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Integrated assessment of mangrove sediments in the Camamu Bay (Bahia, Brazil)

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ABSTRACT

Camamu Bay, an Environmentally Protected Area, may be affected by the pressures of tourism and oil exploration in the adjacent continental platform. The current quality of the mangrove sediments was evaluated by porewater bioassays using embryos of *Crassostrea rhizophorae* and by an analysis of benthic macrofauna and its relationships with organic compounds, trace metals and bioavailability. Porewater toxicity varied from low to moderate in the majority of the samples, and polychaetes dominated the benthos. The Grande Island sampling station (Station 1) presented more sandy sediments, differentiated macrobenthic assemblages and the highest metal concentrations in relation to other stations and guideline values, and it was the only station that indicated a possible bioavailability of metals. The origin of the metals (mainly barium) is most likely associated with the barite ore deposits located in the Grande and Pequena islands. These results may be useful for future assessment of the impact of oil exploration in the coastal region.

1. Introduction

Mangroves are unique ecosystems due to their strong physico-chemical gradients when compared with other ecosystems in which these environmental parameters are less variable (Sanz-Lázaro and Marin, 2009). However, interpreting disturbance effects in mangroves is often complex, since dynamic physical, chemical and geological conditions may interfere with the assessment of anthropogenic impacts on biotic integrity. Thus, in mangroves it is difficult to determine whether structural changes in benthic assemblages are due to natural or anthropogenic stresses, unless the latter are severe (Elliott and Quintino, 2007).

The coast of Brazil has 25,000 km^2 of mangroves distributed over more than 8000 km (Schaeffer-Novelli et al., 2000). The area of mangroves in the State of Bahia (Brazil) is close to 100,000 ha, along a coast of approximately 1100 km, with a human population of around 95,000 inhabitants directly involved with this ecosystem (Ramos, 2002). The mangroves of Camamu Bay (Bahia, Brazil) are considered well conserved and have been investigated in this study because they are important in terms of extension, economic importance and ecological significance (Oliveira, 2000; Hatje et al., 2008). They are also of special interest due the influence of diverse anthropogenic activities in development in the region, which include waste water release, aquaculture, tourism, fishing, boat transport, agriculture, the activities of mining (sand, clay, barium sulfate, manganese, gypsum, carbonaceous concentration exploration) and oil exploration.

Due to their fine grains, the sediments of mangroves are efficient at supplying nutrients and in the absorption and accumulation of organic and inorganic contaminants (such as metals and organic compounds of high molecular weight); thus, they are important reserves of these contaminants and play a basic role in the bioavailability of some chemical compounds that can cause acute and chronic effects in communities that live in or enter into contact with the sediment (Zagatto and Bertoletti, 2006). In this way, since the sediment provides food and a habitat to many infaunal organisms, the assessment of sediment quality is considered necessary for the protection of aquatic life.

Several works have demonstrated sediment characterization in terms of organic matter, grain size, metals (Caccia et al., 2003;

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Gomes et al., 2009; Jaffé et al., 2003; Lu et al., 2005), acid volatile sulfides (AVS), simultaneously extracted metals (SEM) (Fang et al., 2005; Luther III, 2005; Rickard and Morse, 2005) and organic compounds (Brito et al., 2009; Medeiros et al., 2005; Jaffé et al., 2003) to evaluate environmental conditions and bioavailability. However, the effects on the ecosystem can only be determined by biological parameters, including study of the benthic macrofauna assemblage (Barros et al., 2008; Venturini et al., 2008; Peso-Aguiar et al., 2000) and toxicity bioassays (Losso et al., 2009; Beiras et al., 2003; Beiras, 2002; Nascimento et al., 2000).

Toxicity tests allow the evaluation of the interactive effect of the complex mixtures present in the sediment and can be carried out in the aqueous phase (elutriate or porewater) or in the solid phase (whole sediment) (Zagatto and Bertoletti, 2006). Porewater represents a major route of exposure to benthic organisms (Chapman et al., 2002) and substantially influences the bioavailability of contaminants (Whiteman et al., 1996; Long et al., 2003). Porewater toxicity testing has been described as significantly more sensitive than common whole-sediment tests (McDonald, 2005; Nipper et al., 2002; Nipper and Carr, 2001) and highly advantageous due to its overall ecological relevance and ability to avoid some confounding factors (e.g., grain size) common to whole-sediment toxicity tests (Carr et al., 2001).

Toxicity tests on gametes and embryos of bivalves, even if these organisms are not naturally exposed to porewater, are generally accepted and utilized, since larval stages are a good instrument for detecting otherwise unmeasurable sublethal effects (Losso et al., 2009; Nipper, 2000; Carr et al., 2001; Nipper et al., 2002), and provide results that are more realistically predictive of harmful effects at the ecosystem level (Paixão et al., 2007; Beiras and His, 1995; Walsh, 1988). Despite studies in the mangrove sediments of the Camamu Bay having been carried out (Paixão et al., 2010; Oliveira, 2000; Hatje et al., 2008), the existing literature does not record ecotoxicological evaluations together with sedimentary chemistry and their interactive effects on the benthic communities of these sediments.

The goal of this study was to evaluate the sediment quality of mangroves in the Camamu Bay based on the embryo-larval development of the oyster *Crassostrea rhizophorae* through porewater toxicity tests, an analysis of the macrobenthic community distribution and its relationships with natural sediment composition, hydrocarbons (n-alkanes, polycyclic aromatic hydrocarbons (PAH) and total petroleum hydrocarbons (TPH)), trace metal contents (Zn, Cd, Ni, Cu, Ba, Pb, Al and Fe), and bioavailability. The abiotic parameters were chosen considering the information on the area of study (Hatje et al., 2008; Oliveira, 2000), including the current risk of contamination in terms of hydrocarbons and metals due to the changing of oil in boat engines and cleaning storage tanks, as well as the emptying of operational discharges offshore. In this way, the information generated can support intervention, control and environmental security policies in the Camamu Bay.

2. Material and methods

2.1. Study area

Camamu Bay, the fourth largest bay in Brazil (Cirano and Lessa, 2007), is an Environmentally Protected Area located in Bahia state of northeast Brazil. It is situated in the direction north–south, with 20 km of extension between latitudes 13°50′ and 14°6′S and 9 km of maximum width between longitudes 38°57′ and 39°4′W. Camamu Bay is a circular-shaped, shallow bay, with a surface area of approximately 384 km^2 (Hatje et al., 2008) (Fig. 1).

The bay is divided into smaller hydrographic systems, including in the northern section, Serinhaém, a shallow estuarine system with an area of 106 km^2, 48% of which consists totally of mangroves. In the central part of the Bay, there are two systems, Igrapiúna, which receives water from the Igrapiúna, Pinaré and Sorojó rivers, and Sorojó, which receives water from the Pinaré, Acaraí and Conduru rivers. It is a shallow zone, with average depths of 3 m and maximum depths of 7 m within the river channels. The Maraú system, located in the southern part of the Bay, has an area of 120 km^2, consisting of small rivers and the Maraú river (Hatje et al., 2008; Oliveira, 2000). The hydrodynamic circulation inside Camamu Bay is supra-inertially forced and tidally driven, with preferential flow during the dry season (August–February) influenced by a southwestward current (NE winds) (Amorim, 2005). In its interior, the Bay has a rich estuarine ecosystem, with mangroves of great potential for fishing, the remaining Atlantic forest and innumerable islands, the most important being the islands Grande and Pequena (Oliveira, 2000) (Fig. 1).

Six sampling stations (Fig. 1) were chosen as being representative of the meso-littoral region of the Camamu Bay mangroves. Station 1 (S1) was located in the southwest of the Grande Island, a deactivated industrial area (barite exploration). S2 and S3 were situated to the southeast of the city of Igrapiúna. S4 was located in Taipús de Dentro village on the northwest edge (Taipu Mirim Island). S5 was situated in Cajaíba village, and S6 was located on Sorojó Island (Fig. 1).

2.2. Sampling strategy

Meso-littoral surface sediment samples were collected from each station at low tide in December 2007 for toxicity bioassays, benthic community analysis and chemical–physical characterization. For the porewater toxicity test, samples of surface sediment at six sampling stations (S1–S6) were collected with plastic shovels next to the square samplers for benthos collection. Samples of the surface layer of the sediment were collected (<2 cm of depth), corresponding to more recent deposition. The samples were transferred to plastic bags and were kept cool. In this study, ripe oysters *C. rhizophorae* (an euryhaline oyster that inhabits mangrove areas) were collected from mangrove trees in an area of Camamu Bay free from industrial or domestic waste, were cleaned and were kept overnight in an aquarium containing filtered (20 μm) natural seawater taken from the same area.

