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Origin and diagenesis of lignin and carbohydrates in mangrove sediments of Guadeloupe (French West Indies): Evidence for a two-step evolution of organic deposits

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Abstract

The mangroves of Grande Terre Island (Guadeloupe, French West Indies) are known to store large amounts of organic carbon, and organic-rich sediments have been described to several meters depth. The purpose of the present work was to precisely determine the molecular composition (carbohydrates and lignin-derived phenols) of these organic deposits in relationship with environmental conditions. It was found that within the upper meter of the cores, geochemical data displayed the classical degradation pattern of organic matter (OM) deriving from higher plants. On the one hand, carbohydrates from mangrove tissues underwent fast decomposition, other compounds being simultaneously synthesized by bacteria. On the other hand, lignin phenols were lost rather slowly, i.e. at a similar or lower rate than TOC, their distribution with depth evidencing various lignin decomposition pathways depending on redox conditions. The position of the swamp with respect to salt and fresh water tables strongly influenced these conditions. At depth, results revealed an organic-rich layer, which was characterized by surprisingly well-preserved OM with regard to sugar and phenol compositions. We speculate that the preservation of these compounds might be explained by a rapid and permanent flooding of the mangrove stands that may have occurred more than a thousand years ago. We suggest that the geodynamic context, i.e. the recurrent seismic activity recorded in Guadeloupe, may have induced such a flooding, resulting in the preservation of this OM.

Keywords: Mangrove; Carbohydrates; Lignin-derived phenols; Early diagenesis; Guadeloupe

1. Introduction

Mangrove forests, which develop in the intertidal zone of tropical and subtropical coastlines, are among the most productive terrestrial ecosystems, and can be characterized by a strong organic accumulation in their substrate ([Chen and Twilley, 1999], [Bouillon et al., 2003], [Chmura et al., 2003] and [Bouillon et al., 2008]). Additionally, the decay processes of organic matter (OM) in mangrove sediments are highly variable, due to the mixing of marine and fresh water, and to the activity of root systems and macrofauna ([Alongi et al., 2000], [Marchand et al., 2004] and [Kristensen et al., 2008]). Consequently, mangroves constitute a natural laboratory to study present processes of preservation/decomposition of higher plant remains in waterlogged sediments.

The mangrove of “Le Grand Cul-de-Sac Marin”, located on Grande Terre Island (Guadeloupe, French West Indies), is characterized by a clear zonation pattern of mangrove species from saline to fresh water. *Rhizophora mangle* develop on saline sediments, with

salinity values ranging from 30 to 40, *Acrostichum aureum* and *Laguncularia racemosa* on a brackish substrate, with salinity values ranging from 10 to 20, and *Pterocarpus officinalis* and *Cladium marescus* on a nearly fresh water soil, with salinity values lower than 5 (Lallier-Vergès et al., 1998). This mangrove swamp system has been aggrading at the same place for several centuries (Feller et al., 1990). In a previous study (Lallier-Vergès et al., 1998), we showed that the sedimentary record reached about 1400 years BP at 180 cm depth beneath the more marine *R. mangle* stand. Beneath the more continental *P. officinalis* forest, the record reached about 1400 years BP at only 65 cm and 2700 BP at 185 cm depth. Accordingly, this mangrove is characterized by a very high sedimentary organic content, with TOC values ranging from 17 to 48% on 2 m deep profiles, which is among the highest TOC values ever measured in mangrove ecosystems. Using C/N ratios, Rock-Eval pyrolysis data, $\delta^{13}\text{C}$ values and microscopic observations and counts, Lallier-Vergès et al. (1998) demonstrated that there was a strong link between pore water chemistry (i.e. salinity and redox values) and organic matter contents, both in terms of quantity and quality. Finally at depth, an unexpected OM-rich layer, characterized by high C/N ratios and low $\delta^{13}\text{C}$ values, was observed beneath most of the mangrove stands.

Carbohydrates and lignin-derived phenols, which are among the main organic components of vascular plants, are powerful indicators to trace higher plant remains and thus mangrove-derived OM in coastal environments ([Benner et al., 1990], [Opsahl and Benner, 1995] and [Dittmar et al., 2001]). Carbohydrates, which can be divided into storage and structural components, can represent up to 65% of organic carbon in mangrove wood (Opsahl and Benner, 1999). Additionally, clear distinctions can be made between the carbohydrate signatures of mangrove wood and leaves ([Lallier-Vergès et al., 1999] and [Marchand et al., 2005]). However, these signatures tend to disappear rapidly in the early stages of diagenesis with the degradation of the considered constituents (Moers et al., 1990). Compared to sugars, lignin-derived phenols are more resistant to diagenesis (Sarkanen and Ludwig, 1971). Lignin only occurs in higher plants. Its monomeric composition varies between gymnosperms and angiosperms, and between woody and leaf tissues (Hedges and Mann, 1979a). Specific ratios between lignin monomers can also be used as indicators of diagenetic alteration ([Hedges and Ertel, 1982], [Ertel and Hedges, 1984], [Hedges et al., 1988], [Bianchi et al., 1999] and [Miltner et al., 2005]).

Since the studied area exhibits a clear zonation pattern of mangrove species, the first aim of the present study was to compare the distribution of carbohydrates and of lignin-derived phenols in both mangrove plants and sediments in order to evaluate their potential use as mangrove source tracers. The second intent was to assess the fate of these constituents during early diagenesis depending on the respective position of the various stands regarding saline and fresh water input. Finally, the characterization of the OM at the molecular level was undertaken to obtain information on the nature and the origin of the specific OM-rich layer observed at depth.

2. Materials and methods

2.1. Study site and field sampling

Guadeloupe (French West Indies) is situated between 15°57' N and 16°31' N, and between 61°10' W and 61°48' W (Fig. 1). This island is characterized by a tropical climate with a mean annual rainfall ranging from 1500 to 1800 mm year⁻¹ occurring in a bimodal pattern (with a major rainfall period extending from July to November). Sampling was carried out in

June, at the end of the dry season. 2 m long cores were collected at low tide with an Eijkelkamp[®] gouge auger beneath the 5 mangrove species (*R. mangle*, *L. racemosa*, *A. aureum*, *C. marescus*, and *P. officinalis*), along a 2000 m long transect (Fig. 1d). After being collected, cores were wrapped in plastic film and aluminium foil in order to limit gaseous exchanges. Wood and leaves of the various plant species were also picked up from several trees surrounding the coring sites. The elevation of the soil was not measured but we observed that *Cladium* and *Pterocarpus* forests were not daily inundated by tides and were thus at a higher topographic level than the other mangroves. For the bulk analyses the results of which were presented in Lallier-Vergès et al. (1998), cores were sampled at 1 cm intervals in the upper 10 cm, then as 2 cm-thick samples every 10 cm down to 60 cm and every 20 cm below 60 cm. For the molecular analyses presented herein, 6 samples per core were selected as a function of the bulk results.

2.2. Lignin-derived phenol analysis

Air-dried samples were hydrolysed with 2 N NaOH for 4 h at 170 °C in presence of CuO. After addition of 2, 4, 5 trimethoxy benzoic as an internal standard, NaOH was neutralised with 6 N HCl. The phenols were then extracted with di-ethyl ether and were further separated and quantified by capillary zone electrophoresis (thanks to the analysis of an external standard mixture of the studied phenolic compounds; Maman et al., 1996). “X_{lignin}” represents the total yield of 8 simple phenols: vanillyl and syringyl acids, aldehydes and ketones, plus two cinnamic compounds (*p*-coumaric and ferulic acids). This parameter does not take into account the *p*-hydroxy-benzylic moieties that can be derived from non vascular plant material (Goñi and Hedges, 1995). “X_{lignin}” is expressed in mmol of lignin carbon per 100 mmol of total organic carbon (mmol phenolic C/100 mmol TOC). “Σ 11” is the sum of X_{lignin} and *p*-hydroxyl phenols (mmol phenolic C/100 mmol total OC). The C/V ratio is defined as the ratio of the sum of the cinnamic acids over the sum of the vanillic moieties (aldehyde + ketone + acid); the S/V ratio is defined as the ratio of the sum of the syringic phenols over the sum of the vanillic phenols. (Ad/Al)_v is the molar ratio of vanillic acid to vanillin (aldehyde). (Ad/Al)_s is the molar ratio of syringic acid over syringaldehyde.

