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SHORT ORIGINAL COMMUNICATION

Relation of acid-volatile sulfides (AVS) with metals in sediments from eutrophicated estuaries: Is it limited by metal-to-AVS ratios?

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Abstract

Purpose The role of acid-volatile sulfide (AVS) as a factor affecting (or reflecting the environmental conditions influencing) the behavior of metals has been evidenced in anoxic sediments. However, sediment quality studies tend not to consider any potential AVS role when sum of simultaneously extracted metal (ΣSEM) concentrations exceed AVS concentrations, restricting the application of the AVS model to predict toxicity, rather than coupling this model (when applicable) with other possible interpretations of metal–AVS relations.

Materials and methods The relations between total organic carbon (TOC), AVS, and simultaneously extracted Fe, Cd, Cu, Ni, Pb, and Zn were investigated in sediment cores from two eutrophicated estuaries in Guanabara Bay (SE Brazil) in order to contribute to our understanding about metal–AVS relations in conditions of variable ΣSEM and AVS levels, due to gradients of eutrophication and metal contamination.

Results and discussion Correlation analyses indicated a more important role of TOC, AVS, and Fe in the mechanisms affecting trace metal distribution in the less eutrophicated estuary. This suggests that AVS was a more important binding phase, or at least a better proxy for biogeochemical conditions affecting metal distribution, when it exceeds the sum of simultaneously extracted Cd, Cu, Ni, Pb, and Zn concentrations (ΣSEM). However, this potential role of AVS in anoxic estuarine sediments should not be discarded before evaluating individual metals–AVS relations even when ΣSEM levels exceed AVS levels, since the biogeochemical controls on the behavior of individual metals may be also related to metal–AVS associations in this situation (as indicated for Cu and Ni in the more eutrophicated estuary). The same is suggested for all AVS-based approaches, such as the (ΣSEM−AVS)/f_{OC} (organic carbon normalization of excess ΣSEM), since (ΣSEM−AVS)/f_{OC} values were mostly positive and significantly higher in the more eutrophicated estuary.

Conclusions Although the importance of metal relations to AVS in evaluating individual metal behavior in anoxic estuarine sediments may not be restricted to situations in which AVS levels exceed ΣSEM levels (as observed for Ni and Cu in the present study), metal–AVS relations were apparently favored in this situation. Approaches in this way are recommended for future research, coupling the possibilities of metal behavior interpretations (and often predictions) allowed by AVS models.

Keywords Contamination · Estuaries · Metal interactions · Metal–organic matter interaction · Metal–sulfur interaction · Sediments

1 Introduction

The organic carbon, inorganic sulfides, and metal oxides may be considered as main sedimentary phases that influence the behavior of trace metals in coastal sediments (Chapman et al. 1998). However, the development of eutrophicated conditions can change the biogeochemical controls on trace metal behavior within sediments, such as

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metal associations with acid-volatile sulfide (AVS) compounds (Cooper and Morse 1998; Machado et al. 2004). Considering that the proportion between molar concentrations of AVS and some simultaneously extracted metals (sum of Cd, Cu, Ni, Pb, and Zn concentrations or ΣSEM) is a potential indicator of metal availability in pore-water-dissolved phase, due to rapid metal sequestration in solid-phase AVS when ΣSEM do not exceed the AVS levels (Di Toro et al. 1992; Huerta-Diaz et al. 1998), the behavior of metals that can be associated to AVS may vary depending on whether there is sufficient AVS to retain the ΣSEM.

Situations in which ΣSEM levels exceed AVS levels have been interpreted as evidence that factors other than AVS should be considered to explain metal bioavailability and toxicity risk (Wen and Allen 1999; Dalmacija et al. 2006). Recent advances in toxicity prediction approaches have indicated that the excess ΣSEM normalized to organic carbon (i.e., $(\Sigma\text{SEM}-\text{AVS})/f_{\text{OC}}$) predicts free metal activity in the pore water, since organic matter binding can contribute to the prevention of trace metal availability in the dissolved phase (Di Toro et al. 2005; Hansen et al. 2005). On the other hand, an underestimation of the role of AVS as a geochemical tool in investigating the behavior of toxic metals may occur if assessments of metal behavior in anoxic sediments interpret a negligible contribution of AVS based only on an unexpected AVS potential to retain metals when ΣSEM levels exceed AVS levels. While the AVS model for predicting metal toxicity in anoxic sediments has been a matter of debate (Ahlf et al. 2009), since the biological uptake occurs via the dissolved phase, metal complexes, dietary, and particle-bound metals, this model appears to be generally more effective in predicting pore water metal concentrations, allowing its use in metal behavior studies. Therefore, the potential role of AVS as a factor affecting (or a proxy for conditions determining) the distribution of reactive (HCl-extractable) metals was investigated in two sites showing different levels of eutrophication and metal contamination in Guanabara Bay (Brazil).

