Highlights

- Py-GC-MS is used to study organic matter sources and degradation in sediments
- Organic matter in intertidal mangrove sediments is found predominantly terrigenous
- Unusual even-numbered *n*-alk-1-ene distribution is linked to mangrove leaf-waxes
- Vinylguaiacol was the dominant lignin unit detected in mangrove surface sediments
- Early diagenetic products of mangrove-derived lignin and triterpenoids are also found

Biomarkers as indicators of sedimentary organic matter sources and early diagenetic transformation of pentacyclic triterpenoids in a tropical mangrove ecosystem

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Abstract

Mangrove vegetation covers extensive areas along Brazilian tropical coasts and accumulates large amounts of organic carbon in the intertidal sediments. We have investigated the molecular biomarker composition of mangrove sediments from the Potengi estuary North-East Brazil. To characterise sources and fate of sedimentary organic matter (OM), a direct analytical pyrolysis approach was used. The sediment pyrolysates yielded homologous series of aliphatic compounds (*n*-alkane/*n*-alkene doublets, *n*-alkanoic acid and *n*-alkan-2-ones), triterpenoids and lignin-derived methoxyphenols, indicating that most of the sedimentary OM input originates from terrestrial vascular plants. High abundance of long-chain *n*-alk-1-ene series with an even carbon number predominance peaking at C_{28:1}—most likely originated from local mangrove vegetation—is found co-eluted with the saturated odd carbon *n*-alkane series. The occurrence of lignin and *n*-alkan-2-one biomarkers in the sediments has provided parallel information about the input from vascular plants dominating the intertidal zone. This was further corroborated by the presence of the triterpenols (β -amyrin, and germanicol), that provided chemotaxonomic information on mangrove derived leaf wax in sedimentary OM. The unsaturated triterpenoid including teraxerol acetate, olean-12-ene, olean-18-ene, oleana-11, 13(18)-diene, a-neoursa-3(5), 12-diene and aneooleana-3(5), 12-diene, were also observed in sediment pyrolysates. The presence of these unsaturated pentacyclic triterpenoids revealed an early diagenetic alteration of terrestrial OM in the sediments. This study has demonstrated that routine application of analytical pyrolysis may provide important insight into the sources of sedimentary OM and its diagenetic fate in mangrove intertidal sediments.

Keywords: Mangroves; estuary; pyrolysis; aliphatic lipids; methoxyphenols; triterpenoids

1. Introduction

Mangroves forests are mostly intertidal habitats that occur in the tropical and subtropical sheltered coastal environments. Due to their location at the interface between terrestrial and marine ecosystems, they are mainly sensitive to climate change, especially sea level rise, temperature change and rainfall (Alongi et al., 2008; Gilman et al., 2008). They are highly productive ecosystems, with the global net primary production estimated at $218 \pm 72 \text{ Tg C yr}^{-1}$ for a global area coverage estimated at $160,000 \text{ km}^2$ (Twilley et al., 1992; Bouillon et al., 2008a). Recent estimates by Breithaupt et al. (2012) indicate that the rate of organic carbon accumulation in mangrove ecosystems is ca. 26.1 Tg yr^{-1} . Estuarine and oceanic mangrove sediments are disproportionally rich in organic carbon when compared with terrestrial ecosystems. The below-ground carbon storage in estuarine soils is estimated to account for 49-98% of the total organic carbon stored in these ecosystems, including the above ground carbon (Donato et al., 2011). Mangrove forests are highly efficient C sinks and this stable organic carbon pool -preserved, especially in their soils and sediments- is part of the “blue carbon” that is efficiently captured by the world's ocean and coastal ecosystems (McLeod et al., 2011). Therefore, the coastal ecosystems are relevant for climate change mitigation and research towards gaining knowledge about carbon sources and evolution in mangrove sediments is of interest.

Despite their small area relative to other forest types, mangrove forests could account for 11% of the total input of terrestrial organic carbon into the ocean and 15% of the total carbon deposition in modern marine sediments (Jennerjahn and Ittekkot, 2002). It is estimated that mangroves contribute to ca. 10% of the terrestrial dissolved organic carbon (DOC) exported to the ocean globally (Dittmar et al., 2006). The preservation of OM not transported through tidal action in mangrove ecosystem is favoured by an anoxic environment and rapid sediment

178 accumulation (Woodroffe, 1992). On the other hand, the diagenesis of OM in mangrove
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180 sediments is considered to occur mainly due to the mixing of marine and freshwater,
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182 bioturbation, and sulfate-reducing respiration (Lallier-Vergès et al., 1998, Alongi et al., 1999;
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184 Kristensen et al., 2000).
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190 Knowledge of the sources of OM and diagenesis in intertidal sediments is crucial to get a
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192 better understanding of carbon cycling in mangrove habitats. Bulk stable isotope composition
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194 of organic carbon ($\delta^{13}\text{C}$) has been widely used to identify the contribution of mangrove-
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196 vegetation to estuarine sediments (e.g. Gonneea et al., 2004; Bouillon et al., 2008b).
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198 However, organic carbon $\delta^{13}\text{C}$ variation range is narrow, typically of only a few parts per mil,
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200 and overlapping values make difficult to discern precisely the origin OM or its evolution in
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202 estuarine sediments using stable C isotope composition alone. Biomass-specific biomarkers
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204 are more appropriate for studying ecosystems with complex OM inputs such as estuaries,
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206 despite limitations of biomarkers specificity for all major biomass components of an
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208 ecosystem (Mead et al., 2005). Therefore, it seems that a multi-proxy approach could be most
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210 appropriate for tracing the mangrove-derived organic matter to intertidal sediments (e.g Jaffe'
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212 et al. 2001; Ranjan et al., 2015).
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218 The objective of this study was to investigate the molecular distributions of natural product
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220 biomarkers along an intertidal mangrove transect covering mudflat and mangrove forest of
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222 different species from the Potengi estuary at the confluence of the Potengi, Jundiaí and Doce
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224 rivers (NE, Brazil). The study is performed without any extraction or sample treatment by
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226 direct analytical pyrolysis of the sediments. The main goals of the study were twofold: (1) to
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228 assess the natural sources of OM inputs yielded from direct pyrolysis of mangrove intertidal
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surface sediments from tropical estuary and (2) to assess sedimentary diagenesis of pentacyclic triterpenoids.

We have applied analytical pyrolysis- gas chromatography-mass spectrometry (Py-GC-MS) as a powerful tool for fingerprint of complex OM at a molecular level. Many studies have succeeded in identifying pyrolytic source indicators, revealing the origin and transformation of soil/sediments OM (Buurman et al., 2007; Kaal et al., 2008; Jiménez-Morillo et al., 2016). The technique provides several advantages over other methods since no previous treatments (extraction, purification, fractionation, derivatization) are needed, requires only a small amount of sample (less or a few mg), take short analytical time, and provides complementary information as regards wet chemical degradation methods (De la Rosa et al., 2012; Jiménez-Morillo et al., 2016). Few studies have used successfully Py-GC-MS technique to relate the biogeochemical signature of mangrove sediments (e.g. Ferreira et al., 2009; Kumar et al., 2018).

