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2 **Seasonal changes in metal and nutrient fluxes across the sediment-water interface in tropical**
3 **mangrove creeks in the Amazon region**

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26

27

28 **ABSTRACT**

29 Mangrove creeks are considered important routes between terrestrial and adjacent coastal waters
30 regarding the transport of dissolved material to oceans. The present study assessed if Amazonian
31 seasonal rainfall patterns affect the pore water biogeochemistry and the intensity and direction of
32 nutrient (NH_4^+ and PO_4^{3-}) and metal (Fe^{2+} and Mn^{2+}) exchanges from intertidal creek mudflats fringed
33 by pristine mangroves. The results indicate that mangrove-fringed mudflats are effective in retaining
34 iron and nutrients in solid sediment phases compared to export to coastal waters, also potentially
35 comprising a significant manganese contributor to coastal waters. However, nutrient and metal
36 retention are lower during the wet season, as intense rainfall periods reduce pore water salinity and
37 promote increased reducing sediment conditions. Such conditions enhance organic matter
38 degradation and pore water NH_4^+ , PO_4^{3-} , Fe^{2+} and Mn^{2+} concentrations just below the sediment-water
39 interface, generating higher effluxes during this period. Our findings demonstrate that seasonal
40 variabilities drive substantial physicochemical property and pore water biogeochemistry changes,
41 affecting the efficiency of mudflat sediments retaining and exporting nutrients and metals.

42 **Keywords:** Seasonal variations. Intertidal environmental. Organic matter degradation. Pore water
43 exchange. Sediment-water interface.

44 **1 Introduction**

45 Mangroves occur along the land-ocean interface under the influence of both fresh and
46 seawater. These ecosystems, whether pristine or disturbed, can act as sinks and store significant
47 amounts of carbon (Alongi, 2020a), nutrients (Breithaupt et al., 2014; Sanders et al., 2014) and metals
48 (Marchand et al., 2011; Thanh-Nho et al., 2019) in their sediments. Alternatively, mangroves may
49 also play an essential role in exchanging of dissolved and particulate matter between terrestrial and
50 oceanic environments (Dittmar et al., 2006; Jennerjahn and Ittekkot, 2002). The capacity of mangrove
51 systems to act as net sinks or sources of nutrient and metal is influenced by many factors, including
52 the input of terrestrial or oceanic nutrients, shifts in redox conditions, anthropogenic activities, and
53 local environmental factors such as weather conditions, hydrology, tidal range, latitude, mangrove
54 community structure and topographic elevation (Adame et al., 2010; Adame and Lovelock, 2011;
55 Kristensen et al., 2017).

56 Mangrove creeks are considered important routes between forest environments and adjacent
57 coastal waters regarding the transport of dissolved and suspended materials (Dittmar and Lara, 2001;
58 Lacerda et al., 1999). However, mangrove sediment creeks also can act as biogeochemical reactors,
59 and their pore water can become a crucial source of dissolved metals and nutrients to coastal areas, if
60 these elements are not efficiently removed from pore waters by precipitation and sorption processes
61 in the upper sediment layers (Ogrinc and Faganeli, 2006; Rozan et al., 2002). These dissolved
62 elements exchange can take place essentially by spontaneous molecular diffusion across the
63 sediment-water interface (SWI) including in macrotidal regimes (Alongi et al., 2004; Bally et al.,
64 2004; Pan et al., 2020; Pratihary et al., 2021; Thibault de Chanvalon et al., 2017; Wang et al., 2011),
65 through pore water seepage into tidal creek water columns during low and ebbing tides (Holloway et
66 al., 2016; Sanders et al., 2015; Taillardat et al., 2019; Tait et al., 2017) or transported by bioturbation
67 (irrigation from burrows and biodiffusion) (Bouillon et al., 2007; Ovalle et al., 1990).

68 In addition to tides, regional seasonality also influences estuarine water quality. Mangroves
69 developed under the Amazon hydrological regime, for example, are subject to high annual rainfall
70 rates which, in turn, lead to high seasonal freshwater inputs and fluvial water discharges, causing
71 extreme salinity fluctuations within estuaries and tidal creeks. Therefore, the biogeochemistry of these
72 waters alter at both the temporal (seasonal, tidal, diel) and spatial scales, due to seasonal fluvial
73 discharge and organic matter (OM) input from different sources (mainly mangroves and
74 phytoplankton). Previous assessments have reported that the documented seasonal rainfall patterns
75 can lead to seasonal changes in sedimentary physical and chemical properties (Alongi et al., 2004;
76 Berrêdo et al., 2016; Marchand et al., 2004) pore water chemistry (Lee et al., 2008; Taillardat et al.,
77 2019; Thanh-Nho et al., 2020; Wu et al., 2015) and nutrient and metals fluxes to coastal waters
78 (Adame et al., 2010; Alongi et al., 2001; Rao et al., 2018; Yasui et al., 2016). Therefore, local weather
79 conditions in the estimation and management of nutrient and metal budgets, especially in small
80 mangrove rivers (Terada et al., 2017), must be considered.

81 In the present study, Amazonian seasonal rainfall patterns are hypothesized to significant
82 affect the physicochemical properties and pore water biogeochemistry of creek mudflats, as well as
83 metal and nutrient fluxes at the SWI. To assess rainfall effects on creek mudflats sediment and pore
84 water dynamics, field observations were conducted in three intertidal mudflat sediments fringed by
85 pristine mangroves in the Marapanim River Estuary (MRE), northern Brazil, in both the wet (April
86 2017) and dry (September 2017) seasons. To this end, the temporal and spatial distributions of pH,
87 Eh, salinity, Cl^- , SO_4^{2-} , Fe^{2+} , Mn^{2+} , total alkalinity (TA) and nutrients (NH_4^+ and PO_4^{3-}) were first
88 obtained alongside sediment parameters. Diffusive nutrient and metal fluxes between sediment pore
89 waters and the overlying water were subsequently estimated. Finally, rainfall effects on the
90 physicochemical conditions, pore water biogeochemistry and nutrient and metal fluxes at the SWI,
91 and the importance of the creek mudflats to coastal biogeochemical cycles were then assessed.

92

93 **2 Materials and methods**

94

95 *2.1 Study area*

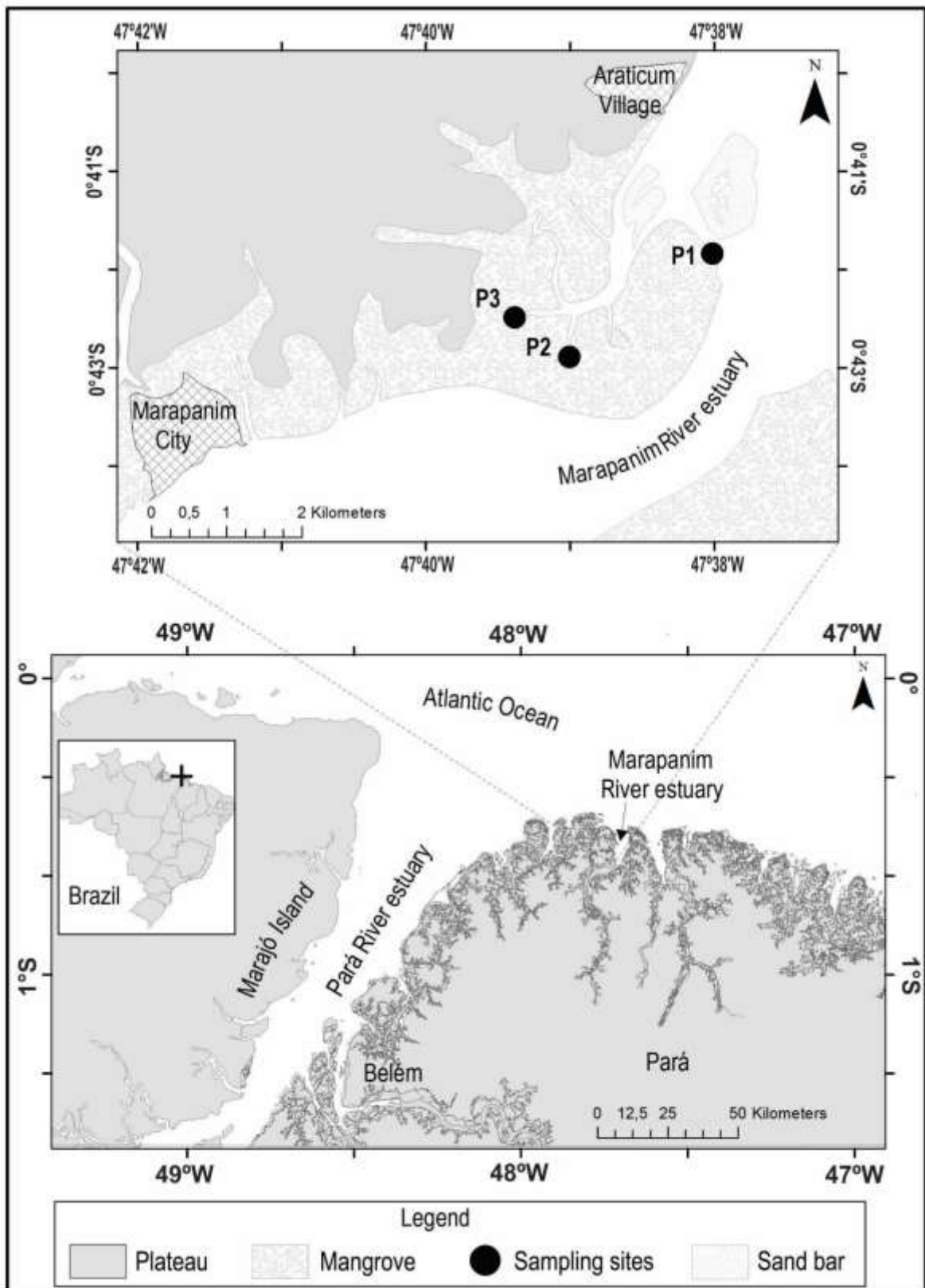
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97 The MRE, located in the state of Pará, northern Brazil (00°30' to 01°00'S and 47°32' to
98 47°00'W, Fig. 1), can be subdivided into three morphologic realms, namely the coastal, estuarine and
99 alluvial plains (Silva et al., 2009). The sedimentary deposits of the Coastal Plateau are represented
100 by cliffs and lateritic soils (Pleistocene) derived from the Barreiras Formation (Tertiary), the main
101 source of sand, silt and clay fractions, comprising quartz, clay minerals (kaolinite and illite), iron
102 oxides, and recent sediments (Holocene) that constitute mangrove substrates (Berrêdo et al., 2008a).
103 The estuarine plain where mangroves are established presents sandy and muddy deposits (Silva et al.,
104 2009).

