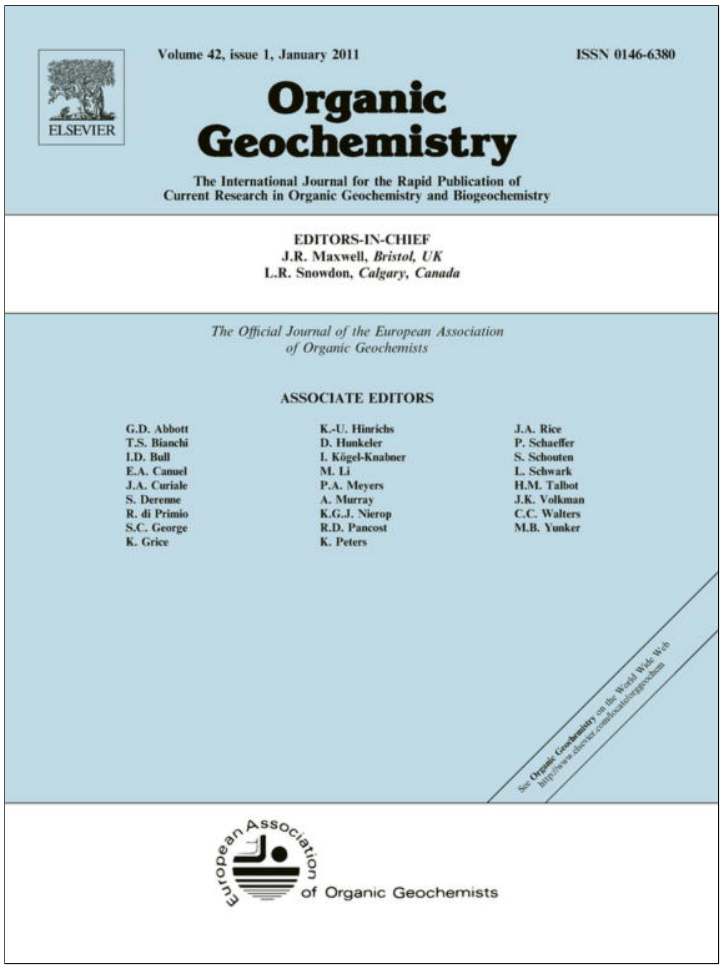

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Triterpenols in mangrove sediments as a proxy for organic matter derived from the red mangrove (*Rhizophora mangle*)

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ABSTRACT

Mangroves are the dominant type of vegetation along many tropical coasts. Organic matter (OM) derived from mangrove leaf litter and root material is stored in sediments and is a major contributor to the amount and chemical composition of sedimentary OM. A set of organic biomarkers in sediments was applied as a palaeo-indicator for the Holocene dynamics of a mangrove Estuary (Rio Caeté, Pará, Brazil). Six sediment cores were collected perpendicular to the present coast line and analysed for triterpenols and sitosterol. The influence of microbial biomarker degradation was implemented from a previous study. Biomarker profiles were validated with pollen data and multivariate statistics to test whether these compounds were suitable indicators for the palaeo-vegetation. Sediments deposited up to 2 Ma BP showed biomarker assemblages similar to those of recent surface sediment. In two cores, the biomarker composition revealed a transition from marsh to mangrove vegetation. Taraxerol, germanicol and β-amyrin provided the most significant chemotaxonomical information and, especially in combination, served as reliable proxies for OM from *Rhizophora mangle* in northern Brazil. The maximum age of the mangrove system ranged between 1000 and 5100 yr depending on the topographic elevation of the drilling location.

1. Introduction

Mangrove ecosystems are the dominant type of coastal vegetation in many tropical regions. They cover 60–75% of the shore in the tropics and subtropics (Spalding et al., 1997) and occur from southern Japan (32°N) to northern New Zealand (38°S; Eisma et al., 1998). The term "mangrove" comprises 70 plant species from 20 families. Some species such as *Rhizophora mangle* (red mangrove) or *Avicennia germinans* (black mangrove) have developed special root systems which support oxygen exchange and stability (Raven et al., 1988). Stilt roots and pneumatophores are capable of reducing erosion and slowing down current velocity, which leads to enhanced sedimentation of suspended material. Therefore, mangroves can expand seawards, occupy new coastal habitats like mud flats (Woodroffe, 1992) and so are important for the protection of tropical coasts. The species occupy a specific niche in the coastal area that is characterised by high salinity in the sediment. Because of their salt tolerance, mangroves can compete with other species in areas regularly flooded by seawater. Further inland, where these conditions change rapidly, vegetation is dominated by terrestrial competitors.

