Environmental changes recorded in the Holocene sedimentary infill of a tropical estuary

Mukesh Kumar a,b, Tomasz Boski a, Francisco P. Lima-Filho c, Francisco H.R. Bezerra c, Francisco J. González-Vila d, José A. González-Pérez d, *

a) CIMA, Univ. do Algarve, 8005-139 Faro, Portugal
b) FUECA, Univ. de Cádiz, Campus de Puerto Real, 11519 Puerto Real, Cádiz, Spain
c) Dept. Geologia, Univ. Federal do Rio Grande do Norte, Natal, RN 59078-970, Brazil
d) IRNAS, CSIC. Avda. Reina Mercedes 10, 41012, Sevilla, Spain

* jag@irnase.csic.es, Tel: +34-954-624-711, Fax: +34-954-624-002

Abstract: Early–to late Holocene sedimentary infill of the Potengi-Jundiai Estuary (Brazil) was studied in a 31.5 m long sediment core. The borehole was drilled in a mangrove area within the central part of the flood tide delta. The sedimentary record, encompassing the last 10 kyrs, was studied for sediment texture and for the \( n \)-alkanes composition of organic matter (OM). Sediments rich in OM and bivalve shells accumulated during the period of sea-level rise, mostly in an intertidal environment of mangrove forest, mudflat and subtidal estuarine flood delta. The characterization of \( n \)-alkanes (\( C_{10} - C_{33} \)) and lignin methoxyphenols by means of direct analytical pyrolysis (Py-GC/MS) technique allowed determining the sources of the extant OM. Downcore fluctuations were observed in \( n \)-alkanes and in several \( n \)-alkane based indices, such as long chain carbon preference index (CPI \( C_{24} - C_{33} \)), long to short chain ratio (L/S) and average chain length (ACL), as well as in the relative proportion of lignin derived compounds. The \( n \)-alkanes distribution points to changing sources of OM input to the estuarine sediments over most of the Holocene period. Major inputs of terrestrial vegetation alternated with periods of mixed input from aquatic macrophytes as the rate of sea-level rise changed over time. The \( n \)-alkanes distribution and the lignin markers were useful for reconstructing paleoenvironmental conditions, particularly during the early Holocene when the lower Potengi River valley (now an estuarine area) could accommodate terrestrial forest vegetation before switching to halophytic mangroves as sea levels rose.
1. Introduction

Understanding the climatically driven sea-level changes is an important aspect for coastal planning and management because it helps to follow estuarine ecosystem responses to climate forcing over centennial to millennial time scales. Such knowledge is essential for planning appropriate adaptation options and consequently to minimise the impacts that sea-level change may cause at the land–ocean interface (Gilman et al., 2008). There has been growing interest in the response of mangrove depositional systems to sea-level and climate change, leading to several studies from the Brazilian continental margin (e.g. Behling et al., 2001, 2004; Angulo et al., 2006; Cohen et al., 2012; Pessenda et al., 2012; França et al., 2013; Boski et al., 2015). Owing to fast sedimentation rates and consequent isolation of OM from bacterial remineralisation (Hedges and Keil, 1999; González-Vila et al., 2003), estuarine sedimentary deposits accreted during the most recent postglacial transgression (Boski et al., 2002) are valuable archives for the investigation of the origins, pathways and fates of sedimentary organic matter (SOM). Where established chronostratigraphic frameworks are available, SOM in estuarine sediments has a high potential to retain a continuous, high-resolution record of environmental change. Environmental changes that took place in coastal zones since the Last Glacial Maximum (LGM) have had a profound impact on the spatial distribution of mangrove vegetation and its associated deposits (Tanabe et al., 2013; Pessenda et al., 2012) at both local and regional scales. Mangrove forests have
unique physiological and morphological adaptations to life in the intertidal zones of tropical and subtropical regions (Alongi, 2008; Sanders et al., 2012; França et al., 2013) that result in very characteristic signatures of their presence in terms of molecular markers. Terrestrial vascular plants are the major source of long chain $n$-alkanes ($C_{25}-C_{33}$), with conspicuous odd-over-even predominance in their carbon chain length (Eglinton and Hamilton, 1967; Riley et al., 1991b). In contrast, mid-chain length ($C_{20}-C_{24}$) markers are attributed to submerged aquatic macrophytes (Huang et al., 1999; Ficken et al., 2000). Long chain $n$-alkanes are particularly resistant to microbial degradation due to post-depositional and diagenetic processes. Therefore, are considered a robust biomarker proxy compared to other hydrocarbons (Meyers, 2003; Garcin et al., 2012) and thus suitable for paleoenvironmental studies in sedimentary archives (Yamamoto et al., 2010). Short chain length ($C_{14}-C_{20}$) $n$-alkane homologues mainly originate from bacteria, algae and fungi. Their distributions show no odd or even carbon number predominance in chain length (Grimalt and Albaiges, 1987; Meyers and Ishiwatari, 1993), whereas the $C_{17}$ alkane is regarded as a biomarker for algae and photosynthetic bacteria (Cranwell et al., 1987; Meyers, 2003).

Other relevant biomarkers for vegetation are the methoxyphenols, released from lignins during pyrolysis and widely used for the direct study this biopolymer (Meier & Faix, 1992; Galetta et al., 2014; Blánquez et al., 2017). Lignin is mainly composed by three precursors: $p$-coumaryl (H), coniferyl (G), and sinapyl (S) alcohols and their proportion differ between groups of plants; whereas the softwood lignin from gymnosperms is made up by G units, that in hardwood from angiosperms contains G and S, and grass lignin G, S and H units.