105 The tidal flats of the MRE are occupied by well-developed mangroves, which are part of the
106 largest continuous and best-preserved mangrove forest in the world (Kauffman et al., 2018;
107 Nascimento et al., 2013). The main river channel is about 70 and 8 km long and wide at the mouth,
108 presenting the incursion of oceanic waves from Atlantic and semi-diurnal macrotides that present a
109 tidal range of 3.5 m during neap tides and over 6 m during spring tides (Silva et al., 2009). Saline
110 waters penetrate approximately 62 km up the main river channel during the dry season and 42 km
111 during the wet season (Berrêdo et al., 2008b).

112 The coastal region of Pará is characterized by a tropical climate with two distinct seasons. The
113 wet season occurs between January and June, when total rainfall often exceeds 2000 mm, with a mean
114 April rainfall of 462 mm. The dry season ranges from July to December, with a mean September
115 rainfall of 5 mm. The annual mean temperature is 27.7 °C. The estuary water temperature ranges from
116 27 to 30 °C. The pH values along the estuarine channel range between alkaline (7.9 to 8.0) to slightly
117 acidic (5.7 to 6.7) during the dry and wet seasons, respectively (Berrêdo 2008b).

118 The samplings were carried out along three intertidal mudflats, numbered according to their
119 distance from the main Marapanim River, with number 1 (P1) comprising the Marapanim River
120 margin, and numberr 2 (P2) and 3 (P3) located at two tidal mangrove creeks along the Marapanim
121 mangrove forest (Fig. 1). Sites P1 and P2 are 2.3 km apart, while site P3 is located ~1 km from P2.
122 The tidal creeks do not receive any direct freshwater inputs except for rainwater and runoff from the
123 Marapanim River during the wet season. They exhibit sinuous bifurcated forms, are shallow (3 m in
124 depth), about 5 km long and 800 m wide, and are under the influence of the semidiurnal tide regime,
125 with 6 hours intervals between the ebb and flood tides. The three sampling sites are frequently
126 exposed during the low tide.



127

128 **Fig. 1.** Map displaying the Marapanim estuary study area, in the state of Pará, Brazil, indicating the

129 P1, P2 and P3 sampling sites.

130

131

132 *2.2 Solid-phase sediment sampling and analyses*

133

134 To assess the effects of contrasting seasons, two replicate cores were collected from the
135 intertidal mudflat at each site, during the wet (April 2017) and dry (September 2017) seasons. Acrylic
136 tubes (50 cm length, 8 cm diameter) were used to recover approximately 35 cm of sediment and 15
137 cm of overlying water at a water column depth of ~0.8 m. One core, dedicated to solid-phase analyses,
138 was sliced at 1-cm (0 – 6 cm), 2-cm (6 – 20 cm), and 5-cm intervals (20 – 35 cm depth). The sub-
139 samples were stored in polyethylene bags at 4 °C until processing. An aliquot of humid sediment was
140 fixed with Zn-acetate, within a N₂-filled glove bag, for the determinations of acid volatile sulfides
141 (AVS, mainly Fe monosulfide/FeS) and chromium reducible sulfur (CRS, mainly pyrite/FeS₂).

142 The most reactive Fe (Fe_R) and Mn (Mn_R) fractions were determined using the ascorbate
143 reagent (50 g NaHCO₃, 50 g Na-citrate, 20 g ascorbic acid to a 1 L solution, buffered at pH 8)
144 (Anschutz et al., 2005; Kostka and Luther, 1994). Extractions were carried out using 500 mg of dried
145 sediment in 10 mL of N₂-degassed ascorbate reagent for 24 h under continuous shaking. The
146 supernatant was diluted 10-fold with HNO₃ (1.0 %), and Fe and Mn concentrations were determined
147 by atomic absorption spectrometry using an external standard prepared in the same matrix. Total
148 organic carbon (TOC) depth profiles were obtained from Matos et al., (2020). AVS and CRS were
149 determined in 1 g of sediment by a two-step distillation with cold 6 N HCl followed by boiling 2 N
150 acidic CrCl₂ solution (Fossing and Jørgensen, 1989). The liberated H₂S was collected in Zn-acetate
151 (20%) traps, and its concentration was determined according to the method of Cline, (1969). Scanning
152 electron microscopy (SEM) coupled with an energy dispersive X-ray spectrometer was used on
153 particles collected from sediments.

154

155 *2.3 Pore water sampling and analyses*

156

157 Regarding the second replicate core, pH and redox potential (Eh) were measured with a pH
158 meter electrode (Metrohm 826 pH mobile) directly in the sediment through holes in one specific
159 predrilled tube, in the same intervals as in the solid-phase, which were covered with tape during the
160 sampling. After determining the redox-pH, following the same intervals, the overlying and pore
161 waters were removed using Rhyzon® collectors (7 cm and 0.1 µm in length and pore diameter,
162 respectively), inserted directly into the sediment through pre-drilled holes along the acrylic tubes
163 (Seeberg-Elverfeldt et al., 2005). The overlying water sampling comprised ~5 cm above the SWI.

164 The pore water samples were treated in a N₂-filled glove bag to prevent oxidation. The
165 overlying and pore water samples were analyzed concerning Cl⁻, SO₄²⁻, Fe²⁺, Mn²⁺, total alkalinity
166 (TA), NH₄⁺ and PO₄³⁻ and total dissolved sulfide ($\Sigma\text{H}_2\text{S} = \text{H}_2\text{S} + \text{HS}^- + \text{S}_0 + \text{S}_x^{-2}$). A total of 2 mL of
167 water samples were deposited in amber vials for the alkalinity analyses. Subsamples (1 mL) were
168 preserved in Eppendorf tubes using 100 µL of a 5% Zn-acetate solution and 10 µL HCl for the $\Sigma\text{H}_2\text{S}$
169 and PO₄³⁻ analyses, respectively. Samples (1 mL) were preserved in Eppendorf tubes for the SO₄²⁻
170 and Cl⁻ analyses. All samples were maintained at 4 °C. Other sub-samples (1 mL) were frozen in
171 amber vials for subsequent NH₄⁺ analyses.

172 Dissolved Fe and Mn concentrations were determined employing an ICP-OES (VISTA-MPX
173 CCD Simultaneous) using 10-fold dilutions. Accuracies were checked using a natural water reference
174 NIST (1640a, 1643e), and were within 5% for Fe and Mn. TA was determined through potentiometric
175 Gran titration using 0.01 mol L⁻¹ HCl immediately after vial removal from the glove-bag. Standard
176 colorimetric methods were used to determine the NH₄⁺ and PO₄³⁻ concentrations (Gieskes et al.,
177 1991). $\Sigma\text{H}_2\text{S}$ concentrations were quantified through the colorimetric method as proposed by Cline,
178 (1969). The SO₄²⁻ and Cl⁻ concentrations were measured by ion chromatography (Dionex DX 120)
179 applying a 500-fold dilution. Salinity was determined using a portable refractometer (Atago).

180

181 *2.4 Sulfate depletion calculation*

182

183 Chloride is a conservative element, as it is not affected by biological or chemical processes.
 184 It was therefore, employed to evaluate sulfate depletion ($SO_4^{2-}_{Dep}$) under freshwater dilution and
 185 microbial removal effects. Sulfate concentrations were normalized according to chloride
 186 concentration changes, according to Eq. 1:

187

$$188 \quad (SO_4^{2-})_{Dep} = [(Cl^-)_{pw} \cdot (R_{sw})^{-1}] - (SO_4^{2-})_{pw} \quad (1)$$

189

190 where $(SO_4^{2-})_{Dep}$ comprised SO_4^{2-} depletion, $(Cl^-)_{pw}$ and $(SO_4^{2-})_{pw}$ consists in the pore water
 191 concentrations of Cl^- and SO_4^{2-} , and R_{sw} is the molar ratio of Cl^- to SO_4^{2-} in surface seawater ($R_{sw} =$
 192 19.33; Weston et al. 2006). Sulfate depletion reveals the net consumption of microbially mediated of
 193 SO_4^{2-} (Weston et al., 2006).