The benthic macrofauna were sampled at six stations (S1–S6) randomly distributed in the intertidal area. Six replicate samples were collected from each station using a square sampler with a 0.9 m^2 area to a depth of 20 cm. At each sampling station next to the square samplers, six sub-samples of sediment were collected for organic analysis. The sediment sub-samples were collected and mixed to obtain one homogenized sample, which was stored in an aluminum container. The samples were stored at 4 ± 2 °C for up to 14 days until the extraction and for a maximum period of 40 days after the extraction. The sediments for analysis of metals and acid volatile sulfides were sampled using a similar procedure to the sampling procedure for the organic analyses but were collected using plastic utensils. At each station, the samples were immediately placed in zip-lock-type plastic bags and were kept chilled (4 ± 2 °C) until analysis.

2.3. Preparation of porewater and toxicity tests

In the laboratory, porewater bivalve larval development toxicity tests were conducted on sediment samples from six sampling stations (S1–S6) in Camamu Bay. Porewater was extracted on the same day as test initiation by centrifuging sediment for 30 min at 6000*g* and a temperature of approximately 15 °C. The resulting supernatant was carefully removed from the centrifuge containers, transferred to a glass receptacle and cooled. Temperature (*T* °C), potential hydrogen—pH, salinity, conductivity (mS/cm), NH_4^+ NH_3^+ (mg L^{-1}), NO_3^- N (mg L^{-1}), oxidation–reduction potential—ORP (mV), total dissolved solids—TDS (g L^{-1}) and dissolved oxygen—DO (mg L^{-1}) were measured in porewater (100%) before the toxicity testing using multiparameter sondes (YSI 6600 model) that had been previously calibrated.

The toxicity values were determined by oyster embryonic development testing based on the number of abnormal oyster D-larvae. Control and all dilutions were prepared with dilution water consisting of seawater collected in the Camamu Bay that was filtered (GF/C 1.2 μm), with the salinity adjusted to 28 part per trillion (ppt) and also sterilized (127 ± 1 °C, 1.5 kg cm^2) and with quality proven for a minimum level of 90% development of sea urchins (*Lytechinus variegatus*) in a fertilization test (Nascimento et al., 2000). The tests ($n=6$) followed the protocol for *C. rhizophorae*, as adapted by Nascimento (2002) from the American Society for Testing and Materials (ASTM, 1995), the recommended standard method for *Crassostrea virginica*. Six replicates consisting of 10 mL of 25%, 50%, 75% and 100% porewater in a test tube were prepared for each sample. The batches of organisms used in the toxicity tests had been used in bioassays for toxicants, with reference toxicant being sodium dodecyl sulfate (SDS), as recommended by the Canadian Environmental Protection Service (Report EPS-1-EE-73-1) to assess the sensitivity of the organisms and increase the reliability of results, at concentrations of 0.32, 0.56, 1.0, 1.8 and 3.2 mg L^{-1}, according to Da Cruz et al. (2007).

Immediately prior to each test, gametes were collected from mature oysters (3–6 individuals). Pooled eggs and sperms were then suspended in a water dilution. Fertilization was accomplished by transferring 2 mL of sperm to 1.0 L of a dense egg suspension (Santos and Nascimento, 1985; Nascimento, 2002). One hour later, embryos having undergone the first cellular division were counted to maintain a density of 1000 viable embryos per 100 mL in the test vessels. At the end of the test period (24 h), the samples were preserved in 5% buffered formalin and were later examined under a compound microscope.

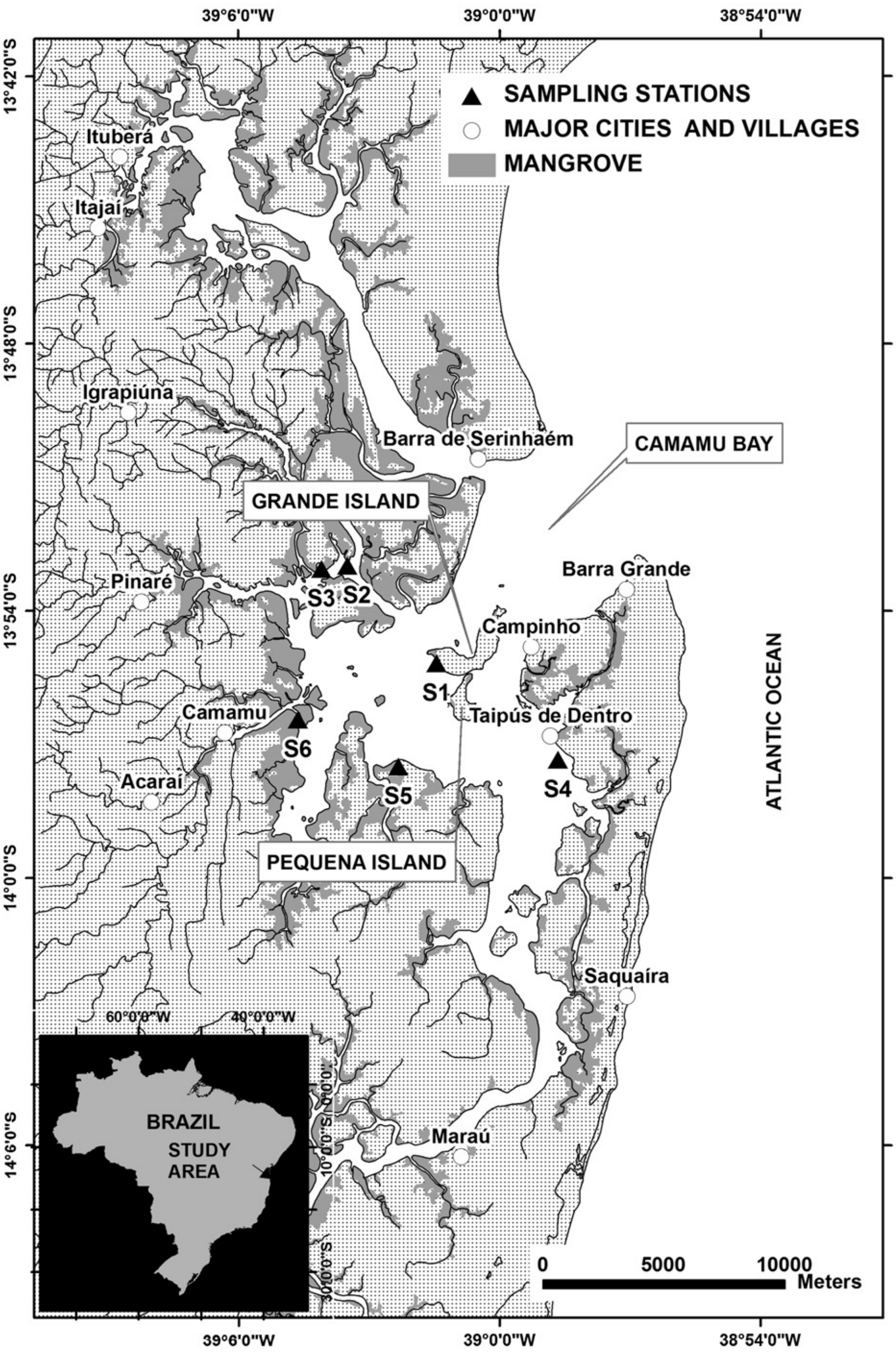

Fig. 1. Area of the study with the location of the six sampling stations.

The numbers of embryos that developed normally and abnormally were counted. Responses to the differentiated treatment were recorded as the percentage of embryos that failed to develop or that developed in an abnormal manner. Embryos, larvae without shells, partly developed larvae or larvae with malformed shells were considered abnormal, while larvae with perfect ‘‘D’’ form shells were considered normal. The acceptability of the test results was fixed at (a) negative control for a percentage of normal D-shape larvae $\geq 75\%$ and (b) EC_{50} (effect concentration 50%) using the reference toxicant (SDS) falling within previously defined acceptability ranges for the reference toxicant (Da Cruz et al., 2007; Paixão et al., 2007; Nascimento, 2002).

2.4. *Macrobenthic community*

The sediment was sieved in situ through meshes with sizes of 1, 2 and 5 mm, and the retained organisms were transferred to plastic recipients, preserved in 70% ethanol and maintained in a freezer (4 °C) for further sorting. The polychaetes found were anaesthetized using 8% magnesium chloride solution and were preserved in a 4% formaldehyde solution. In the laboratory, specimens were counted and identified to the lowest possible taxonomic level, usually species, and were preserved in 4% formaldehyde solution or in 70% alcohol, as specifically required (Peso-Aguiar et al., 2000).

2.5. *Sediment characteristics*

In the homogenized sediment samples, particle size fractions (percentage of sand, silt and clay), carbonates and total nitrogen (EMBRAPA, 1997), TPH, PAH and n-alkanes (SMEWW, 2001; EPA, 1990, 1996) were determined. The analyses were carried out in duplicate. Calibration curves, matrix spikes, apparatus blanks and standard recoveries were employed in the analysis.

