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Sediment quality assessment in a tropical estuary: The case of Ceará River, Northeastern Brazil

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ABSTRACT

The present study aimed to assess the sediment quality in a tropical estuary located in the northeast of Brazil under semi-arid conditions and multiple sources of contamination, using both toxicity bioassays and metal distribution. The metal distribution followed a concentration gradient decreasing one order of magnitude from the inner station toward the outer estuary, with amounts in the following order: Fe > Al > Zn > Cr > Pb > Cu. The index of geoaccumulation indicated a metal enrichment in the Ceará river sediment, mainly at inner sites, considered from moderately to strongly contaminated by Al, Cu, Cr and Zn. Sediment samples were considered toxic by means of whole sediment tests with copepods (reproduction) and amphipods (survival), and also elutriate fraction and sediment–water interface with sea urchin embryos (development). Acute and chronic toxicity did not exhibit a significant correlation with metals, emphasizing the influence of other contaminants mainly related to the pollution sources installed in the mid-estuary.

1. Introduction

Sediment quality assessment is considered a natural and logical extension of programs dedicated to evaluating environmental quality. Thus, many studies have been conducted to evaluate the biological effects of sediment contamination in marine and estuarine ecosystems (Anderson et al., 2007; Carr et al., 1996; Losso et al., 2004; Volpi Ghirardini et al., 2005). The most common contaminants in aquatic environments are metals (Astudillo et al., 2005; Gómez-Parra et al., 2000; González-Fernández et al., 2011; Neto et al., 2006; Silva et al., 2003), hydrocarbons (Anderson et al., 2007; Bebianno and Barreira, 2009; Geffard et al., 2003; Vidal et al., 2011), polychlorinated biphenyls (Chau, 2006; Jones, 2011), biocides (Bejarano et al., 2004; Staton et al., 2002) and ammonia and sulfides (Losso et al., 2007; Machado et al., 2004).

The bioavailability of these contaminants and consequently their toxicity may be strongly influenced by factors such as sediment grain size, salinity, pH, and organic matter content, that can change daily due to the natural dynamics of estuaries (Choueri et al., 2009). Toxicity bioassays have been applied worldwide to contribute to the assessment and monitoring of sediment quality and can provide information on how living systems respond to the influence of contaminants (Anderson et al., 2007; Cesar et al., 2007; Losso et al., 2004).

The pursuit of economic development in countries is frequently related to phenomena such as increasing industrialization and migration to urban centers, which, in turn, cause negative impacts due to environmental pollution. This scenario is especially true for the northeastern Brazilian coastal cities, such as Fortaleza. The Ceará River Basin is one of the three major water sources of the Metropolitan Region of Fortaleza, the Ceará State capital. Despite its ecological and economic importance to the region, this river has suffered considerable degradation caused by intensive and continuous industrial and domestic contamination (Aguiar, 2004; Vaisman et al., 2005). A previous ecotoxicological study performed in this estuary by Nilin et al. (2007) demonstrated that surface water samples collected at the inner portion of this estuary were toxic. Their investigation highlighted the significant ecological alterations in this ecosystem and evidenced the necessity for further

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studies. Therefore, this investigation aimed to assess the sediment quality in a tropical estuary under semi-arid conditions and that is influenced by multiple sources of contamination, including industrial effluents, sewage and agricultural runoff.

2. Material and methods

2.1. Study sites

The Ceará River Basin covers approximately 600 km^2 and the river is approximately 60 km long, passing through three cites: Maranguape, Caucaia and Fortaleza (Brandão, 1998). The estuarine portion of the river is a legally protected area because of its scenic and ecological importance and vulnerability to anthropic impacts (Ceará, 1999). However, this basin is under increasing human pressure due to disorderly cities expansions and lawless constructions that contribute to deforestation, soil erosion and siltation, and degrade the river water quality. Agriculture and small boat traffic are less evident sources of pollutants in the river, whereas untreated sewage, urban drainage and especially industrial effluents from electroplating, textiles, plastics, tanneries and others factories constitute the main sources of contamination.

Three sampling surveys were conducted (campaign ***A*** in October/06 during the dry season; campaign ***B*** in January/07 and campaign ***C*** in May/07 both during the rainy season) at the Ceará river estuary, Fortaleza, Brazil (Fig. 1). Sediments were collected from a recently exposed estuarine bank during low tides at four sampling stations selected based on previous studies (Nilin et al., 2007): **S1** −03°43′076S −038°37′185W, located upstream in an approximately median portion of the estuary nearly 5 km from the river mouth; **S2** 03°42′584S −038°37′110W, farther downstream and situated at the confluence with the Maranguapinho River; **S3** −03°42′116S −038°37′138W, located 3 km from the river mouth; and **S4** −03°41′976S −038°35′525W, near the river mouth. As reference sites, sediment samples were collected at the Malcozinhado River estuary, **MC** −04°05′340S −038°11′611W (campaigns ***B*** and ***C***), and at the Pacoti River estuary, **PT** −03°50′057S −038°24′443W (campaign ***C***). These estuaries were chosen as references because no marked pollution sources have been reported in their vicinities. However, there is currently an increasing development of the area, with new constructions as such as houses, hotels and resorts that may also impact the river quality.

