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Vertical and tidal variability of dissolved organic matter in mangrove soils: influence on dissolved trace metal dynamics

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ABSTRACT:

Mangrove ecosystems are dynamic ecotones that play a key role in organic carbon and trace metals (TM) cycling along tropical coastlines. Tidal pumping is a key process that allows dissolved organic matter (DOM) and dissolved trace metals export towards adjacent ecosystems. While this process is well characterized, DOM-TM relationships and variability within mangrove soils remain poorly studied. In the present study, we investigated the vertical distribution of DOM and TM in a *Rhizophora stylosa* mangrove stand in New Caledonia over 12-hour tidal cycles during both spring and neap tides. DOM quantity and quality were assessed through UV-visible absorbance, fluorescence spectroscopy, total and dissolved organic carbon analysis, and physicochemical measurements. Dissolved TM were quantified using ICP-MS. Our results show a vertical gradient in DOM, with deeper layers concentrated in aromatic and humified compounds, attributed to vertical migration through potential convection process. This gradient (DOM and salinity) is accentuated during neap tide due to lower hydrodynamics. Dissolved TM exhibited distinct vertical trends with depth: Cr and Mn followed DOM trends, suggesting either common vertical transport mechanisms or complexation with humic substances. In contrast, Mo and Ni decreased with depth, suggesting stronger control by physicochemical or mineralogical conditions, and potential precipitation within pyrite in the most anoxic layers. This study highlights the combined effect of vertical soil gradients and tidal fluctuations on DOM-TM interactions, contributing to a better understanding of

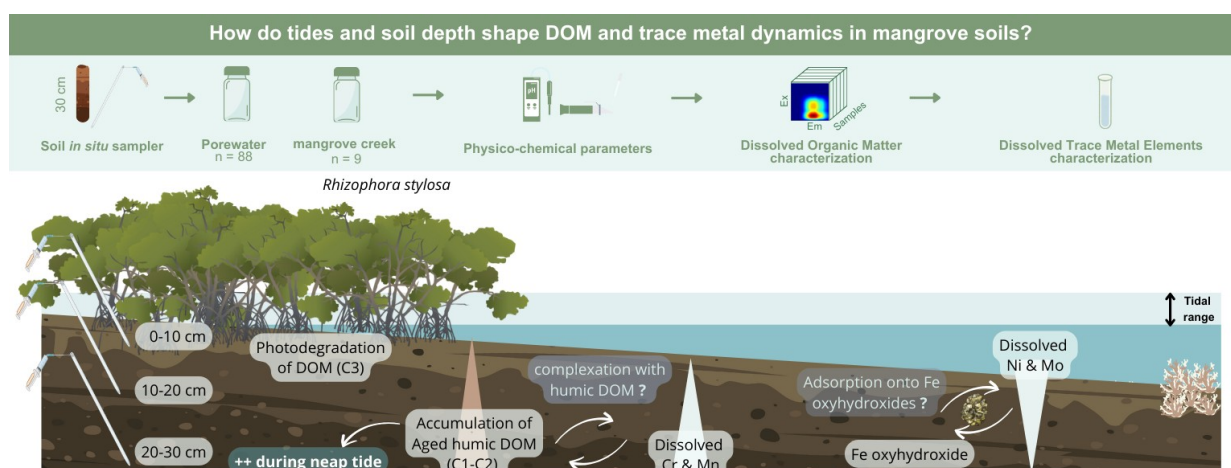
the role of mangroves as biogeochemical filters and as both sources and sinks of trace elements at the land-ocean interface.

Keywords: Porewater, Photochemistry, Fluorescence spectroscopy, *Rhizophora stylosa*, Humic substances

HIGHLIGHTS

- Dissolved organic carbon content is higher in deeper soil layers
- The deep dissolved organic matter is older and more humified than at the surface
- The vertical gradients studied are amplified during neap tides
- Cr and Mn follow the dissolved organic carbon vertical gradient
- Ni and Mo follow an opposite vertical gradient to dissolved organic carbon

GRAPHICAL ABSTRACT



1 Introduction

Mangrove forests develop along tropical and subtropical coasts in the intertidal zone, where they play a crucial role in the dynamics of coastal ecosystem and carbon cycling (Giri et al., 2011). Despite covering less than 0.5% of the Earth's coastal surface (Alongi, 2014), mangroves provide several ecosystem services, including high organic matter (OM) productivity (Bouillon et al., 2008), efficient carbon fixation, and long-term carbon storage in their soils (Donato et al., 2011; Kristensen et al., 2008). However, these carbon stocks can fluctuate under effects of environmental factors such as tidal variations and seasonal changes that can significantly influence the production, storage, and export of OM (Adame et al., 2021).

In mangrove soils, the decomposition of leaf litter represents a primary source of dissolved organic matter (DOM), characterized by a high content in humic-like compounds (Coble, 2007; Maie et al., 2008; Shank et al., 2009). These compounds are known for their high reactivity and ability to form stable complexes with trace metals (TM). Previous studies have demonstrated that DOM from mangrove soils can be exported to adjacent ecosystems via tidal processes, either flushing or pumping (Xiao et al., 2023). In fact, several research papers confirm the significant role of mangroves in exporting DOM to adjacent coastal waters (Adame et al., 2024; Alongi, 2022; Dittmar et al., 2006). However, this export is variable over time, influenced by seasonal dynamics, precipitation, evaporation, and tidal cycles, which in turn affect the production and mobilization of this matter (Cawley et al., 2014; Maie et al., 2012). For instance, Bouillon et al. (2008) observed that DOM export to estuarine waters peaks during ebb and flood tides.

Beyond its role in the carbon cycle, DOM also interacts with trace elements in soils, influencing their mobility, storage and potential export. Several studies have shown that mangrove soils can act as both sinks and sources of TM, depending on environmental conditions (Lacerda et al., 2022; Thanh-Nho et al., 2020). Among the dominant drivers, tidal pumping and porewater exchange, both vertical and lateral, play a key role in the mobilization and export of dissolved metals and DOM to adjacent coastal waters (Knoke et al., 2024; Sadat-Noori and Glamore, 2019). Studies in temperate and tropical mangroves have shown that tidal pumping promotes the release of Fe(d), Mn(d), and DOC, with metal speciation often shifting during transport due to redox and pH changes (Knoke et al., 2024; Thanh-Nho et al., 2020). In mangrove soils, redox conditions, which are highly sensitive to tidal inundation and soil water saturation, primarily control the precipitation-dissolution cycles of TM (Noël et al., 2014). In addition, litterfall decomposition has been shown to increase the mobility of trace elements (Robin et al., 2025). Indeed, the high OM content of mangrove soils both favours DOC

preservation in reducing conditions (Alongi et al., 1998; Marchand et al., 2006b, 2004; Pérez et al., 2021), and strongly influences dissolved trace metals (DTM) behaviour, by either promoting their mobility through complexation or favouring their retention via co-precipitation and stable binding (Mounier et al., 2001; Zhu et al., 2019).

In this context, DOM plays a major role in driving the fate of dissolved DTM in mangrove soils. Through its reactive functional groups such as carboxyl and hydroxyl, particularly abundant in humic substances, it can either enhance metal solubility via complexation or promote their retention through sorption and co-precipitation (Yi et al., 2019). The nature of these interactions depends on DOM characteristics, such as aromaticity and molecular weight, which influence its affinity for dissolved metals like Cu(d) and Fe(d) (Kikuchi et al., 2017; Yamashita and Jaffé, 2008). Understanding these processes is essential to better characterize metal mobility patterns in mangrove environment, especially in this system where humic OM is abundant. While mangroves are known to export substantial amounts of DOM and DTM, especially during tidal exchange, the contribution of soil including leaf litter inputs to these exports remains poorly understood. Moreover, the vertical processes (linked to soil depth and redox driven stratification) and lateral processes (tidal pumping and horizontal porewater exchange) regulating DOM quality and its metal-binding potential in mangrove soils are still underexplored.

This study aims to characterize the vertical distribution of DOM and DTM in mangrove soils under tidal influence, and to investigate their potential interaction across porewater and surface water compartments. We focused on a *Rhizophora stylosa* dominated mangrove, conducting 12-hour tidal cycle monitoring of porewaters during both neap and spring tides. We hypothesize that DOM derived from leaf litter degradation contributes to some TM mobilization through complexation, and that tidal stage modulates DOM and DTM dynamics by changing physico-chemical conditions and porewater exchange. To avoid the effects of allochthonous OM inputs, we selected a study site without riverine or terrestrial inputs, which provides a relevant setting to investigate autochthonous DOM-TM dynamics. The composition and origin of DOM was characterized using spectroscopic techniques, including UV-visible absorbance and excitation-emission matrix (EEM) fluorescence coupled with PARAFAC (Hansen et al., 2016).

