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Using an integrated approach to assess the sediment quality of an estuary from the semi-arid coast of Brazil

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ABSTRACT

The Jundiaí–Potengi Estuary (JPE) on the semi-arid coast of Brazil is influenced by multiple sources of pollution. Sediment quality at 10 JPE sites was evaluated through an integrated approach. Rainy and dry seasons were considered. Collected sediments were analyzed for texture, metal, nitrogen, phosphorus concentrations, and toxicity to invertebrates. Geochemical and ecotoxicological data were integrated using qualitative approaches and multivariate techniques. We observed decreased sediment quality in both seasons, particularly in the mid-estuary. In the dry season, the contamination–toxicity relationship was clearer, as hydrological conditions favor contaminant retention within the estuary. Rainy season conditions were found to be worse, since stormwater drainage from agricultural and urban areas carries the contamination into the estuary. Because of the contamination sources and dissolved and particle-bound metal transport, contamination and toxicity did not correlate as clearly in the rainy season. The results suggest that unmeasured contaminants are contributing to JPE sediment degradation.

1. Introduction

The majority of world's population inhabits coastal areas. As a consequence, the natural environments of these areas have been continuously altered and replaced with industrial facilities, ports, aquaculture ponds, agricultural fields, and urban expansion (Diegues, 2001; Chen et al., 2004; Marshall et al., 2010; Souza and Silva, 2011). Rapid population growth, the disordered occupation of coastal areas, and an economic model based on the consumption of natural resources have all caused the deterioration of these areas. The discharge of chemicals into the environment is one of the main threats to coastal and marine ecosystems. These pollutants include nutrients, pesticides, metals, detergents, oil, plastics, pharmaceuticals and personal care products, among others (Petrovic et al., 2003; Marins et al., 2004).

Despite the advances in environmental legislation to regulate emissions and reduce pollution, and in spite of the frequent insistence among scientists for the need to protect coastal zones, the release of contaminants into the sea and coastal water bodies continues, and many people and governments still believe that the world's coastal water bodies are capable of diluting contaminants to safe levels for both humans and biota (Zagatto and Bertoletti, 2008). This scenario has become a very problematic situation, especially in developing countries, where the establishment of new economic activities is often combined with ineffectiveness and inefficiency of their respective residue treatment systems and thus represents an emerging challenge to sustainable development (Choueri et al., 2009a; Torres et al., 2009).

Within the coastal zone, estuaries have been widely recognized as some of the most important and productive environments on the planet, as they provide different ecosystem products and services (Costanza et al., 1997; Savage et al., 2012). However, estuaries receive both the natural influences of continental terrains and that of human activity. Although estuarine degradation is a matter of global concern, the evaluation of the impacts on these environmental has not been an easy task (Chapman and Wang, 2001; Zonta et al., 1994, 2007; Elliott and Quintino, 2007), largely because estuaries may be susceptible to chemicals of different natures, and also because of estuaries high environmental instability.

Chemicals introduced into estuarine environments are influenced by a set of physical, chemical, and biological processes that may affect their fate and behavior (Chapman et al., 1999). Metals represent substances

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of special interest because they cannot be destroyed and may persist in the environment (Tam and Wong, 2000; Nicolau et al., 2006; Yang et al., 2014). After settling in sediments and waters, metals can be incorporated by the biota and easily spread along the food chain; during this process, these contaminants may have toxic effects on a wide range of organisms.

Most contaminants that are released into estuaries accumulate in the sediments (Bartoli et al., 2012); thus, sediments become not only a repository but also a source of contaminants for the water column and the biota (Adams et al., 1992; Nipper, 1997; Delvalls et al., 2004; Burton and Johnston, 2010). The retention of contaminants in the sediments, their bioavailability, and their potential toxicity are all strongly influenced by environmental factors, such as grain size distribution, salinity, pH, redox potential, and levels of organic matter. In addition, these environmental factors are influenced by winds, tides, freshwater input, bioturbation, and other aspects that characterize natural estuarine dynamics (Chapman and Wang, 2001; Pekey, 2006; Idris, 2008).

Because sediments tend to integrate environmental variations over time, they can be used as an appropriate environmental compartment in environmental assessments. Many studies on sediment quality have been conducted and have provided information on the effects of sediment contaminants on aquatic organisms and ecosystems (Araújo et al., 2009; Cesar et al., 2009; Ré et al., 2009; Langston et al., 2010; Du et al., 2012; Gonçalves et al., 2013; Roig et al., 2015). In Brazil, investigations into sediment quality have been concentrated in some industrial and port zones of the southern and southeastern regions (Carvalho et al., 2002; Machado et al., 2002; Abessa et al., 2005; Pusceddu et al., 2007; Torres et al., 2009; Choueri et al., 2009a; Buruaem et al., 2013a; Fonseca et al., 2013; Rodrigues et al., 2013; Zalmon et al., 2013). On the other hand, studies conducted on the northeastern region of the country are still scarce (Buruaem et al., 2013b; Nilin et al., 2013; Krull et al., 2014), despite the ecological importance of this region to the biodiversity of the South Atlantic. The semi-arid coast is located in the northeastern region of Brazil, between the states of Piauí (PI) and Rio Grande do Norte (RN). It includes the Jundiaí–Potengi Estuary (JPE), which is the largest and most important in RN state. In spite of its socioeconomic and ecological importance, this estuary has been exposed to a variety of anthropic pressures, which include the discharge of untreated industrial and domestic effluents (Souza and Silva, 2011), runoff from agricultural areas, and discharges from shrimp farm effluents. Little is known about the sediment quality of this estuary (Buruaem et al., 2013b). The objective of this investigation was to consider both the dry and rainy seasons in order to assess the sediment quality of an estuary from the semi-arid coast of northeastern Brazil (JPE), which is influenced by multiple sources of contamination. To achieve this objective, different lines of evidence (LOEs), including geochemical and ecotoxicological analyses, were employed.

2. Materials and methods

2.1. Study area

The JPE is located on the eastern sector of the RN coast in northeastern Brazil, between the 5°53′S and 5°43′S latitudes and 35°21′W and 35°09′W longitudes (Fig. 1) (Souza and Silva, 2011). The estuary presents a maximum depth of 15 m and typical marine influence, in which the tidal fluxes range from 5000 to 20,000 $m^3 \cdot s^{-1}$ (Silva et al., 2001; Boski et al., 2015). Freshwater input comes from the Potengi, Jundiaí and Doce Rivers; the Potengi River is the main contributor to the estuary, draining a basin with 3180 km^2 and flow of 5 $m^3 \cdot s^{-1}$ during the rainy period. The Jundiaí River has an intermediate flow but is more heavily influenced by tides. The Doce River presents the smallest freshwater contribution; its mean flow remains at about $2m^3 \cdot s^{-1}$ for most of the year (Silva et al., 2006).

The climate in the region is characterized as tropical and semi-arid, with a dry season (September to February) that has a mean rainfall rate of 220 mm, and with a rainy period (March to August) during which the mean rainfall rate is 1390 mm. The annual mean precipitation rates range from 1300 to 2000 mm (Silva et al., 2007; Boski et al., 2015).

The JPE is approximately 30 km long, and its basin includes the cities of Macaíba, São Gonçalo do Amarante, and Natal, which have a combined population of more than 1.4 million people (IBGE, 2014). Approximately 60% of the raw sewage from Natal is discharged directly into the JPE; in addition, the estuary receives effluents from several industrial sources, such as textile factories, food and beverage producers, pulp mills, and leather and tannery manufacturers (Silva et al., 2006; SEPLAN, 2013). The estuary also receives effluents from shrimp farms and from the dumping sites where residues from urban septic tanks are stored and treated (IDEMA, 2008).

2.2. Sediment sampling

Two sampling surveys were conducted from which 10 sampling sites distributed along the JPE were considered (Fig. 1). The first survey occurred in May 2013 (the rainy season); the accumulated rainfall in that month was 399.1 mm. The second survey was performed in December 2013 (the dry season). The rate of precipitation for that month was 9.8 mm, and the accumulated precipitation for 2013 was 1846.7 mm, according to EMPARN (2013). Sediments from the Galinhos Estuary (150 km northwest of the JPE) were collected to be used as reference sediments; this estuary is not impacted.

