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Role of Redox Processes in the Pedogenesis of Hypersaline Tidal Flat Soils on the Brazilian Coast

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Hypersaline tidal flats (HTFs) represent transitional ecosystems where the ocean, land, and freshwater meet. These places are globally widespread and their soils are an important environmental component controlling chemical reactions in wetland ecosystems. Here, we present a pedogenic study of two HTFs on the Brazilian coast (northeast and southeast) based on the solid-phase geochemistry of Fe and Mn and morphological studies. Broken and irregular topographies and strong expression of redoximorphic concentrations (e.g., mottles, nodules, and pore linings) are present throughout the soil profiles. Although lepidocrocite is the most abundant Fe fraction in these soils (more than 50% of all extractions), deeper horizons show pyrite as the main Fe fraction caused by the presence of buried mangrove soils. The more oxidizing conditions in these deeper horizons indicate that pyrite is not stable and is undergoing degradation. Iron released in this process is moving upward and precipitating as Fe oxides in more oxidized portions of the soil profile. Coprecipitation of Mn and ferrihydrite seems to be an important process controlling the geochemistry of Mn in HTFs. Our data indicate that deeper horizons have been transforming, driven mainly by water table oscillation and, consequently, redox processes. This process allows translocation of Mn^{2+} and Fe^{2+} throughout the soil profile, followed by oxidation and precipitation of $\text{Mn}^{3+/4+}$ and Fe^{3+} oxides in preferential sites.

Abbreviations: CCE, CaCO_3 equivalent; DOP, degree of Fe pyritization; EC, electrical conductivity; Eh, redox potential; ESP, exchangeable Na percentage; F1, exchangeable Fe and Mn; F2, Fe and Mn associated with carbonates; F3, ferrihydrite and Mn associated with this extraction; F4, lepidocrocite and Mn associated with this extraction; F5, crystalline Fe oxides and Mn associated with this extraction; F6, Fe and Mn associated with pyrite; HTF, hypersaline tidal flats; HTF-CE, hypersaline tidal flat at the Acaraú River Basin; HTF-RJ, hypersaline tidal flat in the Sepetiba-Guaratiba coastal complex; P1CE, Soil Profile 1 in HTF-CE; P2CE, Soil Profile 2 in HTF-CE; P1RJ, Soil Profile 1 in HTF-RJ; P2RJ, Soil Profile 2 in HTF-RJ; TOC, total organic C; TPA, total potential acidity.

Coastal wetlands are globally widespread and can be found in almost all climates (Ramesh Reddy and DeLaune, 2008). Active biological, chemical, and physical reactions taking place in these complex environments have a great impact on global biogeochemical processes (Frings et al., 2016; Kolditz et al., 2012; Sperlich et al., 2015). Two examples of coastal wetland are HTFs and mangroves. Although both ecosystems are commonly associated in the estuary, flooding frequency and seawater residence is substantially less notable in HTFs, leading to different pedogenic processes and, consequently, formation of soils with different properties (Albuquerque et al., 2014b; Ferreira et al., 2010; Ridd and Stieglitz, 2002).

Hypersaline tidal flat soils are commonly found in regions where evapotranspiration exceeds precipitation in some months of the year (Albuquerque et al., 2014a; Hadlich and Ucha, 2009). These soils are very common in the northern, northeastern, and southeastern Brazilian coasts and in many other countries

Core Ideas

- Iron and Mn movement followed by oxidation impose strong control on soil transformations.
- Sulfidization is not an active process in hypersaline tidal flat (HTF) soils.
- Coprecipitation of Mn and ferrihydrite controls the geochemistry of Mn in HTF soil.

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around the world (Albuquerque et al., 2014a; Ridd and Stieglitz, 2002). Previous studies evidenced that formation of HTFs is a natural process in which mangrove have been replaced by a new hypersaline environment (Albuquerque et al., 2014a). This process is driven by an increase in soil salinity caused by hydrodynamic alterations in the estuary plain, leading to mangrove dieback followed by formation of hypersaline soils. Pedogenic relationships between mangrove and HTF soils are marked by the presence of deeply buried soils in HTF soils produced by the previous mangrove ecosystem (Albuquerque et al., 2014b; Ucha et al., 2008).

Hypersaline tidal flat soils are different by contrasting morphological, physical, and chemical attributes from mangrove and most well drained and aerated soils (Albuquerque et al., 2014b). Nevertheless, these soils undergo pedogenic processes similar to those of evaporative environments, such as precipitation of CaCO_3 and soluble salts, solonization, salinization, and redox processes (Albuquerque et al., 2014b). Since these environments are under alternating redox conditions, Mn and Fe oxides are very important soil components that act as electron acceptors during microbial respiration under suboxic and anoxic conditions (Ramesh Reddy and DeLaune, 2008). These redox fluctuations lead to the formation of redoximorphic features in the soil profiles, which can be investigated via morphological approaches (Lindbo et al., 2010; Vepraskas, 2001, 2004). Although sulfate reduction and accumulation of authigenic Fe sulfides are important biogeochemical process in coastal wetlands (Berner, 1984),

these processes do not seem to be relevant in these soils because of the more oxidized conditions imparted by the formation of HTFs (Albuquerque et al., 2014b). Investigation of these processes is important to better understand the fundamental properties and mechanisms of these soils and how they control the dynamics of elemental cycles in their respective environments (Barbiéro et al., 2008; Furquim et al., 2017; Santos et al., 2017).

Few studies have investigated the formation and fundamental properties of HTF soils (Hollins and Ridd, 1997; Sanford and Wood, 2001; Ridd and Stieglitz, 2002; Dong et al., 2014; Schile et al., 2017; Xie et al., 2018). We investigated the pedogenesis of two HTFs on the Brazilian coast (northeast and southeast regions). Our discussion is based on morphological and geochemical studies, with the latter focusing on sequential extractions of Fe and Mn to understand the forms and distribution of these redox-sensitive elements in HTF soils.

