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Trace metal pyritization variability in response to mangrove soil aerobic and anaerobic oxidation processes

W. Machado^{a,*}, N.L. Borrelli^{b,c}, T.O. Ferreira^d, A.G.B. Marques^d, M. Osterrieth^{b,c}, C. Guizan^e^a Departamento de Geoquímica, Instituto de Química, Universidade Federal Fluminense, Niterói, RJ 24020-141, Brazil^b Instituto de Geología de Costas y del Cuaternario (IGCyC), Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, CC 722, Correo Central (7600) Mar del Plata, Buenos Aires, Argentina^c Instituto de Investigaciones Marinas y Costeras (IIMyC), Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina^d Departamento de Ciências do Solo, Universidade de São Paulo, ESALQ/USP Piracicaba, São Paulo, Brazil^e Laboratório de Geologia Marinha-LAGEMAR, Departamento de Geologia, Universidade Federal Fluminense, Niterói, RJ 24210-340, Brazil

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ABSTRACT

The degree of iron pyritization (DOP) and degree of trace metal pyritization (DTMP) were evaluated in mangrove soil profiles from an estuarine area located in Rio de Janeiro (SE Brazil). The soil pH was negatively correlated with redox potential (Eh) and positively correlated with DOP and DTMP of some elements (Mn, Cu and Pb), suggesting that pyrite oxidation generated acidity and can affect the importance of pyrite as a trace metal-binding phase, mainly in response to spatial variability in tidal flooding. Besides these aerobic oxidation effects, results from a sequential extraction analyses of reactive phases evidenced that Mn oxidized phase consumption in reaction with pyrite can be also important to determine the pyritization of trace elements. Cumulative effects of these aerobic and anaerobic oxidation processes were evidenced as factors affecting the capacity of mangrove soils to act as a sink for trace metals through pyritization processes.

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Mangrove forests are highly productive ecosystems periodically flooded by tidal water, which result in anaerobic decomposition of accumulated organic matter via bacterial sulfate reduction in mangrove soils, consequently promoting pyrite (FeS₂) formation (Sherman et al., 1998; Alongi et al., 2003). Although substantial sulfide reoxidation can occur at surface layers due to bioturbation, presence of roots and tidal mixing (Holmer et al., 1994), pyrite has been recognized as an important trace metal-binding compound in such soils (Clark et al., 1998; Alongi et al., 2003). Therefore, the production of pyrite and its preservation can be considered important for the retention of trace metals within these environments and metal-sulfur associations can contribute to determine the mangrove ecosystems role as trace metal sinks (Machado et al., 2002; Marchand et al., 2006).

The evaluation of the extent in which reactive (HCl-soluble) Fe is converted in pyrite, i.e. the degree of iron pyritization (DOP), has been extensively used to elucidate Fe geochemistry, after its introduction by Berner (1970). This evaluation was extended to investigations on the degree of trace metal pyritization (DTMP) by

Huerta-Díaz and Morse (1990), improving the knowledge on the trace metal behavior and bioavailability in coastal environments, such as salt marsh soils (Otero and Macías, 2002) and intertidal sediments (Álvarez-Iglesias and Rubio, 2009). However, relatively few studies dealing with DOP evaluation have been performed for mangrove ecosystems (Sherman et al., 1998; Ferreira et al., 2007a,b,c; Otero et al., 2009; Araújo et al., 2012), while remarkably fewer information is available on DTMP for these ecosystems, as has been reported for Mn (Otero et al., 2009; Andrade et al., 2012) and Co, Ni and Zn (Andrade et al., 2012).

This study evaluates the pyritization of Fe, Mn, Cr, Cu, Ni, Pb and Zn in a mangrove area within the São João River estuary (22°34'24"S, 42°00'52"W), Rio de Janeiro State, SE Brazil (Fig. 1). The São João River catchment has nearly 2100 km², mainly covered by pastures, agricultural areas and preserved forests, also holding biological reserves and a water reservoir that supplies drinking water for many municipalities. River channelization, sand mining activities and urbanization have impacted some parts of this catchment. Land erosion and conversion to agriculture and pasture activities have been considered as its main anthropogenic impacts (Oliveira and Mello, 2007). The study site does not present significant point sources of contamination, although it presents physical human impact due to an artificial system of channels and flooding gates used to drain the surrounding soils (formerly wetlands),

* Corresponding author. Tel.: +55 21 26292218; fax: +55 21 26292234.

