

Article

Organic Matter Redox State Driven by Specific Sources in Mangrove Sediments: A Case Study from Peruvian Ecosystems

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Abstract: In order to determine the organic matter redox state in relation to specific sources in mangrove sediments, two 60 cm-long sediment cores were collected from mangrove-covered and mudflat zones within a mangrove forest in Peru. Sediment subsamples from these cores were analyzed to determine $\delta^{13}\text{C}$ values and C:N ratios, whereas two redox indices, namely, electrochemical (f_{EAOM}) and spectroscopical (A_{1650}/A_{3400}) indices, were taken from a previous study and correlated with the geochemical indices obtained from this work. These indices may provide accurate information on sedimentary organic matter diagenesis by oxidative processes through its redox state. The results show that the electrochemical index (f_{EAOM}) and the spectroscopical index (A_{1650}/A_{3400}) for mangrove-covered sediments exhibited a positive correlation with $\delta^{13}\text{C}$ values and a negative correlation with C:N molar ratios. These correlations suggest that the more labile sedimentary organic matter derived from non-terrestrial sources is in a more oxidized state than that derived from mangrove vegetation. However, this was not valid for mudflat zones, where non-significant correlations between geochemical indices were observed. Furthermore, the results suggest that the redox state of the organic matter deposited over time is dependent on source mixing influences, being better preserved in the presence of mangrove-derived organic matter.

Keywords: mangrove sediments; redox state; organic matter source; blue carbon

1. Introduction

The role of mangrove ecosystems in the coastal carbon cycle has been increasingly recognized, as these ecosystems sequester and accumulate large quantities of organic carbon [1,2]. The organic carbon accumulated in these systems is largely influenced by accretion rates [3,4] and geochemical conditions within the sediments [5,6], as well as by the geomorphological and hydrological characteristics [7,8]. As a result, mangrove sediments are estimated to contribute between 15 and 25% of the coastal blue carbon burial [1,9], derived from autochthonous and allochthonous organic matter production [7,10]. These autochthonous and allochthonous organic matter sources are frequently assessed through well-established techniques, including elemental and stable isotope measurements in coastal sediments [3,10].

Alternatively, electrochemical techniques are often used to determine the oxidized and non-oxidized fractions or the redox state of organic matter compounds [11,12]. In addition, spectroscopical techniques allow the determination of the organic matter composition in terms of aliphatic groups and carboxylic acids, providing information on the oxidized state of organic matter [13,14]. The redox state of sedimentary organic matter plays an essential role in geochemical processes, where compounds containing quinones, hydroquinones, aromatic groups and others functional groups are involved in the preservation of organic carbon [15–17]. The proposed methodology is based on the capability of electrochemistry to detect oxidizable organic matter compounds and estimate the antioxidant capability of sediments based on monitoring the reaction of antioxidant compounds with reactive oxygen species, which has only previously been applied to vegetal-derived organic matter [18,19]. However, there have been no previous initiatives to determine the influence of sedimentary organic matter sources on the redox state of organic matter using electrochemical and spectroscopic techniques on mangrove-covered and mudflat sediments. An initial attempt using these techniques was based on the relationship between electrochemical and spectroscopical proxies of the redox state and total organic matter content in mangrove sediments [12].

The Peruvian mangrove ecosystems are located in the mangrove distribution boundary of the eastern South Pacific. This geographical position makes this ecosystem very important and sensitive to climate change and environmental impacts [8,20]. The high accumulation of organic matter in this area is controlled by daily and seasonal hydrological regimes (e.g., tidal forces, seasonal rainfall and freshwater intrusion), as well as by the enclosed geomorphology [8,21]. It is worth noting that during extreme hydrological periods (e.g., ENSO events), this ecosystem may be impacted due to the significant increase in flow of the Zarumilla River [22,23]. These factors may influence the sediment distribution as well as the organic matter accumulation and degradation in the sedimentary environments [4,8,21].