2.2. Sampling and sediment processing

The sampling procedure followed the method described by Burton (1992). Sediments from the 3 cm surface layer (approximately 8–10 samples) were taken with a plastic shovel. The samples were homogenized in plastic trays and split into two subsamples stored separately in polypropylene chambers for

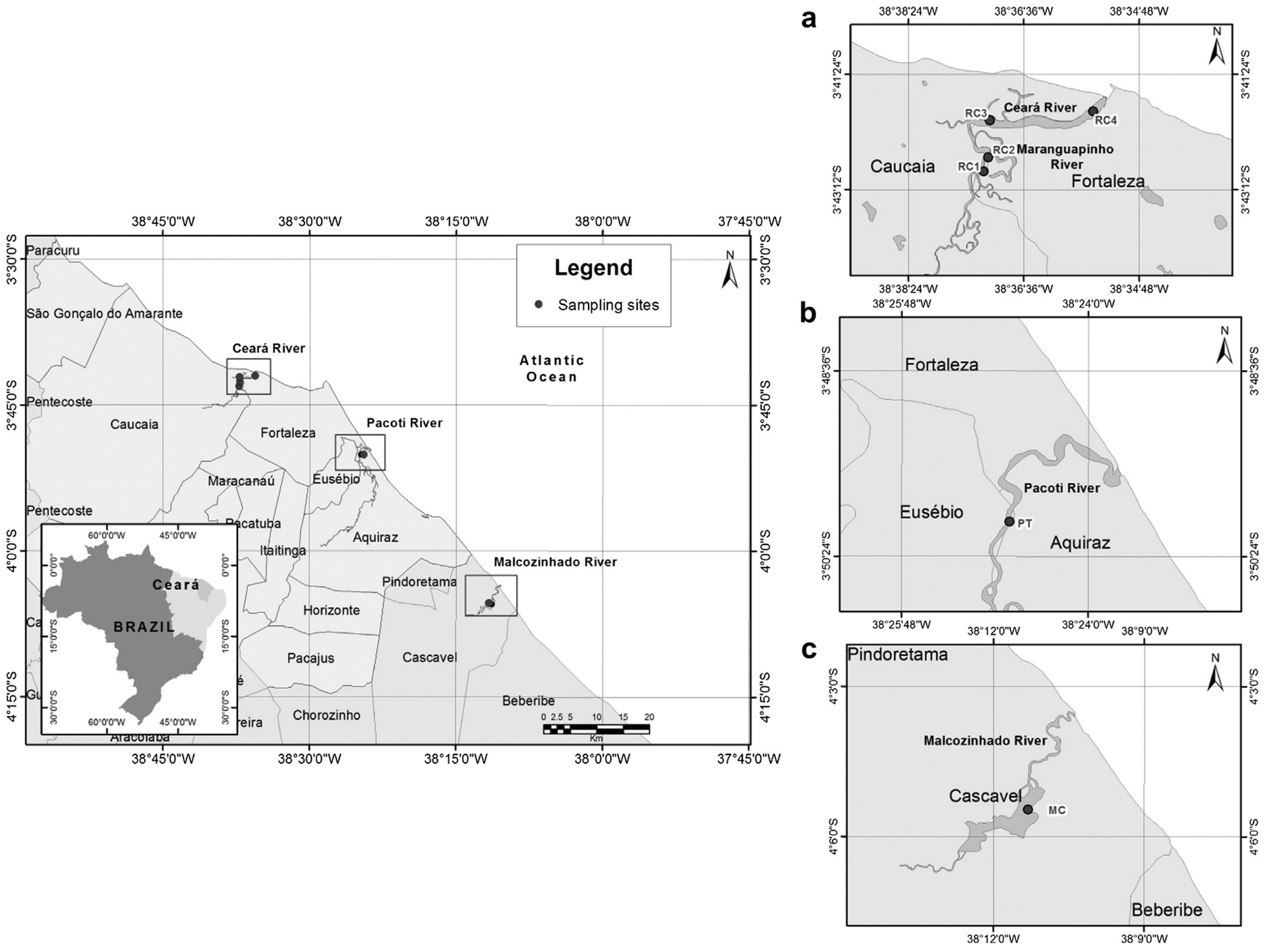

Fig. 1. Map of study area: a. Ceará River, b. Pacoti River and c. Malcozinhado River, Brazil.

sediment characterization and toxicity bioassays. All samples were stored at 4 °C until use. Subsamples used to bioassays were packed in coolers and sent to São Vicente, São Paulo as soon as possible, where were carried out all bioassays.

2.3. Analyses of sediment samples

The samples were dried at 60 °C for 5 days and were subsampled for metal analysis, calcium carbonate ($CaCO_3$) and organic matter (OM) content, and sediment grain size distribution. Approximately 100 g of sediment were wet-sieved to separate silty–clay (<63 μm) and sand fractions (>63 μm). The $CaCO_3$ contents were analyzed by the volumetric method (Bernard calcimeter) by adding 10% (2 mL) chloride acid to the sediment samples (0.5 g). The total organic matter content was obtained by the loss on ignition method (LOI) of two grams of dried sediment at 450 °C for 24 h (Loring and Rantala, 1992).

The concentrations of major (Al and Fe) and trace metals (Cu, Zn, Cr, Pb, Fe, Al) were obtained by the digestion of dried samples (4 g) in aqua regia (50%) for 2 h (Gonçalves, 1993). The extracts from the digestion were analyzed using a flame atomic absorption spectrometer calibrated with respective metal solution standards (AA-6200 Shimadzu). The standard sediment for estuarine sites 1646-A NIST (National Institute of Standards & Technology) was used to validate the procedure analyses.

The detection limit was calculated in terms of metal concentrations from the standard deviations of seven reagent blanks using the equation $DL = 3.14^*s$, where 3.14 corresponds to the t value of the Student table, and s is the standard deviation (APHA, 1995).

