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Use of an Integrated Geochemical and Ecotoxicological Approach to Evaluate Sediment Metal Contamination in Three Protected Estuarine Areas Along the Coast of São Paulo State, Brazil

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Abstract
We compared sediment quality in estuaries at three locations along the coast of São Paulo State, Brazil, using geochemical analyses and whole sediment toxicity tests, during the southern summer and winter of 2013. Each locality is afforded a distinct degree of legal protection, and exhibits a different level of metal pollution: overall, Rio Diana (RD, the most polluted, a Permanent Protection Area) > Rio Itapanhaú (RI, intermediate contamination, an Environmental Protection Area) > Rio Picinguaba (RP, pristine, a State Park). Chronic sediment toxicity tests evaluated reproductive rates of the copepod *Nitokra* sp. RI sediments showed the highest metal concentrations and toxicity in both seasons. Metal concentrations at RD were low but toxic in summer. RP sediments were not contaminated, suggesting effective legal protection from pollution at this locality. RI and RD, although provided some legal protection, showed clear signs of environmental degradation, emphasizing the need for more effective pollution control.

Keywords Sediment quality · Geochemical and toxicity analyses · Legally protected reserves · Differential metal contamination · São Paulo state coast

Coastal regions and estuaries suffer from intense human occupation and anthropogenic activity that especially impact marine and estuarine ecosystems, owing to pollutant discharge. Most contaminants accumulate in sediments, producing toxic effects on the biota (Adams et al. 1992). Because sediments function as deposits of complex contaminant mixtures, interactions among xenobiotics are likely, leading to unpredictable ecological effects (Chapman 1995). Geochemical analyses and toxicity tests are frequently used to assess sediment quality in estuarine and coastal ecosystems, respectively identifying the nature and the degree of contamination, enabling evaluation of sediment toxicity, and providing biological relevance.

Despite the importance of sediment quality assessments for environmental management, other means are also mandatory, such as establishing restricted areas to protect habitats, ecological processes and biodiversity, and to maintain fisheries productivity. Kelleher (1999) defined Marine Protected Areas (MPA) as "any area of intertidal or subtidal terrain, together with its overlying water and associated flora, fauna, historical and cultural features, which has been reserved by law or other effective means to protect part or all of the enclosed environment". Different categories of MPAs have been proposed, providing increasing restrictions on human presence and activities, to minimize anthropogenic impacts (IUCN 1994). However, the effectiveness of different types of MPAs in protecting marine and estuarine environments from pollution is poorly known. Information on pollution is available for only 69 of the 11,169 MPAs designated worldwide (Abessa et al. 2018), emphasizing the need for more inclusive studies.

The State of São Paulo in southeastern Brazil includes 622 km of coastline and 11 coastal municipalities. The

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coastal region harbors a mosaic of uses, including pristine reserves under maximum legal protection to areas suffering intense anthropogenic pressure. Consequently, different levels of pollution occur along the coast, including within some MPAs (CETESB 2018). Establishing whether such MPAs remain uncontaminated and whether conservation policies have been effective in avoiding pollution constitutes an issue of foremost importance. This study aims to evaluate the quality of sediments at three estuarine sites subject to distinct levels of legal protection and anthropogenic impact, using an integrated approach combining geochemical analyses and sediment toxicity testing. We hypothesize that the most restrictive protected areas would exhibit lower degrees of environmental degradation.