Here, the main lipid biomarkers (*n*-alkanes, *n*-alkanoic acids and *n*-alkan-2-ones), lignin-derived phenols, and triterpenoid biomarkers and their relative abundance are identified in intertidal mangrove sediments from the Potengi estuary, NE, Brazil. The study provide insight to the origin of sedimentary OM characterised at a molecular level and its fate in the studied mangrove-ecosystem. To the best of our knowledge, this study represents the first detailed assessment of OM sources based on multiproxy biomarkers of the Potengi estuary. It is also expected that this work contributes to a better general knowledge of the sources and evolution of mangrove's "Blue Carbon" that is effectively preserved in sediments.

2. Materials and methods

2.1. Study area description

The Potengi Estuary is situated in one of the largest embayments of the Brazilian North-Eastern coast, in the state of Rio Grande do Norte at the confluence of the Potengi, Jundiá and Doce rivers (Fig. 1). The three rivers drain a combined area of ca. 5000 km². Over its last 8 km, the main estuarine channel is 900 m wide (Boski et al., 2015). Owing to low freshwater discharge and the gentle gradient of the river bed, tidal influence extends some 30 km upstream of the Jundiá valley (Barbosa, 1983) and forms well-mixed conditions, with overall salinity oscillating between 29.5 and 34.5 PSU during the rainy and dry seasons respectively (De Miranda et al., 2005). The tides are semi-diurnal and tidal amplitude in the estuary is ca. 2.8 m (mesotidal regime) with current velocity approaching 1.0 m/s (Boski et al., 2015). The climate in the region is equatorial hot and humid (Koppens' As climate category) with most precipitation from February to July, the annual average temperature of 26.8 °C and annual precipitation varying from 1300 to about 2000 mm.

The main estuarine zone encompasses a mosaic of mangrove forest, shrimp ponds, mudflats, tidal creeks and channels. Mangroves cover an area of ca. 1488 ha (Souza and Ramos e Silva, 2011). The vegetation cover in the estuarine area consists predominantly of three species of mangrove; *Rhizophora mangle* (red mangrove) is the dominant vegetation in the area, constituting ca. 62% of the total forest cover and is found in close proximity to channel margins. *Avicennia germinans* (black mangrove, 17% of total forest cover) is present throughout the forest as scattered individuals, more towards the internal part of halophytic forest, and *Laguncularia racemosa* (white mangrove, 21% of the forested area) occurs in the highest positions above the maximum tides (Souza and Ramos e Silva, 2011).

Degradation of mangrove forest in the estuarine areas is of major concern and has occurred due to anthropogenic activities in the second half of the 20th century, especially through extensive shrimp farming, heavy metal pollution, and urban waste and sewage effluents from the adjacent three cities (Ramos e Silva et al., 2006). In addition, around 30% of the pre-existing mangrove forests in the estuarine zone have been destroyed over the last three decades (Souza and Ramos e Silva, 2011).

2.2. Site description and sampling strategy

Sampling locations were selected along a 500 m transect in the mangrove intertidal zone from Potengi estuary NE, Brazil (Fig. 1). The study area is situated in the central part of the Potengi mangrove forest. Eight composite samples of surface sediment were collected from the mangrove swamps in the estuary during June-July 2015. Each sample was made up by combining four sub-samples taken within a circular area of ca. 20m². After litter layer removal, top 15 cm were sampled and transported to the laboratory in glass containers.

The sampling sites are referred to as P1, P 2, P3, P4, P5, P6, P7 and P8 (Fig. 1) and were collected to represent the full range of conditions in terms of tidal inundation and vegetation cover. This included: intertidal mudflats, banks of tidal creeks, solitary *Rhizophora mangle* trees, a cluster of mangrove plants (Hammock mangrove) and mangrove-covered pristine areas including *R. mangle* and *Avicennia germinans* species in the estuary, representing all input routes for organic matter and associated spatial variability in the intertidal zone. The geographical location and description of the sediments studied are presented in Table 1.

Although, the number of sediments analysed in this study was not sufficient to cover all parts of the estuary, these included the tidal inundation conditions and vegetation cover and were

considered adequate to distinguish the major aspect of the recent estuarine sedimentary deposits and to test the effectiveness of the multiproxy approach.

2.3. Sediment analyses

2.3.1. pH and electrical conductivity

In the laboratory the sediment samples were lyophilized, crushed and grounded. The pH and electrical conductivity were measured in sediment extracts with deionized water (1:2.5 sediment to water ratio) (Kumar et al., 2018) and readings obtained with a GLP 22 Crison pH meter calibrated before the measurements with commercially prepared buffer solutions of pH 4.00, 7.00 and 10.00. Similarly, electrical conductivity (EC) readings were obtained using a conductivity meter EC-Meter BASIC 30 +.

2.3.2. Analytical pyrolysis (Py-GC-MS)

A double-shot Frontier Laboratories pyrolyser (model 2020i, Fukushima, Japan), directly connected to an Agilent 6890 GC-MS system (Agilent, Santa Clara, CA) was used. Sample aliquots (ca. 10mg) were weighed on a precision balance and placed in crucible capsules. The prepared samples were then introduced into a preheated micro-furnace at 500°C for 1 min. The evolved gases were directly injected, separated and their components identified in the GC-MS system equipped with a DB-5 fused silica column (30 m × 0.25 µm i.d., 250 µm film thickness; J&W Scientific). The oven temperature was programmed as follows: 50 °C for 1 min and then increased to 100 °C at 30 °C min⁻¹, from 100 °C to 300 °C at 10 °C min⁻¹ and stabilized at 300 °C for 10 min. The carrier gas was He at a constant rate of 1 ml min⁻¹. The detector was a mass selective detector Agilent 5973, and the mass spectra acquired with 70 eV ionising energy. Finally, assignment of pyrolysis compounds was done from selected ion

monitoring (SIM), mass spectra comparison with published data and compound libraries (NIST and Wiley).

2.3.3. *n*-Alkanes indices

From the relative abundances of *n*-alkanes determined as chromatographic areas, a number of molecular proxies were inferred.

Average chain length (ACL) is the weighted average of carbon chain lengths calculated for the long *n*-alkane range detected (C₂₅₋₃₇) as:

$$ACL = \Sigma (n \times Cn)_{25-37} / \Sigma (Cn)_{25-37}$$

Chain length ratio (short/long) (S/L) was calculated according to:

$$S/L = \Sigma (Cn)_{10-23} / \Sigma (Cn)_{24-37}$$

where *n* is the number of carbons and [Cn] the relative abundance of each alkane.