E-mail addresses: wmachado@geoq.uff.br (W. Machado), nlborrelli@mdp.edu.ar (N.L. Borrelli), toferreira@usp.br (T.O. Ferreira), gisamarques@yahoo.com.br (A.G.B. Marques), mosterri@yahoo.com.ar (M. Osterrieth), cleverson@igeoq.uff.br (C. Guizan).

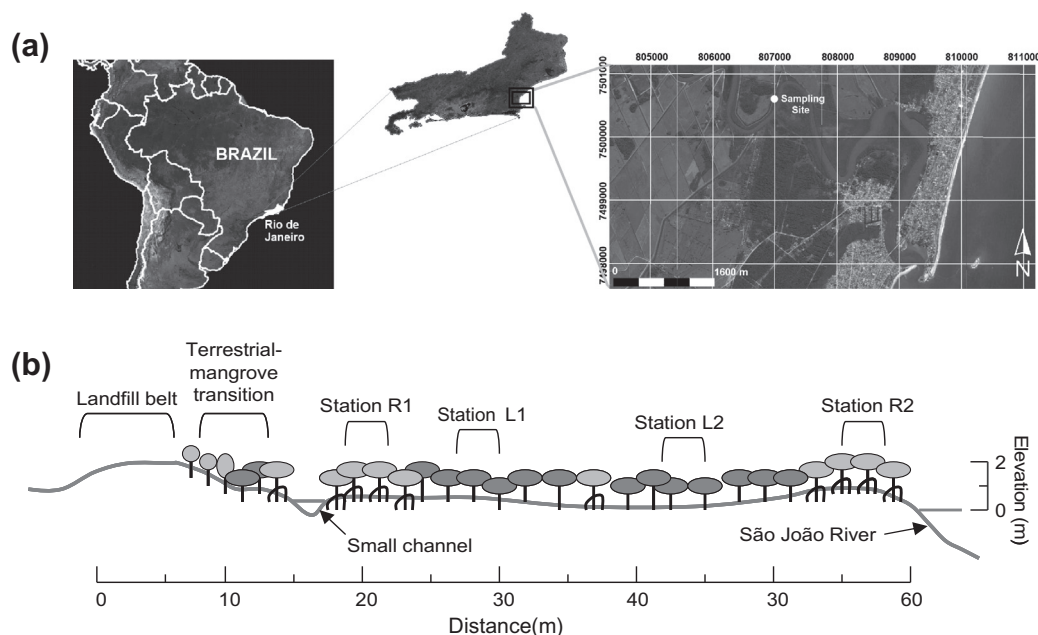


Fig. 1. Location of (a) study area in the São João River (Rio de Janeiro State, SE Brazil) and (b) sampling stations within the transect.

presenting a “landfill belt” built with the soil removed to construct drainage channels (Fig. 1).

Since there is no information on trace metal concentrations in the study area and there are remaining mangrove forests that appear to be not affected by the drainage system changes in São João River estuary, mangrove soils located outside the landfill belt were analyzed to provide information to be used as baseline data in future investigations. In a similar approach to obtain baseline data, Keene et al. (2010) evaluated the trace metal geochemistry in former acid sulfate soils (ASS), which were located behind a sea wall, by comparing these soils with those from surrounding mangrove soils outside the sea wall.

Mangrove soil samples were collected during low tide along a 40-m transect across the study area, in October 2010, perpendicular to the landfill belt. The sampling was carried out at increasing distances from this belt, considering the plant cover variability toward São João River margin. Four sampling stations were established: two colonized by *Rhizophora mangle* (stations R1 and R2) and two colonized by *Laguncularia racemosa* (stations L1 and L2). Field observation of tidal flooding during the field work evidenced that the flooding sequence was L2 → L1 → R1 → R2 (Fig. 1), implying that microtopography variability follows this sequence.

In each station an acrylic tube (6 cm i.d., 25 cm length) was used to collect a short soil profile, during low tide. Each profile was sectioned in three slices (with 4 or 5 cm depth intervals). Redox potential (Eh) and pH were measured in each interval (after probe equilibration during nearly two minutes). The Eh electrode was checked against a standard Metrohm redox solution (250 ± 5 mV at 20 °C), and final readings were corrected by adding the potential (244 mV) of a calomel reference electrode. The pH was measured with a glass electrode after calibration with pH 4.0 and 7.0 standards. After these measurements, the samples were stored under refrigeration until further analysis.