This study aimed to determine the influence of specific organic matter sources on the redox state in mangrove sediments. To accomplish this aim, electrochemical and spectroscopical properties [12], and data on the sources of the sedimentary organic matter [4], were taken from a tropical Peruvian mangrove ecosystem. These analyses were used to test the hypothesis that the redox state of the sedimentary organic matter within mangrove ecosystems may be influenced by the organic matter sources and mixing effects during its deposition in sediments, which may directly impact the blue carbon accumulation capacity of these sedimentary environments.

2. Materials and Methods

The mangrove ecosystem studied in this research is located in Tumbes, which is situated on the northern coast of Peru and is associated with the National Sanctuary “Manglares de Tumbes” (Figure 1a). This estuarine system is influenced by the Zarumilla River and its secondary creeks, which provide fresh water to it and facilitate the continuous transport and deposition of high quantities of particulate organic matter [8,21]. The dominant mangrove species near the creeks are *Rhizophora mangle*, *Rhizophora harrisonii* and *Avicennia germinans*, which are together considered one of the main components of the sedimentary organic matter in this estuarine ecosystem [8].

The fieldwork for this study was carried out in 2014, when two 60 cm-long sediment cores were sampled from a representative area dominated by *Rhizophora mangle*. The first core (Core “ZMu”) was collected in a mudflat zone, whereas the second core (Core “ZMa”) was collected in a mangrove-covered zone (Figure 1b). The sediment cores were obtained using PVC tubes by means of percussion and rotation to minimize compression [4]. While collecting the sediment columns, the presence of mangrove roots was avoided in order to obtain intact sediments that lacked mixing [3,4]. Each sediment column was sectioned on site in 1 cm intervals from the top of the core to 10 cm depth, and then at 2 cm intervals to the base of the core. Subsamples were bagged, placed on ice, returned to the laboratory and

kept frozen at $-20\text{ }^{\circ}\text{C}$, then subsequently lyophilized before analysis. Further subsamples of each core were acidified with HCl 1M to remove carbonate material [3,4]. Subsamples were analyzed for carbon (C), nitrogen (N) and $\delta^{13}\text{C}$ using an isotope ratio mass spectrometer, Thermo Finnigan Model Delta Plus XP, with an analytical precision of C = 0.1%, N = 0.1% and $\delta^{13}\text{C}$ = 0.1‰ [3,4]. It is important to mention that non-decarbonated sediment was used to measure nitrogen content [24]. Data for the redox state indices in sedimentary organic matter (f_{EAOM} and A_{1650}/A_{3400}) were taken from Cebrian-Torrejón et al. (2019) [12]. Higher values of the electrochemically active organic matter index (f_{EAOM}) in the sediment core indicate the occurrence of electrochemically active organic matter resulting from the degradation of vegetal components in a more reducing environment [12,14]. Higher values of the spectroscopical index (A_{1650}/A_{3400}) in the sediment core indicate the presence of more oxidized organic matter [12,14]. The data were first normalized and tested by the Shapiro–Wilk test ($\alpha = 0.05$) [4,8]. After that, analysis of variance (ANOVA) ($\alpha = 0.05$) was used to determine differences between sedimentary environments (mangrove-covered and mudflat zones).