2.3. Carbohydrate analyses

Neutral sugar analyses were carried out in 2 independent steps according to a modified Cowie and Hedges procedure (1984). Both these steps mostly consist in a hydrolysis with dilute acid solution (2.4 N H₂SO₄), but with and without previous soaking of the analysed sample with concentrated acid (24 N H₂SO₄). The first step with previous soaking yields the Total Sugars (i.e. cellulosic + hemicellulosic), whereas the second step which only consists in a simple hydrolysis with dilute acid only releases the most labile hemicellulosic monomers. Finally, the amounts of cellulosic monomers were calculated by subtracting the results of the second step to those of the first step.

Concerning the first step, in a Pyrex tube, 1 ml of 24 N H₂SO₄ was added to 30 mg of plant material or 100 mg of sediments, previously dried. After 16 h at room temperature, the solutions were diluted to 2.4 N H₂SO₄. The tubes were tightly closed under vacuum and heated at 100 °C for 5 h. After cooling, 6-deoxy-d-glucose (400 µg) was then added as an internal standard and the samples were subsequently neutralised with CaCO₃. The precipitate was removed by centrifugation at 3000 rpm for 20 min. After evaporation of the supernatant to dryness, the extracted sugars were dissolved in methanol at 50 °C. After evaporation of the solvent, the residue was stored in a desiccator.

The sample extracts were dissolved in pyridine, derivatised with trimethylsilyl (Sylon BFT Supelco), and immediately analysed using a Perkin Elmer gas chromatograph fitted with a 25 m long, 0.25 mm i.d. DB-1 capillary column (CPSil5CB, 0.25 μm film thickness), and an FID detector. The temperature program began at 60 $^{\circ}\text{C}$, then the oven temperature was raised at a rate of 30 $^{\circ}\text{C min}^{-1}$ up to 120 $^{\circ}\text{C}$ where it was maintained for 1 min, then raised again to 240 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C min}^{-1}$ and finally at a rate of 20 $^{\circ}\text{C min}^{-1}$ up to 310 $^{\circ}\text{C}$ where it was kept for 10 min. The injector split was off at the start time and turned on after 2 min. The injector was maintained at 240 $^{\circ}\text{C}$, the detector at 300 $^{\circ}\text{C}$. Replicate analyses gave an analytical precision lower than 5% for neutral sugar analyses of plant material and between 10% and 15% for sediments. Eight monosaccharides were identified in mangrove plants and in sediments: ribose, arabinose, xylose, rhamnose, fucose, glucose, mannose and galactose. The total neutral sugar concentrations are expressed in mmol of carbon of neutral monosaccharides per 100 mmol of total organic carbon (mmol TCOH-C/100 mmol OC).

3. Results

3.1. Molecular composition of mangrove plant species

The carbohydrate and lignin-derived phenol compositions of wood and leaves of the five mangrove species (*R. mangle*, *L. racemosa*, *A. aureum*, *C. marescus*, and *P. officinalis*) developing along the studied transect are presented in Table 1. TOC values of all plant tissues ranged between 32 and 39%.

Some distinctions in the phenol distribution can be made between the various species. The compositions of *Rhizophora* and *Laguncularia* were quite similar with a balanced proportion of the 4 phenol units (i.e. syringic, vanillic, cinnamic and *p*-hydroxy-benzylic) in leaves, and a dominance of syringic and vanillic units in wood. *Cladium*, which was the richest in lignin oxidation products (9.85 mmol phenolic C/100 mmol TOC), had a composition close to that of *Rhizophora* and *Laguncularia* woody tissues. The fern *Acrostichum* was characterized by a dominance of vanillic units, namely 80% of total phenols in leaves and up to 97% in stems. Finally, *Pterocarpus* was characterized by a low content in cinnamic and *p*-hydroxy-benzylic units, representing together less than 15% of total phenols even in the leaves. Additionally, clear distinctions in the phenol composition can be made between wood and leaves. Woods were richer in lignin oxidation product than leaves. X_{lignin} (see experimental) values ranged from 0.9 to 4.9 and from 4.1 to 8.8 mmol phenolic C/100 mmol TOC in leaves and woody material, respectively. Mangrove woods were relatively poor in cinnamic units, namely between 1 and 5% of total phenols. As a consequence, woody tissues were characterized by very low C/V ratio values, close to 0.1 (Fig. 2). For the three mangrove trees (*R. mangle*, *L. racemosa*, and *P. officinalis*), S/V ratios were higher in woody tissues than in leaf tissues, ranging from 1.07 to 1.82 and from 0.57 to 1.3, respectively. This ratio was close to 0 for the fern *Acrostichum* and was equal to 1.37 for *Cladium* (Fig. 2). Additionally, the acid-to-aldehyde ratios for both the vanillic and syringic units were higher in leaves than in woody tissues for *Rhizophora* and *Laguncularia*, but were similar in the wood and leaves of *Acrostichum* and *Pterocarpus* (Table 1).

The woods of all the mangrove species were almost twice as rich in carbohydrates as their leaves, i.e. from 32.6 to 50.6 mmol TCOH-C/100 mmol TOC and from 15.0 to 32.1 mmol TCOH-C/100 mmol TOC, respectively (Table 1). The fern *Acrostichum* was the richest in carbohydrates. Glucose was the most abundant neutral sugar in all plants, representing

between 26 and 67% of total sugars in leaves and between 47 and 71% in wood. Ribose and the deoxy sugars (rhamnose and fucose) were the least abundant monomers, representing generally less than 5% of total carbohydrates. Leaves were characterized by a higher content in hemicellulosic carbohydrates than wood, e.g. up to 81% of total carbohydrates in the leaves of *Rhizophora*. In addition to glucose, the 3 mangrove tree leaves were also characterized by high proportions, first of arabinose and second of galactose. Conversely, woody tissues were richer in xylose than leaves, with values ranging from 13 to 22% and from 5 to 13%, respectively.

3.2. Distribution of carbohydrates and lignin-derived phenols in mangrove sediments

In the studied mangrove sediments, TOC varied between 17 and 48%, with higher values on the landward side of the mangrove (Lallier-Vergès et al., 1998). Except beneath the *R. mangle* stands, TOC decreased downwards in the upper 40 to 60 cm and then increased up to values as high as those measured in the upper sediment (Fig. 3). Total lignin concentrations ranged between 8 and 78 mg g⁻¹ (Fig. 4), X_{lignin} representing between 1.8 and 10% of TOC (Table 2). The highest concentrations were found in the upper sediment beneath *Rhizophora* and *Laguncularia* and in the sample taken at 132 cm depth beneath *Cladium*, i.e. the deepest one. Total lignin displayed the same evolution pattern as TOC, and the proportion of organic carbon (OC) from lignin in the TOC was also higher at depth than at mid-core. For instance beneath *Pterocarpus*, OC from lignin represented 1.8 and 5.5% of TOC at 103 and 143 cm depth, respectively. The proportions of lignin units in mangrove sediments varied as follows: vanillic (27 to 78%), syringic (11 to 37%), and cinnamic units (2 to 24%) (Table 2). S/V ranged between 0.4 and 0.9 except beneath *Acrostichum*, where they were very low, close to 0.15 in the upper core (Fig. 5). C/V ratios ranged between 0.06 and 0.69, the lowest values having also been measured beneath *Acrostichum*. Beneath *Rhizophora*, *Laguncularia* and *Cladium*, the upper core was characterized by an increase in C/V ratios with increasing depth and a slight increase in S/V ratios (Fig. 5). Beneath *Pterocarpus*, the upper part of the core was characterized by a slight decrease in the C/V ratio and a slight increase in the S/V ratio with depth. When examined in a C/V vs. S/V diagram, the signatures of the deeper samples, appear closest to those of the upper core than to those taken at mid-core, whatever the sampling site (Fig. 5). Ad/Al ratios of both syringic and vanillic units were lower than 1 in every sample except below 1 m depth beneath *Pterocarpus* (Table 2). Beneath *Laguncularia*, *Acrostichum*, and *Cladium*, these ratios increased slightly with depth in the upper core section and then decreased in the layers that were characterized by higher TOC values (Table 2).