Materials and Methods

Three estuarine sites subject to different degrees of legal protection and contamination were chosen (Fig. 1): (i) Rio Diana (RD, 23° 55′ 04.5″ S; 46° 18′ 31.5″ W) and (ii) Rio Itapanhaú (RI, 23° 50′ 0.2″ S; 46° 09′ 10.6″ W), located in the Santos Estuarine System (SES) on the central coast of São Paulo State, and (iii) Rio Picinguaba (RP, 23° 22′ 73.0″ S; 44° 50′ 50.0″ W) situated on the northern coast. All three sites are afforded baseline protection under the Brazilian Forest Code (Federal law number 12.651/2012) and are designated as Permanent Protection Areas (PPA) due to the presence of mangrove forests. This legal designation does not restrict various anthropogenic activities. Additionally, RI is part of the Marine Environmental Protection Area of the central São Paulo coast, a category of MPA that imposes mild restrictions on several human impacts (see São Paulo State decrees #53,526 and #53,528, 2008a, b). Rio Picinguaba lies within the Serra do Mar State Park where most anthropogenic activities are prohibited, according to the Brazilian system of protected areas (Brasil 2000).

Rio Diana is located within the central SES and consists of an area of 2372 km^2; it incorporates one of the most populous and industrialized regions of São Paulo state (IBGE 2007) and includes the Port of Santos. The area was once considered amongst the most polluted estuaries in the world