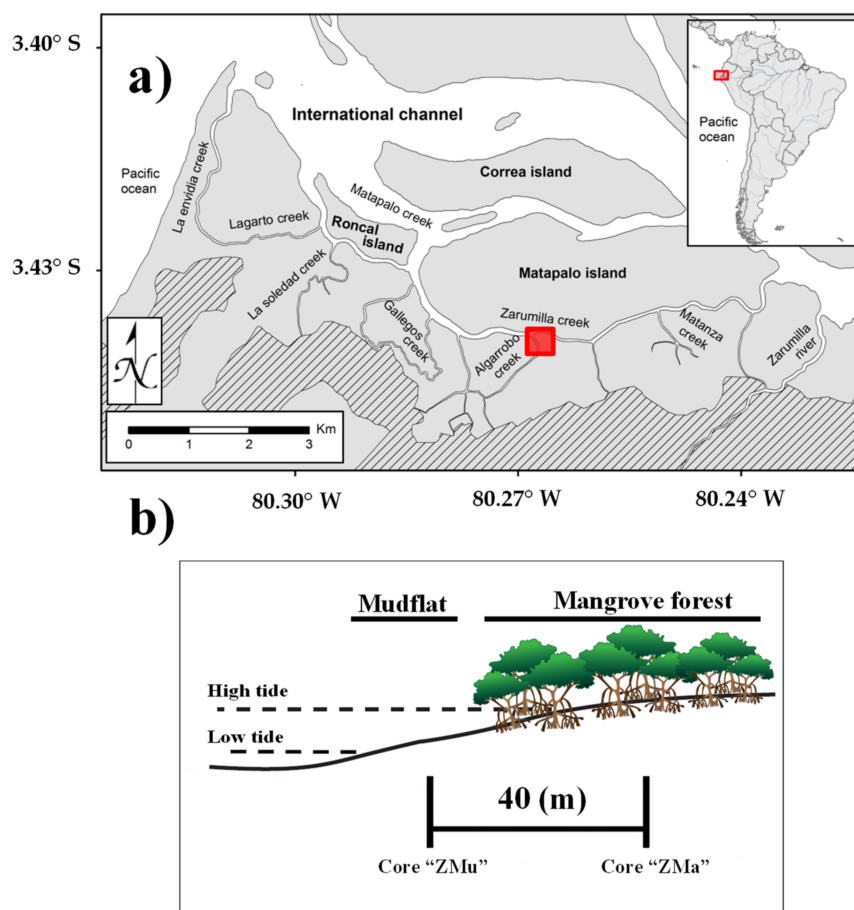


Figure 1. (a) Map of the study area within the mangrove sanctuary. The red square indicates the sampling site. (b) The spatial location of the sampling sites within the two sedimentary environments. Sediment cores were sampled within the mangrove-covered (ZMa) and mudflat (ZMu) zones.

3. Results and Discussion

3.1. Sedimentary Organic Matter Source

Several studies on wetland ecosystems have reported that sedimentary organic matter containing a high proportion of mangrove litterfall may present $\delta^{13}\text{C}$ values between -26 and -30‰ , whereas values between -17 and -24‰ may reflect a high proportion of non-mangrove-derived organic matter in sediments (e.g., phytoplankton, microphytobenthos, saltmarshes and seagrasses) [3,4,6,25]. In this study, the mudflat zone exhibited a higher

proportion of organic matter derived from non-terrestrial vegetation than the mangrove-covered zone (Figure 2), which was likely derived from planktonic and benthic microalgae deposition [3,4]. As expected, the lighter $\delta^{13}\text{C}$ values were found within the mangrove forest (Table 1), with lighter $\delta^{13}\text{C}$ values towards the top of the sediment column (Figure 2), suggesting the dominance of terrestrial or mangrove-derived organic matter in the younger sediments [3,4,6]. These differences were observed within the first 15 cm depth of the sediment profile in the mangrove-covered zone (Figure 2). The results agree with the isotopic $\delta^{13}\text{C}$ values observed in fresh mangrove leaves from the sampling site (Table S1), suggesting that the main proportion of organic matter is derived from mangrove plants.