Total carbohydrate concentrations ranged between 16 and 88 mg g⁻¹ (Fig. 4), and OC from carbohydrates represented between 2 and 9% of TOC contents (Table 3). In all cores, total carbohydrate concentrations as well as their OC contribution to the TOC were at a maximum in the upper 1st cm and displayed the same downward evolution pattern as TOC (Fig. 4; Table 3). For instance beneath *L. racemosa*, OC from carbohydrates represented 2.1 and 3.9% of TOC at 65 and 178 cm depth, respectively (Table 3). The proportions of neutral sugars in the sediment varied as follows: glucose (27 to 57%), arabinose (8 to 26%), xylose (7 to 17%), galactose (6 to 15%), rhamnose (5 to 15%), mannose (3 to 13%), fucose (3 to 6%) and ribose (< 2%) (Table 3). Beneath *R. mangle*, the sediments were characterized by the highest concentrations in xylose and rhamnose. Conversely, on the landward side of the mangrove, the upper sediment was characterized by the highest concentrations in galactose. No specific trend with depth could be observed for any neutral sugar. However, the ratios between xylose

and rhamnose decreased with depth in the upper core and then increased to reach the highest values in layers that were characterized by higher TOC contents (Fig. 6).

4. Discussion

4.1. Mangrove tissues signature

In recent decades, lignin has often been used to trace the input of higher plant remains in riverine, coastal and marine environments ([Hedges and Mann, 1979b], [Hedges et al., 1986], [Dittmar et al., 2001] and [Bianchi et al., 2007]). Some authors have examined the lignin content of possible source material such as the leaves of various mangrove species: *Rhizophora* (Benner et al., 1990), *Avicennia* (Opsahl and Benner, 1995), *Avicennia*, *Rhizophora* and *Laguncularia* (Dittmar and Lara, 2001), and *Avicennia*, *Rhizophora*, *Laguncularia*, *Crenea*, and *Acrostichum* (Marchand et al., 2005). Leaves of *Rhizophora* and *Laguncularia* from Guadeloupe exhibit a typical vascular-plant lignin signature (Hedges and Mann, 1979a) and present a lignin yield close to 1 mmol phenolic C/100 mmol TOC, similar to values from mangrove leaves collected in the Bahamas (Benner et al., 1990), Brazil (Dittmar and Lara, 2001), and French Guiana (Marchand et al., 2005). In contrast to leaves, mangrove wood compositions have seldom been investigated ([Opsahl and Benner, 1995] and [Marchand et al., 2005]). The woody tissues of these species are 4 times richer in lignin than their leaves and contain only a few cinnamic units thus inducing low C/V ratios. Such a composition, which is typical for angiosperm woody tissues ([Hedges and Ertel, 1982] and [Ertel and Hedges, 1984]), is consistently supported by previous results obtained by Opsahl and Benner (1995) and Marchand et al. (2005) for *Avicennia* wood. While we observed that *Pterocarpus* woody tissues have the same composition as *Rhizophora* and *Laguncularia* woods, the low content in cinnamic unit of its leaves is surprising. As observed in other mangroves ([Benner et al., 1990], [Dittmar and Lara, 2001] and [Marchand et al., 2005]), the C/V ratios of mangrove leaves are higher than those of other dicotyledonous angiosperm leaves. S/V ratios of *Rhizophora* and *Laguncularia* leaves are in the same range as in Brazil (Dittmar and Lara, 2001) or in French Guiana mangroves (Marchand et al., 2005). Vanillic and syringic acid-to-aldehyde ratios determined for the leaves of these mangrove species are relatively high. They are also high for the woods, whereas Marchand et al. (2005) observed that mangrove woody tissues were characterized by very low vanillic acid to aldehyde ratios. Conversely to the signature of these mangrove trees, the fern *Acrostichum* is characterized by low C/V and S/V ratios, both close to 0.1 (Fig. 2). The dominance of vanillic units in *Acrostichum* is characteristic of the lignin composition of Pteridophytes. Accordingly, Logan and Thomas (1985) observed that vanillin represented 98% of total aldehydes in 5 out of 6 analysed ferns. Finally, *Cladium* exhibits a typical angiosperm signature close to that of mangrove tree leaves.

Studies dealing with the carbohydrate composition of mangrove tissues are relatively scarce ([Moers et al., 1990], [Benner et al., 1990], [Opsahl and Benner, 1999] and [Marchand et al., 2005]). In our study, total carbohydrate yields, with higher values in wood than in leaves, are in agreement with data previously obtained by Marchand et al. (2005) in French Guiana, except for *Acrostichum* for which higher carbohydrate concentrations were found in the present work. Wood and leaves can be differentiated by their carbohydrate contents. Leaves were always richer than wood in hemicellulosic carbohydrates and especially in galactose. Accordingly, Benner et al. (1990) reported that *Rhizophora* leaves contained 15% of galactose, and Moers et al. (1990) found only 5% of galactose in *Rhizophora* wood, which is

consistent with our own findings. Conversely, high xylose contents, (> 13%) appear characteristic of wood. The high xylose contents determined by Opshal and Benner (1999) and Moers et al. (1990) for *Avicennia* and *Rhizophora* wood (14 and 24% respectively), are in full agreement with our data.

4.2. Lignin and carbohydrates in mangrove sediments: a two-step evolution of organic deposits

The mangrove studied sediments present very high organic contents. They are also characterized by unusual depth profiles, beginning with a classical downward decrease expressing progressive degradation of organic matter, but at depth this profile is followed by a rather surprising increasing trend. This peculiar trend is opposite to usual decay profiles, as described in other mangrove swamps (Marchand et al., 2003).

4.2.1. Sources vs. diagenesis in the upper layer

Along the sea-land transect, xylose and galactose present an opposite trend. The highest xylose concentrations were found beneath *Rhizophora*, the most seaward mangrove plant, whereas the highest galactose content was measured beneath *Pterocarpus*, the most landward plant species. In plant tissues, a high xylose content is a characteristic of wood whereas galactose is more abundant in leaves. Cowie and Hedges (1984) suggested that the sum of arabinose and galactose can be used to distinguish inputs of non-woody vascular plant tissues. Accordingly, the higher galactose contents determined on the landward side of the studied transect may reflect an accumulation of leaf litter, while on the seaward side the contribution of the root system to the organic accumulation may be responsible for its specific sugar composition. Additionally, the high proportion of lignin normalized to TOC recorded in the upper part of the cores collected beneath *Rhizophora* and *Laguncularia* confirms the important contribution of woody tissues to the OM. It must be underlined that the organic accumulation was higher beneath *Cladium* and *Pterocarpus*. This probably results from the fact that in contrast to the most seaward mangroves that were daily flushed by tides, mangroves developing on the landward side were not, thus allowing an accumulation of leaf litter and hence higher galactose contents.