2 Material & Method

2.1 Study site

The Bouraké mangrove, located on the western coast of New Caledonia (21.946°S, 165.999°E), is characterized by a semi-enclosed geomorphology and reflects a typical semi-arid mangrove forest structure

(Adame et al., 2021). This 2.5 km² mangrove is largely dominated by *Rhizophora stylosa* (*R. stylosa*), which forms dense stands along the seaward fringe (Fig. 1). Hydrologically, the system is linked to Pritzbuier Bay by a narrow tidal channel that crosses a coral platform and connects the open sea to the inland mangrove lagoons. Due to its unique hydrological and geomorphological setting, the Bouraké mangrove has served as a model system for studying biological responses to extreme environments (Alessi et al., 2024; Dubuc et al., 2019; Maggioni et al., 2021). However, the role of *R. stylosa*-dominated soils in biogeochemical processes within this semi-enclosed system remains understudied. Bouraké is located on volcano-sedimentary soils (Ullmann et al., 2014) and is not directly influenced by river input. This system is exposed to semidiurnal tidal range (Maggioni et al., 2021).

2.2 Field sampling

Field sampling was conducted in March 2024, during two contrasting tidal periods: neap tide (March 4, 2024 with a maximum tidal range of 0.6 m) and spring tide (March 11, 2024, with a maximum tidal range of 1.25 m) (Fig. S1). For the neap tide campaign, five time points were sampled over a 12-hour period (low, flood, high, ebb, low), and for the spring tide, four time points were sampled (low, ebb, high, flood). Each sampling campaign lasted approximately 12 hours, with samples collected every three hours throughout the tidal cycle.

Porewater sampling zones were located along the inland mangrove creek, with three replicate sites distributed laterally across the creek (Fig. 1). Surface water samples were collected directly in front of each mangrove site. Porewater was extracted in situ using MacroRhizon® samplers (0.1 µm pore size) at three soil depths (0-10, 10-20, and 20-30 cm) beneath *R. stylosa* at each of the three sites. Each MacroRhizon® was fixed on 30 cm PVC pipe, installed in the morning at designated site and depth, and connected to 2 m extension tubes attached to trees to ensure stability during tidal inundation. The system was coupled to 30 mL syringes for extraction. To obtain sufficient sample volume, each collection lasted approximately 1.5 hours (Fig. S1). These sites correspond to GPS locations where sediment cores had previously been collected for a related study (Mouras et al., 2025a, EGU sphere preprint), ensuring consistency across sampling efforts (Table S1). In total, 81 porewater samples were collected (9 samples per sampling moment). Surface water samples were also collected during both campaigns, resulting in a total of 9 samples, taken at various tidal stages when accessible.

Measurements of temperature, pH, and redox potential (Eh) were conducted using sensors directly in a sub-sample of the porewater and surface water by avoiding any contact of the samples with air. The pH and redox parameters could only be analysed for samples taken during spring tide. pH was measured with a WTW® 3320 meter equipped with a SenTix® 81 glass electrode, calibrated beforehand with standard buffer solutions

(pH 4, 7, and 10). Redox potential was assessed using a WTW® pH315i meter fitted with a SenTix® ORP electrode and verified before each field sampling with a 220 mV standard solution. Eh values were adjusted to the standard hydrogen electrode (SHE) scale by adding +220 mV, as recommended for Ag/AgCl reference electrodes. Salinity was measured using a refractometer (ATC) on the collected porewater samples.

After collection, all water samples (porewater and surface water) were immediately filtered in the field. For carbon analysis, including dissolved organic carbon (DOC), chromophoric dissolved organic matter (CDOM), and Fluorescent dissolved organic matter (FDOM), samples were filtered through pre-combusted (450 °C, 4 h) 25 mm Whatman GF/F filters (0.7 µm pore size), following standard methods (Coble, 1996; Halewood et al., 2022; Sharp et al., 2002). For trace metal analyses, samples were filtered through 0.2 µm cellulose acetate filters (Sartorius®). Filtered samples were transported in coolers and stored under appropriate conditions until analysis. DOC samples were acidified with HCl (pH < 2) and stored in 24 mL glass vials with Teflon/silicone septum (Wheaton®) previously cleaned by acid-washing with 10% HCl, rinsed three times with Milli-Q water, and combusted at 450 °C for 6 h. Vials were kept at 4 °C in the dark. CDOM and FDOM samples were stored in glass vials treated following the same cleaning protocol as for DOC (acid-washed, rinsed, combusted), and also kept at 4 °C in the dark. Trace metal samples were acidified with ultrapure HNO₃ (pH < 2) and stored in acid-cleaned 15 mL metal-free polypropylene tubes (Labcon®).



150

151 Figure 1: Map of the Bouraké mangrove site showing the locations of porewater sampling within *Rhizophora stylosa* stands.
152 Sampling was conducted during neap and spring tide periods. Map created using QGIS 3.28.6; base map from ESRI satellite
153 (June 2025).

154 **2.3 Analytical methods**

155 **2.3.1 Dissolved and organic carbon (DOC)**

156 DOC concentrations were measured using a Shimadzu TOC-VCSH carbon analyser based on high-
157 temperature catalytic oxidation and infrared detection, equipped with an auto-sampler. Each sample was
158 analysed in triplicate to ensure precision. Blanks and standard solutions were included every 10 samples for
159 quality control, all replicates showed a relative error below 10%.

160 **2.3.2 Chromophoric dissolved organic matter (CDOM)**

161 CDOM absorption spectra were measured from 200 to 700 nm at 1 nm intervals using a Shimadzu UV-
162 1700® spectrophotometer with a 1 cm quartz cuvette. Milli-Q water was used as a blank, and raw absorbance
163 values were corrected accordingly. Absorption coefficients (m^{-1}) and related indicators were then calculated
164 following the method of Yamashita and Tanoue (2009). In particular, the absorption coefficient at 350 nm (a_{350})
165 was used as a proxy for CDOM quantity. Spectral slopes $S_{275-295}$ and $S_{350-400}$ were calculated to distinguish
166 between marine and terrestrial sources of CDOM (Hansen et al., 2016), and their ratio (S_R) was used to assess
167 molecular weight and photodegradability of the DOM (Hansen et al., 2016; Helms et al., 2008). The E_2/E_3 ratio

was also calculated to indicate aromaticity and molecular weight (Hautala et al., 2000; Rocha et al., 1999; Thomsen et al., 2002). Specific UV absorbance (SUVA) was determined as the absorbance at 254 nm divided by the DOC concentration, it is used as a proxy for aromaticity and humification.

2.3.3 Fluorescent dissolved organic matter (FDOM)

Fluorescence measurements were carried out using a PERKIN ELMER LS 55 spectrofluorometer with a 2 mm pathlength quartz cuvette (Hellma®) to avoid inner filter effect due to high absorbance and dilution. Excitation-Emission Matrices (EEMs) were recorded following the approach of (Coble, 2007, 1996), with emission wavelengths ranging from 280 to 550 nm and excitation wavelengths from 200 to 500 nm, both at 5 nm intervals. The slit widths for excitation and emission were set at 10 nm. Before each run, the cuvette was thoroughly rinsed with 10% HCl, Milli-Q water, and the sample.

EEM datasets were analysed using Parallel Factor Analysis (PARAFAC) to identify distinct fluorescent components, following the method of (Bro, 1997). Analyses were conducted with the ProgMEEF software (developed at the Mediterranean Institute of Oceanography, University of Toulon) with MATLAB R2017a. Prior to modelling, EEMs were corrected by normalizing fluorescence signals to the Raman peak of Milli-Q water at Ex/Em = 275/303 nm, according to Murphy et al. (2010), to correct possible excitation lamp day variations. Fluorescence intensities were converted into Quinine Sulfate Units (QSU) based on a calibration curve measured at Ex/Em = 350/450 nm in 0.1 N H₂SO₄ (Murphy et al., 2010). PARAFAC component selection was guided by the CORCONDIA diagnostic test, choosing the higher number of components with values above 60% indicating model robustness (Luz-Santos et al., 2025). Identified components were compared with reference fluorophores using the OpenFluor database.

In addition, the humification index (HIX) was calculated as described by (McKnight et al., 2001), with values from 0 to 1 reflecting the degree of humification. The biological index (BIX) was calculated following (Parlanti et al., 2000), where values > 1 suggest dominant autochthonous production, while lower values indicate more limited *in situ* biological activity (Huguet et al., 2009).

2.3.4 Trace metal quantification

Trace metals were analysed in the laboratory for physical chemistry of traces in Ruđer Bošković Institute in Croatia. The concentrations of dissolved elements in water samples (V, Cr, Mn, Fe, Co, Ni, Zn, Mo, Pb, U)

were measured by Inductively Coupled Plasma Mass Spectrometer (Agilent 8900), with a 20-fold dilution to reduce salt-matrix effect. He mode was used for analysis of elements. All samples were spiked with an Internal Standard (^{115}In) at concentration of $10\text{ }\mu\text{g.L}^{-1}$. A certified reference material (CASS-6, Nearshore seawater reference material for metals, National Research Council Canada) was used as a quality control (QC). Two separate CASS-6 samples, and two additional QC samples from WEPAL-QUASIMEME Proficiency Test intercomparison studies were measured after every 15 samples. Matrix matching external calibration (in 20-fold diluted seawater sample; 0, 0.1, 1, and 10 ppb standards) was used for concentration quantification. Determined concentrations of metals in QC samples were within 15% of the assigned values.