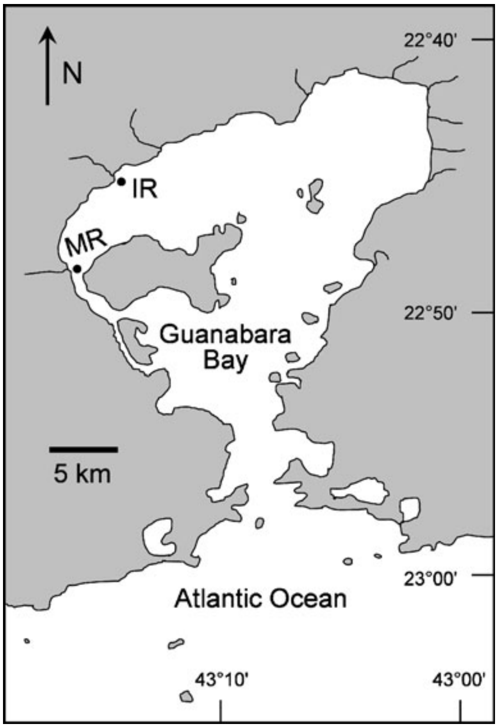

Fig. 1 Location of Iguaçu River (*IR*) and São João de Merití River (*MR*) sampling stations in Guanabara Bay, southeastern Brazil

2 Material and methods

Duplicate sediment cores were collected in June 2005, using acid-cleaned acrylic tubes, in the estuaries of Iguaçu River (station IR; 22° 44.95′ S, 43° 14.46′ W) and São João de Merití River (station MR; 22° 48.12′ S, 43° 16.20′ W) (Fig. 1). Station MR was located in the estuary with a higher degree of eutrophication, due to a greater sewage runoff and less efficient water renewal. The sediments were sectioned in 0−2-, 2−4-, 4−6-, 6−9-, 9−12-, 12−15-, 15−20-, and 20−25-cm depth intervals and kept frozen in order to minimize oxidation. For AVS and metal extractions, wet sediment subsamples were submitted to an acid distillation with 6 mol l^{-1} HCl (Allen et al. 1991). The AVS concentrations were determined spectrophotometrically, while simultaneously extracted metal concentrations were determined by ICP OES. After carbonate removal by acidification, total organic carbon (TOC) concentrations were determined on a Perkin Elmer analyzer. Reproducibility of duplicate analyses of all samples was within 22% (AVS), 15% (metals), and 3% (TOC). The Mann–Whitney *U* test was used to compare data from different stations, and possible data correlations within each station were evaluated employing the Spearman correlation test. A significance level below 0.05 was accepted.

3 Results and discussion

The studied sites presented no significant differences for most sediment properties (Table 1). Median values of AVS and Fe concentrations were significantly higher in station IR, which generally presented AVS concentrations above the theoretical values necessary to bind all reactive trace metals as monosulfides, i.e., AVS levels exceeded ΣSEM levels (Di Toro et al. 1992; Chapman et al. 1998). This contrasts with the lower potential to retain metals in the form of AVS found in most samples from station MR, which presented significantly higher values of all AVS-derived variables. The observed metal, AVS, and TOC data

Table 1 Median, minimum, and maximum values determined for the sedimentary variables studied in duplicate cores from the Iguaçu River (station IR) and the São João de Meriti River (station MR) estuarine areas and results of a Mann–Whitney *U* test for comparisons between stations (n=16 per station)