The index of geoaccumulation (I_{geo}), is an index defined by Muller (1979) as a criterion to evaluate the intensity of heavy metal pollution, taking into account the enrichment of levels compared to reference values and geochemical background (baseline) and is defined as the following:

$$I_{\mathrm{geo}} = \log 2\left(\mathrm{C}n/1,5^*\mathrm{B}n\right)$$

where Cn refers to the sedimentary concentration for a metal n measured, Bn represents the baseline value or reference site for a metal n, and the 1.5 factor corresponds to possible variations to the baseline due to lithological processes.

Hence, for quality classification, I_{geo} results are applied to a qualitative scale of enrichment intensity (*<0 reference levels; 0–1 uncontaminated; 1–2 unpolluted to moderately contaminated; 2–3 moderately contaminated; 3–4 moderately to strongly contaminated; 4–5 strongly contaminated; >5 very strongly contaminated*) and, according to this scale, samples with I_{geo} above 1 show signs of enrichment/contamination. Due to the lack of studies focusing on the geochemical background of metals in sediments of Ceará estuaries, the average values of metal content obtained by Aguiar et al. (2007) for sediments from Fortaleza coast by partial digestion were used as a reference values.

2.4. Sediment toxicity

2.4.1. Solid-phase bioassays

The toxicity of the sediment samples was tested on amphipods and copepods.

The amphipod *Tiburonella viscana* has a burrowing habit and can be found near intertidal seagrass meadows at many sandy beaches of São Paulo State (Melo and Nipper, 2007). The animals were collected at Engenho D'água beach in Ilhabela, São Paulo, southeastern Brazil (23°48′S; 045°22′W), along with the sediment used for acclimation period and also as control in all experiments. The specimens were transported to the laboratory and acclimatized for 2–3 days. The test protocol followed the procedures described by Melo and Abessa (2002). Twenty-four hours before the beginning of the experiment, each sediment sample was homogenized and transferred to polypropylene vessels (4 replicates/sample) with approximately 200 mL of sediment and 700 mL of filtered seawater (0.45 μm). The following day, ten adults were added to each chamber and then maintained without supplementary feeding under continuous illumination and aeration for 10 days. After the exposure time, the material from each test chamber was sieved (0.5 mm), and the numbers of living amphipods were recorded. Physical–chemical analyses were conducted at the beginning and end of the experiments to ensure the minimum requirements for the test acceptability (D.O. > 3.0 mg L^{-1}; salinity 34–37; pH > 7.0 and temperature 25 ± 2 °C).

The benthic harpacticoid copepod *Nitokra* sp. is habitually collected in the intertidal zone of seagrass meadows. These organisms can be used in sediment and also in water phase (interstitial) toxicity tests. In the present study, the animals were acquired from the culture maintained at the Ecotoxicology Laboratory of the Oceanographic Institute of the University of São Paulo a few days before the beginning of the bioassays. Toxicity tests were performed according to Lotufo and Abessa (2002). The test chambers (4 replicates/sample) were prepared 24 h before exposure with nearly 2 g of homogenized sediment and 5 mL of artificial seawater (salinity 17‰). Ten ovigerous females were added to each test chamber, and the supplementary feeding consisted of 100 μL of yeast solution given at the beginning of the tests. The chambers were incubated without aeration and under a constant temperature (25 ± 2 °C) with a 12/12 h dark/light photoperiod for 10 days. After exposure, 10% formalin and Bengal rose stain were added to each test chamber to preserve and identify the animals. After at least 2 days, the whole content (water and sediment) was sieved through a 45 μm mesh. The adults and offspring (copepodites and nauplii) were then counted to evaluate the reproduction rate expressed as the average number of copepodites and nauplii. To validate the test, animals exposed to control sediments should present a minimal fecundity rate of 10 offspring per female (unpublished data). Physical–chemical analyses were conducted at the beginning with the artificial seawater before the sediment addition to guarantee the minimum requirements to test acceptability (D.O. > 3.0 mg L^{-1}; salinity 17; pH > 7.0 and temperature 25 ± 2 °C).

2.4.2. Sediment–water interface (SWI)

The sediment–water interface has a relevant ecological importance, since large quantities of epibenthic and benthic organisms, including gametes and larvae at various development stages live in that environment. So, SWI analysis complements the data obtained in other matrices, allowing a wider evaluation of sediment quality by incorporating sub-lethal effects with the use of standardized bioassays, such as the sea urchin embryo-larvae test, and also evaluate a scenario more similar to the natural habitat of the exposed organisms (Anderson et al., 2001).

Adult sea urchin individuals, from the species *Lytechinus variegatus*, were obtained at Palmas Island, Guarujá, SP, and the toxicity test followed the method outlined by ABNT (2006), adopting the reduced volumes proposed by Cesar et al. (2004). Two grams of sediment were transferred to glass tubes (15 mL) and complemented with 8 mL of filtered seawater (4 replicate/sample). To prevent direct contact between the embryos and the sediment, a mesh (15 μm) was introduced in each tube and placed on the sediment. The tubes were allowed to stabilize for 24 h before exposure. The same procedure was made with control tubes with only clean seawater.

The procedure for inducing the spawning and fertilization of the sea urchin gametes was the same for all experiments (Nilin et al., 2008). The gametes were obtained by osmotic induction (0.5 M KCl), and then the eggs in solution (100 mL) were fertilized by mixing an aliquot of sperm solution containing activated sperm cells (0.05 mL of sperm in 1 mL seawater). After about two minutes, the control samples were checked for fertilization under an optical microscope.

