



Sediment quality in a metal-contaminated tropical bay assessed with a multiple lines of evidence approach[☆]



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ARTICLE INFO

Article history:

Received 8 November 2016

Received in revised form

6 May 2017

Accepted 17 May 2017

Available online 24 May 2017

Keywords:

Metal bioavailability

Equilibrium-partitioning model

Metal toxicity tests

Macrobenthos

Sepetiba Bay

ABSTRACT

A sediment quality assessment was performed near to the main industrial source of metal contamination in Sepetiba Bay, Brazil, which represents one of the worst cases of trace metal contamination reported for coastal areas. Acute and chronic toxicity tests, benthic fauna community analysis and metal bioavailability evaluations were applied to identify risks to the benthic community. Significant amphipod mortality was observed close to the major pollution source and lower copepod fertility was observed for all stations. Equilibrium-partitioning and biotic-ligand models to predict pore water metal toxicity, which were based on acid-volatile sulfide (AVS) and organic carbon fraction (f_{OC}) normalization approaches, suggested that metals are not likely to be available in sediment pore water. However, Cd, Pb and Zn concentrations were mainly (>50%) weakly bound to sediments, suggesting high potential bioavailability. Linking the chemical results with ecotoxicological responses, we observed that sediment-feeding organisms presented acute and chronic toxicities that were positively correlated to the metal concentrations in the sediments. Additionally, benthic fauna composition was dominated by tolerant species, revealing a trophic structure response to environmental contamination. These results reinforce the necessity of a multiple lines of evidence approach to establish sediment quality and to support environmental management decisions that are based on observed effects and potential extrapolation scenarios into the future.

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1. Introduction

Environmental quality assessments are essential to support sustainable development-driven public policies. For instance, these

assessments may benefit watershed committees, coastal management planning and the development of new monitoring programs and protocols (Balthis et al., 2014; ITRC, 2015). In this sense, multidisciplinary approaches to evaluate the quality of aquatic systems have been performed with the aim of improving our capacity to evaluate wide ranges of environmental conditions (e.g., in relation to pollutant availability and biological diversity; Burton, 2017), which have been supported by the application of multiple lines of evidence (LOEs) (Chapman and Hollert, 2006; Campos et al., 2016). Considering the LOEs approach, generally at least three lines of evidence are studied in sediment quality assessments: (1)

[☆] This paper has been recommended for acceptance by Prof. W. Wen-Xiong.

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physical and chemical characterization; (2) ecotoxicity evaluation; and (3) ecological effects.

Biological parameters can provide information about ecosystem quality and also reflect the general ecological condition of the water body (Hale and Helstshe, 2008). For instance, ecological indexes are commonly used to enhance environmental impact assessments in aquatic communities (Dauven, 2007). These indexes reflect the tolerances and relative sensitivities of organisms to different environmental conditions. Macrobenthic species can be used to support the evaluation of environmental quality, representing physiological diversity and a variety of life strategies, as well as long lifecycles and low mobility (Pearson and Rosenberg, 1978).

Sediments have often been applied as matrixes for environmental quality studies since they act as records of aquatic processes and toxic substance discharges. Sediments also behave as a secondary source of contamination, since toxicants may be partly released if desorption processes occur (Roberts, 2012; Eggleton and Thomas, 2004).

For reduced sedimentary conditions, Di Toro et al. (1990, 1992) presented an equilibrium-partitioning model to predict metal toxicity limitation linked to acid-volatile sulfides (AVS). Since FeS is the major AVS constituent, the divalent metals dissolved in pore water can displace the Fe from the FeS, forming more stable metal monosulfides (Di Toro et al., 1990; Allen et al., 1993). Molar differences or ratios between the sum of simultaneously-extracted Cd, Cu, Ni, Pb and Zn (Σ SEM) and AVS concentrations can indicate the occurrence of sufficient AVS to retain Σ SEM (i.e., Σ SEM/AVS ratio < 1) and, consequently, this equilibrium-partitioning model can be used as a tool to predict pore water toxicity, as supported by empirical data from toxicity tests (Di Toro et al., 1992). Di Toro et al. (2005) later proposed a biotic-ligand model derived from the potential role of the organic carbon fraction (f_{OC}) to trap Σ SEM concentrations that exceed the AVS levels in the sediments, represented by $(\Sigma$ SEM – AVS)/ f_{OC} . According to those authors, no toxicity was observed when these ratios were lower than $100 \mu\text{mol g}^{-1} \text{OC}$, regardless of the trace metal identities (Di Toro et al., 2005).

Here, we aimed to provide a sediment quality evaluation based on multiple LOEs in tropical Sepetiba Bay, which has been severely polluted by metals over recent decades. We assessed the influence of a contamination hotspot on macrobenthic community structure and on acute and chronic ecotoxicological effects, coupled with AVS-based evaluations of metal bioavailability. Cd and Zn total concentrations in sediments can reach values as high as 200 and $40,000 \mu\text{g g}^{-1}$, respectively, in a contamination hotspot near to the major source of metals in this coastal system (Barcellos and Lacerda, 1994), representing one of the worst cases yet described of metal pollution in coastal areas. Though chemical contamination of sediments (as reviewed by Molisani et al. (2004)), suspended particulate matter (Lacerda et al., 1987; Araújo et al., 2017a) and benthic organisms (e.g., Lacerda and Molisani, 2006; Araújo et al., 2017b) have previously been studied for this bay, there is a lack of information on multiple LOEs for this impacted system.

The primary motivation of our study is to provide useful information to scientists and environmental managers and to identify critical gaps that need to be filled by future research on sediment trace metal bioavailability in contaminated sediments, as well as the applicability of a multiple lines of evidence approach.

2. Study area

Sepetiba Bay is shallow but has suitable hydrodynamic conditions to allow navigation, which facilitates port, tourist and fishery activities (Calil et al., 2006). Despite the local biological richness and good navigability, public policies for Sepetiba Bay are not

focused on conservation, tourism or fishery development. Instead, industrial and port activities are expanding.

Itaguaí Harbor is located on Madeira Island in the northern region of the bay (Fig. 1). This strategic position has stimulated a variety of industrial settlements. Besides multiple diffuse sources of contamination nearby (e.g., due to urban and industrial discharges into the São Francisco and Guarda channels; Fig. 1), Madeira Island hosted industrial wastes from the Ingá Metallurgical Company (closed in 1998) that produced a metallic alloy of Zn from Calamine ore (Barcelos et al., 1997). In 2010, the waste pile was decommissioned (HAZTEC/USIMINAS, 2010). During this industrial activity, which began in 1958, the dam containing the industrial wastes was breached several times, discharging vast quantities of metal waste into Saco do Engenho Creek (SEC) that flows into the bay. Such discharges also occurred after the industrial activity had ceased. This point source of contamination resulted in extremely elevated inputs of Cd and Zn into the bay, which have mainly dispersed in the northern and northeastern regions of the system (e.g., Marques et al., 2006; Gomes et al., 2009). However, these chemicals also spread to the furthest reaches of the bay (Patchineelam et al., 2011). Concerns regarding metallic pollutants throughout Sepetiba Bay have been reported since the 1980s (Lacerda et al., 1983; Pfeiffer et al., 1985; Souza et al., 1986; Lacerda et al., 1987; Barcellos and Lacerda, 1994; Molisani et al., 2004; Gomes et al., 2009; Ribeiro et al., 2013; Monte et al., 2015). This pollution warrants careful monitoring, given the potential for metal bioaccumulation in organisms, including seafood (Lacerda and Molisani, 2006; Lino et al., 2016).

3. Materials and methods

3.1. Sampling

Surface sediments were sampled in August 2011. Five sampling sites were established near Madeira Island (Fig. 1). At each site, sediment samples (five replicates per site) were taken using a van Veen grab, stored in plastic bags, and refrigerated for transport to the laboratory. Three sites were located around the margins of Madeira Island (stations P1, P2 and P3), with station P2 located at the mouth of SEC. The two other stations were chosen as control areas, and reflect the dominant direction of water circulation into the bay; one site at Coroa Grande Sound (station C1) and another near Itacuruçá Island (station C2). We did not expect these latter two stations to be pristine, since diffuse pollution due to urbanization may occur. Instead, in the absence of proximal pristine conditions, these sites represent sedimentary conditions without the severe influence of metal loading from SEC. For each sediment replicate, subsamples were separated for toxicity tests, benthic community characterization and chemical analyses. For ecotoxicological assays, the sediments were refrigerated (-4°C), whereas aliquots used for chemical analyses were kept frozen.