In the upper cores, total carbohydrate concentrations decrease with depth as well as their proportions normalized to TOC. OC from carbohydrates represents between 15 and 50% of TOC in the mangrove plant species but less than 9% in the mangrove sediments, whatever the forest zone. This result highlights the reactivity of carbohydrates relative to bulk OC as observed in other swamps where degradation of polysaccharides appeared to be very efficient even in waterlogged sediments ([Cowie and Hedges, 1984], [Stout et al., 1988], [Moers et al., 1990] and [Marchand et al., 2005]). Although the present results show that the decomposition of carbohydrates is continuous within the sediment, at least 50% of these compounds were already degraded in the litter, before being readily incorporated to the sediment. The decomposition of carbohydrates in the litter first occurred through leaching processes (Benner et al., 1990). The substance loss between the higher plant sources and the sediments might even have been more important than it appears at first sight since part of the sedimentary hemicellulosic carbohydrates may have been neo-synthesized *in situ* by micro-organisms or expelled by higher plants through their root systems (Cowie and Hedges, 1984). In fact, the studied mangrove sediments here are characterized by higher contents in deoxy sugars (rhamnose and fucose) than mangrove plants. Hedges et al. (1988) showed that deoxy sugars could be derived from bacteria, and later Moers et al. (1990) demonstrated that they can

contribute significantly to mangrove peat. In addition, the ratio between xylose and rhamnose decreases in the upper part of the cores beneath all the mangrove stands (Fig. 6), thus highlighting increasing bacterial contribution to total carbohydrates with increasing depth.

OC from lignin-derived phenols ranges from 1 to 10% TOC in mangrove tissues and varies between 2 and 10% in mangrove sediments, highlighting the relative stability of these compounds compared to carbohydrates and bulk OC ([Benner et al., 1984a], [Benner et al., 1984b], [Hedges et al., 1985], [Cowie et al., 1992], [Dittmar and Lara, 2001] and [Marchand et al., 2005]). Nevertheless, like carbohydrates, phenol concentrations decrease with depth in the upper cores, thus highlighting lignin decomposition. Vanillic units are predominant in the mangrove sediments where they range between 27 and 78% of total phenols, whereas in the plant tissues they are dominant only in the fern. As a consequence, S/V ratios are lower in sediments than in plants. These results might indicate a preferential degradation of syringic phenols by decomposers, with the elimination of one of the 3- or 5-methoxyl group, thus entailing an increase in vanillic units at the expense of syringic ones ([Hedges et al., 1988] and [Goñi et al., 1993]). This lignin decomposition pathway does not seem to be common in all mangroves. For example, in Brazilian mangroves, Dittmar and Lara (2001) found relatively constant S/V values, similar to those of leaf litter. They suggested a similar diagenetic reactivity for syringic and vanillic moieties in anoxic mangrove sediments. The Guadeloupe mangrove upper sediments are also highly depleted in cinnamic phenols relative to vanillic phenols, and thus characterized by very low C/V ratios. On the one hand, these low C/V ratios may partly result from the relative reactivity of the various phenols. Dittmar and Lara (2001) also observed low C/V ratios and, referring to the work of Benner et al. (1990) and Opsahl and Benner (1995), suggested a preferential loss of cinnamic acids known to be rather peripheral to the lignin core to which they are linked by a rather labile ester bond. On the other hand, low C/V ratio values may also result from the introduction of root-derived OM, which originally has low C/V ratios, as already observed in French Guiana mangroves (Marchand et al., 2005). Finally, the low C/V and S/V ratios measured in the upper sediment level beneath *Acrostichum*, more probably reflect some source variation than a diagenetic evolution, since this plant species is characterized by the dominance of the vanillic unit (Table 1). The Ad/Al ratios of both syringic and vanillic units are low and close to those of mangrove tissues, except beneath *Pterocarpus*, where these ratios are relatively high. Low Ad/Al ratios appear typical for lignin decomposition under anoxic conditions. Reversely, high Ad/Al ratio values result from an oxidation of the propyl chain of lignin units, typical for lignin decomposition under oxic conditions ([Hedges and Ertel, 1982] and [Ertel and Hedges, 1984]). Thus, the rationale for these contrasting results might be that *Rhizophora* and *Laguncularia* forests develop under the influence of marine water whereas *Pterocarpus* forest develops under the influence of fresh water and is less frequently inundated by the sea. This difference induces an evolution in the redox conditions in the sediments, with increasing distance from the sea (Fig. 7). In the mangroves of Guadeloupe, seaward sediments are the site for anoxic conditions and organic decomposition processes mainly driven by sulfate reduction processes, as highlighted by high sulfur contents (Lallier-Vergès et al., 1998). Conversely on the landward side, mangrove sediments are oxygenated and have low sulfur contents (Lallier-Vergès et al., 1998). These various observations support the idea that different processes of lignin decomposition occur within the sediments under the various mangrove forests, as a result of their location in the swamp and the respective influence and frequency of fresh and salt water input.

4.2.2. Preservation of OM at depth in relationship with past water-table variation

In previous work (Lallier-Vergès et al., 1998), we observed that mangrove sediments from Le Grand Cul-de-Sac Marin were characterized by higher TOC contents at depth than in the upper levels. The deep organic-rich layer had lower $\delta^{13}\text{C}$ values and higher C/N ratios, highlighting the important contribution of higher plants to its OM. For instance, beneath *Laguncularia*, $\delta^{13}\text{C}$ values decreased from -27‰ to -28‰ , and C/N increased from 17 to 43 (Lallier-Vergès et al., 1998). The present molecular approach provides a more precise description of this organic accumulation. First, it presents higher xylose over rhamnose ratio values than the upper layers (Fig. 6) thus indicating a large contribution from higher plants. Then, the proportion of OC from carbohydrates and phenols in the TOC was also found to be higher in this buried layer compared to the overlying deposits (Table 2 and Table 3). Finally, when examined in a C/V vs. S/V diagram (Fig. 5), the chemical signatures of samples from this deep layer were closer to those taken in the upper sediments than to those taken at mid-core. Consequently, the OM of this layer is chemically well-preserved, nearly as well as in litter. Accordingly, while the organic content of the upper sediment certainly resulted from an *in situ* accumulation of the mangrove system during the last millennia (Lallier-Vergès et al., 1998), a simple aggradational process cannot explain such an OM preservation at depth. We assume herein that only rapid and complete water flooding of the coastal mangrove deposit may account for this exceptional chemical preservation. Such organic matter compositional variations have already been evidenced in ancient sedimentary formations. Accordingly, the vertical and lateral distribution of organic components (macerals) in sequential coal-bearing strata from Campanian coastal deposits exhibited differential organic preservation, which was interpreted as the consequence of very short-term base level changes of probable climatic origin (Buillit et al., 2002). Since climate forcing cannot be invoked during the last two millennia in order to explain a rapid uplift of the water-table, we surmise that the specific geodynamic context of Grande Terre Island could be the main driving force for such a water-table variation. Indeed, we speculate that the intense coupled volcanic and seismic sensitivity of the island ([Feuillet et al., 2001], [Feuillet et al., 2002] and [Feuillet et al., 2004]) might have induced the modification in water tables resulting in the flooding of the most littoral organic formations and thus the preservation of these compounds.

5. Conclusions

This study has allowed us first to precisely define the lignin and carbohydrate composition of some mangrove plant tissues, then to confirm the potential use of some of these compounds as source tracers, and finally to evidence the well-preserved character of the OM in a buried organic-rich layer.

1) Mangrove trees (*Rhizophora*, *Pterocarpus*, and *Laguncularia*) exhibited a typical angiosperm woody tissues signature rich in lignin-derived oxidation products, with very few cinnamic units and high xylose contents. Concerning leaf tissues, C/V ratios were confirmed to be higher than for other dicotyledonous angiosperm leaves, except for *Pterocarpus*, which contains surprisingly low amounts of cinnamic units. The leaves were also characterized by a high content in hemicellulosic carbohydrates, especially galactose. The fern *Acrostichum* was characterized by a very high dominance of vanillic units, while *Cladium* had a signature close to that of mangrove tree leaves. A rather high content in deoxy sugars (rhamnose and fucose) in mangrove sediments compared to mangrove plants might indicate their *in situ* production by bacteria thriving at the expense of higher plant remains. Accordingly, decreasing xylose over rhamnose ratios in the upper part of the cores probably highlights an increasing

contribution of bacterial sugars to total carbohydrates. Finally, the opposite evolution of xylose and galactose contents in upper sediments from the seaward to the landward sides evidences their ability to trace leaf and woody tissues. The farther from the sea, the higher the accumulation of leaf litter, and the higher the galactose content. Conversely, on the seaward side, the main contributor of organic matter was the root system, as highlighted by high xylose contents.