	IR			MR			Mann–Whitney test[a]
	Median	Minimum	Maximum	Median	Minimum	Maximum	
TOC (mmol g^{-1})	3.68	2.43	4.24	3.53	1.59	7.01	NS
AVS (μmol g^{-1})	18.4	5.67	37.4	4.04	0.65	198	0.01
Fe (μmol g^{-1})	212	81	278	123	27.1	288	0.02
Cd (nmol g^{-1})	6.46	3.96	10.8	6.23	2.19	19.5	NS
Cu (μmol g^{-1})	0.80	0.41	1.21	0.47	0.23	1.69	NS
Ni (nmol g^{-1})	58.0	21.2	165	76.9	29.8	450	NS
Pb (nmol g^{-1})	171	110	278	173	83.5	498	NS
Zn (μmol g^{-1})	5.39	2.99	8.42	4.59	1.27	15.8	NS
ΣSEM (μmol g^{-1})	6.42	3.55	10.0	5.31	1.63	18.3	NS
ΣSEM/AVS	0.36	0.17	1.10	1.20	0.08	3.13	0.01
ΣSEM−AVS (μmol g^{-1})	−11.8	−30.9	0.70	0.48	−179.8	11.3	0.02
f_{OC} (kg OC kg^{-1})	0.044	0.029	0.051	0.042	0.019	0.084	NS
(ΣSEM−AVS)/f_{OC} (μmol g OC^{-1})	−242	−772	15.9	10.0	−2,873	268	0.01

NS not significant at a *p* level 0.05

[a] Significance (*p*) levels are shown

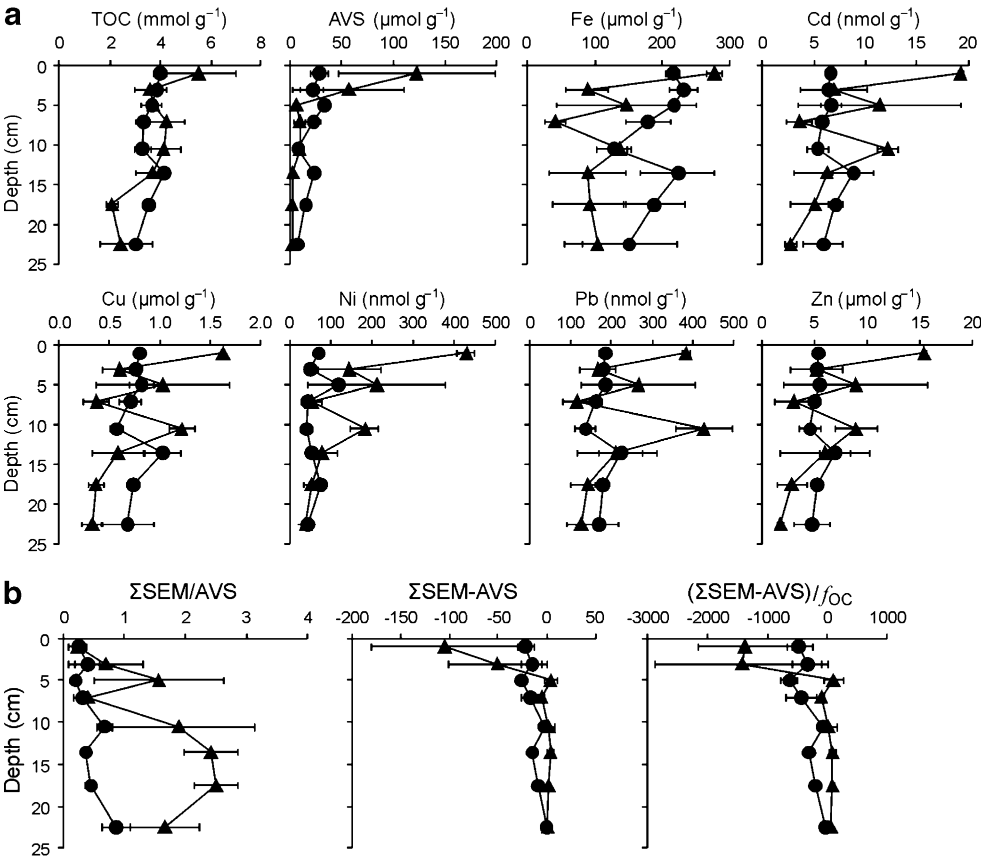

Fig. 2 Depth distribution of **a** TOC, AVS, and reactive metal concentrations and **b** AVS-derived variables (ΣSEM/AVS, ΣSEM−AVS and (ΣSEM−AVS)/f_{OC}) in sediment cores from Iguaçu River (*circles*) and São João de Meriti River (*triangles*) estuaries. *Symbols* indicate mean values, while *error bars* indicate the ranges of duplicate cores

reflected anthropogenic influences in both stations, as previously indicated for the western area of the bay and other impacted areas in Rio de Janeiro coast (Carreira et al. 2002; Maddock et al. 2007; Pereira et al. 2008).