The carbon stable isotope composition ($\delta^{13}C$), has been widely used as a tracer for the organic contribution. The majority of terrestrial plant species have a $C_3$ type photosystem and characteristic low ($^{13}C$ depleted) $\delta^{13}C$ values ranging between -24 and -34 ‰, while $\delta^{13}C$ of plants from tropical, arid and saline environments with $C_4$ photosystem have higher ($^{13}C$
enriched) values in the range −6 to −19 ‰ (Deines, 1980). Hence, variations in SOM δ\textsuperscript{13}C can be related to vegetation changes as well as to SOC dynamics. Additionally, factors like temperature, salinity and moisture can also induce δ\textsuperscript{13}C variations in soils and sediments (Farquhar, 1984 and references therein). Slight isotopic differences occur between the different parts and organs of single plants (Hobbie & Werner, 2004) as well as among the different OM components: alkanes and lipids have light C isotopic compositions, depleted in \textsuperscript{13}C (Collister et al., 1994), while cellulose and lignin present similar values to those from the original vegetation (Hobbie & Werner, 2004). Thus, rapid degradation of certain SOM components may also induce shifts in isotopic composition (Balesdent et al., 1988).

In general, OM becomes \textsuperscript{13}C enriched (less negative δ\textsuperscript{13}C values) during decomposition and evolution processes in sediments. The main hypotheses proposed to explain this δ\textsuperscript{13}C enrichment from plant material to sedimentary organic carbon (SOC) with increasing soil depth are; first, a isotopic fractionation during microbial metabolism of SOM that result in respiration of lighter compounds (Wynn et al., 2005) and second, the Suess effect i.e., the increase of atmospheric \textsuperscript{12}C due to the combustion of fossil fuels causing a depletion of OM δ\textsuperscript{13}C in the soil surface (Feng and Epstein, 1995; Francey et al., 1999).

Direct analytical pyrolysis (Py-GC/MS) is a powerful ‘fingerprinting’ tool that provides rapid and semi-quantitative information relating to the molecular composition of complex organic matter (De la Rosa et al., 2012; González-Pérez et al., 2014). This technique involves no solvents, chemical degradation, fractionation, purification, or derivatisation of products and requires only milligram quantities of dry sediment for direct analysis. The Py-GC/MS technique has been widely applied in the study of SOM (De la Rosa et al., 2012; Faria et al., 2015). It has also been applied to the paleoclimatic studies in peat bogs (McClymont et al., 2011), as well as in carbon sequestration studies (Vancampenhout et al., 2009).
The delivery and deposition of allochthonous and autochthonous OM to NE, Brazilian coastal margin is not well studied, leaving a large gap in our understanding of the fate of OM in coastal environments. In this work, we used a combination of complementary analyses, including conventional SOM characterization, carbon stable isotope composition and analytical pyrolysis, to study Holocene OM inputs into the SOM pool of estuarine mangrove sediments in the Potengi Estuary (NE Brazil) to track the Holocene development of this vegetation type.

2. Geological setting and general description of the study area

The Potengi Estuary forms one of the largest embayments of that type on the Brazilian north-eastern coast. It is situated in the state of Rio Grande do Norte, northern Brazil and is formed at the confluence of the Potengi, Jundiaí and Doce rivers. The three rivers jointly drain an area of about 5000 km². Over its final 8 km, the main estuarine channel attains the width of 900 m (Boski et al., 2015). Fig. 1 shows the geological settings of the study area. Owing to limited freshwater discharge and the low gradient of the river bed, tidal influence extends up to 30 km upstream of the Jundiai mouth (Barbosa, 1983). The estuary exhibits well-mixed conditions with an overall salinity oscillating between 29.5 to 34.5 ‰ during rainy and dry seasons respectively (De Miranda et al., 2005). Tides are semidiurnal and tidal amplitude in the estuary is about 2.8 m (mesotidal regime) with current velocity approaching 1.0 m/s. The climate in this region is equatorial hot and humid (Köppen AS’ climate category), with precipitation concentrated in the months from February to July. The annual average temperature is 26.8 °C and precipitation varies from 1300 to about 2000 mm per annum. The main estuarine intertidal zone encompasses patches of mangrove forest, shrimp ponds, mudflats, tidal creeks and channels. Mangrove forest has been reduced to 40% of its original
extent by shrimp aquaculture and currently occupies ca. 1488 hectares (Souza and Ramos e Silva, 2011). It is composed of three arboreal species: i) *Rhizophora mangle* (red mangrove), the dominant species (approximately 62% of the total forest cover) found in proximity to channel margins; ii) *Avicennia germinans* (black mangrove, 17% of the total forest cover) present throughout the forest as scattered individuals more towards the higher lying part of halophytic forest; and iii) *Laguncularia racemosa* (white mangrove, 21% of the forested area) occurring in the highest positions above the maximum tide. Heavy metals, urban waste and sewage effluents from adjacent three cities contribute to low conservation status of the mangrove area.

### 3. Methodology

#### 3.1 Borehole drilling, sampling and granulometric analysis

Borehole IG-8 was drilled by means of a rotary drilling rig (TECOINSA –TP-50-D with core diameter 2 ½ inch). The 2 ½ inch-diameter core was extracted from 1m-long sections of core barrel, sealed in plasticized cardboard for transport and sectioned in two halves in the laboratory. After sampling, the samples were dried at 40°C and kept in the refrigerator until further analyses. Granulometric analyses were performed after carbonate removal through application of 10% hydrochloric acid (HCl). The samples were sieved through a 250 µm sieve and the fractions <250 µm were analysed in a Malvern Mastersizer Microplus instrument using demineralised water with 1 g of Calgon l⁻¹, added to avoid flocculation of clay minerals. The results of granulometric analyses are presented together with core profiles in the form of mean grain size plots.

#### 3.2 pH and electrical conductivity
The pH and electrical conductivity were analysed in 1:2.5 sediment to water ratio extracts and readings were obtained from the GLP 22 CRISON pH-meter which was calibrated before the measurements with commercially prepared buffer solutions of pH 4.00, 7.00, and 10.00. Similarly, conductivity readings were obtained from a conductivity meter (EC-Meter BASIC 30+).