2.3.5 Scanning electron microscopy (SEM-EDX)

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) was used to observed the mineralogical composition of mangrove soil samples. Dried soil fragments were mounted on aluminium stubs using conductive carbon tape and coated with a thin carbon layer to prevent surface charging. Observations were performed using a JEOL JSM-IT300LV scanning electron microscope equipped with an Oxford EDX detector at the Electronic Microscopy Platform of the University of New Caledonia. SEM imaging was used to describe mineral morphology and associations, while EDX analyses provided semi-quantitative elemental information on mineral phases.

2.3.6 Statistics

All statistical analyses were carried out using R software (version 4.0.3). Descriptive statistics were first used to summarize the dataset. Data normality and homogeneity of variances were assessed with the Shapiro-Wilk and Levene's tests, respectively. When these assumptions were met, one-way ANOVA was used to test for differences across sediment depths, followed by Tukey's HSD post-hoc test when relevant. For non-normally distributed data or when homoscedasticity was not met, the Kruskal-Wallis test was applied, with Wilcoxon pairwise comparisons for post-hoc analysis. To compare variables between spring and neap tide conditions, Student's t-test was used for parametric data, and the Mann-Whitney U test for non-parametric data.

To explore the combined effects of tidal period (spring vs neap), tidal stage (low, flood, high, ebb), and sediment depth on the full set of environmental parameters, including carbon-related variables (TOC, DOC, CDOM, FDOM) and trace metal elements concentration, a Permutational Multivariate Analysis of Variance (PERMANOVA) was performed using the `adonis2` function from the `vegan` package. The analysis was based on

223 Bray-Curtis dissimilarities calculated from fourth-root transformed data, with 999 permutations. Pairwise
224 comparisons were run when significant main effects were found. For all statistical tests, a significance threshold
225 of $p < 0.05$ was applied.

226 **3 Results**

227 **3.1 Overall pattern of variability**

228 A PERMANOVA was performed to test the effects of tidal period (spring vs. neap), tidal stage (low, flood, high,
229 ebb), and sediment depth on porewater and mangrove surface water composition. The analysis showed that
230 sediment depth had the strongest influence on sample differentiation ($R^2 = 34.8\%$, $p = 0.001$), followed by the
231 tidal period ($R^2 = 7.8\%$, $p = 0.001$). In contrast, the effect of tidal stage was negligible and not significant ($R^2 =$
232 2.3% , $p = 0.3$), indicating that intra-day variations related to the tidal cycle were less important than the depth
233 and period related effects (Table S2 and S3). As most parameters did not show statistically significant
234 differences between spring and neap tides, we grouped both tidal periods in the figures, displaying their average
235 values. For parameters showing significant tidal differences, DOC, CDOM a_{350} , BIX, and HIX, results are shown
236 separately for spring and neap tides, either in the main figures or in the supplementary material. The tidal stage
237 factor was omitted from the other figures due to its negligible influence.

238 **3.2 Variability of physicochemical parameters and DOM quantity**

239 Salinity increased with depth in mangrove porewater for both spring and neap tides (average values are shown;
240 Fig. 2A). In surface waters, values were on average for both tidal period 36.5 ± 2.9 . In the soil, salinity ranged
241 from 41.9 ± 2.7 (0-10 cm) to 46.5 ± 2.5 (20-30 cm). This vertical increase was statistically significant (Kruskal-
242 Wallis, $p < 0.05$). Between tidal periods, only surface waters differed significantly (t-test, $p < 0.05$; table S6),
243 with salinity averaging 33.3 ± 2.1 during neap tide and 38.1 ± 1.5 during spring tide. Redox potential (Eh)
244 showed contrasting patterns between surface and porewaters during spring tide (Fig. 2B).

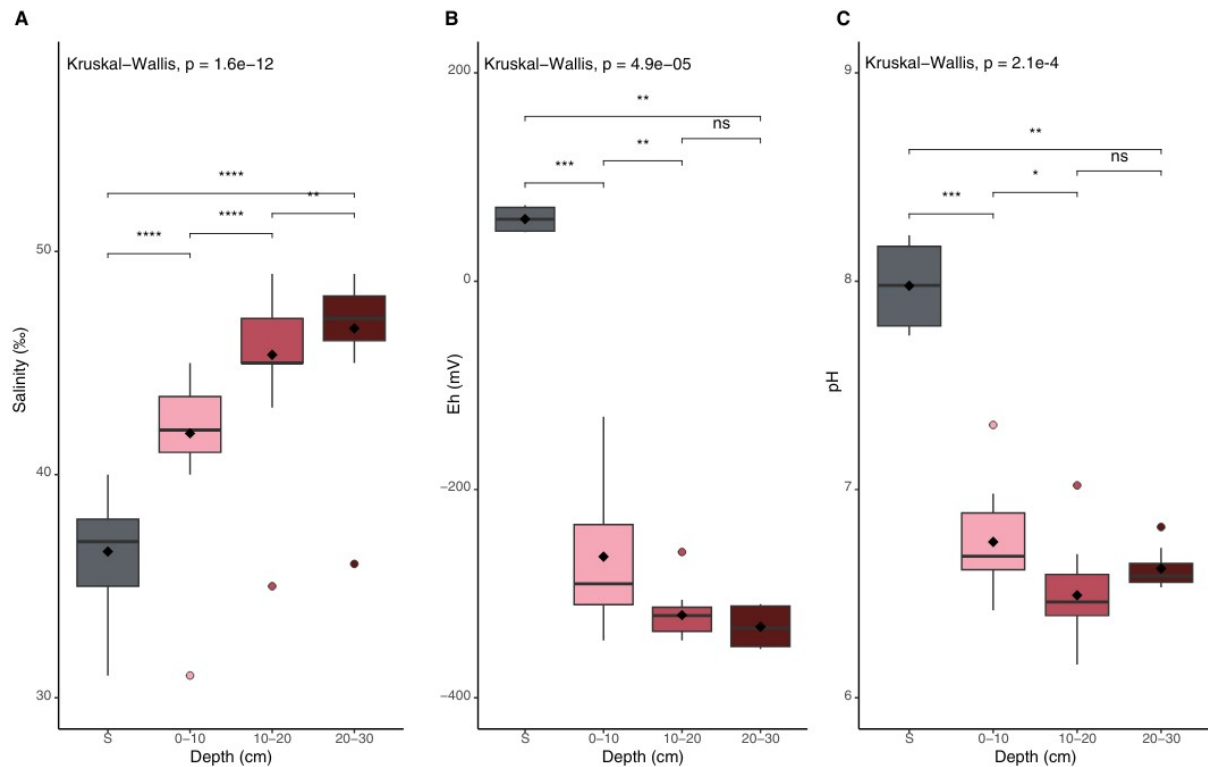


Figure 2 : Salinity (A), Redox potential (Eh) (B), and pH (C) in mangrove porewater (0-10, 10-20, and 20-30 cm; $n = 81$) and surface water (S, grey; $n = 9$). Data from spring and neap tides are pooled for A due to similar trends. Eh (B) and pH (C) measured during spring tide only.

In surface waters, Eh values were significantly higher and positive (59.6 ± 12.9), whereas in the soil, conditions were strongly reducing, with values decreasing with depth from -264.6 ± 69.1 (0-10 cm) to -320.5 ± 23.3 (10-20 cm), and -331.8 ± 19.0 (20-30 cm) (Kruskal-Wallis, $p < 0.05$). Similarly, pH values were significantly lower in porewater compared to surface waters (7.9 ± 0.23), showing a decreasing trend with depth, from 6.7 ± 0.25 (0-10 cm) to 6.5 ± 0.23 (10-20 cm), and 6.6 ± 0.10 (20-30 cm) (Kruskal-Wallis, $p < 0.05$) (Fig. 2C).

Regarding the quantity of OM, both DOC and a_{350} showed similar depth-related patterns, with overall accumulation in porewaters with depth when data from both tidal periods were combined (Table S7). However clear differences emerged between tidal conditions (Fig. 3). During neap tide, DOC concentrations increased significantly with depth (Kruskal-Wallis, $p < 0.05$), ranging from $39.6 \pm 7.1 \text{ mg} \cdot \text{L}^{-1}$ at 0-10 cm to $159.3 \pm 156.7 \text{ mg} \cdot \text{L}^{-1}$ at 20-30 cm. This represents an enrichment of about 6.5 times between surface waters and the deepest soil layer. In contrast, during spring tide, DOC concentrations were still higher in porewaters than in surface waters, but the vertical trend was inverted: the upper layer (0-10 cm) displayed the highest concentrations ($74.4 \pm 81.2 \text{ mg of C L}^{-1}$), followed by a slight decrease with depth to $52.0 \pm 9.5 \text{ mg of C L}^{-1}$ at 20-30 cm. The corresponding enrichment between surface waters and deep soil porewaters was only about 2.5-fold. This decrease, however, was not statistically significant. On average, porewater DOC concentrations in the topsoil

layer (0-10 cm) were about 2.5 times higher than in surface waters, and up to 5 times higher in the deepest layer (20-30 cm).