For the toxicity test approximately 500 eggs were added to each vessel and then incubated for 24 h with constant temperature (25 ± 2 °C) and a 16 h light/8 h dark photoperiod. Afterward, all water content was transferred to other vessels to preserve the larvae (500 μL formaldehyde). Then, one hundred embryos were counted for each replicate, and the percentage of normal embryos was calculated. Normal plutei were detected based on typical larval development, considering the branch symmetry, shape and size of the skeleton (Perina et al., 2011).

2.4.3. *Elutriates*

Tests using elutriates, an important matrix derived from sediment, were initially developed to assess the potential toxic effects of contaminants released from dredged material disposed in the open sea. This method has been recently applied to evaluate the potential effects of bioavailable pollutants in the water column, simulating a natural sediment resuspension phenomenon (Losso et al., 2004, 2007).

Elutriates were prepared on all sediment samples in accordance with U.S. EPA (1998). Sea urchin embryos were obtained as described above. The homogenized sediments were mixed with 1:4 (v:v) filtered seawater and placed in a mechanical shaker for 30 min. Thereafter, the samples were allowed to rest for 24 h at 4 °C. The supernatant was removed carefully, and physical–chemical analyses (D.O., salinity and pH) were performed. The incubation of embryos with elutriates was realized by using sterile polystyrene 24-well tissue culture plates with lids (TPP, Switzerland) according to Nilin et al. (2008). The toxicity of the samples was analyzed in 3 dilutions: 100, 50 and 25% (3 replicates/samples). When the control showed >80% of well-formed pluteus larvae, about 24–28 h after fertilization, 125 μL of formaldehyde was introduced in each cavity to fixate the embryos. Subsequently, 100 embryos were counted from each replicate, and the percentage of normal pluteus larvae was calculated.

2.5. *Data analysis and interpretation*

The mean amphipod survival, mean offspring per female of copepods and normal sea urchin embryo-larval development in SWI and elutriate samples in the three campaigns were compared using one-way ANOVA followed by Dunnett's test at a 5% significance level. To search for possible relationships between sediment properties and chemical and ecotoxicological aspects, a data matrix (clustered from all campaigns) was constructed and a principal component analysis (PCA) was performed using the program PC-ORD 6.0. Before all the analysis, the percentage data were arcsine transformed.

3. Results and discussion

3.1. *Sediment characteristics*

The sediment characterization results are presented in Table 1. In general, an estuarine gradient could be observed for all campaigns in the Ceará river estuary, with organic matter (1.6–24.8%) and fine fractions (0.0–92.3%) decreasing from the inner station toward the outer estuary (S1–S4). In contrast, the $CaCO_3$ contents were higher at the marine influenced zones. Other studies have shown different textural patterns with a predominance of sandy

Table 1
Concentrations of metals (μg g^{-1}), sediment characteristics (percentage of fines fraction, carbonates and organic matter) and toxicity of whole sediment (copepod *Nitokra* sp. reproduction and amphipod *Tiburonella viscana* survival.), sediment–water interface (SWI) and elutriates (Elu) (sea urchin *Lytechinus variegatus* embryo-larvae development) from stations 1, 2, 3 and 4 of the Ceará River estuary and the reference sites (the Malcozinhado-MC and Pacoti-PT river estuaries) in the three campaigns. The metal data are presented as the mean ± standard deviation. NT indicates nontoxic; T indicates toxic; UT indicates uncertain toxicity: n.p. indicates not performed. n.c. indicates not considered because the low quality of data.