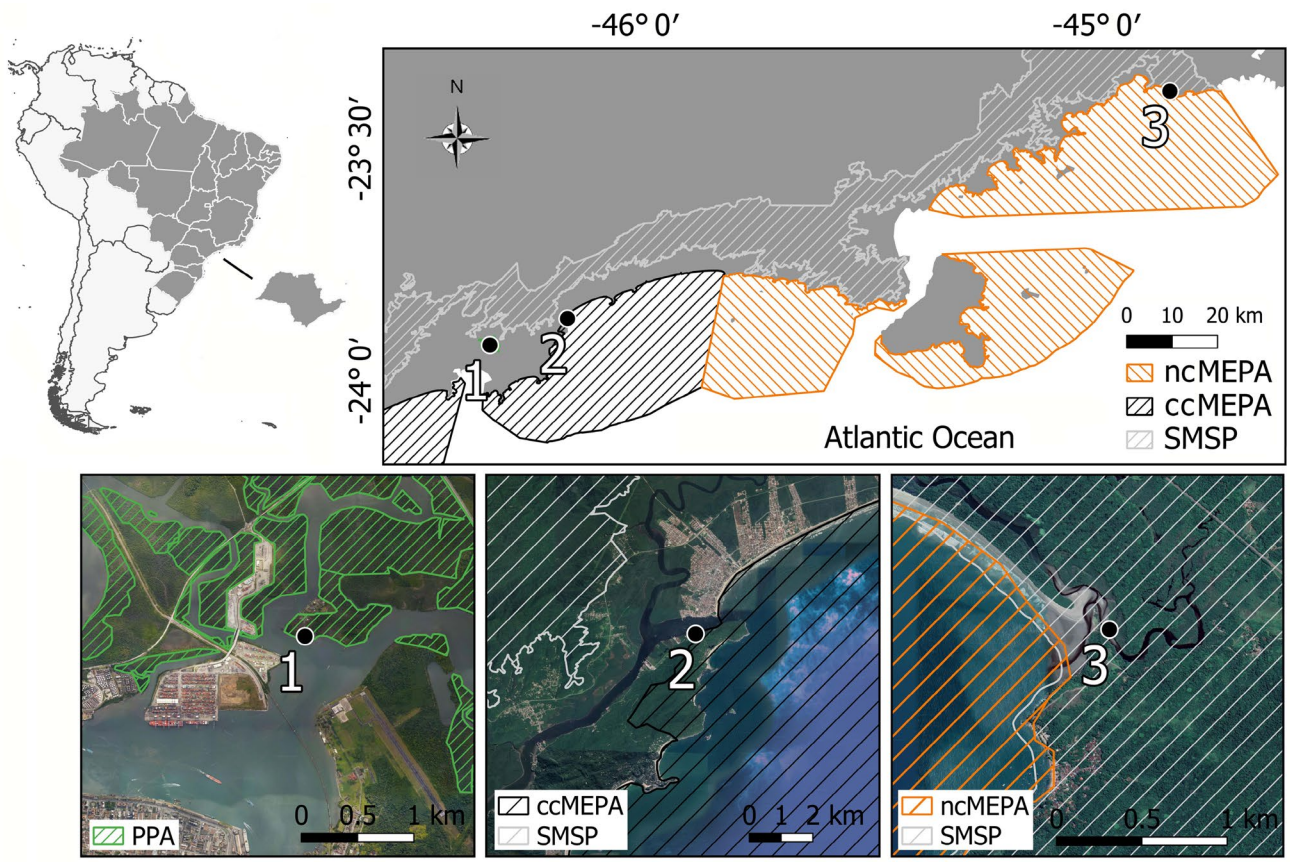

Fig. 1 Sediment sampling sites on the Atlantic coast of the State of São Paulo, Brazil (1, Rio Diana, Santos; 2, Rio Itapanhaú, Bertioga; 3, Rio Picinguaba, Ubatuba). *ncMEPA* northern coast Marine Environmental Protection Area. *ccMEPA* central coast Marine Environmental Protection Area, *SMSP* Serra do Mar State Park, *PPA* permanent protection areas, including mangrove forests in the Santos Estuarine System

(CETESB 1985) due to multiple pollution sources, such as uncontrolled urbanization, port and industrial activities and agricultural discharges like metals, fertilizers and pesticides. Despite programs to control and reduce pollution, many sectors of the SES remain severely polluted (Abessa et al. 2019; Ribeiro et al. 2016).The Rio Itapanhaú estuary that delimits the northern edge of Bertioga is also part of the SES, but is in a better state of conservation (Eichler et al. 2006). Metal contamination has not been encountered in sediments near the river itself (Gonçalves et al. 2013), although local fiddler crabs like *Minuca rapax* show high metal concentrations in their soft tissues (Capparelli et al. 2019). The main threats to this estuary include the urban growth of Bertioga, erosion of mangrove forest margins by boat traffic, pollution from marinas, fishing terminals, sewage and urban drainage (Cunha-Lignon et al. 2009). Rio Itapanhaú is included in the Marine Environmental Protection Area of the central coast (São Paulo 2008a, b), a mildly restrictive MPA focused on reconciling conservation demands and anthropogenic activities.

Rio Picinguaba is situated in the northern region of the São Paulo state coast near Ubatuba and lies within the Serra do Mar State Park (São Paulo 1977), an even more restrictive protected area aimed at conserving the Atlantic rainforest and its associated ecosystems.

Surveys at the three sites were undertaken during the southern summer (January) and winter (June) of 2013. Sediment sampling sites were chosen based on the degree of anthropogenic contamination, legal protection status and distance from known sources of pollution. Sediments were also collected from Praia Engenho d'Água (23° 47′ 15.4″ S; 45° 21′ 48.7″ W) facing the São Sebastião Channel on São Sebastião Island off the central coast of São Paulo to serve as negative controls in the toxicity tests. All sediments were sieved (1 mm mesh), washed in filtered seawater and stored at 4°C for a maximum of 1 month.

Approximately 150 g of surface sediment were collected from sand banks in each estuary. The samples were transferred to 50-mL falcon tubes and transported to the laboratory in an isoprene container. For metal analyses, aliquots were frozen at − 20°C; for toxicity experiments, aliquots were refrigerated at 4°C and tested within 10 days.

For granulometric analyses, each sediment sample was kiln-dried at 60°C for three days, and then macerated and sieved using a sieve set of known mesh diameters. Sediment granulometry was classified according to the Wentworth scale (Wentworth 1922). Calcium carbonate ($CaCO_3$) was analyzed following the digestion of duplicate, previously-dried, 2-g aliquots in 50% hydrochloric acid for 16 h. The difference between the initial and final sample masses provides the $CaCO_3$ content, and is given as a percentage. Total organic matter (TOM) was analyzed following the method of Loring and Rantala (1992). Duplicate, 10-g sediment samples, previously dried in an oven at 60°C for 3 days, were heated in a muffle furnace at 500°C for 3 h. The percentage TOM was calculated as the difference between the initial and final masses.