Fresh soil subsamples were used for metal extractions and the results were expressed in dry weight basis, after correction for water content (61–72% for all samples) as determined by drying soil subsamples to constant weight. A combined sequential extraction method was carried out, adapted from Tessier et al. (1979), Fortin et al. (1993); Huerta-Díaz and Morse (1990). This procedure

includes six operationally- defined phases, as previously applied to study Fe and Mn biogeochemistry (Ferreira et al., 2007a,b,c; Otero et al., 2009; Araújo et al., 2012):

- F1—Exchangeable metals: shaken for 30 min in 30 ml of 1 M MgCl_2 solution (pH 7.0);
- F2—Metals associated with carbonates: shaken for 5 h in 30 ml of 1 M NaOAc solution (pH 5.0);
- F3—Fe—ferrihydrite and metals associated to this fraction: shaken for 6 h at 30 °C in 30 ml of 0.04 M hydroxylamine + acetic acid 25% (vol/vol) solution;
- F4—Fe—lepidocrocite and metals associated to this fraction: shaken for 6 h at 96 °C in 30 ml of 0.04 M hydroxylamine + acetic acid 25% (vol/vol) solution;
- F5—Fe—goethite/hematite and metals associated to this fraction: shaken for 30 min at 75 °C in 20 ml of 0.25 M sodium citrate + 0.11 M sodium bicarbonate solution with 3 g of sodium dithionite;
- F6—Metals associated to the pyritic fraction: after a silicate phase (10 M HF extraction) and organic phase (H_2SO_4 extraction) elimination (see Huerta-Díaz and Morse, 1990 for details), the pyritic phase was extracted by shaking for 2 h at room temperature in 10 ml of concentrated HNO_3 .

This procedure is an alternative to the conventional extraction in 1 M HCl to determine metal reactive phases for DTMP evaluation (Huerta-Díaz and Morse, 1990), being hypothesized that the estimates of different reactive phases can help in elucidating specific biogeochemical processes associated to trace metal pyritization.

Metal concentrations were determined by ICP OES. The DOP was calculated by considering the $\Sigma\text{F1–F5}$ as the reactive-Fe phase (Ferreira et al., 2007a,b; Otero et al., 2009; Ferreira et al., 2010). This principle was applied for DTMP calculation (Otero et al., 2009). The degrees of Fe and trace metal (Me) pyritization were calculated according to the following equations:

$$\text{DOP (\%)} = (\text{pyrite Fe} / (\text{pyrite Fe} + \text{reactive Fe})) \times 100$$

$$\text{DTMP (\%)} = (\text{pyrite Me} / (\text{pyrite Me} + \text{reactive Me})) \times 100$$

Physicochemical characteristics found in studied soils are presented in Table 1. All samples presented acidic (pH = 5.0–6.3) and suboxic to oxic (Eh = 105–401 mV) conditions. The more elevated site (R2) showed more oxidized and acidic conditions. In the other stations, pH values did not present noticeable differences, while Eh values were lower in the less elevated site (L2). During low tide periods, aerobic sulfide oxidation may take place and generate acidity, as indicated by the negative correlation between Eh and pH in the study area ($r = -0.86$, $p < 0.01$), as also reported for other mangrove areas (Ferreira et al., 2010; Araújo et al., 2012). Depth variations of Eh values may also be related to aeration by roots (Otero et al., 2006) and/or bioturbation (Ferreira et al., 2007a). However, the most probable process that has affected the redox conditions is the flooding variability, in response microtopography (Ferreira et al., 2010).

The sums of metal concentrations from all phases ($\Sigma F1-F6$) were low, with a generally very low variability (Table 1). The $\Sigma F1-F6$ values for Cr, Cu, Ni, Pb and Zn were always below the ranges of background concentrations for coastal sediments from Rio de Janeiro State, which were ≥ 3.3 , 14.6, 10.6, 4.0 and 93 nmol g^{-1} for Cu, Cr, Ni, Pb and Zn, respectively, as supported by coupled ^{210}Pb dating and land use history data (Marques et al., 2006; Gomes et al., 2009; Monteiro et al., 2012). Although the organic matter-bound phase, which might be expected to occur in mangrove soils (e.g., Clark et al., 1998), have not been accounted in the present study, the results did not indicate anthropogenic contamination influence for the partial extraction procedure used.