The sediment collection followed the recommendations described by Burton (1992). Composite sediment samples were collected from each site (with at least 3 subsamples) through the use of a stainless steel Van Veen grab sampler. From the material retained in the sampler, only the first 5 cm of the surface layer was separated. The sediments were transferred to plastic trays, thoroughly homogenized, and split into aliquots. The aliquots to be used for toxicity tests were conditioned in polyethylene flasks and stored at 4 °C in the dark until the assays were performed. The aliquots for the metal, organic carbon, and grain size distribution analyses were kept in polyethylene flasks and stored at −20 °C.

2.3. Geochemical analyses

The sediment samples were dried at 45 °C for 5 days, and aliquots were then separated for the following analyses: grain size distribution, organic matter (OM) contents, concentrations of total nitrogen (N) and phosphorus (P) and metal concentrations (Fe, Mn, Cd, Cr, Cu, Pb, Ni, and Zn). 100 g sediments were used to assess grain size distribution, in which quantities of mud (<0.063 mm) and sand (>0.063 mm) were determined (ABNT, 1988). OM levels were measured using the volumetric method described by EMBRAPA (1998), which is an adaptation of the Walkley-Black (1965) method. Concentrations of N and P were measured using the colorimetric method (Grasshoff et al., 1999).

For the chemical analysis, 5 g of the fine fractions (<0.063 mm) from the sediments were dried and digested using a mixture of HCl 0.05 M and H_2SO_4 0.0125 M (EMBRAPA, 1998). The extracts were analyzed via atomic absorption spectrophotometry (model: Varian Spectr-AAS-220-FS). The spectrophotometer was calibrated based on the reading the absorbance of six standards prepared for each element. The analytical precisions were established by analyzing a certified sediment (NIST 1646-A); the recoveries ranged from 80.7 to 114% (see supplementary material), values which are considered acceptable, and their uncertainties were below the acceptable limits (between 7% and 18%). Metal concentrations in the JPE sediments were compared to those obtained at the reference site, and a risk quotient (RQ) was established based on the ratios between these concentrations (Roig et al., 2015). This quotient aims to evaluate both the pollution load and the potential risk to the biota as a result of the contribution of the eight elements measured, by defining four risk categories: low risk ($RQ < 1$), moderate

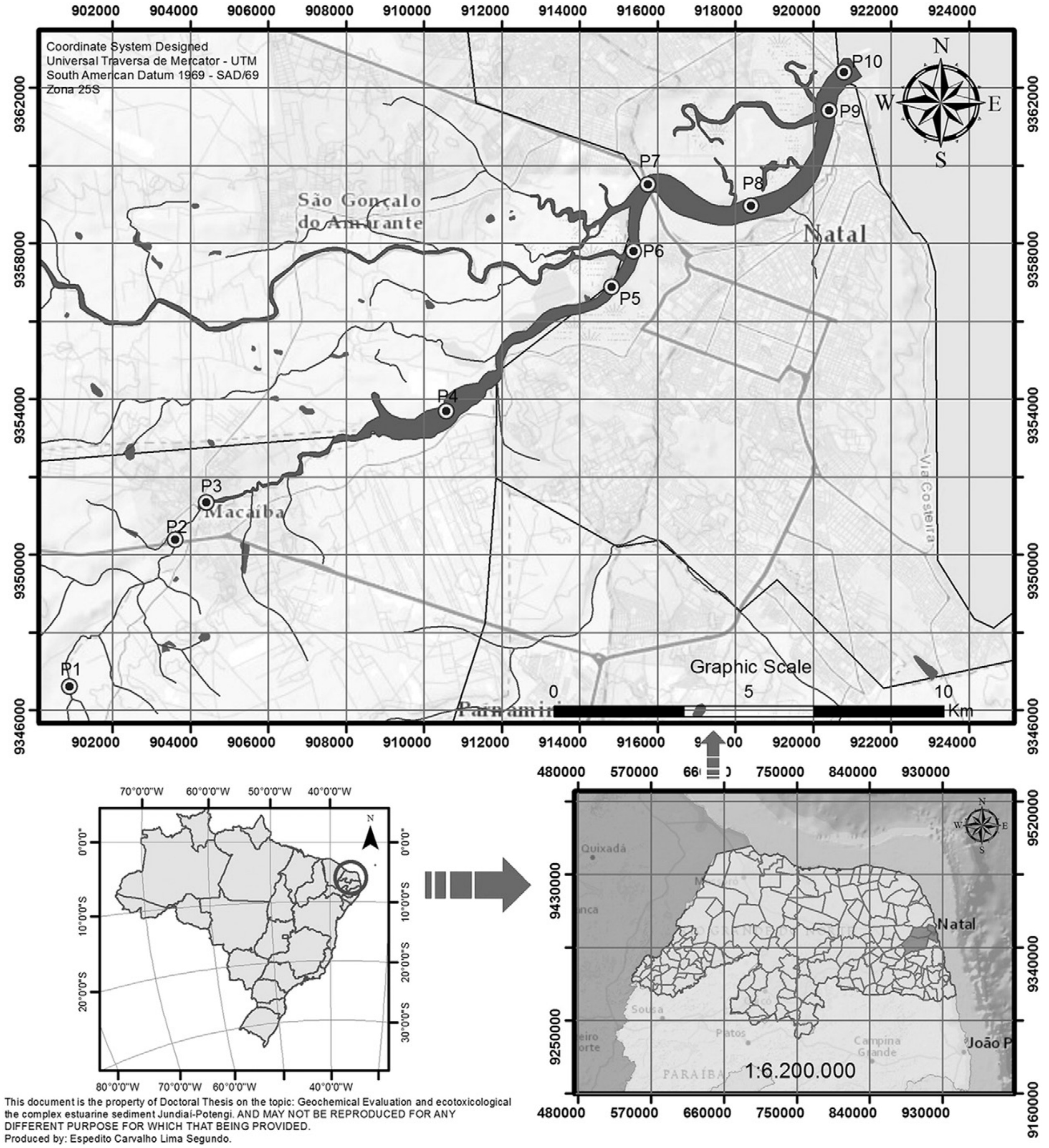


Fig. 1. Map of the study area and position of the sampling sites.

risk ($1 \leq RQ < 3$), considerable risk ($3 \leq RQ < 6$), and very high risk ($RQ \geq 6$) (Loska et al., 1997; Islam et al., 2015).

Due to the considerable anthropic interferences in the study area, the evaluation of sediment contamination was made using the percentage enrichment factor (%EF) defined by Zonta et al. (1994) and further used by Loska and Wiechuła (2003). The percentage enrichment factors (EFs) were calculated according to the following equation:

$$EF\,(\%) = [(C - Cmin)/(Cmax - Cmin)] \times 100 \qquad (1)$$

where C indicates the mean concentration of the concerned element, Cmin and Cmax indicate the respective minimum and maximum concentrations determined during the period of investigation. To evaluate the metal load at each site, the EFs of all of the elements were added together, as suggested by Adamo et al. (2005).

2.4. Sediment toxicity

Sediments were tested for acute toxicity (AT) and chronic toxicity (CT), in which organism exposure to whole-sediment (WS) and sediment–water interface (SWI) was considered. For all toxicity tests, physical and chemical parameters — which included pH, salinity, dissolved oxygen (DO), and temperature — were determined at the beginning and end of each experiment. The original tables containing this information can be seen in the supplementary material.

2.4.1. Whole-sediment acute toxicity

The whole-sediment acute toxicity tests were conducted using the amphipods *Leptocheirus plumulosus* and *Tiburonella viscana* and following the protocols described by ABNT (2008) and Melo and Abessa (2002), respectively. *T. viscana* specimens were collected from the Engenho D'água Beach (Ilhabela, São Paulo, Brazil) and were then acclimated to laboratory conditions over 3 days. Sediment from this beach was collected to be used as internal control. *L. plumulosus* specimens were obtained from a culture maintained in laboratory.

The tests consisted of exposing the amphipods (20 juvenile *L. plumulosus* specimens and 10 adult *T. viscana* specimens per replicate) to the sediments for a 10–day period. Test chambers consisted of polyethylene flasks containing approximately 200 ml of homogenized sediment and filtered sweater (salinities of 20‰ for *L. plumulosus* and 34‰ for *T. viscana*). The system was kept under constant lighting and aeration and at a temperature of 25 ± 2 °C. At the end of the test, the contents of each test chamber were sieved, and the surviving organisms were counted. Missing organisms were considered dead. Three replicates were used for each sample.