Campaign/site	Pb	Cu	Zn	Cr	Al	Fe	Fines fraction	Carbonates	Organic matter	Copepod toxicity	Amphipod toxicity	Sea urchin (SWI/Elu)
Campaign ***A***												
S1	30.59 ± 1.00	35.38 ± 0.55	109.54 ± 2.98	76.06 ± 3.06	22,902.06 ± 923.05	21,736.55 ± 83.88	63.9	2.2	24.8	NT	T	n.p.
S2	11.17 ± 0.53	11.44 ± 0.48	59.41 ± 3.35	18.97 ± 1.41	12,116.20 ± 1492.04	11,814.73 ± 307.93	70.5	1.6	10.4	NT	NT	n.p.
S3	22.36 ± 0.97	11.78 ± 0.09	74.86 ± 3.80	27.33 ± 3.56	11,991.22 ± 228.16	16,215.13 ± 312.62	41.7	18.6	15.4	NT	NT	n.p.
S4	2.70 ± 0.41	0.63 ± 0.04	5.47 ± 0.36	5.12 ± 0.64	753.87 ± 53.57	902.86 ± 12.39	9.2	0.0	1.6	NT	NT	n.p.
Campaign ***B***												
S1	25.75 ± 1.43	31.15 ± 2.02	93.80 ± 1.30	68.34 ± 6.93	14,211.77 ± 626.98	20,184.04 ± 207.61	92.3	5.5	24.1	T	T	(UT/UT)
S2	11.91 ± 1.28	11.93 ± 0.38	68.75 ± 10.71	22.81 ± 1.50	6336.94 ± 263.81	9011.05 ± 510.41	89.1	0.6	10.8	NT	T	(UT/UT)
S3	8,49 ± 2.05	5.34 ± 1.15	36.34 ± 1.62	13.74 ± 4.11	5170.91 ± 150.19	8800.23 ± 199.46	34.8	9.6	8.2	NT	T	(UT/UT)
S4	4.11 ± 0.08	1.91 ± 0.07	7.94 ± 0.11	6.07 ± 0.76	1169.19 ± 155.24	2421.22 ± 153.27	2.7	5.5	2.5	NT	T	(UT/UT)
MC	11.11 ± 0.28	4.63 ± 0.24	118.33 ± 7.00	13.98 ± 0.82	6193,05 ± 195.31	8875.55 ± 77.65	58.2	0.0	5.1	NT	NT	(NT/NT)
Campaign ***C***												
S1	26.43 ± 0.23	5.41 ± 0.04	106.44 ± 1.17	63.54 ± 0.90	17,287.93 ± 1399.55	24,892.49 ± 286.91	90.2	0.6	21.1	n.c.	T	(UT/UT)
S2	22.95 ± 1.06	4.81 ± 0.18	110.10 ± 0.48	28.55 ± 0.39	9846.23 ± 209.60	15,538.87 ± 680.11	63.8	0.0	13.9	n.c.	T	(UT/UT)
S3	15.24 ± 0.76	2.24 ± 0.10	74.81 ± 6.12	25.96 ± 0.00	11,464.88 ± 1422.46	14,737.27 ± 1222.52	56.6	6.0	12.6	n.c.	T	(UT/UT)
S4	3.58 ± 0.03	0.67 ± 0.00	8.16 ± 0.13	9.73 ± 0.14	859.74 ± 124.91	2127.72 ± 3.21	0.0	0.0	2.1	n.c.	T	(UT/UT)
MC	7.00 ± 0.02	1.13 ± 0.00	24.61 ± 2.46	18.00 ± 0.40	4068.37 ± 169.61	7963.64 ± 502.54	24.4	2.2	5.7	n.c.	NT	(UT/UT)
PT	9.33 ± 0.09	1.46 ± 0.04	4.99 ± 0.24	22.43 ± 0.32	6168.19 ± 263.24	13,236.99 ± 126.29	40.4	3.3	9.7	n.c	T	(UT/UT)

fractions in the inner sites, suggesting a surface sediment shift driven by tidal currents, river flows and wind processes (Aguiar, 2004). The organic matter levels found by Aguiar (2004) along the Ceará River estuary were also lower (0.82–3.96%) than those obtained in the present study (1.6–24.8%), showing a significant increase, mainly in the stations near Maranguapinho River (S1 and S2).

The metal distribution followed the gradient described above with values one order of magnitude higher in S1 decreasing toward S4, in the following order: Fe (902.86–24,892.49 μg g^{-1}) > Al (753.87–22,902.06 μg g^{-1}) > Zn (5.47–110.10 μg g^{-1}) > Cr (5.12–76.06 μg g^{-1}) > Pb (2.7–30.59 μg g^{-1}) > Cu (0.63–35.38 μg g^{-1}). Marins et al. (2002) investigated mercury distribution in surface sediments from Ceará river estuary and found a similar gradient distribution with metal decreasing toward the river mouth and, according their analyses, the values found were similar to those from moderately contaminated sites. The metal concentrations obtained in the present study are in agreement or a bit higher than those of Aguiar (2004) and a Technical Report of the Ceará State government (Marins et al., 2005) that found enriched levels of Pb (4.45–10.89 μg g^{-1}), Cu (0.6–20.4 μg g^{-1}), and Zn (1.80–29.85 μg g^{-1}) in the Ceará River estuary. This result shows that although the Ceará estuary is an important natural resource to the region, the sources of the metals have remained active since 2004, and the system has a significant accumulation capacity for these contaminants (Aguiar, 2004; Marins et al., 2005). Additionally, the index of geoaccumulation showed the metal enrichment in Ceará river sediment, mainly at inner sites by Al, Cu, Cr and Zn, and then considered from moderately to strongly contaminated (Table 2). In general, sediments from reference sites (MC and PT) showed lower contamination being classified as uncontaminated to moderately contaminated.

One of the many sources of the metals could be due the shipping traffic in this portion of the river and the presence of a marina, where antifouling paints based on Cu and Zn are most likely used (Huggett et al., 1992). Turner (2010) has demonstrated that antifouling paint can be a source of Cu, Cd, Pb and Zn increases in sediments and emphasizes that release of those metals is generated during boat maintenance and cleaning. Al and Fe are considered particle size proxies because they are conservative elements and a major constituent of clay minerals (Aloupi and Angelidis, 2001; Burton et al., 2005; Rubio et al., 2000), and their gradients in estuaries can be related to continental inputs of matter from urban drainages.

Table 2
Index of geoaccumulation of metals in sediment samples from stations 1, 2, 3 and 4 of the Ceará River estuary and the reference sites (the Malcozinhado-MC and Pacoti-PT river estuaries) in the three campaigns.

Campaign/site	Al	Fe	Cr	Cu	Pb	Zn
*Campaign **A***						
S1	3.4	0.2	3.3	4.8	1.7	4.9
S2	2.5	−0.7	1.3	3.1	0.3	4.0
S3	2.5	−0.2	1.8	3.2	1.3	4.3
S4	−1.5	−4.4	−0.6	−1.0	−1.8	0.5
*Campaign **B***						
S1	2.8	0.1	3.1	4.6	1.8	4.6
S2	1.6	−1.1	1.5	3.2	0.4	4.2
S3	1.3	−1.1	0.8	2.0	−0.8	3.3
S4	−0.8	−3.0	−0.4	0.6	−2.3	1.1
MC	1.6	−1.1	0.8	1.8	−1.0	5.0
*Campaign **C***						
S1	3.0	0.4	3.0	2.1	1.5	4.8
S2	2.2	−0.3	1.8	1.9	1.3	4.9
S3	2.4	−0.3	1.7	0.8	0.7	4.3
S4	−1.3	−3.1	0.3	−0.9	−1.4	1.1
MC	1.0	−1.2	1.2	−0.2	−0.4	2.7
PT	1.6	−0.5	1.5	0.2	0.0	0.4

<0 reference levels; 0–1 uncontaminated; 1–2 unpolluted to moderately contaminated; 2–3 moderately contaminated; 3–4 moderately to strongly contaminated; 4–5 strongly contaminated; >5 very strongly contaminated (Muller, 1979).

