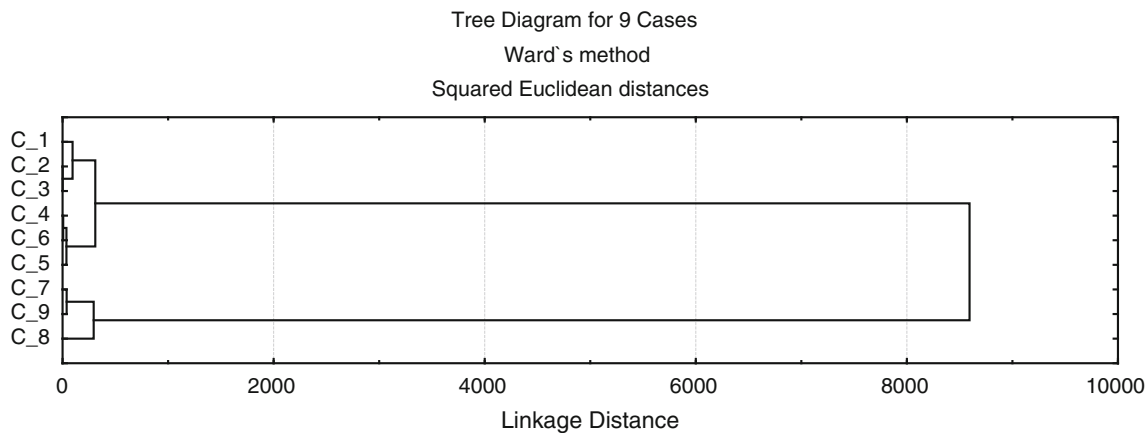


Fig. 2 The Ward squared Euclidean distance (Cluster Analysis) based on the observed hydrochemistry ($n = 18$) along the studied tidal creek in NE Brazil

sediment were digested with 10 mL of concentrated HNO_3 in Teflon vials and a MARS-Plus microwave furnace. The detection and quantification limits were 0.03 and 1.7 ng g^{-1} , respectively. The total Hg (Hg-T) determination was validated with a standard reference material (NIST 2976-Mussel tissue and NIST 1646a-Estuarine Sediment). The analytical results were precise and accurate at $94 \pm 3\%$ and $102 \pm 3\%$, respectively. The data were subjected to Cluster analysis with Ward's method by applying the Euclidian square distance to test the link between the Hg concentrations in water, superficial sediments and hydrochemical variables. A p value of <0.05 was considered to be statistically significant.

Results

Cluster analysis of the hydrochemical parameters measured along the creek revealed the existence of three sectors (Fig. 2). The first sector (stations 1, 2 and to a lesser extent, 3) is located near the main Jaguaribe river channel. The second sector is located in the intermediate region (stations 5, 6 and to a lesser extent, 4), and the third sector is located near the shrimp farms effluent release point (stations 7, 8

and 9). The hydrochemistry results showed increasing average dissolved oxygen (5.3, 6.2, and 8.9 mg L^{-1}) and salinity (22.9, 23.3, and 24.2) and decreasing pH (7.7, 6.1, and 6.1) from sector one at the Jaguaribe River to sector two in the middle of the creek and to sector three at the effluent area, respectively.

Suspended particle concentrations were higher in sectors two and three. However, the Hg species concentration distributions followed a bi-modal pattern with the highest values in sector three (near the effluents), including the total particulate and dissolved Hg concentrations. The Hg concentrations decreased in the middle section of the creek and increased again in sector one near the Jaguaribe River (Table 1). The highest Hg-D and Hg-T values were observed in sector three but were highly variable. The Hg-P concentrations were higher in sectors two and three. These concentrations were lower than those reported for highly contaminated estuaries but higher than those reported for background concentrations at other pristine sites on the Brazilian coast Paraquetti et al. (2004). This result and the spatial Hg distribution patterns suggest that shrimp farm effluents impact Hg distribution. In fact, the maximum Hg concentrations occurred near the shrimp farm discharge. Others have previously reported Hg concentrations in

Table 1 Range, average and standard deviation of suspended particulate matter (SPM) (mg L^{-1}) and dissolved (Hg-D), particulate (Hg-P) and total (Hg-T) Hg concentrations (ng L^{-1}) in the SPM (Hg-SPM) (ng g^{-1}) waters along the studied tidal creek at the Jaguaribe River estuary, NE Brazil

Sector	SMP	Hg-D	Hg-P	Hg-T	Hg-SPM
1 ($n = 6$)	28.1–53.2	4.6–17.0	3.2–5.4	7.7–21.7	78.5–167.4
	40.6 ± 12.6	8.7 ± 7.2	4.4 ± 1.1	13.1 ± 7.5	115.7 ± 46.2
2 ($n = 6$)	60.4–146.5	2.0–4.9	4.4–15.0	6.6–17.0	72.2–139.9
	105.1 ± 43.1	3.1 ± 1.6	9.4 ± 5.3	12.4 ± 5.3	95.4 ± 38.5
3 ($n = 6$)	55.8–100.3	1.1–23.5	5.2–11.5	6.3–32.1	87.7–147.7
	79.1 ± 22.3	9.2 ± 12.4	8.4 ± 3.2	17.6 ± 13.2	106.9 ± 29.4