For elemental analyses, the sediment samples were digested using a microwave-assisted decomposition system (Milestone MSL Ethos Synth 1600, Sorisole, Italy): a 0.10 to 0.25 g aliquot from each sample was weighed in a PTFE flask, and 4 mL HNO_3/H_2O_2 (2 mL 14 mol/L HNO_3 + 2 mL 30% (v/v) H_2O_2) were added. The flasks were sealed and a specific heating program was set to decompose the samples for ≈30 min. The elements were identified and quantified by mass spectrophotometry using a plasma source (Elan DRC II ICP-MS, Perkin Elmer, CT, USA). All reagents were of analytical grade, except HNO_3 and HCl, which were previously purified using a quartz sub-boiling distillation system (Kürner Analysentechnik, Rosenheim, Germany). High purity deionized water was obtained from a Milli-Q water purification system (Millipore, MA, USA). All solutions were stored in high-density polyethylene bottles. Plastic materials were cleaned by immersion in 10% (v/v) HNO_3 for 24 h, washed five times with Milli-Q water and dried in a class 100 laminar flow hood before use. A multi-element solution containing 1000 µg/mL of each element (PerkinElmer Pure IV, N9303941 Multi-Element Standard Solution, PerkinElmer, CT, USA) was used as certified reference material to construct the calibration curves. The calculated limit of detection (LOD) was 0.001 µg/g. Validation was performed by analyzing percentage metal recovery from the certifed reference material (> 80%). All data are given as µg/g sediment dry weight.

A whole sediment toxicity test using the harpacticoid copepod *Nitokra* sp. was employed to evaluate sediment toxicity at the 'Laboratório do Núcleo de Estudos em Poluição e Ecotoxicologia Aquática' (UNESP), according to the protocol standardized by Lotufo and Abessa (2002). Four replicate samples of homogenized sediment of ≈2 mL each were placed in scintillation flasks, and 8 mL of dilute seawater (19‰ ± 2‰S) were added, giving a final volume of 10 mL. The seawater was collected at the Laje de Santos Marine State Park, located about 35 km off the central São Paulo State coast (24° 18′ 51.9″ S; 46°11′ 4.2″ W), and considered a pristine site. Salinity was adjusted by diluting this seawater with distilled water. After 24 h, 10 ovigerous female copepods were separated from our copepod culture and introduced into each replicate. The long-term copepod culture is maintained under constant conditions of temperature (25 ± 2°C), photoperiod (12 h light: 12 h dark) and salinity (15‰–17‰S) (see Lotufo and Abessa 2002), and the copepods are fed with a commercial brand yeast extract (Fleischmann, Associated British Foods plc) and microalgae twice a week. The test system was maintained in a photoperiod chamber (16 h light: 8 h dark), without aeration, at

25 ± 2°C. Chronic toxic effects of the sediment on copepod reproduction were assessed on culture day 10. The test copepods were fed at the beginning of the experiment by adding 100 µL of yeast extract prepared in a mixture of 50% dechlorinated, filtered tap water and 50% distilled water (1: 100 w/v). At the end of the experiment, the contents of each replicate were fixed in 10% formalin, stained with Rose Bengal stain and analyzed.

Physico-chemical parameters were measured at the beginning and end of the experiments (Table 1), i.e., dissolved oxygen and temperature (Digimed DM-4P, São Paulo, Brazil), pH (Lutron PH-206 pH meter, Taipei, Taiwan) and salinity (Index Instruments US, Inc., FG-211 Portable Refractometer, Fl, USA). The copepods were sieved from the sediment using a 45-µm diameter mesh sieve and examined under a stereomicroscope to identify and quantify the adult females and nauplii and copepodites.