3.2. *Sediment toxicity*

The Ceará River sediment toxicity was analyzed by means of whole sediment tests with copepods (reproduction) and amphipods (survival), the elutriate fraction and the sediment–water interface with sea urchin embryos (development).

In general the sediment samples from the Ceará River were toxic to amphipods except for S2, S3 and S4 in the campaign ***A*** (Table 2). It is important to highlight that campaign sampling was performed in October/06, during the dry season (June to December). The pluviometric index for the whole season was about 270 mm, but only 3.2 mm in October (FUNCEME, 2008). Otherwise, campaigns ***B*** and ***C*** were performed during the rainy season, which showed a normal rainfall pattern in 2007 with total of 1056.8 mm (36.5 mm in January/07, campaign ***B***; and 181.6 mm in May/07, campaign ***C***). Rainy events in tropical regions are important to sustain the continuous river flux that can decrease during the dry periods. Also, these events contribute to the surface runoff of pollutants and may resuspend the sediment due to the increased turbulence. The inner stations S1 (campaign ***B***) and S2 (campaigns ***B*** and ***C***) exhibited elevated toxicity with 100% mortality. The analyses of the reference sites showed that while the MC samples were not toxic, PT showed toxicity to amphipods (55.0 ± 5.8% of survival, campaign ***C***).

Regarding the chronic effects on copepod reproduction, the reproduction of organisms exposed to control sediments (Ilhabela) showed a great fluctuation along samplings campaigns with 49.5 ± 4.3 offspring in the campaign ***A*** (5 female exposed), 292.0 ± 11.0 offspring in the campaign ***B*** and 18.0 ± 13.0 offspring in the campaign ***C***, both with 10 females exposed (Table 3). So, the results of Ceará river sediment were compared

Table 3
Amphipods survival (%) and copepods reproduction (offspring) after 10 days of exposure to sediments of four stations at the Ceará river estuary (S1–S4) and the Malcozinhado (MC) and Pacoti (PT) river estuaries as reference sites, in the three campaigns. All results are expressed as the mean values ± standard deviation.

Campaign/site	Copepods reproduction (copepodites and nauplii)	Amphipods survival (%)
*Campaign **A***		
S1	14.3 ± 13.1#	35.0 ± 30.0*
S2	4.3 ± 4.8#	52.5 ± 15.0
S3	26.3 ± 15.2	75.0 ± 19.1
S4	71.0 ± 29.2	85.0 ± 17.3
Ilhabela	49.5 ± 7.7	80.0 ± 8.2
*Campaign **B***		
S1	10.0 ± 5.4*	0*
S2	235.5 ± 60.5	0*
S3	28.5 ± 12.8*	40.0 ± 23*
S4	75.5 ± 28.2*	10.0 ± 11.5*
MC	167.8 ± 32.7	66.6 ± 5.7*
Ilhabela	292.0 ± 11.0	82.5 ± 5.0
*Campaign **C***		
S1	37.3 ± 9.8*	47.5 ± 9.6*
S2	8.3 ± 2.6*	0*
S3	9.0 ± 4.3*	45.0 ± 31.1*
S4	73.8 ± 47.7*	12.5 ± 15.0*
MC	164.0 ± 24.4	87.5 ± 5.0
PT	n.p.	55.0 ± 5.8*
Ilhabela	18.0 ± 13.6	85.0 ± 12.9

#Indicates a significant difference between the station and sediment control from Ilhabela and ($p < 0.05$. ANOVA followed by Dunnett's test).
*Indicates a significant difference between the station and reference sediment from MC ($p < 0.05$. ANOVA followed by Dunnett's test).
n.p. indicates not performed.

Table 4
Effects of samples from stations 1, 2, 3 and 4 of the Ceará river estuary and the reference sites (the Malcozinhado-MC and Pacoti-PT river estuaries) on the development of sea urchin pluteus in the campaigns ***B*** and ***C***. Data are presented as normal larvae mean (%) ± standard deviation (SD) of three replicates. n.p. indicates not performed. *Indicates a significant difference between the station and sediment control from Ilhabela ($p < 0.05$, ANOVA followed by Dunnett's).