2.4.2. Whole-sediment chronic toxicity

The copepod *Nitocra* sp. was used as the test organism for the whole-sediment chronic toxicity tests, based on the protocol developed by Lotufo and Abessa (2002). The copepods were obtained from a culture kept in the laboratory. Four replicates were set up for each sample, and 15 ml of high density polyethylene test chambers filled with 2 ml of sediment and 8 ml of filtered sea water (salinity 17‰) were used. Ten healthy ovigerous females were introduced into each replicate. The entire test system was incubated at 25 ± 2 °C with a 12 h:12 h (light:dark) photoperiod for 10 days. Next, the content of each replicate was fixed with formaldehyde (10%) and Rose-Bengal dye (0.1%). Finally, the adult females and their offspring (nauplii and copepodits) were counted using a stereomicroscope.

2.4.3. Chronic toxicity of the sediment–water interface

The sediment–water interface chronic toxicity test was conducted following the method described by Anderson et al. (2001) and adapted by Cesar et al. (2004) for small volumes. This treatment assesses the effects of contamination that arises from sediment and which may affect organisms in the adjacent water column. In this procedure, the test system was set up in test tubes containing sediment and water 1:4 (v:v).The samples were then tested for toxicity by analyzing the embryo-larval development of the sea urchin *Lytechinus variegatus* according to ABNT NBR protocol No. 15350 (ABNT, 2012). Sea urchin spawning was induced and subsequent in vitro fertilization was implemented. The test was conducted by introducing approximately 400 embryos in each of the four replicates, as well as in a negative control (filtered seawater). After the test (24 h), embryos were analyzed microscopically for morphological abnormalities and delayed development.

2.5. Interpretation and integration of the ecotoxicological data

The results of all toxicity data were checked for normal distribution using the Chi-Square test. Variance homogeneity was assessed using Fisher's exact test. Student's t-test was then used to compare each sample to its respective control. Sediments were considered significantly toxic when the value for the respective endpoint (mortality, fecundity, embryo development) was lower than the value observed in the control (e.g. when $p \leq 0.05$). The analyses were run using the STATISTICA 7 software tool.

The results of all of the tests were then combined, and the qualitative conclusions of each test were considered. The criteria for classifying the sediments based on their toxicities are shown in Table 1. For the amphipod tests, non-toxic sediments were considered good, and the significantly toxic sediments were classified as poor (<50% difference from the control) or very poor (≥50% in common with the control). A similar criterion was used in the copepod test. Meanwhile, for the sea-urchin embryo test, there were four classes (good: not toxic; moderate: development inhibition rates ranging from 30 to 49%; poor: development inhibition rates between 50% and 74%; very poor: development inhibition equal or greater than 75%). Finally, to determine the sediment quality at each site based on the combination of toxicity tests, the results regarding acute and chronic toxicity were combined in order to produce five possible sediment quality classes (Fig. 2). Because acute toxicity generally indicates severe responses, our approach was conservative and gave more weight to the results of acute toxicity.

2.6. Integration of geochemical and ecotoxicological data

Geochemical and toxicity data were integrated using cluster analyses (CAs), with the Euclidean distance and the Ward's method, and also using factor analysis with data extracted with the principal component analysis (FA–PCA). The data matrix used for these analyses was comprised of the results on OM, muds, Nitrogen, Phosphorus, and metals (Fe, Mn, Cd, Cr, Cu, Pb, Ni, Zn) concentrations, amphipod mortality, reduction in copepod fecundity, and the abnormal development rate of sea-urchin embryos. In the FA–PCA, we used 0.4 as the cut-off value (Comrey and Lee, 1992), which is equal to or higher that the criteria used by Choueri et al. (2009a, 2009b, 2010) and Rodrigues et al. (2013). The selection of the number of principal components was based on the Scree plot method, and the analysis considered the normalized Varimax rotation. Prior to both the CAs and the FA–PCA, the data was auto-scaled in order to reduce the magnitude differences between variables.

2.7. Quality assurance/quality control (QA/QC)

The QA/QC procedures included the use of replicates and repeatability tests in the analyses of total N and P, as well as the use of analytical blanks and standard reagents. In the case of metals, the calibration curve was adjusted using linear regression, and the curves obtained for each element showed the relationships between the absorbances and the concentrations of the known solutions. Method validation included the analysis of a standard sediment (NIST 1646-A). The analytical precisions were within the acceptable limits for uncertainty and ranged from 7% to 18%. In the ecotoxicological tests, the experimental variables (pH, DO, temperature, salinity, and luminosity) were monitored. Tests with reference substances were run for each species or

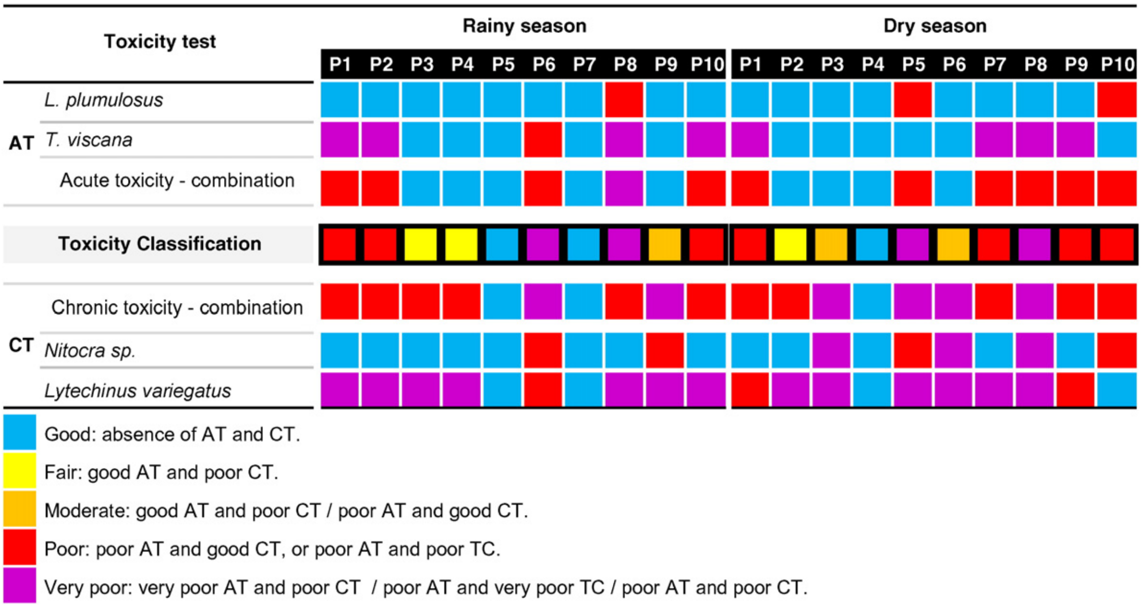
Table 1
Criterion for classifying the sediment quality in the Jundiaí–Potengi Estuary based on the toxicity to marine/estuarine invertebrates.

Test type	Endpoint	Species	Sediment classification for toxicity			
			Good	Moderate	Poor	Very poor
Acute	% mortality	*L. plumulosus* *T. viscana*	NT	–	<50%[a]	≥50%
Chronic	fecundity ((nauplii + copepodits)/female)	*Nitocra* sp.	NT	–	<50%[b]	≥50%
	% abnormal development	*L. variegatus*	NT	30–49%	50–74%	>75%

NT: not significantly toxic in relation to the controls.

[a] Mortality below 50%, but significantly different from the reference sediment.

[b] Significantly toxic (in comparison with the controls) but the difference from the control group is less than 50%.



