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Tannin as a New Indicator of Paleomangrove Occurrence within an Amazonian Coastal Region

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ABSTRACT


Three sediment cores, sampled from a (1) mangrove zone, (2) mangrove–várzea zone, and (3) várzea zone at the Marajó Island–Amazonian coastal region were studied to compare the pollen and the sedimentological signals with tannin concentrations in sediments accumulated during the last millennium. The integration of these data allowed the interpretation of mangrove paleoecology based on pollen content along stratigraphic sequences. Most stratigraphy of the cores indicated a direct relationship between Rhizophora mangle (red mangrove) pollen content and tannin content. Some stratigraphic intervals showed a high percentage of R. mangle pollen, which may be interpreted as the mangrove forest mainly being occupied by R. mangle. A decrease of tannin content suggests a decrease of R. mangle density or a late mangrove colonization. The spectrophotometric method using tannin concentrations, proposed in this paper and supported by pollen data, may be considered an additional tool for the paleoenvironmental reconstruction of mangrove areas and an innovative tool that will allow reduction of costs in the studies of paleomangrove environment identification.

ADDITIONAL INDEX WORDS: Mangrove, paleoenvironmental reconstruction, palynology, polyphenol, Rhizophora mangle.

INTRODUCTION

Tannins are polyphenolic secondary metabolites of higher plants (Krauss, Allen, and Cahoon, 2003), which comprise as much as 20% of leaves (Benner, Hatcher, and Hedges, 1990), roots, and bark tissue (Kelsey and Harmon, 1989), all major contributors to terrigenous organic matter cycling (Hernes et al., 2001). Tannins are estimated to be the fourth-most abundant compound produced by vascular plant tissue after cellulose, hemicellulose, and lignin (Maie, Pisani, and Jaffé, 2008). Mangrove species, such as Rhizophora mangle, that have presented high tannin concentration (Benner, Hatcher, and Hedges, 1990; Godoy et al., 1997; Maie, Pisani, and Jaffé, 2008), which prevents damage from herbivory (Hernes et al., 2001), are known to suppress microbial activity (Hättenschwiler and Vitousek, 2000; Krauss, Allen, and Cahoon, 2003; Kuiters, 1990) and thus can affect biogeochemical cycling in these ecosystems.

Mangroves are coastal ecosystems colonized by trees and shrubs that form dominant plant communities in tidal and other saline wetlands along sheltered tropical and subtropical shores (Blasco, Saenger, and Janodet, 1996). These ecosystems are highly susceptible to climatic changes and sea-level oscillations (Alongi, 2015; Cohen et al., 2012; Fromard, Vega, and Proisy, 2004), and they have undergone almost continual disturbance as a result of fluctuations in sea level over the last 11,000 years (Behling, Cohen, and Lara, 2001; Cohen et al., 2005, 2015; França et al., 2013; Lamb, Wilson, and Leng, 2006; Rossetti et al., 2015). Therefore, these are relevant ecosystems to paleoenvironmental studies attempting to understand the coastal dynamics that may be associated with sea-level fluctuations and climate change. Thus, new tools, as proposed in this work, will be important to integrating with more data and strengthening the study of coastal environments.

Palyngnology and isotope and geochemical analyses have been the main tools supporting regional paleoenvironmental reconstructions (Cohen et al., 2012; França et al., 2013, 2015; Guimarães et al., 2012, 2013; Pessenda et al., 2012; Smith et al., 2011, 2012). However, other techniques have been developed, such as application of triterpenols as biomarkers for mangrove deposits in northern Brazil (Koch et al., 2011) and spectral analysis of sediment in the central portion of the Pacific Ocean to study variation of planktonic foraminifera and the benthic community in sediment cores (Ujiié, 2003).

Considering palynological studies, the composition of fossil pollen in sediments depends on several factors, such as sedimentary environment, composition of the vegetation from which the pollen originates, pollen production of the individual plant species, pollen dispersion, and preservation (Phuphumirat et al., 2015). Paleoecological studies developed along the
Brazilian coastal zone have indicated that lakes, tidal flats, and fluvial floodplains are sedimentary environments suitable for accumulation of muddy sediment and preservation of pollen sourced from vegetation present when the sediment was deposited (Alizadeh, Cohen, and Behling, 2015; Cohen, Behling, and Lara, 2005; Cohen et al., 2008, 2009a, 2014; Vedel et al., 2006).