Pyritization values (Table 1) ranged in one order of magnitude, except for Cu, and were clearly associated with physicochemical gradients. Significant positive correlations between pH and the pyritization of Fe ($r = 0.76$, $p < 0.05$), Cu ($r = 0.93$, $p < 0.01$), Mn ($r = 0.75$, $p < 0.05$) and Pb ($r = 0.75$, $p < 0.05$) were observed. The pyritization of Zn, Cr and Ni did not present significant correlations with physicochemical conditions, while only Cu pyritization was

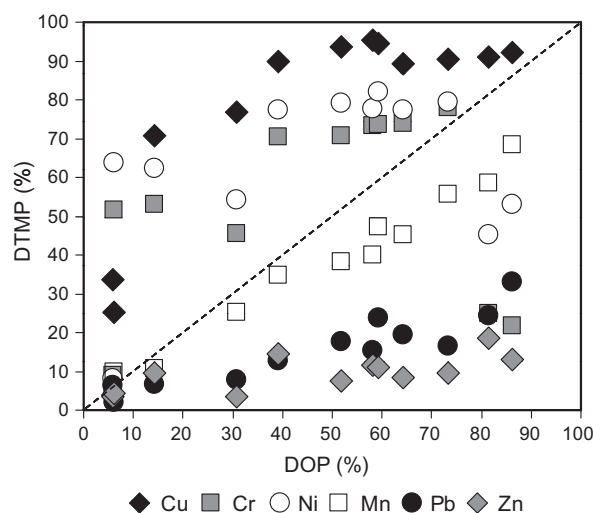


Fig. 2. Relationships between DTMP and DOP data.

significantly correlated with Eh values, showing a negative relationship ($r = -0.77$, $p < 0.05$). Copper geochemical partitioning was chosen by Clark et al. (1998) to illustrate their conceptual model on the sensitivity of trace metals to redox conditions within mangrove soils, since the predominance of oxide or sulfide phases of this metal oscillated following Eh vertical variability. The present results are in good agreement with this Cu geochemical partitioning sensitivity to physicochemical conditions.

Both thermodynamics and water exchange reaction kinetics have allowed predictions on trace metal incorporation into pyrite (Morse and Luther, 1999). According to such conceptual predictions, Mn, Cr, Zn, Pb and Cd generally do not undergo high incorporation

Table 1

Depth variability of Eh (mV), pH, sums of sequential extraction phases ($\Sigma F1-F6$) (nmol g^{-1} for trace metals and $\mu\text{mol g}^{-1}$ for Fe) and degrees of iron and trace metals pyritization (%), followed by means and standard deviations (SD) in bold.