	Toxicity test	Rainy season										Dry season									
		P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10
AT	*L. plumulosus*	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟥	🟦	🟦	🟦	🟦	🟦	🟦	🟥	🟦	🟦	🟦	🟦	🟥
	T. viscana	🟪	🟪	🟦	🟦	🟦	🟥	🟦	🟪	🟦	🟪	🟪	🟦	🟦	🟦	🟦	🟦	🟪	🟪	🟪	🟦
	Acute toxicity - combination	🟥	🟥	🟦	🟦	🟦	🟥	🟦	🟪	🟦	🟥	🟥	🟦	🟦	🟦	🟥	🟦	🟥	🟥	🟥	🟥
	Toxicity Classification	🟥	🟥	🟨	🟨	🟦	🟪	🟦	🟪	🟧	🟥	🟥	🟨	🟧	🟦	🟪	🟧	🟥	🟪	🟥	🟥
CT	Chronic toxicity - combination	🟥	🟥	🟥	🟥	🟦	🟪	🟦	🟥	🟪	🟥	🟥	🟥	🟪	🟦	🟪	🟪	🟥	🟪	🟥	🟥
	Nitocra sp.	🟦	🟦	🟦	🟦	🟦	🟥	🟦	🟦	🟥	🟦	🟦	🟦	🟪	🟦	🟥	🟪	🟦	🟪	🟦	🟥
	Lytechinus variegatus	🟪	🟪	🟪	🟪	🟦	🟥	🟦	🟪	🟪	🟪	🟥	🟪	🟪	🟦	🟪	🟪	🟪	🟪	🟥	🟦

🟦 Good: absence of AT and CT.
🟨 Fair: good AT and poor CT.
🟧 Moderate: good AT and poor CT / poor AT and good CT.
🟥 Poor: poor AT and good CT, or poor AT and poor TC.
🟪 Very poor: very poor AT and poor CT / poor AT and very poor TC / poor AT and poor CT.

Fig. 2. Classification of sediment samples from the Jundiaí-Potengi Estuary in the rainy and dry seasons based on the combination of the conclusions obtained for each individual toxicity test (amphipod mortalities, inhibition of copepod reproduction, and reduction in normal sea urchin embryo development).

survey in order to evaluate the sensitivity of the test organisms. Tests were used to determine *L. plumulosus* and *T. viscana* sensitivities to zinc sulfate and potassium dichromate, respectively. The LC50-48 h for *T. viscana* was estimated to be 8.2 mg·L^{-1} (6.25–9.37 mg·L^{-1} $K_2Cr_2O_7$), while the LC50-96 h for *L. plumulosus* was estimated to be 0.89 mg·L^{-1} (0.67–17 mg·L^{-1}). Both values were within the acceptable ranges defined by the respective control charts. *Nitocra* sp. sensitivity to $K_2Cr_2O_7$ was determined as well, and the LC50-96 h was estimated to be 26.92 mg·L^{-1} (16.25–33.33 mg·L^{-1}, which is within the acceptable range. Finally, *L. variegatus* sensitivity to zinc sulfate was estimated, and EC50-24 h values ranged from 0.20 to 0.43 mg·L^{-1}, values which were within the range established in the control chart.

3. Results and discussion

3.1. Sediment properties

The results of the geochemical characterization of the sediment samples are summarized in Table 2. The sediment textures along the estuary were heterogeneous overall, particularly in the second survey (dry season). Fine sediments were predominant in the mid-estuary (P4–P7) and in the lower estuary (P8–P10). This high percentage of mud is an indication of the low hydrodynamic energy in these portions of the JPE, as is the presence of a dense mangrove forest, which increases fine particle retention. In addition, the narrow mouth of the JPE may contribute to the siltation process within the estuary.

The quantities of OM in the sediments ranged from 0.05 to 12.67%. The highest values were observed during the dry season, possibly finding which may be due to the lower turbulence and higher deposition rate during this period. In both sampling campaigns, the highest levels of OM occurred in the mid-estuary (P4–P7). However, all along the JPE, OM levels were within the range expected for tropical estuaries from northeastern Brazil (0.76–38.9%) (Freire et al., 2004; Lacerda and Marins, 2005; Marques et al., 2008; Nascimento et al., 2010). The distribution of OM in the sediments presented a pattern similar to that exhibited by the fine sediments, a finding which reinforces the possibility that the lower and mid-estuarine zones are depositional areas. Moreover, in these portions of the JPE, both human activity and natural sources may be contributing to the increase in OM levels. OM input to the JPE is influenced by the seasonal population increase resulting from tourism, especially during the dry season. In addition, effluents and residues from the shrimp farms are continuously released into the JPE. There are 61 shrimp farms in the vicinity of the JPE basin; they cover approximately 1440 ha (Medeiros, 2009), and are most frequent along the banks of the mid- and lower-estuary.

3.2. Nutrients (total nitrogen and phosphorus)

Phosphorus concentrations were highest in the internal portion of the estuary, and they decreased progressively as the sites became closer to the mouth of the JPE. The P2 and P6 sites presented the highest concentrations in both seasons. In general, the concentrations were higher during the rainy season. When nitrogen levels were assessed, there was no clear pattern for the element's distribution in the sediments in either season, but the concentrations tended to be higher during the rainy season. In the dry season, sediments from the mid-estuary (P4 and P6) and from the lower estuary (P8–P10) presented the highest concentrations, particularly those from P8 (2580 mg·kg^{-1}). P8 is close to the mouth of the Baldo Channel, which carries a large amount of untreated sewage and other domestic residues into the JPE (Silva et al., 2001).

The relatively high levels of nitrogen and phosphorus in the sediments from P2 and P7, particularly in the first campaign, may be a result of leakage from agricultural areas or urban drainage during rainstorms. According to Singh et al. (1997) and Walker et al. (1999), urban drainage contributes to pollution loads in estuaries that cross urban areas. Nitrogen and phosphorus are important nutrients for organisms, but they can be introduced into coastal environments through sewage and urban effluents (Mackenzie and Chou, 1993), and high values can cause eutrophication. Tavares et al. (2014) observed the phenomenon of eutrophication in the JPE, which was dependent on tidal conditions and rainfall precipitation levels. Shrimp farms also represent important sources of nitrogen and phosphorus for the JPE; large amounts of fertilizer and shrimp food are employed to accelerate shrimp growth (Lacerda et al., 2006a; Silva et al., 2010; Marins et al., 2011). Thus, we can infer that there are multiple sources of N and P contributing to the JPE.

Table 2
Geochemical variables (percentage of organic matter, mud, nitrogen, phosphorus and metals) of the sediment samples collected in the Jundiaí–Potengi Estuary and in the reference site (Galinhos Estuary) during the rainy and dry seasons.

Sampling Sites	Geochemical analyses											
	N	P	Mn	Cr	Cu	Cd	Ni	Pb	Zn	Fe	OM	Mud
	$(\mathrm{mg \cdot kg^{-1}})$									(%)		
Rainy season												
P1	340	17	21.74	<0.01	0.90	0.02	0.86	1.29	2.47	0.569	0.59	12.7
P2	1340	175	9.26	<0.01	7.46	0.15	3.58	6.51	30.17	0.598	3.15	23.6
P3	1120	85	9.65	<0.01	3.81	0.12	2.31	3.05	6.30	0.443	4.43	32.2
P4	280	136	23.39	0.27	3.08	0.19	2.21	3.30	11.36	0.611	5.53	36.7
P5	1680	113	15.00	0.74	2.42	0.25	2.82	2.87	10.41	0.392	6.22	39.5
P6	900	117	52.62	0.37	2.72	0.22	1.83	2.44	8.68	0.494	4.57	34.7
P7	1230	29	22.57	0.51	1.82	0.37	2.18	3.12	13.23	0.281	5.04	34.6
P8	950	2	8.16	0.64	6.63	0.26	1.29	4.74	26.22	0.471	3.12	17.9
P9	1060	1	22.96	<0.01	0.41	0.36	1.22	2.24	1.82	0.011	4.55	31.7
P10	780	1	18.36	<0.01	0.40	0.33	0.98	2.17	1.27	0.005	1.78	39.8
GAL	220	2	11.23	<0.01	0.48	0.25	1.11	1.24	1.45	0.007	3.72	30.4
Dry season												
P1	340	9	78.50	<0.01	1.63	<0.01	1.76	1.05	2.53	0.579	0.35	17.6
P2	220	17	21.11	<0.01	0.29	<0.01	0.38	0.25	2.13	0.437	0.05	3.5
P3	170	47	10.35	0.26	17.90	0.08	1.56	1.85	4.96	0.253	2.18	18.9
P4	1960	141	98.60	0.93	2.46	0.38	4.14	3.92	14.46	0.655	11.38	67.8
P5	170	94	46.62	0.94	0.64	0.47	3.10	2.70	10.61	0.336	12.67	61.0
P6	1570	34	34.03	0.70	1.64	0.29	1.92	2.18	8.84	0.456	8.58	45.6
P7	390	1	21.32	0.39	0.40	0.35	1.24	1.96	3.67	0.054	4.04	40.5
P8	2580	1	29.33	0.53	0.65	0.49	1.51	2.45	2.21	0.005	6.39	69.9
P9	1010	2	15.48	0.42	0.42	0.36	1.06	2.02	1.61	0.010	4.98	58.4
P10	1120	1	20.90	0.41	0.43	0.35	1.07	1.79	1.25	0.005	3.04	46.3
GAL	140	2	12.55	0.42	0.46	0.25	1.11	1.06	1.19	0.008	3.46	31.1

GAL: Reference site — Galinhos Estuary northeastern Brazil.