2) Concerning the behavior of the studied compounds regarding diagenesis, our results show the reactivity of carbohydrates relative to bulk OC, with at least 50% of carbohydrates being readily degraded before being incorporated to the sediment. Conversely, lignin-derived phenols were lost at a similar or lower rate than bulk OC. Various decomposition processes have been evidenced for phenols. In most mangroves, decomposers preferentially utilized syringic phenols, and eliminated the 3- and/or 5-methoxyl group. Beneath the landward forests, processes of lignin decomposition under oxic conditions were also observed, as evidenced by high Ad/Al ratios. As a consequence, the position of the mangrove stand in the swamp regarding the fresh and saline water inputs appears predominant in OM decay processes.

3) A deep organic-rich layer has been confirmed to derive from higher plants by high xylose over rhamnase ratio values. Additionally, the proportion of OC from carbohydrates and phenols in TOC, and the C/V and S/V signatures of this layer evidences the chemically well-preserved character of this OM. We speculate that a catastrophic event linked to regional geodynamics may have induced modifications in the water-table, leading to the rapid and complete flooding of mangrove swamps, and thus to the preservation of these compounds.

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Figures and Tables

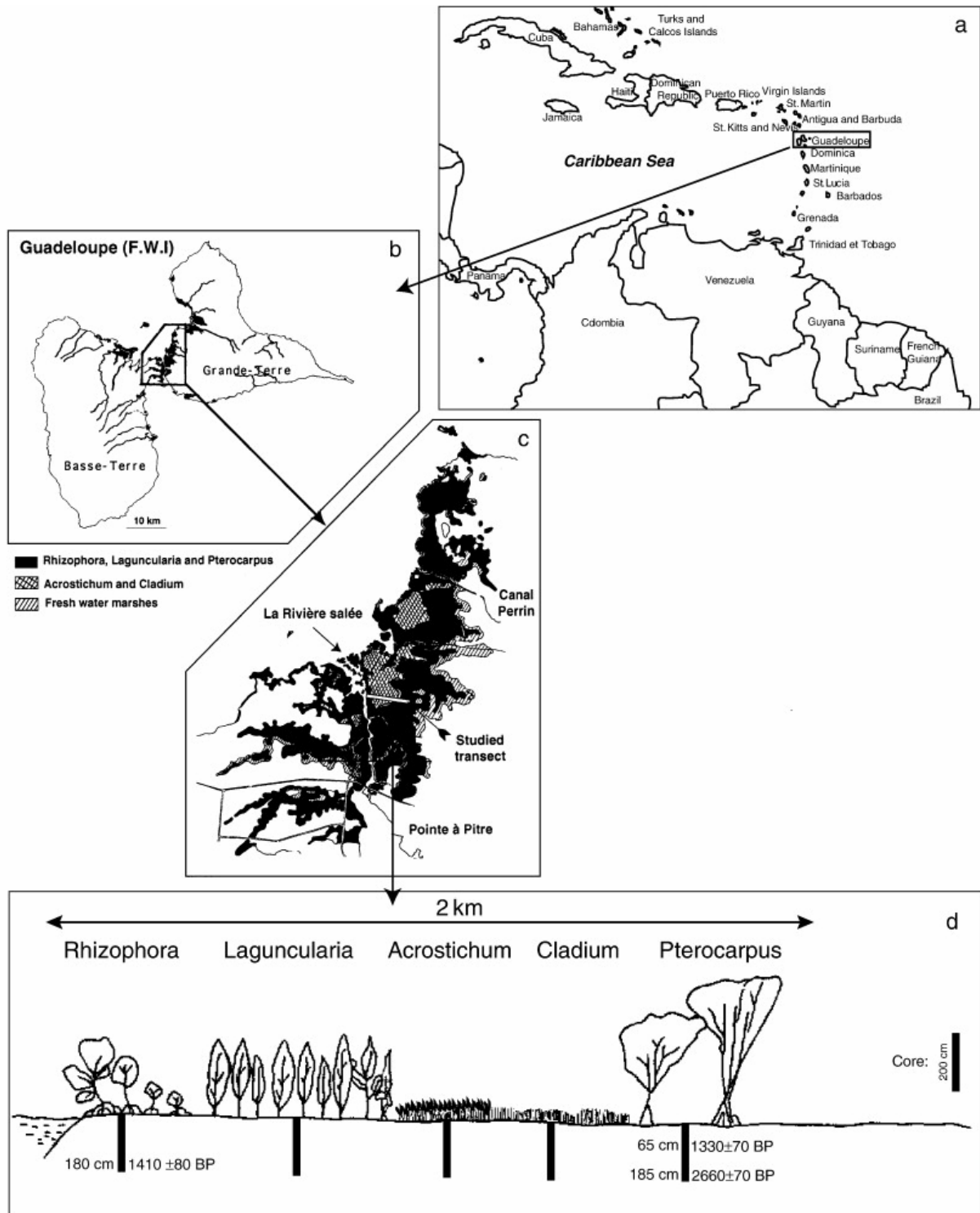


Fig. 1. Maps of the studied area: a) situation of the Guadeloupe Island in the Caribbean Sea; b) situation of the mangrove studied in Guadeloupe; c) surface map of the studied mangrove showing the position of the transect; d) distribution of the various mangrove species along the transect, and radiocarbon dates (from Lallier-Vergès et al., 1998).

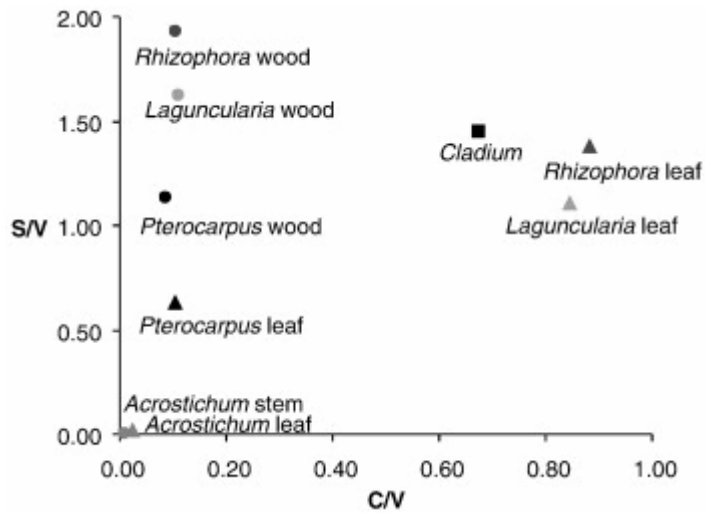


Fig. 2. C/V vs. S/V diagram of the mangrove leaf and woody tissues (*Rhizophora mangle*, *Laguncularia racemosa*, *Acrostichum aureum*, *Cladium marescus*, and *Pterocarpus officinalis*).