3.2. Grain size

Sediment grain size analysis was carried out using 2 g subsamples of wet sediments, after agitation for 24 h in 30 mL of a dispersant solution (Na_3PO_3). This analysis was performed using a laser diffraction particle analyzer (CILAS 1064). The results were analyzed using the software GRADISTAT version 8 (Blott and Pye, 2000), with equations proposed by Folk and Ward (1957). Grain size classification follows the Shepard diagram (Shepard, 1954).

3.3. Total organic carbon (TOC)

TOC concentrations were determined using a Shimadzu

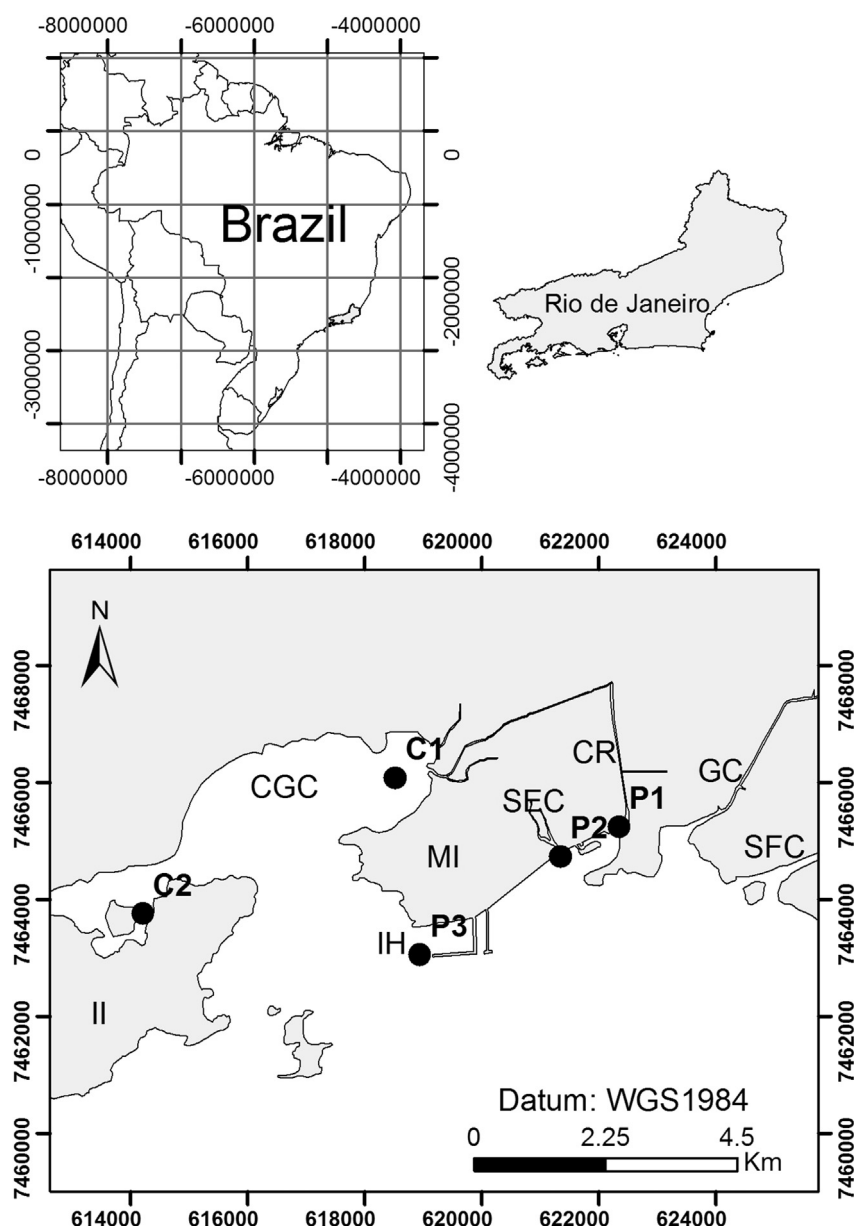


Fig. 1. Map of South America highlighting Rio de Janeiro state in grey. Below: study area location, with black circles indicating the positions of sampling sites. Abbreviations: CGC – Coroa Grande Cove; CR – Cação River; GC - Guarda Channel; II – Itacuruça Island; IH – Itaguaí Harbor; MI - Madeira Island; SEC - Saco do Engenho Creek; SFC - São Francisco Channel.

analyzer, with a module for solid samples. This analysis was carried out after removal of carbonates from sediment subsamples by acidification, which was achieved by agitation for 16 h in a 0.1 mol L^{-1} HCl solution.

3.4. AVS, ΣSEM and residual metal concentrations

The sediment subsamples used for SEM and AVS analyses were kept frozen in glass flasks. These sediments were submitted to a purge and trap extraction technique (USEPA, 1991). Wet samples were submitted to a cold acid distillation with 6 mol L^{-1} HCl solution and the released H_2S was trapped in 0.5 mol L^{-1} NaOH, using N_2 as a carrier gas. Afterwards, the AVS concentrations were determined using a UV FEMTO model 700 PLUS spectrophotometer (São Paulo, Brazil). The acid sediment suspensions were centrifuged

and filtered for determination of simultaneously-extracted metals ($\Sigma\text{SEM} = \text{SEM}_{\text{Cd}} + \text{SEM}_{\text{Cu}} + \text{SEM}_{\text{Ni}} + \text{SEM}_{\text{Pb}} + \text{SEM}_{\text{Zn}}$). The residual sediment was dried at 60°C and submitted to a new extraction according to the EPA 3051A method (i.e., a microwave-assisted digestion in concentrated HNO_3). A Jobin Yvon Horiba Ultima 2 model (Longjumeau, France) ICP OES was used to determine the metal concentrations (Fe, Mn, Cd, Cu, Ni, Pb and Zn) from both extractions. These metal determinations have been suggested by Di Toro et al. (1990, 1992) to calculate the $\Sigma\text{SEM}/\text{AVS}$ index. The sum of metal concentrations obtained by the HCl extraction and the USEPA 3051A extraction of residues were conducted to facilitate comparisons with sediment quality guidelines, as performed elsewhere (Machado et al., 2010; Monte et al., 2015).

3.5. Sediment Quality Guideline Quotients (SQGQs)

Fairey et al. (2001) proposed an integrated application of SQGs as Sediment Quality Guideline Quotients (SQGQs) to estimate how many of these thresholds were exceeded on average. According to the authors, these quotients are average values of the ratios between contaminant concentrations and the respective SQG value for each element measured. Values greater than 1.0 indicate that the chemical concentrations in that sample likely exceed the respective thresholds. Here, we evaluated five trace metals in relation to SQGs adopted in Brazilian legislation (CONAMA, 2012), according to the equation:

$$SQGQ = \sum_{n=1}^5 \left(\frac{[Cd]}{L2_{Cd}} + \frac{[Cu]}{L2_{Cu}} + \frac{[Ni]}{L2_{Ni}} + \frac{[Pb]}{L2_{Pb}} + \frac{[Zn]}{L2_{Zn}} \right) / 5$$

where L2 corresponds to Level 2 of the CONAMA guidelines, which is the threshold for a high probability of adverse biological effects. The classification criteria for SQGQs, adapted from Fairey et al. (2001) by Abessa et al. (2008), include four possible conditions of environmental risk: non-risk (SQGQ between 0 and 0.1), discrete risk (SQGQ between 0.1 and 0.25), environment under risk of impact (SQGQ values from 0.25 to 1), and strong risk of impact (values >1).

3.6. Whole sediment toxicity tests

Whole sediment toxicity tests have been used routinely to evaluate the sediment quality at sites influenced by contaminant release as well as dredged materials. These tests can assess both chronic and acute toxicities. Chronic toxicity involves effects that affect different phases of the lifecycle of an organism, whereas the acute toxicity involves severe effects in exposed individuals within a short time period (Zagatto and Bertoletti, 2006).