Environmental Settings

Two HTFs were studied along the Brazilian coast (Fig. 1). One site is in the Acaraú River Basin (northeast region) and is referred as the HTF-CE. The regional geology of the Acaraú River Basin consists of pre-Cambrian metamorphic rocks (gneisses, schists, and phyllites). The study area is encompassed by the Barreiras Tablelands, which is composed of Cenozoic sand- and clay-sized sediments (Bezerra et al., 2001; Hesp et al., 2009). Rainfall distribution is irregular, with a dry season between July and December. Climate is mild semiarid

Fig. 1. Location of the study sites and soil profiles. The white and black dashed lines delineate the mangrove forests and HTFs, respectively. Images source: Google Earth 2015 version (<https://earth.google.com/web/>, accessed 29 June 2018).

(Bw, according to Köppen) with an average annual precipitation of about 1200 mm and evapotranspiration of about 1700 mm. The tidal regime is semidiurnal with the amplitude varying between 1.4 and 2.6 m. The area is flooded several days throughout the month, with the maximum tidal flooding occurring during spring tides.

The second study site is in the southeast region of Brazil and is included in the Sepetiba-Guaratiba costal complex (referred as HTF-RJ). The regional geology is composed of Quaternary coastal plains and pre-Cambrian crystalline basement (granites, gneisses, and migmatites; Borges and Nittrouer, 2015). The estuary, which includes mangroves and HTFs, is a semiconfined environment that is physically protected from the Atlantic Ocean (Muehe et al., 2006). The rainfall distribution is more homogeneous than that of HTF-CE, with a shorter dry season taking place from June to August. Climate is tropical wet-dry (Aw, according to Köppen) and the average annual precipitation and evapotranspiration are about 1016 and 1450 mm, respectively.

Previous studies have shown that the topography of HTFs in Brazil is around 0 to 3% (Hadlich et al., 2010; Albuquerque, 2015). Both HTFs have an irregular distribution of halophyte plants on the soil surface.

MATERIAL AND METHODS

Description of the soil morphology (Schoeneberger et al., 2012) and soil sampling were performed during low tide in two soil pits at each site. The soil profiles were labeled as P1CE and P2CE (HTF-CE) and P1RJ and P2RJ (HTF-RJ). Samples were taken by horizon and were maintained at $\sim 4^{\circ}\text{C}$ during transportation to the laboratory, where part of each sample was air-dried and another part was stored at low temperature (-5°C) to minimize Fe and Mn oxidation.

Soluble salts were removed from the samples with ethanol (70%) prior to chemical and physical analysis. Particle size distribution was determined by the pipette method after removal of organic matter with H_2O_2 (30%) (Gee and Or, 2002). Calcium carbonate equivalent (CCE) was determined by titration of the solution with NaOH after dissolution of carbonates with HCl (AOAC International, 1970). Total organic C (TOC) was determined by wet oxidation (Walkley et al., 1934). Exchangeable K^+ and Na^+ were extracted with a solution of $0.0125 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.05 \text{ mol L}^{-1} \text{ HCl}$ and determined by flame spectroscopy (Digimed DM-62, Digimed, São Paulo-SP, Brazil), whereas exchangeable Ca^{2+} and Mg^{2+} were extracted with a $1.0 \text{ mol L}^{-1} \text{ KCl}$ solution and determined using atomic absorption spectroscopy (PerkinElmer 1100B, Perkin Elmer, Bordenseewerk, Überlingen, Germany). Potential acidity ($\text{H}^+ + \text{Al}^{3+}$) was measured by titration of the solution with NaOH after extraction with Ca acetate at pH 7.0. Cation exchange capacity was calculated by the sum of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and $\text{H}^+ + \text{Al}^{3+}$. Electrical conductivity was measured in a saturation extract in the laboratory (USDA, 2014) with a Digimed DM-32 conductivity meter (Digimed). The pH and redox potential (Eh) were determined in the field immediately after sampling with a glass

electrode (Hanna HI 98121, Hanna Instruments, Woonsocket, RI) and an oxidation–reduction potential Pt electrode (Eutech Instruments, Vernon Hills, IL), respectively. The final readings for Eh measurements were corrected by adding the potential of a calomel reference electrode (+244 mV). To investigate presence of sulfidic material, total potential acidity (TPA) was determined after oxidation of the samples with H_2O_2 (30%) at pH 5.5 (a soil/solution ratio of 1:5), followed by pH measurement after oxidation was accomplished (Konsten et al., 1988).

Iron and Mn extractions were performed with wet samples previously stored at low temperatures. Throughout this paper, Fe oxides is used to describe oxides, hydroxides, and oxide-hydroxides. Extractions were performed via a sequential extraction procedure derived from the combination of methods proposed by Fortin et al. (1993), Huerta-Díaz and Morse (1990), and Tessier et al. (1979). This methodology has been used widely for wetland soils [see Ferreira et al. (2010) and Otero et al. (2009) for more details] and allows differentiation of six operationally-defined fractions: F1: exchangeable Fe and Mn, extracted with 30 mL of a 1 mol L^{-1} solution at pH 7.0; F2: Fe and Mn associated with carbonates, extracted with 30 mL of a $1 \text{ mol L}^{-1} \text{ NaOAc}$ solution at pH 5.0; F3: ferrihydrite and Mn associated with this extraction, extracted with 30 mL of a solution of 0.04 mol L^{-1} hydroxylamine + 25% (v/v) acetic acid under agitation at room temperature; F4: lepidocrocite and Mn associated with this extraction, extracted with 30 mL of a solution of 0.04 mol L^{-1} hydroxylamine + 25% (v/v) acetic acid under agitation at 96°C ; F5: crystalline Fe oxides and Mn associated with this extraction, extracted with 20 mL of a solution of 0.25 mol L^{-1} sodium citrate + $0.11 \text{ mol L}^{-1} \text{ NaHCO}_3$, with 3 g of sodium dithionite; F6: Fe and Mn associated with pyrite, extracted with 10 mL of concentrated HNO_3 . The degree of Fe pyritization (DOP) was calculated as follows:

$$\text{DOP}(\%) = \left(\frac{\text{Fe}_{\text{pyrite}}}{\text{Fe}_{\text{reactive}} + \text{Fe}_{\text{pyrite}}} \right) \times 100 \quad [1]$$

This equation determines the percentage of reactive Fe incorporated in the pyritic fraction (Berner, 1970). In this study, reactive Fe was defined as $\Sigma(\text{F1} - \text{F5})$.