3.3. Elemental analysis

Total Carbon (%C) content of sediment samples was analysed using a Flash 2000 HT elemental micro-analyser (Thermo Scientific, Bremen, Germany: C, H, N, O and S) coupled to a thermal conductivity detector (TCD). Each sediment aliquot of ca 7 mg was weighted in a precision balance and the calibration curve for each element made by taking triplicate readings of acetonilide for C used as standard.

3.4. Analytical Pyrolysis

Py-GC/MS was performed using a double-shot Frontier Laboratories pyrolyser (model 2020i, Fukushima, Japan), directly connected to an Agilent 6890 GC/MS system (Agilent, Santa Clara, CA). Aliquots of ca. 10 mg were weighed on a precision balance, placed in crucible deactivated steel pyrolysis capsules and introduced into a preheated micro-furnace at 500 °C for 1 min. The evolved gases were directly injected into the GC/MS system for analysis. The GC was equipped with a low polar-fused silica (5%-phenyl-methylpolysiloxane) capillary column (Agilent J&W HP-5ms Ultra Inert, of 30 m × 250 μm × 0.25 μm film thickness). The oven temperature was held at 50 °C for one minute and then increased up to 100 °C at 30 °C /min, from 100 to 300 °C at 10 °C/min and was stabilised at 300 °C for 10 min. The carrier gas was helium at a controlled flow of 1 mL/min. The detector consisted of an Agilent 5973 MSD (mass selective detector), and mass spectra were acquired with a 70 eV ionising energy.
The identification of individual compounds was achieved by single ion monitoring for different homologous series, via low-resolution mass spectrometry and comparison with published data. Additionally, individual compound assignment was done by comparison with National Institute of Standards and Technology (NIST) and Wiley libraries data.

From the relative abundances of the chromatographic areas for \(n\)-alkane peaks, a number of molecular markers were inferred: S/L (short/long) ratio of the relative abundance of short to long hydrocarbon chains was calculated according to the following the formula (Jiménez-Morillo et al., 2016).

\[
\frac{S/L}{= \sum (C_n)_{10-23}/ \sum (C_n)_{24-33}}
\]

Where \(n\) is the number of carbon atoms and \([C_n]\) is the concentration of each alkane. CPI (24-33) (carbon preference index) is an estimation of the relative abundance of odd to even C chain numbers. This index allows inferences to be drawn on the original source of SOM; a CPI value >1 means that odd C chain numbers prevail over even C chain numbers and OM input to the soil/sediment is of plant origin, while a CPI value <1 means bacterial, algal and degraded OM input to the soil/sediments. In this research, CPI was calculated in the range from 24 to 33 carbons.

\[
\text{CPI (24-33)} = \frac{\sum (C_n \text{ odd})_{24-31}}{\sum (C_n \text{ even})_{24-33}}
\]

Where \([C_n \text{ odd}]\) is the hydrocarbon abundance with odd-numbered C chain and \([C_n \text{ even}]\) is the hydrocarbon abundance with even-numbered C chain (Bray and Evans, 1961).

For the study of lignin biomarkers, a set of 12 index-methoxyphenols was analysed by searching by their specific diagnostic ions. These are considered to have discriminant potential to discern between lignin origin (Tinoco et al., 2002), comparable to other classical phenolic indexes used to study the lignin signature from sedimentary organic based in time-consuming, wet chemical degradation methods (Goñi & Hedges, 1990).
3.5. **Carbon stable isotope analysis (δ\(^{13}\)C)**

The bulk carbon isotopic signature (δ\(^{13}\)C) was analysed using a Flash 2000 HT/IRMS system (Thermo Scientific, Bremen, Germany) coupled via a ConFlo IV interface unit to a continuous flow Delta V Advantage isotope ratio mass spectrometer. The results were reported in the delta notation (δ) as per mil deviation (‰) from corresponding international standards of PeeDee Belemnite (\(^{13}\)C/\(^{12}\)C, PDB). The standard deviation of bulk δ\(^{13}\)C was typically less than ± 0.05‰.

3.6. **Sea level and depth/age relation in the sedimentary profile**

The depth/age relation for the studied bore hole profile was obtained from published \(^{14}\)C datings of Bezerra et al. (2003) in the 7000 – 1000 yrs. cal BP interval and Boski et al. (2015) in the 8200 – 7000 yrs. cal B.P. interval. Two additional disseminated organic matter samples were dated. The data are reported in Table 1 and plotted in Fig. 2.

4. **Results**

4.1. **Downcore pH and electric conductivity (EC) variations**

Downcore variations of pH and electric conductivity of sediment water suspensions are depicted in Fig. 5a & b respectively. Measured pH values for the core sediment samples ranged from 3.71–7.74. From surface to 22.80 m downcore depth, pH values remained alkaline, whereas in the interval from 22.80 m to 31.5 m depth they became clearly acidic.

4.2. **Characterization of sedimentary units**

After a geological analysis of borehole IG-8 sediments five sedimentary units were described in ascending order of depth (Fig. 4). Depth is referred to borehole mouth whose coordinates
established by means of DGPS were as follows: lat: 5°46'30,15100"S; long: 35°13'22,80693"W; orthometric z: 1,83m. These five sedimentary units consist of mangrove, mud flat, tidal creek and flood tidal delta deposits. Each sedimentary unit and facies were recognised by lithology, sediment characteristics, texture and fossil components (presence of vegetal remains and shell fragments). The characteristics and depositional environments of these sedimentary units are described below.

Unit-I (depth: 31.5-31 m). This unit embraces the lowermost part of the core and consist of poorly interlaminated sand and silt, of grey greenish colour with scarce disseminated organic detritus. The greenish colour of these sediments, described in several estuarine boreholes in the estuary (Boski et al., 2015), is interpreted as a transition from fluvial to estuarine conditions. It is marked by the presence of acid volatile sulphides finely dispersed through the silty, kaolinite containing, sediment matrix.