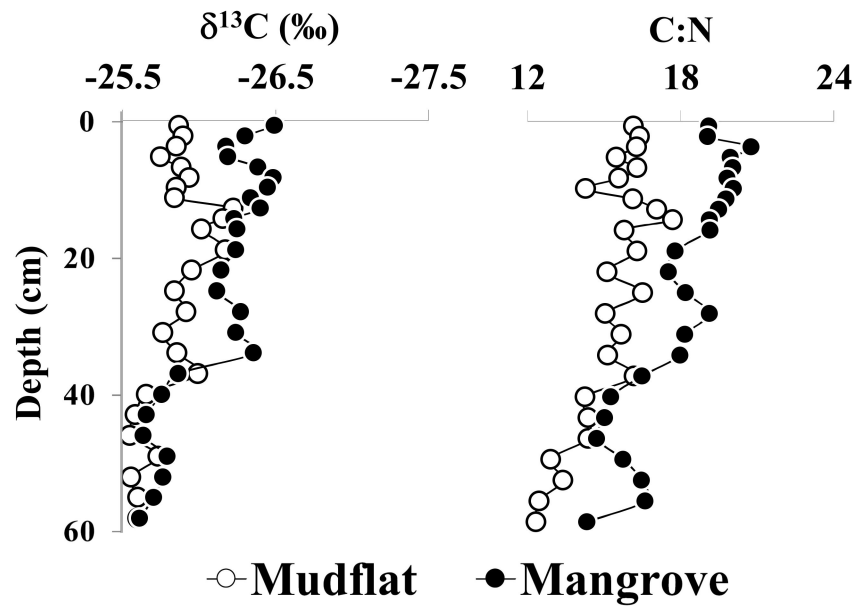


Figure 2. Vertical distribution of isotopic values of carbon ($\delta^{13}\text{C}$) and molar ratios of carbon and nitrogen (C:N) obtained from cores from the mudflat (ZMu) and mangrove-covered (ZMa) sediment zones.

Table 1. Analysis of variance (ANOVA) results for the geochemical proxies in each sediment core. ZMa: mangrove-covered zone. ZMu: mudflat zone. $p < 0.05$; Significant correlation (*); N.S.: non-significant. n : number of subsamples of each sediment core.

Variables	n	Average Values	Statistical Significance
f_{EAOM}	30	ZMa: 0.47 ± 0.24 ZMu: 0.63 ± 0.26	N.S.
A_{1650}/A_{3400}	30	ZMa: 1.02 ± 0.25 ZMu: 0.74 ± 0.08	ZMu < ZMa (*)
C:N	30	ZMa: 15.48 ± 4.96 ZMu: 14.76 ± 2.03	N.S.
$\delta^{13}\text{C}$ (‰)	30	ZMa: -26.15 ± 0.45 ZMu: -25.67 ± 0.46	N.S.

In addition, the C:N molar ratios observed during this research exhibited non-significant differences between sedimentary environments (Table 1). However, lower than average C:N ratios were noted from the mudflat zone in comparison with the mangrove-covered zone (Table 1), whereas the sediment profiles that showed lower C:N molar ratios were observed towards the top of the sediment core (Figure 2). These results suggest there was a higher proportion of non-terrestrial organic matter (e.g., phytoplankton- and microphytobenthos-derived organic matter) in the mudflat zone throughout the sediment column [3,4]. It is worth noting that these C:N molar ratios were negatively correlated with the obtained $\delta^{13}\text{C}$ values

during this study (Figure 3), suggesting that in both sedimentary zones, lighter isotopic values are associated with more refractory organic matter (e.g., terrestrial- or mangrove-derived), which may present less nitrogen content [3,6,25]. It is also important to mention that several reports have found an inverse relationship between the C:N molar ratios and the $\delta^{13}\text{C}$ values derived from mangrove litterfall, indicating that the more refractory mangrove litter degradation is strongly dependent on the availability of nitrogen [6,25]. Our results are consistent with other studies that showed the sedimentary organic matter in mangrove systems is mainly composed of mangrove litterfall and roots (~70%), which is efficiently accumulated within mangrove-covered zones due to their highly productive root systems [6,26]. Finally, it is important to consider that the occurrence of organic matter mixing in surficial sediments is also likely in these dynamic mangrove ecosystems, exhibiting values between the intervals described above [27,28].