Contrasting concentration profiles between sites were found for all sediment constituents (Fig. 2a), mainly due to higher values and higher concentration variability in upper layers of station MR, above 12-cm depth. Station IR profiles generally presented maximum values in deeper layers (below 12-cm depth), except for AVS and Ni, which presented maximum levels in the 4–6-cm depth layer. These metal distribution differences possibly reflect a coupling of variable metal sources in the western bay area (Machado et al. 2004) and different metal extractabilities in the HCl solution (Burton et al. 2006). The observed lower levels of AVS and Fe in deeper layers may be explained by a replacement of reactive Fe and AVS by less reactive or crystalline fractions with increasing sediment depth, such as pyrite (Rickard and Morse 2005). Moreover, elevated levels of all sediment constituents presented in the top sediment layer from station MR (see Fig. 2a) were possibly favored by a 1-cm-thick surface nepheloid layer, which was not found in station IR sediments.

Trace metals were significantly correlated with each other in stations IR (r_s=0.74 to 0.98) and MR (r_s=0.88 to 0.98), suggesting a similarity in its sources and/or binding processes to the sediments. Significant correlations of Cd, Cu, Pb, and Zn with TOC (r_s=0.71 to 0.90), Cu, Ni, Pb, and Zn with AVS (r_s=0.71 to 0.83), and Cu, Pb, and Zn with Fe (r_s=0.73 to 0.86) were also observed in station IR. The TOC was correlated with AVS (r_s=0.74) and Fe (r_s=0.86), but there was no significant correlation of AVS with Fe. In addition to correlations between trace metals, in the station MR, there were significant correlations only for Cu and Zn with TOC (r_s=0.71 to 0.74), Cu and Ni with AVS (r_s=0.71 to 0.74), and TOC with AVS (r_s=0.74). Correlations between geochemical phases potentially involved in trace metal trapping are expected, as previously observed for TOC, AVS, and Fe (e.g., Machado et al. 2008; Keene et al. 2010). However, the results remarkably suggest a more important role of organic matter and reactive sulfides in the mechanisms affecting trace metal accumulation within sediments under the less eutrophicated conditions of station IR.

Vertical profiles of AVS-derived estimates (see Fig. 2b) demonstrated that AVS concentrations were generally more than two times higher than those of ΣSEM in station IR, in which $(\Sigma\text{SEM}-\text{AVS})/f_{\text{OC}}$ values were negative (with just one exception, at the deeper layer). The ΣSEM levels in station MR exceeded AVS levels in most depths, due to comparatively lower levels of AVS with increasing depth (see Fig. 2a). These results indicated that, even in situations in which ΣSEM concentrations exceed AVS concentrations, the geochemical controls on the behavior of individual metals may be related to metal–AVS associations, as suggested for the AVS-correlated distributions of Cu and Ni in station MR. However, a higher importance of AVS as a binding phase (or as an indicator of favorable conditions for metal retention) was observed for station IR, suggesting a limitation of AVS role in station MR.

4 Conclusions

The correlation of fewer individual trace metals with TOC, AVS, and Fe was observed in the station with more eutrophicated conditions (in which a higher importance of AVS could be expected), higher ΣSEM/AVS ratios, and lower reactive Fe and AVS levels (possibly due to reactive phases replacement by phases not extracted in the HCl solution). Although the importance of metal–AVS relations in evaluating individual metal behavior may not be restricted to situations in which ΣSEM levels exceed AVS levels, these relations were apparently favored in this situation.

5 Recommendations and perspectives

This pilot study indicated that further research is required to improve our understanding of metal–AVS relations, involving conditions of variable ΣSEM and AVS levels. Approaches in this way are recommended for future research, contributing to the characterization of the actual role of AVS, rather than a restricted interest in the application of the AVS models to predict toxicity (when applicable), coupling the possibilities of metal behavior interpretation (and possible predictions) allowed by AVS models. These approaches may support interpretations about what is expected for future eutrophication scenarios, as well as for future oligotrophication scenarios, if effective water quality restoration practices occur.

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