Carbon preference index (CPI) is an estimation of the relative abundance of odd/even chain numbers. It is a marker of the *n*-alkane source in soil/sediments; values > 1 means that odd C chain numbers prevail over even C chain numbers and organic matter input to the soil/sediment is of plant origin; values < 1 means bacterial, algal and degraded organic matter input to the soil/sediments (Bray and Evans, 1961). However, petrochemical derived *n*-alkanes also show usually no predominance of odd over even chains and CPI values close to unity (Aboul-Kassim and Simoneit, 1996). Here the CPI was calculated for *n*-alkanes in the range from 24 to 37 carbons as follows:

$$CPI_{(24-37)} = [\Sigma (Cn \text{ odd})_{25-37} / \Sigma (Cn \text{ even})_{24-34} + \Sigma (Cn \text{ odd})_{25-37} / \Sigma (Cn \text{ even})_{26-36}] / 2$$

where [Cn odd] is the hydrocarbon abundance with odd-numbered chains and [Cn even] the hydrocarbon abundance with even-numbered chains (Duan and He, 2011; Jiménez-Morillo et al., 2016).

Terrigenous/aquatic ratio (TAR) for *n*-alkanes is an index initially proposed by Bourbonniere and Meyers (1996) to distinguish the relative contributions between land plants and algal inputs.

$$\text{TAR} = (C_{27} + C_{29} + C_{31}) / (C_{15} + C_{17} + C_{19})$$

Paq proxy was defined by Ficken et al. (2000) and is based on the proportions of aquatic macrophyte vs. emergent and terrestrial plant inputs to lacustrine sediments and is calculated using the equation:

$$\text{Paq} = (C_{23} + C_{25}) / (C_{23} + C_{25} + C_{29} + C_{31})$$

Other geochemical proxy to reflect the relative proportion of *n*-alkane is that comparing hydrocarbons derived from herbaceous (H) vs woody (W) plants as described in Zhang et al. (2008):

$$\text{H/W} = C_{31} / (C_{27} + C_{29} + C_{31})$$

Other indexes calculated from the distribution of waxy hydrocarbons and that may give an idea of terrestrial vs aquatic contribution to the sediments were ratios C_{31}/C_{17} and C_{27}/C_{17} for grass and woody plants vs aquatic respectively (Moldowan et al., 1985).

3. Results

3.1. Physicochemical parameters of sediments

The pH and conductivity values of the mangrove intertidal sediments are summarized in Table 2. The pH for the sediments ranged from 5.81 to 8.27. Out of the 8 sites, 5 had alkaline pH values, while the remaining 3 were acidic. Sediment electrical conductivity ranged from 5.05 to 9.59 $\mu\text{S}/\text{cm}$.

3.2. Homologous aliphatic lipids biomarker composition and distributions

3.2.1. *n*-Alkane molecular distribution and indices

The total current ion chromatograms resulting from the direct pyrolysis of sediments can be found in Sup. Fig. 1. The pyrograms were dominated by series of *n*-alkane/*n*-alk-1-ene doublets, that seem to be a major constituent of sedimentary SOM. At a first sight, the chromatograms for most samples exhibited an unusual strong even-to-odd predominance in the long chain *n*-alkane series with apparent $C_{\max}$ at C_{24} , C_{28} or C_{30} , but for sediment samples P5 and P8 that displayed the conventional *n*-alkane odd-to-even predominance peaking at C_{31} and C_{29} respectively, but both with a high abundance of C_{28} alkyl chains (Sup. Fig. 2). A more careful examination of the chromatograms and the analysis of single ion current chromatograms for specific molecular fragments for *n*-alkane and *n*-alk-1-ene moieties (ions m/z 57 and 55 respectively), revealed the occurrence of coelution of long chain alkyl structures and the presence of high amounts of unsaturated chains that were partly disguising the real abundance of *n*-alkanes (Sup. Fig. 3). Therefore, to show the distributions of *n*-alkanes more clearly, the relative abundance for each sample is presented in the form of histograms prepared from single current ion chromatograms for fragment m/z 57 ($\text{CH}_3\text{-(CH}_2\text{)}_3\text{-}$) (Fig. 2). The different geochemical indexes calculated from the *n*-alkane relative abundances are listed in Table 2.

Well resolved *n*-alkane series were present in all the samples, with a tri- or bi-modal distribution of homologous series and ranging from C_{10} to C_{37} . This points to organic matter contributions from multiple sources. No clear carbon number predominance was found in the short chain range ($< C_{20}$) peaking ($C_{\max}$) in the range $C_{12}\text{-}C_{15}$. The *n*-alkane carbon preference index ($\text{CPI}_{(25-37)}$) calculated for all sediment samples varied from 0.87 to 1.47 and average chain length ($\text{ACL}_{(25-37)}$) from 27.16 to 31.38 (Table 2).

3.2.2. Fatty acid and fatty acid methyl esters (FAMES) molecular distribution

An example for the fatty acid and FAME distribution released after the direct pyrolysis of the sediments is depicted in Fig.3. The fatty acid series consisted mainly of saturated species and exhibit a unimodal distribution with maxima at the C₁₆ homologue and the typical strong even-over-odd carbon number predominance in chain length ranging from C₈ to C₁₈ (Fig. 3A). Fatty acid methyl esters, were also identified in the sedimentary OM but with a different distribution to that of fatty acids and ranging from C₁₄-C₃₂ with bimodal distribution peaking at C₁₆ and C₂₈. (Fig. 3B).

3.2.3. *n*-Alkan-2-ones (2-methyl ketones) molecular distribution

A series of *n*-alkan-2-ones was only found in the pyrolysed of sediment sample P5. This was a well resolved homologue series with bimodal distribution in the range C₁₅ to C₃₃, maxima at C₂₀ and C₃₁ and a strong predominance of odd chain-lengths in the long chain range (Fig. 4).

3.3.4. Lignin-derived phenols

The main methoxyphenols lignin units identified in the sediment samples includes both 2-methoxyphenol (guaiacol “G”) and 2, 6-dimethoxyphenol (syringol “S”) type lignin. An example of the lignin signature found in the sediments is shown in Fig.5 as overlaid mass chromatograms *m/z* 124+138+152+150+164+166 for the G-lignin-derived pyrolysis products and overlaid mass chromatograms *m/z* 154+168+182+180+194+196 for the S-lignin products. A semi-quantitative assessment of both guaiacyl and syringyl main derivatives are presented in Table 3. The relative abundance of guaiacol derivatives were found comparatively more abundant than the syringol derivatives in all sediment samples.

3.3.5. Pentacyclic triterpenoids

Alcohols, acetate and unsaturated terpenoids, which are typically found in higher plants were also found in the sediments. An example pyrogram for sample P5 is depicted in Fig. 6 and in more detail in the supplementary data (Sup. Fig. 5). The most abundant pentacyclic triterpenoids identified in the sediments were taraxerol acetate (D: Friedoolean-14-en-3 β -yl acetate) (d), germanicol (olean-18-en-3 β -ol) (f) and β -amyrin (olean-12-en-3 β -ol) (n). Other homologues found included unsaturated triterpenes with one or two double bonds like olean-12-ene (o), olean-18-ene (e), oleana-11, 13(18)-diene (T₂) a-neoursa-3(5), 12-diene (T₃) and a-neooleana-3(5), 12-diene (T₄).