Stations	Pluteus normal larvae (mean ± SD)						
	S1	S2	S3	S4	MC	PT	Ilhabela
Sediment–water interface							
*Campaign **B***	0*	0*	0*	0*	93.4 ± 2.1	n.p.	92.2 ± 4.6
*Campaign **C***	0*	0*	0*	0*	79.7 ± 2.6 *	72.8 ± 3.6 *	95.0 ± 2.0
Elutriates							
*Campaign **B***							
100%	0*	0*	0*	0*	95.5 ± 2.4	n.p.	94.5 ± 2.2
50%	0*	0*	0*	0*	96.0 ± 1.4	n.p.	
25%	64.0 ± 18.2*	0*	88.6 ± 5.6	90.0 ± 5.3	96.0 ± 1.7	n.p.	
*Campaign **C***							
100%	0*	0*	0*	0*	27.3 ± 7.6*	83.7 ± 2.9 *	98.0 ± 1.0
50%	0*	0*	14.0 ± 3.6*	13.3 ± 3.5*	91.0 ± 4.0	94.0 ± 2.7	
25%	92.0 ± 3.6	47.3 ± 6.0*	95.3 ± 4.7	90.0 ± 2.7	96.3 ± 1.1	98.3 ± 0.6	

with the reference sediment from Malcozinhado river that showed a quite similar reproduction between campaigns (167.8 ± 32.7 in ***B*** and 164.0 ± 24.4 in ***C***). The female survival during the exposure was affected by sediment toxicity, showing less than 70% survival in the campaign ***A*** (S2 and S3), ***B*** (S1, S3 and S4) and ***C*** (S1, S2 and S3), suggesting an acute toxicity (data not shown). Chronic toxicity was also observed in all campaigns (S1 and S2 in ***A***; S1, S3 and S4 in ***B***; S1, S2, S3 and S4 in ***C***) with reduction in the reproduction (offspring) exceeding 70% to S1 (***A***, ***B*** and ***C***), S2 (***B*** and ***C***) and S3 (***B*** and ***C***), and 50% to S4 (***B*** and ***C***) when compared with MC results. It is important to emphasize that despite of acute toxicity observed, the chronic results were capable of discriminating the sites.

In general, the sediments from S1 were the most toxic to both amphipods and copepods, and presented also the higher levels of metals, which may have contributed, at least partially, to the toxicity. Abessa et al. (2006) suggested that for sediments from tropical environments, toxicity may occur even when metals levels are below "threshold effect level" (TEL). Buruaem et al. (2012), using geochemistry criteria, showed that for toxic sediments from Mucuripe Harbor (Ceará State), moderate concentrations of metals could cause environmental impact. However, the observed toxicity in Ceará river sediments indicates that it is possible that the toxic effects were also caused by other contaminants or stressors than the measured metals. According to official data (SEMACE, 2005), there is an agriculture area nearby Ceará River (S1, see Fig. 1), which could be responsible for an input of pesticides into the estuary. Davanso et al. (submitted to this issue) showed a cholinesterase inhibition in gills of the crab, *Goniopsis cruentata*, collected near the S1, what could be due to the influence of such pesticides. Nevertheless, there is no published work that has discussed the types and quantities of pesticides in this area.

Therefore, all these data emphasize the importance of toxicity tests for the protection of delicate environments such as the tropical ones and protected areas, since they could detect effects, which were not detected through the geochemical, analyzes.

The results of the SWI and elutriate toxicity tests are shown in Table 4. For both treatments, sea urchin embryo-larval development was strongly affected after exposure to the samples (Table 4), with 100% abnormal larvae in all samples. The adverse effects observed in the SWI treatments included cell destruction, delayed development and the absence of zygote development. In the SWI tests, the MC sediment samples showed a pluteus larvae development of 93.4 ± 2.1% and 79.7 ± 2.6% in the campaigns ***B*** and ***C***, respectively, while PT had 72.8 ± 3.6% normal pluteus larvae in the campaign ***C***. The elutriates were toxic in all campaigns, with no larvae development at 100% and 50% dilutions for the S1 and S2 sediments. At 25% dilution, the effects were significant for S1 in the campaign ***B*** and S2 in both the campaigns ***B*** and ***C*** (Table 4). The samples from stations 3 and 4 exhibited more than 85% of developed larvae (25% dilution) in all campaigns and 14.0 ± 3.6% (S3) and 13.3 ± 3.5% (S4) in the 50% dilution. The reference sites generally showed over 80% of normal pluteus development, except for MC (100%) in the campaign ***B***, which presented only approximately 27% normal larvae (Table 4).

The release of metals from sediment to water phase can be driven by physical and biological forces and in estuaries, processes as waves, tides, currents, bioturbation, dredging and ship traffic, could entrain large amounts of matter into the water column (Burgess and Kester, 2002). Particularly in the case of the Ceará estuary, these processes also contribute to contamination alerts because the estuary sediments show a retention behavior throughout the monitored years.

Moreover, Losso et al. (2007) emphasized that volatile compounds (sulfides and ammonia) can interfere with toxicity bioassays on the early life stages of sea urchins, which was demonstrated by Prósperi (2002) with *L. variegatus* embryos. Such compounds may originate from anthropogenic or natural sources, especially in transitional environments such as mangroves, where the organic enrichment and redox conditions in depositional zones (reducing or oxidizing) favor their production (Mopper and Kieber, 2002; Siqueira et al., 2006). Nor sulfides or ammonia were measured in matrixes used for toxicity tests; and consequently it

Table 5
Eigenvectors and correlation coefficient from principal component analysis (PCA) based on environmental variables and sediment toxicity from all sampling sites in campaign ***A***, ***B*** and ***C***. Marked (bold) results are >0.65.