The a_{350} parameter followed a similar trend, with accumulation in depth from $37.3 \pm 21.8 \text{ m}^{-1}$ at 0-10 cm to $50.5 \pm 21.9 \text{ m}^{-1}$ at 20-30 cm, an effect more pronounced during neap tide. Overall, a_{350} values in porewaters were generally higher during neap tide. In surface waters, however, concentrations differed significantly between tidal periods, with higher values during spring tide ($41.7 \pm 3.2 \text{ m}^{-1}$) compared to neap tide ($8.8 \pm 0.6 \text{ m}^{-1}$).

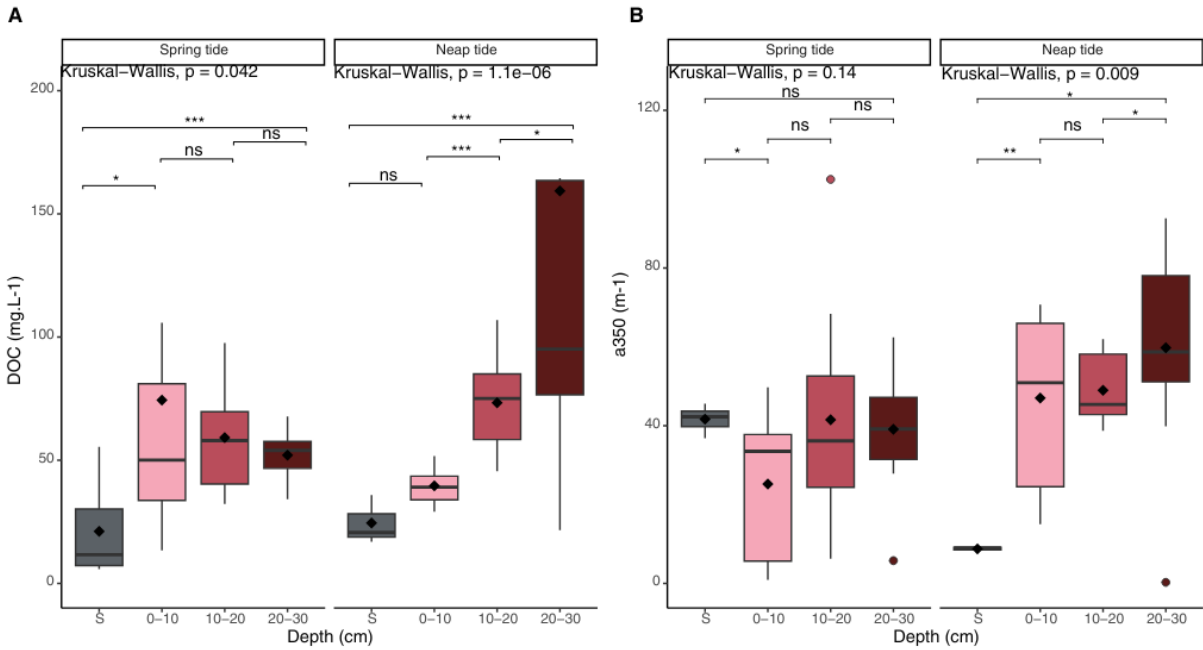


Figure 3 : Mangrove surface water and porewater properties: (A) (DOC, $\text{mg}\cdot\text{L}^{-1}$) and (B) (a_{350} , m^{-1}) variability with depth (0-10, 10-20, and 20-30 cm) in porewaters ($n=81$) and in mangrove surface waters S (grey, $n=9$), measured during spring and neap tides.

3.3 DOM quality

In porewaters and mangrove surface samples collected during both tidal periods, three fluorescent components (C1 to C3) were identified and validated by PARAFAC analysis, based on 90 EEMs. The contour plots of these components, along with their concentrations expressed in quinine sulphate units (QSU), are shown in figure 4, spectrums are presented in figure S2. Spectral characteristics of the components were compared with literature and the OpenFluor database (Murphy et al., 2014), revealing strong matches for all three components (Tucker's correlation coefficients > 0.95 ; Table S6). Components C1 and C2 were assigned to humic-like fluorophores, with excitation maxima at 250 (325) nm and 210 (275, 380) nm, and emission peaks at 447 nm and 484 nm, respectively. Component C3 had spectral characteristic consistent with photodegraded humic-like material (Amaral et al., 2020; Lambert et al., 2016). It exhibited excitation below 200 nm, with a secondary peak near 275 (410) nm, and emission at 469 nm.

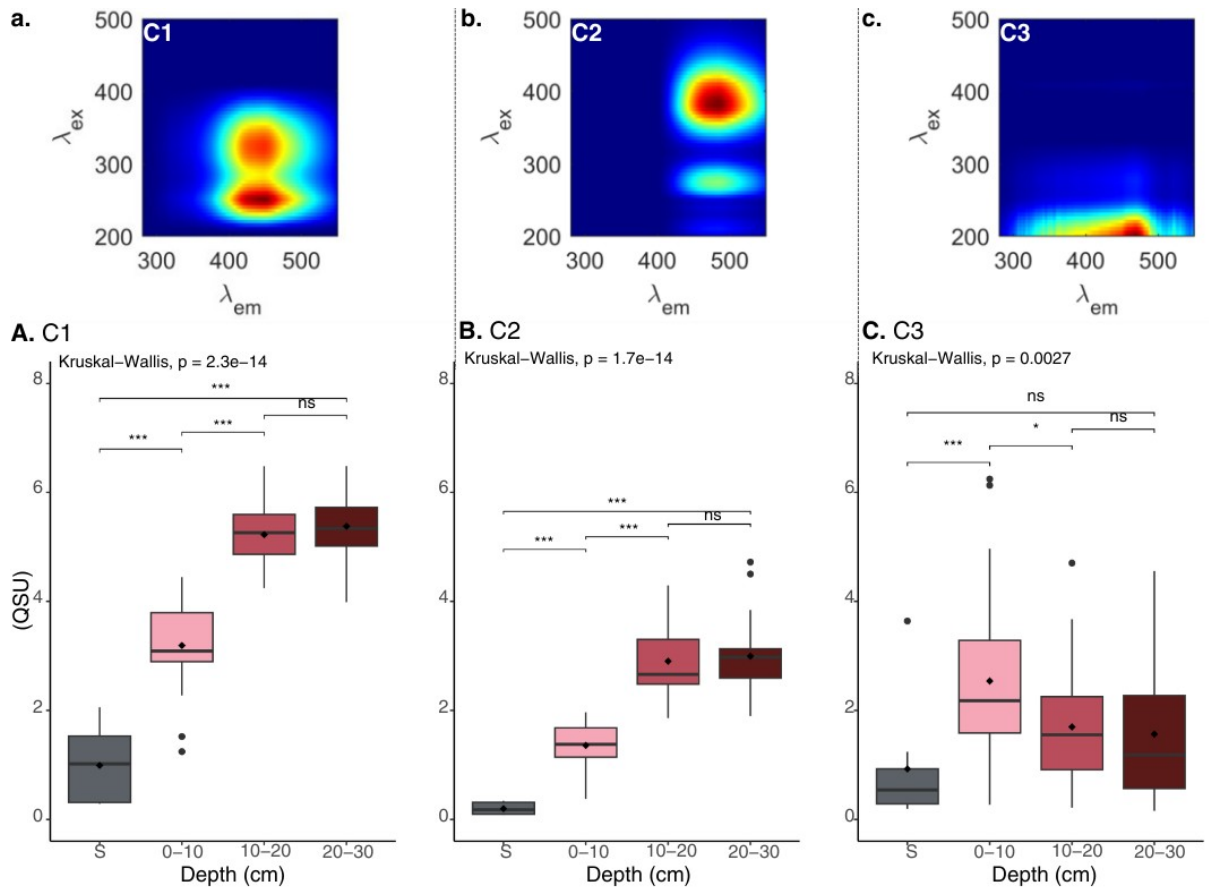


Figure 4: Vertical distribution and variability of three FDOM components in mangrove porewater ($n = 81$) and surface water (grey, $n = 9$). Data from spring and neap tides were pooled due to similar trends. Contour plots of the three PARAFAC components are shown in panels a-c, while panels A-C show corresponding boxplots of component fluorescence in QSU (C1-C3).