Station/depth	Eh	pH	$\Sigma F1-F6$							Degrees of pyritization						
			Fe	Mn	Cr	Cu	Ni	Pb	Zn	Fe	Mn	Cr	Cu	Ni	Pb	Zn
<i>Station R1</i>																
0–5 cm	285	5.9	101	93	87	22.0	35.8	7.25	139	73.4	55.7	78.1	90.3	79.4	16.4	9.7
5–10 cm	214	6.1	88	84	27	18.9	10.2	5.80	141	81.5	58.6	24.8	91.0	45.2	24.4	18.6
10–15 cm	194	6.3	119	147	31	25.2	11.9	6.76	132	86.1	68.3	21.7	92.2	53.1	33.0	12.9
Mean	231	6.1	102	107	48	22.0	18.7	6.76	138	80.3	60.9	41.5	91.2	59.2	24.6	13.7
SD	48	0.2	16	35	33	3.1	13.6	0.97	5	6.4	6.6	31.7	1.0	17.9	8.3	4.5
<i>Station L1</i>																
0–4 cm	231	6.1	125	113	100	20.5	35.8	7.25	171	39.1	34.8	70.5	89.8	77.5	12.7	14.4
4–8 cm	203	6.2	119	127	96	25.2	35.8	7.25	147	64.2	45.2	74.0	89.4	77.3	19.3	8.3
8–12 cm	249	6.0	111	124	94	25.2	35.8	7.73	164	58.2	40.1	73.3	95.5	77.7	15.4	11.6
Mean	228	6.1	118	122	96	23.6	35.8	7.25	161	53.8	40.0	72.6	91.6	77.5	15.8	11.4
SD	23	0.1	7	7	4	3.1	0.0	0.48	12	13.1	5.2	1.9	3.4	0.2	3.3	3.1
<i>Station L2</i>																
0–4 cm	105	6.1	102	87	56	17.3	15.3	7.73	151	30.7	25.2	45.4	76.9	54.1	7.7	3.4
4–8 cm	159	6.3	108	116	90	17.3	32.4	6.76	168	51.7	38.4	70.8	93.7	79.2	17.7	7.5
8–12 cm	114	6.1	110	111	92	20.5	34.1	6.28	208	59.3	47.3	73.6	94.6	81.9	23.7	10.9
Mean	126	6.2	107	106	79	18.9	27.3	6.76	176	47.2	37.0	63.3	88.4	71.7	16.4	7.3
SD	29	0.1	4	16	21	1.6	10.2	0.97	29	14.8	11.1	15.5	10.0	15.3	8.1	3.8
<i>Station R2</i>																
0–4 cm	376	5.4	188	133	69	25.2	15.3	9.66	216	5.8	5.3	9.0	33.7	8.2	6.4	3.5
4–8 cm	401	5.0	177	109	137	22.0	39.2	10.6	243	6.1	9.8	51.7	25.2	63.8	1.9	4.4
8–12 cm	281	5.7	173	142	131	22.0	40.9	10.1	269	14.3	10.6	53.1	70.8	62.4	6.8	9.7
Mean	353	5.4	179	127	112	23.6	32.4	10.1	243	8.7	8.6	37.9	43.2	44.8	5.0	5.9
SD	63	0.4	8	16	37	1.6	13.6	0.48	28	4.8	2.9	25.1	24.2	31.7	2.7	3.4