The toxicological testing data were verified for normality of distribution and homoscedasticity using the Shapiro-Wilk and Bartlett tests, respectively. Toxicity effects were evaluated using a One-Way Analysis of Variance followed by Dunnett's multiple comparisons post-hoc t-test. Effects and differences compared to the control sediment were considered significant at $p = 0.05$. The data were further analyzed using a principal components analysis. All data were analyzed employing an R software package (R Core Team 2017).

Results and Discussion

The composition and metal concentrations quantified in the sediments at sites from Rio Picinguaba (RP), Rio Itapanhaú (RI) and Rio Diana (RD) during the southern summer and winter of 2013 are provided in Table 2. All metal concentrations fell below the toxic effect threshold (CCME 2001). Only the nickel concentration in the summer RI sediment was moderately high, according to the regional sediment quality values proposed by Choueri et al. (2009) (i.e., > 3.89 µg/g, level 1/moderately polluted; and > 6.02 µg/g, level 2/highly polluted). Percentage $CaCO_3$ ranged from 23% to 28% in most samples except for RP in summer that reached 87.5%. Rio Picinguaba sediments showed the lowest percentages of TOM, and exhibited considerable seasonal variation (3.5% summer, 58% winter). At RI and RD, TOM varied between 60% and 70% during summer. The RP sediments were sandier than at the other locations in both seasons (> 90%). Congruently, sediments at RD and RI showed higher percentages of mud (= silt + clay) (29% to 40%, and 16% to 27%, respectively). The high TOM levels are indicative of depositional processes at all sites, while $CaCO_3$ suggests marine influence. Muds, TOM and $CaCO_3$ are geochemical carriers and are likely associated with contaminant accumulation (Abessa et al. 2019; Cruz et al. 2019).

All physico-chemical parameters fell within acceptable ranges (Lotufo and Abessa 2002) during the experiments, except for low pH values for the RI site during both summer and winter (pH 1.2 and 3, see Table 1). Low pH values may reflect the influx of acid leachate from a nearby garbage dumpsite. High sulfur titers, whose oxidation can generate H_2SO_4 also may be present, or organic matter from the surrounding mangrove forest, including humic and fulvic acids, or sewage, may have contributed to the low pH (Wren and Stephenson 1991; Schubauer-Berigan et al. 1993). The toxicity test findings are given in Fig. 2. The hatching rates of *Nitokra* sp. exposed to the site sediments were significantly lower for the RI sediments in both summer and winter, and for RD in summer. The toxicity of the RD sediments in summer may be related to the high TOM concentrations (69%), which can accumulate toxic contaminants. The toxicity of the RI sediments may derive from the overall higher metal concentrations at this site, although only Ni exceeded the

Table 1 Physico-chemical parameters measured at the beginning (T_i) and end (T_f) of the 10-day sediment toxicity tests performed using *Nitokra* sp. during the southern summer (S) and winter (W) of 2013

Site	Season	Salinity (‰S)		Dissolved O_2 (mg/L)		pH		Temperature (°C)	
		T_i	T_f	T_i	T_f	T_i	T_f	T_i	T_f
Control	S	17.0	18.0	6.7	5.0	7.4	7.6	25.0	25.0
	W	17.0	18.0	6.7	5.0	7.4	7.6	25.0	25.0
RD	S	17.0	20.0	4.5	5.3	7.1	7.1	25.0	25.0
	W	17.0	20.0	4.3	5.2	7.0	7.0	25.0	25.0
RI	S	16.0	17.0	4.9	5.3	**3.0**	**1.2**	25.0	25.0
	W	17.0	17.0	5.4	3.7	7.4	4.7	25.0	25.0
RP	S	17.0	17.0	4.4	5.0	7.0	7.1	25.0	25.0
	W	17.0	18.0	5.4	4.5	7.5	7.2	25.0	25.0

Sediments were collected from Rio Diana (RD), Santos, Rio Itapanhaú (RI), Bertioga, and Rio Picinguaba (RP), Ubatuba. Control sediments were collected from Praia Engenho d'Água, São Sebastião Island, off the northern coast of São Paulo State. Only the two pH values indicated in bold exceed the limits recommended by Lotufo and Abessa (2002)