194

195 *2.5 Metal and nutrient flux estimations*

196

197 The diffusive metal and nutrient flux estimates between sediment pore waters and the
 198 overlying water were calculated from the interfacial concentration gradients, according to Fick's first
 199 law of diffusion (Berner, 1980) below:

200

$$201 \quad F = -\emptyset D_s (\Delta C / \Delta Z) \quad (2)$$

202

203 where F ($mmol \cdot m^{-2} \cdot d^{-1}$) is the diffusive flux, \emptyset (dimensionless) is the porosity at the sediment
 204 surface (depth = 0-1 cm), D_s ($m^2 \cdot s^{-1}$) is the molecular diffusion coefficient in sediment, and $\Delta C / \Delta Z$
 205 comprises the concentration gradient across the SWI. According to these calculations, negative fluxes

206 reflect sediment uptake processes (*i.e.*, downward fluxes), whereas positive fluxes indicate benthic
207 recycling (*i.e.*, outward fluxes to overlying waters). Porosity was expressed and calculated as the
208 water volume fraction in the wet sediment, which was identified by the weight difference between
209 wet sediment samples before and after drying at 60 °C. $\Delta C/\Delta Z$ consists in the concentration gradient
210 in the overlying water and pore water. The diffusion coefficient (D_s) was calculated from the
211 molecular diffusion coefficient in free water D_0 corrected for sediment porosity and temperature (Li
212 and Gregory, 1974). The upper sediment layers presented porosities between 0.51 and 0.76, and
213 overlying waters ranged between 28.0 and 29.3 °C.

214

215 *2.6 Statistical analyses*

216

217 Statistical assessments were carried out using the statistical package PAST version 3.26
218 (Hammer et al., 2001). Potential differences regarding dissolved and solid-phase concentrations
219 between the sampling sites (P1, P2, and P3) and seasons (wet and dry) were assessed by a variance
220 analysis (ANOVA). Data distribution normality of was first verified applying Shapiro-Wilk. Non
221 normally distributed variables were log-transformed to fit a normal distribution. A statistical
222 significance of $\alpha < 0.05$ was used for all statistical analyses. Pearson's correlation coefficient was
223 employed to determine the strength of the associations between each pair of variables, where
224 correlation coefficients higher than 0.5 were interpreted as significant.

225

226 **3 Results**

227

228 *3.1 Sediment geochemistry*

229

230 Sedimentary compositions and OM sources at each sampling site were previously
 231 characterized by Matos et al., (2020), and the mean values \pm standard deviations are presented in
 232 Table 1. The estuarine mudflat (P1) presented very different sedimentary characteristics compared to
 233 the creek mudflats (P2 and P3). Located in the lowest topographic area, P1 exhibited a slightly higher
 234 sedimentation rate (1.8 cm yr^{-1}). Its grain size, however, is represented by a higher sand content (\sim
 235 52%) and significant contributions from marine OM (wet: 76.4% and dry: 79.6%). Both P2 and P3
 236 are located in topographically higher tidal flats ($\sim 2 \text{ m amsl}$), where sediments are strongly oxidized
 237 during the dry season. The P2 site is located in a more confined area, presenting a lower sedimentation
 238 rate of 1.3 cm yr^{-1} , finer grain size of $\sim 68\%$ (silte+clay) and marine OM contributions of 54.5% in
 239 the wet season and 69% in the dry season. The P3 site, located closer to the mainland, presented a
 240 sedimentation rate of 1.5 cm yr^{-1} , finer particle size of $\sim 66\%$ and marine OM contributions of 60%
 241 in the wet season and 78% in the dry season.

242
 243 **Table 1**

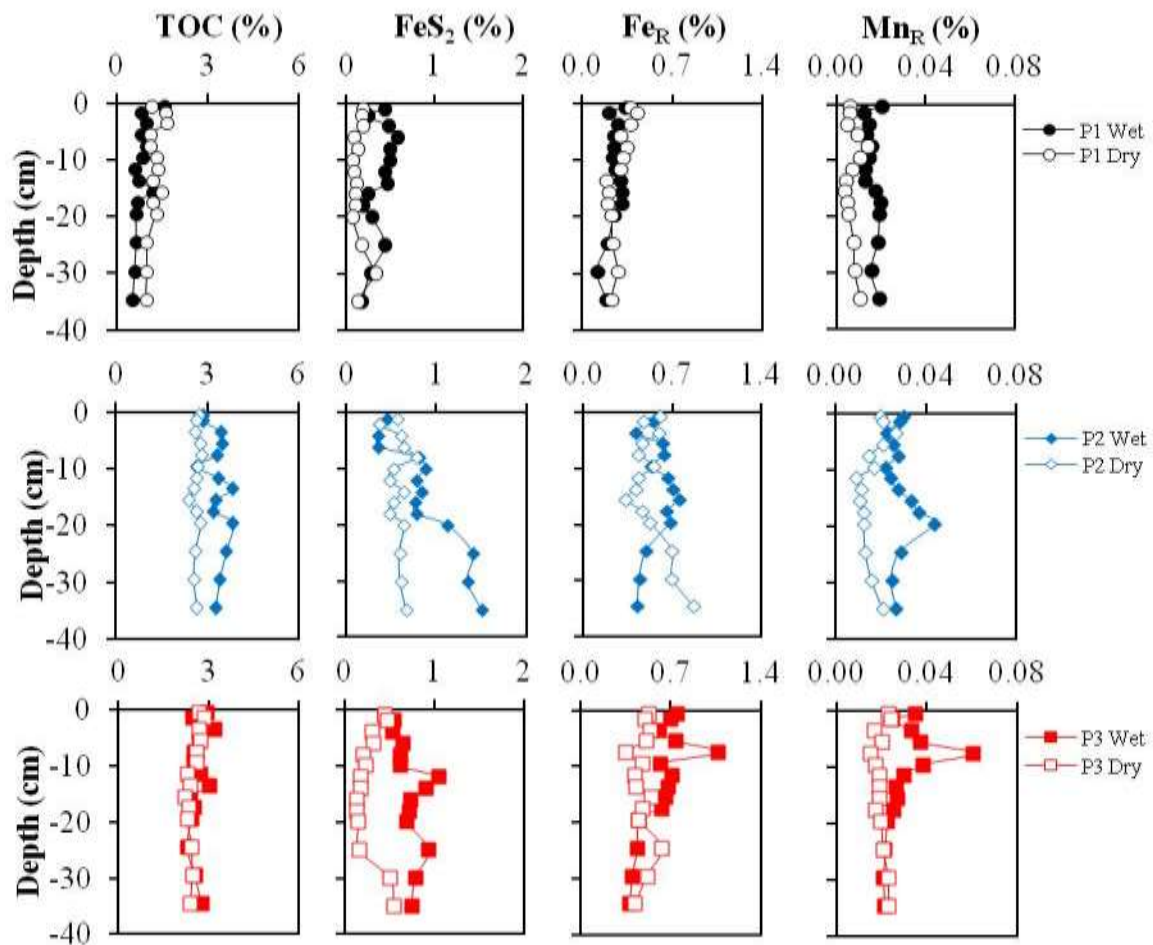
244 Sedimentary characteristics of the P1, P2 and P3 sampling sites, during the wet and dry seasons.

Properties	P1		P2		P3		References
	Wet	Dry	Wet	Dry	Wet	Dry	
FeR (%)	0.25 ± 0.6	0.29 ± 0.8	0.59 ± 0.11	0.54 ± 0.14	0.63 ± 0.18	0.48 ± 0.07	This study
MnR (%)	0.016 ± 0.003	0.007 ± 0.003	0.029 ± 0.006	0.016 ± 0.005	0.030 ± 0.011	0.020 ± 0.003	
TOC (%)	0.9 ± 0.3	1.3 ± 0.2	3.4 ± 0.3	2.6 ± 0.2	2.7 ± 0.2	2.5 ± 0.2	Matos et al. (2020)
Sand (%)	51.7 ± 10.4	52.6 ± 5.6	36.8 ± 7.4	26.5 ± 7.7	32.4 ± 10.3	35.6 ± 8.9	
Silt (%)	46 ± 9.3	46.3 ± 5.3	58 ± 6.6	71.5 ± 6.9	60.2 ± 9.3	62.2 ± 8.6	
Clay (%)	2.3 ± 1.3	1.0 ± 0.4	5.2 ± 1.0	2.0 ± 1.0	7.4 ± 1.5	2.2 ± 0.5	
OM _{terr} (%)	23.6 ± 6.0	20.4 ± 6.2	45.5 ± 3.4	31.0 ± 9.5	40.1 ± 3.9	21.8 ± 8.7	
OM _{mar} (%)	76.4 ± 6.0	79.6 ± 6.2	54.5 ± 3.4	69.0 ± 9.5	59.9 ± 3.9	78.2 ± 8.7	
SAR (cm.yr^{-1})	1.8		1.3		1.5		

245

246 Sediment-depth profiles of TOC, FeS₂, Fe_R and Mn_R in different seasons are presented in Fig.
 247 2, and the mean values \pm standard deviation are displayed in Table 1. Sediment concentrations were
 248 different between sites, seasons, and depth. Overall, the TOC, FeS₂, Fe_R and Mn_R ranges were lower

249 at site P1 compared to the sites P2 and P3. At all three sites, TOC concentrations decreased slightly
 250 with depth, ranging from 3.84 to 0.53 %. FeS₂ content showed large fluctuations between the sites
 251 and seasons varying from 0.06 to 1.52 %, with the highest concentrations during the wet season. AVS
 252 concentrations were below the detection limit (<0.01 wt%) in all sediment profiles. At P1, Fe_R
 253 concentrations in both seasons decreased slightly with depth, varying from 0.43 to 0.11 %. At P2 and
 254 P3, Fe_R and Mn_R concentrations presented a clear seasonal trend, with the lowest Fe_R concentrations
 255 (0.34 % at -16 cm to P2 and 0.34 % at -8 cm to P3) determined during the wet season, and the highest
 256 concentrations (0.76 % at -16 cm to P2 and 1.07 % at -8 cm to P3) found in the dry. Mn_R
 257 concentrations ranged from 0.004 to 0.061 %, and presented almost the same depth distribution
 258 patterns as Fe_R, with one peak of 0.044 % at -20 cm to P2 and another of 0.061 % at -8 cm to P3.