Several studies have been carried out to reconstruct palaeovegetation distribution and relative sea level dynamics along the Brazilian coast (Suguio et al., 1985; Behling and da Costa, 2000, 2001; Behling et al., 2001; Cohen et al., 2005; Souza Filho et al., 2006, 2009). For the mouth of the Amazon River it was shown that a strong sea level decline of about 100 m below modern mean sea level (MSL) occurred during the last glacial maximum (Vital and Stattegger, 2000). The lowest level of the order of 120 m below MSL during the last glacial maximum was confirmed by several studies using various methods (e.g. Flint, 1971; Shackleton, 1987; Fairbanks, 1989). After the glacial maximum, the sea level in the Amazon fan rose from ca. 80 m below MSL during the late Pleistocene (ca. 12,000 yr BP) to 10 m below MSL in the early Holocene (8000 yr BP; Vital and Stattegger, 2000). About 6000 yr BP (mid Holocene) the relative sea level in the Amazon region reached

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the present height and largely remained stable (Vital and Stattegger, 2000).

Triterpenols and sterols occur in the cuticle of terrestrial plants (e.g. Kulshreshtha et al., 1972; Moyna et al., 1983; Killops and Frewin, 1994; Dodd et al., 1995; Rafii et al., 1996; Wollenweber et al., 1999; Koch et al., 2003). Owing to their stability during diagenesis these compounds are frequently used to characterise sources of sedimentary organic matter (OM; e.g. Pant and Rastogi, 1979; Das and Mahato, 1983; Volkman, 1986; Johns et al., 1994; Killops and Frewin, 1994; Munoz et al., 1997). Taraxerol in particular is abundant in some mangrove species and is suitable for identifying mangrove-derived OM in sediments (ten Haven and Rullkötter, 1988; Johns et al., 1994; Koch et al., 2003; Versteegh et al., 2004; Kim et al., 2005; Scourse et al., 2005; Jaffé et al., 2006; Volkman et al., 2007). However, it has been shown that even very stable biomarkers like pentacyclic triterpenols are subject to degradation and that degradation products such as 3-oxytriterpenols can be detected in sediments (Jaffé et al., 1996). It is therefore essential to assess microbial degradation before applying triterpenols as biomarkers for mangroves (Koch et al., 2005).

For this study, we selected a suite of five lipid biomarkers, which were validated in two earlier studies, for their chemotaxonomic potential and for their persistence to microbial decomposition (Koch et al., 2003, 2005). Taraxerol and germanicol are useful chemotaxonomic biomarkers since they occur in *R. mangle* but are absent from the two other mangrove species in the study area. However, taraxerol occurs in many other higher plant species, so the combination of several compounds increases their reliability as biomarkers for single species. Using sitosterol and lupeol as additional dominant biomarkers in the samples enabled us to differentiate mangrove-derived OM from that contributed by other plant species. Betulin was also analysed previously and shown to be a good chemotaxonomic biomarker for the mangrove species *A. germinans* in the study area. However, as betulin can be degraded quickly during early diagenesis (Koch et al., 2005), it was excluded from this study.

The aim was to improve the application of triterpenols as biomarkers for mangrove deposits in northern Brazil by combining sedimentological, palynological and organic geochemical techniques to sediment core studies. The use of several independent mangrove proxies greatly strengthens the validity of palaeoecological reconstruction (e.g. Xu et al., 2006; Dittmar et al., 2009; Koch et al., 2010). Biomarkers are especially valuable where macro- and microfossil structures have not been preserved. Considering that mangroves only colonise a relatively narrow coastal strip, their OM in the sediment can be a useful indicator for ancient coastlines.

2. Material and methods

2.1. Study area

All sampling was carried out in the Rio Caeté estuary in the state of Pará in northern Brazil (0.9°S, 46.7°W; Fig. 1). The main study site was the Bragança peninsula, with a total area of ca. 166 km^2, which is bordered by the Caeté River in the east and Maiaú Bay in the west. The peninsula is cut by several tidal channels, but most of the area is inundated only bi-weekly during spring tides. Mangroves cover 88% of the total area. The three major species are *R. mangle* (red mangrove), *A. germinans* (black mangrove) and *Laguncularia racemosa* (white mangrove), the latter being the least abundant. Total litter fall amounts to ca. 3.7 g dry wt (DW) m^{-2} d^{-1} (Mehlig, 2006).

In the centre of the peninsula, approximately 2.5 m above MSL, an extensive marsh area [Campo Salgado (CS); Fig. 1] of ca. 6.5 km^2 has developed, with a vegetation dominated by halophytic herbaceous plants such as *Sporobolus virginicus* (seashore dropseed) and *Eleocharis geniculata* (spikerush). At the southwestern end of the peninsula a palaeo-cliff indicates the transition from the coastal plain to the coastal plateau. North of the cliff mangrove vegetation dominates, whereas in the south (2–3 m higher elevation) non-halophytic species prevail. In the upper north of the peninsula, ancient dune-beach ridges [cheniers (RKS-2); Fig. 1], which mainly host halophytic herbaceous plants, indicate an ancient coastline and transgressive sea level conditions (Souza Filho and El-Robrini, 2000).

