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Trace metal bioavailability in sediments from a reference site, Ribeira Bay, Brazil

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ABSTRACT

Surface sediments were collected near potential contamination sources impacting Ribeira Bay (Brazil), a system considered as a 'reference site' for trace metals. Physicochemical properties (pH and Eh), grain size and concentrations of total organic carbon (TOC), total phosphorus (TP), acid-volatile sulfides (AVS) and simultaneously-extracted metals (Fe, Mn, Cd, Cu, Ni, Pb and Zn) were analyzed. Although relatively low metal concentrations were found, correlations of Zn and Ni with high TP levels suggested an association with sewage inputs, while other metals presented associations with specific geochemical carriers (TOC, Fe and Mn compounds). AVS levels exceeding those of the sums of Cd, Cu, Ni, Pb and Zn (ΣSEM) by at least one order of magnitude and TOC-normalized differences between ΣSEM and AVS ($(\Sigma\text{SEM}-\text{AVS})/f_{\text{OC}}$) near to or below than $-200 \mu\text{mol g OC}^{-1}$ indicated that there were sufficient AVS and TOC levels to control trace metal bioavailability in sediment pore water.

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Trace metal accumulation, bioavailability and toxicity to sediment dwelling organisms are largely influenced by the physicochemical conditions and geochemical properties of sediments. This relationship allow us for the use of predictive equilibrium-partitioning models to determine the behavior of these elements (e.g., Burton et al., 2006; Machado et al., 2008; De Jonge et al., 2012). In coastal sedimentary environments where reducing conditions occur, acid-volatile sulfides (AVS) can play an important role in trapping many trace metals in the sediment solid phase, mediating the extent to which they can become dissolved in sediment pore waters and, consequently, regulating their bioavailability and toxicity (Chapman et al., 1998). Therefore, AVS-derived models for predicting metal toxicity risks have been developed (as supported by empirical data from metal toxicity tests), initially based on the molar ratios or differences between the sums of simultaneously-extracted metal concentrations (i.e., ΣSEM , usually considering Cd, Cu, Ni, Pb and Zn) and AVS concentrations (i.e., AVS/ ΣSEM or AVS- ΣSEM models; e.g., Di Toro et al., 1992). Care is requested in applying AVS-based models for predicting toxicity, since the heterogeneity in feeding modes, feeding habits and food preferences of benthic organisms is not taken into account (e.g., Ahlf et al., 2009). However, their effectiveness in predicting pore water metal concentrations supports the predictability on metal toxicity risks (Chapman et al., 1998).

The coupling of this equilibrium-partitioning model with a biotic ligand model (BLM) was proposed to allow predictions on acute and chronic metal toxicities, based on the normalization of the difference between ΣSEM and AVS to the fraction of total organic carbon (TOC) in the sediments (i.e., $(\Sigma\text{SEM}-\text{AVS})/f_{\text{OC}}$; Di Toro et al., 2005; USEPA, 2005). However, although several studies on this extended model can be found in the literature (e.g., Machado et al., 2010; Zhuang and Gao, 2013; Chandler et al., 2014), very few have dealt with pristine or near-pristine coastal environments for comparative analysis with impacted sites (Pereira et al., 2008; Li et al., 2014).

This study examined the factors affecting the distribution and the potential bioavailability of trace metals in sediments from the Ribeira Bay estuarine system, located in Angra dos Reis municipality, Rio de Janeiro State (SE Brazil). This system is a fishing and touristic area that has been considered as a 'reference site' for trace metal studies since the 1980s (Lacerda et al., 1982; Cardoso et al., 2001; Gomes et al., 2009; Freret-Meurer et al., 2010). However, some potential contamination sources within the bay may possibly be changing the sediment quality of this coastal region. These sources include four rivers with human occupation in the catchments (Fig. 1) and some marinas, generally located in the river mouths or within ~400 m from them. In addition, potential diffuse sources are found nearby the bay, including other marinas and a commercial harbor eastward (within ~13 km) and two nuclear power plants westward (~2 km). Since there is no information on the potential importance of AVS in determining trace metal behavior in this system, surface sediments were analyzed here for grain size, physicochemical conditions (pH and redox potential, Eh) and concentrations of TOC, AVS, simultaneously-extracted metals