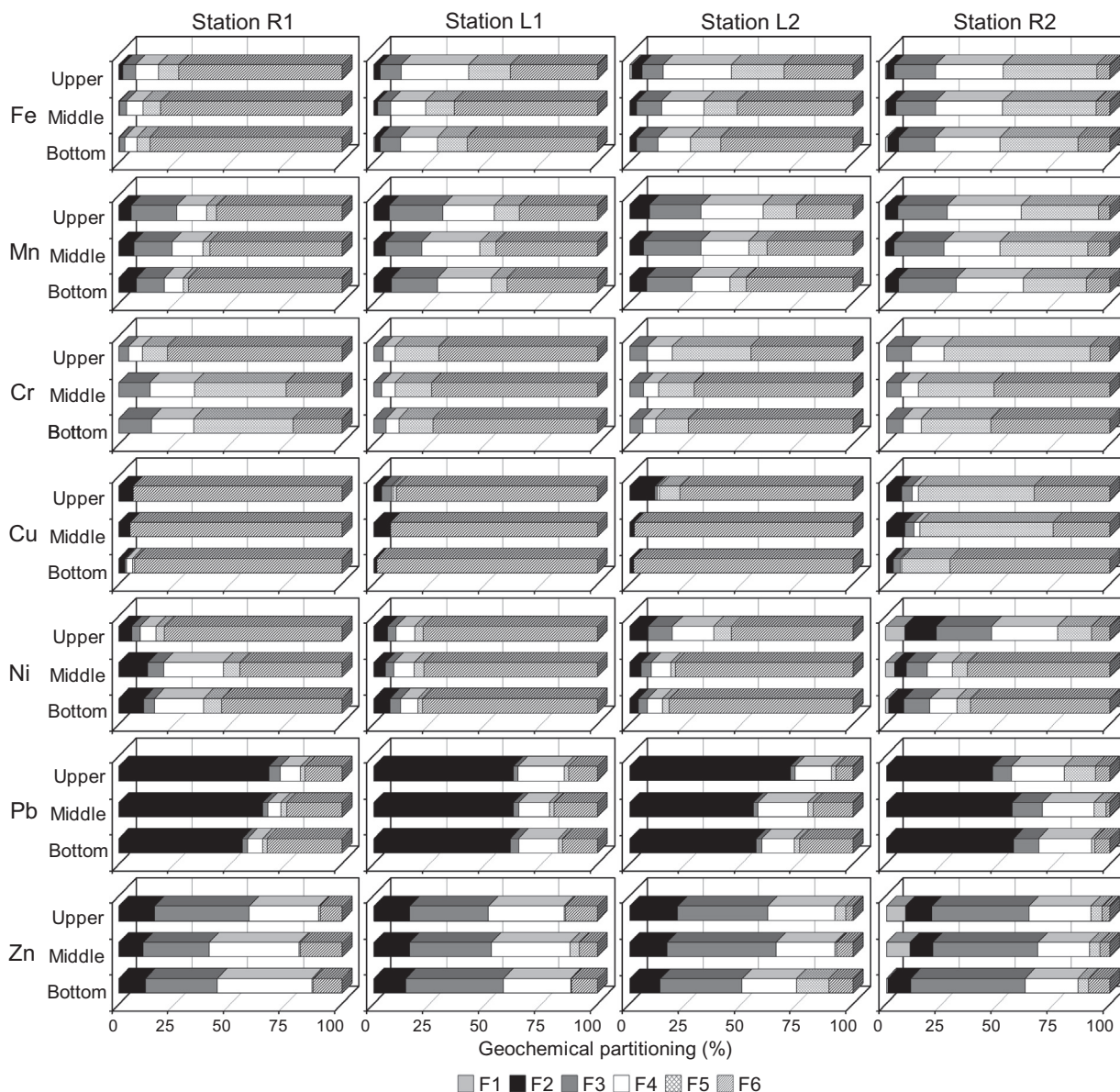


Fig. 3. Variability in the percent geochemical partitioning among the sequential extraction phases from mangrove soils (F1, exchangeable; F2, carbonate-bound; F3, ferrihydrite-bound; F4, lepidocrocite-bound; F5, goethite/hematite-bound; F6, pyritic). Upper, middle and bottom soil layers correspond to 0–5, 5–10 and 10–15 cm depth (station R1) or 0–4, 4–8 and 8–12 cm depth (stations L1, L2 and R2), respectively. Note that the percent contributions of F6 correspond to DOP and DTMP values.

into pyrite, while Ni and Cu can be more readily susceptible to be incorporated (Morse and Luther, 1999), as it was supported by data from diverse sedimentary environments (Huerta-Diaz and Morse, 1992). However, unpredicted high pyritization levels have been previously observed (e.g., for Cr in Galveston Bay, USA; Morse et al., 1993), since metals not expected to undergo high pyritization can co-precipitate with pyrite (Morse and Luther, 1999). This can explain the often high pyritization (exceeding 60% in some cases) presented by Mn and Cr (Table 1).

Fig. 2 presents the relationships of DTMP with DOP values, while geochemical partitioning data are showed in Fig. 3. The DTMP was correlated with DOP ($r = 0.68$, $p = 0.05$, for Zn; $r = 0.82$, $p = 0.01$, for Cu; $r = 0.92$, $p < 0.01$, for Pb; $r = 0.99$, $p < 0.01$, for Mn), except for Cr ($r = 0.17$) and Ni ($r = 0.36$). This general trend is consistent with previous studies, reflecting gradual incorporation into pyrite (Huerta-Diaz and Morse, 1992). Most samples presented a trend of decreasing pyritization in the order $\text{Cu} > \text{Ni} > \text{Cr} > \text{Fe} > \text{Mn} > \text{Pb} > \text{Zn}$ (Fig. 2). Exceptions to this general

order can be elucidated by the geochemical partitioning trends from specific samples. For example, Cr and Ni pyritization values were lower than DOP values only in the 5–15 cm depth intervals of station R1 (Table 1; Fig. 3). In these samples, both metals were more associated to oxidized phases (Fig. 3), which may be explained by subsurface oxidation processes, as can be promoted by bioturbation (Ye et al., 2011) and/or oxygen release by *R. mangle* roots (Otero et al., 2006). If significant bioturbation occurs, this process can possibly contribute for trapping of metals, e.g. by enhancing the metal diffusion into depths in which the mangrove rhizosphere can retain these elements (Suzuki et al., 2012).

