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Long-Term (2002–2015) Changes in Mercury Contamination in NE Brazil Depicted by the Mangrove Oyster *Crassostraea rhizophorae* (Guilding, 1828)

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Abstract Mercury concentrations in oysters from four estuaries in northeastern Brazil varied following source changes during the past 13 years. Concentrations were higher in urban estuaries relative to rural areas, but decreased in the 13-years interval following improvements in solid wastes disposal and sewage treatment. In rural estuaries, the one located in an environmental protection area showed no changes in Hg concentrations in the period. However, in the Jaguaribe estuary, remobilization from soils and sediments due to regional environmental changes, increased Hg concentrations in oysters to values similar to the most contaminated metropolitan sites.

Keywords Monitoring · Estuaries · Metals · Oysters

Biomonitoring is the preferred strategy for accompanying trends in pollution processes, since rather than total concentrations, biomonitors reflect the fraction of the contamination concentration actually available for biological uptake and, therefore, a measurement of environmental exposure and toxicological risk. Successful examples of this strategy involve the use of plants for the biomonitoring of the emissions of metals and other compounds to the atmosphere (Frati and Brunialt 2006; van Dijka et al. 2015), whereas in aquatic environments one of the best examples is the Mussel Watch Program (NOAA 2016) that monitors the concentration of contaminants in bivalves (mussels and oysters) and sediments in the coastal waters of the U.S. This program was followed by younger companion studies in South Africa (Sparks et al. 2014), Korea (Choi et al. 2010) and a few other counties. Unfortunately, a global IOC-UNESCO initiative started in the 1970s, mostly involving developing countries failed to establish a similar network as the one presently run by NOAA in the USA (Tripp 1993). Therefore, few examples of long term, at least decade-scale studies, are available to assess the long term impacts of pollution processes in the marine environment in most developing countries.

In Brazil, although a potential participant of the international IOC-UNESCO effort (Porte et al. 1990) only a few long-term studies at the local level are available, mostly restricted to the industrialized south and southeastern coasts (Costa et al. 2000; Marins et al. 2004; Lacerda and Molisani 2006). In Brazil, most anthropogenic drivers of environmental contamination by Hg are no longer related to industrial uses. Rather, present day Hg sources to Brazilian coastal environments are associated with land-use changes in watersheds, unplanned urban development resulting in untreated sewage inputs and inadequate solid wastes disposal, agriculture and aquaculture and atmospheric deposition (Marins et al. 2004; Lacerda et al. 2011), thus affecting other stretches of the Brazilian coast regarded as relatively pristine such as the northeastern coast.

Prior to the present century very little information existed on the Hg contamination in the northeastern Brazil coastline. Even today, studies are restricted to sites receiving special attention due to the presence of past point sources of Hg. For example, Meyer et al. (1998) and Cavalcanti (2003) measured Hg concentrations in oysters from a contaminated estuary that had received from 22 to 35 t of Hg between 1963 and 1987 from a chlor-alkali plant and found high concentrations, similar to those frequently observed in sites affected by industries

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(136–3748 ng g^{-1} d.w.). Oysters from estuaries receiving diffuse Hg emissions from large metropolitan areas in NE Brazil showed concentrations 2–20 times lower (84–154 ng g^{-1}) (Vaisman et al. 2005).

There is only, to our knowledge, a single biomonitoring study at the regional level measuring Hg concentrations in oysters from a long stretch of the northeastern coastline of Brazil performed in 2002 by Vaisman et al. (2005). In that study four estuaries were selected to measure the concentrations of Hg in the mangrove oysters *Crassostraea rhizophorae*. Two of the estuaries were located within the metropolitan area of Fortaleza, State Capital of Ceará, and two others in relatively pristine areas where major anthropogenic activities were agriculture and husbandry. As expected the areas within the metropolitan area showed higher Hg concentrations compared to the rural sites. During the 15 years from that study significant changes have occurred in all four estuaries and the present study was deployed to check the effect of environmental control measures and changing intensity of specific drivers on Hg concentrations in oysters of the same four areas.