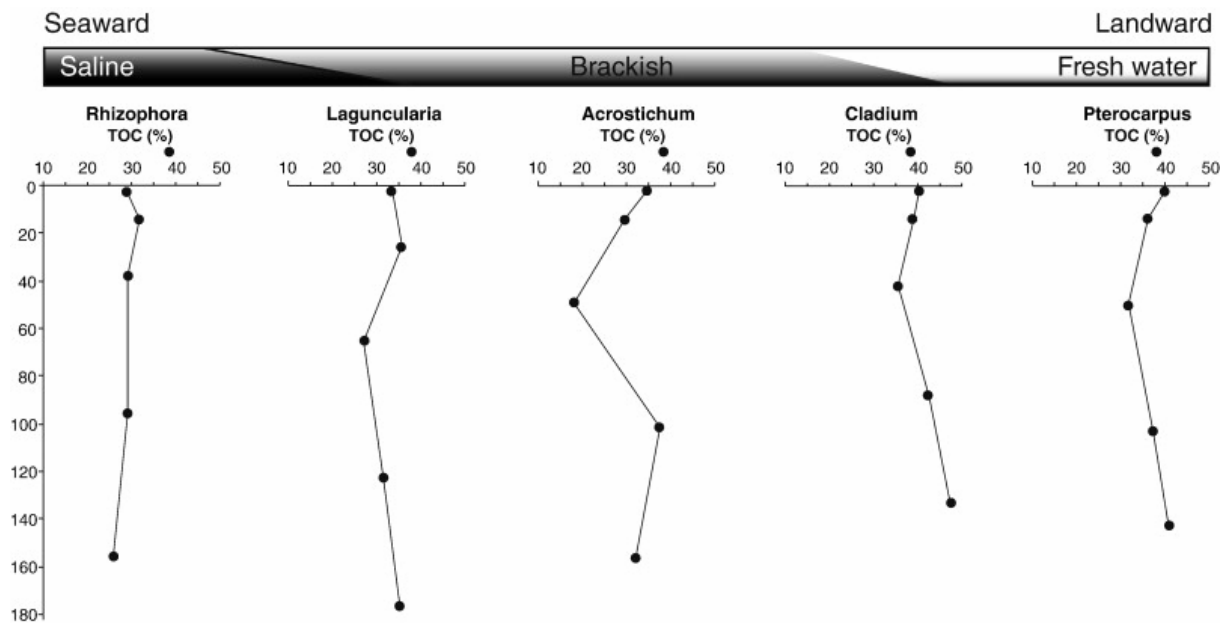


Fig. 3. TOC (%) depth profiles beneath the different mangrove swamps, i.e. *Rhizophora mangle*, *Laguncularia racemosa*, *Acrostichum aureum*, *Cladium marescus*, and *Pterocarpus officinalis* (Data from Lallier-Vergès et al., 1998).

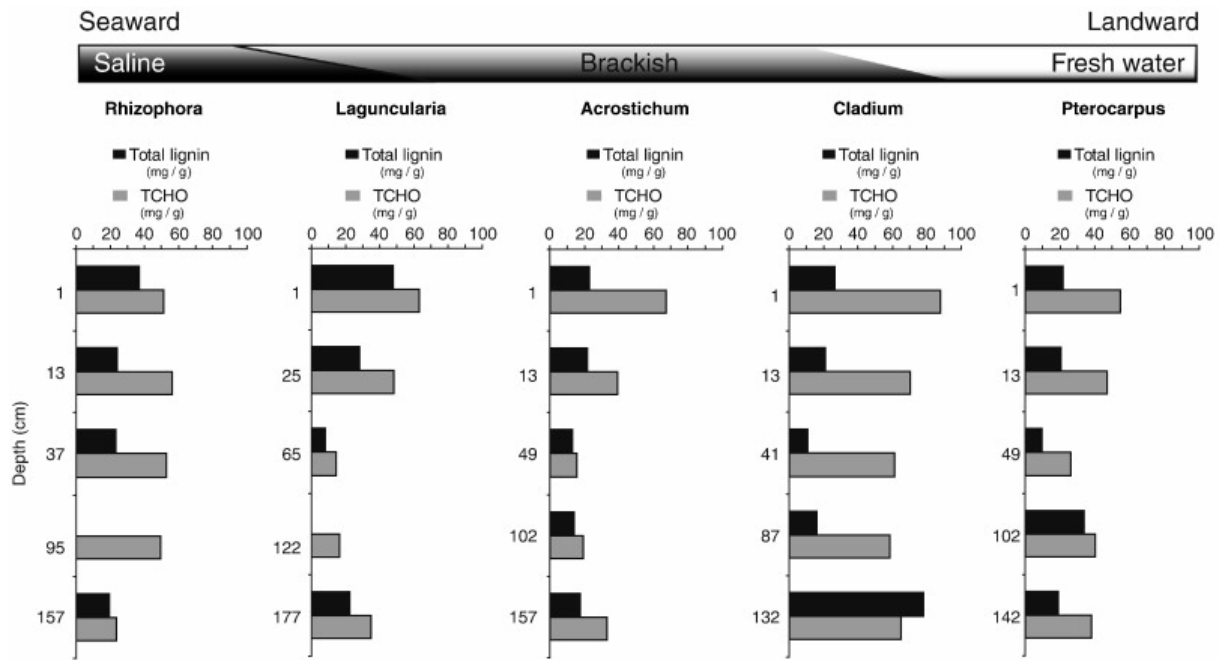


Fig. 4. Depth profiles beneath the different mangrove swamps, i.e. *Rhizophora mangle*, *Laguncularia racemosa*, *Acrostichum aureum*, *Cladium marescus*, and *Pterocarpus officinalis*: sum of the vanillic, syringic, and cinnamic phenols (in mg phenol/g sediment), and sum of the eight monosaccharides (TCHO) (ribose, arabinose, xylose, rhamnose, fucose glucose mannose and galactose) in mg sugar/g sediment. (No lignin analyses were performed at 95 cm depth beneath *Rhizophora* and at 122 cm beneath *Laguncularia*).