Previous studies (Souza and Silva, 2011) showed that the region between the cities of Natal and São Gonçalo do Amarante (close to P8, P9 and P10) corresponds to a portion of the estuary that has been increasingly degraded over the last few decades. According to theses authors, the main causes of degradation include urban expansion, the release of raw sewage, and the replacement of mangrove forests with shrimp farms and with anaerobic ponds from sewage effluent plants; these sources explain the high levels of nitrogen that were found in the lower JPE in the current study.

3.3. Metals

Most of the metal concentrations found in the sediments were higher in the rainy season, with the exception of Mn, Cd, and Cr (see Table 2). During the rainy season, the higher concentrations tended to occur in sediments from P2–P8 (sites which represent almost the entire length of the estuary). Meanwhile, in the dry season, the highest levels of metals were observed in the sediments from P4–P6. The difference in levels between dry and rainy seasons suggests an influence of the drainage from urban and agricultural areas on the distribution of metals along the JPE. Rainstorms in tropical areas are considered important for sustaining river flows and contribute to contaminant runoff from the surrounding areas (Nilin et al., 2013). Ambrozevicius and Abessa (2008) observed that storm water runoff and urban drainage have contributed to the degradation of water quality in some urban channels located in the Santos Bay (southeast Brazil).

However, the long dry season on the semi-arid coast causes the rivers to be perennial only in their estuarine portions, since the freshwater input drops to minimum levels. Thus, the reduced river flow is not strong enough to reach the sea and remains blocked within the estuarine zone by the marine waters (Lacerda et al., 2012), thus increasing the water's residence time in this region. Under these conditions, contaminants tend to be retained within the estuary during the dry season, and only a small fraction is carried to the sea as dissolved metals. This phenomenon can explain the higher concentrations of metals in the intermediate portions of the JPE, especially in the sediments collected between P4 and P6 (Table 4). On the other hand, the exportation of contaminants toward the sea tends to occur predominantly during the rainy season, when the flow becomes strong enough to break the resistance imposed by marine waters (Lacerda et al., 2007, 2012). This explains, at least partially, the larger number of sampling sites affected by metal contamination. For this reason, it can be inferred that the presence of multiple contamination sources along the entire JPE do not support the idea of metal retention in the sediments from the sites located upstream.

Many studies have reported that the physical and chemical properties of surface waters also can regulate metal precipitation or solubilization and thus influence the mechanisms involved in the temporal geochemical variability of coastal sediments (Cooper and Morse, 1998; Warnken et al., 2001). Lau (2000) concluded that salinity and temperature variations influenced the dynamics of metals through the sediment–water interface in a subtropical estuary, thus increasing metal availability to the biota. There is a consensus that other factors, such as the redox potential and pH, may influence metal precipitation and mobilization in coastal sediments, since they alter the stability of some compounds involved in the contaminant retention process in sediments (Chapman and Wang, 2001), as is the case of sulfides (Otero and Macias, 2002). However, these factors cannot be considered the only factors responsible for the changing behavior of metal concentrations in sediments. Human activity must also be considered, since multiple point and diffuse sources are present along the JPE, and their contributions of metals vary over time, as observed by Guedes (2012). Marins et al. (2004) found a similar situation in other estuaries from northeastern Brazil.

Metal concentrations in sediments from the JPE were lower than global geological reference levels (Turekian and Wedepohl, 1961) and were also lower than those adopted by the Brazilian government as standards for sediment dredging and disposal (CONAMA, 2012); these results are consistent with those obtained by Dantas (2009). The concentrations were comparable to levels found in other estuaries of Brazil and lower than those observed around the world (Table 3). Possible reasons for relatively lower levels of nutrients and metals in JPE in comparison to other sites worldwide may include the fact that our study the metals were extracted by weak acid digestion; and the regional concentrations of these elements are low, as suggested by the results for the reference site and by previous studies in JPE (Sindern et al., 2007; Buruaem et al., 2013b). International sediment quality guidelines must be used with caution, since they may not represent the best basis for comparison (Marins et al., 2004). Abessa et al. (2008) observed that more than 75% of the sediments from the Santos Estuarine System that exhibited concentrations above the Canadian threshold effect levels (TELs) were toxic to marine invertebrates, and these authors stated that the sediment quality guidelines (SQGs) for tropical regions may need to be lower than those of temperate zones. Choueri et al. (2009b) and Buruaem et al. (2012) showed that site-specific SQGs could be much more reliable for predicting toxicity than those adopted by the Brazilian legislation. Thus, we adopted risk quotients (Loska et al., 1997; Islam et al., 2015) and enrichment factors (Zonta et al., 1994) to evaluate the geochemical conditions of the JPE.

Risk quotient (RQ) and enrichment factor (EF) values are shown in Table 4. Total EF values ranged from 16.9 to 67.2% during the rainy season and were between 10.6 and 97.1% during the dry season. The most enriched sediments (%EF > 50) during the rainy season were P2 > P8 > P5 > P6, while in the dry season, the most enriched samples were those from P4 > P5 > P6. The RQ values indicated that the sediments from sites P2–P8 were of considerable or very high risk during the rainy season, and that those from P4–P6 were of considerable risk (RQ ≥ 3) during the dry season. Results obtained for %EF and RQ were in agreement and presented similar metal accumulation patterns. The enrichment of metals in the sediments was clearly demonstrated, a result which indicates the influence of human activity, particularly in the mid-estuary, where sediments were found to be of considerable or very high risk. The mid-estuary also coincides with the regions where deposition and accumulation of organic matter, fine particles, and nutrients would be expected due to the hydrological regime.

Many sources of pollution are established along the JPE, particularly near the mid-estuary. These include 26 factories representing different sectors (textile, food and beverages, pulp, and leather and tannery), and most of them discharge their effluents along the intermediate estuarine zone (IDEMA, 2008; Souza and Silva, 2011). The contribution of effluents from the textile factories is the most relevant source of pollution. Alencar et al. (2005) and Vandevivere et al. (1998) reported that their composition includes organic compounds (such as detergents), carbonates, sulfates and chlorides, and also metals (Zn, Ni, Cr, Cd, Pb, and Fe), among other substances. These effluents may be associated with enrichment of metals in the JPE sediments, particularly in the region between P4 and P6.

Metal contamination may be linked to the surrounding shrimp farms as well. This activity occurs close to the mid-estuary and the low estuary (Silva et al., 2007; Souza and Silva, 2011), and it is associated with a series of contaminants, including copper-based fungicides and algaecides (Boyd and Massaut, 1999), as well as with shrimp feed, which presents high levels of Cu, Zn, and Mn (Lacerda et al., 2006b; Cunha, 2010).

Therefore, the enrichment of metals in sediments from the JPE may be a result of a combination of human activity and natural factors.

3.4. Sediment toxicity

Sediment toxicity tests have been widely used as a line of evidence (LOE) to evaluate the quality of sediments and the bioavailability of chemicals (Cesar et al., 2009). The combined use of different toxicity tests has been recommended by Abessa et al. (2008) in order to provide more reliable information on sediment quality. For this reason, we used 4 different species and considered both acute and chronic toxicities. As shown in Table 5, sediments from P1, P2, P6, P8, and P10 presented chronic and acute toxicities for at least one of the tested organisms. The sediments from P3, P4 and P9 were chronically toxic. In the dry season, sediments from P2, P3, and P6 presented only chronic toxicity. In both campaigns, there was not any sediment that showed only acute toxicity — as expected, more samples presented chronic toxicity than acute toxicity. This fact highlights that more weight should be placed upon acute toxicities when sediment quality is assessed.