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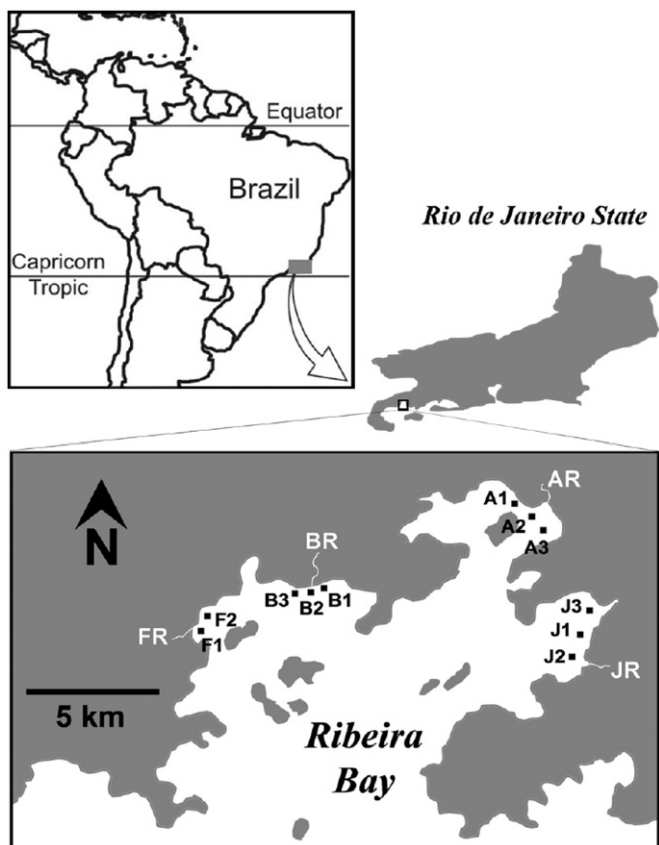


Fig. 1. Location of sampling stations along the Ribeira Bay coastline, Rio de Janeiro State, Brazil. FR, Frade River; BR, Bracuí River; AR, Ariró River; JR, Japuiba River.

(Fe, Mn, Cd, Cu, Ni, Pb and Zn) and total phosphorus (TP). TP concentrations were used as a proxy for sewage inputs (e.g., Church et al., 2006; Borges et al., 2009).

Sediment samples were collected with a stainless steel Van Veen grab in 11 sampling stations distributed along four coves from Ribeira Bay, in July 2013 (Fig. 1). After careful conditioning under refrigeration within zip-lock plastic bags in the field, the samples were kept frozen in the laboratory until analysis, in order to minimize oxidation. There is a known potential methodological limitation when the sampling procedures are not performed under strictly anoxic conditions, since the derived AVS results may represent minimal estimates, due to some partial oxidation. The susceptibility to occur or to not occur a significant AVS oxidation can be dependent on the combined degrees of: (1) AVS accumulation in the whole sediment sample; (2) O₂ diffusion and consumption into the stored sample; (3) heterogeneity in the AVS distribution within the sample; and (4) anaerobic AVS oxidation (e.g., in reaction with metal oxides; e.g., Machado et al., 2008). The last cited process may possibly affect the AVS levels even under strictly anoxic conditions.

The sampling sites were located in shallow areas close to the mouths of the most important rivers discharging freshwater and urban effluents into Ribeira Bay. The Bracuí Cove (stations B1, B2 and B3), Ariró Cove (stations A1, A2 and A3), Japuiba Cove (stations J1, J2 and J3) and Frade Cove (stations F1 and F2) were included in this sampling, located near to the cited river mouths and marinas (Fig. 1; Table 1). The Eh and pH of sediments were determined in situ immediately after sampling, by using Metter Toledo SG78 and WTW pH340i/set electrodes, respectively. These electrodes were inserted in a subsample separated from that stored for AVS analysis to avoid possible effects of oxidation due to their insertion and removal.