3.6.1. Acute toxicity test with *Tiburonella viscana*

We applied the method described by Swartz et al. (1985) and adapted to the amphipod *T. viscana* by Melo and Abessa (2002). The technique consists of exposing adult amphipods to sediment samples for 10 days. During this period, animal survival and condition (e.g. burrowing) are assessed. Amphipods were collected from Ilha Bela (an unpolluted site located on the north coast of São Paulo State, SE Brazil), and were acclimated in the laboratory under the test conditions for 3–5 days.

One day before starting the test, sediment samples and clean control sediments (from Ilha Bela) were homogenized, and sub-samples were distributed into test chambers (1 L polyethylene beakers). Sediments were not sieved. A sediment layer of 2 cm depth and 750 mL of filtered seawater were introduced into each test chamber. On the following day, 10 amphipods were added to each test chamber. Amphipods that did not bury themselves into sediments within 1 h were removed and replaced. Five replicates per test sediment were prepared. The overlying water used in the test chambers was monitored to control physico-chemical parameters according to the *T. viscana* test acceptability criteria reported by Melo and Abessa (2002). After ten days, lethal effects were recorded by sieving the contents of the test chambers through a 0.5 mm mesh and counting the surviving amphipods. Missing organisms were considered as being dead.

3.6.2. Chronic toxicity test with *Tisbe biminiensis*

Chronic toxicity tests with the copepod *T. biminiensis* followed the method of Araújo-Castro et al. (2009). Each test flask contained a sediment layer of 2 cm depth comprising sediment samples or

control sediments from Ilha Bela covered with 30 mL of filtered seawater. These systems underwent a 24 h stabilization period in a hatchery at 25 °C, with a 12 h/12 h photoperiod. After this time, 10 ovigerous age-matched (~12 days) female *T. biminiensis* were placed in each flask. *T. biminiensis* specimens were obtained from a laboratory-based permanent cultivation (Núcleo de Estudos em Poluição e Ecotoxicologia Aquática, NEPEA/UNESP). After 7 days, 4% formaldehyde with rose Bengal was added to test flasks. The sub-lethal effects were assessed as fecundity estimates, corresponding to the number of individuals (copepodits + nauplii) produced by females over the course of the test.

3.7. Macrobenthic community characterization

The five replicates of sediments collected at each station were sieved (0.5 mm mesh) and the remaining material was fixed with 4% formaldehyde in situ. In the laboratory, the samples were washed, preserved in 70% ethanol and sorted under a stereomicroscope to isolate the benthic macrofauna. Identification of macrofaunal specimens was done to the lowest possible taxonomic level with the aid of identification keys and confirmed by experts. The macrobenthic assemblage was characterized by the following biotic indexes: Shannon diversity, Pielou evenness, Simpson dominance, and Richness (number of species), according to Magurran (2004).

3.8. Statistical analyses

Statistical treatments were performed using the software *Statistica 8.0*. Variance analyses were applied for metal concentrations, grain size, Σ SEM/AVS, and total organic carbon, with the aim of identifying differences between the sites. Normality was checked with the Shapiro-Wilk test, and any datasets that had to be modified were log-transformed (base 10 logarithm). Analysis of variance (ANOVA) followed by a Tukey HSD test was applied to identify differences between the averages of *T. biminiensis* tests. Data from the *T. viscana* test did not achieve normality so a Kruskal-Wallis test was applied. The significance level for all tests was 0.05.

Trends in spatial distribution of the benthic fauna were explored by n-MDS ordination of our Bray-Curtis index database on abundance (fourth root-transformed). Principal Component Analyses (PCA) were performed to identify possible associations between datasets from the different LOEs.

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

Adopted QA/QC procedures included the use of replicates and repeatability tests for TOC, as well as the use of blanks and standards for these analyses. For metals, standard curves were established using fortified solutions of known concentrations. To validate the analytical procedure used for metal analyses, the standard certified sediment (NIST 2782) was analyzed, and recoveries of Cu, Fe, Mn, Ni, Pb and Zn ranged from 95% to 107%. However, the certified sediment we used does not have a certified value for Cd.

For toxicity tests, additional bioassays were conducted with reference substances (ABNT, 2006) to estimate detection limits. Reference substance tests (48-h, potassium dichromate, $K_2Cr_2O_7$) were performed for *T. viscana* in aqueous solution and the estimated median lethal concentration (LC_{50}) value was 13.92 mg L^{-1} of $K_2Cr_2O_7$. Lower and upper confidence limits for these tests corresponded to 11.45 and 16.91 mg L^{-1} , respectively, which are within the range defined by the internal control chart (5.86 – 14.83 mg L^{-1} of $K_2Cr_2O_7$) and are comparable to values previously estimated for this species (Abessa and Sousa, 2005). The LC_{50} for the *T. biminiensis* test was estimated with $K_2Cr_2O_7$ using the Trimmed-Sperman-

Karber program and the value obtained was 14.38 mg L^{-1} . Lower and upper confidence limits for these tests of 11.59 and 16.87 mg L^{-1} are near to those estimated by Araújo-Castro et al. (2009).

4. Results and discussion

4.1. Sediment geochemistry

Bulk sediment properties are presented in Table 1. Poorly-sorted silt-sand was the predominant grain size, with an average 70% of fine sediments (silt + clay), except for station P3 (classified as fine silt, with 99% of fine sediments). TOC content ranged from 1.5% to 4.3%, with higher concentrations observed at stations P1 and P2 and lowest values found at stations C1 and P3. All sediment samples presented reduced conditions with a redox potential ranging between -136 and -281 mV .

The sum of metal concentrations obtained by the SEM and USEPA 3051A procedures are given in Table 1. Fig. 2 presents the percentages of HCl-soluble and residual fractions. Iron and manganese concentrations presented the same pattern, with the residual fractions predominating at all sites except for the Mn HCl-soluble fraction at P2 (Fig. 2). Lead and copper concentrations also evidenced accumulation at station P2 but, at stations P3 and C1, more than half of the content of these two metals were assigned to their respective residual fractions (Fig. 2). Nickel concentrations ranged from 2.7 to 5.9 mg kg^{-1} in the study area and followed the pattern for Fe (Fig. 2), suggesting natural occurrence of this element. Total concentrations of cadmium ranged from 0.55 to 16.11 mg kg^{-1} and zinc from 168 to 3039 mg kg^{-1} , both of which exhibited the same pattern over all stations, with higher percentages in the HCl-soluble fraction.

Overall, the highest metal concentrations were found at station P2 (Table 1), which lies at the mouth of SEC. Since the 1960s, this tidal channel receives land-based input from an old industrial waste pile located on Madeira Island (Barcellos and Lacerda, 1994; Gomes et al., 2009; Ribeiro et al., 2013).

We compared our metal concentrations with national Sediment Quality Guidelines (SQG) (CONAMA, 2012). Only cadmium and zinc concentrations exceeded SQGs. Cd values exceed thresholds for both low probability of adverse biological effects (Level 1: 1.2 mg kg^{-1}) and for high probability of adverse biological effects

(Level 2: 7.2 mg kg^{-1}). Station P2 had a maximum Cd concentration 19 times higher than Level 1 and 3 times higher than Level 2. Zn concentrations exceeded Level 1 (150 mg kg^{-1}) for all sites. The maximum Zn concentration observed at station P2 was 30 times higher than Level 1 and 11 times higher than Level 2 (410 mg kg^{-1}).

SQGs exhibited considerable spatial variability (Fig. 3). The values found for station P2 (at the mouth of SEC) were around 2, which was higher than for station P1 (with an average value of 1.38). Therefore, both these stations were classified as highly contaminated. By comparison, stations P3, C1 and C2 presented low level contamination, with average SQGs of 0.21, 0.13 and 0.19, respectively.