Materials and Methods

Samples for Hg determination were collected from oyster beds located at the lower estuary of the four rivers. A total of 303 individuals were collected and pooled in composite samples containing from 2 to 6 individuals of each size class and lyophilized. Approximately 0.5 g of lyophilized oyster homogenate were digested with 10 ml of concentrated HNO_3 in Teflon vials in a MARS-Plus microwave furnace. Mercury concentrations were quantified by cold vapor atomic absorption spectrophotometer (CVAAS) in a NIC RA-3 NIPON spectrophotometer, after reduction of oxidized Hg species to Hg^0 with a $SnCl_2$ acidic (20 % HSO4) solution. The detection and quantification limits were 0.27 ng (three times the standard deviation of 14 blank readings), equivalent to 1.07 ng g^{-1} dry weight (10 times the standard deviation of 14 blank readings), respectively (USEPA, 2000). All glass- and plastic ware 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 HNO_3 (10 % v/v) solution for 3 days and rinsed with Milli-Q water. The digested samples, blanks, and reference material were diluted with Milli-Q water to a final volume of 20 mL.

All samples were analyzed in duplicate. The differences between duplicate samples were consistently below 20 %. For quality assurance of Hg in oysters, certified reference material (National Research Council, Canada, DORM-2 (fish muscle) and DOLT-3 (fish liver) were analyzed simultaneously, 1 set each of 24 samples. These analyses showed average Hg recoveries varying from 93.4 % to 96.7 % (Table 1). The reported concentrations were not corrected for the recoveries of the certified materials. Normality tests (Kolmogorov–Smirnov) were performed on the biometric data of oysters and the Hg concentrations, a Mann–Whitney test was used to compared differences in Hg concentrations between size classes, whereas comparisons of the average concentrations between estuaries and size classes were assessed by Kruskal–Wallis comparisons of means using a Statistica 13 software package. A $p < 0.01$ level of significance was used in the statistical tests.

Results and Discussion

The total 303 individual oysters collected in the four estuaries were separated according to their length and height size classes (Table 2). Variance within pooled samples was small and varied from 8.5 % to 16.1 % and was, in general, higher in larger size classes with less individuals per pooled sample. In relation to the limits established by the Brazilian legislation (500 ng g^{-1}, ANVISA 1998) for seafood, most values were between 1 and 2 tenths of that limit, whereas even the highest concentrations measured in the Ceará estuary oysters, were 5-times lower. Thus, the resulting human exposure is very small, even considering local artisanal fishermen and their associated communities. If the reference dose for Hg (Hg = 0.47 μg kg^{-1} body weight day^{-1}; BCS 2007) is considered and the average ingestion rate per capita of fisheries of 35.6 g day^{-1} (Sartori and Amâncio 2012), a huge overestimation since oyster consumption is over ten-times lower; the estimated hazard quotients (HQ) (Newman and Unger 2002) would be well below to the critical limit of 1.0 and varying from 0.06 in the more pristine sites to 0.11 in the most contaminated Ceará river estuary.

There was no difference between Hg concentrations observed in the two size classes at the rural Pacotí and Jaguaribe estuaries, while larger size classes at the metropolitan estuaries (Cocó and Ceará) presented significantly higher ($p < 0.01$) Hg concentrations, although there was no observed trend of increasing Hg concentrations with size when all size classes in the four estuaries are considered. Previous work with the same species in such far apart sites such as NE Brazil (Vaisman et al. 2005) and Cuba (Olivares-Rieumont et al. 2012) showed no relationship between shell size and Hg concentrations, which is in agreement with the trophic level of this species as a filter feeding organisms exposed to Hg present in suspended particles, mostly inorganic, rather than from live preys, where Hg occurs mostly as organic complexes. Kehrig

Table 1 Mercury concentrations (ng g^{-1} dry weight) obtained in standard reference materials analyzed according to the described methodology

Reference standard	n	Certified values	Obtained values	Recovery (%)
NRCC–DOLT—3	3	3370	3237 ± 293	96.7 ± 8,7
NRCC–DORM—2	3	4640	4333 ± 34	93.4 ± 0.7