Values measured for F6 in the Mn extractions were very low (the mean value for all samples was $0.07 \pm 0.1 \text{ mmol kg}^{-1}$) and thus were not considered in this study. Iron and Mn concentrations in the extracts were determined by atomic absorption spectroscopy (AAAnalyst 400, PerkinElmer).

Redox concentration samples from 12 horizons were selected for diffuse reflectance spectroscopy to identify the Fe oxides present in the redox concentrations (mottles) of the selected soil horizons and thus support the Fe sequential extractions. Diffuse reflectance spectroscopy was used as an additional technique to determine the composition of the samples but other analysis is needed for more precise mineral identification. The spectra were obtained from freeze-dried and ground powders. Spectra were taken from 350 to 840 nm at 1 nm increments with a 110 mm integrating sphere using a Varian Cary 5 Spectrophotometer

Table 1. Morphological attributes of the soil profiles.

Horizont†	Depth cm	Matrix color	Redox concentrations and mottles		Structure§	Boundary¶	Shiny peds#
			Color	Quantity and contrast‡			
Agknz	0–10	5Y 5/2	–	–	gr, m	g,s	–
P1CE: tidalic episalic endogleyic fluvisol (thapto-thionic, sodic); haplic Sulfaquent							
C1gknz	10–29	5Y 6/2	–	–	m	g,w	–
C2gknz	29–51	5Y 6/2	5YR 3/4, 10YR 6/8	c/p	m	g,w	–
C3gknz	51–71	5Y 6/4, 5Y6/2	5YR 3/4	m/p	m	c,i	–
2C3/C4gknz	71–85	5Y 6/4, 10YR 4/4, 2.5Y 5/4, 5B 4/1	–	–	m	c,b	–
3C4gknsez	85–104+	5B 4/1	–	–	m	–	–
P2CE: tidalic episalic endogleyic fluvisol (thapto-thionic, sodic); sulfic Fluvaquent							
Agknz	0–9	10YR 4/1	–	–	gr, m	g,s	–
C1gknz	9–26	5Y 6/2	10YR 4/6	c/p	m	c,i	–
2C2gknz	26–38	10G 4/1	5YR 3/4, 7.5 YR 4/6	c/p	m	c,b	–
3C3gknsez	38–66	10B 3/1	–	–	m	d,s	–
4C4gknsez	66–90+	10B 3/1	–	–	m	–	–
P1RJ: tidalic episalic endogleyic fluvisol (thapto-thionic, sodic, epiclayic); sulfic Fluvaquent							
Agknz	0–13	10YR 3/2	–	–	gr, pl	g,s	+
C1gknvz	13–30	2.5Y 6/2	7.5YR 3/3	m/p	m	g,s	–
C2gknvz	30–56	5Y 6/2	2.5YR 3/2, 7.5YR 4/6	m/p	m	a,w	–
2C3gknsez	56–120+	5B 3/1	–	–	m	–	–
P2RJ: tidalic episalic endogleyic fluvisol (thapto-thionic, sodic, epiclayic); sulfic Fluvaquent							
Agknz	0–11	10YR 4/2	2.5YR 3/4, 7.5YR 4/6	c/p	gr, pl	g,s	+
C1gknz	11–30	2.5Y 5/1, 10BG 4/1	2.5YR 3/4, 7.5YR 4/6	m/p	m	g,i	–
2C2gknz	30–51	5GB 4/1	7.5YR 5/6, 2.5Y 5/1	m/p	m	d,s	–
3C3gknsez	51–105+	10GB 3/1	–	–	m	–	–

† P1CE, Soil Profile 1 in the hypersaline tidal flat in the Acaraú River Basin; P2CE, Soil Profile 2 in the hypersaline tidal flat in the Acaraú River Basin; P1RJ, Soil Profile 1 in the hypersaline tidal flat in the Sepetiba-Guaratiba coastal complex; P2RJ, Soil Profile 1 in the hypersaline tidal flat in the Sepetiba-Guaratiba coastal complex.

‡ Quantity and contrast: common (c), many (m), prominent (p).

§ Structure: granular (gr), massive (m), platy (pl).

¶ Boundary: gradual (g), clear (c), diffuse (d), abrupt (a), smooth (s), wavy (w), irregular (i), broken (b).

Shiny peds: present (+), absent (–).

(Varian, Palo Alto, CA). The reflectance function was transformed into a remission function by applying the Kubelka–Munk theory and the second derivative was calculated via a cubic spline fitting procedure (Malengreau et al., 1996).

RESULTS

Characterization of the Soil Profiles

The morphological data are shown in Table 1 and the soil profiles can be visualized in Fig. 2. The P1CE and P2CE profiles were classified as Tidalic Episalic Endogleyic Fluvisol (Thapto-Thionic, Sodic), whereas P1RJ and P2RJ profiles were classified as tidalic episalic endogleyic Fluvisol (thapto-thionic, sodic, epi-

Fig. 2. Morphology of the soil profiles.

Fig. 3. Particle size distribution of the soil profiles.

clayic) (International Union of Soil Sciences Working Group WRB, 2006). In terms of soil taxonomy (Soil Survey Staff, 2014), the P1CE profile was classified as haplic Sulfaquent and the P2CE, P1RJ, and P2RJ profiles as sulfic Fluvaquent.

Topographies of the horizon boundaries varied widely among and within the soil profiles. Broken topographies (tongues) appeared above the 3C4 (P1CE) and 3C3 (P2CE) horizons, which are related to the buried mangrove soil. Wavy and irregular boundaries were found in the C2 (P1RJ) and C1 (P2RJ) horizons. As in the HTF-CE profiles, these boundaries appeared above the buried mangrove soils. The existence of buried mangrove soils is discussed in more detail below.