Acid volatile sulfide (AVS) and simultaneous extracted metal (SEM) were determined by the method of Allen et al. (1993). Sediment samples were acidified for 30 min with a 1 M HCl solution to form H_2S that was collected in a 0.5 M NaOH solution. The dissolved sulfide concentration was measured by spectrophotometric analysis. The metal contents were obtained by atomic absorption spectroscopy with flame atomization (AAS-F) for Fe, Al, Ni, Ba, Cd, Pb, Cu and Zn (ASTM, 2002), in duplicate. The results were expressed as $\mu g\ g^{-1}$.

2.6. Data and statistical analysis

Oyster embryo responses to toxic porewater were expressed as a percentage net risk of abnormality, corrected for effects in control tests by applying Abbott's formula (Finney, 1971). The effects were calculated based on concentration–response curves and were analyzed by the Trimmed Spearman–Karber (Hamilton et al., 1977) computer statistical method. This was done to provide EC_{50} values (with 95% confidence limits), equivalent to the porewater concentrations that may cause abnormalities in 50% of the exposed embryos. Toxicity data, originally expressed as EC_{50} values, were transformed to Toxicity Units ($TU = 100/EC_{50}$) to obtain a direct relationship between the toxic effect and the measurement system used.

The faunistic data was produced by calculating common community descriptive univariate parameters as follows: total abundance (A), number of species (S), Pielou's evenness index (J') (Pielou, 1966) and Shannon diversity index (H') (Shannon and Weaver, 1963).

The total metal contents in the sediment were compared with two guideline values, the effects range—low (ERL) and the apparent effects threshold (AET) for Amphipod of NOAA—National Oceanic and Atmospheric Administration/Screening Quick Reference Tables (NOAA, 1999). The ERL is indicative of concentrations below which adverse effects rarely occur, while the AET is equivalent to the concentration observed in the highest non-toxic sample.

Varieties of ordination methods were utilized to compare the results, including detrended correspondence analysis (DCA), canonical correspondence analysis (CCA), principal component analysis (PCA) and non-metric multidimensional scaling (nMDS) analysis. Detrended correspondence analysis (DCA) was used to compare the species composition (relative abundances) at six sites using 36 samples collected in December 2007. All species with less than two individuals were deleted from the DCA to avoid possible overemphasis of the importance of rare taxa. DCA of samples and taxa was carried out using the statistical package CANOCO version 4.5. Non-transformed abundance data were used.

A PCA ordination was performed using the computer software PRIMER (Clarke and Warwick, 2001) to ordinate the samples based on the metals (Fe, Al, Zn, Cd, Cu, Ni, Pb, Ba), n-alkanes (C10–C28), total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs), organic matter, grain size, total nitrogen, AVS and SEM concentrations in sediments of Camamu Bay, using the correlation matrix to standardize each variable, meaning the analysis was not influenced by differences in data magnitude and measurement scales (Emmerson et al., 1997; DelValls et al., 1998; Webster, 2001, Ledauphin et al., 2004). In this way, significant factors were then selected based on the Kaiser principle of accepting factors with eigenvalues > 1 (Arambarri et al., 2003; Kuppusamy and Giridhar, 2006). Factor loadings were considered to be significant if they were > 0.6 (DelValls et al., 1998).

The canonical correspondence analysis (CCA), a combination of CA of taxa (non-parametric) and PCA of the environmental variables (parametric) was run after detrended correspondence (DCA) and principal component analyses (PCA) for assessment of the effects of environmental variables on the species abundances. Sample scores were expressed as weighted means of species scores, and CCA axes were scaled accordingly. Through this analysis, the significant variables in the explanation of the data were selected. The importance of environmental data was decided by their intraset correlations with CCA axes and by their p-values obtained from a Monte Carlo significance test, rather than by their canonical coefficient because canonical coefficients were likely to be influenced by other collinear environmental variables (Ter Braak, 1986).

3. Results

3.1. Porewater chemistry

The results of pH, $NH_4^+\ NH_3^+$ ($mg\ L^{-1}$), NO_3^- N ($mg\ L^{-1}$), temperature (°C), ORP (mV), TDS ($g\ L^{-1}$), OD ($mg\ L^{-1}$) and conductivity (mS/cm) measured in porewater (100%) are presented in Table 1. These parameters could not be measured in all test containers because there was insufficient porewater volume to conduct chemical analyses in all of the samples. Dissolved oxygen, salinity, temperature and pH measured in dilution water—water used to obtain concentrations of 25%, 50% and 75% porewater—were maintained at $> 4.0\ mg\ L^{-1}$, 28 ppt, 27 ± 2 °C and 7.0–8.5, respectively, according to the test protocol presented by Nascimento (2002). For 100% porewater, the concentrations of $NH_4^+\ NH_3^+$ ($mg\ L^{-1}$) varied from 23.4 (S2) to 39.72 (S4) $mg\ L^{-1}$.

3.2. Embryo-larval bioassays data—toxicity of porewater

The control results showed a "natural" abnormality in oyster embryo-larval development of 11%, meeting the minimum percent normality in negative seawater controls for the test acceptability criterion (Nascimento, 2002; PSEP, 1995). Experiments using SDS as reference toxicant confirmed the good repeatability of all assays. SDS EC50 values from the reference toxicant tests ranged from 0.77 to 1.12 mg/L, which was within the mean based on the previous tests and also within the SDS EC_{50} acceptability range for *C. rhizophorae*, which ranged from 0.78 to 1.94 $mg\ L^{-1}$ (Da Cruz et al., 2007).

The *C. rhizophorae* embryonic development test results at six sample stations were expressed in $EC_{50,24\ h}$—estimate concentrations that can cause abnormalities in 50% of the exposed population—and the 95% confidence range not exceeding 30% of the EC_{50}. The least toxic among the samples of the six stations tested were S2 and S6 ($EC_{50,24\ h}$ values of 67.35 and 65.37, respectively) and the most toxic were S4 ($EC_{50,24\ h}$ estimated at 34.98%). Intermediate $EC_{50,24\ h}$ values were found for S5, S3 and S1 ($EC_{50,24\ h}$ estimated at 48.90, 46.86 and 42.04, respectively). Toxic unit data are presented in Fig. 2, which allows visualization of the central trend and variability of the toxicity results of the porewater samples at each sampling station to the oyster embryos. The TU_{50} results of stations S1, S3, S5 and, mainly, S4 were higher, differing significantly from the results of stations S2 and S6 ($p = 0.0012$). The coefficients of variation among tests ($n = 4$), calculated for each porewater sample of the six stations, were low (varying from 5.05% for S1 to 10.47% for S5).

3.3. Macrobenthic infauna data

Thirty-six species distributed in 526 individuals of the macrobenthic community were found in the area studied. In terms of species, the macrobenthic community was dominated by polychaetes (16 species, accounting for 43.24% of total species). The total abundance, number of species, Pielou's evenness index and Shannon diversity index per station are presented in Table 2. The total abundance at each station varied from 25 (S6) to 218 individuals (S1). The abundance of the macrobenthic community in S1 was significantly higher than that in the sediment of the other stations. However, the diversity index was lower in S1 as compared

Table 1
Physical–chemical characteristics of porewater at six sampling stations in the sediment mangroves of Camamu Bay.

Stations	Parameters									
	pH	$NH_4^+\ H_3^+$ ($mg\ L^{-1}$)	NH_3 ($mg\ L^{-1}$)	NO_3^- N ($mg\ L^{-1}$)	Temp (°C)	Sal (‰)	ORP (mV)	TDS ($g\ L^{-1}$)	OD ($mg\ L^{-1}$)	Cond (mS/cm)
S1	8.85	25.92	6.91	924.5	26.4	40.99	215	39.63	9.64	60.97
S2	8.54	23.4	3.60	938.8	26.7	36.98	211.9	36.26	7.27	57.67
S3	8.65	23.97	4.81	1048	27.58	37.72	210.8	36.91	9.92	59.62
S4	8.85	39.72	10.94	1039	27	41.84	191.5	40.73	8.28	65.18
S5	8.87	36.4	10.36	1150	27.03	41.94	166.1	40.53	8.42	64.78
S6	8.74	33.86	8.59	850.3	28.6	33.57	205.7	33.24	11.8	54.96

to the other stations. The second highest abundance occurred in the sediment of Station 4 (113 individuals). The variation in the number of species among the stations was relatively low, from 9 (S6) to 17 species (S3). The highest number of species was registered in the sediment of S3. S1 and S5 registered an equal number of species in the second position, followed by equal numbers at S2 and S4. Finally, S2 showed the highest evenness and S5 registered the highest diversity. Table 3 presents the main species found in the sediments and their order of abundance between the sampling stations. *Leonereis culveri* and *Ophioglycera* sp. appeared in all station samples.