259

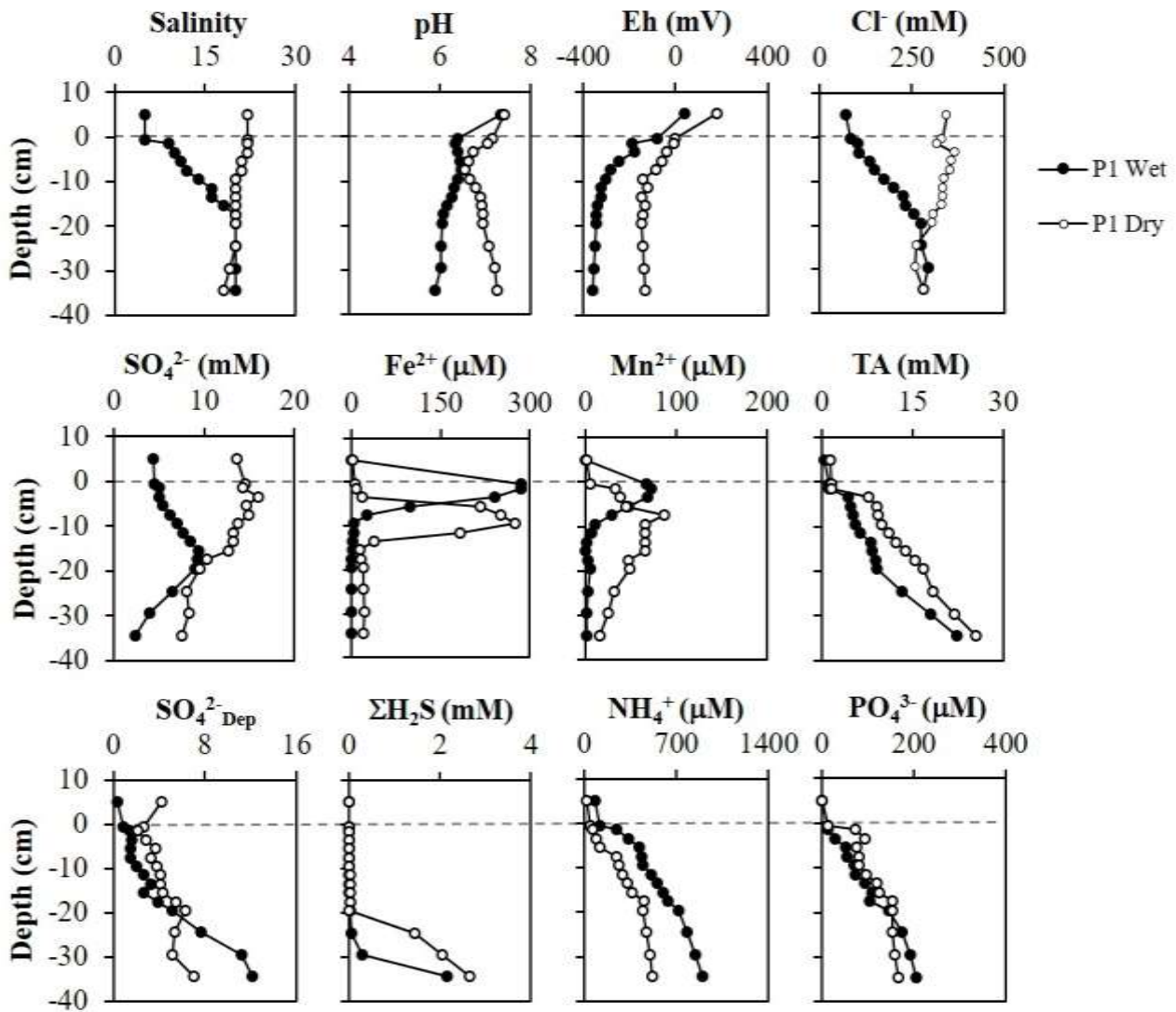
260 **Fig. 2.** Sediment TOC, FeS₂, Fe_R and Mn_R profiles at the P1 (black), P2 (blue) and P3 (red) sampling
 261 sites during the wet (solid markers) and dry (open markers) seasons.

262 3.2 Physicochemical characteristics

263

264 Depth salinity, pH, and Eh profiles in the overlying and pore waters in different seasons are
265 presented in Fig. 3, 4, and 5. A clear seasonal signal was noted through the upper -15 cm, with the
266 highest values detected in the dry season compared to the wet season. In the wet season, the overlying
267 water salinity was of, on average, 4, and pore water salinity increased with depth (5-20 at P1, 4-13 at
268 P2, and 4-15 at P3). In the dry season, the overlying water salinity was of, on average, 23, and pore
269 water salinity exhibited a distinct vertical pattern, decreasing with depth (24-19 at P1, 22-18 at P2
270 and 25-20 at P3). Furthermore, a significant difference between sampling sites was observed during
271 the dry and wet seasons ($p < 0.05$). At P1, salinity remained constant below -18 cm in both seasons,
272 while P2 and P3 exhibited stable salinity values below -35 cm in depth.

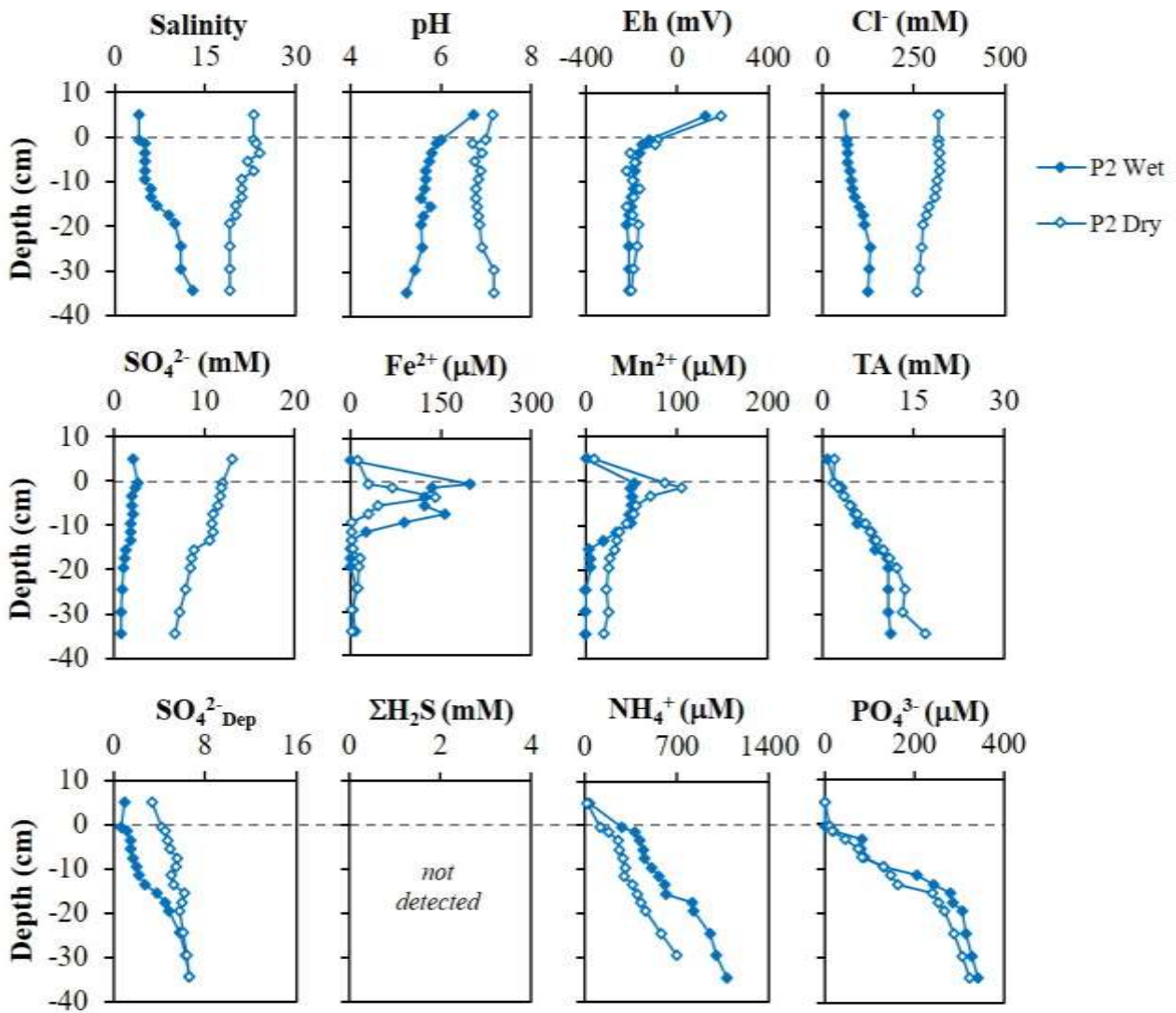
273 pH values were slightly acidic to neutral (6.7 to 7.4), and no seasonal variations were observed
274 for the overlying water. Pore water pH values decreased with depth below the SWI during the wet
275 season. In contrast, pH values slightly increased with depth during the dry season. The determined
276 pH values were slightly more acidic during the wet season (5.9-6.5 at P1, 5.3-6.0 at P2 and 4.7-6.0 at
277 P3) compared to the dry season (6.6-7.3 at P1, 6.7-7.2 at P2 and 6.6-7.0 at P3). Eh values in the
278 overlying water were suboxic in both seasons at all sites, ranging from 40 to 190 mV. Eh values
279 dropped very strongly from the SWI and tended to decrease with depth, ranging from -357 to -80 at
280 P1, -220 to -125 at P2, and -180 to -95 at P3 in the wet season and from -146 to 0 at P1, -222 to -85
281 at P2 and, -265 to -55 at P3 in the dry season. A significant seasonal difference was noted only for P1
282 ($p < 0.05$), which exhibited more reducing conditions during the wet season, and no significant
283 seasonal differences were observed for the other sites ($p > 0.05$).