The low pollen preservation in sediments may be caused by various external factors (sediment grain size, microbial attack, oxidation, and mechanical forces), as well as factors inherent to the pollen grains (sporopollenin content and chemical and physical composition of the pollen wall; Havinga, 1967). However, anaerobic conditions (low Eh value) in the fine-grained sediment of mangroves provide a suitable environment for pollen to be preserved (Bryant et al., 1994; Ellison, 2008; Grindrod, 1988; Tschudy, 1969). Sediment with high salinity and low Eh and pH values seems to be ideal for pollen preservation (Bryant et al., 1994; Campbell and Campbell, 1994; Dimbleby, 1957; Phuphumirat, Mildenhall, and Purin-tavara, 2009). However, other substrates, including unweathered rock platforms, coral rubble, and sandy sediments, also occupied by mangroves are not suitable for pollen preservation (Grindrod, 1988). For instance, pollen tends to rapidly decay in sandy sediment because of better drainage caused by large interstitial pores, which allows pollen grains to be abraded during soil hydration–dehydration cycles (Faegri, 1971; Grindrod, 1988).

Therefore, in some cases, the pollen content within a stratigraphic sequence may not reflect the dynamics of a coastal wetland or this analysis alone may not be appropriate for paleoenvironmental reconstructions. However, studies of the chemical composition of R. mangle leaves during decomposition in tropical estuarine waters indicated that tannin, a phenolic compound, had intermediate resistance to decomposition and maintained a constant concentration during leaf decomposition (Benner, Hatcher, and Hedges, 1990). Thus, tannin concentrations within stratigraphic sequences could be used as indicators of old R. mangle–dominated mangrove areas (Cohen et al., 2009b).

To assess the viability of implementing tannin analysis as a new indicator of R. mangle trees during tidal flat development, this paper presents pollen and sediment results previously published by França et al. (2012), as well as tannin analyses as a potential tool for paleoenvironmental studies. The study uses three sediment cores sampled from eastern Marajó Island, located at the mouth of the Amazon River.

### METHODS

**Study Site**

The study sites are located on Marajó Island, northern Brazil, covering about 39,000 km² (Cohen et al., 2008). This island is situated at the mouth of the Amazon River. The sediment cores were sampled on the coastal plain of Soure (Figure 1; Table 1). The study area occupies the central-eastern part of the coastal plain and covers approximately 380 km². The eastern portion of the island is characterized by lowlands with altitudes averaging only 4 to 6 m above modern sea level (Rossetti et al., 2008; Rossetti, Valeriano, and Thales, 2007) and is dominated by Holocene sedimentation (Behling, Cohen, and Lara, 2004).

The region is characterized by a tropical warm and humid climate with annual precipitation of around 2300 mm (Lima et al., 2005). The rainy season occurs between December and May, and a drier period occurs between June and November. Annual mean temperatures range from 25 to 29°C. The region is dominated by meso- and macrotides, with a range during spring tide between 3.6 and 4.7 m (Beardsley et al., 1995).

The modern coastal vegetation of eastern Marajó Island is represented by the following units: Amazon coastal forest (ACF), herbaceous flats, mangroves (tree heights reaching ~20 m), restinga (shrubs and herbaceous vegetation that occur on sand plains close to the shoreline), and várzea (swamp seasonally and permanently inundated by freshwater; Cohen et al., 2008). These units are distributed within specific inundation regimes, sediment types, and porewater salinities (Cohen and Lara, 2003).

**Spectrophotometric Measurement by Uvikon 941**

The method to determine tannin in sediment is adapted from Price and Butler (1977) and based on the reduction by tannin of ferric ion to ferrous ion, followed by the formation of a ferricyanide–ferrous ion complex (reactions 1 and 2). The colored product, commonly known as Prussian blue, absorbs maximally at 720 nm. The same reagents in a more concentrated form are often used to visualize phenolic compounds on
paper chromatograms. For the preparation of the calibration standards, stock tannin solutions were prepared at concentrations of 0.005, 0.01, 0.015, and 0.02 mg g\(^{-1}\) tannin solutions. After preparing the calibration standard solutions, the absorbances of each solution were read. The wavelength used was 720 nm. The absorbances were taken in triplicate for each solution. These absorbances were then averaged and plotted to form a calibration curve (Figure 2). The standard deviation for the mean of the absorbances was about 0.01:

\[
\text{tannin} + n\text{FeCl}_3 \rightarrow \text{Fe}_n\text{[Fe(CN)]}_6 + n\text{H}_2 + \text{Fe}
\]  