Table 2 Mercury concentrations (ng g^{-1} dry weight) in different size classes of oysters (*C. rhizophorae*) sampled from four estuaries along the coast of Ceará State, NE Brazil

Estuary	Size class (length/height) (cm)	n_s	Average Hg (ng g^{-1} dry weight)	Minimum–Maximum (ng g^{-1} dry weight)
Pacoti	<30/20–40	12	52.7 ± 4.5[a]	45.1–59.7
	>35/40–60	8	51.1 ± 7.1[a]	40.2–59.4
Cocó	<30/20–40	8	56.1 ± 7.7[a]	43.9–67.2
	<35/40–60	16	65.8 ± 7.2[b]	53.6–76.3
Jaguaribe	<30/20–40	8	75.6 ± 12.2[a]	55.5–86.0
	>35/40–60	8	74.5 ± 7.4[a]	67.0–85.8
Ceará	<30/20–40	12	84.5 ± 12.1[a]	59.7–96.9
	>35/40–60	16	101.7 ± 14.7[b]	74.9–120.9

Different superscript letters mean significant different average concentrations with $p < 0.01$ between size classes. (n_s = number of polled sample; the number of individuals per pooled sample varied according to size class between 2 and 7)

et al. (2006), for example, found Methyl–Hg, the most toxic Hg species, to amount only from 31.9 % to 64.5 % of the total Hg content in oysters from SE Brazil, much lower than typical Methyl–Hg content in predatory fish (>95 %), which generally present highly significant positive relationships between concentrations and size (Yamashita et al. 2005). Lack of relationships between size and Hg concentrations in oysters suggest that Hg levels are a function of environmental pressures rather than age- or size-specific factors of individuals, confirming their usefulness as biomonitors, as previously verified for othe oyster species (Osuna-Martínez et al. 2010).

Oysters from the Ceará estuary, located at the metropolitan area of Fortaleza city, presented the highest Hg concentrations in the two size classes (84.5 and 101.7 ng g^{-1} for small and large size classes, respectively); whereas the lower concentrations were observed in oyster form the relatively pristine Pacotí estuary, where oysters of all size classes presented average Hg concentrations varying from 51.1 to 52.7 ng g^{-1}. Interesting to note is the relatively high concentrations found in the rural Jaguaribe estuary, where oysters presented Hg concentrations higher than those found in the metropolitan Cocó estuary and similar to those observed in smaller oysters from the Ceará estuary.

Figure 1 compares Hg concentrations in oysters from the small and large size classes from all four estuaries. It is clear that significantly higher concentrations occur in the metropolitan Ceará estuary in both size classes and the lowest in the pristine Pacotí estuary. At the Jaguaribe estuary, Hg concentrations in oysters were significantly higher than those from the other rural river and even higher that those observed in the metropolitan Cocó estuary.

Although differences in Hg concentrations due to different oyster species may impede a direct comparison between areas within the same genera, it is possible with caution to compare our results with others using oysters worldwide. Concentrations observed in the mangrove oysters from the three of the Ceará coast estuaries in this study are mostly similar to those observed in pristine environments (30–80 ng g^{-1}; Jara-Marini et al. 2008; Garcá-Rico et al. 2010; Bilandzic et al. 2015). The single exception are the oysters from the Ceará river estuary, which showed consistently higher concentrations than those pristine sites. In all studied sites Hg concentrations in oysters were lower than most other values reported in the literature from areas affected by human activities. Páez-Osuna and Osuna-Martínez (2015) found Hg concentrations varying from 170 to 540 ng g^{-1} in mangrove oysters from ten locations along the Gulf of California, Mexico, and although other trace metals presented a clear seasonal variation, Hg concentrations showed no significant difference between rain and dry period. In contaminated estuaries receiving industrial effluents in Brazil and the USA, Crassostraea species frequently achieve Hg concentrations that may reach up to 2000 ng g^{-1} (Meyer et al. 1998; Aguilar et al. 2012); whereas in urban estuaries along other tropical coasts in Africa, Asia and in Brazil, oysters