The combination of the results from the chronic and acute toxicity tests showed that sediments from P6 and P8 (during the rainy season) and from P5 and P8 (during the dry season) were toxic to the point of negatively affecting amphipod survival, copepod reproduction, and the development of sea urchin embryos (Fig. 2). On the other hand, sediments from P5 and P7 (during the rainy season) and from P4 (during the dry season) were not toxic. These results showed that toxicities of sediments from the mid-estuary change over time, despite the higher levels of metals and nutrients in this portion of the JPE.

Sediments from the lower and upper portions of the JPE were toxic in both seasons. These findings corroborate the study conducted by Buruaem et al. (2013b), in which chronic toxicity was found along the length of the estuary, while acute effects were associated only with sediments from the inner portion of the estuary. Previous studies found metal bioaccumulation in bivalves, barnacles and crabs collected along the JPE (Silva et al., 2001, 2006; Lopes, 2012), and foraminiferal assemblages from the estuary exhibited signs of environmental stress.

Table 3
Concentrations of metals (mg·kg^{-1}) in sediments from different estuarine zones of the world (iron concentrations are expressed in %).

Region	Fe	Mn	Cr	Cu	Cd	Ni	Pb	Zn
Jundiaí–Potengi Estuary (Brazil)[1a]	0.005–0.61	8.1–52.2	<0.01–0.74	0.4–7.4	0.02–0.37	0.8–3.5	1.2–6.5	1.2–30.1
Jundiaí–Potengi Estuary (Brazil)[1b]	0.005–0.65	10.3–98.6	<0.01–0.94	0.29–2.4	<0.01–0.49	0.3–4.14	0.2–3.9	1.1–14.4
Potengi River (Brazil)[2]	0.47–0.6	–	7.2–20.8	1.6–3.7	<0.01–0.013	3.8–11.8	1.67–4.67	6.7–12
Guaratuba Bay (Brazil)[3]	–	–	–	0.58–8.49	0.07–0.40	–	1.38–2.51	0.39–2.14
Paranaguá Estuarine System (Brazil)[4]	–	–	14,5–58	<0.04–16.2	<0.01	6.6–21.9	<0.3–29.7	26.9–80
Parnaíba River Delta (Brazil)[5]	0.3–2.5	145–1356	1.5–38	1.5–48	–	–	1.5–28	2.6–31
Tapacurá River (Brazil)[6]	0.7	53.8	1.7	12.5	0.3	1.1	0.2	18.9
Port of Rotterdam (Netherlands)[7]	–	–	–	<5–40	0.5–1.8	<5–20	<10–60	15–190
Port of Cádiz (Spain)[8]	–	–	0.1–14.9	7–202	0.92–1.3	0.06–21.3	2.3–86.9	21.27–378
Daya Bay (China)[9]	–	–	–	20.8	0.05	31.2	45.7	113
River Ganges (India)[10]	–	–	1.8–6.4	0.98–4.4	0.14–1.4	–	4.3–8.4	–
Toxicity reference value[11]	–	–	26	16	0.6	16	31	–
World average[12]	4.7	850	90	45	–	–	20	95

References: [1a] this study (rainy season), [1b] this study (dry season), [2] Sindern et al. (2007), [3] Rodrigues et al. (2013), [4] Choueri et al. (2009b), [5] Paula Filho et al. (2015), [6] Aprile and Bouvy (2008), [7] Van Den Hurk et al. (1997), [8] Casado-Martínez et al. (2009), [9] Gao and Chen (2012), [10] Gupta et al. (2009), [11] USEPA (1999), [12] Turekian and Wedepohl (1961).

Table 4
Enrichment factors for metals (%EF) and risk quotients of toxicity (RQ) obtained for the sediments collected from the Jundiaí–Potengi Estuary in the rainy and dry seasons.

Seasons	Enrichment Factor (%EF)								EF-total	Risk Quotient (RQ)								RQ-total	Classification
	Fe	Mn	Cr	Cu	Cd	Ni	Pb	Zn		Fe	Mn	Cr	Cu	Cd	Ni	Pb	Zn		RQ
Rainy season																			
P1	93	31	0	7	0	0	0	4	16.9	8.1	1.0	0	1.9	0.1	0.8	1.0	1.7	1.9	Moderate
P2	98	3	0	100	37	100	100	100	67.2	8.5	0.8	0	15.5	0.6	3.2	5.3	20.8	6.8	Very high
P3	72	3	0	48	29	53	34	17	32.1	6.3	0.9	0	7.9	0.5	2.1	2.5	4.3	3.1	Considerable
P4	100	34	36	38	49	50	39	35	47.5	8.7	2.1	0.3	6.4	0.8	2.0	2.7	7.8	3.8	Considerable
P5	64	15	100	29	66	72	30	32	50.9	5.6	1.3	0.7	5.0	1.0	2.5	2.3	7.2	3.2	Considerable
P6	81	100	50	33	57	36	22	26	50.5	7.1	4.7	0.4	5.7	0.9	1.6	2.0	6.0	3.5	Considerable
P7	46	32	69	20	100	49	35	41	49.0	4.0	2.0	0.5	3.8	1.5	2.0	2.5	9.1	3.2	Considerable
P8	77	0	86	88	69	16	66	86	61.1	6.7	0.7	0.6	13.8	1.0	1.2	3.8	18.1	5.8	Considerable
P9	1	33	0	0	97	13	18	2	20.6	0.2	2.0	0	0.9	1.4	1.1	1.8	1.3	1.1	Moderate
P10	0	23	0	0	89	4	17	0	16.6	0.1	1.6	0	0.8	1.3	0.9	1.8	0.9	0.9	Low
Dry season																			
P1	88	77	0	62	2	37	22	10	37.2	7.2	6.3	0	3.5	0	1.6	1.0	2.1	2.7	Moderate
P2	66	12	0	0	0	0	0	7	10.6	5.5	1.7	0	0.6	0	0.3	0.2	1.8	1.3	Moderate
P3	38	0	28	63	16	31	44	28	31.0	3.2	0.8	0.6	3.6	0.3	1.4	1.7	4.2	2.0	Moderate
P4	100	100	99	100	78	100	100	100	97.1	8.2	7.9	2.2	5.3	1.5	3.7	1.7	12.2	5.6	Considerable
P5	51	43	100	16	96	72	67	71	64.5	4.2	3.9	2.2	1.4	1.9	2.8	2.5	8.9	3.5	Considerable
P6	69	27	74	62	59	41	53	57	55.4	5.7	2.7	1.7	3.6	1.2	1.7	2.1	7.4	3.3	Considerable
P7	8	12	41	5	71	23	47	18	28.2	0.7	1.7	0.9	0.9	1.4	1.1	1.8	3.1	1.5	Moderate
P8	0	21	56	17	100	30	60	7	36.5	0.1	2.3	1.3	1.4	2.0	1.4	2.3	1.9	1.6	Moderate
P9	1	6	45	6	73	18	48	3	25.0	0.1	1.2	1.0	0.9	1.4	1.0	1.9	1.4	1.1	Moderate
P10	0	12	44	7	71	18	42	0	24.2	0.1	1.7	1.0	0.9	1.4	1.0	1.7	1.1	1.1	Moderate

3.5. Integration of geochemical and ecotoxicological data

The cluster analyses showed 4 groups for the rainy season and 3 groups for the dry season (Fig. 3). In the rainy season, CA separated P1 from the resting sites, probably due to the low levels of metals and nutrients found. Sites P9 and P10 formed a second group that presented intermediate quantities of OM, a high percentage of muds, high nitrogen content, low phosphorus levels, and low metal concentrations (except in the case of Cd). The third group included P2 and P8, with intermediate quantities of OM and muds, high nitrogen levels, high metal concentrations, and poor quality according to the toxicity tests. The fourth group included sites P3, P4, P5, P6, and P7 (mid-estuary) the sediment of which presented high metal concentrations and OM levels, moderate to high quantities of nitrogen and phosphorus, and variable toxicities. This CA suggests that other contaminants (not analyzed herein) may be contributing to the sediment toxicities, especially in the lower and upper portions of the JPE.

In the dry season, the first group included P4, P5 and P6, with high levels of metals, nutrients, and OM, as well as variable toxicities. The second group included P7 and P10, where the sediments presented low phosphorus concentrations, moderate concentrations of OM, Cr, Cd and Pb, high amounts of muds, high total nitrogen content, and high toxicity. The third cluster included sites P1, P2 and P3, where metals, nutrients and OM were low but where the toxicities were moderate to high. As well as in the rainy season, non-measured contaminants may be contributing to the toxicity levels.