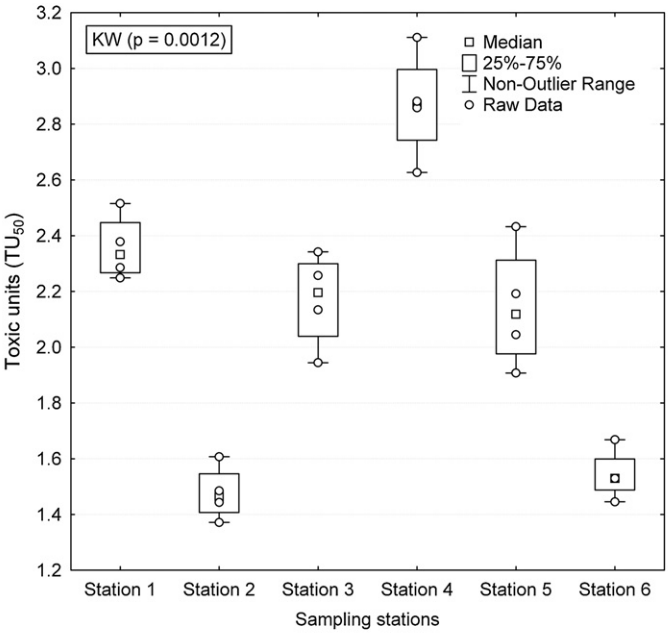

Fig. 2. Box plots show the effects of porewater on *Crassostrea rhizophorae* embryos: values of TU_{50} are reported as raw data ($n=4$).

Table 2
Total abundance (*A*), number of species (*S*), Pielou's evenness index (*J'*) and Shannon diversity index (*H'*) measured at the six sampling stations of Camamu bay.

Index	Stations					
	S1	**S2**	**S3**	**S4**	**S5**	**S6**
Total abundance (*A*)	218	35	64	113	71	25
Number of species (*S*)	15	12	17	12	15	9
Pielou's evenness index (*J'*)	0.63	0.85	0.70	0.75	0.81	0.79
Shannon diversity index (*H'*)	1.71	2.10	1.98	1.85	2.19	1.73

Because of these results of abundance per station, in the data set, the most abundant taxa were *Neritina virginea*, which accounted for 19.96% of the total abundance. This was followed by *L. culveri* (15.02%), a polychaete from the family Nereididae and by *Anomalocardia brasiliana* (12.74%), a bivalve from the family Veneridae. The most diverse stations (S5 and S2) showed 15 and 12 taxa, respectively. The most abundant taxonomic group was Mollusca (282 individuals; 10 taxa). The second most abundant and most diverse group was Polychaeta (208 individuals; 16 taxa). Crustacea (Malacostraca) presented 30 individuals distributed in 22 taxa. Fig. 3 presents the main Phylum/Classes found in the collected samples of mangrove sediments of the Camamu Bay.

Among the taxonomic groups, Polychaeta and Bivalvia presented a widespread distribution, although gastropods and crustaceans were also important groups (Fig. 3). Bivalves appeared in all the samples, in the greatest abundance at S1, a station that was dominated by Gastropoda (mainly by *N. virginea*, a species that also occurred at S3, but in significantly lesser numbers). Polychaetes occurred at all the stations, mainly at S4, followed by S3, because of the abundance of *L. culveri* at these stations. S5 was dominated by Polychaeta and by Bivalvia. S7 and S6 were dominated by Malacostraca, and S2, by Bivalvia. In all the stations, Malacostraca crustaceans were found, with prominent occurrence of the crab *Uca rapax* at S6 (12 individuals).

3.4. *Trace metals concentrations, sediment quality guidelines and bioavailability data*

The quality control analytical studies revealed satisfactory recoveries for all metals (each metal was analyzed according to its individual analytical quality control, with the results showing verification standards above 94.3% and spikes above 96% for all metals). The organic matter contents are presented in Fig. 4a. S6 registered the highest values of organic matter followed by S5,

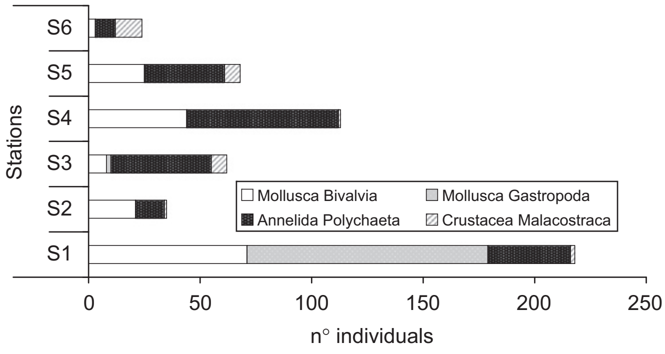

Fig. 3. Values of individual number per taxon (Phylum/Family) measured at the six sampling stations of the Camamu Bay.

Table 3
Main species registered in the sediments of the Camamu bay, classified by their abundance among the sampling stations.

Class	Family	Specie	Order of abundance, no. of individuals
Bivalvia	Veneridae	*Anomalocardia brasiliana*	**S1**(39) > **S4**(12) > **S2**(10) > **S3**(6)
		Ventricolaris sp.	**S4**(24) > **S5**(16) > **S1**(7) > **S3**(1)
	Tellinidae	*Tellina* sp.	**S1**(25) > **S5**(3) > **S6**(2) > **S4**(1)
Gastropoda	Neritidae	*Neritina virginea*	**S1**(103) > **S3**(2)
Polychaeta	Nereididae	*Laeonereis culveri*	**S4**(40) > **S3**(32) > **S1** = **S2** = **S6**(2) > **S5**(1)
	Goniadidae	*Ophioglycera* sp.	**S1**(20) > **S4**(15) > **S5**(10) > **S2**(7) > **S3**(4) > **S6**(3)
	Pilargidae	*Sigambra grubei*	**S4**(7) > **S1** = S3(4) > **S5**(3) > **S6**(2)
	Terebellidae	Terebellidae unidentified	**S5**(18)
Malacostraca	Ocypodidae	*Uca rapax*	**S6**(12) > **S3** = **S5**(2)

while S3, S4 and S2 registered intermediate values and S1 the lowest values. Grain size analysis indicated that coarse sediments (sand, loamy sand, sandy loam) dominated the stations (Fig. 4b). S1–S4 were dominated by sand (94.04%—sand, 67.15%—sandy loam, 77.22%—loamy sand and 66.22%—sandy loam, respectively). S5 (silt loam) and S6 (sandy loam) were dominated by sand (48.33% and 54.40%, respectively), followed by silt (46.08% and 40.19%, respectively).

The metals results are presented in Fig. 4c–j, which shows the mean values for all stations. Sediment contents of the metals were compared with the sediment quality guidelines, effects range—low (“ERL”) and apparent effects threshold (“AET”) for amphipods, as shown in Fig. 4c–j. ERL values for zinc and cadmium did not appear in the graph because they were above the *Y*-axis scale. S1 had the highest values of Ni, Cu, Ba (followed by S5) and Pb, while S3 had the highest values of Zn, Cd (followed by S5), Al and Fe. S1 presented the lowest values of Al and Fe, and registered concentrations above the ERL for Ni and Cu. S4 had the lowest values of Zn, Ba and Pb, and S2 had the lowest values of Cd, Ni and Cu.

S5 and S6 had intermediate metal contents, but a value above the ERL for Ni was observed at S5. Barium in all of the samples showed concentrations close to or above the AET levels. Iron, aluminum and barium had the highest concentrations in Camamu sediments of the studied metals. The highest concentrations for Al (medium value