Correlation coefficient			
Variables	Axis 1	Axis 2	Axis 3
Mud	**−0.83**	0.15	0.32
$CaCO_3$	−0.18	**−0.84**	−0.36
OM	**−0.98**	−0.14	−0.05
Al	**−0.95**	−0.15	−0.15
Fe	**−0.94**	−0.18	0.16
Pb	**−0.96**	−0.08	0.06
Cu	**−0.76**	0.007	−0.41
Zn	**−0.83**	0.06	0.26
Cr	**−0.91**	0.002	0.10
Acute	0.32	−0.52	**0.66**
Chronic	0.14	**−0.82**	−0.02
Eigenvalues	6.59	1.77	0.96
% of variance	59.94	16.04	8.78
Total variance	59.94	75.99	84.77

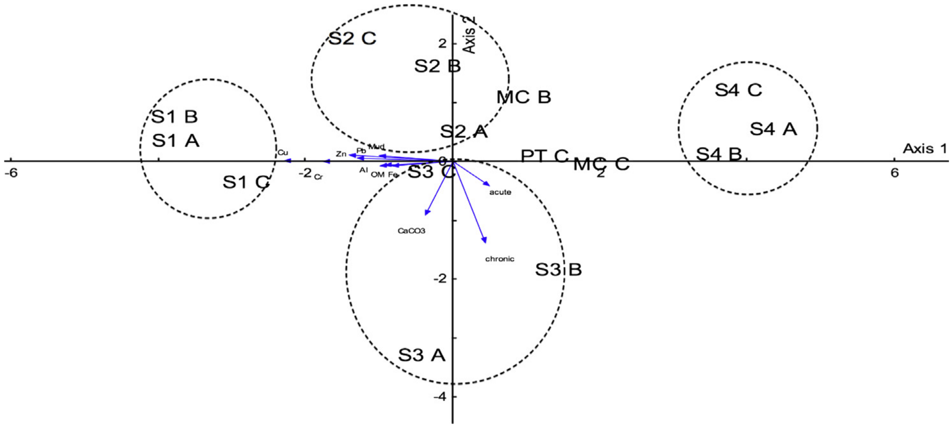

Fig. 2. Ordination results of the principal component analysis (PCA) based on environmental variables and sediment toxicity from stations 1, 2, 3 and 4 of the Ceará river estuary and the reference sites (the Malcozinhado-MC and Pacoti-PT river estuaries). Acute results refer to the amphipod test (*Tiburonella viscana*) and chronic results refer to the copepod test (*Nitokra* sp.).

was not possible to determine whether the observed effects were due to sulfides and ammonia or to other contaminants. Therefore, due to uncertainty, the integration of data gave greater importance to the whole sediment test results.

It must be considered that the observed toxicity in the present study may be associated with pollutants not measured in this investigation. Vaisman et al. (2005) found high Hg concentrations (154 ± 60 ng g^{-1}) in tissues of the mangrove oyster *Crassostrea rhizophorae* at sampling stations similar to those described in this study, when compared with three other estuaries in Ceará State (Cocó, Pacoti and Jaguaribe rivers). Also, in the same area of the Ceará River, Cavalcante et al. (2009) found moderate to high concentrations of polycyclic aromatic hydrocarbons (PAHs) ranging from 3.34 to 1859.21 mg kg^{1}. The synergistic effects produced by metals and organic pollutants have been well documented (Doney, 2010) and can't be excluded from the observed toxic impact in the present study.

3.3. Integrated analyses and temporal trends

The results of the PCA analysis are presented in Table 5. The three first axes together explained 84.77% of the overall variance for all campaigns. The first axis clearly represents an association between metals with the deposition of fine sediments through positive correlations with mud, organic matter and metals. These data indicate a gradient trend for the stations 1 and 4 (inversely) of the Ceará river estuary, as seen in the PCA (Fig. 2), where stations are ordinated along the first axis. This trend is related to higher levels of metals and toxicity at stations located in the river inner portion, whereas the levels of contamination and toxicity were lower toward the river mouth (Fig. 2). Acute and chronic toxicity did not exhibit a significant correlation with metals that emphasize the influence of other contaminants.

The metal contents for the reference estuarine samples (Malcozinhado and Pacoti) were similar to those found in S3 and S4. The Brazilian tropical estuaries, specifically in the semi-arid region, exhibit a particular hydrogeochemical behavior. Due to the long dry season in the second semester, the rivers are perennial only in the estuarine portion, but are intermittent upstream. Thus, contaminants tend to be retained within the upper estuary during the dry season, and exportation to the sea occurs only during rainy periods (Marins et al., 2002; Lacerda et al., 2007). In this study, however, the concentration of metals did not exhibit relevant temporal variations, and similar levels were observed for dry and rainy periods.

Possible explanations for such unexpected results include the characteristics of industrial effluents, which are expected to be continuous let out, suggesting that in the Ceará River estuary, the metal sources are continuously increasing. The contaminants tend to be retained within the upper estuary with metal concentrations decreasing toward the S3 and S4, with associated lower toxicity at this outer portion of the estuary, corroborating the results of Marins et al. (2002) and Lacerda et al. (2007). Moreover, present data suggest that the metals, although present at increasing concentrations, could not be considered the main cause of toxicity at the low estuarine portion of the Ceará River; and reinforce the presence of contaminants discharged upstream threatening local biota.

4. Conclusion

Sediments from the Ceará River estuary are considered toxic in spite of the species used (copepods, amphipods and sea urchin), the fraction analyzed (whole sediment, sediment–water interface and elutriate) or end-point (reproduction, development or survival). The metal distribution indicated that contaminants are predominantly retained in the estuary and that the contamination fingerprint shows an increase in metal contents during the last decade. Although the toxicity gradient is similar, with higher toxicity in the inner portion of estuary, toxicity could not be attributed to the metal concentration. These findings strongly suggest the contribution of other contaminants mainly related to the pollution sources installed in the mid-estuary in the observed biological effects.

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