As sewage is discharged into the JPE, some pollutants would be expected to occur, as pharmaceuticals and personal care products (PPCPs), detergents, chloramines and other chemicals (Bound and Voulvoulis, 2005; Wise et al., 2011). A previous study found high concentrations of HPAs in sediments collected along the JPE (Queiroz, 2011), and since this group of substances is widely known as toxic and carcinogenic, they may have contributed to the observed toxicity. In addition, we measured the concentrations of ionized ammonia in the sediments and the concentrations reached levels capable of inducing negative biological effects; however three of test-organisms used in this study are relatively insensitive to ammonia. Campos et al. (2016) showed that in estuarine sediments rich in ammonia, inputs of low amounts of metals may induce sediment toxicity. Therefore, many chemicals may be present in JPE sediments, interacting with metals and contributing to the observed toxicity. Further studies should be conducted with the purpose of identify and quantify such substances.

The results of the FA–PCA for both campaigns are shown in Figs. 4 and 5. For the results of the rainy season, the first three factors explained 74.82% of the variances. Each axis explained a relatively low percentage of variances (Table 6), which is expected in heterogeneous

Table 5
Results of the tests on sediments from the Jundiaí–Potengi Estuary and the experimental control (C) during the rainy and dry seasons. The values shown are the means.

Rainy season			C	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10
AT	% mortality	*L. plumulosus*	3.3	0	5	3.3	13.3	16.7	1.7	11.7	30	1.7	1.7
		T. viscana	10	73.3	83.3	30	33.3	33.3	46.7	40	76.7	36.7	56.7
CT	fecundity ((nauplii + copepodits)/female)	*Nitocra* sp.	33.1	46.8	35.4	29.7	27.9	34.7	19.3	25.1	24.2	17.1	20.6
	% abnormal development	*L. variegatus*	15	95.2	100	100	91.5	33.2	54.7	26.2	100	79.2	83.7
Dry season													
AT	% mortality	*L. plumulosus*	1.7	5	3.3	1.7	16.7	21.7	20	15	13.3	10	45
		T. viscana	16.7	96.7	46.7	60	55	40	53.3	73.3	73.3	83.3	40
CT	fecundity ((nauplii + copepodits)/female)	*Nitocra* sp.	43.7	35.6	37.5	17	33.4	22.7	18.6	34.7	20.7	36.5	22.1
	% abnormal development	*L. variegatus*	19.2	64.2	94.7	92.5	36.7	92	81	88.7	100	74.7	41.7

AT: acute toxicity.
CT: chronic toxicity.
C: control.

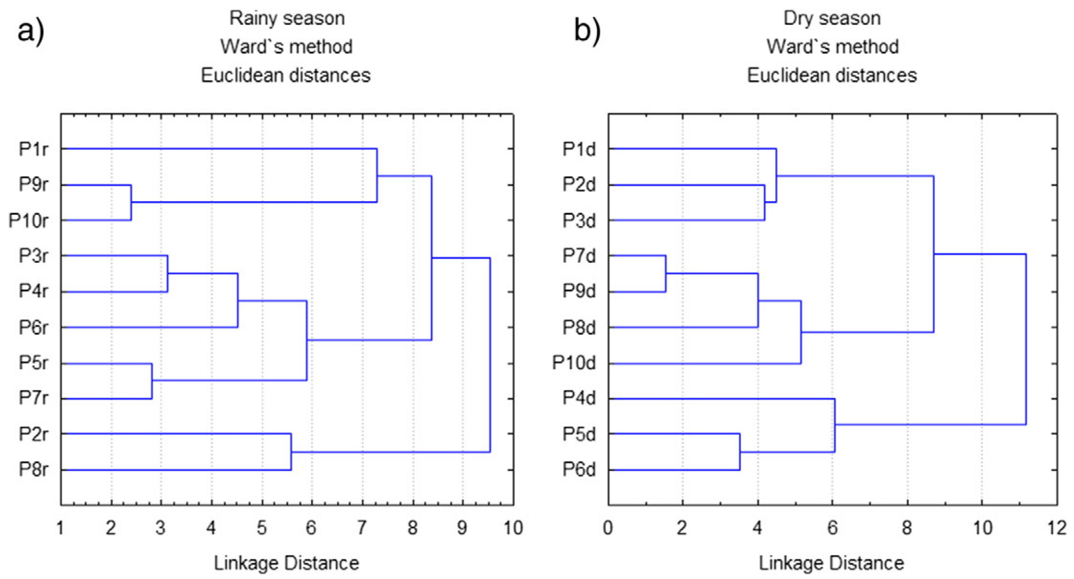


Fig. 3. Results of the cluster analysis with geochemistry and toxicity data of sediments from 10 collection sites along the Jundiaí–Potengi Estuary (a) = rainy season; (b) = dry season.

environments where interactions between variables are intense and complex. The first factor (F1) explained 34.19% of the variances and showed associations between nitrogen, Cr, Cu, Pb, Zn, and amphipod mortality (Table 6); sites P2 and P8 made the highest contribution to this factor (Fig. 5). Mn correlated negatively with F1, a finding which suggests that the positive correlations mentioned above indicate an anthropic component, since Mn naturally occurs in high concentrations and is not typically associated with human activity (Niencheski et al., 1994). These findings are consistent with the EF results, which showed enrichment of metals in sediments from P2 and P8 (Table 4). The second factor explained 26.38% of the variances and showed positive correlations with nitrogen, Cr, Cd, Ni, OM, and muds (Table 6). Negative correlations with this factor were obtained in the case of *T. viscana* mortality and abnormal sea urchin embryo development. Site P1 was the most important to F2 (Fig. 5). This result corroborates those from the CA and suggests that, during the rainy season, P1 is not directly influenced by the deposition of OM and muds or, consequently, by the elements associated with suspended particles, such as nitrogen, Cr, Cd, and Ni; under these conditions, toxicity may have been caused by unmeasured contaminants (Table 6 and Fig. 2). The third factor (F3) explained only 14.3% of the variances and showed an association between Fe, Cu, Ni, Pb, and phosphorus. This finding may indicate a common source for these elements, such as sewage or urban drainage. Copepod fecundity was found to be negatively correlated with this factor, a result which indicates that the elements above may be linked to chronic toxicity; on the other hand, the negative correlation observed in the case of Cd may be a mathematical artifact, since the concentrations of this element were low.

When the dry season was considered, the first three factors explained 78.95% of the variances (Fig. 5). The first factor explained 46.33% of the variances and showed positive correlation for Fe, Mn, Cr, Cu, Ni, Pb, Zn, phosphorus, and OM (Table 6). Abnormal *L. variegatus* development was found to be negatively correlated with F1; thus, these results suggest that the main causes of toxicity for this species were

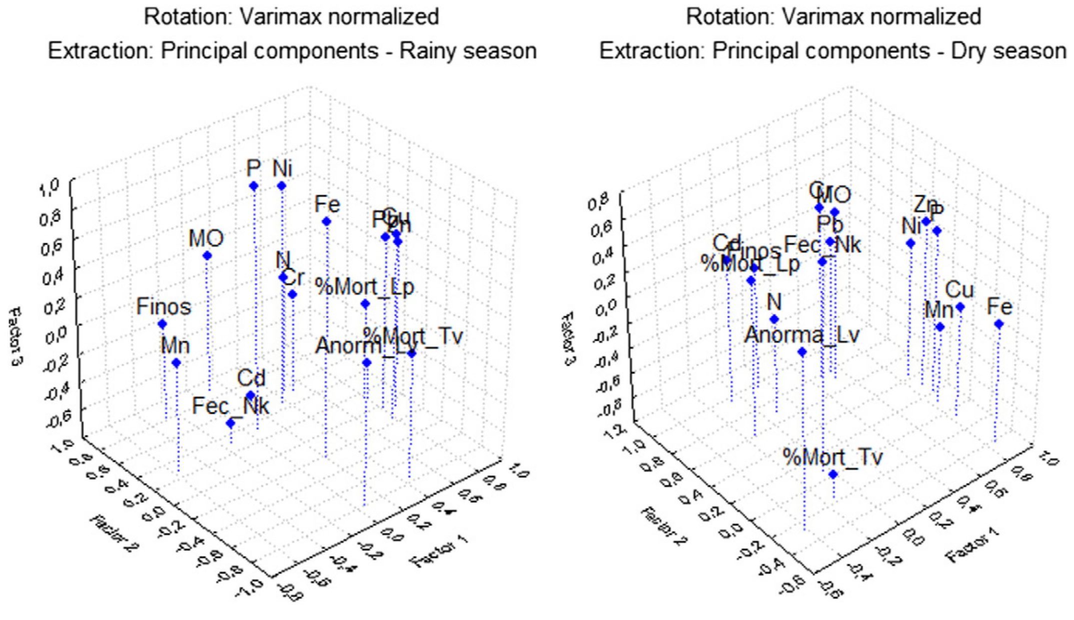


Fig. 4. Three-dimensional projection of geochemical and ecotoxicological variables from the Jundiaí–Potengi Estuary for the rainy and dry seasons after the factor analyses.