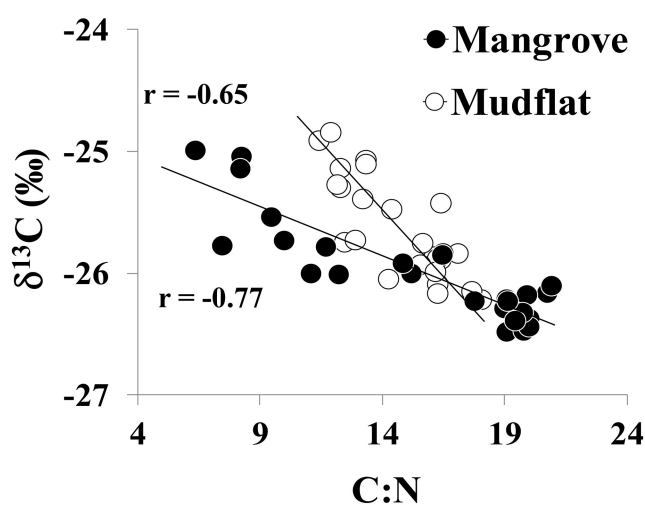


Figure 3. Isotopic values of carbon ($\delta^{13}\text{C}$) plotted against C:N molar ratios for sediment cores within the mangrove-covered (ZMa) and mudflat (ZMu) zones.

3.2. Redox State of Sedimentary Organic Matter

The f_{EAOM} index in mangrove ecosystems exhibited higher values below 20 cm depth in the mangrove-covered and mudflat zones (Figure S1). This reflects that the sedimentary organic matter in the deeper layers is electrochemically active due to oxidative degradation and natural bioturbation [12]. In the mangrove-covered zone, this degradation may occur through hydrolysis or bacterial respiration, which may be enhanced by oxygenation produced by the mangrove rhizosphere [29–31]. In the mudflat zone, the organic matter degradation may be facilitated by oxygenation driven by tidal and hydrological regime energies in this study area [8,21]. It should be noted that within the mangrove-covered zone, the f_{EAOM} values exhibited a negative correlation with the C:N molar ratios, and a positive correlation with the $\delta^{13}\text{C}$ values (Figure 4a). This indicates less oxidative degradation of mangrove- or terrestrial-derived organic matter than non-terrestrial organic matter, which is explained by the more refractory composition of the mangrove vegetation in comparison with the non-terrestrial material [6]. In addition, higher f_{EAOM} values were associated with heavier $\delta^{13}\text{C}$ values mainly within the mangrove-covered zone (Figure 4a), suggesting that the presence of terrestrial organic matter may trigger lower oxidative degradation rates [12,29]. In addition, f_{EAOM} values and C:N molar ratios were not correlated in the mudflat zone (Figure 4a) because this environment is more exposed to creek water flow and tidal forces and, therefore, more prone to organic matter suspension, mixing and subsequent transport [8,21]. Under this context, a higher proportion of organic matter remains efficiently sequestered within the mangrove-covered zone, facilitating the accumulation of more refractory organic matter as compared to that within the more dynamic mudflat zone.