Unit-II (depth: 31-20.4 m). This unit consists of interbedded layers of dark grey silt and fine to medium sand, with several layers of poorly preserved, corroded bivalve shells. Tidal laminations are frequent. Abundant OM in silt layers is present in the form of finely disseminated, decomposed plant detritus, which exudes a pronounced sulphurous smell. These characteristics point to a confined environment of mangrove forest and tidal creeks, which lasted for about one thousand years from ca 10 kyrs cal. B.P. Elemental analyses of samples derived from Unit-II show large variations in TOC content from 4.1% to 1.3% (Fig. 5c). Total inorganic carbon (TIC) values range from 0.7% to 0% (Fig. 5d). The highest TIC content (0.7%) was observed at 22.75m downcore depth, while lowest (0%) at 28.40m. Large fluctuations in bulk $\delta^{13}$C values were observed in this unit from -25 to 17.1‰ (Fig. 5e). The downcore depth interval from 30.95 to 29.70 m shows minor fluctuations in bulk $\delta^{13}$C values (-25 to -24 ‰). More pronounced fluctuations are marked by highly enriched values (−
at 29.45 m downcore depth followed by depleted values -23.9‰ and -25.1‰ at 28.65 m and 28.40 m downcore depth respectively. In the remainder of Unit-II, slight enrichment in δ¹³C values is observed from -23.5‰ to -22.3‰. Both unimodal and bimodal homologous series of n-alkane distribution patterns were observed in Unit-II. Unimodal distributions are characterised by maximum abundance (Cmax) at C₁₁, C₁₂ and C₁₃ respectively, while bimodal distribution with Cmax at C₂₅, C₂₇ and C₂₉ (Fig. 6). The most striking feature of n-alkane distribution patterns in this Unit-II below 30 m downcore is the co-dominance of both long chain as well as short n-alkanes with Cmax at C₁₃, C₂₅, C₂₇ and C₂₉, together with the abundance of lignin markers that include mainly guaiacyl (G) type but also syringyl (S) derived methoxyphenols (Table 2).

Disseminated organic matter was extracted for dating from 2 core samples in this unit, at 23.17 m and 28.41 m down-core depth (Table 1 and Fig. 4). These samples yielded ¹⁴C ages of 9306 and 9552 cal. yr B.P respectively and represent the oldest Holocene sea-level indicative points so far established along the Brazilian littoral. Assuming a linear trend in accumulation of the sediments the entire unit could be deposited in less than 500 years with an accumulation rate around 20 mm/yr⁻¹. However, that figure, require further confirmation by more datings.

Unit-III (depth: 20.4 – 12.3 m). The third unit has a sharp contact with the underlying fine sediments and consists of a monotonous packet of fine, light grey quartz sands, occasionally containing small fragments of shells and very scarce vegetal fragments. These sediments were deposited in the environment of inner estuarine flood tidal delta, which formed between 9 and 8 kyrs cal. B.P, i.e. in the final stage of the postglacial transgression. Unit-III is characterised by a narrow range of TOC fluctuation between 2.5 and 2.2% (Fig. 5c), whereas TIC content displays constant values of 0.5% (Fig. 5d). Slight enrichment in bulk δ¹³C values is observed between -21.30‰ and -20.10‰ (Fig. 5e). Unit-III has a unimodal distribution...
pattern with predominance of short chain \( n \)-alkanes, \( C_{\text{max}} \) at \( C_{11}, C_{12} \) and \( C_{13} \) (Fig. 6). Lignin markers are very scarce and only detected as traces in the deepest sample of this Unit (Table 2).

Unit-IV (depth: 12.3 – 6.1 m). This unit embraces two sandy, shell-containing layers interpreted as tidal creek sediments within dark grey silty sediments with abundant vegetal remains, deposited in a mangrove mudflat environment. TOC values oscillate within a narrow range from 2.2 to 2 % (Fig. 5c), while TIC values fluctuate between 0.5 and 0.3 % (Fig. 5d). Notable enrichment in bulk \( \delta^{13}C \) values from \(-22.3 \) to \(-26 \)‰ (Fig. 5e) is observed at 11.50 m downcore depth. Unit-IV exhibits similar \( n \)-alkane distribution patterns to Unit-III with \( C_{\text{max}} \) at \( C_{11}, C_{12} \) and \( C_{13} \) (Fig. 6). The deposition of both Unit-IV and the overlying Unit-V occurred during the last 8 kyrs (Fig. 2) and was interrupted by periods of erosion/non-sedimentation, after the sea level stabilized or slightly exceeded the present one. No lignin markers were detected in this Unit (Table 2).

Unit-V (depth: 6.1 – 0 m). The upper sedimentary unit of the core consists of fine to very fine to silty sand with shell fragments (Fig. 4). It corresponds to the modern flood tide delta deposits. TOC content varies from 2 to 3.9 % (Fig. 5c), while TIC remains constant at 0.3 % (Fig. 5d). Notable enrichment in bulk \( \delta^{13}C \) value is observed from \(-23.3 \) to \(-19.3 \)‰ (Fig. 5e).

Unit-V displays similar \( n \)-alkane distribution patterns to Unit-IV, with \( C_{\text{max}} \) at \( C_{11}, C_{12} \) and \( C_{13} \) respectively (Fig. 6).