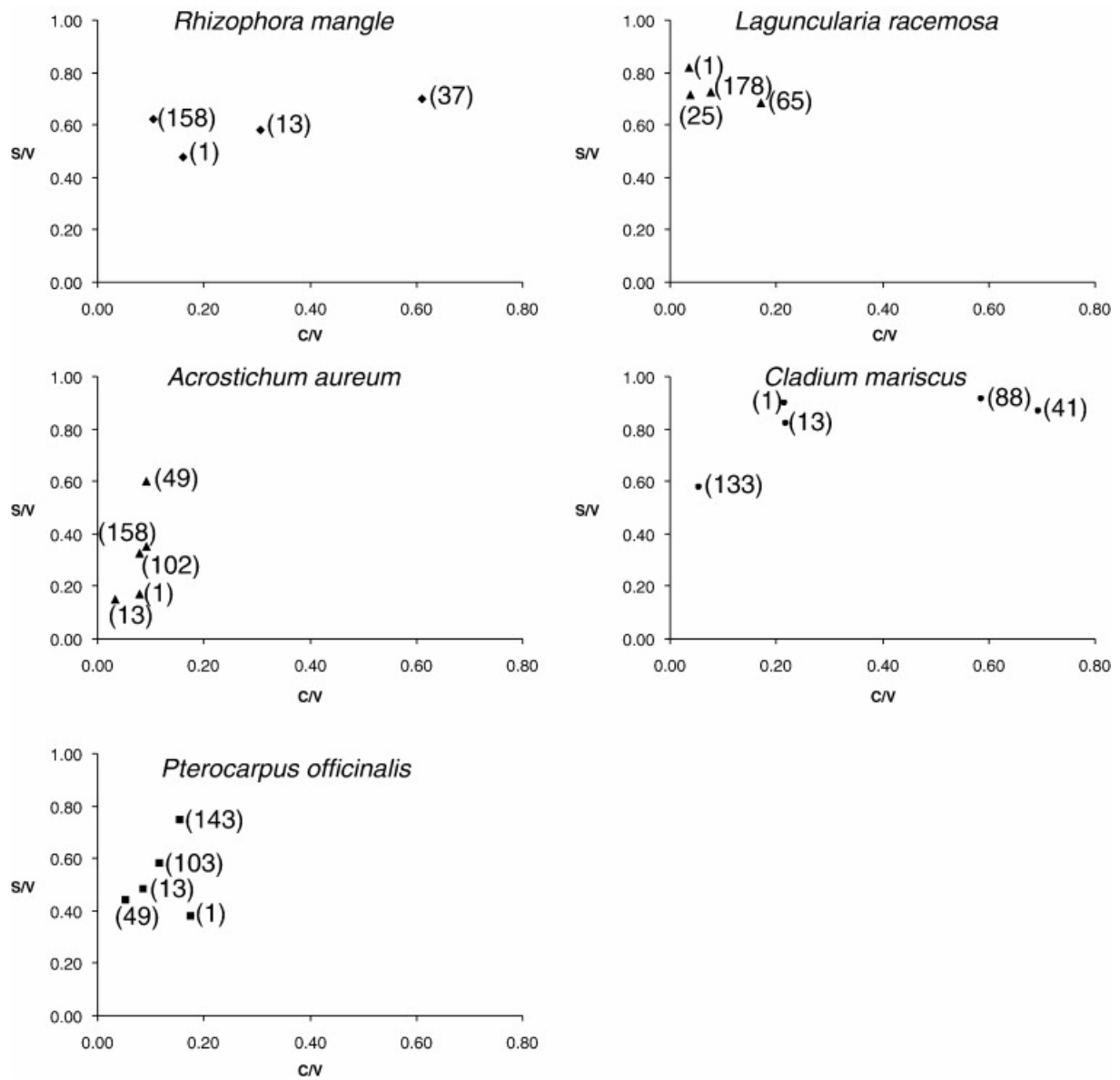


Fig. 5. C/V vs. S/V diagram of sediment samples collected beneath the various mangrove swamps, i.e. *Rhizophora mangle*, *Laguncularia racemosa*, *Acrostichum aureum*, *Cladium mariscus*, and *Pterocarpus officinalis*. The numbers in bracket indicate the depth of the sample.

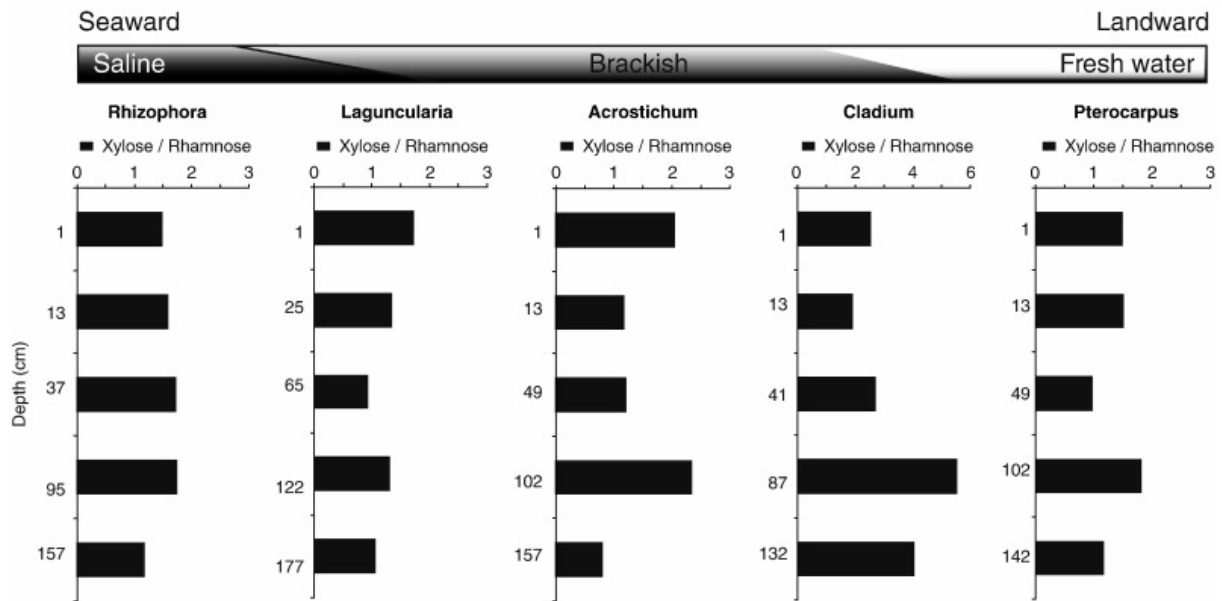


Fig. 6. Depth profiles of xylose over rhamnose ratios beneath the different mangrove swamps, i.e. *Rhizophora mangle*, *Laguncularia racemosa*, *Acrostichum aureum*, *Cladium marescus*, and *Pterocarpus officinalis*.

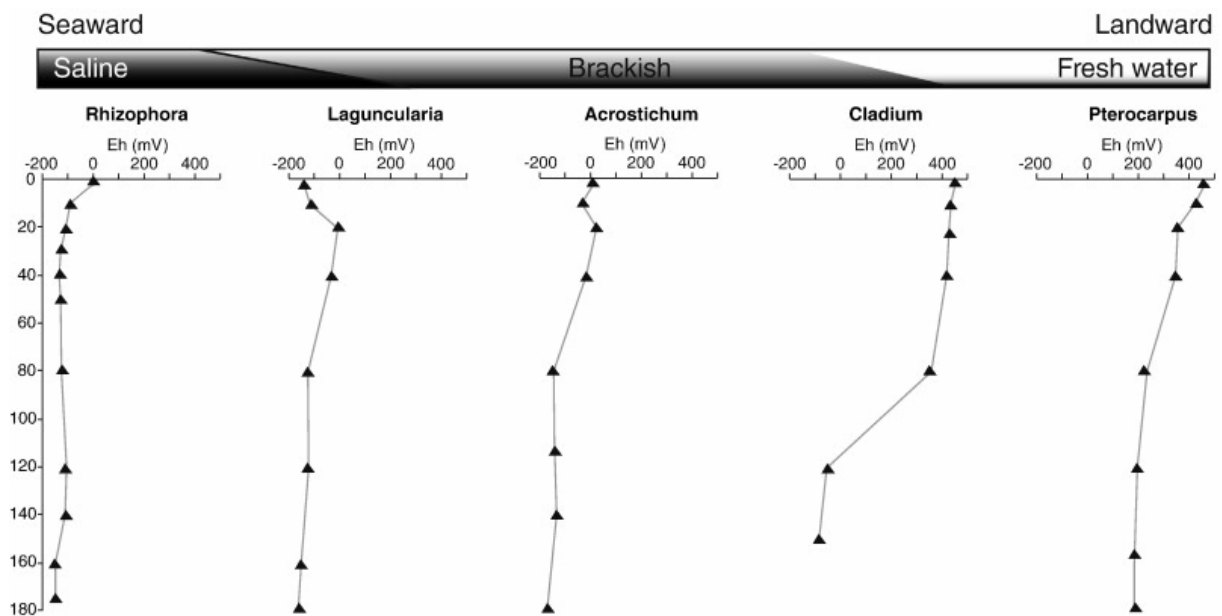


Fig. 7. Redox (mV) depth profiles beneath the different mangrove swamps, i.e. *Rhizophora mangle*, *Laguncularia racemosa*, *Acrostichum aureum*, *Cladium marescus*, and *Pterocarpus officinalis* (Data from Lallier-Vergès et al., 1998).