4. Discussion

The aim of the present study was on the sources and cycling of natural product biomarkers deposited in surface sediment of the mangrove ecosystem. For that reason, anthropogenic sources of OM and biomarkers will not be discussed here.

4.1. Sediments pH and conductivity variation

The pH and conductivity values of the mangrove intertidal sediments are summarized in Table 2. The more acidic pH values recorded in this study are thought to be mainly due to the release of organic acids upon decomposition of OM (mangrove litter) (Tam et al., 1995) and also may be attributed to the oxidation of pyrite (FeS₂ and FeS) minerals promoted by the release of O₂ from mangrove plant pneumatophores, especially in surface layers (Marchand et al., 2003). On the other hand, alkaline pH value of the sediments are due to the buffering by CaCO₃ in the form of foraminifera carapaces (Boski et al., 2015), which readily dissolve during the preparation of suspensions and regular input of seawater of basic pH (pH>8). Among sampling sites, an increasing salinity is observed from South (6.6 μ S/cm) to North

(9.4 $\mu\text{S}/\text{cm}$) (Samples P1-P5), whereas conductivity remained more or less constant at $6.0 \pm 0.6 \mu\text{S}/\text{cm}$ in transect West to East (Samples P5-P8).

4.2. Aliphatic lipid biomarkers and source assignments of sedimentary OM

4.2.1. Sources of *n*-alkanes in sediment

The occurrence of long chain *n*-alkanes in the range C_{23} to C_{35} with an odd-chain carbon number predominance is attributed to epicuticular wax from terrestrial vascular plants (Eglinton and Hamilton, 1967) and this distribution has been also found for soils and sediments under mangrove (Canuel et al., 1997; Mead et al., 2005; Belligotti et al., 2007). On the other hand, unusual even over odd carbon number predominance peaking at the C_{28} hydrocarbon has been found in the epicuticular waxes of mangrove leaves from Guyana and also in mangrove sediments (Rafii et al., 1996; Dodd et al., 1998), however this is a controversial issue. High abundance of monounsaturated alkane (alkene) series with even carbon number predominance and peaking at $\text{C}_{28:1}$ been also found in estuarine plants and sediments (Canuel et al., 1997; Hernandez et al., 2001; Jaffé et al., 2001), to the point that this $\text{C}_{28:1}$ alkene can be considered a specific biomarker surrogated to mangrove environments. Microbial mediated reductions of these alkenes can occur in the sediments producing the corresponding *n*-alkanes (Jaffé et al., 2001). Also, Belligotti et al (2007) noticed that although *R. Mangle* epicuticular *n*-alkane distribution was similar to that of other species -the typical odd over even chain length predominance- indicated that the identification requires more analytical care due to the co-elution of branched and / or unsaturated compounds. For both abovementioned effects -a microbial mediated conversion of alkenes or the occurrence of co-elution- the final result would be a reduction of *n*-alkane CPI values to unrealistic values, as well as a bias towards an even/odd carbon number

predominance of *n*-alkane distributions, like that reported for several coastal environments elsewhere (e.g. Nishimura and Baker, 1986; Kennicutt and Brooks, 1990).

For this study, and considering that we are probably at the edge of our instrument resolution, after a careful observation and re-examination of the pyrograms, we observed a co-elution for the alkane/alkene doublets (Sup. Fig. 3). These are well resolved and separated at low retention times and progressively co-elute more or less up to the C₂₈ alkane. Therefore, under our chromatographic conditions, we confirm the predominance of the C_{18:1} alkene and the occurrence of co-elution of long chain alkanes in the pyrolysis of sediments; the mass spectra for the major peak (ret time = 21.57 min) corresponded to the C_{18:1} alkene 1-octacosene (*m/z* 392), whereas that at 21.59 min corresponded with the *n*-alkane C₂₈ octacosane, with a consistent loss of -CH₂ fragments (*m/z* 14) and a clear molecular ion at *m/z* 394.

With respect to the short chain *n*-alkanes (C₁₀-C₂₀), even-numbered molecules may reflect a reduction of fatty acids (and alcohols) under anoxic conditions (Dastillung and Corbet, 1978). On the contrary, oxidative decarboxylation of fatty acids under oxic environments would also result in the formation of predominantly odd-numbered hydrocarbons (Guoqing et al., 1980). Surface sediments in a mangrove intertidal zone have little chance to develop anoxic conditions because mangrove roots diffuse oxygen into the rhizosphere, increasing redox potential in the sediment (Koch, 1997). Moreover, processes like periodically sediment drying out or aeration by bioturbating-fauna, further limit the anoxia. In this regard, a reduction of biogenic even-numbered fatty acids / alcohols into hydrocarbons is not feasible. In highly saline, carbonate environments, fatty acids (including short- and long-chain acids) may be more sensitive to degradation and modification and can be converted to *n*-alkanes (Shimoyama and Johns, 1972). Gobe et al. (2000) used pyrolysis and thermochemolysis

techniques to investigate a series of *n*-alkane/*n*-alk-1-ene doublets, ranging from C₁₆ to C₃₆ with even-numbered predominance found in an acid soil sample (anmoor soil). The authors suggested that this even C numbered hydrocarbon series probably derived from fatty acid or alcohol reduction. However, the short/mid chain *n*-alkane (C₁₄-C₁₈) distribution found in our study does not resembles that of the fatty acids /FAMES in chain length (Fig. 3A and B). Therefore, the high relative abundance of short chain homologues (C₁₀ to C₂₀) without a noticeable carbon preference most likely reflects a highly reworked autochthonous organic matter contribution (Grimalt et al., 1988) or, alternatively, an input from fossil fuel (Jaffe et al., 2001).

The high relative abundance of mid chain *n*-alkanes (particularly C₂₁ and C₂₄ homologues) recorded in many sediment samples, points to the input from marine macrophytes (Cranwell, 1984; Ficken et al., 2000).

No clear carbon number predominance was found in the short chain range (< C₂₀) peaking (C_{max}) in the range C₁₂-C₁₅. For most samples, long chain *n*-alkanes exhibited the usual odd-to- even predominance (CPI₍₂₅₋₃₁₎ > 1) with C_{max} at C₂₅, C₂₉ or C₃₁ (Fig. 2). Values of CPI >1 indicate that they are predominantly of plant origin (Eglinton et al., 1962), while low values <1 indicate the prevalence of low molecular weight *n*-alkanes derived from phytoplankton, algae, bacteria, fungi and/or contamination with petroleum (Kennicutt et al., 1987; Saliot et al., 1988). Microbial degradation and diagenesis of OM is slow under cold and dry climatic conditions, which lead to high CPI values because soil OM is usually well-preserved (Kuder and Krueger, 1998; Xie et al., 2004). Likewise, low CPI values may also result from rapid microbial degradation and diagenesis of soil OM, which is likely to occur under a warm and wet climate.