C1 and C2 contributions increased with depth, showing significantly higher values in the deeper layer compared to the surface (0-10 cm) across both tidal periods (Kruskal-Wallis, $p < 0.05$) (Fig. 4). However, no significant difference was found between the mid (10-20 cm) and deep (20-30 cm) layers. In contrast, C3 showed no significant variation with depth or tide, and no clear vertical trend could be identified.

The relationship between the two humic-like components, C1 and C2, is characterized by a strong co-variation across all samples (Fig. 5). Although their concentrations change with depth (Fig. 4), the two components increase and decrease together, with a common behaviour within the mangrove soils. The strong correlation between C1 and C2 is best described by a quadratic model ($y = -0.24x^2 + 2.33x + 0.58$) with a high coefficient of determination ($R^2 = 0.91$, $n = 90$, $p < 0.01$), highlighting their linked dynamics in the system.

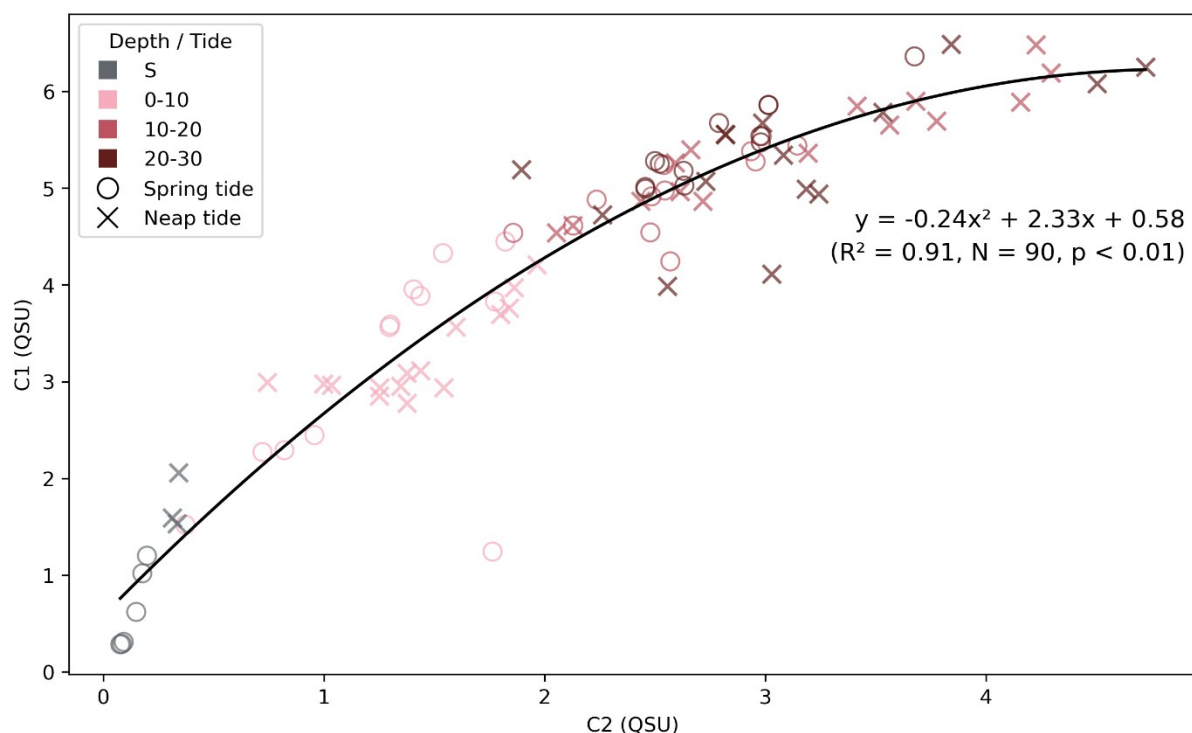


Figure 5: Relationship between humic-like FDOM components C1 and C2 across mangrove soil depths ($n = 81$) and surface water ($n = 9$). Symbols represent spring and neap tides, and colours indicate soil depth.

The biological index (BIX) and humification index (HIX), which respectively indicate the biological origin and humification state of DOM, revealed distinct vertical patterns (Table 1). BIX values were highest in the mangrove surface waters, averaging 0.65 ± 0.23 . Within the soil, BIX was lower, showing a slight decrease with depth. The surface layer (0-10 cm) exhibited higher BIX values 0.49 ± 0.05 than the deeper layer with 0.46 ± 0.06 , with no significant differences observed for the two deeper layer (Table S5).

For the HIX index (Table 1), values were lower in surface water (7.04 ± 2.79) than in soils, where HIX increased with depth from 14.7 ± 6.03 at 0-10 cm to 18.9 ± 5.32 at 10-20 cm (Kruskal-Wallis, $p < 0.05$). Between tidal periods, HIX was significantly higher during neap tides in surface waters (9.7 ± 1.3 vs. 5.7 ± 2.3 during spring tides) and in the 10-20 cm layer (19.7 ± 3.5 vs. 17.6 ± 7.1). In contrast, the deepest layer showed higher values during spring tides (21.2 ± 5.4 vs. 11.7 ± 7.3 during neap tides) (Table S6, Fig. S4).

Table 1: Average and standard deviation values for mangrove surface water and porewater properties: BIX, HIX, and S_R index across soil depths (0-10, 10-20, and 20-30 cm; $n = 81$) and in mangrove surface waters (S, $n = 9$).

Depth (cm)	BIX		HIX		S_R	
	Mean	SD	Mean	SD	Mean	SD
S	0.66	0.23	7.04	2.79	1.15	0.08
0-10	0.49	0.05	14.72	6.04	1.17	0.24
10-20	0.46	0.07	18.82	5.33	1.22	0.16
20-30	0.47	0.06	15.95	8.03	1.14	0.10

S_R ratios remained relatively stable across the soil profile, with values close to 1 at all depths and no significant trends or statistical differences observed between tidal periods (Tables 1, S5 and S6). A slight variation with depth was only detected during spring tide conditions, where the surface layer (0-10 cm) showed significantly higher S_R values compared to both the mangrove surface water and the deepest soil layer (20-30 cm).

3.4 Dissolved trace metals dynamics

The vertical distribution of selected dissolved trace metals is shown as averaged values across neap and spring tides, as no significant tidal differences were observed (Fig. 6). The vertical profiles reveal contrasting depth-related trends depending on the element. Nickel (Ni(d)), and molybdenum (Mo(d)), exhibit decreasing concentrations with depth. In surface waters, Ni(d) concentrations were $4.10 \pm 1.19 \mu\text{g}\cdot\text{L}^{-1}$. Within soil porewaters, Ni(d) decreased from $2.45 \pm 1.77 \mu\text{g}\cdot\text{L}^{-1}$ at 0-10 cm to $1.30 \pm 0.82 \mu\text{g}\cdot\text{L}^{-1}$ at 10-20 cm, and $1.14 \pm 0.60 \mu\text{g}\cdot\text{L}^{-1}$ at 20-30 cm. Mo followed similar decreasing profiles, with highest values in the 0-10 cm layer and lower concentrations in deeper layers. In contrast, chromium (Cr(d)) and manganese (Mn(d)) showed an opposite pattern. [Cr] increased with depth in both tidal conditions. Cr(d) increased from $1.23 \pm 0.35 \mu\text{g}\cdot\text{L}^{-1}$ at 0-10 cm to $2.00 \pm 0.25 \mu\text{g}\cdot\text{L}^{-1}$ at 20-30 cm. Surface water showed lower Cr(d) concentrations overall, with $0.46 \pm 0.06 \mu\text{g}\cdot\text{L}^{-1}$. Mn also exhibited general enrichment with depth (Fig. 6). These depth-related patterns were supported by significant correlations (Fig. S6): Ni(d) and Mo(d) were strongly positively correlated ($r = 0.83$), Cr(d) was negatively correlated with both Ni(d) ($r = -0.47$) and Mo(d) ($r = -0.66$), and positively correlated with Mn(d) ($r = 0.40$). Mn(d) did not show significant correlations with Ni(d) or Mo(d).

Some of the studied trace metals element (V(d), Zn(d), Pb(d), U(d), Co(d)) did not show any specific trends or correlations with the studied parameters/variables (Fig. S3). Cadmium (Cd(d)) and copper (Cu(d)) were not included in this analysis, as their concentrations were below the laboratory's recommended quantification limits and therefore considered unreliable (below $1 \text{ ng}\cdot\text{L}^{-1}$).

