



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



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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)

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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 $100 \mu\text{mol g}^{-1}$ 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 ($-4 \text{ }^\circ\text{C}$), 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

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