5. Discussion

5.1. Depth-age relation in the sedimentary profile and the inferred sea-level changes

In order to obtain a chronostratigraphic framework for the studied sedimentary column this information was integrated with previously published geochronological data by Boski et al.
(2015) and Bezerra et al. (2003). All points plotted as depth in relation to the present sea level are at the intersection of error bar in age determination (Table 2) and error of the past sea surface position with respect to the present sea level. The three main sources of error in past sea level reconstruction and the respective error margins may be estimated as follows: i) elevation of the borehole mouth with respect to the present MSL ±10 cm, ii) actual depth in the borehole, from which the dated item was recovered ±20 cm, (due to the incomplete core recovery), iii) position of dated items with respect to the past MSL ±140 cm (equal to the half of present maximum tidal range). All 14C ages used in plotting the curve depicted in Fig. 2, are summarised in Table 1. The depth-age graph for the borehole points, presented as linear regression line, was obtained by tying the new IG8 datings to those previously studied by Boski et al. (2015) and Bezerra et al. (2003) and obtained from boreholes located some 4 km to east, in the mangrove area of Jardim Lola. The first point of the line set at 0-m relative sea level (RSL) was 7500 cal. yr BP. This figure is in agreement with the generally accepted slackening Holocene sea-level rise, as for instance in Australia, where Lewis et al. (2013), indicated that the last Mid Holocene period of an accelerated sea-level rise (SLR) terminated after reaching the present sea level 7400±200 cal. yrs BP. This connection point predates the death assemblage of bivalve shells, in the study of Bezerra (2003), encrusted in shoreline exposed beach rock elevated 0 m +/- 1 m with respect to the present RSL and all remaining, more recent reference points. The plot (Fig. 2), displays the regression line for the pre-7.5 kyrs points and a two segment band depicting the sea-level change along the entire period. The lower segment corresponds to the fast sea-level rise with a rate of ca. 20 mm yr⁻¹, and the upper, from 7500 cal yrs BP onwards suggesting possible Mid-Holocene highstand and progressive sea-level fall since 6000 cal yrs BP. The first trend seems to be in excess of the usually proposed values i.e. between 6 and 10 mm yr⁻¹. (Murray-Wallace and, Woodroffe, 2014). Milne et al. (2005) critically assessed SLR after the removal of the non-eustatic
glacio-isostatic adjustment (GIA) component from the available data on SLR from 2 Caribbean and 6 South American records and obtained a uniform sea-level rise during the early Holocene period of 7-8 mm yr$^{-1}$, similar to the trends proposed by Tanabe et al. (2003) for the South China Sea Basin.

However, in our case the estimation of SLR was based on only 2 dated points and without considering the decomaption and therefore must be complemented by more data. Rapid changes in global sea level around 8.2 kyrs have been linked to the final drainage of glacial Lake Agassiz in north-central North America. It has been suggested that freshwater release from Lake Agassiz into the North Atlantic Ocean centred at around 8.2 kyrs B.P (melt water pulse 1C), was responsible for a sudden jump of some 4-5 m in sea level and an abrupt climate change during the early Holocene (Törnqvist and Hijma, 2012).

Over the one millennium timespan corresponding to the deposition of Unit II sedimentary dynamics were apparently in equilibrium with the development and stability of mangrove forest, which could withstand rapid sea level rise. Most probably the massive input of shelf sands since ca 9 kyrs BP onwards (Unit III), which created a flood tide delta in the central portion of the estuary, did not permit the maintenance of mangroves in this part of estuary. It could also correspond to a period of faster SLR as discussed above, that permanently drowned the halophytic forest. The renewed appearance of mangrove vegetation in the upper section of the sedimentary profile, followed by another disruption, follows the sequence of events observed in the inner more sector of the estuary reported by Boski et al. (2015) and thus may indeed correspond chronologically to the Lake Agassiz event.

5.2. Downcore pH and electric conductivity (EC) variations

Acidic pH values (3.71–6.24) observed in the core sediments could be attributed to two possible processes. First, the acidity may be produced by microbial decomposition and
hydrolysis of OM, accompanied by release of fulvic and humic acids (Tam and Wong, 2000).

Second, it may result from the bacterially mediated oxidation of acid volatile sulphides (AVS). The latter form in the early diagenetic reaction of iron, brought to the sedimentary environment from nearby lateritic crust outcrops, and H₂S produced as a metabolite in anaerobic sulphate-reducing respiration. Conductivity oscillations between 5.69 –13.56 (µS/cm) are depicted in Fig. 5b. Conductivity was higher in the upper section of the cored sediments and displayed only minor downcore variation until 25.60 m, then decreasing drastically in the lower core sections. The high EC in the upper horizon is attributed to the presence of ionic components (Na⁺, Cl⁻, SO₄⁻² and Ca⁺⁺) present in interstitial waters of marine origin, which easily penetrate through the uppermost packet of fine sands and/or are readily leached from sediments during the laboratory suspension process.

5.3. Organic carbon in sedimentary units

The OM in the IG-8 core sediments has two principal sources: autochthonous (mangrove litter, marine algae and phytoplankton) and allochthonous (terrestrial OM transported by rivers) in the estuarine catchment areas.

Changes in the TOC content of core sediments during the Holocene would indicate changes in the amount of terrestrial and marine OM input. Percentage TOC content is an indicator of both primary production in area of deposition and efficient preservation of OM in sediments. It indicates the amount of organic matter transferred to long-term geological storage after cessation of diagenesis. Relatively high TOC content in this sedimentary unit is due to preservation of vegetal remains in the clay/silt layer. Particle size is a crucial factor in controlling the preservation of OM in sediments (Dean, 1999), with a generally positive correlation between the proportion of silt/clay and preserved organics (Mayer, 1994). Lower
TOC content in Unit-III and Unit-IV is probably due to the switching off of the supply of terrestrial OM to the estuary as sea level rose during mid-late Holocene.