There was no systematic trend in ACL in the Potengi samples for long chain alkanes (C₂₅-C₃₇); site P5 (within the pneumatophoric root system of *Rhizophora mangle*) yielded the highest value of 31.38, indicative of a predominantly vascular plant input, while at other sites, point to a stronger marine influence, which was also evident in the greater contribution of shorter chain *n*-alkanes. Thus, the ACL value found is probably linked to source vegetation indicating mixed coastal/terrestrial input of OM in the surficial sediments. Terrestrial plant (C3) leaf wax components normally exhibit a C_{max} at C₂₇ and therefore tend towards lower ACL values, while grasses (C4) have C_{max} at C₃₁ and thus tends to higher ACL values (Rommerskirchen et al., 2006). It has also been found that ACL values are related to temperature and humidity and point to diverse biosynthetic pathways of *n*-alkanes under different climate conditions (Rommerskirchen et al., 2003; Bush and McInerney, 2015). Vascular land plants in warm climates tend to biosynthesise longer chain *n*-alkane wax coatings (Gagosian and Peltzer, 1986) compared with those in a cold climate (Schefus et al., 2003). Zhou et al. (2005) suggested that regional pluviosity can also influence the *n*-alkane chain length distribution in leaf wax. Furthermore, the modal carbon number of higher plant *n*-alkane distribution is broadly related to latitude (Poynter and Eglinton, 1990), with higher modal carbon numbers occurring at lower latitudes. Our findings for ACL calculated for long chain molecules (C₂₅-C₃₇) ranged between 27.16 and 31.38 with average in 28.23±1.37. These results are in line with previous findings from mangrove biomass in equivalent warm climates like in Belligotti et al. (2007) for leaves of *R. mangle*, *A. schaueriana* and *L. racemosa*, collected in Sepetiba and Guanabara bays (Rio de Janeiro, Brazil). The authors also suggested that this ACL proxy could be a useful tool for biogeochemical, eco-physiological and palaeoceanography studies in coastal environments.

Complex intertidal estuarine aquatic systems receive significant soil OM contribution from mangrove vegetation, marine macrophyte and riparian aquatic inputs. Soil OM input assessments beyond the terrestrial and microbial end members are therefore needed. We also examined the SOM contribution from aquatic macrophytes using the *Paq* proxy. This proxy is based on the fact that submerged/floating species have abundant mid chain length *n*-alkanes (C_{23} and C_{25}) while in emergent macrophytes and terrestrial plant vegetation C_{29} and C_{31} *n*-alkanes prevail (Ficken et al., 2000). As seen in Table 2, *Paq* values between 0.28 and 0.74 were observed in sediments from the Potengi Estuary. The *n*-alkanes at site P5 showed the lowest *Paq* value, suggesting that this site has a clear input from the mangrove vegetation (Mead et al., 2005). On the other side, sites P1 & P7 with the highest *Paq* value of 0.74 & 0.71 respectively, indicate an input from submerged/floating macrophytes. The sediments of the other sites (P2, P3, P4, P6 and P8) exhibited mid *Paq* values in the range 0.51-0.66, indicating that these sites are mainly influenced by inputs from the mangrove vegetation with some contributions from other submerged and floating-leaved species with enhanced abundances of mid-chain length, C_{23} and C_{25} *n*-alkanes. The *Paq* index (also known as *Pmar-aq*) has been previously used to study coastal SOM in a subtropical estuary (Hauraki Gulf, northern New Zealand) dominated by *Avicenna marina* mangrove forest (Sikes et al., 2009). The authors also found that low *Paq* values (0.01- 0.25) were indicative of OM mainly from a terrigenous input, mid values (0.4-0.6) from emergent aquatic plants including mangroves, and high values (> 0.6) from aquatic plants and marine macrophytes.

The TAR values for all sampling sites are presented in Table 2. The maximum value (> 2.0) was found for P5, indicating that an arboreal (terrestrial) input was predominant, while low values at the other sites (< 1.0) suggest a lesser contribution from a terrigenous input and increased marine influence. According to this index, a terrigenous contribution was relatively

abundant, resulting from sediments transported into the intertidal zone in quantities more or less proportional to the distance from the source.

The H/W ratio represents the autochthonous molecular fossil between grass and woody plant and values are listed in Table 2. Higher values (c. 0.5) indicating preferential contributions from grass biomass were found for samples P5 and P3 and lower values (<0.2) for P7 and P4 pointing to contributions from woody biomass. No clear trends were found in the transects studied.

The C_{31}/C_{17} or C_{31}/C_{19} ratios can serve as a measure of the relative proportions of allochthonous and autochthonous inputs in sedimentary environments. Higher values are thought to be indicative of a non-marine sources, whereas lower values indicate a predominance of different marine biogenic sources (Moldowan et al., 1985; Gonzalez Vila et al., 2003). Sites P2, P3, P6 and again P1 and P7 exhibited low values for ratios C_{31}/C_{17} or C_{31}/C_{19} indicating probable marine contributions to sedimentary OM.

4.2.2. Source assignments of sedimentary OM based on fatty acid distribution

Fatty acids chain lengths and carbon number predominance vary as a function of their source; therefore, fatty acids have been used as biomarkers surrogate to OM origin. It is known that pyrolysis has major limitations in the detection of *n*-alkanoic acid due to two main reasons: i) incompatibility with the apolar columns used in GC and ii) secondary reactions, which may occur at high temperatures (Dignac et al., 2006). However, in the Potengi samples we found well resolved and comprehensive series of fatty acids ranging from C_8 to C_{18} , with the typical strong even-over-odd carbon number predominance in mid chain length molecules (C_{14} - C_{18}) (Fig. 3A). This indicate that, under the experimental conditions used here, known pyrolysis

drawbacks are not limiting the study of lipids in sediments. Generally, short-chain *n*-fatty acids ($> C_{20}$) derived from algae and bacteria (Matsuda, 1978; Cranwell, 1984) but palmitic acid (C_{16}) is ubiquitous in nature and is found in terrestrial plants, algae, bacteria and other microorganisms (Meyers, 1997). The relative high abundance of fatty acid C_{16} found here in all sediment samples may result directly from mangrove leaves, which are known to be enriched in C_{16} *n*-fatty acid (Mfilinge et al., 2003).

Apart from multiple possible source inputs to sediment, we believe that the most likely source for the fatty acids could be derived from the oxidation of lipids from vegetation (Amblès et al., 1994). The low soil pH in mangrove sediments further promote the formation of fatty acids. Nonetheless, Potengi estuary is adjacent to Natal City and large quantities of industrial wastewater and municipal sewage is discharged into the estuary that can bring C_{16} and C_{18} fatty acids to coastal areas and add them to the natural OM pool (Quemeneur and Marty, 1992). The source of short chain fatty acid detected (C_8 - C_{12}) is more difficult to attribute, because they are widely found in multiple sources, including algae, higher plants, bacteria and fungi (Meyers and Ishiwatari, 1993). Besides, fatty acids are prone to degradation in coastal /marine sediments owing to their labile characteristics of rapid loss through bacterial degradation and zooplankton grazing (Cranwell, 1984; Carrie et al., 1998).