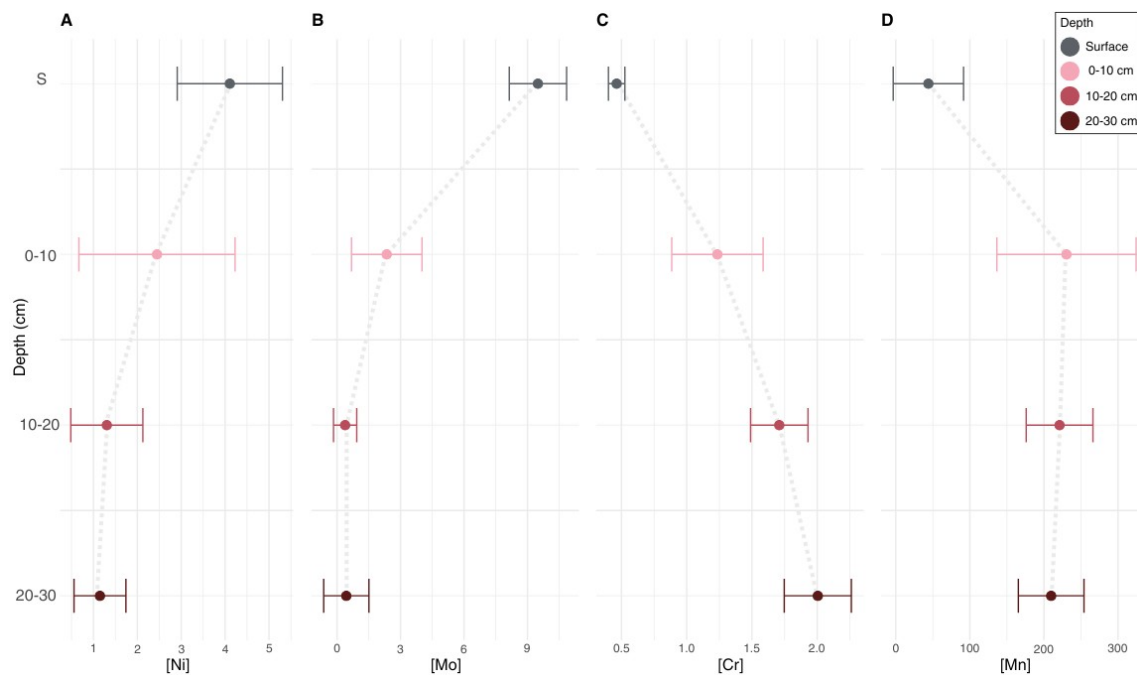


Figure 6: Mean concentrations ($\mu\text{g}\cdot\text{L}^{-1}$) of dissolved nickel (Ni): A, molybdenum (Mo): B, chromium (Cr): C, and manganese (Mn): D in mangrove porewaters at different soil depths (0-10, 10-20, and 20-30 cm) and in mangrove surface water (S). Points represent mean values, and horizontal error bars indicate standard deviations.

3.5 Relationships between DOM properties and dissolved trace metals

Relationships between DTM and DOM optical properties were studied using correlation analyses (Fig. 7). Dissolved Cr concentrations showed a significant positive correlation with the humic-like fluorescent component C1 ($R^2 = 0.65$, $p < 0.01$; Fig. 7A), with Cr(d) concentrations increasing with humic substances (C1 and C2 values). Weaker but significant positive correlations were also observed between Mn(d) and both C1 ($R^2 = 0.28$) and C2 ($R^2 = 0.33$; Fig. S6). In contrast to Cr(d) and Mn(d), dissolved Mo showed a strong and significant negative correlation with the humic-like fluorescent component C1 ($R^2 = 0.77$, $p < 0.01$; Fig. 7B), and its concentrations decreased with depth.

Mineralogical observations using SEM-EDX analyses (Fig. 8) revealed the presence of abundant framboidal pyrite in mangrove soil under *R. stylosa*. EDX spectra revealed detectable Ni and Cu incorporation in some pyrite grains from the upper soil layers (Fig. 8B).

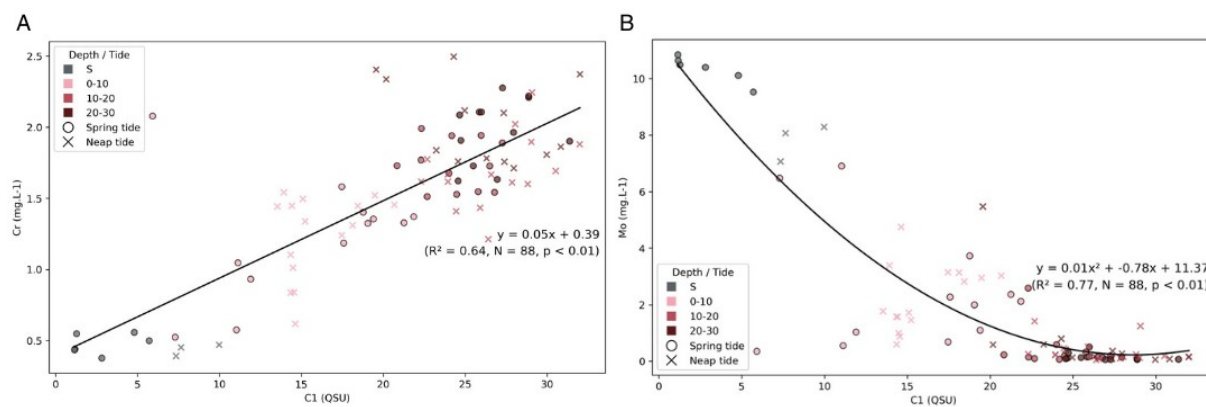


Figure 7: Vertical relationships between trace metals (Cr, Mo) and humic-like DOM (component C1) in mangrove porewaters. (A) Positive correlation between Cr and C1, both increasing with depth. (B) Negative correlation between Mo and C1.

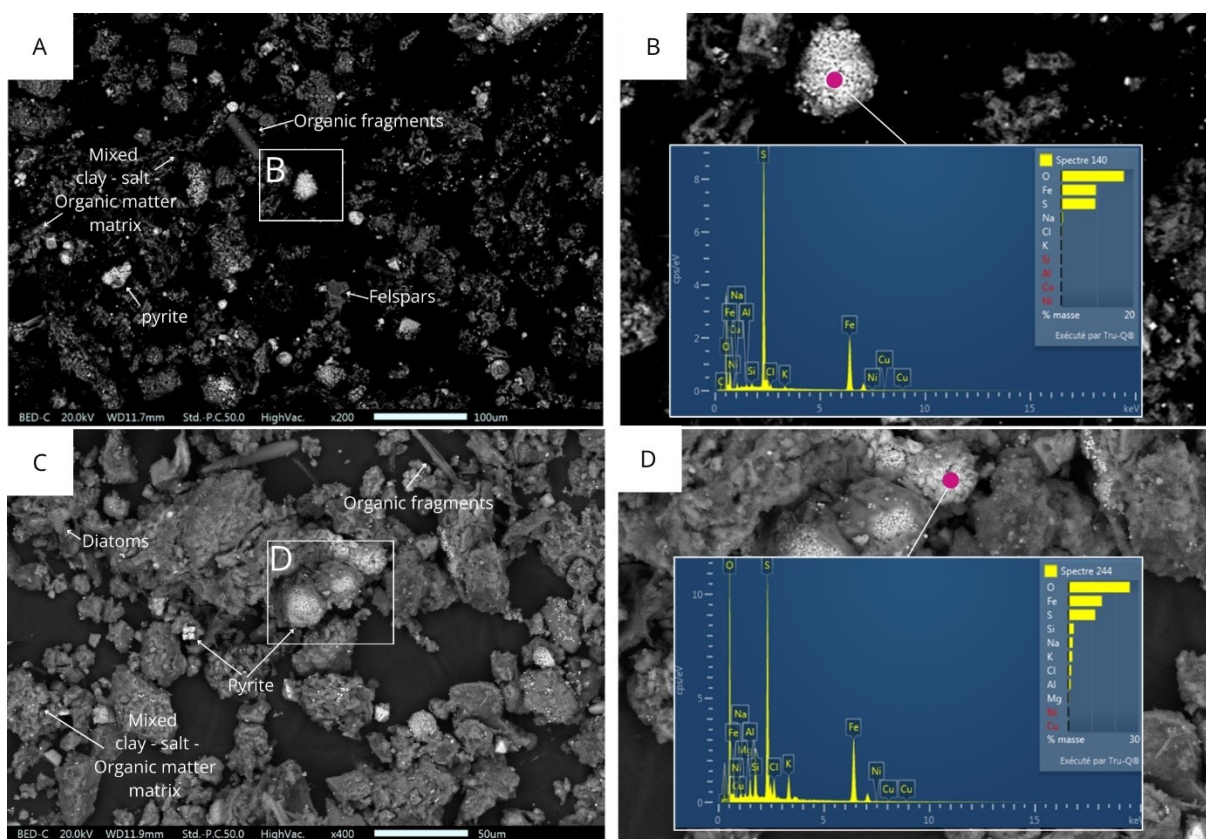


Figure 8: SEM-EDX analyses of soil samples (Rh-1) collected under *R. stylosa*. (A) General view of the 0-10 cm layer showing numerous framboidal pyrites (tens of μm). (B) Representative EDX spectrum of a pyrite grain from 0-10 cm, showing incorporation of Ni and Cu (as observed in several, though not all, pyrites from this depth). (C) General view of the 10-20 cm layer, also containing framboidal pyrites of similar morphology. (D) EDX spectrum of a pyrite grain from 10-20 cm, displaying detectable but low (<1%) Ni and Cu signals. At 20-30 cm, pyrite remains abundant but trace metal incorporation was not consistently visible in EDX spectra.