The exchangeable phase (F1) was generally negligible for all metals, reaching a maximum contribution at the two upper layers of station R2 for Ni and Zn, but always $\leq 10\%$ of $\Sigma\text{F1–F6}$. Carbonate phases (F2) were quantitatively important only for Pb ($> 50\%$ of $\Sigma\text{F1–F6}$), whereas the other metals presented negligible or small carbonate phase contributions to determine the $\Sigma\text{F1–F6}$ (essentially $< 20\%$ of $\Sigma\text{F1–F6}$), probably due to the slightly acidic

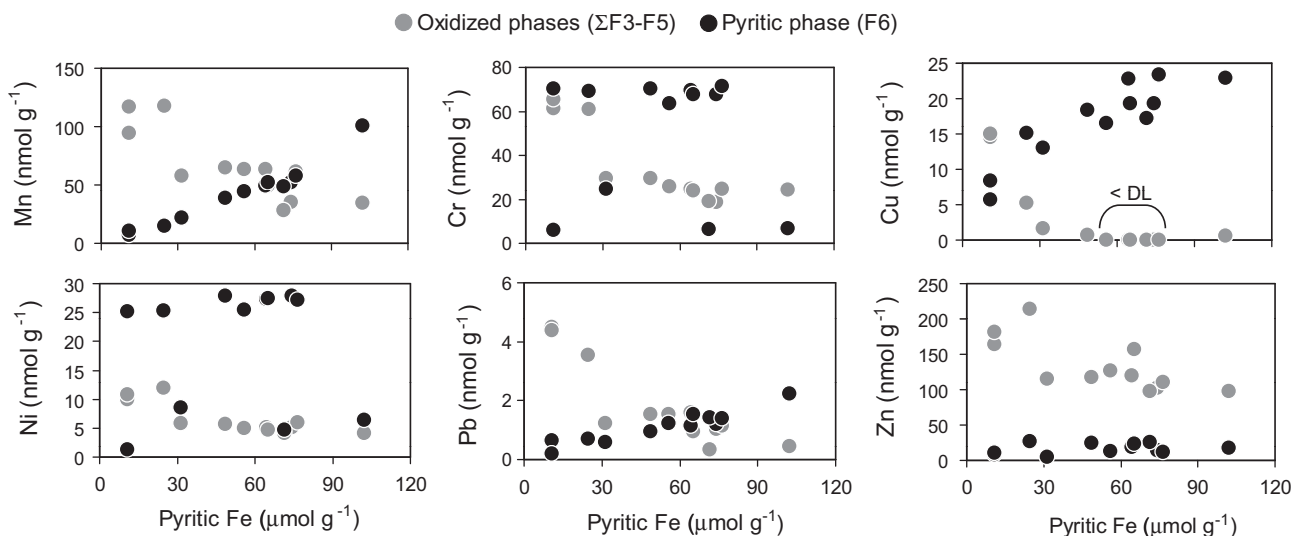


Fig. 4. Relationships of the sums of oxidized phases ($\Sigma F3-F5$) and sums of all reactive phases ($\Sigma F1-F5$) of trace metals with Fe pyritic phase. Note that some samples presented $\Sigma F3-F5$ data below the detection limits (DL) found for Cu oxidized phases (ranging from 0.1 to 0.3 nmol g⁻¹ for such phases).

characteristic of the short soil profiles. In fact, there were significant negative correlations of pH with the concentrations of Fe ($r = -0.76$; $p < 0.05$) and Pb ($r = -0.71$; $p < 0.05$) in the carbonate fraction. The more easily-extractable phases can be interpreted as more mobile (e.g., [Marcovecchio et al., 2010](#)), and consequently more bioavailable forms of metals. These phases are expected to be low in mangrove soils due to the frequently observed capacity of these environments to conserve metals in more strongly-bound phases, such as sulfides, oxides and organic compounds, depending on the stability of these phases in response to physicochemical conditions ([Lacerda et al., 1993](#); [Clark et al., 1998](#)).

Oxidized phases were important in most sampling stations for all studied metals (with the exception of Cu), but showed variable proportions between the ferrihydrite (F3), lepidocrocite (F4) and goethite/hematite (F5) fractions, reflecting different crystallization levels of the oxidized metal fractions. Considering these three fractions, some metals generally presented a predominance of F4 (Fe, Ni and Pb), F5 (Cr) and F3 (Zn), while other metals did not present a clear trend. Disregarding the previously discussed exceptional increase in oxidized forms of Cr and Ni at deeper layers from station R1, the metal oxidized phases' contributions to determine $\Sigma F1-F6$ were frequently consistent with the expected redox effects (i.e., generally higher contributions of $\Sigma F3-F5$ under more oxidized conditions). These general trends are reflected by significant correlations of Eh values with $\Sigma F3-F5$ concentrations for the studied metals ($r = 0.60-0.90$; $p < 0.05$ or lower), except for Zn ($r = 0.47$). It is important to note that most metals presented a change from a predominant pyritic phase (F6) to predominant crystalline oxidized phases with increasing Eh ([Table 1](#); [Fig. 3](#)), while Zn presented a ferrihydrite phase predominance.