Table 2 Sediment composition ($CaCO_3$, Total Organic Matter [TOM], Sand and Mud [silt + clay], as percentages) and metal concentrations (μg/g dry weight) in sediment samples (N = 1) from Rio Picinguaba, Ubatuba (Serra do Mar State Park), Rio Itapanhaú, Bertioga (Marine Environmental Protection Area), and Rio Diana, Santos (Permanent Protection Area) collected during the southern summer (January) and winter (June) of 2013

	Rio Picinguaba		Rio Itapanhaú		Rio Diana	
	Summer	Winter	Summer	Winter	Summer	Winter
$CaCO_3$	85.7	28.6	27.8	25.1	23.7	25.6
TOM	3.5	58.0	59.6	64.2	69.8	63.2
Sand	92.8	97.3	72.3	83.4	70.7	59.1
Mud	7.2	2.7	27.7	16.7	29.3	40.9
Aluminum	1562.4	968.7	3785.7	4041.5	296.3	428.2
Arsenic	1.1	0.9	0.4	0.9	0.1	0.4
Barium	1.8	2.4	30.3	18.9	2.0	2.3
Cadmium	0.0	0.0	0.2	0.0	0.0	0.0
Lead	1.1	1.2	3.9	5.8	1.5	2.2
Cobalt	0.6	0.6	2.0	1.7	0.1	0.2
Copper	1.2	0.9	4.2	3.2	1.6	1.3
Chromium	5.0	3.8	4.4	4.1	0.7	1.1
Iron	2374.2	1764.2	5170.7	5851.8	291.0	459.5
Magnesium	728.0	764.1	1,267.0	1,321.6	189.1	538.0
Manganese	15.0	11.2	61.0	7.2	3.6	2.7
Nickel	1.0	4.2	**5.1**	2.7	0.8	1.2
Rubidium	2.4	2.8	25.1	24.8	1.0	1.4
Uranium	0.2	0.2	0.8	1.8	0.1	0.4
Vanadium	3.0	11.5	25.8	19.7	14.1	14.0
Zinc	7.5	7.6	28.5	24.6	2.8	3.1

The bold value indicates a nickel concentration that exceeds the Canadian Environmental Quality Guidelines for sediments (CCME 2001; Choueri et al. 2009)

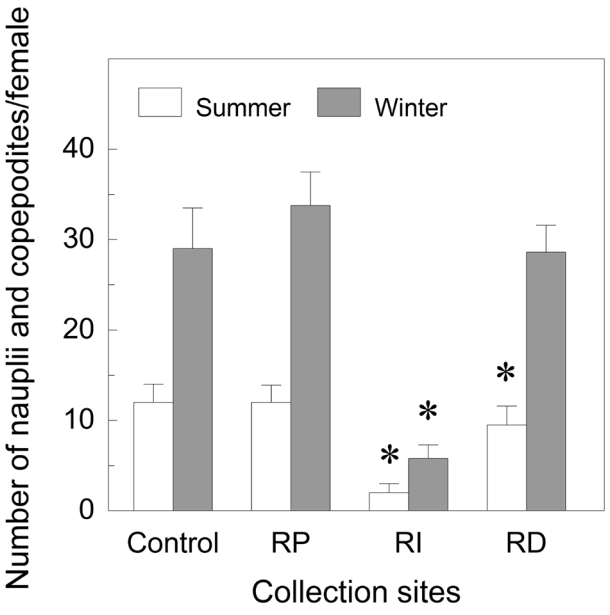

Fig. 2 Chronic toxicity effects on copepod (*Nitokra* sp.) reproduction, using sediments collected from the Rio Picinguaba (RP), Rio Itapanhaú (RI) and Rio Diana (RD) during the southern summer and winter of 2013. Data are mean (± SEM, N = 4) hatching rates (number of nauplii and copepodites divided by the total number of females [10]). *$p \leq 0.05$ compared to the respective control group (sediment from Praia Engenho d'Água, São Sebastião Island) for each season

threshold guidelines, in addition to the low pH (see Table 1). In this more acidic environment, metals may not be in a steady-state equilibrium, and may be bioavailable and toxic.