All profiles had yellowish, reddish, or brownish hues (2.5Y, 5Y, and 10YR) in the uppermost horizons, with strong expression of redoximorphic concentrations (2.5YR, 5YR, 7.5YR, and 10YR hues, with high chroma; see Table 1). A reduced matrix (5B, 10B, 5GB, and 10GB hues) occurred in the buried mangrove soils (Table 1 and Fig. 2). Most of the horizons were structureless (massive), with only the surface horizons displaying granular structure (all soil profiles) and platy structure with shiny peds (but only in the HTF-RJ soil profiles). The particle size distribution was erratic throughout the soil profiles at HTF-CE (Fig. 3), with clay content varying from 12 to 55% and sand from 21 to 70%. In contrast, sand content was less than 3% and clay was more than 55% at HTF-RJ, with a clayey texture in all soil horizons. The high base cation content and low values of $H^+ + Al^{3+}$ led to a base saturation above 70% in most of the soil horizons. Overall, the soils displayed high Na saturation (exchangeable Na percentage, ESP), with mean values of 11% (P1CE), 32% (P2CE), 46% (P1RJ), and 31% (P2RJ).

The pH values are similar throughout the soil profiles, being slightly higher in the surface horizons (Fig. 4), and ranged from 7.7 to 8.3 in the HTF-CE soils and 6.8 to 7.1 in the HTF-RJ soils. Total potential acidity values less than 2.5 (Fig. 4) indicated

Fig. 4. pH values measured in the field (field), total potential acidity (TPA), and redox potential (Eh) of the soil profiles.

the presence of sulfidic materials in the 3C3 and 4C4 horizons of P2CE, the 2C3 horizons of P1RJ, and the 3C3 horizon of P2RJ. As indicated by the Eh values (Fig. 4), the 3C4 horizon of P1CE, the 3C3 and 4C4 horizons of P2CE, the 2C3 horizon of P1RJ, and the 3C3 horizon of P2RJ are under suboxic conditions (~ 100 – 400 mV), whereas the other horizons are under oxic conditions (>400 mV). Soil profiles displayed low TOC content in the uppermost horizons (less than 1.0%), increasing with depth to up 4.4% (Fig. 5), caused by the presence of buried mangrove soils (Ucha et al., 2008; Albuquerque et al., 2014b).

Fig. 5. Total organic C (TOC) of the soil profiles.

Table 2. Chemical attributes of the soil profiles. †

Horizon	Depth cm	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	H ⁺ +Al ³⁺	CEC	Base saturation -%-	ESP	CCE g kg ⁻¹	EC dS m ⁻¹
P1CE: tidalic episalic endogleyic fluvisol (thapto-thionic, sodic); haplic Sulfaquent											
Agknz	0–10	2.9	2.0	6.2	23.1	0.0	34.1	100.0	8.4	107.5	105.3
C1gknz	10–29	2.9	2.5	4.7	21.5	1.6	33.2	95.2	8.7	77.5	102.3
C2gknz	29–51	6.2	7.9	7.6	29.9	5.0	56.6	91.2	11.0	40.4	104.6
C3gknz	51–71	3.3	5.9	5.2	25.6	3.6	43.7	91.8	7.7	35.2	111.1
2C3/C4gknz	71–85	7.2	9.6	9.0	35.8	9.2	70.8	87.0	10.1	27.3	134.4
3C4gknsez	85–104+	29.7	16.6	18.1	72.3	9.0	145.7	93.8	20.4	107.5	126.5
P2CE: tidalic episalic endogleyic fluvisol (thapto-thionic, sodic); sulfic Fluvaquent											
Agknz	0–9	23.9	8.4	13.2	23.1	0.0	68.6	100.0	34.9	110.5	84.2
C1gknz	9–26	11.5	7.6	8.1	25.5	1.4	54.1	97.4	21.2	72.4	95.0
2C2gknz	26–38	108.6	26.4	21.7	29.4	13.0	199.2	93.5	54.5	22.9	134.7
3C3gknsez	38–66	62.7	19.7	23.2	29.5	48.4	183.5	73.6	34.2	8.2	157.3
4C4gknsez	66–90+	23.4	10.1	12.9	23.2	75.0	144.6	48.1	16.2	5.7	156.3
P1RJ: tidalic episalic endogleyic fluvisol (thapto-thionic, sodic, epiclagic); sulfic Fluvaquent											
Agknz	0–13	63.9	74.9	21.4	9.2	10.0	179.4	94.4	35.7	30.9	106.4
C1gknvz	13–30	78.6	57.5	22.8	9.2	23.4	191.5	87.8	41.0	20.0	74.6
C2gknvz	30–56	157.1	46.6	26.1	11.8	22.2	263.8	91.6	59.6	22.3	89.0
2C3gknsez	56–120+	107.8	51.2	33.3	14.6	18.6	225.4	91.8	47.8	20.6	118.5
P2RJ: tidalic episalic endogleyic fluvisol (thapto-thionic, sodic, epiclagic); sulfic Fluvaquent											
Agknz	0–11	31.1	64.9	17.0	7.1	9.0	129.1	93.0	24.1	23.1	102.6
C1gknz	11–30	53.0	33.8	19.4	7.8	40.6	154.6	73.7	34.3	17.3	95.5
2C2gknz	30–51	68.5	33.8	23.2	10.0	54.2	189.7	71.4	36.1	21.7	130.5
3C3gknsez	51–105+	68.5	49.3	31.9	23.3	55.8	228.8	75.6	30.0	3.8	135.0

† CEC, cation exchange capacity; ESP, exchangeable Na percentage; EC, electrical conductivity; CCE, CaCO₃ equivalent; P1CE, Soil Profile 1 in the hypersaline tidal flat in the Acaraú River Basin; P2CE, Soil Profile 2 in the hypersaline tidal flat in the Acaraú River Basin; P1RJ, Soil Profile 1 in the hypersaline tidal flat in the Sepetiba-Guaratiba coastal complex; P2RJ, Soil Profile 2 in the hypersaline tidal flat in the Sepetiba-Guaratiba coastal complex.