The regional background value for Zn is 54 mg kg^{-1} , as estimated by Gomes et al. (2009), which is up to 80 times lower than the maximum Zn concentration observed at station P2. The HCl-soluble fractions for Cd and Zn were clearly dominant at stations P1, P2 and C2 (Fig. 2). Monte et al. (2015) also reported high concentrations of Cd (17.77 mg kg^{-1}) and Zn (3854 mg kg^{-1}) in samples taken near to SEC and analyzed in an HCl 1 mol L^{-1} solution.

4.2. $\Sigma\text{SEM}/\text{AVS}$ and organic carbon fraction

AVS concentrations were detected at all sites and ranged from 14.26 to $41.46 \text{ } \mu\text{mol g}^{-1}$, with higher values at stations P2 and P1 (Table 2). The sum of simultaneously extracted metals (ΣSEM) varied from 1.5 to $37.66 \text{ } \mu\text{mol g}^{-1}$, with highest values at station P2 and lowest values at station C1. $\Sigma\text{SEM}/\text{AVS}$ ratios were above 1.0 at P1 (ranging between 1.10 and 2.30). According to the Di Toro et al. (2005) model, $(\Sigma\text{SEM}-\text{AVS})/f_{\text{OC}}$ values below $100 \text{ } \mu\text{mol gOC}^{-1}$ predict non-significant chronic and acute effects on benthic organisms. Station P1 showed $(\Sigma\text{SEM}-\text{AVS})/f_{\text{OC}}$ ratios significantly higher than observed at the other sites ($p < 0.02$), reaching an average value of $295 \text{ } \mu\text{mol gOC}^{-1}$. Both AVS and TOC contents were not sufficient to support that metals would not accumulate in pore water, which does not support a prediction of non-toxicity at station P1. All other sites presented average $\Sigma\text{SEM}/\text{AVS}$ ratios below 1.0 and average $(\Sigma\text{SEM}-\text{AVS})/f_{\text{OC}}$ ratios below $100 \text{ } \mu\text{mol gOC}^{-1}$, suggesting non-toxicity arising from metal availability in sediment pore water (Di Toro et al., 1992; Di Toro et al., 2005). However, it is important to highlight that lower ΣSEM levels do not necessarily imply free pore water metal toxicity (Di Toro et al., 1992; Ribeiro et al., 2013).

Table 1

Sediment chemical composition, grain size and redox potentials obtained for 5 replicates from each sampling site. The sum of SEM + residual metal concentrations is compared with SQGs (CONAMA, 2012), values exceeding guidelines were in bold. Metal concentrations are in mg kg^{-1} .

| | | Fe | Mn | Cd | Cu | Ni | Pb | Zn | TOC (%) | Sand (%) | Silt (%) | Clay (%) | Eh (mV) |
|----|------|--------|--------|--------------|-------|------|-------|-------------|---------|----------|----------|----------|---------|
| P1 | Mean | 29,011 | 225.33 | 10.71 | 15.25 | 2.77 | 26.83 | 2118 | 3.76 | 26.05 | 65.48 | 8.47 | -136 |
| | Min. | 26,621 | 211.54 | 8.88 | 13.36 | 2.46 | 22.49 | 1808 | 2.51 | 0 | 56.89 | 2.23 | -130 |
| | Max. | 31,299 | 241.65 | 11.97 | 16.73 | 3.14 | 29.46 | 2329 | 4.79 | 40.01 | 70.07 | 29.93 | -155 |
| | SD | 1973 | 12.06 | 1.22 | 1.33 | 0.29 | 2.7 | 225 | 0.84 | 15.48 | 5.56 | 12.01 | 10.67 |
| P2 | Mean | 35,495 | 282.27 | 16.11 | 25.29 | 3.22 | 44.66 | 3039 | 4.31 | 23.16 | 71.75 | 5.09 | -281 |
| | Min. | 29,420 | 238.35 | 12.21 | 17.02 | 2.71 | 34.47 | 2152 | 3.8 | 20.79 | 67.3 | 4.84 | -280 |
| | Max. | 39,184 | 423.64 | 23.5 | 33.32 | 3.6 | 63.58 | 4567 | 4.79 | 27.63 | 74.38 | 5.37 | -295 |
| | SD | 3847 | 79.37 | 4.36 | 5.8 | 0.34 | 11.19 | 914 | 0.36 | 2.65 | 2.66 | 0.21 | 11.13 |
| P3 | Mean | 34,160 | 226.81 | 1.03 | 12.31 | 5.94 | 19.61 | 260 | 1.49 | 0.7 | 83.02 | 16.28 | -168 |
| | Min. | 31,914 | 208.81 | 0.55 | 10.84 | 5.61 | 18.76 | 127 | 1.45 | 0.25 | 80.64 | 13.03 | -160 |
| | Max. | 37,816 | 239.23 | 2.67 | 15.38 | 6.36 | 20.31 | 740 | 1.53 | 1.45 | 86.53 | 19.11 | -178 |
| | SD | 2345 | 12.47 | 0.92 | 1.81 | 0.29 | 0.67 | 268 | 0.04 | 0.56 | 2.79 | 2.97 | 7.24 |
| C1 | Mean | 34,978 | 228.92 | 0.54 | 9.9 | 3.98 | 11.5 | 168 | 1.85 | 24.65 | 71.17 | 4.18 | -239 |
| | Min. | 30,789 | 195.38 | 0.48 | 8.56 | 3.53 | 9.73 | 132 | 1.72 | 23.58 | 69.33 | 3.75 | -210 |
| | Max. | 39,401 | 254.11 | 0.61 | 10.98 | 4.88 | 14.96 | 191 | 1.93 | 25.38 | 72.41 | 5.3 | -264 |
| | SD | 3072 | 22.2 | 0.05 | 1.1 | 0.54 | 2.24 | 22 | 0.08 | 0.74 | 1.21 | 0.64 | 24.31 |
| C2 | Mean | 32,647 | 234.28 | 1.1 | 10.61 | 3.54 | 12.39 | 268 | 3.16 | 27.9 | 68.12 | 3.98 | -239 |
| | Min. | 28,920 | 189.04 | 0.74 | 8.57 | 3.2 | 10.1 | 197 | 3.08 | 26.02 | 66.01 | 3.8 | -218 |
| | Max. | 37,440 | 327.07 | 2.11 | 16.35 | 4.02 | 19.33 | 502 | 3.25 | 30.19 | 69.58 | 4.4 | -258 |
| | SD | 3761 | 57.33 | 0.57 | 3.24 | 0.34 | 3.96 | 132 | 0.06 | 1.6 | 1.44 | 0.24 | 19.94 |