(1)

\[
4\text{Fe} + 3\text{K}_2\text{Fe(CN)}_6 \rightarrow \text{Fe}_4\text{[Fe(CN)]}_3 + 12\text{K}
\]  

(2)

Sediment samples (60 mg) were shaken constantly for 60 seconds with 3 ml of methanol in a test tube and then filtered using a Buchner funnel. The tube was quickly rinsed with an additional 3 ml of methanol, and the contents were immediately poured into the funnel. The filtrate was mixed with 50 ml of water and analyzed after 1 hour. Next, 3 ml of 0.1 M FeCl\(_3\) in 0.1 N HCl were added to the extract, followed immediately by the addition of 3 ml of 0.008 M K\(_2\)Fe(CN)\(_6\). The optical density was read after 10 minutes in 1-cm glass cells at 720 nm on the Uvikon 941 Plus spectrophotometer. Ten minutes was allowed for color development, because the rate of reaction was considerably slower after that time and because a precipitate often formed after 15 to 20 minutes. A blank of identical composition, omitting the sediment, was analyzed and subtracted from all other readings. The tannin concentrations of the samples were obtained by comparison of its spectrum with the sample spectrum of known tannin concentrations (Price and Butler, 1977). To check the reproducibility of this method, five determinations were made for each 5-cm depth; the means of these replicates had standard deviations between 0 and 0.007.

RESULTS

The pollen and the sedimentological signals with tannin concentrations (Figure 3) in sediments accumulated during the last millennium in the Marajó Island–Amazon coastal region.
The results consist of three subsections: mangrove and várzea transition (R-1 core), mangrove (R-2 core), and várzea (R-3 core). The cores present dark gray and light brown muddy and sandy silt with an upward increase in grain size. These deposits are massive, parallel laminated, or heterolithic bedded (Table 2).

**Mangrove (R-2 Core)**

The R-2 deposits consist typically of massive mud (facies Mm), bioturbated mud (facies Mb), and coarse to fine sand (facies Sb), with an increase in sandy sediments at the surface layers (França et al., 2012). The core also presents many roots and root marks with dwelling structures. The core typically shows five ecological groups, according to the pollen and spore analyses (Figure 4). The sedimentation rate for this deposit was 1.2 mm/y.

The tannin values oscillate between 0.05 and 5.6 mg g\(^{-1}\). According to those results, the sediment core registered three zones. The first zone (T2#1) shows increases of the tannin values and *R. mangle* pollen percentages from 0.2 to 5.6 mg g\(^{-1}\) and from 10 to 75%, respectively. The second zone (T2#2) registers an oscillation of tannin content (from 7.6 to 14.8 mg g\(^{-1}\)) and *R. mangle* pollen percentages (from 25 to 100%) occur. The subsequent zone (T1#3) was characterized by high *R. mangle* pollen percentages. However, it presents a decrease of tannin concentration (from 14.8 to 0.01 mg g\(^{-1}\)) and tannin was not detected close to the top, between the 35-cm depth and the surface (T1#4). The pollen diagram from the 150-cm R-1 core also shows the concentration and accumulation rates were from 5000 to 100,000 grains/cm\(^3\) and 100 to 2500 grains/cm\(^2\)/y, respectively (Figure 5).

**Várzea (R-3 Core)**

The R-3 core consists of bioturbated mud (facies Mb), which are interbedded with lenticular muddy sediments (facies Hl) and sand cross-lamination (facies Sc). Near the top, it is possible to record fine to medium-grained sand (facies Sb), with an upward increase in grain size (Figure 6). The interval between 150 and 15 cm is marked by a dominance of mangrove pollen, while the top is marked by an increase in herbaceous pollen, trees, and shrubs from ACF (França et al., 2012). The sedimentation rates for this core were 0.8 and 11 mm/y.

Based on tannin concentration (Figure 6), this core shows two zones (T3#1 and T3#2). The first zone, between a 150-cm and a 40-cm depth, presents a decrease of tannin concentrations from 23 to 1 mg g\(^{-1}\), while the *R. mangle* pollen percentages present stable values of about 90%. In the second zone (T3#2), tannin concentration was not detected upward and was followed by a decrease of *R. mangle* pollen percentages.
The concentration and accumulation rates were from 3000 to 80,000 grains/cm³ and 6000 to 10,000 grains/cm²/y, respectively (Figure 6).