Formation of CaCO₃ was more extensive at HTF-CE, with a CCE of ~109 g kg⁻¹ in the surface horizons, decreasing to less than 30 g kg⁻¹ in the deeper horizons (Table 2). The 3C4 horizon of P1CE profile displayed high CCE, probably because

of the presence of broken and shattered shell fragments in this soil horizon. For HTF-RJ, the CCE values were ~ 27 g kg⁻¹ in the surface horizons. All soil profiles had high electrical conductivity (EC) in all horizons (Table 2), with a mean value higher than 100 dS m⁻¹, which is greater than the EC of seawater (~ 50 dS m⁻¹).

Solid-Phase Distribution of Fe

Iron concentrations of the exchangeable (F1) and carbonate fractions (F2) were very low in all soil horizons (mean values of all horizons: 1.0 ± 0.2 mmol kg⁻¹ for F1 and 0.5 ± 0.2 mmol kg⁻¹ for F2), generally representing less than 3% of the extractions (Fig. 6). The mean concentrations of the lepidocrocite fraction (F4) for all horizons at each site were 31.7 ± 10.9 mmol kg⁻¹ at HTF-CE and 34.9 ± 15.4 mmol kg⁻¹ at HTF-RJ, comprising more than 50% of all extractions. In general, the concentration of this fraction increased with depth and decreased again in the buried mangrove soils. The highest concentrations of the lepidocrocite fraction occurred in the 2C3/C4 (P1CE), 2C2 (P2CE), C2 (P1RJ), and 2C2 (P2RJ) horizons, where the redoximorphic features were more evident. Higher concentrations of the pyrite fraction (F6) were found in the deeper horizons, comprising buried mangrove soils, as supported by the higher DOP values. These values ranged from less than 2% in the uppermost horizons of all profiles to ~57% in P1CE and P2CE, 30% in P1RJ, and 73% in

Fig. 6. Sequential Fe extractions and degree of pyritization (DOP) of the soil profiles.

Fig. 7. Second-derivative spectra of the redox concentrations sampled from Soil Profile 1 in the hypersaline tidal flat at the Acaraú River Basin (P1CE, right) and Soil Profile 1 (P1RJ) and Soil Profile 2 (P2RJ) in the hypersaline tidal flat in the Sepetiba-Guaratiba coastal complex (left) profiles. The range of crystal field band positions (ETP) for lepidocrocite and goethite (a), ferrihydrite (b), and hematite (c) (Scheinost et al., 1998).

P2RJ. The concentrations of the ferrihydrite fraction (F3) were highest in the uppermost horizons, with mean concentrations for the surface horizons of $21.1 \pm 3.8 \text{ mmol kg}^{-1}$ (HTF-CE) and $7.5 \pm 0.3 \text{ mmol kg}^{-1}$ (HTF-RJ). The concentrations of the crystalline Fe oxides fraction (F5) displayed a more homogenous distribution throughout the soil profiles and varied from ~ 3.0 to 9.0 mmol kg^{-1} in P1CE, P2CE and P1RJ. The C1 horizon of P2RJ had an anomalous concentration of the crystalline Fe oxide fraction ($138.0 \text{ mmol kg}^{-1}$). This horizon had a higher number of nodules, which probably explains the high concentration of this fraction. The other horizons of P2RJ had concentrations between 6.0 and $12.0 \text{ mmol kg}^{-1}$.

The diffuse reflectance spectroscopy data corroborated the Fe sequential extraction data (Fig. 7). The most intense absorption bands (electronic transition of pair band) were associated with the presence of lepidocrocite or goethite in the samples. The most intense absorption band for lepidocrocite is between 485 and 490 nm (Scheinost et al., 1998), the same range detected for the A, C1, C2, and C3 horizons (P1CE). Goethite is probably the dominant crystalline Fe mineral in these soils (Schwertmann and Taylor, 1989), which contributed to the absorption band shown in the diffuse reflectance spectroscopy spectra ($\sim 488 \text{ nm}$, Fig. 7). Diffuse reflectance spectroscopy does not allow a precise distinction between goethite and lepidocrocite, and other analysis is necessary to distinguish these minerals. Furthermore, the absorption band indicative of hematite was not evident in either spectrum.

Solid-Phase Distribution of Mn

The results of the sequential Mn extractions are shown in Fig. 8. Unlike the Fe pool, the highest concentrations of Mn were in the exchangeable fraction (F1) in all horizons at HTF-CE ($2.5 \pm 0.8 \text{ mmol kg}^{-1}$). In general, this fraction increased with depth and comprised 63% of the extracted Mn. The concentrations of Mn associated with the ferrihydrite (F3,

$0.6 \pm 0.5 \text{ mmol kg}^{-1}$) and lepidocrocite (F4, $0.4 \pm 0.3 \text{ mmol kg}^{-1}$) fractions were much smaller than the exchangeable Mn fraction. The latter, by contrast, was not the main fraction at HTF-RJ. Manganese associated with the ferrihydrite ($5.7 \pm 5.1 \text{ mmol kg}^{-1}$) and the lepidocrocite ($5.8 \pm 4.3 \text{ mmol kg}^{-1}$) fractions made up more than 90% of total Mn extracted in the HTF-RJ soils. These fractions were present in higher concentrations in the uppermost horizons and decreased substantially with depth. For example, the concentration of Mn associated with the ferrihydrite fraction dropped from $18.9 \text{ mmol kg}^{-1}$ in the C1 horizon to less than 0.1 mmol kg^{-1} in 2C3 (P1RJ), and 9.0 mmol kg^{-1} in A to less than 0.1 mmol kg^{-1} in 3C3 (P2RJ). The amount of Mn associated with the pyrite fraction (F6) was negligible in all soil profiles,

Fig. 8. Sequential Mn extractions of the soil profiles.

even in the buried mangrove soils, with a mean value of 0.07 ± 0.1 mmol kg⁻¹. This value comprised less than 1.0% of all extractions.