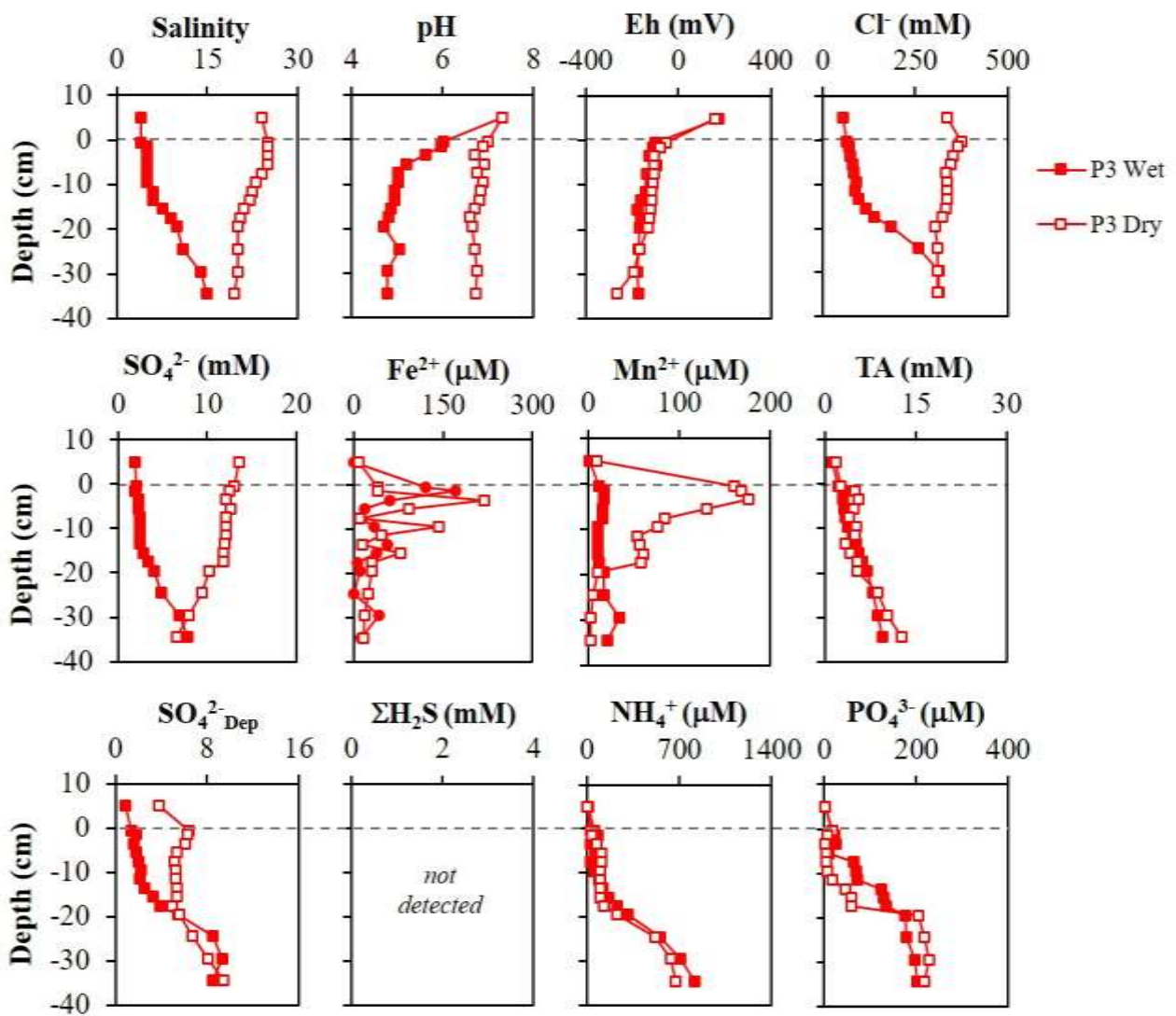
284

285 **Fig. 3.** Overlying and pore water profiles concerning physicochemical parameters (salinity, pH and
 286 Eh), Cl⁻, SO₄²⁻, redox-sensitive trace metals (Fe²⁺ and Mn²⁺), total alkalinity (TA), sulfate depletion
 287 (SO₄²⁻_{Dep}) and nutrients (NH₄⁺ and PO₄³⁻) at sampling site P1 during the wet (filled circles) and dry
 288 (open circles) seasons. Dashed horizontal lines represent the SWI.

289



290 **Fig. 4.** Overlying and pore water profiles concerning physicochemical parameters (salinity, pH and
 291 Eh), Cl⁻, SO₄²⁻, redox-sensitive trace metals (Fe²⁺ and Mn²⁺), total alkalinity (TA), sulfate depletion
 292 (SO₄²⁻_{Dep}) and nutrients (NH₄⁺ and PO₄³⁻) at sampling site P2 during the wet (filled circles) and dry
 293 (open circles) seasons. Dashed horizontal lines represent the SWI.



294

295 **Fig. 5.** Overlying and pore water profiles concerning physicochemical parameters (salinity, pH and
 296 Eh), Cl^- , SO_4^{2-} , redox-sensitive trace metals (Fe^{2+} and Mn^{2+}), total alkalinity (TA), sulfate depletion
 297 ($\text{SO}_4^{2-}\text{-Dep}$) and nutrients (NH_4^+ and PO_4^{3-}) at sampling site P3 during the wet (filled circles) and dry
 298 (open circles) seasons. Dashed horizontal lines represent the SWI.

299

300 3.3 Pore water dissolved species profiles

301

302 Overlying and pore water profiles concerning Cl^- , SO_4^{2-} , redox-sensitive trace metals (Fe^{2+}
 303 and Mn^{2+}), total alkalinity (TA), sulfate depletion ($\text{SO}_4^{2-}\text{-Dep}$), and nutrients (NH_4^+ and PO_4^{3-}) at three
 304 sampling sites during the wet and dry seasons are shown in Fig. 3, 4 and 5. The Cl^- concentrations

305 were positively correlated with salinity values at all sites and in both seasons ($0.81 < r < 0.91$,
306 Supplementary Table S1 and S2). At all sites, Cl^- concentrations increased from the overlying water
307 to the pore water depth during the wet season (90-294 mM at P1, 59-143 mM at P2 and 54-314 mM
308 at P3) and decreased with depth during the dry season (332-260 mM at P1, 317-260 mM at P2 and
309 376-310 mM at P3). The SO_4^{2-} concentrations exhibited a similar trend regarding salinity only during
310 the dry season, with decreasing concentrations from the overlying water to the pore water with depth
311 (16.0-7.5 mM at P1, 13.1-6.8 mM at P2 and 13.6-6.6 mM at P3). During the wet season, however,
312 the downcore pore water SO_4^{2-} concentrations displayed different characteristics at each site (Fig. 3-
313 5).

314 During the wet season, sites P1, P2, and P3 featured the highest pore water Fe^{2+} concentrations
315 closer to the SWI, reaching 285.1, 198.8, and 170.1 μM , respectively. During the dry season, pore
316 water Fe^{2+} concentrations were very low in the upper centimeters, followed by a 275 μM peak in -10
317 cm at site P1, 140.2 μM in -4 cm at site P2, and 219.3 μM in -4 cm at site P3. During the wet season,
318 pore water Mn^{2+} concentrations were also higher closer to the SWI, except for P3, reaching 72.2 at
319 site P1 and 53 μM at P2, respectively. During the dry season, Mn^{2+} peaks were located above the Fe^{2+}
320 peaks, reaching 86.7 μM in -8 cm at site P1, 104.7 μM in -4 cm at site P2 and 175.7 μM in -4 cm at
321 site P3. Fe^{2+} and Mn^{2+} concentrations drastically decreased below the peaks with increasing depths
322 at the three sampling sites.

323 TA concentrations varied from 0.4 to 2.0 mM in the overlying water, and increased sharply
324 with depth below the SWI, ranging from 1.1 to 25.4 mM. Pore water TA concentrations did not differ
325 significantly between seasons ($p > 0.05$). The SO_4^{2-} _{Dep} values increased with sediment depth at all sites,
326 ranging from 0.6 to 12.1. SO_4^{2-} _{Dep} did not differ considerably between sites ($p > 0.05$), but were
327 significantly different between seasons at sites P2 and P3 ($p < 0.05$), exhibiting slightly higher values
328 in the dry season. Pore water $\Sigma\text{H}_2\text{S}$ concentrations at P2 and P3 were negligible ($< 1 \mu\text{M}$), while a
329 high peak of 2 mM was recorded at the -35 cm depth at site P1.

330 NH_4^+ concentrations varied from 3.1 to 79.2 mM in the overlying water. The pore water NH_4^+
 331 range was highest at sites P1 (119.2-900.8 μM), and P2 (286.2-1083.8 μM) compared to site P3 (72.5-
 332 349.2 μM). Seasonal patterns were significant ($P < 0.05$) only at P1 and P2, where pore water
 333 concentrations were higher in the wet season. Pore water NH_4^+ concentrations increased with
 334 sediment depth at all sites. PO_4^{3-} concentrations ranged from 0.2 to 1.0 mM in the overlying water.
 335 Pore water PO_4^{3-} concentrations were not significantly different between seasons ($p > 0.05$), while
 336 differing significantly between sites ($p < 0.05$), with the highest concentrations at P2 (1.2-342.9 μM)
 337 compared to P1 (12.5-205.0 μM) and P3 (1.2-227.5 μM).