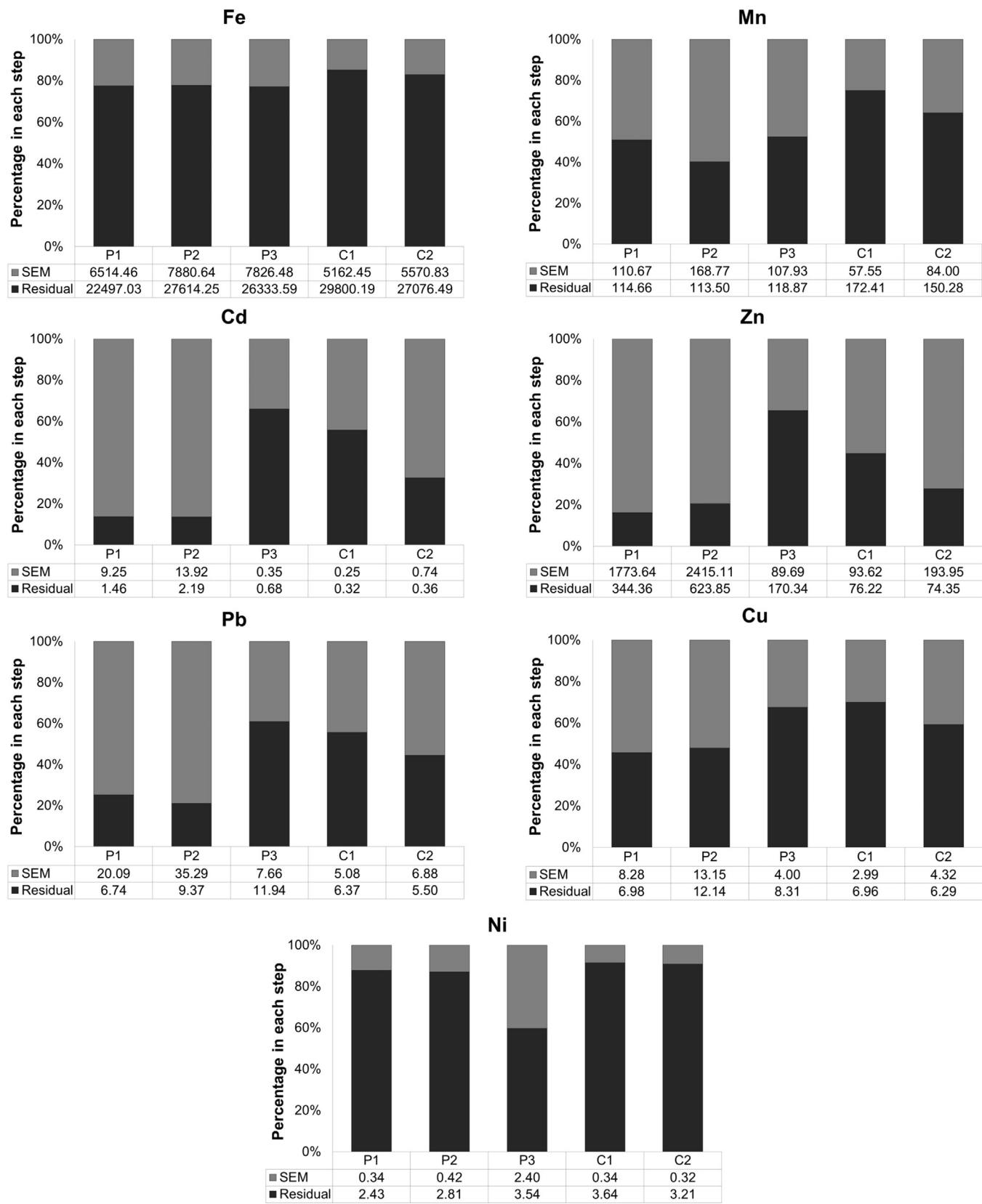


Fig. 2. Percentages of metals (Fe, Mn, Cd, Cu, Pb, Ni and Zn) in each extraction for all sampling sites. The number below each bar corresponds to the mean of five replicates per site in the SEM and residual fractions. Concentrations are expressed in mg kg⁻¹.

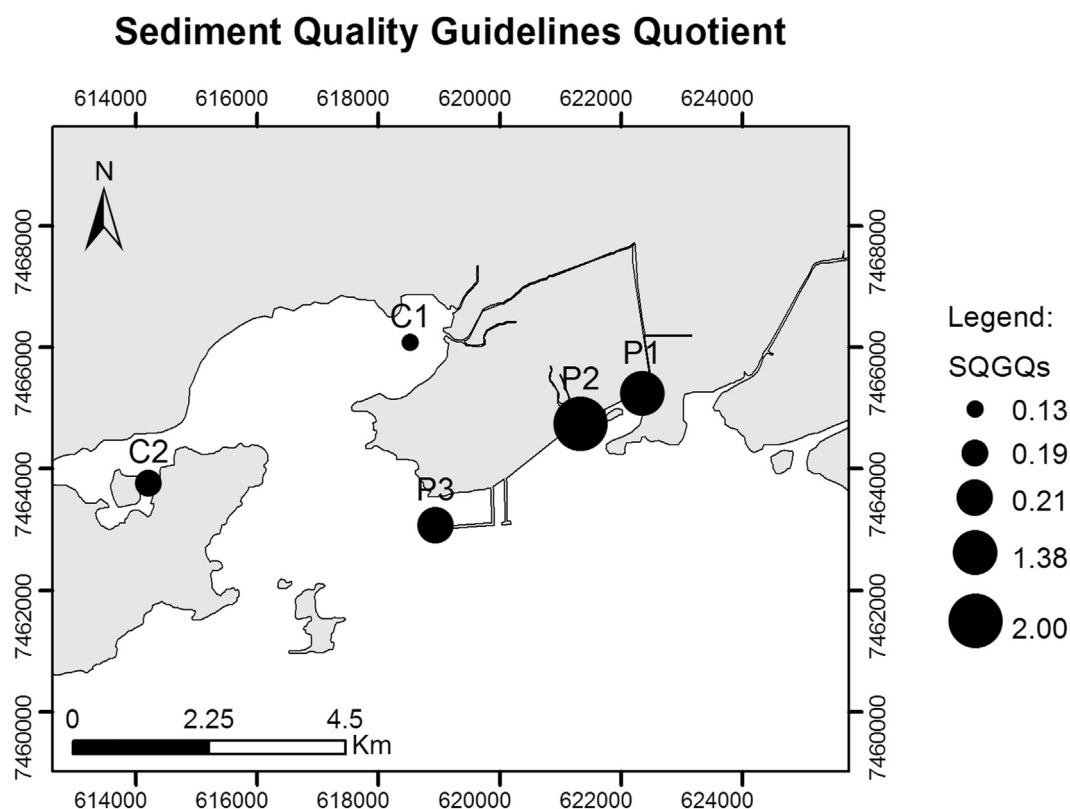


Fig. 3. The mean of Sediment Quality Guideline Quotients (SQGQs) for each sampling site.

Table 2

Means, minimum, maximum and standard deviation for all variables used to $\Sigma\text{SEM}/\text{AVS}$ and $\Sigma\text{SEM}-\text{AVS}/f_{\text{oc}}$ models to estimate metals availability and bonding phases in superficial sediments. The bold values are above de model threshold. Each site has 5 replicates.

| | | ΣSEM ($\mu\text{mol g}^{-1}$) | AVS ($\mu\text{mol g}^{-1}$) | $\Sigma\text{SEM}/\text{AVS}$ | $(\Sigma\text{SEM}-\text{AVS})/f_{\text{oc}}$ ($\mu\text{mol g OC}^{-1}$) | f_{oc} (kg OC kg^{-1}) | Cd (nmol g^{-1}) | Cu ($\mu\text{mol g}^{-1}$) | Fe ($\mu\text{mol g}^{-1}$) | Ni (nmol g^{-1}) | Pb (nmol g^{-1}) | Zn ($\mu\text{mol g}^{-1}$) |
|----|------|--|-----------------------------------|-------------------------------|--|---|--------------------------------|----------------------------------|----------------------------------|--------------------------------|--------------------------------|----------------------------------|
| P1 | Mean | 27.60 | 17.70 | 1.69 | 295.06 | 0.04 | 82.56 | 0.13 | 31.47 | 5.36 | 97.05 | 27.29 |
| | Min. | 23.24 | 11.60 | 1.10 | 71.02 | 0.03 | 68.14 | 0.11 | 28.67 | 4.79 | 80.97 | 22.98 |
| | Max. | 30.54 | 27.15 | 2.30 | 688.54 | 0.05 | 90.96 | 0.14 | 34.48 | 5.93 | 105.39 | 30.20 |
| | SD | 3.10 | 6.47 | 0.48 | 233.68 | 0.01 | 9.19 | 0.01 | 2.29 | 0.49 | 9.74 | 3.06 |
| P2 | Mean | 37.66 | 41.46 | 0.91 | −95.31 | 0.04 | 124.29 | 0.20 | 38.07 | 6.65 | 170.49 | 37.16 |
| | Min. | 28.05 | 26.63 | 0.80 | −232.85 | 0.04 | 95.20 | 0.15 | 27.53 | 4.22 | 134.80 | 27.67 |
| | Max. | 60.44 | 57.56 | 1.05 | 64.98 | 0.05 | 188.87 | 0.30 | 60.86 | 9.94 | 265.50 | 59.67 |
| | SD | 13.09 | 11.43 | 0.13 | 135.74 | 0.00 | 37.54 | 0.06 | 13.21 | 2.72 | 54.50 | 12.94 |
| P3 | Mean | 1.52 | 22.41 | 0.15 | −1414.57 | 0.01 | 3.11 | 0.06 | 37.81 | 38.02 | 37.03 | 1.38 |
| | Min. | 1.34 | 2.92 | 0.04 | −2558.13 | 0.01 | 2.51 | 0.05 | 34.12 | 32.26 | 32.10 | 1.22 |
| | Max. | 1.74 | 38.60 | 0.46 | −103.41 | 0.02 | 3.58 | 0.08 | 43.12 | 41.98 | 42.06 | 1.58 |
| | SD | 0.16 | 14.78 | 0.18 | 1002.40 | 0.00 | 0.48 | 0.01 | 3.38 | 3.89 | 4.58 | 0.14 |
| C1 | Mean | 1.49 | 14.26 | 0.11 | −691.32 | 0.02 | 1.98 | 0.05 | 25.01 | 5.38 | 24.76 | 1.41 |
| | Min. | 0.86 | 11.16 | 0.08 | −1003.03 | 0.02 | 1.31 | 0.04 | 21.08 | 2.80 | 21.39 | 0.79 |
| | Max. | 1.85 | 20.32 | 0.13 | −547.50 | 0.02 | 2.63 | 0.05 | 30.42 | 13.78 | 28.80 | 1.76 |
| | SD | 0.38 | 3.69 | 0.03 | 183.89 | 0.00 | 0.57 | 0.01 | 4.71 | 4.75 | 3.08 | 0.37 |
| C2 | Mean | 3.10 | 15.20 | 0.20 | −386.07 | 0.03 | 6.64 | 0.07 | 26.91 | 5.15 | 33.25 | 2.98 |
| | Min. | 1.80 | 7.91 | 0.13 | −708.65 | 0.03 | 3.90 | 0.04 | 20.74 | 3.39 | 22.07 | 1.73 |
| | Max. | 6.80 | 28.59 | 0.27 | −177.21 | 0.03 | 15.18 | 0.15 | 45.37 | 10.86 | 65.32 | 6.56 |
| | SD | 2.10 | 7.83 | 0.06 | 196.38 | 0.00 | 4.80 | 0.05 | 10.48 | 3.21 | 18.21 | 2.03 |