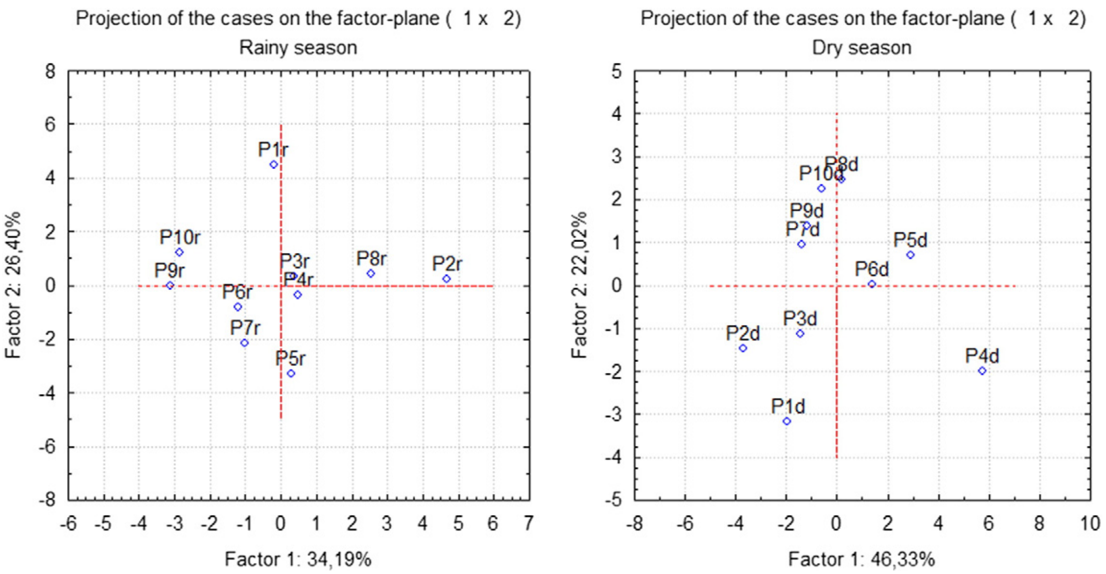


Fig. 5. Scores of the two first factors obtained in the factor analyses using geochemical and ecotoxicological variables of the Jundiaí–Potengi Estuary for the rainy season and the dry season.

unmeasured contaminants. Sites P4, P5, and P6 were the most important to this factor (Fig. 5). The results also suggest, at least partially, that the metals and phosphorus may have a natural source. Since sediments from P4, P5, and P6 presented the highest EF values, this portion of the JPE is likely being influenced by both natural and human inputs during the dry season. Moreover, sediments from P4 were not toxic in this campaign, which indicates that metals were not bioavailable. Chapman and Wang (2001) reported that the increased metal concentrations in relation to the background levels do not necessarily indicate toxicity. The second factor explained 22.01% of the variances and showed an association between nitrogen, OM, muds, Cr, Cd, Pb, Ni, and *L. plumulosus* mortality (Table 6); thus, F2 essentially provides evidence of the human causes of environmental degradation and its effects. These correlations also showed that OM and muds are important geochemical carriers during the dry season, as suggested by Lacerda et al. (2012) in a study on other estuaries from the semi-arid coast of Brazil. Iron was found to be negatively correlated with to F2, a finding which corroborates that the source of metals was human activity. The third factor explained 10.60% of the variances. *T. viscana* mortality was found to be negatively correlated with this factor, while the abnormal sea-urchin embryo development was found to be positively correlated. This result suggests that, during the dry season, other variables (unmeasured contaminants, confounding factors) contributed to sediment toxicity.

Table 6

Eigenvalues and correlations obtained in the factor analysis–principal component analysis (FA–PCA) using geochemical and ecotoxicological data on sediments from the Jundiaí–Potengi Estuary from the rainy and dry seasons. Bold fonts indicate significant correlations (for a cut-off value of 0.40).

Variable	Rainy season			Dry season		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Fe	0.20	−0.22	**0.84**	**0.87**	**−0.40**	−0.06
Mn	**−0.56**	0.28	−0.03	**0.85**	0.12	−0.39
Cr	**0.51**	**0.54**	−0.10	**0.48**	**0.79**	0.35
Cu	**0.79**	−0.15	**0.51**	**0.85**	−0.05	−0.13
Cd	0.20	**0.57**	**−0.73**	−0.06	**0.97**	0.13
Ni	0.38	**0.46**	**0.73**	**0.88**	**0.43**	0.07
Pb	**0.82**	−0.02	**0.41**	**0.54**	**0.79**	0.06
Zn	**0.89**	−0.06	0.38	**0.88**	0.31	0.30
N	**0.47**	**0.58**	0.02	0.08	**0.70**	−0.25
P	0.08	0.34	**0.89**	**0.89**	0.22	0.27
MO	0.11	**0.91**	0.17	**0.53**	**0.72**	0.32
Fines	−0.28	**0.83**	−0.12	0.13	**0.97**	−0.04
Mort_*L. plumulosus*	**0.80**	0.16	−0.13	−0.14	**0.61**	0.23
Mort_*T. viscana*	**0.45**	**−0.75**	0.08	−0.13	−0.16	**−0.81**
Fec_*Nitocra*	−0.14	0.31	**−0.66**	−0.04	0.07	**0.63**
Abnormal_*L. variegatus*	0.07	**−0.79**	0.19	**−0.42**	−0.27	0.38
Eigenvalues	5.47	4.22	2.27	7.41	3.52	1.69
% Total variance	34.19	26.39	14.23	46.33	22.01	10.6
% Cumulative var.	34.19	60.59	74.82	46.33	68.34	78.95

The analyses showed that sediments from the JPE are especially enriched by the mid-estuarine portion. We were not able to not detect clear gradients along the estuary, because the JPE presents multiple contamination sources that create a complex and heterogeneous geochemical and ecotoxicological dynamic. A similar situation was observed by Rodrigues et al. (2013) in Guaratuba Bay (southern Brazil), as well as in other sites around the world (Du et al., 2012; Araujo et al., 2013; Roig et al., 2015). We also observed that, in both seasons, the sediment quality of the JPE was altered, and that nutrients and metals have both natural and anthropic sources, similar to other estuaries from the semi-arid coast of Brazil (Marins et al., 2002; Lacerda et al., 2007, 2012). Metal concentrations tended to occur in sediments from sites located close to sources of human activity, a finding which corroborates previous data on the JPE (Silva et al., 2001, 2003, 2006). These other studies reported that the main sources of pollution for this estuary are untreated sewage, industrial effluents, and agricultural residues, which include fertilizers and pesticides. Further studies are recommended to determine which chemical groups are responsible for the sediment toxicity in the JPE, as well as to determine if the microbenthic community is being affected by the contaminants.

4. Conclusions

Our results indicate that the sediments from the JPE present some degree of degradation. These sediments are toxic and enriched by metals and nutrients, and this situation is produced by a combination of natural sources and human activity. The mid-estuary is considered to be the most altered portion of the JPE, regardless of the season. Conditions are worse during the rainy period, when urban and agricultural runoffs are more intense and carry other contaminants to the estuary. The dry season shows a more clear relationship between contamination and toxicity, because the conditions favor the retention of contaminants within the estuary. In this study, toxicities did not correlate highly with metal concentrations, a result which suggests that unmeasured contaminants are contributing to the environmental degradation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.marpolbul.2016.02.009.

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