Fatty acid methyl esters ranging from C_{14} - C_{32} , were also identified in the sedimentary OM, with a bimodal distribution and maxima at C_{16} and C_{28} (Fig. 3B) and distinct distribution to that of fatty acids. We believe that this distribution reflects a double origin; samples having FAME chains larger than C_{24} suggest a high terrestrial input to sediments, while, FAME series peaking at C_{16} and C_{18} are attributed to microbial/ algal inputs (Grasset et al., 2002).

4.2.3. Alkan-2-ones as natural product biomarker

A conspicuous series of alkyl ketones was only found in sample P5 (Fig. 4). The homologue series had a bimodal distribution in the range C₁₅ to C₃₃, with maxima at C₂₀ and C₃₁. The *n*-alkane- 2-ones are common lipid components in estuarine sedimentary environments (e.g., Gonzalez Vila et al., 2003; Xu et al., 2006). Our long chain *n*-alkane- 2-ones series, characterized by high odd-to-even predominance and dominant peaks at C₃₁ and C₂₉, are very similar to that depicted in Hernandez et al. (2001) for *Rhizophora mangle* samples from the Everglades National Park (Florida, USA). This distribution suggests that the long chain homologues at site P5 originate mainly from the standing red mangle, while the other sites were also influenced by marine or microbial inputs. Similar distributions have been reported in many terrestrial and aquatic depositional environments (Jaffe et al., 1995; Hernandez et al., 2001) and particularly high relative abundance of C₃₁ has also been previously reported in mangrove plant biomass (Mead et al., 2005; Xu et al., 2006). The *n* -alkan-2-one distribution in aquatic sediments has usually been interpreted as a product of post- depositional modifications from original precursors (Cranwell et al., 1987; Hernandez et al., 2001). The long chain *n*-alkanes molecular distribution found in sediment sample P5 resembles that for *n*-alkan-2-ones pointing to a probable origin from microbial mediated α -oxidation of *n*-alkanes rather than from β -oxidation and decarboxylation of *n*-alkanoic acids (Cranwell et al., 1987). Nonetheless, *n*-Alkan-2-ones from C₁₅ to C₃₃; with an odd-to-even carbon number predominance has been reported in organic aerosols (Gogou et al., 1996; Oros and Semoneit, 2001). Thus, atmospheric fallout could be another source of *n*-alkan-2-ones in sediments.

4.3. Lignin-derived phenols

Lignin is an unambiguous molecular tracer for terrigenous OM (Hedges and Mann, 1979) and has been widely used to trace the transport and fate of terrigenous organic matter in the

mangrove sediments (Dittmar and Lara, 2001; Lallier-Vergès et al., 2008; Kumar et al., 2018). Lignin in hardwoods is composed of syringyl (S) and guaicyl (G) units in varying ratios whereas in softwoods and grasses is composed of mostly guaiacyl (G) units and small amounts of p-hydroxyphenyl (H) units. In all sediment samples G units prevailed over S units. However, the presence of S units in all sediment samples suggests OM inputs from hardwood species (Hedges and Mann, 1979; Obst, 1982). The most abundant methoxyphenol unit in all sediment pyrolysates was 4-vinylguaiacol (VG) (Table 3), which is derived from cinnamic units and considered as markers of lignin from monocotyledon herbaceous plants (Saiz-Jimenez and De Leeuw, 1986), although this could be also originating from aquatic plants spores (Nierop et al., 2011) and higher plants pollen grains (Hu et al., 1999). Pollen grains from red mangrove are highly resistant to microbial degradation and remains preserved in sedimentary OM for long time (Versteegh et al., 2004) being a relevant lignin contributor to mangrove sediments. Although possible, pollen as source of VG to mangrove sediments can't be discarded but needs to be analytically explored.

The methoxyphenols composition recorded in this study is consistent with previous reports from soil organic matter extracted under different vegetation types from a Brazilian mangrove (Pai Matos Island, São Paulo State) using Py-GC/MS techniques (Ferreira et al., 2009). Studies using alkaline CuO oxidation method for the molecular characterization of lignin-derived phenols from sediment of a North Brazilian mangrove ecosystem, indicated that *Rhizophora* mangle leaves are characterised by high cinnamyl phenol and low content in vanillic units (Dittmar and Lara, 2001). However, other studies reported that lignin-derived phenols in *Rhizophora* and *Laguncularia* leaves have a balanced proportion of the 4 phenol units (i.e. syringic, vanillic, cinnamic and p-hydroxy-benzylic), and a dominance of syringic and vanillic units in wood (Lallier-Vergès et al., 2008).

Other lignin derived pyrolysis products such as vanillin, vanillic acid, and the catecols (1, 2-benzenediol) were also identified in the sediments (Sup. Fig. 4). These indicate the presence of biodegraded lignins (Saiz-Jimenez and de Leeuw, 1984; Hedges et al., 1988). However, catechol can be also ascribed as pyrolysis products of tannins (Galletti and Reeves, 1992) and has also been reported in *Rhizophora* spp. (Ferreira et al., 2009).

The sediment samples revealed higher relative abundance of guaiacols than syringols (Table 3) and this feature is characteristic of lignin degradation in aerobic soils (Chefetz et al., 2002; Nierop et al., 2005). Lignin degradation under sulfate-reducing conditions is slower (Dittmar and Lara, 2001) and shows large preservation potential under anoxic conditions (Benner et al., 1984). Although, lignin decomposition under anaerobic conditions may occur due to microbial degradation (Marchand et al., 2005). In Potengi estuary, mangrove sediments within a few centimeters of the sediment-water interface were clearly aerobic whereas deeper layers below the surficial aeration zone have anoxic condition. The probable process of lignin decomposition in is that for suboxic conditions. Intertidal mangrove sediment may be oxygenated by *Avicennia* species because of their extensive radial cable roots with pneumatophores, which create a pathway for the oxygen exchange between atmosphere and sediment. Moreover, bioturbation by crabs may also contribute to oxygen gas exchanges between atmosphere and sediment (Marchand et al., 2003).

4.4. Pentacyclic triterpenoids and early diagenetic transformation products

Pentacyclic triterpenoids are widespread in terrestrial higher plants and their occurrence has been reported in several marine sediments (e.g. Brassell and Eglinton, 1983; Volkman et al., 1987). Studies across the world have shown that triterpenoids are efficient biomarkers for

identifying the source of the organic matter in sediments derived from mangrove forests (Killops and Frewin, 1994; Koch et al., 2005, Ranjan et al., 2015). Taraxerol, β -amyrin and germanicol are the main triterpenoids found in the leaves of *R. mangle* (Killops and Frewin, 1994). Taraxerol has been reported in surface sediments from the Camamu Bay, NE Brazil (Carreira et al., 2016) and also from the Rio Caete estuary (Para, N Brazil) dominated by fringe mangrove forests (Koch et al., 2003, 2005, 2011). Taraxerol, germanicol and β -amyrin in combination, provided relevant chemotaxonomical information for OM from *R. mangle* in northern Brazil (Koch et al., 2005). In contrast, *A. germinans*, which occurs in the upper intertidal zone, contains mainly betulin, lupeol and the phytosterol sitosterol. The former two have also been reported in *L. racemosa* from the supratidal environment (Koch et al., 2003; 2011). These three-arboreal species are dominant in the mangrove forest of the Potengi Estuary (Souza and Ramos e Silva, 2011). The interpretation of these taxa as the major source of germanicol and β -amyrin in the sediments is in agreement with other findings from mangrove ecosystems in Brazil (Koch et al., 2005, 2011).