4 Discussion

4.1 Vertical distribution and dynamics of DOM in mangrove soils

4.1.1 Depth variability of DOM quality and hypothesis on its origin

Regarding the quality of the DOM, the semi-enclosed nature of the Bouraké mangrove system, with no significant external OM input from upstream catchments, suggests that the main source of DOM is autochthonous, likely originating from mangrove vegetation. This assumption is supported by absorbance indicators such as the S_R index, whose values close to 1 are indicative of DOM derived from higher terrestrial plants (Helms et al., 2008). Furthermore, fluorescence results reveal a clear accumulation of humic-like fluorophores (C1 and C2) with increasing soil depth (Figs. 4 and 5). The strong correlation between these two components ($r^2 = 0.91$) points to a common origin (Zhang et al., 2011; Zhao et al., 2017; Zhou et al., 2019), most likely the degradation of mangrove leaf litter. Interestingly, the relationship between C1 and C2 is not linear (Fig. 5), with C2 increasing relatively faster with depth. This suggests a shift in the relative contribution of these two humic-like pools along the soil profile, with a progressive enrichment in C2, which may represent a more refractory and humified DOM fraction. This correlation supports the hypothesis of a joint progressive decomposition and humification of mangrove-derived OM, leading to the accumulation of older, more refractory DOM in deeper soil layers. In addition, higher HIX values at depth corroborate the shift toward more aromatic and recalcitrant DOM. The spectral characteristics of C1 and C2 components reinforce this hypothesis. Both components exhibited a red shift in their fluorescence signatures, indicative of increased aromaticity or extended conjugated double bonds, which are typical features of aged and oxidized OM. Similar red shift phenomena have been reported by Burdige et al. (2004) and more recently in a mangrove study by (Knoke et al., 2024), where molecular-level characterization using FT-ICR-MS revealed the presence of highly unsaturated compounds with relatively high O/C ratios, consistent with a refractory, aged DOM pool. This interpretation is further supported by lower C/N ratios of the soil samples observed at 20-30 cm, which are commonly associated with highly humified OM (Fig. S5). In the Bouraké site, all C/N ratios were higher than 12, suggesting a vascular plant origin, rich in lignin, as previously demonstrated in Amazonian systems (Fig. S5; Hedges et al., 1986).

These patterns align with the physicochemical conditions observed in the soils under *R. stylosa* (Fig. 2), where pH and redox potential decreases with depth, creating less favourable conditions for aerobic microbial degradation (Wu et al., 2023). The more acidic environment may limit microbial processes, leading to a reduced rate of litter decomposition. In contrast, the surface layer (0-10 cm) is less acidic that can enhance microbial activity. *Rhizophora* soils are known to be mainly anoxic, with sulfate-reduction being the main decay process of

organic matter, except in the upper centimetres where suboxic processes were described (Kristensen et al., 2017). Conversely, surface waters were characterized by high BIX values, which are inversely related to HIX, suggesting fresher and more recently produced DOM (Table 1). Together, these findings suggest a vertical gradient in DOM composition, with fresher material near the surface and more degraded, older material accumulating at depth. Such patterns are consistent with previous findings in mangrove soils. In New Caledonia, Robin et al. (2024a) reported the presence of preserved, aged OM layers in deep *Rhizophora spp.* soils. Similarly in the dissolved phase, (Ray et al., 2023) showed that deeper DOC tends to be more humified and less mobile, highlighting the capacity of mangrove soils to retain and stabilize DOM over time.

Overall, the vertical distribution of DOM quality in the mangrove soils appears to be shaped by physicochemical conditions, with more oxidized and aromatic matter accumulating at depth due to limited oxygen availability and microbial degradation. In contrast, surface layers exhibit fresher DOM signatures, likely reflecting more recent production and faster turnover. In the following section, we explore the processes that may control the quantity of DOM in mangrove soils that vary with depth and tidal conditions.

4.1.2 Variability of DOM quantity with depth and hypothesis on its accumulation

Our findings highlight a clear vertical variation in porewater DOC concentrations. Several processes may be explained this pattern and will be discussed in the following section: (i) *in situ* production, and decomposition of OM, (ii) dilution and mobility of dissolved compound along soil profile, and (iii) the influence of tidal hydrodynamic with contrasted effect between neap and spring tides.

The vertical distribution of fluorophores points to differences in their production zones. Component C3, typically associated with photodegradation products, was most concentrated in the surface layer (0-10 cm), consistent with exposure to solar UV radiation. This pattern is in line with previous studies that identified this component as a product of photo-degradation (Amaral et al., 2020; Chen et al., 2017; Lambert et al., 2016) (Tab. S6). In contrast, humic-like components C1 and C2 were more abundant at depth (Fig. 5). In addition to their likely origin from the degradation of mangrove leaf litter (Hinsinger et al., 2003; Robin et al., 2024a, 2024b), these compounds may also be produced locally in deeper soil layers. In particular, root exudates from *Rhizophora* stand have been shown to result of the formation of humic acid (Arnaud et al., 2023). Moreover, soil organic matter in deeper layers may be less affected by tidal leaching compared to the upper soil, allowing for its accumulation and long-term preservation.

Lower CDOM concentrations expressed as a_{350} in the upper soil layers may also result from dilution by tidal inflows. During flood tides, incoming lagoon waters, are poor in DOM. Martias et al. (2018) reported a_{350} values (averaging $1.38 \pm 4.59 \text{ m}^{-1}$ in lagoon waters from the west coast of New Caledonia, where our study site is situated. The input of such DOM-poor water may dilute the porewater DOM in surface soil and mangrove surface waters. In contrast, our recent findings (Mouras et al., 2025b) showed that porewaters in mangrove soils, especially beneath *Rhizophora spp. stands*, are highly enriched in CDOM, with a_{350} values reaching $19.2 \pm 5.75 \text{ m}^{-1}$. In this present study this proxy confirmed a marked increase of CDOM with depth (Fig. 3) suggesting that dilution effects are likely most pronounced in the upper 10 cm of the soil profile, where tidal mixing is more intense. Such dilution processes could partly explain the lower DOC concentrations observed in surface layers compared to deeper horizons. In our study, deeper porewaters were markedly enriched in DOC compared to surface waters (Fig. 3). Similar patterns have been reported in other mangrove systems. In China, for example, DOC concentrations were found to be 1.6 to 2.1 times higher in porewater than in surface water, indicating vertical enrichment (Xu and Zhang, 2025).

This vertical accumulation of DOC may be partially explained by downward mobility processes driven by salinity-induced convection. In our study, salinity was consistently higher in deeper porewaters than in surface layers. This profile likely reflects the result of previous downward transport. Indeed, several studies have shown that salinity in mangrove soils is highly dynamic and can become elevated at the surface due to intense evaporation and evapotranspiration (Marchand et al., 2004). Such surface salinity enrichment may also be reinforced by biotic mechanisms, such as transpiration and ion exclusion by *Rhizophora stylosa* roots, which filter Na^+ via suberization and the Casparian strip (Kim et al., 2016; Reef and Lovelock, 2015). This root-mediated exclusion contributes to hypersaline conditions in surface porewaters (Ridd and Stieglitz, 2002), creating a density contrasts with deeper layers that can induce convective porewater exchanges (Santos et al., 2012). This convection facilitates the downward migration of salts and associated DOM. Similar mechanisms have been observed in other mangrove systems in Mexico (Chan-Keb et al., 2023). These processes could explain the DOC build-up in deeper layers under *R. stylosa* in this present study. In a similar context, Marchand et al. (2006a) reported increased DOC concentrations in the deeper mangrove soils of French Guiana, associated with more aged, recalcitrant, and hydrophobic DOM fractions. These findings support the idea that DOM is not only produced *in situ* but may also migrate vertically through convection-driven transport. In addition to vertical convection, horizontal exchanges of porewaters may also occur. These transfers could be driven by density contrasts associated with salinity gradients between adjacent mangrove stand, with more saline porewaters from

Avicennia marina zones or salt flats migrating laterally and accumulating at depth beneath *Rhizophora* stands (Mouras et al., 2025a, EGU sphere preprint).