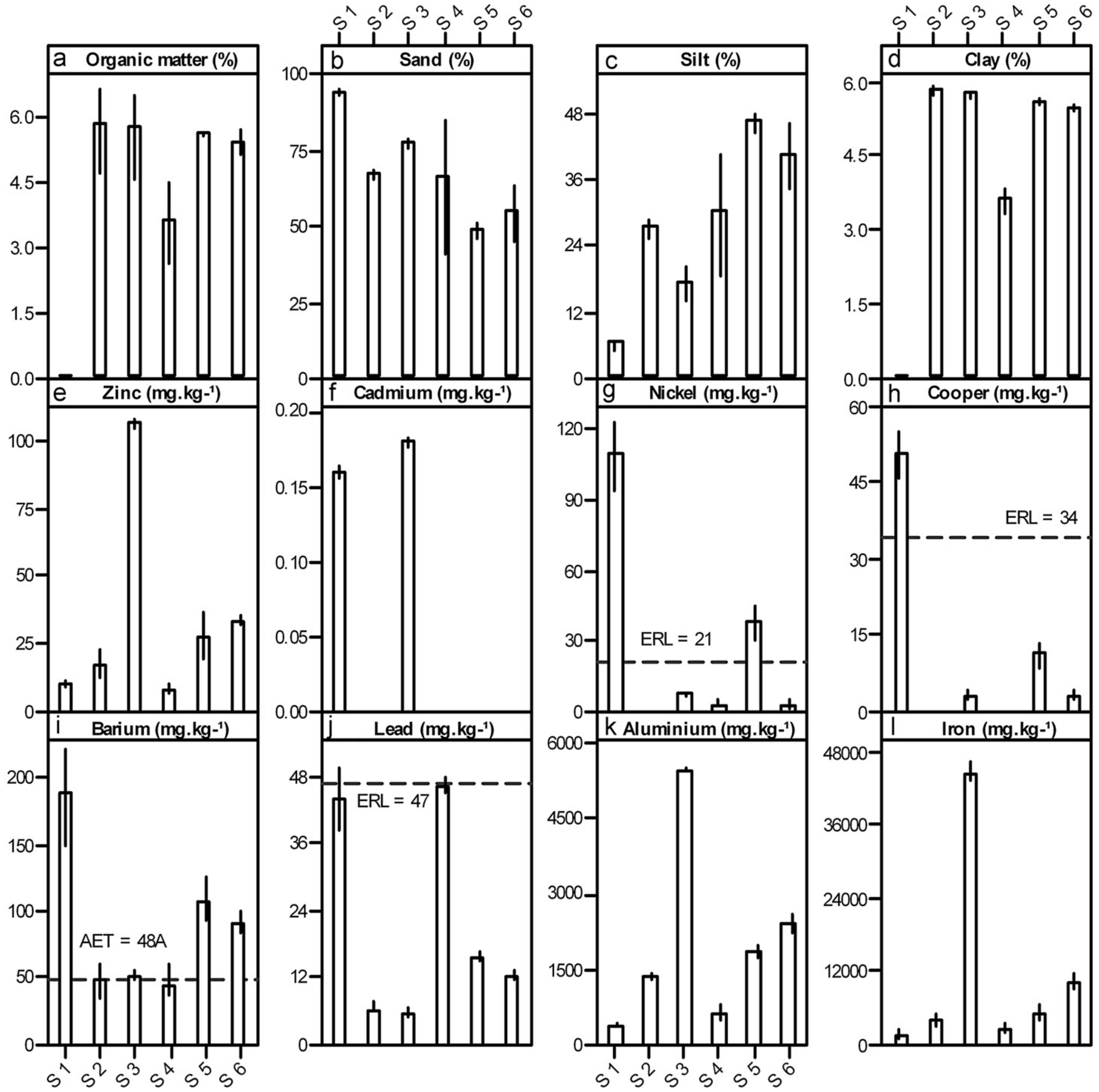

Fig. 4. Organic matter (a), grain size fraction (b) and metals (c–j) (average and standard deviation) at the six sampling stations. Dashed lines represent the effects range—low (ERL) and apparent effects threshold (AET) values for each metal. The presence of outliers could indicate possible contamination.

of 5515 µg g^{-1}) and Fe (medium value of 44,950 µg g^{-1}) were found at S3 (Fig. 4i–j).

The AVS and SEM concentrations are shown in Table 4. The highest AVS values were registered in the southwestern region (S5 and S6) of the bay, followed by the AVS values obtained in the central and northwestern regions (S1–S3). The concentrations of AVS were lowest in the station located in the southeast region of Camamu Bay (S4, in Taipus de Dentro village) (Fig. 1). The ratio of SEM to AVS was less than one at the majority of stations, suggesting that sediment toxicity is not due to metals. A SEM/AVS of greater than one was observed at S1, compatible with possible bioavailability and potential toxicity of the sediment.

3.5. n-Alkanes, total petroleum hydrocarbons and polycyclic aromatic hydrocarbons concentrations

The TPH and n-alkanes concentrations are presented in Fig. 5. The n-alkanes of all chain lengths C10–C28 were detected. Total n-alkane sediment concentrations varied from 772.82 (Station 4) to 6782.74 (Station 2) µg kg^{-1} (Fig. 5a). TPH concentrations were highest in the sediment samples of S6 (average value of 305 µg L^{-1}), and the lowest were obtained at S1 (medium value of 52 µg L^{-1}) (Fig. 5b). n-alkanes (C10–C28) were found in high concentrations among sediments from all stations, with Station 5 showing the highest value (55,172 µg L^{-1}), while the concentrations at other stations varied from 7204 (S2) to 13,151 (S1) µg L^{-1}. These results indicated that other hydrocarbon sources (except n-alkanes (C10–C28) and PAH) were present in the sediments of Station 6, a situation that should be further investigated.

Results of the PAH concentrations in the studied sediments are shown in Table 5. PAH concentrations were less than analytical detection limits or substantially less than the TEL and ERL levels in the majority of samples collected in the Camamu Bay, with the exception of Dibenz [a,h] anthracene (carcinogenic) at S5, where the levels (18.5 and 18.9 µg L^{-1}) were higher than the TEL limit for this hydrocarbon. Conversely, these values were lower than ERL for this PAH, the level that represents the value at which toxicity may begin to be observed in sensitive species.

Benzo [k] fluoranthene, benzo [a] pyrene, benzo [b] fluoranthene, benz [a] anthracene, chrysene, indeno [1,2,3-cd] pyrene and pyrene were detected in the sediments from S4 and S5 (Table 5), located in Taipús de Dentro and Cajaíba village (Fig. 1), respectively. Benzo [g,h,i] perylene, dibenz [a,h] anthracene and phenanthrene were present in S5 sediment. Naphthalene was determined in the S2 (southeast of Igrapiúna city) and S6 (Sorojó Island) sediments (Table 5).

Table 4
Acid volatile sulfide (AVS), simultaneously extracted metals (SEM) and SEM/AVS (average ± SD) at the six sampling stations.

Stations	**SEM** (µmol g^{-1})	**AVS** (µmol g^{-1})	**SEM/AVS** (µmol g^{-1})
S1	3.89 ± 3.11	2.16 ± 1.27	1.80
S2	0.29 ± 0.11	3.36 ± 1.93	0.09
S3	1.83 ± 0.06	2.48 ± 1.13	0.74
S4	0.20 ± 0.09	0.92 ± 0.38	0.22
S5	1.32 ± 1.54	43.90 ± 1.54	0.03
S6	0.67 ± 0.08	67.19 ± 0.08	0.01

3.6. Multivariate approach

The results of the DCA ordination showed that 57.4% of species abundance was accounted for by the two first ordination axes used in the analyses. Explanation of axis 1 and axis 2 were 42.6% and 14.8%, respectively (Fig. 6). Considering that DCA can produce stronger distortions than a two-dimensional non-metric multidimensional scaling analysis (nMDS) in some of the simulations (Hill and Gauch, 1980), nMDS testing was performed regarding the significance of the relationships of taxa relative to the sampling stations. Both procedures yielded the same results. However, DCA ordinations are more interpretable than those from nMDS, and for this reason, only the results based on the first procedure are shown (Fig. 6). DCA axis 1 indicated that the macrofauna at S1 were substantially different from communities at other stations. Benthic samples were associated mainly with polychaeta, bivalvia, gastropoda and malacostraca.

The PCA (Fig. 7) performed with the abiotic data showed that the first component (PC1) explained 49.4% of the data variance, being positively correlated with sand, SEM, Cu, Ni, Pb, Cd, Ba, total nitrogen and n-alkanes concentration in the sediments, and showed negative correlation with Fe, Al, Zn, AVS, PAH, TPH, clay, silt and organic matter. Although many of the variables showed a slight negative skew in PC1 (Fe, Zn, Al, PAH, AVS), some variables showed a stronger negative skew (TPH, Clay, Silt and OM). The second component (PC2) explained 28.4% of the variance and was negatively correlated with Cu, Ni, Pb, Ba, SEM, AVS, PAH, TPH, silt and organic matter.