Table 1. : Geochemical characterization of the mangrove plant species developing along the studied transect: percent total organic carbon (TOC); X_{lignin} (sum of the vanillic, syringic and cinnamic phenols in mmol phenolic C/100 mmol total OC); $\Sigma 11$ (sum of X_{lignin} and *p*-hydroxyl phenols in mmol phenolic C/100 mmol total OC); Vanillic unit, Syringic unit, Cinnamic unit, *p*-hydroxyl unit in % of total phenols; vanillic acid/vanillin ratios (Ad/Al)_v, syringic acid/syringaldehyde (Ad/Al)_s; total neutral sugars in mmol TCHO-C/100 mmol total OC; hemicellulosic carbohydrates, total ribose, total arabinose, total xylose, total rhamnose, total fucose, total glucose, total mannose and total galactose in % of total carbohydrates

	<i>Rhizophora</i> leaf	<i>Rhizophora</i> wood	<i>Laguncularia</i> leaf	<i>Laguncularia</i> wood	<i>Acrostichum</i> leaf	<i>Acrostichum</i> stem	<i>Cladium</i> whole plant	<i>Pterocarpus</i> leaf	<i>Pterocarpus</i> wood
TOC (%)	35.82	35.53	32.16	34.49	33.48	34.76	35.66	38.86	37.54
X _{lignin} (mmol phenolic C/100 mmol TOC)	0.95	4.16	1.09	4.63	2.34	8.88	9.85	4.99	6.57
Σ 11 (mmol phenolic C/100 mmol TOC)	1.27	4.49	1.41	4.82	2.76	9.09	14.47	5.41	6.70
V (%)	23.28	31.55	26.50	36.36	81.13	96.80	22.21	54.06	45.48
S (%)	30.31	57.48	27.85	55.53	1.76	0.00	30.37	32.36	48.52
C (%)	21.23	3.44	23.12	4.17	2.09	0.97	15.47	5.84	4.12
P (%)	25.17	7.50	22.50	3.92	15.01	2.23	31.94	7.72	1.87
(Ad/Al) _v	2.41	0.62	0.64	0.32	0.98	0.95	0.42	0.47	0.47
(Ad/Al) _s	1.49	0.76	1.03	0.32	0.01	0.02	0.31	0.55	0.50
Total carbohydrates (mmol TCHO- C/100 mmol TOC)	20.89	33.76	15.04	32.69	32.17	50.60	28.98	21.58	42.79
Hemicellulosic carbohydrates (%)	81.46	55.72	62.67	45.98	51.62	35.97	50.70	49.22	37.56
Total ribose (%)	0.69	0.77	0.80	0.67	0.18	0.24	0.60	0.32	0.30
Total arabinose (%)	18.11	12.07	20.18	10.90	2.63	1.32	7.47	7.92	6.16
Total xylose (%)	7.05	22.04	5.62	16.85	6.61	13.20	31.19	13.07	13.82
Total rhamnose (%)	11.24	3.60	4.84	2.76	2.76	0.57	0.73	3.87	2.08

	<i>Rhizophora</i> leaf	<i>Rhizophora</i> wood	<i>Laguncularia</i> leaf	<i>Laguncularia</i> wood	<i>Acrostichum</i> leaf	<i>Acrostichum</i> stem	<i>Cladium</i> whole plant	<i>Pterocarpus</i> leaf	<i>Pterocarpus</i> wood
Total fucose (%)	4.43	2.90	3.72	2.84	0.96	0.49	1.58	2.00	1.45
Total glucose (%)	26.35	47.74	44.65	53.94	67.96	71.56	48.69	59.47	65.93
Total mannose (%)	3.95	4.63	6.94	3.92	9.65	9.55	6.65	4.82	4.69
Total galactose (%)	28.14	6.23	13.23	8.11	9.22	3.03	3.05	8.54	

Table 2. : Lignin phenols depth distribution beneath the various mangrove swamps studied, i.e. *Rhizophora mangle*, *Laguncularia racemosa*, *Acrostichum aureum*, *Cladium marescus*, and *Pterocarpus officinalis*: X_{lignin} in mmol phenolic C/100 mmol total OC, Vanillic unit, Syringic unit, Cinnamic unit in % of total phenols, vanillic acid/vanillin ratios (Ad/Al)_v, syringic acid/syringaldehyde (Ad/Al)_s

Mangrove species	Depth (cm)	X_{lignin} (mmol phenolic C/100 mmol TOC)	V (%)	S (%)	C (%)	(Ad/Al) _v	(Ad/Al) _s
<i>Rhizophora</i>	1	7.7	50	23	8	0.26	0.23
	13	4.5	47	25	15	0.42	0.35
	37	4.8	37	25	24	0.10	0.32
	158	4.5	53	31	6	0.31	0.29
<i>Laguncularia</i>	1	8.6	47	37	2	0.37	0.27
	25	4.7	53	36	2	0.63	0.59
	65	1.8	48	31	8	0.90	0.58
	178	3.8	50	34	4	0.30	0.28
<i>Acrostichum</i>	1	4.0	66	11	5	0.42	0.37
	13	4.5	78	11	3	0.48	0.27
	49	4.4	56	32	5	0.53	0.39
	102	2.3	65	20	5	0.55	0.44
	158	3.3	59	20	6	0.37	0.30
<i>Cladium</i>	1	4.0	35	30	8	0.33	0.37
	13	3.2	39	30	9	0.58	0.35
	41	1.8	27	22	20	0.54	0.43
	88	2.3	31	26	19	0.19	0.33
	133	10.0	59	32	3	0.47	0.45
<i>Pterocarpus</i>	1	3.3	46	33	7	0.38	0.38
	13	3.5	61	25	3	0.53	0.42
	49	1.8	53	29	6	0.78	0.58
	103	5.5	58	27	5	1.13	1.12
	143	2.9	58	21	10	1.20	1.00

Table 3.

Neutral carbohydrates depth distribution beneath the various mangrove swamps studied, i.e. *Rhizophora mangle*, *Laguncularia racemosa*, *Acrostichum aureum*, *Cladium marescus*, and *Pterocarpus officinalis*: total carbohydrates in mmol TCHO-C/100 mmol total OC; total ribose, total arabinose, total xylose, total rhamnose, total fucose, total glucose, total mannose, total galactose, hemicellulosic carbohydrates in % of total carbohydrates

Mangrove	Depth (cm)	Total carbohydrates (mmol TCHO-C/100 mmol TOC)	Total ribose (%)	Total arabinose (%)	Total xylose (%)	Total rhamnose (%)	Total fucose (%)	Total glucose (%)	Total mannose (%)	Total galactose (%)	Hemicellulosic carbohydrates (%)
<i>Rhizophora</i>	1	7.0	2	14	14	10	3	41	10	6	40
	13	7.0	2	16	15	9	5	36	10	7	27
	37	7.2	< 1	18	15	9	4	35	9	10	45
	95	7.0	< 1	17	14	8	4	40	8	9	–
	158	3.6	< 1	26	17	15	5	27	3	6	73
<i>Laguncularia</i>	1	7.5	< 1	18	8	5	6	40	10	11	27
	25	5.4	1	17	7	5	5	45	9	11	36
	65	2.1	1	17	7	7	3	42	13	9	47
	123	2.1	2	13	11	9	3	42	10	9	53
	178	3.9	1	19	10	10	5	36	8	11	58
<i>Acrostichum</i>	1	7.7	< 1	10	10	5	3	47	13	11	39
	13	5.3	< 1	11	8	7	4	40	15	15	40
	49	3.5	1	15	8	6	3	44	13	10	54
	102	2.1	1	10	7	3	4	57	12	6	27
	158	4.1	< 1	20	9	12	5	36	9	8	56
<i>Cladium</i>	1	8.8	1	10	12	5	4	40	13	15	63
	13	7.2	1	10	10	5	4	43	13	14	73
	41	6.9	1	8	11	4	3	51	11	11	60

Mangrove	Depth (cm)	Total carbohydrates (mmol TCHO-C/100 mmol TOC)	Total ribose (%)	Total arabinose (%)	Total xylose (%)	Total rhamnose (%)	Total fucose (%)	Total glucose (%)	Total mannose (%)	Total galactose (%)	Hemicellulosic carbohydrates (%)
	88	5.6	1	13	17	3	3	44	8	11	58
	133	5.5	< 1	12	15	4	3	45	8	12	60
<i>Pterocarpus</i>	1	5.5	< 1	15	8	5	4	44	9	13	41
	13	5.2	< 1	12	8	6	4	46	10	13	42
	49	3.3	2	20	6	7	4	37	11	12	65
	103	4.4	< 1	20	7	4	5	44	7	11	40
	143	3.7	< 1	18	6	5	5	50	7	9	51