338

339 *3.4 Metal and nutrient fluxes at the sediment-water interface (SWI)*

340

341 The diffusive metal and nutrient fluxes estimates at the SWI at the three sites during the wet
 342 and dry seasons are exhibited in Table 2. The Fe^{2+} , Mn^{2+} , NH_4^+ , and PO_4^{3-} fluxes in both seasons at
 343 all sites were positive, indicating sediment pore water exports to the overlying water. Overall, Fe^{2+} ,
 344 Mn^{2+} , NH_4^+ , and PO_4^{3-} exhibited the highest fluxes in the wet season, except for Mn^{2+} at site P3. Fe^{2+} ,
 345 Mn^{2+} , NH_4^+ , and PO_4^{3-} fluxes ranged from 6 to 723 $\mu\text{mol m}^{-2} \text{d}^{-1}$, from 16 to 189 $\mu\text{mol m}^{-2} \text{d}^{-1}$, from
 346 90 to 1,433 $\mu\text{mol m}^{-2} \text{d}^{-1}$, and from 2 to 35 $\mu\text{mol m}^{-2} \text{d}^{-1}$, respectively (Table 2).

347

348 **Table 2**

349 Fe^{2+} , Mn^{2+} , NH_4^+ , and PO_4^{3-} fluxes ($\mu\text{mol m}^{-2} \text{d}^{-1}$) across the SWI at sampling sites P1, P2 and P3,
 350 during the wet and dry seasons.

	P1		P2		P3	
	Wet	Dry	Wet	Dry	Wet	Dry
Fe^{2+}	723	6	595	24	238	75
Mn^{2+}	92	32	73	64	16	189
NH_4^+	415	90	1,433	155	201	121
PO_4^{3-}	24	18	35	14	19	2

351 Positive numbers indicate fluxes from the sediment (effluxes) and negative numbers indicate fluxes
352 to the sediment (influxes).

353

354 **4 Discussion**

355

356 *4.1 Seasonal physicochemical properties and Cl⁻ variabilities*

357

358 Salinity oscillations detected herein were associated to seasonal rainfall rate variations. Due
359 to increasing rainfall rates and runoff from the Marapanim River, surface salinity values were five
360 times lower in the wet season relative to the dry season, indicating greater saline water dilution by
361 freshwater, as observed at the Sinnamary mangrove by Marchand et al., (2004) and at the Marapanim
362 mangrove by Berrêdo et al., (2016). The seasonal effects controlled the conservative Cl⁻ and salinity
363 values, especially in the upper sediment intervals (< 15 cm). Spatial variations were observed only
364 during the wet season, with lower salinity and Cl⁻ values detected at the creek mudflats (P2 and P3)
365 compared to the estuarine mudflat (P1). Spatial salinity and Cl⁻ variabilities can be explained by
366 spatial grain size variability. The fine-grained sediments identified at P2 and P3 promote high
367 freshwater retention capacity, while P1, characterized by sandy sediments (>50%), favored saline
368 water recharge during rising tides. At P1, pore water salinity remained constant below -18 cm in both
369 seasons, while pore water salinity remained constant below the -35 cm depth at P2 and P3.

370 The increased rainfall trend observed during the wet season led to a decrease in pH values,
371 which may be explained by a more intense OM decomposition, as well as the reoxidation of reduced
372 products that result in lower pH (Gueiros et al., 2003; Otero et al., 2006), such as Fe sulfide (pyrite,
373 FeS) and pore water sulfide (HS) oxidation during the wet season. Acidity was higher at P2 and P3,
374 reaching values lower than 5 (Fig. 4-5). These sites are located in topographically higher areas,
375 leading to strong sediment oxidation. Sediments more acidic during the wet season have been reported
376 in other tropical intertidal environments (Alongi et al., 2004, 1999). During the dry season, saline

377 water recharges influence pore water quality, buffering the pH close to neutrality (6.6 to 7.3), with
378 no significant difference noted between sites. Redox potential values indicate suboxic to anoxic
379 conditions at all sampling sites. Eh values were very sensitive to seasonal changes only at site P1,
380 significantly lower in the wet season than dry season (Fig. 3).

381

382 *4.2 Biogeochemical processes and seasonal variations*

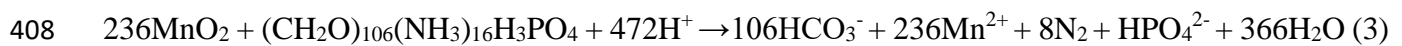
383

384 Irrespective of the pathways, all mangrove OM not exported by tidal action enters the
385 sediment and is degraded or chemically modified by microorganisms (Kristensen et al., 2008).
386 Microbes in the sediment surface use electron acceptors (for example, O₂, MnO₂, Fe-oxides, SO₄²⁻)
387 in order of declining energy yields from OM respiration (Froelich et al., 1979). High OM
388 accumulation in mangrove sediments enhances intense microbial activity, sedimentary mineralization
389 rates are high, often leading to oxygen depletion within the upper few sediment millimeters (Glud,
390 2008; Kristensen et al., 1994; Meiggs and Taillefert, 2011) and favoring the prevalence of anaerobic
391 OM mineralization pathways, such as iron reduction and sulfate reduction (Alongi, 1995; Kristensen
392 et al., 2011).

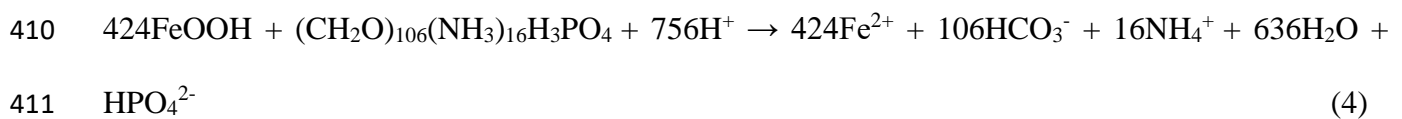
393 The gradual decrease observed for TOC concentrations and redox potential with depth in all
394 sampled cores likely reflect microorganisms OM degradation. The pore water profiles allowed for
395 the assessment of the redox sequence associated to OM mangrove mudflat sediment degradation.
396 Based on downcore Fe²⁺ and Mn²⁺ variations, the sediment cores were subdivided into two distinct
397 zones, as follows: Zone 1 (from 0 to -15 cm) presents peaks with high dissolved Fe²⁺ and Mn²⁺
398 concentrations, revealing a suboxic zone in these sediments. This mobilization is due to Fe and Mn
399 oxyhydroxides use as terminal electron acceptors in bacterial OM oxidation (Eq. 3 and 4) (Froelich
400 et al., 1979), resulting in decreased Mn_R and Fe_R concentrations (referred to in the equations as MnO₂
401 and FeOOH/Fe(OH)₃) in the solid-phase in this zone (Fig. 2). High Mn²⁺ and Fe²⁺ concentrations

402 depth sequences were recorded during the dry season, as Mn^{2+} appeared vertically in solution before
 403 Fe^{2+} . However, during the wet season, Mn^{2+} and Fe^{2+} appeared simultaneous and closer to the SWI,
 404 probably due to strong resuspension and the effect of tidal pumping caused by intense rainfall rates.
 405 Marchand et al., (2006) also observed Fe^{2+} and Mn^{2+} variations with depth associated to seasonal
 406 fluctuations.

407



409



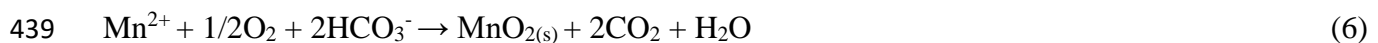
412

413 Pore water Fe^{2+} reached higher concentrations at P1 (285.1 μM) compared to P2 (198.8 μM)
 414 and P3 (219.3 μM). Although freshwater discharge penetration during the wet season significantly
 415 decreased pH values, which would enhance oxyhydroxide dissolution (Holloway et al., 2016; Otero
 416 et al., 2009), the highest Fe^{2+} concentrations did not indicate significant difference between seasons,
 417 probably due to the high Fe supply from the continent (Barreiras Formation, Vilhena et al., 2010).
 418 However, Fe^{2+} peaks were typically deeper during the dry season. Low Fe^{2+} concentrations were
 419 observed at the top pore water (0 to -2 cm) during the dry season, increasing in the surface solid
 420 phase, probably due to Fe^{2+} oxidation and precipitation in the form of oxyhydroxides, likely
 421 associated to high oxygen sediment exposure during the low tide due to lower river discharges.

422 During tidal oscillations, multiple reduction-oxidation reactions may occur, and Fe^{2+} and Mn^{2+}
 423 may be removed from the pore water by oxidation to form oxyhydroxides (Liu et al., 2019), which
 424 explains the Fe_R and Mn_R peaks around -20 cm at P2 and -8 cm at P3 during the wet season (Fig. 2).
 425 A percentage of the dissolved Fe and Mn encounters oxygen from the sediment surface and
 426 precipitates back to Mn and Fe oxyhydroxides (Eq. 5 and 6). These peaks also seem to mark the

427 transition zone between suboxic and anoxic phases. Only pore water Mn^{2+} at P3 showed much lower
 428 concentrations during the wet season, consistent with higher reactive Mn_R concentrations in the solid-
 429 phase (Fig. 2). At this site, Mn_R precipitation was probably enhanced by bioturbation activities.
 430 Sediment mixing (i.e. physical or/and biological mixing) was noted in the surface sediment layers at
 431 P3, determined through the excess ^{210}Pb profiles reported by Matos et al., (2020), masking the
 432 production of pore water Mn^{2+} at the SWI. This mixing can also explain the top pore water Fe^{2+}
 433 concentration variations observed at P3. Gueiros et al., (1999) also observed higher Mn^{2+} profile
 434 intensities during the dry season compared to wet season in mudflat sediments. On the other hand,
 435 Thanh-Nho et al., (2020) and Lacerda et al., (1999) observed the highest dissolved Mn concentrations
 436 during the wet season.