**DISCUSSION**

Based on the main results, the relationship between tannin and paleomangrove deposits is discussed in Marajó Island as an innovative additional tool to the paleoenvironmental reconstruction of mangrove areas.

**Relationship between Tannin and Rhizophora Trees**

The vegetation changes proposed by the pollen records from the lakes probably represent regional vegetation dynamics, while the pollen profiles from tidal flats present a smaller spatial representativeness of the vegetation (Cohen et al., 2008). Modern pollen accumulation rates in tidal flats adjacent to mangrove stands indicate that *R. mangle* (Rhizophoraceae) is a high pollen producer, while *Avicennia* spp. (Acanthaceae) and *Laguncularia racemosa* (L.) C.F. Gaertn. (Combretaceae) are low producers (Li et al., 2008; Tomlinson, 1986). Pollen traps placed at an Amazonian herbaceous plain located 1 to 2 km from a *R. mangle*-dominated stand and near (~100 m) a *Avicennia* shrub zone captured averages of 410 and 8 grains/cm²/y for *R. mangle* and *Avicennia* spp., respectively. This indicates high pollen productivity for *R. mangle*, whereas *Avicennia* pollen is low (Behling, Cohen, and Lara, 2001). The presence of *Avicennia* pollen within the sediment core also suggests *Avicennia* trees near the sampling site during sediment accumulation (Cohen et al., 2009b).

**Table 2. Facies description of cores R-2, R-1, and R-3.**

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<th>Facies</th>
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<tr>
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<td>Massive mud (Mm)</td>
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(from 90 to 40%). The concentration and accumulation rates were from 3000 to 80,000 grains/cm³ and 6000 to 10,000 grains/cm²/y, respectively (Figure 6).

**Figure 4.** Results for the R-2 core, showing chronology, sedimentation rates, lithological profile, pollen ecological groups, *Rhizophora* and *Avicennia* pollen and tannin chemical data, mean value of tannin concentration, and its standard deviation.

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A high tannin concentration during the early stages of sediment deposition observed in the cores was the result of the *R. mangle* trees present. The direct trend between tannin concentration values and *R. mangle* pollen percentages identified in the studied cores may be used as an indicator of *R. mangle* tree density in the study site. The absence of trends between tannin and *R. mangle* pollen along the upper part of the sediment cores may indicate late *R. mangle* trees near the study sites or may be associated with a decrease of *R. mangle* tree density and a decrease of mangroves (França et al., 2012, 2013) or with oxidation and biochemical modification of the upper part of the sediment profile altering the ratio of tannin and *Rhizophora* pollen.

**Relation between Tannin and Iron**

As described by Cohen et al. (2009b) in the sediment cores from the Amapá–northern Brazilian coastal zone, despite the probable relationship between tannin content in sediment and *R. mangle* pollen in the stratigraphic sequences, the natural presence of Fe within the cores available to react with K₂Fe(CN)₆ may also cause the appearance of Prussian blue after the addition of the reagents. This can then generate incorrect conclusions about tannin concentration.

Iron is highly reduction–oxidation (redox) sensitive (Lacerda, Ribeiro, and Gueiros, 1999; Mortimer and Rae, 2000). Wetlands may change the redox characteristics of sediments, such as occurs in mangroves from French Guiana, where suboxic to oxic processes continuously lead to Eh values averaging 300 mV to a depth of 30 cm, resulting in a Fe concentration of 180 μmol L⁻¹ in the soluble form (Marchand et al., 2004), while in the upper 5 cm, in which Eh values are close to 0 mV, Fe is present in concentrations of up to 1120 μmol L⁻¹ in the soluble form. This is caused by a higher content of organic matter (Scholander, Dam, and van Scholander, 1955), probably deposited under anoxic conditions. These changes in Fe concentrations reflect the reduction of Fe oxyhydroxides by bacteria, using them as electron acceptors in the reaction of organic matter decay. Therefore, authigenic-reduced sulfide minerals, such as amorphous FeS, mackinawite (FeS), greigite (Fe₃S₄), and pyrite (FeS₂), occur in wetland sediments.

Similarly, in the *várzea* vegetation, large variations in redox conditions occur that partially control the solubility of minerals such as Fe oxyhydroxides that are located in the bed sediments (Viers et al., 2005). This directly affects the concentrations of Fe in the *várzea* sediments (Balistrieri, Murray, and Paul, 1992; Tonkin, Balistrieri, and Murray, 2004). However, the spectro-photometric measurement along the upper part of core R-3, sampled from under *várzea* vegetation, did not indicate the occurrence of tannin or of Fe (Figure 5).