DISCUSSION

Pedogenic Processes

Traditionally, soils from saline and arid sites are classified as saline ($EC > 4$ dS m⁻¹, $ESP < 15\%$, $pH < 8.5$), saline-sodic ($EC > 4$ dS m⁻¹, $ESP > 15\%$, $pH < 8.5$), or alkaline soils ($EC < 4$ dS m⁻¹, $ESP > 15\%$, $pH > 8.5$) (Richards 1954). According to this classification, HTF soils correspond to saline (P1CE) and saline-sodic soils (P2CE, P1RJ, P2RJ). The P1CE profile showed ESP values lower than 15% in most of the profile and was therefore classified as saline but not sodic. This soil profile is positioned at a higher elevation in a convex portion of the microrelief and has a higher sand content than P2CE and thus water drains more rapidly from the soil profile and generally transported laterally away from it. These conditions cause the water to move from P1CE toward the lower portion of the microrelief, where the soils are saturated with water for a longer period of time (concave surface). Since Na⁺ is more susceptible to leaching (more soluble) and the exchangeable divalent cations (Mg²⁺ and Ca²⁺) have more binding affinity to clays (Rytwo et al., 1996), it appears that Na⁺ has been leached and replaced by Ca²⁺ and Mg²⁺ on the particle surfaces in the P1CE profile. As can be seen in Table 2, exchangeable Mg²⁺ and Ca²⁺ occupied more than 70% of the cation exchange capacity throughout the P1CE profile.

Salinization is easily recognizable by the EC values in all horizons and accumulation of salts on the soil surface (van Breemen and Buurman, 2003). In general, the diagnostic criterion defining a salic horizon in the soil taxonomy (Soil Survey Staff, 2014) and a hypersalic horizon in the World Reference Base for Soil Resources (International Union of Soil Sciences Working Group WRB, 2006) is a horizon that has an EC of 30 dS m⁻¹ or higher. Hypersaline tidal flat soils display ECs between 75 and 157 dS m⁻¹, which implies that HTF soil are strongly affected by salinization. This is explained by the flat relief, the higher soil elevation in the estuarine plain than mangroves, the constant input of seawater, and high evapotranspiration rates associated with low soil permeability. These conditions enable seawater to remain in the soil profiles and on the soil surface after the tide recedes, which favors concentration of soluble salts in the interstitial water by evapotranspiration and therefore the increase in soil salinity.

The high Na⁺ concentrations in cation exchange sites in P2CE, P1RJ, and P1RJ indicate that a solonization process is taking place in these soils. A high correlation between ESP and clay content ($r = 0.83$, $n = 19$, $p < 0.01$) demonstrates that higher clay content and seawater–clay mineral exchange equilibria reactions has led to a higher proportion of Na⁺ at the exchange site in HTF soils (Sayles and Mangelsdorf, 1977). Although this process often leads to an increase in pH values over 8.5 and has been reported by Albuquerque et al. (2014b) in these ecosystems, no pH values higher than 8.3 were measured in this study. In general, high pH values are achieved when the concentration of Ca is depressed by calcite precipitation, and the soil solution remains

dominated by HCO₃⁻ and Na⁺ (van Breemen and Buurman, 2003). This reaction probably does not play a significant role in the HTF soils because of the removal of alkalinity from the soil solution through precipitation of carbonates, keeping the pH from reaching higher values.

There is a strong correlation between the clay content and cation exchange capacity in both sites ($r = 0.82$, $n = 19$, $p < 0.05$), and no such correlation exists between TOC and cation exchange capacity, which means that the clay fraction exerts a strong control on the cation exchange in HTF soils.

Accumulation of secondary CaCO₃ (calcification process) is an active process in HTFs. The concentration of interstitial water by strong evapotranspiration leads to precipitation of carbonates, which is shown by the CCE values. This pedogenic process is likely to be an important factor controlling the geochemistry of Mn in HTF soils, mainly in surface horizons at HTF-CE (more than 20% of the Mn extracted was associated with carbonates). Previous studies have shown that relatively high concentrations of Mn associated with carbonates control the solubility of Mn²⁺ in environments driven by either CaCO₃ adsorption or coprecipitation (Böttcher, 1998; Mucci, 1988; Otero et al., 2003).

Low TPA and high DOP values indicate the presence of sulfidic material in deeper horizons. In general, pyrite formation is favored in environments under anaerobic conditions where metasulfides are produced by bacteria that use organic compounds as reducing agents and energy sources (Berner, 1984). This implies that organic matter can be a limiting factor for pyrite precipitation in soils. The strong correlations between TPA and TOC, TPA and Eh, Eh and TOC, and DOP and TOC (Fig. 9) indicate that sulfidic material is mostly present deeper in the soil profiles, where the buried mangrove soils are present (Eh values are lower and TOC contents are higher, Fig. 4 and Fig. 5). Nevertheless, the present soil physicochemical conditions (high Eh and pH values) are not favorable for pyrite formation. Plotting soil Eh and pH values in the stability diagram for the Fe–S–O–H system shows that pyrite is probably undergoing oxidation in HTF soils (Fig. 10). Therefore, our data suggest that the pyrite in HTF soils is inherited from the buried mangrove soils and its occurrence deeper in the soil profiles is a consequence of a “paleo-sulfidization process” and pyrite formation is not an active process in HTF soils. The morphology of pyrite was studied by Albuquerque et al. (2014b) in the same estuary (HTF-CE). They suggest that pyrite has undergone some morphological alteration caused by the conditions in HTF soils being more oxidizing than those in mangrove soils, which corresponds with our findings. Therefore, the oxidation of sulfide-bearing minerals seems to be an active process in HTF soils, and the Fe released gradually to the soil solution through this process may be precipitating as Fe oxides in more oxidized zones of the soil profiles (Fitzpatrick et al., 1996), and on the surfaces of preexisting solids as coatings (Bonnissel-Gissinger et al., 1998). The latter is expected to slow down oxidation of pyrite in deeper horizons, since Fe oxide coatings can block oxidant

Fig. 9. Correlation between total organic C (TOC) and total potential acidity (TPA), redox potential (Eh) and TPA, TOC and Eh, and TOC and degree of pyritization (DOP).

transport from the solution to the pyrite surface, reducing the rate of pyrite oxidation (Huminicki and Rimstidt, 2009). This process helps to explain the presence of sulfidic material in HTF soils (Albuquerque et al., 2014b).