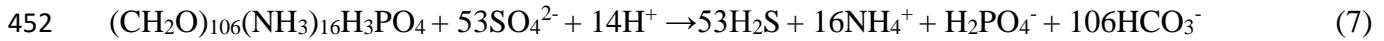
437



440

441 In zone 2 (below -15 cm), the concurrent decreases in Fe^{2+} and Mn^{2+} were accompanied by a
 442 steady increase in TA, $\text{SO}_4^{2-}_{\text{dep}}$, PO_4^{3-} and NH_4^+ toward the base of the core, suggesting an anoxic
 443 zone, with rapid OM mineralization in deeper sediment layers (Fig. 3-5). Regression analyses
 444 between $\text{SO}_4^{2-}_{\text{Dep}}$ as an estimate for the metabolic amount of sulfate reduction (SR) and TA as a
 445 terminal metabolic product were performed. According to Eq. (7), where OM is sourced from
 446 phytoplankton (Redfield et al., 1963), OM degradation is mainly related to SR. Thus, a TA: $\text{SO}_4^{2-}_{\text{Dep}}$
 447 ratio of 2 would be expected. $\text{SO}_4^{2-}_{\text{Dep}}$ in pore waters was positively correlated to total alkalinity at
 448 all sites (see Supplementary Table S1 and S2). The TA: $\text{SO}_4^{2-}_{\text{Dep}}$ ratio revealed by the regression
 449 analysis slope ranged between 1.0 and 2.6. According to the Redfield ratio, this range indicates sulfate
 450 reducing conditions.

451



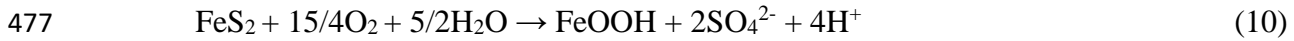
453

454 Considering the pore water is devoid of free sulfide at sites P2 and P3, and appear at site P1
 455 only in deeper layers, a tight coupling between sulfide production via SR and sulfide consumption by
 456 pyrite formation may be proposed (Raiswell and Canfield, 1998). The $\Sigma\text{H}_2\text{S}$ can react with Fe^{2+} and
 457 Fe_R to form iron sulfides, e.g., FeS (Eq. 8) and FeS_2 (Eq. 9). However, the low $\Sigma\text{H}_2\text{S}$ and AVS (mainly
 458 FeS) concentrations can also be due to intense oxidation and pore water exchange during the air
 459 exposure in the low tides. As reported by Pan et al., (2019) the formation and reoxidation of sulfide
 460 in surface layers in the intertidal zones are regulated by tide-induced redox changes.

461 In the wet season, when the reducing conditions become pronounced, at sites P2 and P3 pyrite
 462 concentrations increase dramatically in the solid phase below Fe^{2+} and Fe_R peaks (Fig. 2). Thus, the
 463 consumption of Fe_R and Fe^{2+} in deeper sediments occurs due to iron sulfide precipitation. Lower
 464 pyrite concentrations in the dry season, especially at sites P2 and P3 are probably due to these sites
 465 being located in topographically higher areas and their sediments are strongly oxidized during the dry
 466 season, promoting the pyrite oxidation (Eq. 10), thus Fe_R concentrations increase with depth reaching
 467 higher concentrations in the dry season than the wet season in deeper sediment layers. The oxidation
 468 of Fe sulfides to Fe oxyhydroxides occurred in the dry season is similar to the seasonal changes
 469 observed in other studies (Luther et al., 1992; Rozan et al., 2002). Pyrite oxidation was previously
 470 observed in Marapanim mangrove sediments by Vilhena et al., (2010), they observed oxidation of
 471 pyrite grains surface and the presence of jarosite mineral as a product of pyrite oxidation. Mn
 472 consumption at deeper layers is likely associated to pyrite coprecipitation, as reported in other
 473 assessments (Huerta-Diaz, 1992; Otero and Macias, 2003; Santos-Echeandia et al., 2009).

474





478

479 Seasonal effects, mainly controlled by freshwater discharges, affected the downcore profiles
480 of pore water SO_4^{2-} Dep in the investigated sediments. Sulfate depletion was not appreciable in the top
481 sediment layers (above -15 cm) at all sites during the wet season, due to the dilution-mixing process,
482 that results in a more efficient sulfate removal than bacterial SR in these layers. On the other hand,
483 sulfate depletion increased abruptly below the dilution-mixing layers. Similar seasonal trends were
484 also reported by Wu et al., (2015) at the Pearl River estuary. SR products (TA, NH_4^+ and PO_4^{3-})
485 indicated no simple mixing trend in the dilution-mixing layer (Fig. 3-5), suggesting that pore waters
486 TA, NH_4^+ and PO_4^{3-} are substantially altered by diagenetic reactions, such as Fe and Mn reduction.
487 However, only pore water NH_4^+ exhibited any seasonal variability, with the highest concentrations
488 detected in the wet season. A similar phenomenon was reported by Meiggs and Taillefert, (2011),
489 who investigated seasonal effects on estuarine sediments biogeochemical processes, indicating that
490 dilution-mixing does not cause seasonal SR product alterations.

491 Suboxic to anoxic sediment conditions limit aerobic OM degradation. Iron reduction and SR
492 are energetically less favorable degradation processes, thus enhancing OM burial. As previously
493 observed by Matos et al., (2020), the sampling sites exhibit higher potential regarding TOC, TN and
494 TP sediment accumulation, especially the creek mudflats (P2 and P3). The mudflat sediment in the
495 Marapanim River margin (site P1) presented lower TOC, higher sand contents and high marine OM
496 contributions compared to P2 and P3 (Table 1). P1, however, reached higher terminal metabolic end-
497 products of OM mineralization concentrations, such as Fe^{2+} , SO_4^{2-} Dep, H_2S and TA, suggesting that
498 the OM of this estuarine mudflat is more susceptible to degradation compared to the mangrove creek
499 mudflats. Typically, organic-rich sediments present high OM degradation rates. However, due to the
500 enhanced OM and oxygen input by advective processes at the sediment surface, sandy sediments
501 containing low organic carbon contents often exhibit OM degradation rates comparable to organic-

502 rich muds (Beck et al., 2008; Rusch et al., 2006). OM degradation rates further depend on sedimentary
503 OM sources. For example, previous studies have demonstrated that marine-derived OM (fresher or
504 more labile) is more susceptible to degradation by microorganisms than terrestrial OM (more
505 refractory) (Hedges et al., 1997; Matos et al., 2020; Ranjan et al., 2011). Therefore, coarse-textured
506 sediment and higher available labile OM likely contributed to more susceptible OM degradation at
507 P1, resulting in low TOC concentrations.

508

509 *4.3 Seasonal diffusive flux variability at the SWI*

510

511 High amounts of Fe^{2+} and Mn^{2+} are produced by microbial Fe and Mn reduction processes,
512 respectively, which then diffused from the sediment pore waters into the overlying water, indicating
513 that the studied mudflats comprise a source of Fe^{2+} and Mn^{2+} . The changes in diagenetic processes
514 induced by increasing rainfall rates, therefore, lead to variable diffusive fluxes. Concerning the wet
515 season, the highest Fe^{2+} concentration was noted just below SWI, generating higher fluxes during this
516 period (Table 2). On the other hand, Fe^{2+} concentrations in the dry season were lower in the top
517 sediment layers, probably due to high oxygen sediment exposure during the low tide, enhancing
518 oxidized solid phase severely limiting its diffusion to the overlying water. Mn^{2+} fluxes followed the
519 same trend as Fe^{2+} fluxes, except at P3, which presented lower fluxes in the wet season due to
520 sediment mixing, resulting lower Mn^{2+} concentrations in the surface sediment. Marchand et al. (2006)
521 also reported higher dissolved Fe and Mn fluxes in the wet season compared to dry season, as a result
522 of vertical redox status oscillations.

523 Sediment pore waters constituted a source of PO_4^{3-} and NH_4^+ to the water column at all sites,
524 with higher fluxes in the wet compared to the dry season (Table 2). As reported by Taillardat et al.
525 (2019), intense rainfall events reduce pore water salinity and enhance OM degradation, which is likely
526 to increase phosphate and nitrogen mineralization. The high NH_4^+ pore water concentrations and the

527 strong correlation between NH_4^+ and SO_4^{2-} _{Dep} pore water detected in both sampling seasons ($r = 0.61$
528 $- 0.70$, Supplementary Table S1 and S2) reveal high OM mineralization (ammonification), more
529 intense during the wet season, with higher downcore pore water concentrations. Mangrove sediments
530 generally comprise NH_4^+ sinks (Alongi, 2020b and references within), mostly due to N- NH_4^+ uptake
531 by vegetation, although an efflux for NH_4^+ is often noted (Gleeson et al., 2013; Matos et al., 2016;
532 Sadat-Noori and Glamore, 2019; Tait et al., 2017), as observed herein for the investigated mangrove
533 mudflats, as no permanent macrophytic vegetation in the mudflat is available to consume dissolved
534 nutrients (Taillardat et al., 2019).

535 Pore water PO_4^{3-} concentrations were also significantly and positively correlated with SO_4^{2-}
536 _{Dep} pore water in the wet season ($r = 0.64$, Supplementary Table S1). This positive correlation receded
537 in the dry season ($r = 0.48$, Supplementary Table S2), due to enhanced SO_4^{2-} _{Dep} in the upper layers,
538 that did not affect downcore pore water PO_4^{3-} . Other studies have indicated that the release or
539 adsorption of P in coastal sediments is associated with the iron redox cycle (Ding et al., 2016;
540 Sherman et al., 1998). Fe oxy-hydroxides potently adsorb P under more oxidizing conditions. In
541 contrast, more reducing conditions favor its mobility from sediments to pore waters (Bava and
542 Seralathan, 1999). However, low PO_4^{3-} remobilization in the upper layers where Fe reduction occurs
543 implies that PO_4^{3-} release was not associated to Fe-bound P at our investigated study sites. A low
544 negative correlation between PO_4^{3-} and Fe^{2+} , and significant positive correlations between PO_4^{3-} and
545 NH_4^+ and TA (Supplementary Table S1 and S2) reinforces the assumption that PO_4^{3-} release to pore
546 water was mainly derived from OM mineralization by SR.