4.3. Toxicity results

Results from the *T. viscana* toxicity test only showed an effect for station P2 ($p < 0.0001$), whereas the *T. biminiensis* toxicity test exhibited sublethal effects that differed from the laboratory control for all sites ($p < 0.05$) (Fig. 4). Despite stations P1 and P2 showing the lowest fecundity rates, there were no significant differences between sites.

In a short-term evaluation, negative impacts on early life-stages

are far less obvious whereas, in the long-term, irreversible changes can occur in biological populations as well as in entire communities (Chapman, 2002). If development of an organism or spawning is inhibited at each new generation, population decrease or even extinction of sensitive species can occur.

We found that the biological community of Madeira Island has been affected by metal contamination, with sublethal effects on copepods that are a key species and play an important role (primary consumers) in the food chains of most aquatic estuarine

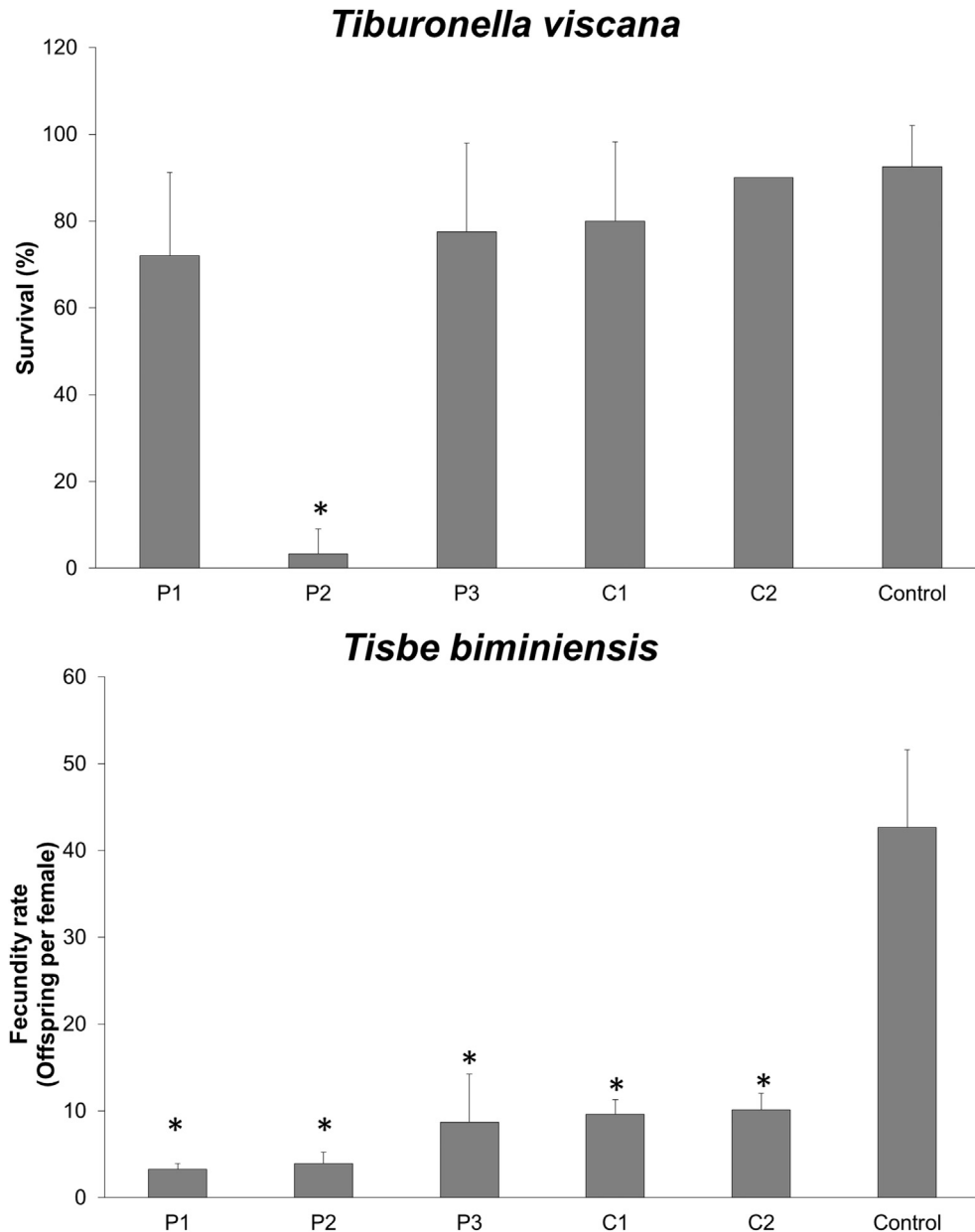


Fig. 4. *T. viscana* survival (above) and fecundity rate of *T. biminensis* (below). The columns indicate means ($n = 25$) from 5 sites and the bars are the standard deviation for each of the five sites.

environments. Chapman (2002) stated that a key species can be identified as any whose impact on its community is disproportionately high relative to its population size. We found up to 10-fold lower fecundity (spawning) between Sepetiba Bay samples and control sediments. Stations P1 (3.3) and P2 (3.9) had fecundity ratios less than half those of P3 (8.7), C1 (9.6) and C2 (10.1), as shown in Fig. 4. These results raise concerns about the extent of trace metal contamination around Madeira Island and its potential impact on sensitive species.

Although our AVS-based evaluations of toxicity risk (i.e., $\sum \text{SEM}/\text{AVS}$ and $(\sum \text{SEM}-\text{AVS})/f_{\text{OC}}$ approaches) predicted no occurrence of toxicity associated with metal availability in pore water, our toxicity results imply a strong negative effect for the area under the direct influence of SEC. *T. viscana* is a detritivore (Abessa et al., 1998), ingesting silt and clay particles, organic matter, bacteria, and microphytobenthos. This diet greatly exposes the species to

contaminated sediments. Moreover, Decho and Fleeger (1988) observed that harpacticoid copepods, such as *T. biminensis*, feed on sedimentary organic matter, mud particles and microphytobenthos. Therefore, metal uptake is not limited to a pore water source, but is also derived from particles containing metals. Considering that the tested benthic organisms were exposed to a variety of potentially toxic sedimentary constituents, the low amphipod survival in sediments from near to SEC (station P2) is probably due to concurrently higher levels of Cd, Zn, Pb and Cu, suggesting a synergistic effect of these metals.