Table 2 Concentrations of organic matter (O.M.), Al and total Hg in surface sediments along the studied tidal creek at the Jaguaribe River, NE Brazil

Stations	O.M. (%)	Al (mg g ⁻¹)	Hg (ng g ⁻¹)
1	6.3 ± 0.0	9.3 ± 0.8	5.1 ± 0.3
2	7.0 ± 0.1	16.0 ± 0.4	6.6 ± 0.2
3	16.2 ± 0.1	24.2 ± 0.3	10.3 ± 0.4
4	13.3 ± 0.3	21.8 ± 0.4	7.4 ± 0.1
5	4.7 ± 0.2	13.8 ± 0.7	4.5 ± 0.4
6	2.0 ± 0.0	3.5 ± 0.9	2.1 ± 0.7
7	3.6 ± 0.0	8.1 ± 0.1	2.8 ± 0.8
8	1.9 ± 0.2	4.2 ± 0.5	1.6 ± 1.2
9	5.2 ± 0.3	10.5 ± 0.7	2.3 ± 0.1

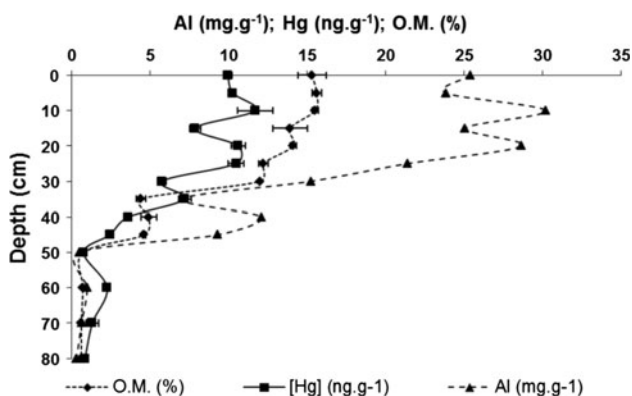


Fig. 3 Vertical distributions of total Hg, Al, and organic matter (O.M.) concentrations in a sediment core that was collected at station 3 in the tidal creek of the Jaguaribe River, NE Brazil. Data points represent the average values of duplicate samples at each depth

shrimp farm effluents and ponds (Lacerda et al. 2011; Soares et al. 2011). In addition, trace concentrations of metals have been reported as impurities in aquafeeds and chemicals that are used in the shrimp production process. These impurities enrich the effluents and change the environmental concentrations of these metals when these effluents are released from shrimp farms (Silva et al. 2003;

Lacerda et al. 2009; Dorea 2007). These elevated metal concentrations impact the environmental dynamics and change the metal mobility and bioavailability for aquatic organisms.

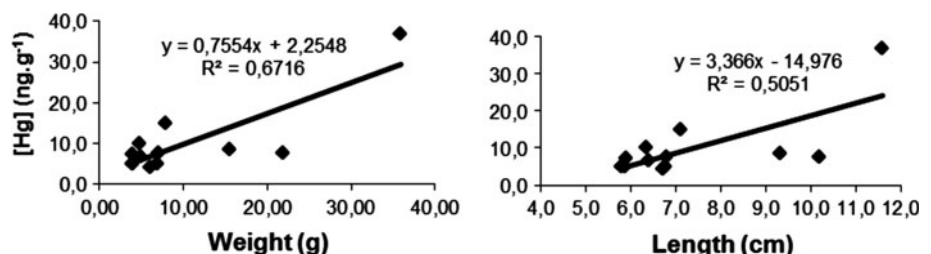
Average Hg concentrations in the surface sediments increased from sector three (1.6–2.8 ng g⁻¹) to sectors two [stations 3 (7.4 ng g⁻¹) and 4 (10.3 ng g⁻¹)] and decreased in sector five near the Jaguaribe River (5.1–6.6 ng g⁻¹) (Table 2). These concentrations are similar to those that were observed in the water and were lower than those reported in contaminated areas (Marins et al. 1998). However, these concentrations were slightly higher than the regional background values (Vaisman et al. 2005).

The Hg concentrations in the sediments were significantly correlated with organic matter ($r = 0.9407$; $p > 0.05$) and Al ($r = 0.9338$ $p > 0.05$) concentrations, which suggests that a similar source and transport mechanism occurred. Shrimp farm effluents are characterized by high organic matter concentrations from excess aquafeed and animal excreta and total suspended solids that result from pond wall erosion by aerators (Dierberg and Kiattisimkul 1996).

The Hg distribution in the sediment core that was obtained in sector two shows that higher concentrations occurred in the top 35 cm. These concentrations varied from 7.2 to 11.7 ng g⁻¹ and were compared to values that ranged from <0.5 to 3.6 ng g⁻¹ (Fig. 3). Sedimentation rates are unknown for this area, but have been estimated to reach 0.3 cm year⁻¹ in other muddy banks in the estuary. Thus, the Hg concentration began to increase in the early 2000s, which agreed with the increase in the intensive shrimp farming area (Lacerda et al. 2011).