The first two principal components explained ≈83% of the total variance (Fig. 3), PC1 accounting for 62.2%. Most metals showed high positive correlations with PC1, while copepod fecundity correlated negatively, suggesting that metals contributed to toxicity. PC1 also separated RI (positive scores) from the other sites. Principal component 2 accounted for 22.8% of the variance, and revealed an association of sediment factors with positive correlations for TOM and Mud, with a negative correlation for $CaCO_3$ and toxicity, and for As and Cr. Rio Diana and Rio Itapanhaú showed positive scores during summer and winter, and were associated with muddy and organically enriched sediments. Rio Picinguaba showed negative scores.

The Rio Picinguaba site showed no relevant contamination. Given that this area is subject to the most restrictive level of legal protection as a state park, our findings suggest that the current protection policies are effective in avoiding pollution here. Lack of contamination and/or toxicity in marine and estuarine areas subject to more strict protective measures have been documented in other marine parks along the coast of São Paulo State (Moreira et al. 2019a, b; Abessa et al. 2017). Rio Diana is located within the SES, an area with a long history of environmental impact (Abessa

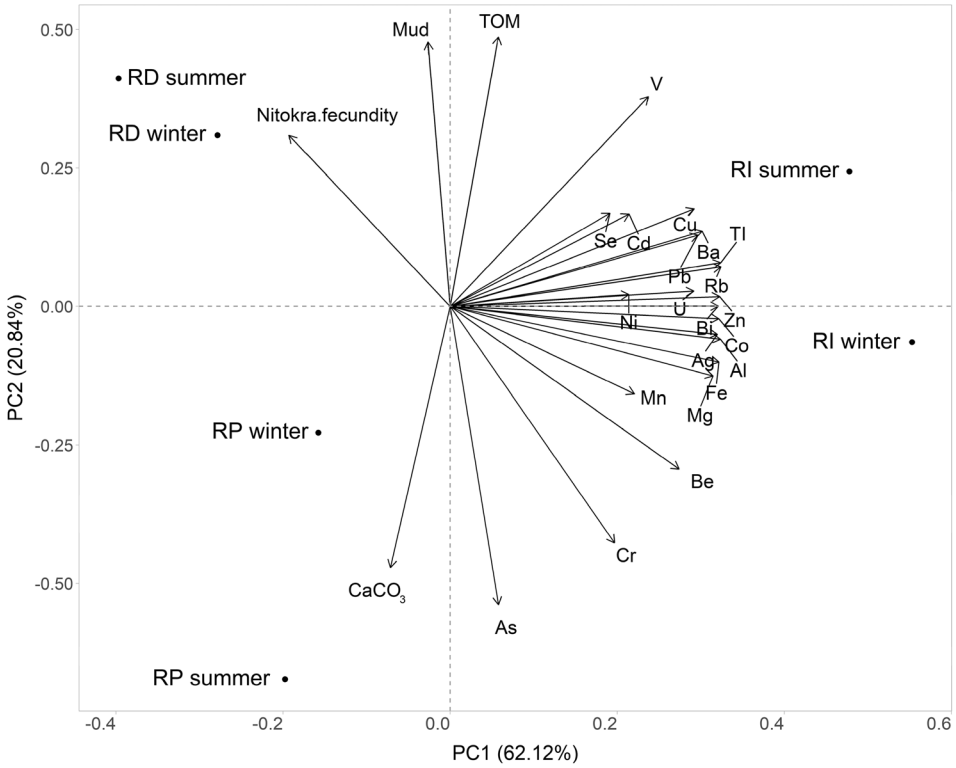

Fig. 3 Principal components analysis of sediment composition, elements and toxicity for samples collected from Rio Diana (RD, severely contaminated site), Santos, Rio Itapanhaú (RI, moderately contaminated site), Bertioga, and Rio Picinguaba (RP, pristine site), Ubatuba, during the southern summer and winter of 2013