Regardless of the known high stability of triterpenols in sediments, these are subject to degradation producing a variety of degraded components that retain significant features of their structure or stereochemistry that permit the recognition of their biological origins (Brassell et al., 1983). Degradation products of pentacyclic triterpenols i.e. 3-oxytriterpenols were detected in sediments by Jaffe et al., 1996. Many studies have focused in the early diagenetic products of taraxerol in mangrove sediments to establish relationship linking the precursor triterpenoids and the diagenetic transformation products like taraxerone (Killops and Frewin, 1994; Medeiros and Simoneit, 2008; Pisani et al., 2013; He et al., 2018). Thus, taraxerol as a sole quantitative marker for mangrove plants has been questioned by many studies (e.g. Versteegh et al., 2004, Boot et al., 2006). Although taraxerol was not found in

our study, taraxerol acetate (m) was found in all sediment samples (Fig. 6 and Sup. Fig. 5).

This compound is thought to be produced by the diagenetic alteration of taraxerol. Thus, our finding suggests that taraxerol is degraded in the Potengi estuary yielding the acetate derivative that is therefore an indicator of *Rhizophora mangle* species.

Other unsaturated triterpenoids with one or two double bonds recorded in this study were olean-12-ene (o), olean-18-ene (e), oleana-11, 13(18)-diene (T₁), a-neoursa-3(5), 12-diene (T₃) and a-neooleana-3(5), 12-diene(T₄) (Fig. 6 and Sup. Fig. 5), are considered as early diagenetic intermediates, which points to rapid diagenetic transformation of mangrove-derived triterpenoids in the sediments (He et al., 2018). Olean-12-ene (o) is an early diagenesis product of β -amyrin (n) (Ten Haven and Rullkotter, 1988) and its presence in the sediments indicates that mangrove-derived organic matter is probably at an early stage of diagenetic transformation (Neto et al., 2006). Dehydration of higher plant triterpenes gives triterpene dienes, also indicative of early stages of diagenesis, as observed in buried mangroves and modern marine sediments (Ten Haven et al., 1992a, b). The unsaturated triterpenoids recorded in this study, provide a better understanding of the diagenetic fate of mangrove derived triterpenoids in Potengi estuary recent sediments. Moreover, many studies have widely observed diagenetic alteration products of mangrove-derived triterpenoids in sediments from other mangrove ecosystems in Brazil (e.g. Koch et al., 2003, Koch et al., 2005, Boot et al., 2006).

5. Conclusions

The sedimentary OM accumulated in the intertidal zone of Potengi estuary is found mainly formed from autochthonous sources. The presence of aliphatic lipid biomarkers such as *n*-alkanes, *n*-alka-2-ones, fatty acids, and triterpenoids, supports the substantial input of OM to

the surface sediments from terrestrial vascular plants and mangrove vegetation in particular. This was clearly marked by an unusual high abundance of long-chain *n*-alk-1-ene series ($C_{24:1}$ - $C_{30:1}$) with an even carbon number predominance and normally peaking at $C_{28:1}$. In this aspect our findings are in line with those reported by Reddy et al. (2000) and Belligotti et al. (2007) in that previously reported unusual CPI values in mangrove sediments may be caused by the co-elution of olefins and other unsaturated hydrocarbons. Moreover, the presence of triterpenoids (germanicol and β -amyrins), in combination with the diagenetic product (taraxerol acetate) also corroborates major contribution of OM from mangroves to the sediment. More recalcitrant component of sedimentary OM (lignin and pentacyclic triterpenoids) were found in degraded state in the surface sediments. The presence of catechol's, vanillin and vanillic acid in the sediment pyrolysates pointed out to degraded lignin. Early diagenetic degradation products of pentacyclic triterpenoids, including mono- and di-unsaturated triterpenes, and taraxerol acetate reflected terrestrial OM degradation through oxidation, photochemical reactions and/or microbial process. The fluvial discharge of terrestrial OM to the estuarine zone by rivers Potengi, Jundiaí and Doce is probably responsible for the deposition of the remaining terrestrial OM. Further studies of the suspended particulate material and sedimentary OM from upper catchment of the Potengi estuary, are needed to study degradation process in a greater detail. This study also demonstrated that Py-GC-MS technique can provide rapid and detailed fingerprinting for unraveling complex sedimentary OM macromolecular structure in diverse intertidal with potential applications for the recognition of sediment degradation processes and monitoring of carbon cycling in mangrove intertidal sediments.

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Table captions

Table 1. Description of surface samples collected in a transect covering mangrove vegetation's and mudflat from Potengi Estuary, North-East Brazil.

Table 2. Physical parameters (pH & Conductivity) and biogeochemical indexes calculated from the *n*-alkane series.

Table 3. Semi quantitative assessment of lignin pyrolysis products recorded in surface sediment samples (P1 to P8) from Potengi Estuary, North-East Brazil. Selected ion traces for the lignin derived 12 index-methoxyphenols as described in Tinoco et al. (2002).

Figure captions

Fig.1. Location of study area and sampling sites in a transect from Potengi estuary, North-East Brazil.

Fig.2. Histograms showing the relative abundance of individual *n*-alkanes released from the direct pyrolysis of intertidal mangrove sediments.

Fig.3. Partial selected ion chromatograms of *m/z* 73 and 74 showing the distribution of *n*-alkanoic acid and fatty acid methyl ester (FAME) reconstructed for sediment sample P5.

Fig.4. Partial selected ion chromatograms of *m/z* 59, showing the distribution and relative abundance of *n*-alkan-2-ones reconstructed for sediment sample P5.

Fig.5. Reconstructed single current ion chromatogram to illustrate the relative abundances of methoxyphenols (guaiacol and syringol) derivatives of sediment sample P5. Molecular structure and diagnostic ions of main methoxyphenols released by direct pyrolysis of the sediment are included. The example chromatogram corresponds to sample P5. G: guaiacol; S: syringol; MG: methylguaiacol; MS: methylsyringol; EG: ethylguaiacol; ES: ethylsyringol; VG: vinylguaiacol; VS: vinylsyringol; PG: propenylguaiacol; PS: propenylsyringol; AG: acetoguaiacone and AS: acetosyringone.