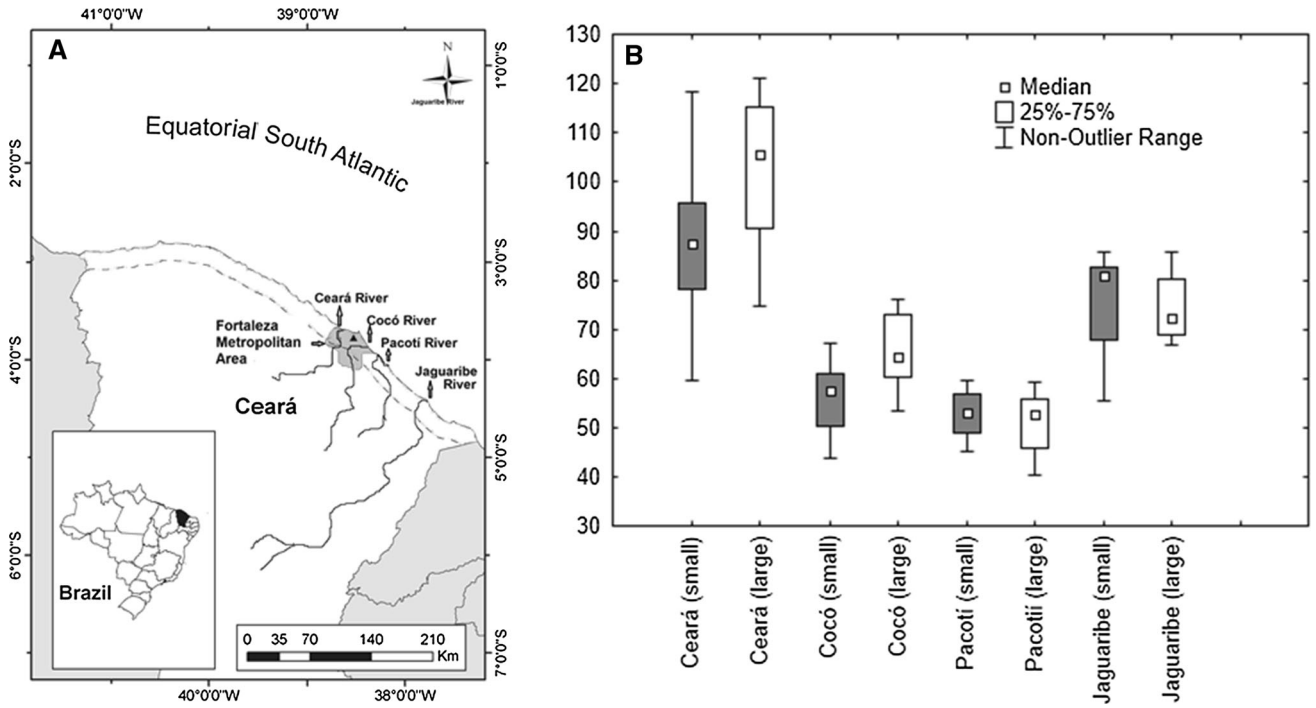

Fig. 1 Location of the four studied estuaries in the Ceará coast, NE Brazil (**a**) and Hg concentrations (ng g^{-1} d.w.) in oysters of different size classes in the four studied estuaries

achieve Hg concentrations (96–270 ng g^{-1}) that are within the higher range of values observed in this study (Jeng et al. 2000; Joris et al. 2000; Curtius et al. 2003, respectively). Olivares-Rieumont et al. (2012) also found higher concentrations in oysters in a gradient from impacted to more pristine areas in the coast of Cuba.

When compared Hg concentrations within a given size class, between the earlier study by Vaisman et al. (2005) and the present survey, differences between the estuaries are much clearer and statistically significant (Fig. 2). Whereas oysters from the Ceará estuary are still the most contaminated, average Hg concentrations decreased by 35 % from 2002 (median of 145 ng g^{-1}) to 2015 (median of 94 ng g^{-1}) in this estuary. A similar decrease was observed in the other urban estuary in the Cocó River (median of 84 ng g^{-1} in 2002 and 61 ng g^{-1} in 2015). In the Pacotí estuary, located in an environmental protection area, Hg concentrations in oysters were virtually equal between the two sampling dates and were the lowest observed in the two sampling periods. A different trend was observed in the Jaguaribe estuary with median Hg concentrations increasing about 65 % from 49 ng g^{-1} to 76 ng g^{-1}, in 2002 and 2015, respectively.

