



Baseline

Are acid volatile sulfides (AVS) important trace metals sinks in semi-arid mangroves?

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ABSTRACT

Acid-volatile sulfides (AVS) formation and its role on trace metals bioavailability were studied in semi-arid mangroves. The semi-arid climatic conditions at the studied sites, marked by low rainfall and high evapotranspiration rates, clearly limited the AVS formation (AVS contents varied from 0.10 to 2.34 $\mu\text{mol g}^{-1}$) by favoring oxic conditions ($E_h > +350$ mV). The AVS contents were strongly correlated with reactive iron and organic carbon ($r = 0.84$; $r = 0.83$ respectively), evidencing their dominant role for AVS formation under semi-arid conditions. On the other hand, the recorded $\Sigma\text{SEM}/\text{AVS}$ values remained > 1 evidencing a little control of AVS over the bioavailability of trace metals and, thus, its minor role as a sink for toxic metals.

Acid-volatile sulfides (AVS) consist in a complex and dynamic biogeochemical fraction, composed by a variety of dissolved (e.g., S^{2-} , Fe^{2+} , and polysulfides; FeS) and solid (e.g., greigite and mackinawite) sulfur species (Rickard and Morse, 2005). This fraction is commonly associated with anoxic soils and sediments of intertidal ecosystems (e.g., mangroves, seagrasses, and saltmarshes), resulting from the sulfate reduction microbial pathway (Hammerschmidt and Burton, 2010; Holmer and Storkholm, 2001). The AVS formation and stability depend on anoxic conditions, a supply of sulfate and labile organic matter (e.g. low-molecular-weight organic acids) that lead to a high activity of sulfate-reducing bacteria (Gonzalez, 2002; Oehm et al., 1997).

The AVS, along with pyrite, is considered one of the most important mineral fraction controlling trace metals dynamic/bioavailability in mangroves, lagoons, and saltmarshes (Di Toro et al., 1990; Hare et al., 1994; Meysman and Middelburg 2005). In fact, the ability of coastal wetland soils and sediments in retaining trace metals is widely recognized, mostly due to the sulfide formation that characterizes these ecosystems (Alongi, 2002; Bayen, 2012; Clark et al., 1998; Robertson and Alongi, 1992). However, AVS fraction is a meta-stable mineral fraction (Rickard and Morse, 2005), usually ephemeral (Rickard and Morse, 2005) and affected by several factors, such as the activity of roots (e.g., roots exudates and rhizospheric oxidation); frequency and duration of tidal flooding and bioturbation (De Jonge et al., 2009; Ferreira et al., 2007a; Ferreira et al., 2007b; Otero et al., 2006; Otero and Macias, 2002).

Furthermore, previous studies have shown that the sulfate-reducing pathways may be rather sensitive to seasonal variations (Kristensen

et al., 2008; Leonard et al., 1993; Nóbrega et al., 2013), due to changes in temperatures and water input. In this context, the uppermost soil layers of mangrove forests at semi-arid coasts may exhibit some of the harshest redox environments by reaching highly oxic conditions ($E_h > +350$ mV; see Júnior et al., 2016; Bomfim et al., 2015; Nóbrega et al., 2013), which may considerably affect the ability of AVS fraction to control trace metals dynamics. In this context, the objective of this study was to determine a baseline for AVS and simultaneously extracted metals (SEM) contents in semi-arid mangrove soils from NE-Brazil and evaluate how this fraction (and its function as a metal sink) is affected by the semi-arid climatic conditions.

Soil samples were collected in three mangrove forests under different settings at the Brazilian NE semi-arid coast (Ceará state; Fig. 1): i.e., Cocó River (an urban mangrove, located in the largest city of the state with 2.6 million habitants; UM); Jaguaribe River (a mangrove characterized by an intense shrimp farming activity; SFM); and Timonha River, (a mangrove free from anthropogenic impacts; FAI) (da Silva and Souza, 2006). Samples were collected using PVC tubes attached to a sampler for flooded soils, after the sampling, tubes were hermetically sealed and transported in a vertical position under refrigeration (approximately 4 °C). At the laboratory, soil samples were sectioned into 0–10 and 30–40 cm sections, representative of the uppermost and lowermost soil layers. During samples collections, the redox potential (E_h) and pH values were obtained in situ. The E_h values were obtained using a platinum electrode, corrected for the calomel reference electrode adding the value of +244 mV, whereas the pH readings were obtained with calibrated glass electrode calibrated with