Despite the observed trace metal contamination at all other sites, severe short-term effects were not observed, as indicated by the absence of acute toxicity for all sites except station P2. However, benthic deposit-feeders (i.e., species feeding on organic matter, meiofauna and bacterial biofilms) ingest sediment particles, which explains the observed chronic toxicity at all sites and may also

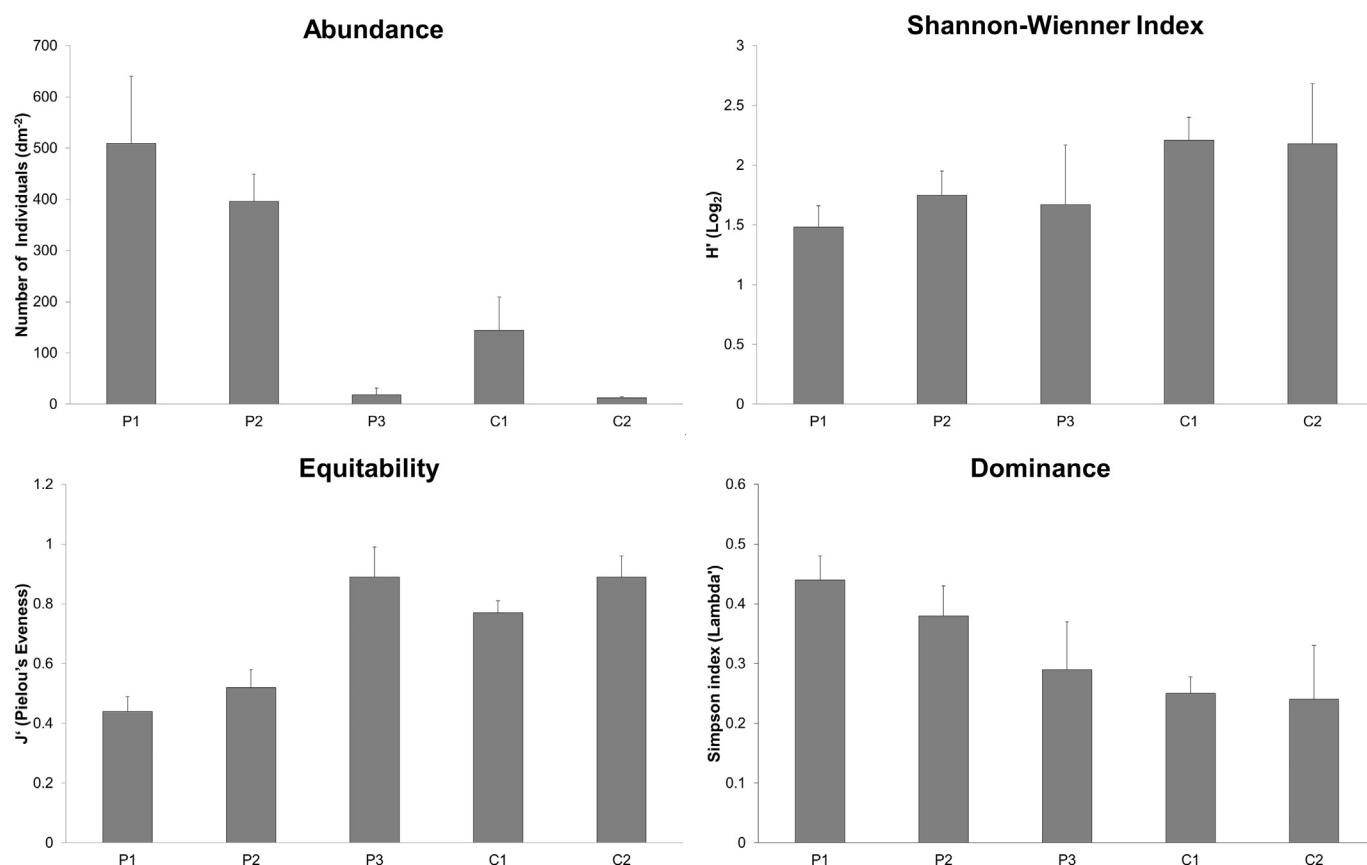


Fig. 5. Means of Species abundance (A), Shannon-Wiener index (H'), equitability (J' – Pielou Evenness) and Simpson Dominance (D) found in the samples ($n = 25$) from five sites near Madeira Island.

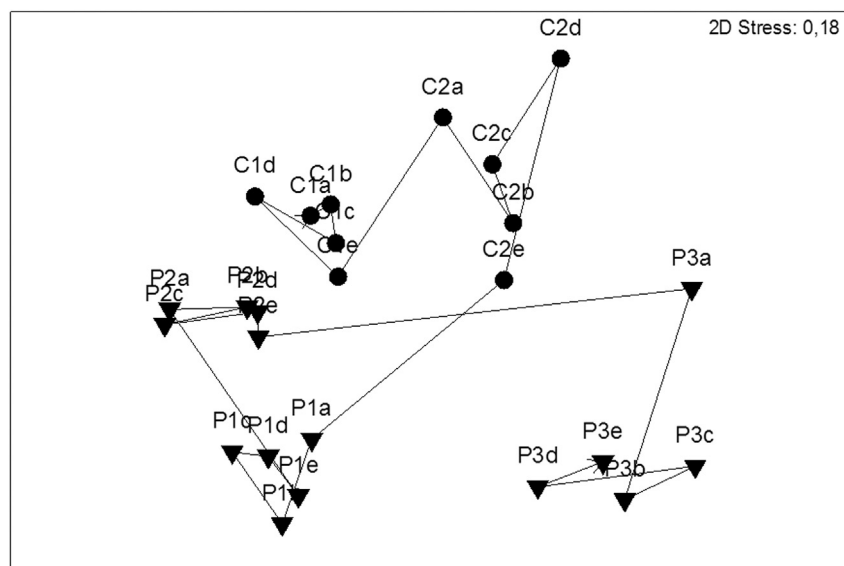


Fig. 6. n-MDS plot of the macrobenthos, based on fourth root-transformed abundance data and the Bray-Curtis similarity index.

explain why chronic toxicity was not associated with theoretical predictions from our $\sum\text{SEM}/\text{AVS}$ and $(\sum\text{SEM}-\text{AVS})/f_{\text{OC}}$ results. Similar results were observed by Torres et al. (2015) and Cruz et al. (2014), who suggested that the $\sum\text{SEM}/\text{AVS}$ and $(\sum\text{SEM}-\text{AVS})/f_{\text{OC}}$ models may not be suitable for predicting toxicity when exposure to contaminants is via dermal contact and ingestion. Metals

weakly-bound to sediments can be released into the digestive tubes of organisms. Ahlf et al. (2009) emphasized that the metal association phase can also influence metal bioavailability. This indicates that metal normalization to TOC fractions and AVS contents does not necessarily reflect metal bioavailability, particularly in the case of sediment-feeding organisms. Sediment properties can affect