Although the accumulation trend of DOM is observed under both tide conditions, it appears to be more pronounced during neap tides. DOC concentrations and a_{350} values were higher during neap tide conditions (Fig. 3). In deeper soil layer, this enrichment was greater than in surface waters, particularly during neap tide. A similar pattern was observed for CDOM, with stronger increases in a_{350} values during neap tide in the soil layer (Fig. 3). This enhanced build-up of DOM during neap tide conditions may result from reduced tidal flushing and pumping and slower porewater renewal, which increase residence times and limit DOM export. Such mechanism has been highlighted by Bouillon et al. (2008), who emphasized the role of tidal dynamics in regulation of DOM accumulation and export in mangrove soils. More recently, Xiao et al. (2023), linked reduced tidal energy to DOM build-up in mangrove soils, while Sippo et al. (2016) reported that longer porewater residence times during neap tides promoted higher DOC concentrations and enhanced autochthonous DOM production. In contrast, the higher a_{350} observed in mangrove surface waters during spring tide may suggest enhanced CDOM export from soils, driven by stronger hydrodynamic forcing under these tidal conditions.

Taken together, these findings highlight a complex interaction of production, dilution, and transport processes controlling DOM accumulation in mangrove soils. As DOM composition and concentration vary with depth and hydrological conditions, they are also likely to influence the geochemical behaviour of DTM. In the following section, we explore potential links between DOM and DTM dynamics in mangrove soils, highlighting two contrasting behaviours: some DTM appear to follow the same trend as DOM, while others show an inverse distribution, reflecting distinct mobility and complexation processes.

4.2 Dissolved trace metal dynamics and their relationship with DOM

Mangrove soils act as active biogeochemical reactors where hydrological dynamics, vegetation type, and redox processes shape the mobility and transformation of DOM, as well as the mobility and speciation of DTM. In our study, several DTM presented vertical trend along the soil profile, suggesting specific processes of mobilization or retention. Cr and Mn tended to increase with depth, following a similar trend to DOC and showing positive correlations with it (Fig. S6), whereas Ni, and Mo decreased with depth (Fig. 6), and were negatively correlated to DOC and humic-like component C1 and C2 (Fig. S6). While these trends highlight vertical dynamics, other metals did not show clear trends or significant correlations with the environmental variables studied (Figs. S3 and S6). These behaviours may also reflect the complex interplay of physical, chemical, and biological drivers in mangrove soils.

4.2.1 Potential complexation between DOM and some DTM

Our results suggest that the physicochemical conditions in mangrove soils may promote the accumulation of Cr(d) and Mn(d) at depth in porewaters, with low pH and negative Eh. The relationships observed between dissolved Cr and Mn and humic-like DOM components (Fig.7A) suggest an potential association between the distribution of these metals and the presence of humified OM in mangrove porewaters. This association is consistent with the increasing dominance of humic DOM in deeper soil layers. Humic substances are known to exhibit strong metal-binding capacities due to their high content of functional groups such as carboxyl, hydroxyl, and phenolic moieties (Yi et al., 2019).

As previously described, DOM at depth appears older and more humified, which may enhance its capacity to interact with dissolved metals. DOM enhances the solubility of DTM by forming stable complexes, which reduces their adsorption to soil particles (Kalbitz et al., 2003; Yu et al., 2023). These interactions are governed by various geochemical and environmental factors, including pH and redox conditions. In acidic environments, excess protons can compete with metals for binding sites, reducing their complexation and potentially enhancing metal mobility (Huang et al., 2014; Liu et al., 2019; Sauvé et al., 1998). Redox conditions also affect metal behaviour in mangrove soils. Under acidic and reducing environments, Cr(d) predominantly occurs as Cr(III), which is relatively soluble and can form stable complexes with DOM (Gorny et al., 2016; Gustafsson et al., 2014; Nakayama et al., 1981). Complexation of Cr(III) with DOM is kinetically slow and pH-dependent (Dai et al., 2009), but once formed, these complexes are generally more stable and resistant to oxidation (Gorny et al., 2016). As a result, Cr tends to remain trapped in its less toxic form in deeper soils. For Mn(d), the observed vertical distribution may also reflect early diagenetic processes. As redox potential decreases with depth, Mn(IV) oxides are reduced to soluble Mn^{2+} , leading to a peak of dissolved Mn just below the oxic layer (Vinh et al., 2019). Such behaviour is consistent with Mn cycling redox stratified sediments (Torres et al., 2014; Widerlund and Ingri, 1996).

Although the complexation with humified DOM appears to be the most plausible explanation for the behaviour of Cr(d) and Mn(d), an alternative hypothesis cannot be excluded. DTM may simply follow similar distribution patterns as DOM without direct complexation, potentially undergoing the same downward transport processes. For example, convective porewater circulation driven by salinity induced density gradients, as previously described for DOM, could also facilitate the downward transport of dissolved trace metals into deeper soil layers.

4.2.2 Vertical distribution and immobilization of dissolved trace metal elements

In contrast to Cr(d) and Mn(d), dissolved Mo exhibited an inverse relationship with humic-like DOM component, with lower concentration observed in deeper soil layers (Fig. 7B). Although some variability was observed between tidal periods at specific depths, the overall relationship with DOM was consistent across both neap and spring tides. As discussed in the previous section, this pattern is consistent with the more reducing and alkaline conditions in deeper soil layers (especially 20-30 cm), where pH increases and redox potential decreases (Fig. 2). These geochemical conditions are known to reduce the solubility of some trace metals, including Mo, by promoting their immobilization through various processes such as precipitation with sulfides, adsorption onto iron oxyhydroxides, and complexation with organic matter (Alongi, 2021; Pan et al., 2016; Wichard et al., 2009). Supporting this, XRD analysis (Mouras et al., 2025a, EGU sphere preprint; Fig.S5) and SEM analysis (Fig. 8) confirmed the presence of pyrite and secondary iron sulfate minerals such as jarosite under *R. stylosa*. These minerals are typical of sulfur cycling and oxidation processes occurring under suboxic to anoxic conditions in mangrove soils (Kristensen et al., 2017), and they may play a role in trapping Mo and other trace metals such as Ni. Moreover, the detection of iron oxyhydroxides further suggests a potential for metal retention through sorption mechanisms. Although we lacked quantitative mineralogical data, the presence of pyrite crystals with Ni and Cu incorporations (Fig. 8) suggests a potential role of sulphide minerals in the immobilization of Mo and Ni at depth in the solid phase, which is in line with previous findings (Noël et al., 2015). The ability of divalent cations to incorporate into pyrite has been well documented, following the general affinity order $\text{Co}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+} > \text{Ca}^{2+} > \text{Zn}^{2+}$ (Kornicker and Morse, 1991), which further support this hypothesis. In addition to mineral interactions, Mo can also be complexed by plant-derived organic compounds. Wichard et al. (2009) showed that Mo binds strongly to tannins and tannin-like compounds, which are abundant in mangrove systems due to leaf litter degradation. Therefore, both mineralogical and organic pathways may contribute to the reduced Mo(d) concentrations observed in deeper porewaters.

5 Conclusion

In mangrove soils, both the quantity and quality of DOM vary with depth and tidal period. Tides influence DOM dilution, export, and residence time within the soil profile. DOM is primarily produced in surface layers, where it originates mainly from the leaching of mangrove litter, as supported by our fluorescence indicators. The upper soil layers are characterized by suboxic conditions that promote the decomposition of the most labile DOM fractions. We suggest that more refractory, humified compounds migrate downward through tidal-driven water table fluctuations and convective porewater movements. In these deeper, more anoxic layers, the humified

DOM is preserved over longer timescales. This accumulated pool may then be remobilized and exported during spring tides, when tidal pumping is more intense.

The distribution of DTM further supports the influence of these vertical and tidal processes. While elements like Cr(d) and Mn(d) tend to increase with depth, possibly due to complexation with humic-like DOM or with convective processes, others such as Mo(d) and Ni(d) show a decreasing pattern, possibly link to geochemical processes of precipitation and sorption to mineral phases, as supported by SEM and XRD results. The potential for DOM-metal interactions, through both complexation and mineral association, points to a key role for DOM in modulating metal mobility and retention within mangrove soils. Although we did not directly quantify porewater or tidal fluxes, the vertical patterns and metal distributions suggest that some DTM, such as Ni(d) and Mo(d), may be laterally exported to surface waters via tidal mixing. However, geochemical conditions within the soil, such as the presence of iron oxyhydroxides and pyrite and the stability of humified DOM, may act as sink by promoting precipitation or retention of metals. Overall, our findings highlight mangrove soils are dynamic biogeochemical compartment where DOM not only reflects OM processing, but also influence trace metal cycling. These processes contribute to the role of mangroves as potential sinks for trace metals, with implications for coastal water quality and fluxes under changing environmental conditions.

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7 Authors contributions: CRediT

Naïna Mouras: Conceptualization, Methodology, Formal analysis, Investigation, Visualization, Writing- Original draft, Writing- Reviewing and Editing. **Cyril Marchand:** Conceptualization, Validation, Supervision, Writing- Reviewing and Editing, Funding acquisition. **Maximilien Mathian:** Formal analysis, Writing- Reviewing and Editing. **Chloé Factou:** Investigation, Writing- Reviewing and Editing. **Stéphane Mounier:**

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