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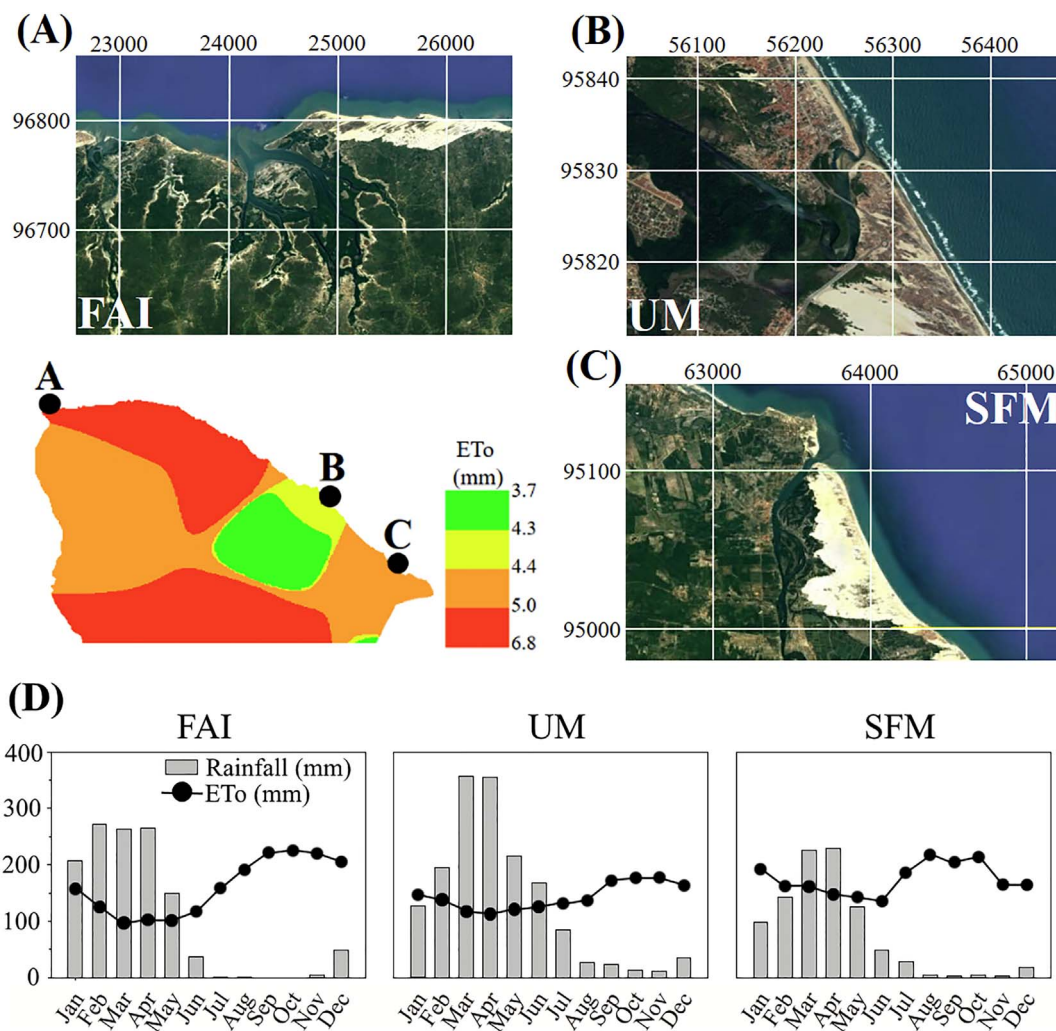


Fig. 1. Sampling sites location and climatic classification for the three studied mangrove forests. (A) Timonha River (FAI), (B) Cocó River (UM), (C) Jaguaribe River (SFM), (D) annual rainfall distribution and evapotranspiration (ETo) at the studied sites.

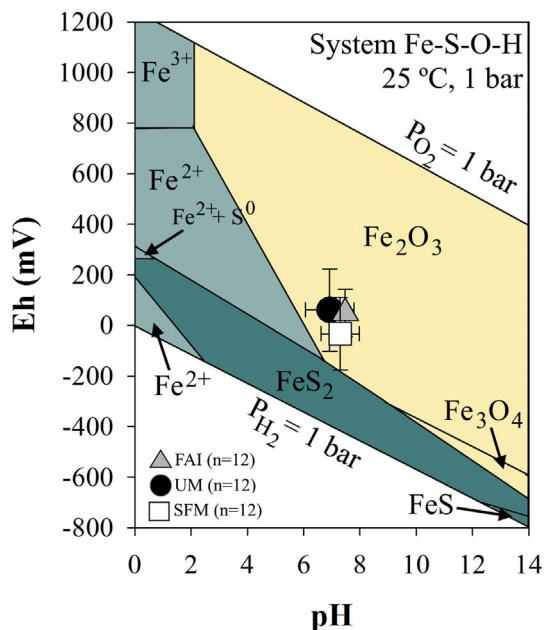


Fig. 2. Mean values (\pm S.D.; $n = 36$) of Eh and pH for the studied sites and the diagram for the stable phases of iron in the system Fe-S-O-H (adapted from Brookins, 1988).

pH = 4.0 and 7.0 standard solutions. Sampling occurred in triplicate during low tide during the wet (from January to May) and dry seasons (June to December), accounting 12 samples for each studied site (Fig. 1D).

All samples were analyzed to determine the total organic carbon content (OC), reactive and pyritic Fe, AVS and simultaneously extracted metals (SEM). The OC contents were obtained by an elemental analyzer (LECO-CNS 2000) after the removal of inorganic C using 1 M HCl (Howard et al., 2014). The reactive and pyritic iron contents were sequentially extracted by the method proposed by Lord (1982), in which the reactive Fe ($Fe_{REACTIVE}$) was extracted with a solution of 0.25 M Na-citrate + 0.11 M Na-bicarbonate adding 3 g of Na-dithionite; whereas pyritic Fe ($Fe_{PYRITIC}$) was extracted with concentrated HNO_3 , after the removal of sheet silicates and organic matter using HF 10 M and concentrated H_2SO_4 , respectively.

The AVS fraction was extracted using 3 M HCl, avoiding higher acid concentrations (e.g., 6 M HCl) and, thus, preventing pyrite and Fe-oxhydroxides dissolution (Allen et al., 1993; Cooper and Morse, 1998a; Luther, 2005). The evolved H_2S was trapped in a Zn acetate solution (25%) and the AVS content was quantified colorimetrically (Cline, 1969), whereas the simultaneously extracted metals (SEM) (i.e., Mn, Cu, Cr and Pb) were determined by ICP-OES. In order to compare the results among the sites, the mean values were compared by one-way ANOVA, followed by Tukey test. Association and relationship among the variables were assessed by principal component analysis (PCA) and

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