Table 1

Identification, location and water column depth of sampling stations along the coves from Ribeira Bay.

Cove	Sampling station	Geographical coordinates	Water depth (m)
Ariró	A1	22°55'54.5"S, 44°20'8.8"W	2.5
	A2	22°56'8.8"S, 44°19'56.9"W	4.3
	A3	22°56'27"S, 44°19'46"W	3.5
Bracuí	B1	22°57'24.8"S, 44°23'46.7"W	3.5
	B2	22°57'24.7"S, 44°24'6.6"W	0.6
	B3	22°57'22.6"S, 44°24'23.8"W	3.6
Frade	F1	22°57'54.8"S, 44°25'56.8"W	4.0
	F2	22°58'16.5"S, 44°26' 2.8"W	3.8
Japuiba	J1	22°58'10"S, 44°18'47.7"W	2.5
	J2	22°58'37.7"S, 44°19'2.8"W	2.0
	J3	22°57'43.5"S, 44°18'36.9"W	2.2

Sediment grain size was determined using a laser analyzer CILAS model 1064, employing the software GRADISTAT version 4.0. TOC determinations were performed using a Shimadzu TOC-VCPH analyzer, coupled with a SSM-5000A module for solid samples. TP levels were extracted as previously described by Aspila et al. (1976) and these concentrations were quantified employing a UV-Vis Agilent 8453 spectrometer at 880 nm (Grasshoff et al., 1999). The TP extractions were performed in triplicate with a precision <12%. The accuracy was evaluated by triplicate analyses of NIST 1646a and MESS-3 certified reference materials, for which the mean recoveries were 102% and 94%, respectively.

The AVS and SEM analyses were performed according to the cold distillation method described by Allen et al. (1991). The extractions were carried out in duplicates, with the addition of 20 mL cold 6 M HCl to 2 g wet sediment. Apparatus blanks, reagent blanks (distilled water), calibration curves, and standard recoveries were employed in the analysis. Quality control of AVS extraction was assured by calibrating the procedure against a known amount of Na₂S·9H₂O (0.44 and 1.75 mg mL⁻¹). The obtained mean recovery was ≥89%. The 6 M HCl suspensions of sediments were filtered for the determination of the simultaneously-extracted metals (Fe, Mn, Cu, Pb, Zn, Ni and Cd) by flame atomic absorption spectrometry (AAS, Varian model AA240). The reproducibility of duplicate metal concentration determinations was within 14%. Pearson correlation analysis was performed to evaluate possible relationships between sediment properties and metals. A significance level of p < 0.05 was accepted.

All results of physicochemical, grain size and chemical analyses are presented in Table 2. Negative Eh values found in the studied sediments ranged from -186.8 mV to -1.1 mV, indicating their reducing nature, while pH values varied within a very narrow, near-neutral range (7.06 to 7.55). Grain size analysis revealed predominant silt contents (66% to 86.6%), except at station B2, where the sand content was 95.6%. Consequently, this station presented the least negative Eh value and its chemical constituents generally showed levels one order of magnitude lower than those found at most other sampling stations (Table 2). Therefore, the statistical analyses presented below were carried out without accounting the data from station B2 and without the Ni data below the analytical detection limit (station F1).

The highest AVS concentrations (above 100 μmol g⁻¹) were observed in the stations A1 and J1, which were similar to those also reached in anaerobic sedimentary conditions elsewhere (Machado et al., 2004; Burton et al., 2006). Station A1 presented the highest TOC content (5 mmol g⁻¹; Table 2), possibly due to the influence of mangroves in the vicinity of this station (e.g., Sanders et al., 2010). Effluent discharges near river mouths in the study area may have also served to enhance TOC concentrations, which fuel a higher production of AVS (Cooper and Morse, 1998; Machado et al., 2008).

The ΣSEM concentrations ranged from 0.42 μmol g⁻¹ (at station B2) to 2.29 μmol g⁻¹ (at station J1) (Table 2), with Zn as the dominant

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