Transformation of Subsurface Horizons

The morphological and chemical data presented in this study suggest that the subsurface horizons of both HTF soils are undergoing transformations driven mainly by redox processes. The predominance of redox concentrations and variegated color in the intermediate portion of the soil profiles are caused by oxidation–reduction cycles, which, in turn, are caused by oscillation of the water table in these soil sections. It was noticed during fieldwork that the deeper horizons are continually saturated with water even during the dry season and at low tide, a condition that does not favor the occurrence of redoximorphic features (Schwertmann and Fanning, 1976). Transformations can be better understood when a comparison is made between the deeper horizons (buried mangrove soils) and the overlying horizons at each site. These can be seen in P1CE and P2RJ (Fig. 11). Figure 11a (arrows) shows the occurrence of Fe concentrations following the boundary of the tongues in the C3 and 2C3/C4 horizons, indicating that Fe is precipitating in some preferential

sites. Reduction of ferric iron to ferrous iron is favored at deeper horizons (buried soils) where TOC is higher and Eh is lower, which enable Fe^{2+} to move through the soil and precipitate in more oxidized sites of the soil profiles. Similar redox concentrations occur in the P2RJ profile (Fig. 11b,c). It can be seen that

Fig. 10. Redox potential (Eh)–pH diagram for the Fe–S–O–H system (adapted from Brookins, 1988)

Fig. 11. Redoximorphic features in Soil Profile 1 in the hypersaline tidal flat at the Acaraú River Basin (P1CE) and Soil Profile 2 in the hypersaline tidal flat in the Sepetiba-Guaratiba coastal complex (P2RJ) soil profiles. (a) Fe concentrations along tongues boundaries in the C3 and 2C3/C4 horizons (arrows), (b) nodule surrounded by a reduced matrix in the 2C2 horizon (P2RJ), (c) Fe or Mn pore linings in root channels in the 2C2 horizon (P2RJ), and (d) transversal section showing the tubular mottles in the 2C2 horizon (P2RJ).

Mn and/or Fe concentrations occur as pore linings and nodules in the reduced matrix of the 2C2 horizon, which indicates that an accumulation of Fe and Mn along root channels was probably left by dead roots from previous mangrove trees (more oxidized zones). The tubular and vertical shapes of the Fe and Mn concentrations (Fig. 11b–d) also suggest the formation of pedofeatures influenced by roots (Sundby et al., 1998). Iron and Mn tubular concretions in salt marshes originate from oxidation of metals at the root surface, increasing radially outward from the root channel as Fe precipitates (Sundby et al., 1998). This process is likely to have taken place in P2RJ.

The formation of redox concentrations at the boundary of the tongues in C3 and 2C3/C4 (P1CE) and formation of nodules and pore linings in 2C2 (P2RJ) are favored by soil endosaturation and water table oscillation throughout the soil profiles.

These processes allow Fe^{2+} to diffuse through and within the soil solution. As the water table goes down, the pore channels are aerated and the higher redox conditions lead to the precipitation of Fe oxides in preferential sites (e.g., tongues and root channels), resulting in redox concentrations. The more oxidizing conditions in the tongues were confirmed by the measured Eh values (>400 mV). Furthermore, the soil matrix displayed chroma of 2 or less and values of 4 or more, and redox concentrations with a diffuse boundary were present, indicating that redox features are still forming in the soil profiles (Vepraskas, 2001). These observations support our interpretation that the water table oscillates and, consequently, allows the Fe^{2+} to move through the profile followed by precipitation as Fe oxides in preferential sites along the root channels and on the tongue boundaries. These processes are supported by Fe and Mn extractions and are discussed in

Fig. 12. Pedological evolution of hypersaline tidal flat (HTF) soils.

more detail throughout the paper. Figure 12 shows the pedological evolution of HTF soils based on our data.

Other observations are pertinent to the transformation of HTF soils. Some portions of the 2C3/C4 horizon (P1CE) display a color of 5B 4/1, which is the same reduced color as the 3C4 horizon. The increases in TOC values with depth (0.1, 0.5 and 2.7% throughout C3→2C3/C4→3C4, respectively) indicate that the 2C3/C4 horizon still preserves the characteristics of the previous mangrove soil. On the other hand, the oxic conditions in 2C3/C4 (462 mV) and the predominance of lepidocrocite and ferrihydrite in the Fe pool (90% of the Fe extraction) indicate periods of recent oxidation in the deeper horizons.

The P2CE profile also shows evidence of transformations in the intermediate portion of the soil profile, especially in the 2C2 horizon. As in P1CE, there is a depth-dependent increase in TOC (0.2, 1.1 and 4.3% throughout C1→2C2→3C3, respectively) and the presence of irregular and broken boundaries (tongues) in the soil profile. In addition, the 2C2 horizon has a reduced color (10G 4/1) caused by gleization processes, with a predominance of yellowish mottles caused by a higher concentration of the lepidocrocite fraction than in other horizons. These features indicate that the 2C2 horizon still maintains the characteristics of the buried mangrove soil. On the other hand, Eh and TPA values and presence of yellowish redox concentrations indicate oxidation and transformation of the 2C2 horizon, similar to 2C3/C4 (P1CE).

In P1RJ, the C1 and C2 horizons have many redox concentrations and nodules, the latter occupying ~1 to 2% of the horizon. The nodules (2–5 cm) in these horizons are possibly related to precipitation of Fe and Mn in air-filled pores or channels caused by oscillation of the water table in this section of the profile (D'Amore et al., 2004). Although there is only subtle morphological evidence of oxidation in the 2C3 horizon, the presence of redox concentrations in the C2 horizon, wavy

boundaries (C2→2C3), and high Eh values in 2C3 (345 mV) suggest that some transformations may be occurring deeper in the soil profile.