While all reactive and pyritic phases can often be considered as bioavailable phases (e.g., see [Álvarez-Iglesias and Rubio \(2009\)](#); [Ye et al. \(2011\)](#) for different considerations on these possibilities), a degree of increase or decrease in metal bioavailability can be inferred from multiple steps of sequential extraction procedures. The results evidenced that a higher potential bioavailability occurred for Zn and Pb, which were found in more mobile (non-crystalline) forms that were predominant in all samples. On the other hand, the use of the pyritization data as an estimation of bioavailability is dependent on redox conditions and deserves caution. If reducing conditions are predominantly maintained or even enhanced the study area (e.g., in response to future eutrophication

and/or sea level rise and flooding time increase), the inverse order of the pyritization trend can be considered as the order in which the metals are potentially bioavailable, but this trend is modifiable by temporal and spatial physicochemical changes.

While the studied mangrove soils accumulate pyrite, there was a consistent depletion in $\Sigma F3-F5$ of all trace metals ($r = -0.72$ to -0.92 ; $p < 0.05$) in association with F6 levels of Mn, Cu and Pb significantly correlated with pyrite Fe ($r = 0.89-0.97$; $p < 0.01$), though this correlation was not significant for Ni, Cr and Zn ($r = -0.07-0.30$) ([Fig. 4](#)). These results indicate that some Mn, Cu and Pb phases have been produced at the expenses of other phases (e.g., reducible reactive phase consumption allowing metal incorporation into pyrite; [Huerta-Diaz et al., 2011](#)). Experimental evidences derived from resuspension experiments have demonstrated that aerobic oxidation processes can affect strongly the DTMP, which can be also expected to occur due to other processes (e.g., bioturbation) that imply in oxidation ([Morse, 1994](#)). However, an anaerobic oxidation process can be inferred from the observed relationships of pyrite Fe with oxidized phases ($\Sigma F3-F5$) and pyrite phase (F6) of trace metals. Manganese oxides can be consumed in reaction with pyrite ([Schippers and Jørgensen, 2002](#)), possibly releasing associated metals that can undergo pyritization. In fact, Mn oxidized phases were correlated with oxidized phases from all other trace metals ($r = 0.86-0.94$; $p < 0.01$). However, Ni, Cr and Zn oxidized phases depletion trend was not consistently associated to an increased uptake by pyrite ([Fig. 4](#)), suggesting that other binding phases may be more important for these metals (e.g., organic matter). Solid phase and pore water analyses of mangrove soils have evidenced such mechanisms of oxidized phase release of metals, followed by incorporation by organic matter and sulfide phases ([Marchand et al., 2012](#)).

Manganese redox cycling has been well characterized previously in mangrove soils ([Gueiros et al., 2003](#); [Otero et al., 2009](#)), as well as possible associations of trace metals to this cycling ([Harbison, 1986](#); [Marchand et al., 2006](#)), but not for the observed negative Mn-pyrite interactions. Such negative interactions between trace metal binding phases may be a previously unsuspected mechanism affecting the efficiency of metal trapping within Mn oxides and Fe pyrite in mangrove areas. The implications of these interactions can possibly be also valid for other environments that can have an analogous role in trapping trace metals in the coastal zone, such as salt marsh and seagrass ecosystems.

The following main conclusions were derived from the present study: (i) pyrite can be oxidized by both aerobic and anaerobic biogeochemical processes, possibly affecting its role as a trace metal sink; (ii) the difference of soil elevation between the different stands (and thus the flooding pattern) is one of the main factor controlling the oxidation, as an major aerobic effect; and (iii) the role of manganese oxide in pyrite oxidation was evidenced, as an additional anaerobic effect, which probably involve the role of both compounds as trace metals sinks. This variability can affect the whole role of mangrove soils as metal sinks, as well as can influence metal potential bioavailability, since less or noncrystalline geochemical phases are more susceptible to release metals.

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