5.4. Holocene environmental changes and isotopic records

The sedimentary sequence between 31.95 and 29.70 m showing relatively depleted bulk $\delta^{13}$C values in the range of $-24.40$ to $-24\%$ (Fig. 5e), suggests that brackish conditions existed, with relatively unrestrained influx of terrestrial OM derived from C$_3$ vascular vegetation (Mackie et al., 2005; Yu et al., 2010). However, an abrupt shift in the $\delta^{13}$C values from $-24$ to $-17.1\%$ at the 29.45 m downcore depth indicates more inputs from carbonate in sedimentary units. The sedimentary sequence in Unit-II, between 29.45 and 28.40 m shows a trend towards depletion in $\delta^{13}$C values (from $-17.1$ to $-25.1\%$) and is explained by the continuous input of C$_3$ plant-derived OM. Therefore, within Unit-II it clearly shows a transition of depositional environment from brackish water to freshwater depositional environments between 29.45 and 28.40 m downcore depth.

There is a trend towards enriched $\delta^{13}$C values (from $-25.1$ to $-22.3\%$) observed up to 20.50 m downcore depth, with an exception at 22.80 m, where depletion in $\delta^{13}$C values ($-23.8\%$) was observed. Intermediate $\delta^{13}$C values (from $-23.8\%$ to $-22.30\%$) could indicate that sedimentary OM deposits consist of an admixture of both C$_3$ and C$_4$ plants. The sedimentary sequence between 20.4 to 11.50 m downcore depths is characterised by enriched $\delta^{13}$C values from $-22.30\%$ to $-26.1\%$. These values indicate a transition of brackish to freshwater environment in an estuarine zone, clearly distinguishable between Unit-III and Unit-IV. This interpretation is further supported by the presence of vegetal remains in Unit-IV that correspond to bulk $\delta^{13}$C values of $-26.1\%$ (Fig. 5e). Furthermore, in Unit-IV, the $\delta^{13}$C-record varies between $-24$ and $-23.80\%$ from 10.40 to 6.50 m downcore depth which suggests the reappearance of a brackish environment, with OM inputs from both C$_3$ and C$_4$ plants.
In Unit–V, $\delta^{13}$C values increase from -23.8 to -19.3‰ as a response to increased marine influence, resulting in a decline in OM contribution from $C_3$ plants and increased OM inputs from $C_4$ plants at the top of the core sediment.

Down-core trends for Holocene environmental changes inferred from stable isotope ($\delta^{13}$C) records suggest mixed sources of OM in the sedimentary units of core sediments. Bulk $\delta^{13}$C values are often used to distinguish between terrestrial and aquatic plant sources because of their different photosynthetic fixation pathways and the net fractionation against $^{13}$C (Filley et al., 2001). But also, different classes of compounds i.e. polysaccharides, proteins or lipids, with the same carbon source exhibit dissimilar $\delta^{13}$C values (Deines, 1980; Hayes, 1993; Schouten, 1998, Megens et al., 2002) and processes occurring during humification leads to slight $\delta^{13}$C enrichment (2–4‰) from the top to the bottom of soil profiles (Lallier-Vergès et al., 1998).

5.5. Sources of sedimentary organic matter

High-resolution $n$-alkanes records as well as lignin biomarkers presented in Fig. 7 and Table 2, show a sudden change below 29.60 m downcore depth, with an increase of the relative abundance of both long chain $n$-alkanes and lignin methoxyphenols. With respect to the trend observed in sedimentary Unit–II, relative abundances of the long-chain $n$-alkanes ($C_{27}$ and $C_{29}$) is found conspicuously higher in the deepest 2m of the profile than in the remaining upper portion of the sedimentary column. This prominence of long chain $n$-alkanes is caused by changes in the vegetation cover of the source regions. It witnesses shift away from the higher land plant leaf waxes (Eglinton and Hamilton, 1967). The striking feature of the $n$–alkanes distribution pattern in the sedimentary Unit–II below 30 m downcore is also the co–dominance of long chain and short $n$-alkanes with $C_{max}$ at $C_{13}$, $C_{25}$, $C_{27}$ and $C_{29}$. These distribution patterns of $n$-alkanes indicate multiple sources of OM inputs in this unit, which
probably was deposited in parallel to the colonization of the area by mangrove vegetation. The high relative abundances of $C_{25}$, $C_{27}$ and $C_{29}$ $n$-alkanes in the sediments are characteristic of mangrove vegetation (Heenandiz et al., 2001; Mead et al., 2005). Additionally, soil erosion followed by transport from the neighbouring higher lying areas may also add to the sediment OM from more continental source regions. The abundance of lignin markers both of the guaiacyl and syringyl type, indicate contributions from hardwoods (Saiz-Jiménez & De Leeuw, 1986). Throughout sedimentary Unit-III, Unit-IV and Unit-V short chain $n$-alkanes predominance is very noticeable. These short chain alkanes originate mainly from phytoplankton and are typically enriched in the $n$-alkane homologues series from $C_{15}$ to $C_{20}$, with dominance of $C_{17}$ for algae, and $C_{19}$ for cyanobacteria (Belpi et al., 1970 and Cranwell et al., 1987). On the other hand, $n$-alkanes in the range $C_{14}$-$C_{22}$, without odd-over-even predominance, have been linked to photosynthetic and non-photosynthetic bacterial inputs (Grimalt and Albaiges, 1987). The $n$-alkanes from submerged and floating aquatic macrophytes are characterized in mid chain lengths by $C_{\text{max}}$ at the $C_{21}$, $C_{23}$, or $C_{25}$ (Ficken et al., 2000). Consequently, the OM inventory of the IG-8 core represents material derived from aquatic, intertidal and continental sources.