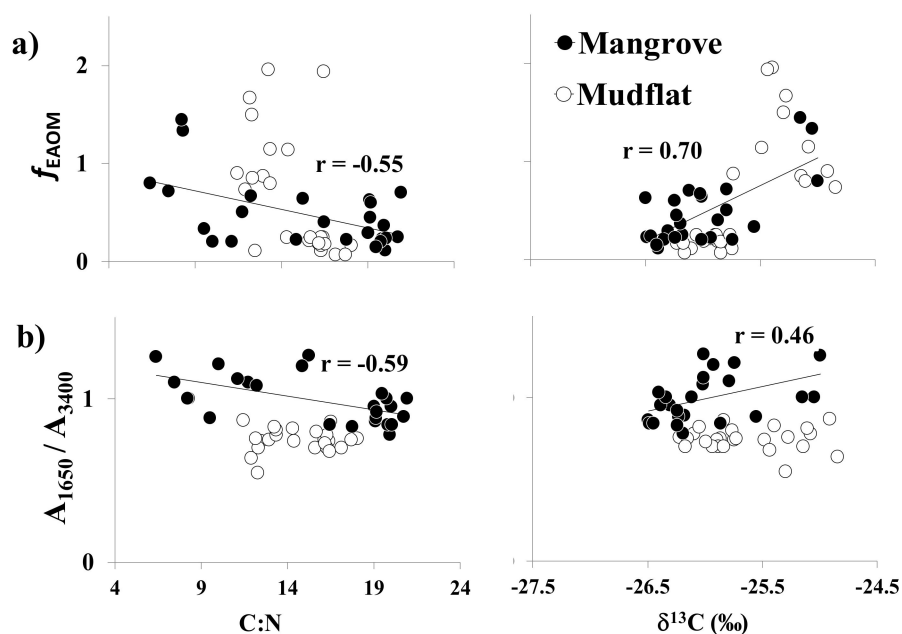


Figure 4. (a) f_{EAOM} vs. C:N molar ratios and $\delta^{13}C$ values. (b) A_{1650}/A_{3400} vs. C:N molar ratios and $\delta^{13}C$ values. The trend lines and correlation coefficients refer to the cores from the mangrove-covered (ZMa) and mudflat (ZMu) zones.

The A_{1650}/A_{3400} index exhibited significantly higher values in the mangrove-covered zone than those in the mudflat zone (Table 1). These results indicate that the organic matter in the mangrove-covered zone may contain higher carbonyl/hydroxyl ratios, as expected in the presence of more degraded organic matter [12,14]. It should be mentioned that the vertical distribution of the A_{1650}/A_{3400} index presented higher values towards the bottom of the sediment column for both sedimentary zones (Figure S1). This agrees with the vertical distribution of f_{EAOM} values (Figure S1), indicating that the sedimentary organic matter in deeper intervals suffered more oxidative degradation [6,29]. Finally, the A_{1650}/A_{3400} index within mangrove-covered sediments was negatively correlated with C:N molar ratios and positively correlated with $\delta^{13}C$ values (Figure 4b). These correlations indicate lower organic matter degradation in the intervals with higher proportions of terrestrial-derived organic matter [4,12]. These correlations were not validated in the mudflat zone, indicating that, in spite of the hydrological and textural differences between the zones [4], the organic matter transported and deposited within the mudflat zone has a lower residence time than the organic matter deposited within the mangrove-vegetated zone, being partially transported by the tidal forces and creek water outflow [8,21].

4. Conclusions

The assessment of the influence of organic matter sources on the redox state in mangrove sediment ecosystems was made possible through the coupled applications of electrochemical and spectroscopical indices, along with C:N molar ratios and isotopic $\delta^{13}C$ analyses. The results show that the sedimentary organic matter derived from mangrove and terrestrial sources was associated with a less oxidized state than the non-terrestrial organic matter. However, this association was not valid for mudflat sediments, where the non-significant correlations indicate the more dynamic conditions in these sedimentary zones. Stable carbon isotope ratios combined with C:N molar ratios identified the susceptibility of sedimentary organic matter to oxidation, wherein both mangrove and algal organic matter deposition may occur. Further research is recommended for other coastal vegetated systems (such as mangrove, salt marsh and seagrass habitats) to better understand the carbon accumulation capacity of blue carbon systems.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/jmse9121438/s1>: Figure S1: Vertical distribution of the electrochemical and the spectroscopical indices obtained from cores in the mudflat and man-grove-covered sediment zones. Table S1: The isotopic values \pm SD for carbon ($\delta^{13}\text{C}$) from fresh *Rhizophora* mangle leaves. The samples were collected in duplicate from trees in the interior and at the border of the mangrove-covered zone (30 m distance) in the sampling site.

Author Contributions: A.P.: conceptualization, writing—original draft preparation. G.C.-T.: conceptualization, review and editing. N.M. and J.P.-C.: methodology and validation. C.J.S.: conceptualization, methodology, review and editing. A.D.-C.: methodology, review and editing. W.M.: conceptualization, review and editing. All authors have read and agreed to the published version of the manuscript.

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