Fig.6. Partial chromatograms (*m/z* 204, 218 and 393) showing distributions and relative abundances of saturated and unsaturated triterpenoids. (a) A-neoursa-3(5), 12-diene; (b) Aneooleana-3(5), 12-diene; (c) A: D-neoolean-12, 14-diene; (d) Taraxerol Acetate/ D-Friedoolean-14-en-3 β -yl acetate; (e) Olean-18-ene / Germanicene; (f) Germanicol; (g) Allobetulin-1-ene; (h) Fridooleanan-3-one or Friedelan-3-one; (k) A-neoursa-3(5), 12-diene; (l) α -Amyrin; (m) Taraxerol Acetate/ D-Friedoolean-14-en-3 β -yl acetate; (n) β -Amyrin; (o) Olean-12-ene; (p) Methyl Commate A; (q) 3-keto- urs-12-ene / α -Amirenone; (r) D: Afriedoolean-3-one. (T₁) Oleana-11, 13(18)-diene; (T₂) A-Neoursa-3(5), 12-diene; (T₃) A-Neooleana-3(5), 12-diene; (T₄) A: D-Neooleana-12(14)-diene; (T₅) Germanicol.

Relative abundance (% chromatographic area)

n-Alkane carbon number

Table 1.

Sampling site	Location	Description of sediment samples
P1	5°46'26.26"S, 35°13'58.98"W	Between root trap material of mangrove tree
P2	5°46'26.20"S, 35°13'59.40"W	Sediment deposited around prop roots of red mangrove (<i>R. mangle</i>)
P3	5°46'26.23"S, 35°14'0.05"W	Natural cluster of Mangrove trees (mangrove hammock) with <i>Avicennia</i> and <i>Rhizophora</i>
P4	5°46'26.32"S, 35°14'0.57"W	From a bare mudflat site without mangrove vegetation
P5	5°46'26.06"S, 35°14'1.09"W	Underneath a solitary red mangrove tree (<i>R. mangle</i>)
P6	5°46'25.21"S, 35°14'1.5"W	Below mangrove tree line (mangrove forest-mudflat transition zone)
P7	5°46'23.88"S, 35°14'2.64"W	Beneath pneumatophores in an area with black mangrove stands (<i>A. germinans</i>)
P8	5°46'23.19"S, 35°14'2.74"W	Mudflat site between black (<i>A. germinans</i>) and red (<i>R. mangle</i>) mangrove stands

Table 2.

Sampling site	pH	EC ($\mu\text{S}/\text{cm}$)	Range	C _{max}	CPI ₍₂₅₋₃₇₎	E/O ₍₁₀₋₃₇₎	ACL ₍₂₅₋₃₇₎	S/L	<i>Paq</i>	TAR	H/W	C ₃₁ /C ₁₇	C ₂₇ /C ₁₇
P1	7.57	5.83	C ₁₀ -C ₃₃	C ₁₃ , C ₂₅	1.07	0.98	27.28	3.06	0.74	0.49	0.23	0.39	0.71
P2	5.81	6.34	C ₁₀ -C ₃₂	C ₁₁ , C ₂₅	0.96	1.02	27.60	2.58	0.66	0.66	0.27	0.59	0.89
P3	6.73	5.97	C ₁₀ -C ₃₂	C ₁₅ , C ₃₁	0.87	1.03	28.71	2.86	0.46	0.57	0.48	0.88	0.38
P4	8.18	5.05	C ₁₀ -C ₃₁	C ₁₃ , C ₂₆	1.18	0.92	27.47	2.41	0.59	0.88	0.18	0.50	1.24
P5	8.27	6.60	C ₁₀ -C ₃₇	C ₁₂ , C ₂₅ , C ₃₁	1.35	0.86	31.38	0.63	0.28	2.15	0.54	4.00	1.00
P6	7.15	8.38	C ₁₀ -C ₃₃	C ₁₃ , C ₂₄ , C ₂₉	1.47	0.92	28.04	2.89	0.57	0.72	0.35	0.79	0.58
P7	8.09	9.59	C ₁₀ -C ₃₂	C ₁₅ , C ₂₅ , C ₂₉	1.47	0.91	27.16	3.30	0.71	0.60	0.13	0.26	1.02
P8	6.48	9.40	C ₁₀ -C ₃₃	C ₁₃ , C ₂₄ , C ₂₉	1.24	0.92	28.17	2.03	0.51	1.01	0.27	0.85	1.04
Mean	7.29	7.15			1.20	0.95	28.23	2.47	0.57	0.89	0.31	1.03	0.86
STD	0.90	1.73			0.22	0.06	1.37	0.84	0.15	0.54	0.14	1.22	0.28

CPI: carbon preference index; E/O: even to odd ratio; ACL: average chain length; S/L: short to long chain ratio; *Paq*: Ficken's aquatic macrophyte vs. emergent and terrestrial plants; TAR: terrigenous to aquatic ratio; H/W: herbaceous to woody vegetation ratio; C₃₁/C₁₇: grass vs aquatic contribution; C₂₇/C₁₇: woody vs aquatic contribution.

Table 3.

Methoxyphenol	m/z	Sampling site							
		P1	P2	P3	P4	P5	P6	P7	P8
G	124	++	++	+	++	++	++	++	++
S	154	+/-	+/-	-	+/-	+/-	+/-	+/-	+/-
MG	138	++	++	+	++	++	++	++	++
MS	168	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-
EG	152	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-
ES	182	-	-	-	-	-	-	-	-
VG	150	+++	+++	++	+++	+++	+++	+++	+++
VS	180	+/-	+	-	+	+	+	+	+
PG	164	+	+	+/-	+	+	+	+	+
PS	194	+	+	-	+	+	+	+	+
AG	166	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-
AS	196	+/-	+/-	-	+/-	+/-	+/-	+/-	+/-

G: guaiacol; S: syringol; MG: methylguaiacol; MS: methylsyringol; EG: ethylguaiacol; ES: ethylsyringol; VG: vinylguaiacol; VS: vinylsyringol; PG: propenylguaiacol; PS: propenylsyringol; AG: acetoguaiacone and AS: acetosyringone.

Semiquantitative assessment: (+++) most abundant; (++) abundant; (+) present; (+/-) trace; (-) not detected.

Sup. Fig.1 Total current ion pyrograms of sediments

Sup. Fig.2

m/z 57.00 (56.70 to 57.70)

Sup. Fig.3

Sup. Fig.4

Sup. Fig.5

Partial chromatograms (m/z 204, 218 and 393) showing distributions and relative abundances of saturated and unsaturated triterpenoids.

(a) A-neoursa-3(5), 12-diene (b) A-neooleana-3(5), 12-diene; (c) A: D-neoolean-12, 14-diene; (d) Taraxerol Acetate/ D-Friedoolean-14-en-3 β -yl acetate; (e) Olean-18-ene / Germanicene; (f) Germanicol; (g) Allobetulin-1-ene; (h) Friedooleanan-3-one or Friedelan-3-one; (k) A-neoursa-3(5), 12-diene; (l) α -Amyrin; (m) Taraxerol Acetate/ D-Friedoolean-14-en-3 β -yl acetate; (n) β -Amyrin; (o) Olean-12-ene; (p) Methyl Commate A; (q) 3-keto- urs-12-ene / α -Amirenone; (r) D: Afriedo-olean-3-one. (T1) Oleana-11, 13(18)-diene; (T2) A-Neoursa-3(5), 12-diene; (T3) A-Neooleana-3(5), 12-diene; (T4) A: D-Neooleana-12(14)-diene; (T5) Germanicol.