CPI ($C_{25}$-$C_{33}$) values for $n$-alkanes vary between 0.8 - 1.4 in the down core profile (Fig. 7a). Alteration in CPI value can also be used to trace OM inputs in sediment/soil from a variety of sources. Only sedimentary Unit-II in the core sediments shows a CPI ($C_{25}$-$C_{33}$) value $> 1$, indicating that the OM deposited at this depth interval originates mainly from epicuticular waxes of higher plants (Eglinton and Hamilton, 1967). The remaining units of the sedimentary profile have a CPI ($C_{25}$-$C_{33}$) value $< 1$ or close to unity, indicative of greater input from microorganisms, recycled OM, and/or petroleum (Nishimura and Baker, 1986; Kennicutt et al., 1987), this is also supported by the almost total absence of lignin markers. It is worth reporting that during the opening of sediment core we have noted a distinct
hydrocarbon smell that could support the latter possibility. Even if there is no proven hydrocarbon reservoir below the Quaternary infill of the estuary, one must bear in mind that Potengi Estuarine area is overlying the oil-rich and intensely exploited Potiguar Basin. Finally, Meyers and Ishiwatari (1993) pointed to the usefulness of CPI as an indicator of the degree of diagenesis in the group of straight chain geolipids. CPI is a numerical representation of how much of the original biological chain length specificity is preserved in geological lipids.

5.6. Average n-alkanes chain length

Considerable down-core variability is observed for ACL values (Fig. 7c) that fluctuate between 19.4 and 13.3. Large variation in ACL values between 19.4 and 14 were observed in Unit-II. The variations in ACL values (19.4 –17) were especially small below 30m downcore depth, because of contributions from high molecular weight n-alkane C27 and C29 homologues that may be attributed to the predominance of hardwood –as indicated by the presence of S lignin lignin biomarkers– arboreal vegetation in the catchment areas of the Potengi Estuary. This finding is also in agreement with the palynological findings of Behling et al. (2000), which suggest that Rhizophora mangrove was dominant vegetation along the NE Brazilian coastal zone since the early Holocene period. Subsequent decrease in ACL values (14.6) was observed until 28.65 m downcore depth, followed by an increase in the ACL value (16.5) at 26.60 m downcore depth. This ACL decrease in Unit-II may be also related to the replacement of C3 by C4 plants, which have relatively lower ACL value than C3 plants. In Unit-III ACL values range between 14.7 and 16.8 that can be attributed to terrestrial, relatively degraded OM inputs. This is also in agreement with the scarce lignin markers found, and the presence of organic remains in this sedimentary unit may correspond with algal biomass. For Unit-IV ACL values oscillated
between 16.8 and 13.3, implying the major contribution of low molecular weight alkanes. ACL and values recorded for Unit-V (13.3–18.6) indicate a reduced contribution of low molecular weight and relatively high contribution of long chain n-alkanes at the top of the core sediment. Shifts in ACL values are often also related to changes in climatic conditions (temperature, humidity and aridity) that determine the dominant vegetation in a given area (Poynter et al., 1989; Hughen et al., 2004).

5.7. Relative sea level changes during early to middle Holocene: evidence from n-alkane input

The relative abundance of the total odd $\Sigma (C_{25}-C_{33})$ n-alkanes was used to characterize the total input of terrigenous n-alkanes to the studied sedimentary environment. The total abundance $\Sigma (C_{25}-C_{33})$ of odd n-alkanes is shown in Fig. 7d, indicating predominantly terrigenous OM inputs at the beginning of the early Holocene, followed by a significant decrease in terrigenous OM inputs from the early to mid Holocene. Summed odd $\Sigma (C_{25}-C_{33})$ n-alkanes fluctuations in sedimentary sequences of the core suggest that they were closely associated with Holocene sea-level change along the NE Brazilian coast. The high abundance of total odd $\Sigma (C_{25}-C_{33})$ n-alkanes at the very beginning of the Holocene identifies pre-inundation conditions. Rapid decrease in the total odd $\Sigma (C_{25}-C_{33})$ n-alkanes indicates progressive drowning of the Potengi paleovalley, which lasted through mid to late Holocene period. Seki et al. (2010) have shown that the flux of terrestrial plant-derived biomarkers $\Sigma (C_{25}-C_{33})$ n-alkanes deposited in coastal sediments bears information about changes in the past terrestrial ecosystems within a given catchment. In that sense, an enhanced relative abundance of individual odd n-alkanes (C_{25}, C_{27} and C_{29}) indicates major inputs attributed to the immediate proximity of mangrove vegetation in the local intertidal zone. Mangrove swamps are sensitive to sea level changes and are solely represented by *Rhizophora* (red
mangrove) pollen distribution in many sedimentary archives. Establishment of mangrove swamps along the NE Brazilian coast occurred during the early Holocene period, when the marine/brackish waters reached the area of the present estuaries. This interpretation is in good agreement with Kim et al. (2005), who reached similar conclusions based on taraxerol concentrations and lipid biomarker (C\textsubscript{29}-alkane, and C\textsubscript{28}-alcohol) analyses, showing maximum values ca. 10 kyr cal. BP in marine sediment core of ODP Leg 175 Site 1078C, off tropical West Africa (west of Angola). While, an abrupt decrease in taraxerol concentrations and lipid biomarker (C\textsubscript{29}-alkane, and C\textsubscript{28}-alcohol) were observed from ca. 10 k -7 kyr cal. BP. An increase in \textit{Rhizophora} pollen percentages during the early Holocene were also reported by Dupont et al. (2000) in the Niger delta. Our findings also show an abrupt reduction in relative abundance of odd \textit{n}-alkanes (C\textsubscript{25}, C\textsubscript{27} and C\textsubscript{29}) alongside dominance of mid chain and short chain length \textit{n}-alkanes and loss of lignin markers that reflects the intensifying inputs of marine phytoplankton, algae and bacteria-derived OM, in line with marine transgression into the estuary during mid to late Holocene. The high stand during the mid to late Holocene after the last pulse of deglaciation in the Northern Hemisphere corresponds to much reduced mangrove forest cover, evidenced by diminished total odd \textit{n}-alkanes in the core sediments and the reduction of methoxyphenols. Other lines of evidence based on integrated sedimentological, geochemical and paleontological research suggest that, after the peak of transgression, terrigenous sediment supply and coastal dynamics became the dominant factor in the evolution of the estuary (Boski et al., 2015), permitting the re-establishment of mangrove forest. Martin et al. (2003), demonstrated that RSL exceeded the present level on the Brazilian coast about 7700 cal yr BP and 5600 cal yr BP and was followed by drop in sea level between 5300 and 4200 cal yr BP. Studies of terrigenous \textit{n}-alkane input in the southern South China Sea suggest that sea-level changes during the last three glacial-interglacial cycles pointed to higher concentrations of C\textsubscript{25}-C\textsubscript{35} \textit{n}-
alkanes during glacial sea-level lows and lower concentrations during interglacial sea-level highs (Pelejero, 2003; Huang and Tian, 2012). A sediment core taken from the Okhotsk Sea, on the western North Pacific rim, showed an increase in \((C_{25}-C_{35})\) \(n\)-alkanes inputs in glacial (low sea level stand) and, in early deglacial periods (Ternois et al., 2000). Our findings indicate that total odd \(\sum (C_{25}-C_{33})\) \(n\)-alkanes in the Holocene sedimentary infill of Potengi Estuary and lignin markers released by Py-GC/MS, closely follow sea-level changes on a geological timescale. As yet, studies linking \(\sum (C_{25}-C_{33})\) \(n\)-alkanes records with climate and sea level changes along the Brazilian coast are very insipient, further research is needed to understand coastal processes on wider spatial and temporal framework.