The Hg concentrations in the fish that were captured in the tidal creek were strongly and positively correlated with weight and size, which suggests bioaccumulation by *S. testudineos* (Fig. 4). The relatively low values mainly occurred in juvenile fish. The Hg concentrations in the fish of this region have been previously reported, and the observed concentrations were similar to the previously reported values (Braga 2006). Because this species eventually migrates to the Jaguaribe River, its Hg content is a poor indicator of environmental Hg concentrations.

Fig. 4 Correlation between Hg concentrations and the morphometric parameters of *S. testudineos* that were captured in the tidal creek at the Jaguaribe River, NE Brazil



Conclusions

The distribution of Hg along the tidal channel of Cumbe's creek reflects the export of Hg from intensive shrimp farming. The partitioning of the geochemical Hg water column was not explained by chemical-physical characteristics in this study. However, the surface sediments at station 3 characterized this area as a preferential deposition area. The correlation between the Hg, Al and O.M. levels suggested the origin of Hg in the sediments. In contrast, the evaluation of sediment cores provided additional evidence that indicated Hg concentrations had recently increased in the area. Due to the predominance of the dissolved fractions, environmental bioindicators should be monitored in this area to minimize the damage caused by the consumption of contaminated fish. These environmental bioindicators would preferably consist of species that are consumed by the population.

References

- Braga TMB (2006) Preliminary assessment of mercury contamination of fish commercialized at the Mucuripe Beach fish market and in the Jaguaribe River estuary, CE. Monografia de Graduação em Engenharia de Pesca, Fortaleza: Universidade Federal do Ceará, p 58. Available at: http://www.institutomilenioestuarios.com.br/pdfs/Monografias/6_BragaTMB2006Contaminacao.pdf
- Burford MA, Costanzo SD, Dennison WC, Jackson CJ, Jone AB, McKinnon AD, Preston NP, Trott LA (2003) A synthesis of dominant ecological processes in intensive shrimp ponds and adjacent coastal environments in NE Australia. *Mar Pollut Bull* 46:1456–1469
- Dierberg FE, Kiattisimkul W (1996) Issues, impacts, and implications of Shrimp Aquaculture in Thailand. *Environ Manag* 20:649–666
- Dorea JG (2007) Fish meal in animal feed and human exposure to persistent bioaccumulative and toxic substances. *J Food Prot* 69:2777–2785
- FAO – Food and Agriculture Organization of the United Nations (2010) The state of world fisheries and aquaculture, Rome, 218 pp
- Gräslund S, Holmström K, Wahlström A (2003) A field survey of chemicals and biological products used in shrimp farming. *Mar Pollut Bull* 46:81–90
- Lacerda LD, Santos JA, Madrid RM (2006) Copper emission factor from intensive shrimp aquaculture. *Mar Pollut Bull* 52:1823–1826
- Lacerda LD, Santos JA, Lopes DV (2009) Fate of copper in intensive shrimp farms: bioaccumulation and deposition in pond sediments. *Braz J Biol* 69:851–858
- Lacerda LD, Soares TM, Costa BGB, Godoy MDP (2011) Mercury emission factors from intensive shrimp aquaculture and their relative importance to the Jaguaribe River Estuary, NE Brazil. *Bull Environ Cont Toxicol* 87:657–661
- Marins RV, Lacerda LD, Paraquetti HHM, Paiva EC, Villas Boas RC (1998) Geochemistry of mercury in sediments of a sub-tropical coastal lagoon, Sepetiba Bay, southeastern Brazil. *Bull Environ Cont Toxicol* 61:57–64
- Marins RV, Paraquetti HH, Ayres GA (2002) Analytical alternative for the physical-chemical speciation of mercury in tropical coastal waters. *Quím Nova* 25:372–378
- Paraquetti HHM, Ayres GA, Almeida MD, Molisani MM, Lacerda LD (2004) Mercury distribution, speciation and flux in the Sepetiba Bay tributaries, SE, Brasil. *Water Res* 38:1439–1448
- Silva CAR, Rainbow PS, Smith BD (2003) Biomonitoring of trace metal contamination in mangrove-lined Brazilian coastal systems using oyster *Crassostrea rhizophorae*: comparative study of regions affected by oil, salt pond and shrimp farming activities. *Hydrobiologia* 501:199–206
- Soares TCM, Coutinho DA, Lacerda LD, Moraes MO, Rebelo MF (2011) Mercury accumulation and metallothionein expression from aquafeeds by *Litopenaeus vannamei* Boone, 1931 under intensive aquaculture conditions. *Braz J Biol* 71:131–137
- Vaisman AG, Marins RV, Lacerda LD (2005) Characterization of the mangrove oyster *Crassostraea rhizophora*, as a biomonitor for mercury in tropical estuarine systems. *Bull Environ Cont Toxicol* 73:582–588