et al. 2019; Luíz-Silva et al. 2006). Although the sediment quality of the main estuarine channels is well known, few studies have addressed the tributaries and smaller inlets of the SES. We found no relevant metal contamination at the RD site, although sediment was toxic in the summer. Since the RD sediments showed a high TOM concentration, organic contaminants like polycyclic aromatic hydrocarbons (PAHs) may have been present, causing the summer toxicity (Abessa et al. 2019; Gusso-Choueri et al. 2018). Rio Diana sediments are considered to be low to moderately contaminated (Perina et al. 2018) and chronic toxicity is associated with the Santos Port operations, which lead to high sediment concentrations of acenaphthene, acenaphthylene and lead. The northeastern segment of the SES that includes Rio Diana suffers the indirect influence of a large steel plant, considered to be the main source of PAHs and some metals, together with discharge from fertilizer plants.

The sediments at the Rio Itapanhaú site were the most toxic and exhibited the highest concentrations of metals in both summer and winter, compared to the other locations While below the thresholds of sediment quality guidelines, these metals appear to be bioavailable and cause toxicity. Although the Rio Itapanhaú estuary is separated from the more contaminated segments of the SES, its sediment quality is considered moderately impacted (Zaroni 2006; Pozo et al. 2011). The Rio Itapanhaú area presents increasing degradation, exhibiting augmented levels of organic matter, fecal bacteria and contaminants like mercury and arsenic (CETESB 2006; Sousa et al. 2014; Ferraz et al. 2017). Thus, while protected by the Brazilian Forest Code as a PPA, and included within a less restrictive MPA, this area shows clear signs of environmental impact, revealing that these means of legal protection are ineffective. Other estuarine areas under similar protection such as the Cananéia-Iguape-Peruíbe Environmental Protection Area (Cruz et al. 2019) and Paranaguá Bay estuary (Rodrigues et al. 2013) also show environmental contamination and toxicity.

The designation of a given location as a protected area often includes not only restrictions on physical destruction, but also on polluting activities (see Kelleher 2005). Since different categories of MPA may endorse different levels of restriction, our study aimed to evaluate whether the current restrictions are effective in preventing or reducing pollution. State Parks are very restrictive and prohibit most human activities, including pollution of any kind. Such parks also impose restrictions in their buffer zones to aid in assuring effective protection. This is the case for Rio Picinguaba. At Rio Itapanhaú, human activities are less restricted than in the Serra do Mar State Park, although pollutant discharge is prohibited. However, since some human activities are permitted such as fishing, marinas, tourism and housing, among others, this type of MPA requires closer monitoring and control to ensure that its ecosystems are kept healthy. Finally, Permanent Protection Areas such as mangrove forests, established by the Brazilian Forest Code, do not explicitly mention the control of pollution sources. However, this law

does establish that mangroves and their surrounding ecosystems cannot be destroyed, producing an indirect effect on pollution sources, by inhibiting their installation in or near mangroves, and in riverine or other coastal ecosystems. This is the main legal protection for Rio Diana; the mangroves at Rio Itapanhaú and Rio Picinguaba are also protected by the Brazilian Forest Code in addition to their MPA status. Although our study areas are located in protected areas, some may be affected by contaminants generated externally, which are then carried into the MPAs by river currents.

Our findings also reveal that although the metal concentrations measured at the Rio Itapanhaú and Rio Diana sites lie below the threshold limits of established quality guidelines, these sediments are toxic. We conclude further that the mere designation of estuarine localities as PPAs or as less restrictive types of MPAs does not provide an effective safeguard against contamination. Other management practices are necessary to assure the effectiveness of estuarine protection measures.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could influence the present investigation.

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