Between 2002 and 2015 improvements occurred in sewage treatment and solid waste disposal in the city of Fortaleza. In 2000 sewage disposal and treatment covered 49 % of the housing and increased to 61 % in 2013. Solid waste collection and disposal increased from 95.2 % to

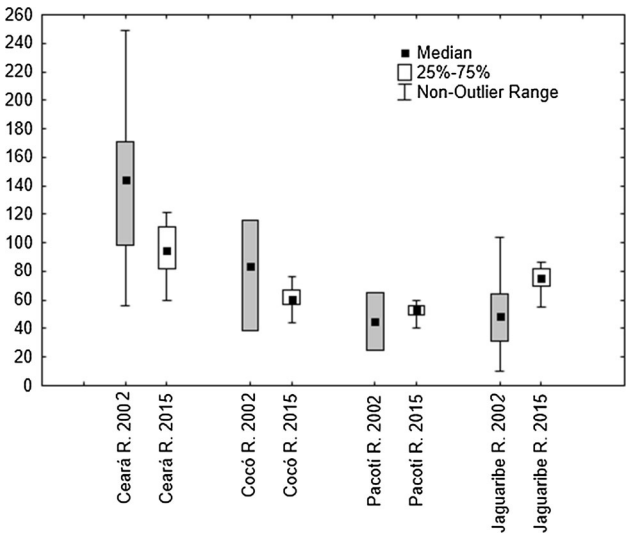

Fig. 2 Mercury concentrations (ng g^{-1} d.w.) in oysters from the four studied estuaries in the Ceará coast, NE Brazil in 2002 (Vaisman et al. 2005) and in 2015 (present study)

98.8 % of all addresses in the city. In the Ceará and Cocó River basins, sewage collecting system increased from 434 km and 560 km in 2000 to 730 km and 866 km in 2012, respectively (Fortaleza 2014). Sewage and solid wastes inadequate disposal were recorded as the most significant Hg sources to both river systems (Lacerda and Sena 2005) and their improvement in the metropolitan area

of Fortaleza may have caused the observed decrease in oysters Hg concentration in their estuaries.

At the Jaguaribe estuary, Hg emissions for the year 2009 were estimated by Lacerda et al. (2011) and reported major sources from inadequate solid waste disposal (150 kg yr^{-1}), untreated sewage (75 kg yr^{-1}) and shrimp aquaculture (0.35 kg yr^{-1}). Relative to 2002, only shrimp farming, the least important source, showed increasing intensity. In Aracati, the most populous (72,700 inhab.) municipality in the lower Jaguaribe Basin, sewage treatment, although restricted to the urban area, has increased by 70 % per year from 2000 to 2013 and reaches nearly 40 % of the total population. Similarly, as for 2010 onwards the Regional Plan for Solid Wastes Disposal has been improving collection and treatment of urban solid wastes (Deepask 2016). Thus, these two major sources were either unaltered or decreased their Hg emissions during the period. Even considering the increase of shrimp farming area from about 940 ha in 2003 to nearly 3000 in 2015, this would still contribute to <1.0 kg of Hg annually to the estuary, hardly explaining the observed increase in Hg oyster's concentrations.

Increasing Hg mobilization and bioavailability has been observed along the Jaguaribe River lower basin, mostly due to soil use alterations including intensive irrigated agriculture resulting in augmenting soil erosion and transport. Also, decreasing annual rainfall due to global climate change reduced fluvial flow in the past three decades and its effects are further aggravated by river damming and reservoir construction upstream of the estuary (Lacerda et al. 2013; Costa and Lacerda 2014). These mechanisms could explain the increase in Hg concertation in oysters from the Jaguaribe river estuary and add a global dimension to the use of these organisms as a biomonitors of Hg environmental concentrations changes.

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