PCA ordination resulted in the separation of stations: Station 1 was characterized by sandy sediments, low organic content and relatively high metal concentrations in one extremity, and the remaining stations in the other extremity. Station 2 presented high concentrations of Al, Zn and Fe and a relatively high percentage of clay and organic matter content (Fig. 4). Station 3 presented the highest Al, Fe and Zn contents, and also the highest total nitrogen and n-alkanes concentrations (Fig. 5). Station 4 showed the

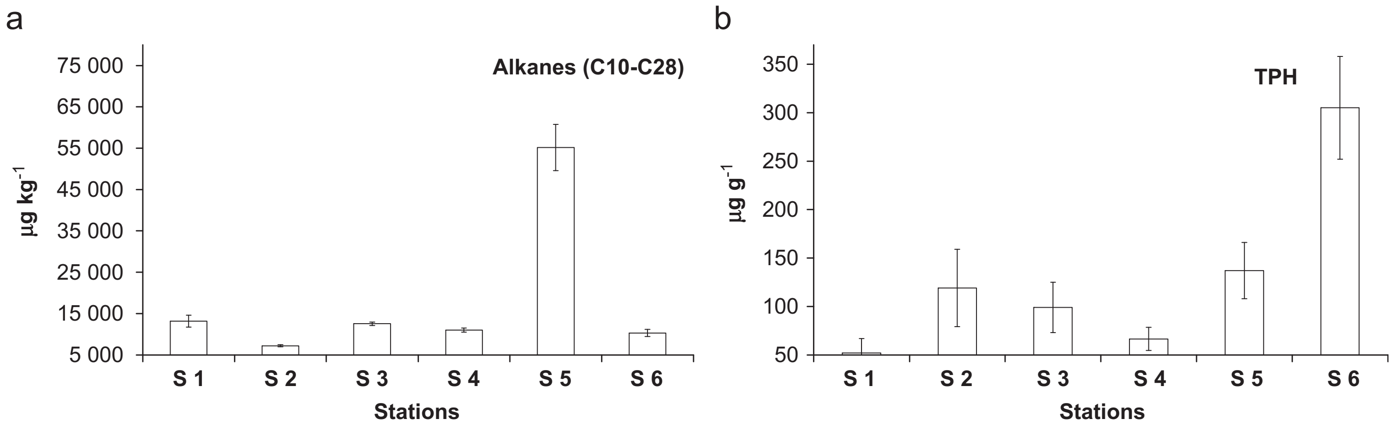

Fig. 5. TPH (a) and ∑alkanes (b) (average and standard deviation) concentrations at the six sampling stations.

Table 5
Distributions of polycyclic aromatic hydrocarbons (PAHs) in sediments of Camamu Bay. Threshold effects level (TEL) and effects range—low (ERL) based National Oceanic and Atmospheric Administration (NOAA/Screening Quick Reference Table for Organics (Buchman, 1999) are indicated.

Stations	PAHs (μg L^{-1})															
	Acenaphthene	Acenaphthylene	Anthracene	Benzo [k] fluoranthene	Benzo [a] pyrene	Benzo [b] fluoranthene	Benzo [g,h,i] perylene	Benz [a] anthracene	Chrysene	Dibenz [a,h] anthracene	Fluoranthene	Fluorene	Indeno [1,2,3-cd] pyrene	Naphthalene	Phenanthrene	Pyrene
S1	< 0.16	< 0.22	< 0.11	< 0.18	< 0.33	< 0.28	< 0.43	< 0.25	< 0.41	< 0.2	< 0.24	< 0.76	< 0.4	< 0.62	< 0.28	< 0.55
	< 0.16	< 0.22	< 0.11	< 0.18	< 0.33	< 0.28	< 0.43	< 0.25	< 0.41	< 0.2	< 0.24	< 0.76	< 0.4	< 0.62	< 0.28	< 0.55
S2	< 0.16	< 0.22	< 0.11	< 0.18	< 0.33	< 0.28	< 0.43	< 0.25	< 0.41	< 0.2	< 0.24	< 0.76	< 0.4	4.6	< 0.28	< 0.55
	< 0.16	< 0.22	< 0.11	< 0.18	< 0.33	< 0.28	< 0.43	< 0.25	< 0.41	< 0.2	< 0.24	< 0.76	< 0.4	4.8	< 0.28	< 0.55
S3	< 0.16	< 0.22	< 0.11	< 0.18	< 0.33	< 0.28	< 0.43	< 0.25	< 0.41	< 0.2	< 0.24	< 0.76	< 0.4	< 0.62	< 0.28	< 0.55
	< 0.16	< 0.22	< 0.11	< 0.18	< 0.33	< 0.28	< 0.43	< 0.25	< 0.41	< 0.2	< 0.24	< 0.76	< 0.4	< 0.62	< 0.28	< 0.55
S4	< 0.16	< 0.22	< 0.11	14.1	16.8	29.5	< 0.43	20	24.5	< 0.2	< 0.24	< 0.76	19	7.7	< 0.28	33
	< 0.16	< 0.22	< 0.11	14.6	18	29.9	< 0.43	20.2	24.9	< 0.2	< 0.24	< 0.76	18.9	7.57	< 0.28	33.6
S5	< 0.16	< 0.22	< 0.11	17.2	22	28	15.6	20.1	17.2	18.5[a]	< 0.24	< 0.76	70	5.7	12.7	24.8
	< 0.16	< 0.22	< 0.11	17.5	21.6	28.1	15.4	20.9	17.2	18.9[a]	< 0.24	< 0.76	70	5.74	10.5	29.6
S6	< 0.16	< 0.22	< 0.11	< 0.18	< 0.33	< 0.28	< 0.43	< 0.25	< 0.41	< 0.2	< 0.24	< 0.76	< 0.4	2.9	< 0.28	< 0.55
	< 0.16	< 0.22	< 0.11	< 0.18	< 0.33	< 0.28	< 0.43	< 0.25	< 0.41	< 0.2	< 0.24	< 0.76	< 0.4	2.91	< 0.28	< 0.55
TEL	6.71	5.87	46.85		88.81			74.83	107.77	6.22	112.82	21.17		34.57	86.68	152.66
ERL	16	44	85.3		430			261	384	63.4	600	19		160	240	665

[a] Concentration that exceeds the threshold effects level (TEL defined by NOAA (Buchman, 1999)).

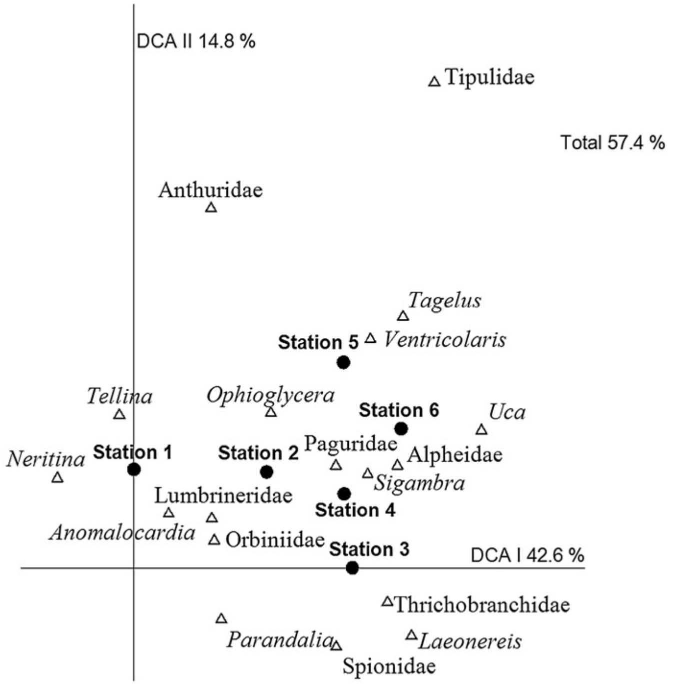

Fig. 6. DCA plot showing the major axes of variation in the benthic data set. Stations closer together on the graph were more similar in their benthic macrofauna.

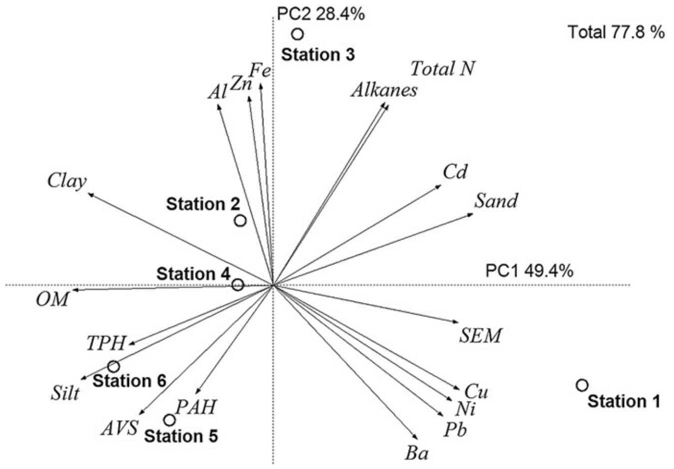

Fig. 7. PCA ordination diagram for the six sampling locations based on sediment variables, metals, AVS, SEM, hydrocarbons (HTP, PAH and n-alkanes), grain size, total nitrogen and organic matter.

strongest correlation with the fine sediment fraction and organic matter; however, it did not present a high metals content. Stations 5 and 6 showed similar percentages of silt, AVS, TPH and PAH. Al, Fe and Zn and TPH, PAH, AVS and organic matter showed the strongest correlation with the fine sediment fraction, clay and silt, respectively (Fig. 7).