Considering that anoxic conditions occur along the studied wetland sediments and that the Fe content in the soluble form...
is subject to the same reduction conditions in mangrove and várzea sediments, it would be acceptable that Fe concentrations in the soluble form within the analyzed cores are not affecting the measurements of tannin content based on spectrophotometric methods.

**Tannin Concentration**

The highest tannin concentrations occur in the base and in the intermediary levels of the studied sedimentary successions, which may indicate that the mangrove colonized by *R. mangle* was present. Tannins are of intermediate resistance to decomposition and have remained in fairly constant proportion during decomposition (Benner, Hatcher, and Hedges, 1990). Degradation may be responsible for alteration of mangrove tannins during the decomposition of leaf litter (Zhou et al., 2012). In mangroves, the tidal flood has been shown to be an important process in the initial stages of leaf degradation (Benner, Hodson, and Kirchman, 1988). Tannin loss from the mangrove leaf material was ~30% in surficial sediment of a tropical estuary in the Bahamas. The tannin remaining in the leaves is potentially more diagenetically labile (Hernes et al., 2001). This organic compound contributes to the dissolved organic matter in the porewater (Cundell et al., 1979), and the soluble tannin tends to be bound to clay and silt particles. In addition, muddy sediments are more impermeable than sandy deposits; furthermore, concentrations of soluble tannin are generally higher in the low and midintertidal zones (Alongi, 1987). Protein- and fiber-bound condensed tannins tended to increase with leaf decomposition, with condensed tannins binding more strongly to protein than to fiber. In addition to having a biomarker potential, tannin greatly contributes to the properties of bulk organic matter, including color, astringency, and reactivity (Lin et al., 2006).

Considering cores R-1 and R-2, the grain sizes are regularly distributed along the studied sedimentary intervals, and they are mainly represented by silt and sand. No trends between grain size and tannin concentration were identified along these cores. This suggests that grain size has not significantly influenced tannin concentrations in the studied cores and that the effects of partial tannin loss from mangrove leaf and migration of soluble tannin to lower levels do not occur.

Core R-3 presents an upward increase in grain size, with some levels exhibiting 60 to 70% of sandy sediments. This probably results from the mangrove disappearing and being replaced by várzea (Fran¸ca et al., 2012). Because tannin was not detected along the 40- to 0-cm interval, it may have been associated with a decrease of *R. mangle* tree density and a decrease of mangroves (Fran¸ca et al., 2012, 2013) or with oxidation and biochemical modification of the upper part of the sediment profile altering the ratio of tannin and *Rhizophora* pollen.

Regarding the sediment cores studied, the spectrophotometric measurement probably is indicating predominantly tannin content sourced from the *R. mangle* leaves deposited during sedimentation of the layer that was analyzed. Then, it is likely that the changes in tannin concentrations along the studied cores mostly reflect *R. mangle* tree density, according to mangrove development at the sampling site. Therefore, the spectrophotometric method for tannin analysis, in association with pollen analysis, may be used as an additional indicator of *R. mangle* tree density in mangrove zones.

**Figure 6.** Results for the R-3 core, showing chronology, sedimentation rates, lithological profile, pollen ecological groups, *Rhizophora* and *Avicennia* pollen and tannin chemical data, mean value of tannin concentration, and its standard deviation.

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*Journal of Coastal Research, Vol. 35, No. 1, 2019*
CONCLUSION

The integration of tannin contents and pollen data supported by features of sediment types and sedimentary structures from three sediment cores indicates a tidal mudflat colonized by herbaceous vegetation and mangrove, with changes in the R. mangle tree density since at least 1150 cal yr BP. Despite the high R. mangle pollen percentage, the tannin data may indicate a decrease of R. mangle tree density in the sampling sites or late mangrove colonization with young trees. Thus, the elevated R. mangle pollen percentage during the last 700 to 500 years probably resulted from a new mangrove colonization area. The absence of tannin near the top also may result from the oxidation and biochemical modification of the upper part of the sediment profile altering the ratio of tannin and Rhizophora pollen. Thus, the tannin analyses supported by the pollen data may be considered additional tools for the paleoenvironmental reconstruction of tropical coastal zones and identification of palgeomarine zones.

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