547 Overall, the short but remarkable climate fluctuations influenced pore water concentrations
548 and physicochemical properties and, consequently, the intensity of metal and nutrient exchange rates
549 at the SWI in our study sites. It is, therefore, essential to take consider local weather conditions when
550 estimating and managing nutrient and metal budgets. Climatic variability (e.g., changes in rainfall
551 and the frequency and intensity of storms) can exacerbate factors affecting mangrove responses to

552 sea level, altering freshwater inflow to mangroves, sediment and nutrient inputs and salinity regime
553 (Alongi, 2018; Mcleod and Salm, 2006). Studies in Bragança Peninsula, 110 km distant from the
554 study area, indicated that mangroves have invaded higher tidal flats since 1984 due to a relative sea
555 level rise (Cohen et al., 2021, 2018, 2009; Cohen and Lara, 2003).

556 Metals and nutrients fluxes at the SWI have been estimated in other mangrove systems
557 worldwide (Supplementary Table S3), but their direction and intensity vary among sites. For example,
558 diffusive Fe^{2+} fluxes in Marapanim mangrove mudflats are low compared to temperate mangrove
559 creeks (Holloway et al., 2018; Sadat-Noori and Glamore, 2019), while diffusive Mn^{2+} fluxes present
560 the same order of magnitude as those reported for other mangrove creeks (Holloway et al., 2016; Pan
561 et al., 2019a). NH_4^+ and PO_4^{3-} fluxes are comparable to those determined in subtropical mangrove
562 forest (Kaiser et al., 2015), temperate mangrove creeks (Tait et al., 2017) and tropical mangrove-
563 fringed estuaries (Pratihary et al., 2021), but are lower than other subtropical mangrove creeks
564 (Gleeson et al., 2013; Pan et al., 2019a, 2019b) and temperate mangrove wetlands (Sadat-Noori and
565 Glamore, 2019). These variations may be due to many factors, including differences in terrestrial or
566 oceanic nutrient inputs, redox condition shifts, anthropogenic activities and local environmental
567 factors, such as weather conditions, hydrology, tidal ranges, latitudes, mangrove community
568 structures and topographic elevations (Adame et al., 2010; Adame and Lovelock, 2011; Kristensen et
569 al., 2017). In addition, this comparison must be cautiously considered, due to different analysis
570 methods and high inter-site variability.

571

572 *4.4 Pore water solute flux versus depositional fluxes*

573

574 The diffusive fluxes in $\text{mmol m}^{-2} \text{d}^{-1}$ were converted to $\text{g m}^{-2} \text{yr}^{-1}$ for comparisons to
575 depositional fluxes. Total nitrogen and total phosphorous depositional fluxes were obtained from
576 Matos et al. (2020). Fe and Mn depositional fluxes were estimated from reactive Fe and Mn

577 concentrations, sediment accumulation and dry bulk density reported previously by Matos et al.,
 578 (2020). The average between the three study sites, propagate to the average between the wet and dry
 579 season dataset, of the calculated diffusive fluxes from the pore water to the overlying water column
 580 for N (as NH_4^+), P (as PO_4^{3-}), Fe (as Fe^{2+}) and Mn (as Mn^{2+}) were 2.6, 0.5, 5.7, and 1.6 $\text{g m}^{-2} \text{yr}^{-1}$,
 581 respectively. Regarding N, P, Fe and Mn depositional fluxes were 15.3, 3.2, 42.3 and 1.8 $\text{g m}^{-2} \text{yr}^{-1}$,
 582 respectively (Table 3). The release of dissolved NH_4^+ , PO_4^{3-} , Fe^{2+} and Mn^{2+} from the pore water to
 583 the overlying water corresponds to averages of ~17, 16, 15 and 90 % (% recycling) of the total amount
 584 of N, P, Fe and Mn deposited in the sediment (% burial), respectively (Table 3).

585

586 **Table 3**

587 Upward diffusive NH_4^+ , PO_4^{3-} , Fe^{2+} and Mn^{2+} fluxes and depositional total N and P and reactive Fe
 588 and Mn fluxes at P1, P2, and P3 sampling sites.

Site	Diffusive flux				Depositional flux				Recycling				Burial			
	$(\text{g m}^{-2} \text{yr}^{-1})$				$(\text{g m}^{-2} \text{yr}^{-1})$				%				%			
	N	P	Fe	Mn	N	P	Fe	Mn	N	P	Fe	Mn	N	P	Fe	Mn
P1	1.4	0.7	7.5	1.3	11.0	2.7	37.2	1.8	12.8	27.2	18.6	70.2	87.2	72.8	81.4	29.8
P2	5.2	0.4	6.3	1.4	16.4	3.1	42.7	1.6	31.9	11.7	18.8	86.1	68.1	88.3	81.2	13.9
P3	1.1	0.4	3.2	2.1	18.4	3.9	47.0	2.1	5.8	9.4	6.7	112.3	94.2	90.6	93.3	-12.3
Average	2.6	0.5	5.7	1.6	15.3	3.2	42.3	1.8	16.8	16.1	14.7	89.5	83.2	83.9	85.3	10.5

589

590 Marapanim mangrove sediments contain high Fe concentrations, with a mean of 6.5 %
 591 (Vilhena et al., 2010). The reactive Fe concentrations found in these mudflat sediments correspond
 592 to <10 % to those detected in the mangrove forest, highlighting Fe burial efficiency (85 %) in
 593 Marapanim mudflats. In contrast, Berrêdo et al., (2008a) observed lower total Mn concentrations
 594 (0.03%) than those detected in the investigated mudflat, of 0.06%. This high recycling potential of
 595 ~90 % corroborates with Holloway et al., (2016), who state that undisturbed mangrove creeks may
 596 be a major source of Mn^{2+} to coastal oceans. N and P burial efficiency (~84 %) is driven by suboxic

597 conditions, where Fe and Mn reductions appear to limit PO_4^{3-} and NH_4^+ pore water mobilization and
598 their fluxes to overlying surface waters.

599 Additionally to spontaneous diffusive exchange at the SWI, transport of dissolved elements
600 by advective pore water seepage and bioturbation (irrigation from burrows and biodiffusion) can also
601 be take place. Intertidal mudflat sediments are submitted to intense oscillations associated to tidal
602 heights, which may enhance nutrient and metal dissolved losses by lateral tidal drainage, advection
603 or groundwater transport (Holloway et al., 2016; Sanders et al., 2015; Tait et al., 2017). Thus, the low
604 PO_4^{3-} and NH_4^+ pore water mobilization in the upper layers can also be due to tidal-induced pore
605 water seepage from the upper layers into the creek water columns during low and ebbing tides. Pore
606 water exchange can be reduced by geochemical factors such as absorption, precipitation etc. (Ogrinc
607 and Faganeli, 2006; Rozan et al., 2002). In our study, low dissolved metal concentrations and their
608 low fluxes across the SWI during the dry season, affected by seasonal rainfall patterns, indicate
609 considerable oxidation and metals trapping into solid-phases. Bioturbation activities may increase
610 sediment oxygen supplies and a fraction of the produced Fe^{2+} , Mn^{2+} and NH_4^+ may be oxidized in the
611 upper layers where suboxic conditions can be found. On the other hand, crab burrows have been
612 demonstrated to increase the hydraulic conductivity of mangrove sediments and create a larger
613 effective surface area enhancing diffusive fluxes (Bouillon et al., 2007). Therefore, diffusive fluxes
614 based only on molecular diffusion and gradient concentrations at the SWI represent only a minimal
615 estimate of how these mudflat pore waters can act as a water column source.

616

617 **5 Conclusions**

618 The present study demonstrates that pore water concentrations, physicochemical properties,
619 and the intensity of metal and nutrient exchange rates at the SWI in intertidal mudflat sediments
620 fringed by pristine mangroves in northern Brazil are influenced by Amazonian seasonal rainfall
621 patterns. A seasonal shift from the dry to the wet season was observed, with increasing acidic and

622 reducing conditions, pore water salinity declines, and increased elemental concentrations within the
623 pore water and sediments. The redox zonation of sediments oscillated vertically in response to rainfall
624 patterns, affecting pore water species and their fluxes across the sediment-water interface. Under
625 suboxic conditions, the mudflat pore waters constitute a source of Fe^{2+} , Mn^{2+} , NH_4^+ and PO_4^{3-} to the
626 water column, and the magnitude of these effluxes increased in the wet season. However, when
627 compared with burial fluxes, the release of dissolved NH_4^+ , PO_4^{3-} , Fe^{2+} and Mn^{2+} from the pore water
628 to the overlying water corresponded to ~17, 16, 7 and 90 % of the amount of TN, TP, Fe_R and Mn_R
629 deposited in the sediment, respectively. This demonstrates that Marapanim mudflats are effective in
630 retaining nutrients and Fe in their sedimentary solid phases compared to coastal water exports, while
631 also potentially comprising significant Mn contributor to coastal waters. These findings evidence the
632 role of mangrove-fringed tidal creeks as sites exhibiting intense biogeochemical processes, rather
633 than simple dissolved material routes between mangroves and coastal oceans, which are strongly
634 influenced by rainfall events.

635

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643

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653 final version.

654

655 **Appendix A. Supplementary data**

656 Supplementary data to this article can be found online at

657

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