The first axis of canonical correspondence analysis explained 60.2% of the variation, selecting TPH and organic matter (OM) as explicative variables. Samples were distributed accordingly, with taxa associated to high silt/clay, organic content and with the highest TPH concentrations in the right quadrant (e.g., *L. culveri*, *Ventricolaris* sp., *U. rapax*, *Sigambra grubei*; Fig. 8), and species more dependent upon opposite conditions (arenaceous sediments, with higher metal concentrations of Station 1) in the lower left (e.g., *A. brasiliana*, *N. virginea* and *Tellina* sp.). The Monte Carlo significance

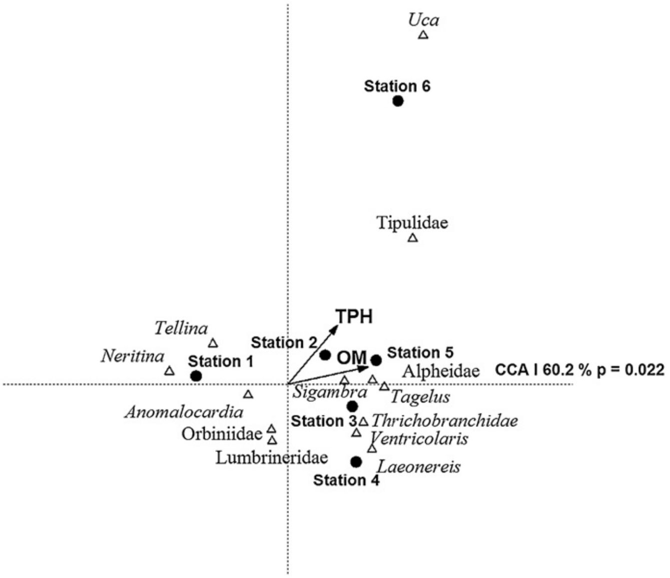

Fig. 8. Representation of the first axis of the CCA, presenting the biological samples (triangles) in their environmental settings (vectors). Samples were grouped by station (1–6, circles).

test resulted in a *p*-value of 0.022, which was considered significant.

4. Discussion

In relation to the ecotoxicological evaluation, comparison between the embryo-larval test results and toxicity classes for bioassays with embryos of *C. gigas* for porewater samples ($TU_{50} < 1.7$—low; $1.7 \leq TU_{50} < 2.6$—medium; $2.6 \leq TU_{50} < 17.2$—-high; $TU_{50} \geq 17.2$—very high) presented in Losso et al. (2009) indicated that TU_{50} values at S2 and S6 might be considered of low toxicity, while the sample at S4 was of high toxicity. Intermediate TU_{50} values were found at S1, S3 and S5, classifying the samples of these stations as having medium toxicity to the oyster embryos (Fig. 2). However, the TU_{50} raw values for the S4 sample were lower than 3.5, which is next to the lower limit of the category "high".

The results of salinity (33.5–41.94) and pH (8.54–8.87) measured in porewater up to 100% (Table 1) demonstrated the occurrence of protocol deviations in the test recipient containing 100% porewater and suggested the possibility of deviations in porewater samples at 75%, 50% and 25% (for which these variables were not analyzed), suggesting that these parameters may have affected the toxicity of samples from all stations.

Although porewater plays an important role in sediment toxicity assessment using bioassays, the potential contribution of confounding factors to the real toxicity needs to be studied (e.g., ammonia) (Losso et al., 2009). Ammonia is a potentially toxic naturally occurring constituent of sediment porewaters and has been identified as a common toxic agent in many porewater toxicity tests (McDonald, 2005; Ho et al., 2002; Stronkhorst et al., 2003; Van Sprang and Janssen, 1997; O'Day and Head, 2000). In anoxic, high organic environments, the nitrogen transformation reactions stop at the conversion of organic nitrogen to ammonia. Since ammonia is highly soluble, it is recycled via the porewater to the water column (Batley and Simpson, 2009). For sediment porewaters, a guideline trigger value of 3.9 mg total NH_3-N L^{-1} was derived from the 80th percentile of background data from Sydney Harbor (and for acute effects, a PC95 and PC90 value of, respectively, 1.55 and 2.26 mg total NH_3-N L^{-1}) (Batley and Simpson, 2009). Taking into account that the Australian and New Zealand guideline for marine and estuarine waters is 910 μg NH_4^+ H_3^+ L^{-1} for 95% species protection (at 20 °C and pH 8) (ANZECC/ARMCANZ, 2000), and that the United States Environmental Protection Agency (USEPA) chronic saltwater criterion is 35 μg NH_3/L (equivalent to 760 μg NH_4^+ H_3^+ L^{-1} at 20 °C and pH 8.0) (EPA, 1989), the concentrations of total ammonia in the 100% porewater samples of the present study (that varied from 23.4 to 39.72 mg L^{-1} (Table 1) were significantly higher than the cited Australian and USEPA guideline values.

However, unionized ammonia (and not NH_4^+ H_3^+) is the most toxic form and comprises 3.8% of the total ammonia (in seawater at 20 °C, pH 8 and 30‰ salinity) (ANZECC/ARMCANZ, 2000), although there is evidence that the ammonium ion (NO_3^- N) also contributes to toxicity (EPA, 1999), although less than 1% of the total toxicity (EPA, 1989). The Puget Sound Estuary Program (PSEP, 1995) specified a BLD ammonia threshold value of 0.13 mg L^{-1} unionized N. Conversely, the PSEP (1995) threshold value was based on data from the Pacific oyster (*Crassostrea gigas*) (EPA, 1993), not *C. rizophorae*.

Data of total ammonia (NH_4^+ H_3^+) and unionized ammonia (NH_3, the most toxic form) obtained porewater samples at 100% of Stations 1–6 (ranging from 23.4 to 39.72 mg L^{-1} and from 3.06 to 10.94 mg L^{-1}, respectively, Table 1) were very high when compared to Australian and USEPA guideline values (of 0.91 and 0.76 mg L^{-1} of total ammonia, respectively). The highest concentration of unionized ammonia was 10.94 mg L^{-1} at S4. This result was about 80 times higher than the limit of unionized ammonia PSEP (1995), at 0.13 mg L^{-1} for *C. gigas*. Considering the bioassay results (Fig. 2), these data suggested that ammonia can be considered a confounding factor for the sample toxicity and must have contributed strongly to the sample toxicity of S4 (TU_{50} raw values: $2.6 \leq TU_{50} < 3.5$, considered of high toxicity) to *C. rhizophorae*, as well to toxicity of samples from other stations, albeit to different extents.

Macrofaunal assemblages represent the integrated response of biological effects of the pollutant content in a sediment sample (Cesar et al., 2007) and are subject to changing environmental conditions and anthropogenic impacts, resulting in a possible reduction in the abundance of some species and an increase in the abundance of opportunistic taxa (Barros et al., 2008; Harvey et al., 1998; De Grave and Whitaker, 1999; Lenihan et al., 2003). In this study, two species, the gastropod *N. virginea* and venerid clam *A. brasiliana*, that together with the nereid polychaete *L. culveri*, were numerically dominant in Camamu Bay (Table 3), representing nearly half the community, appear to prefer sand habitats such as those from Station 1. Higher levels of fine sediments that occur in the other stations may have effectively reduced or excluded them from these environments. Thus, the abundance value observed at S1 (Table 2) was influenced by the density of *N. virginea* (103 individuals), followed by *A. brasiliana* (39 individuals). *A. brasiliana* lives in the muddy sands of mangroves (Moriëza et al., 1999) and is abundant in Camamu Bay, serving as an important source of food for many local communities. This species has been frequently used as an indicator of heavy metals (Waltner-Kersanach et al., 2000) and is common in areas affected by organic pollution (Schaeffer-Novelli, 2000; Denadai et al., 2000), including the Todos os Santos Bay, Bahia, Brazil (Peso-Aguiar et al., 2000), located around 100 km north of the study area. Among the stations, *L. culveri* represented 73% of the worms sampled, suggesting opportunistic behavior, with S4 (40 individuals) and S3 (32 individuals) numerically dominated by this polychaete (Table 3). S4 was located in the Taipus de Dentro village on the island of Taipus-Mirim (Fig. 1), a fishing village with urban infrastructure directed toward tourism, while S3 was located southwest of the city of Igrapiúna, of which 84.1% of the population are found in the agricultural region, in provincial and coastal areas (SEMARH/HYDROS, 2005). Data integration by DCA

(Fig. 6) and CCA (Fig. 8) also showed that the benthic macrofauna of S1 was differentiated in comparison with other stations.