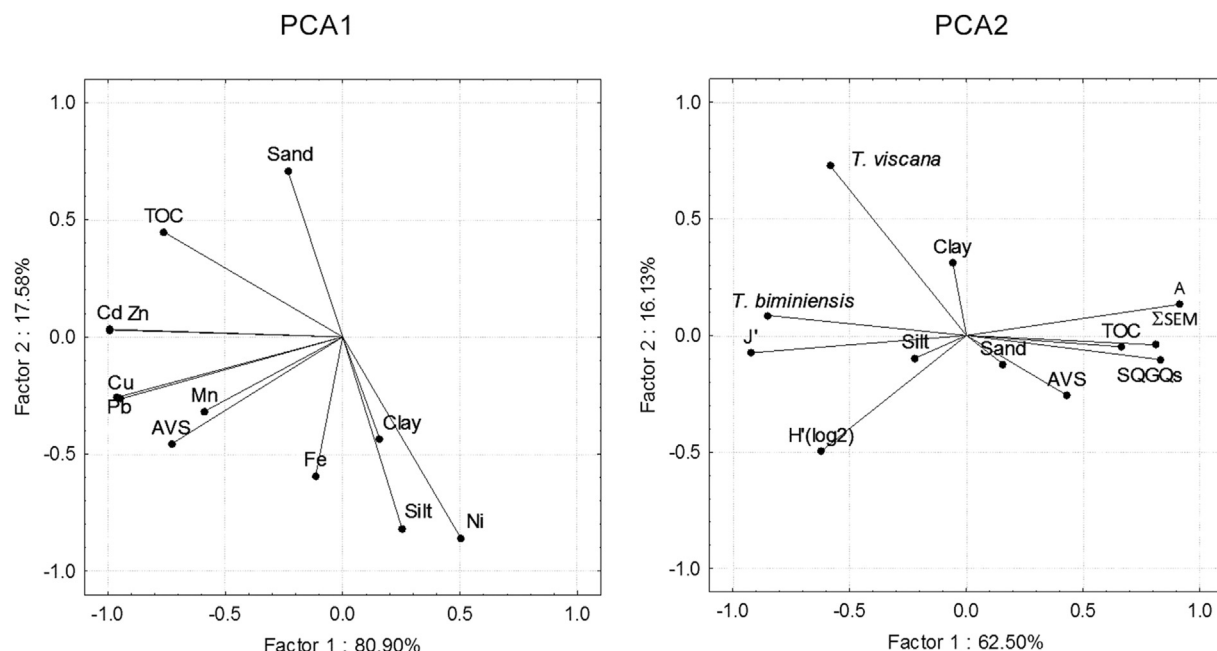


Fig. 7. Bi-dimensional ordination of PCA1 results (at left) using geochemical data obtained from Madeira Island sediments ($n = 25$) and bi-dimensional ordination of PCA2 results (at right) using the sum of trace metals (Σ SEM), SQGQ results, organic carbon content, grain size percentage, ecological indexes and toxicological data obtained from Madeira Island sediments ($n = 25$) from 5 sites.

metal geochemical partitioning, and metal uptake is partly dependent on animal physiology (Ahlf et al., 2009). For instance, species that ingest sediments with higher amount of metals in organic phases, or even silt-clay material with large amounts of adsorbed metals, can absorb these elements because their gastric content is likely able to promote metal desorption from sediment particles.

4.4. Macrobenthic community

A total of 5404 individuals from 11 taxa belonging to 6 zoological groups (Nematoda, Crustacea, Polychaeta, Molluscs and Foraminifera) were sampled (see [supplementary material](#)). Macrobenthic communities are mostly shaped by organic enrichment and grain size characteristics (Gray et al., 1990). However, the occurrence of benthic organisms in our study area was apparently influenced by metal contaminants, given the predominance of opportunistic species (Nematoda, *Monokalliapseudes schubartii*, *Streblospio cf benedicti*, *Scolecopsis* sp., *Bulla striata*, *Heleobia australis*, *Sternaspis* sp.) (see [supplementary material](#)). Most taxa had a low frequency of occurrence and only *B. striata*, *S. cf benedicti*, and *Capitella capitata* were found at all sampling sites. In fact, the macrobenthic assemblages we report are typical of impacted sites, with few species and a predominance of opportunistic species.

Amphipod abundance in the study area was very low since these crustaceans are sensitive to pollution and tend to disappear from polluted sites (Bellan-Santini, 1980; Swartz et al., 1986). Deposit-feeding organisms, such as polychaeta, are abundant in areas enriched with organic matter (Kennish, 2000), and we found that the tanaid *K. schubartii* was dominant at station P1. *K. schubartii* is considered pollutant-resistant and has also been described as dominant in the estuary of Cubatão River, a heavily polluted site from SE Brazil (Nipper et al., 1990). Near Madeira Island, higher OC contents were found at stations P1, P2 and C2, where higher abundances of *B. striata*, Nematoda and *Streblospio* sp. were found, all of which are opportunistic species. The diversity index (H') and

equitability index (J') values for stations P1 and P2 were low (Fig. 5). Our low values of equitability can be related to the high dominance of certain species at stations P1 and P2 (Fig. 5). Benthic communities presenting low diversity and high dominance have been described from polluted sites elsewhere (Reish, 1986; Abessa et al., 2008; Bian et al., 2016).

Conceptually, communities living in a healthy environment present a higher probability of being more diverse and abundant (Jhingan et al., 1989). Although, lower diversity can be found in impacted ecosystems, abundance may also be high due to the occurrence of tolerant species that have the capacity persist in hostile environments (Jhingan et al., 1989).

Our n-MDS analysis showed a clear spatial gradient for macrobenthic community composition in the study area (Fig. 6). Higher diversity was found at stations C1 and C2, with lower values near to SEC (station P2), and lowest values at station P3 (Itaguaí Harbor) (Fig. 5). Station P3 presented more fine-grained sediments (>80%) than the other sites (Table 1), so this low diversity may be associated with grain size differences.

4.5. Principal Component Analysis

A Principal Component Analysis on HCl-soluble metal concentrations (PCA1) revealed two factors that explained 98.5% of the data variation (Fig. 7, see also the [supplementary material](#)). The first factor mainly represented trace metals, except for Ni. Cadmium, zinc, copper and lead were correlated to AVS values, as well as TOC, Fe and Mn concentrations, indicating the presence of exchangeable sulfide forms. The second factor represented clay and silt fractions and Ni concentration. The association of Ni with the fine sediments, as well as the lower concentrations of this element in the samples, could indicate that concentrations of this metal are naturally-occurring. However, Gomes et al. (2009) reported background values for Ni that were 6-fold higher than the concentrations in our findings.

A second PCA (PCA2) was performed using the SQGQs values,

ecological indexes, toxicity results, grain size, TOC, AVS and SEM (Fig. 7). The first two factors explained 79% of the data variation. The toxicity tests (i.e., copepod fecundity and amphipod survival) were not correlated, possibly due to different responses to contaminants, types of exposure and species sensitivity. However, both toxicity endpoints were associated with metal concentrations (SQGs and SEM). The abundance (D) of the macrobenthic communities suggested the presence of opportunistic and resistant species, which were dominant mainly near to SEC. A relationship between the diversity and evenness indexes and the toxicity results was also revealed by PCA2 (Fig. 7). This ecological response to contamination exposure is also illustrated in the lower values of diversity and evenness at contaminated sites.

5. Conclusions

Cadmium and zinc concentrations in sediments from Sepetiba Bay were above SQG thresholds adopted in Brazil, reaching levels nearly 80-times higher (Zn) and 55-times higher (Cd) than pre-industrial background concentrations close to SEC. Sublethal toxicity effects were observed in all samples, with 10-fold less spawning in Sepetiba Bay sediments compared to control samples. Since early life-stages (i.e., larval and/or juvenile phases) of key species may be at risk, permanent loss or damage to benthic community structure can be expected for the region around Madeira Island.

Our application of a multiple LOE approach was successful for comprehensively evaluating metal availability in Madeira Island sediments. In a gradient towards the contamination source, the macrobenthic community presented a predominance of opportunistic and tolerant species. Moreover, we found an association between ecotoxicological results and ecological indices, which reinforces the importance of different LOEs to identify communities under environmental risk.

According to our $\sum \text{SEM}/\text{AVS}$ and $(\sum \text{SEM}-\text{AVS})/\text{foc}$ results, trace metals in sediments at Coroa Grande (C1), Itaguaí Harbor (P3) and Itacuruçá (C2) are predicted to be unavailable in the pore water. SEC (P2) and the mouth of Guarda River (P1) have very high concentrations of trace metals, implying that AVS and organic carbon contents at these sites are not sufficient to trap and retain these elements bound to sediment solid phases.

Our findings based on combined LOEs and cited previous works call for urgent environmental monitoring and a restoration program for Sepetiba Bay, since both the ecosystem structure and human health are under risk from trace metal contamination.

Acknowledgements

We acknowledge financial support from the Brazilian Education Ministry (CAPES) to SKR and APCR. RES, DMSA and WM received financial support from the National Research Council (CNPq).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2017.05.045>.

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