On the basis of evidence from the sequential extractions, the lepidocrocite fraction is predominant in the soil profiles. This supports seasonal alternations of reducing and oxidizing conditions at both sites and provides a good indicator of saturation, reduction, drying, and oxidation events in the soils (Bigham et al., 2002). These conditions favor the formation of Fe^{2+} , which moves into oxygenated zones of the soil profiles where lepidocrocite precipitates (Cornell and Schwertmann, 2003). The horizons with the highest concentrations of the lepidocrocite fraction are 2C3/C4 (P1CE), 2C2 (P2CE), C2 (P1RJ), and 2C2 (P2RJ). These horizons, situated right above the buried mangrove soils, display evidence of transformation driven by redox processes. This result supports the idea that dissolved Mn and Fe are migrating out the reduced matrixes and precipitating as oxides in more oxidized sites in the uppermost horizons. This tendency is also visualized in Fig. 13. Considering the sum of the fractions strongly affected by redox processes (F3 + F4 + F5), the higher concentrations of these fractions combined (F3 + F4 + F5) are present in the intermediary horizons of the soil profiles (where the water table oscillates), and lower concentrations are found in the deeper horizons (buried mangrove soils). This distribution of extracted Fe and Mn (F3 + F4 + F5) can be explained by the movement of Fe and Mn through the soil profile, which supports the discussion previously reported.

The participation of Mn in the redox processes seems to have greater influence at HTF-RJ, since it has a similar trend to that of Fe. Low concentrations of the exchangeable Mn fraction and F3 + F4 + F5 fractions (Fig. 13) in the deeper horizons and higher concentrations in the uppermost horizons suggest that Mn is moving upward in the profile and precipitating. We hypothesize that the Mn^{2+} produced from reductive processes in the deeper horizons precipitates as Mn oxides in the up-

Fig. 13. Concentration of ferrihydrite, lepidocrocite, and crystalline Fe oxide fractions (F3 + F4 + F5) throughout the soil profiles. Horizon numbers on the y-axis refer to the order of horizons with depth for each profile (see Table 1 and Table 2). ; e.g., for Soil Profile 1 in the hypersaline tidal flat at the Acaraú River Basin (P1CE): 1 = A horizon, 2 = C1 horizon, 3 = C2 horizon, etc.

Fig. 14. Regression between the ferrihydrite (F3) and Mn-ferrihydrite (F3) fractions for the soils of the hypersaline tidal flat in the Sepetiba-Guaratiba coastal complex (HTF-RJ).

permost horizons where the Eh values are higher, especially in the upper fringe where the water table oscillates (Smeck et al., 2002). Furthermore, Mn^{2+} has relatively low oxidation kinetics, which favors Mn^{2+} moving through the soil profiles even in more oxidizing conditions (Otero et al., 2003; Stumm and Morgan, 1981). Figure 14 indicates that part of the Mn is precipitating along with ferrihydrite during the formation of Fe oxides at HTF-RJ, where the nodules have strong effervescence when treated with H_2O_2 . No correlation was found for HTF-CE soils ($R^2 = 0.06$, $n = 11$, $p < 0.05$). Ferrihydrite is a poorly ordered mineral and is characterized by its high specific surface area and the proportion of reactive sites, which can catalyze surface adsorption reactions. These Mn precipitates may be very reactive and their low crystallinity favors coprecipitation with iron oxides (Uzochukwu and Dixon, 1986). The nucleation and growth of Fe and Mn nodules is favored in soils with ferrihydrite (McKenzie, 1989) and surfaces that have negative charges where divalent Mn can be adsorbed and precipitated as oxides (Hem, 1978). These two conditions lead to a marked association of Fe and Mn in the nodules at HTF-RJ. However, we do not know which Mn species are forming in soils and if Mn is precipitated as a separated mineral (as an occlusion or as isomorphic substitution within ferrihydrite).

The same does not occur in the HTF-CE soils, which present exchangeable Mn as the most abundant fraction. McKenzie (1975, 1989) pointed out that accumulation of Mn tends to occur in soils where both Mn and Fe oxides are present. Therefore, the lower concentration of the F3 + F4 + F5 fraction for Mn extractions (Fig. 13) and the absence of nodules in the HTF-CE soils suggest that Mn precipitation is less favorable in the HTF-CE soils than in the HTF-RJ soils, which is likely to explain the maintenance of Mn in the exchangeable form at HTF-CE. Considering the horizons above the buried soils, these values (F3 + F4 + F5) fall between 9.5 and 40.4 mmol kg^{-1} for HTF-RJ soils and 0.6 and 2.6 mmol kg^{-1} for HTF-CE soils. Therefore, the presence of nodules and a higher concentration of the F3 + F4 + F5 fraction in the HTF-RJ soils indicate a soil environment that is more propitious

for Mn precipitation, and Mn withdrawal from the soil solution is caused by occlusion and sorption by Fe precipitates (Collins and Buol, 1970). In addition, the composite Eh–pH stability diagram for Mn shows that Mn tends to occur as Mn^{2+} in the deeper horizons (buried mangrove soils), which is mobilized through the soil profile and then precipitates in the uppermost horizon where the Eh values are higher (Fig. 15).

CONCLUSIONS

The present investigation of soil morphology and Fe and Mn geochemistry highlights the importance of redox reactions in controlling the pedogenesis of HTF soils. Even though some physical and chemical parameters differed greatly between the studied HTF soils (e.g., pH, particle size distribution, cation proportions, Mn concentration), pedogenesis in both HTFs shows similar trends. Salinization, solodization, and redox reactions are the main pedogenic processes taking place in HTF soils. Buried mangrove soils make up the deeper part of the soil profiles and redox reactions have been transforming these buried soils as a result of the more oxidizing conditions within the soil profiles. Overall, water table oscillation has led to mobilization of Fe^{2+} and Mn^{2+} upward in the soil profiles, followed by oxidation and precipitation as oxides. In addition, these reactions are leading to pyrite oxidation; formation of mottles, nodules, and pore lining; and formation of irregular and broken topography throughout the soil profiles. The participation of Mn in redox concentrations is more notable in HTF-RJ soils, where Mn precipitates with Fe during the formation of redox concentrations. Although lepidocrocite comprises more than 50% of total Fe extractions, co-precipitation of Mn and Fe seems to be related to ferrihydrite formation.

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Fig. 15. Redox potential (Eh)–pH diagram for the Mn–water system, adapted from Collins and Buol (1970).

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