Fine fractions tend to be deposited in areas with low hydrodynamic energy (Venturini and Tommasi, 2004; Suguio, 1973), such as mangroves. However, the mangroves studied were dominated by sandy sediments (mainly at S1), and aluminum, iron and organic matter concentrations were high, making broad trends difficult to resolve. These results differ from those obtained by Oliveira (2000), who found a strong correlation between trace metals (Cr, Pb, Zn, Mn, Al and Fe), fine particles and organic matter in Camamu Bay sediments of mangroves. A notable difference in substrate nature was apparent between Station 1 (that presented the highest sandy and lowest organic matter, silt and clay contents) and the other stations (with the greatest concentrations of silt corresponding to S5 – Cajaíba village and S6 – Sorojó Island, respectively). Considering that the sampling stations in the present study were situated near the mouths of the rivers, it is probable that the coarse size was influenced by their inflow. PCA analysis (Fig. 7) also indicated separation between sediments of S1 (sandier, with low organic matter content and the highest metal concentrations) and the sediments of the other stations.

It has been reported that Camamu Bay is naturally enriched with Ba (Oliveira, 2000; Hatje et al., 2008), and for this reason mining was started in 1940 on Grande and Pequena islands and was carried out for 40 years in the interior of the Bay (Fig. 1). The metal concentrations in sediments showed a gradient related to the location of the barite ore (barium sulfate, $BaSO_4$) in the Grande and Pequena islands, since the sediment concentrations of metals at S1 (Grande island) presented the highest levels recorded. The comparison between trace metal concentrations and reference values revealed that most of the trace metal concentrations, in general, were conservative, below levels at which adverse effects are expected to occur (ERL values). Barium was an exception and presented concentrations above AET levels. Nevertheless, in this study, some other stations beyond S1 also presented metal results above ERL and AET levels, but even when exceeded, only low or moderate biological effects were found in oyster embryos. Although the metal values were the highest in the S1 sediments, the results of the toxicity tests did not clearly reflect these results. A possible explanation is the grain size, which in the sample of S1 was sandier in relation to the others, presenting a lower potential for trace metal retention. Analysis of barite samples from the Pequena and Grande islands showed high concentrations of Ba, Pb and Zn, i.e., 39–58%, 31–5000 mg/kg and 54–4950 mg/kg, respectively (Campos, 1984). These results suggest that barite is the main source of this element and that the distribution of metals in Camamu Bay not only is linked to deposits or accumulation zones but also is a function of point sources and the transport routes of contaminants (Hatje et al., 2008).

Unfortunately, pre-mining data is not available to elucidate if the metal concentration results of the present study are influenced by the impact of barite exploration in the past (and to what extent) or are natural. Currently, a major part of the reserve, estimated at 25 million tons, is submersed and most of it has not yet been explored (Oliveira, 2000). It is important to point out that the values of metals could also be related to the continental input and runoff from the rivers influenced by urban and rural development areas located in the cities around Camamu Bay. Many of these metals (Cu, Pb, Zn, Ni) are components of fertilizers (Förstner and Wittmann, 1981).

Compared to other coastal systems, the metal results obtained in this study for Camamu Bay were higher than levels for the same mangroves reported by Oliveira (2000) and for the region of the infra-littoral of this bay by Hatje et al. (2008). They also are slightly elevated compared to levels found in São Francisco estuary, NE-Brazil (Sabadini-Santos et al., 2009), Grande island, Rio de Janeiro, Brazil (DePaula and Mozeto, 2001), Singapore's mangrove sediments (Cuong et al., 2005) and also background values in Todos os Santos Bay (CRA, 2004). However, the metal results of this study were lower than those found by numerous authors at impacted sites such as Guanabara Bay, Rio de Janeiro, Brazil (Kehrig et al., 2003) and the Pearl River estuary (Liu et al., 2002).

In sediment, contaminant concentrations may be several orders of magnitude higher than those in overlying water; however, bulk sediment concentrations are not highly correlated to bioavailability (Burton, 1992). In this study, only Station 1 presented a ratio SEM/AVS > 1, which indicates the possible bioavailability of metals. The other stations showed a result < 1, for which a toxic effect is not expected from Cd, Cu, Ni, Pb or Zn.

Activities such as tourism and the exploration of offshore oil and gas reserves have been increasing in the Camamu Bay (Hatje et al., 2008). Recently, 12 blocks of oil and derivatives exploration have been granted in the Camamu Basin—the basin where the Camamu Bay is located. The maritime fields of Camarão, Pinaúna and Sardinha are at the stage of production phase development, while the field of Manati is already in the production phase (ANP, 2008). Many species will be threatened if accidents occur during the operation of oil and gas fields located in the continental platform (Hatje et al., 2008), considering the numerical simulations with oil spills performed by Amorim (2005) that have shown that the bay could be affected within periods of less than one day in the worst scenarios. In the same way that oil and gas activities may further contaminate the bay, the increasing of flow boats related to regional tourism is also associated with fossil fuel combustion and oil-related contamination, suggesting that polycyclic aromatic hydrocarbons (PAHs) might be released to the coastal environment, although no data on PAH contamination of sediments in the mangroves of Camamu Bay were available before this study. PAHs are rarely found as biosynthetic products and are known to have carcinogenic and mutagenic potential (UNEP, 1991). Sediment-associated PAHs exhibit narcotic effects in benthic organisms (Di Toro and McGrath, 2000) and result in malformation induction in many organisms, including oysters (Vahl et al., 1995; Jeong et al., 2005). Our results suggested that PAHs were not the primary contributors to porewater toxicity, due the remarkably low concentrations of these compounds (only one greater than numerical standards and the majority were less than the analytical detection limits) in the whole sediment (Table 5). The results showed that for the majority of the study sites, concentrations of PAHs in the sediments were below TEL values, with the only exception being dibenz [a,h]anthracene at Station 5, and were near background values (Table 5).

In this study, the n-alkanes concentrations (Fig. 5a) were consistent with the fact that the continental platform adjacent to the bay is rich in oil deposits with high paraffinic content (Oliveira, 2000) and confirmed that the terrestrial n-alkane level is predictably higher near the mouths of rivers (Sikes et al., 2009). The n-alkanes are common biomarkers found in sedimentary organic matter and are known to be biosynthesized by a wide variety of both marine and terrestrial plants (Sikes et al., 2009). The short chain n-alkanes have phytoplanktonic origin (Meyers and Ishiwatari, 1993), while marine macrophytes have dominant mid-chain length n-alkanes (C23–C27) and mangroves have slightly longer mid-length chains (C27–C29) (Ficken et al., 2000; Mead et al., 2005). However, the molecular weight alkane distribution did not show a carbon number preference and the input of mid-chain n-alkanes in Camamu Bay, suggesting that a portion comes from coastal sources such as mangroves that are important sources of organic carbon to the sediments (Alfaro et al., 2006), but also could be derived from petrogenic sources and marine primary productivity. Due to many species exhibiting resistance, adaptability or resilience to the levels of n-alkanes in the sediments, masking or delaying the small changes acquired for a certain time (Peso-Aguiar et al., 2000) and due to known PAH toxicity, it is important that information about the contents of these organic compounds in mangroves sediments of Camamu Bay be available.

5. Conclusions

The present study is the first sediment quality assessment of Camamu Bay mangroves using the weight-of-evidence approach. Despite some metal concentrations being found above ERL levels in the mangrove sediments of Camamu Bay, in general, our results showed that the samples were lowly to moderately toxic for *C. rhizophorae* embryos. However, the toxicity may not be due to metals, but to ammonia, organics and other unmeasured contaminants. The use of *C. rhizophorae* embryos in sub-chronic toxicity testing was shown to be an important tool for assessment of the sediment toxicity through porewater due to their high sensitivity.

Benthic distribution patterns indicated differences in macrofauna at S1 associated with sandier sediments in comparison to other stations, and showed the occurrence of opportunistic species (mainly at S1) in these sediments. There was also a clear multivariate relationship between samples at S1 and the metal concentrations. The ore barite located at S1 could be a principal source of trace metal (mainly barium) concentrations in the sediments of Camamu Bay, but it is not possible to affirm that the deactivated barite mining is the contributor of metal contamination, although the highest concentrations of metals were found close to the ceased industrial area.

Taken as a whole, these findings provide a good insight into the integrated evaluation of the sediment quality of the Camamu Bay mangroves and may be useful for future comparisons of metals and organic compounds (PAH, TPH and n-alkanes) and their impacts on mangroves. From an environmental perspective, attention should be paid to the inorganic and organic contamination in Camamu Bay, which could have negative impacts on wildlife in these areas, which are protected by Conselho Nacional de Meio Ambiente (CONAMA) no. 303/2002 Resolution (BRASIL, 2002). This study provides baseline information to assess the impact of recently commenced industrial oil exploration in the continental platform adjacent to Camamu Bay and for the planning of management actions in this area.

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