6. Conclusions

This study presents new information regarding the source of OM deposition and preservation within the context of Holocene relative sea-level fluctuations in the Potengi Estuary, NE Brazil. The use of complementary analytical techniques and mainly of lignin biomarkers and simple \(n\)-alkane derived geochemical proxies obtained from the direct pyrolysis of sediments (Py-GC/MS), was particularly relevant to distinguish between SOM sources. In surface, high \(n\)-alkane ACL value indicate a neat terrestrial vegetation influence. From 6.5 to 11.5 m depth (Cal. Age c. 7800-8000 yr BP), progressive ACL increase together with a \(\delta^{13}C\) depletion indicate reworked or partially degraded OM contributions. At 22.8 m depth and at 28.40 m (Cal. Age c. 8200-9200 yr BP) inputs from terrestrial plants were detected, but for short periods of time. Below 28.4 m (Cal. Age c. 9300 yr BP), the influence is clearly marine that ends at 29.45 m, with absence of organic markers and a \(^{13}C\) enriched layer, indicating the occurrence of sedimentary conditions favouring carbonate formation. Below this depth (Cal. Age > 9500 yr BP), the OM in the sediments shows a conspicuous terrestrial influence.
(depleted conductivity and $\delta^{13}$C, abundance of lignin markers from hardwood and a conspicuous increase in n-alkanes ACL and L/S ratio) that increase towards bottom of the core down at 30.95 m, pointing to a drastic sea-level change during Early-Middle Holocene. This compositional variability of OM reflects the evolutionary history of the Estuary and eventually to better understanding of the depositional processes during the infilling of Potengi palleovalley in which the following stages are distinguished: fluvial to i) estuarine transition, ii) unrestricted access of marine waters, iii) fast sea level rise possibly reflecting melt water pulse 1C, accompanied by mangrove migration iv) terminal infilling of the estuary.

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Table 1. Summarised information for $^{14}$C age determinations showing, depth H with respect to the present sea level, conventional age, $\delta^{13}$C & $2\sigma$ range and midpoint. Radiocarbon ages were calibrated using the program CALIB v. 6.0 (Stuiver et al., 2009; Reimer et al., 2009). Laboratory codes are from Leibniz Labor für Altersbestimmung und Isotopenforschung, Kiel, Germany. Sample source: (1) this study; (2) Boski et al. (2015) and (3) Bezerra et al. (2003).

Table 2. Semi quantitative assessment of lignin pyrolysis products found in sediments along IG-8 core from Potengi Estuary, NE Brazil. Selected ion traces for the lignin derived 12 index-methoxyphenols as described in Tinoco et al. (2002).
Fig. 1. Geological setting, core IG-8 location and description of study area (Modified after Boski et al., 2015.)

Fig. 2. Depth age relation in the Holocene sedimentary record from Potengi–Jundiaí Estuary. The linear regression line corresponds to the dated points from boreholes (Boski et al., 2015) and this study which predate the attainment of present sea level. The more recent sea-level indicative points correspond to emerged coastal settings (Bezerra et al., 2003). The shaded band corresponds to the evolution of sea-level within the established error margins.

Fig. 3. Reconstructed single current ion chromatogram to illustrate the lignin signature of sediment samples. The molecular structure and diagnostic ions of the main methoxyphenols releases by direct pyrolysis of the sediment are also included. The example chromatogram corresponds to sample IG-8 30.65-30.70 m. G: guaiacol; MG: methylguaiacol; EG: ethylguaiacol; VG: vinylguaiacol; PG: propenylguaiacol; PS: propenylsyringol.

Fig. 4. Sediment profile from borehole IG-8 drilled in the mangroves of the central part of Potengi–Jundiaí Estuarine valley.

Fig. 5. Downcore plots of pH, conductivity and bulk characteristics (% TOC, % TIC and bulk δ13C) of sediments from borehole IG-8.

Fig. 6. Histograms of n-alkane series mass fragment (m/z 57) obtained by direct pyrolysis (Py-GC/MS) of sediments from borehole IG-8.

Fig. 7. Downcore plots of n-alkanes indices obtained by direct pyrolysis (Py-GC/MS) of sediments from borehole IG-8.
$y = 1.058x + 7691.8$

$R^2 = 0.9584$
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<td>IG-8 30.30-30.40</td>
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<td>IG-8 30.60-30.65</td>
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<tr>
<td>IG-8 30.65-30.70</td>
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<tr>
<td>IG-8 30.90-30.95</td>
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</tbody>
</table>

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: (+++) very abundant; (++) abundant; (+) present; (+/–) trace; (–) not detected.