2.2. Sampling

In 1998, three cores were collected on a transect perpendicular to the present coastline from the OM-rich layer of the marsh and two mangrove areas (Fig. 1) using a Russian Sampler (Behling et al., 2001). Sampling locations were at a tidal creek ["Furo do Chato" (FDC); 1.9 m above MSL; 1.60 m core depth], in an extended marsh area in the centre of the peninsula ["Campo Salgado" (CS);

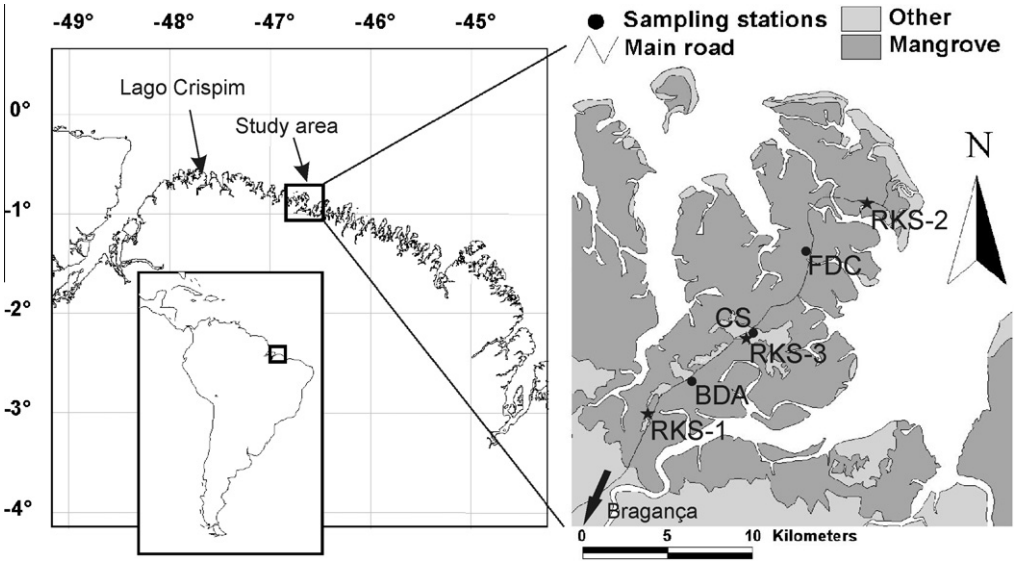

Fig. 1. Sampling area. Deep cores RKS-1 to RKS-3 (asterisks) and shallow cores (dots): BDA, Bosque de Avicennia; CS, Campo Salgado; FDC, Furo do Chato.

2.7 m above MSL; 1.23 m core depth] and in a monospecific *Avicennia* forest ["Bosque de Avicennia" (BDA); 2.4 m above MSL].

In 1999, the BDA drilling depth was extended from initially 5.40 m to a total depth of 6.33 m (for core descriptions see Behling et al., 2001). Three additional cores were drilled in December 2000 (Fig. 1). Core RKS-1 (Rammkernsonde-1; 2.0 m above MSL; 17.90 m core depth) was located in a forest with dense *A. germinans* vegetation near a tidal creek (Furo do Taici) in the transition between the coastal plateau and the coastal plain. RKS-2 (17.50 m) was located on a palaeo-dune (elevation: 2.6 m above MSL) in the northern part of the peninsula, and core RKS-3 (17.90 m depth) was taken in the marsh area at the same site as the CS core. The cores were collected in 0.8–2.0 m sections by using a pneumatic hammer (Cobra MK1) and a piston sediment corer with a plastic liner (50 mm i.d., 1 m length) for the upper sediment layers (up to 6.70 m for RKS-1) and a hollow stem auger drilling device (Rammkernsonde, RKS) for deeper and more consolidated layers (all equipment from Stitz GmbH, Gehrden, Germany). After retrieving the cores with a hydraulic device (S-2003, Stitz), the plastic core liner was removed and sealed with plastic caps.

The shallow cores were taken to the laboratory and immediately frozen at −10 °C. For sampling, cores were cut into two halves with a circular saw. In order to minimise potential contamination, the outer sediment layer was removed and 4 cm^3 of sediment were taken for lipid analysis. RKS cores were sampled in the field. Sediment was filled into clean glass vials and frozen at −10 °C in the lab. For lipid analysis, RKS-1 was sampled with higher resolution at irregular intervals (total of 55 samples; cf. Section 3), whereas only silty layers of RKS-2 and RKS-3 were sampled.

For the deep cores RKS-1 to RKS-3, a few additional samples were analysed for pollen and the resulting data were compared with the lipid distributions. For the shallow cores pollen data were taken from Behling et al. (2001).

2.3. Analytical procedures

Prior to geochemical analysis, all sediment samples were freeze-dried for 72 h and ground with a planetary mill (Fritsch, Pulverisette 5). Total organic carbon (TOC) content was measured with an elemental analyser (Fisons, NA 2100); sediment (2–15 mg) was weighed into tin cups and organic carbon was determined after removing inorganic carbon by way of acidification with 0.1 M HCl and evaporation at 60 °C for 12 h. TOC is expressed as % of g dry sediment.

For recovery of total lipids, samples were saponified with 5% KOH in $MeOH/H_2O$ (4:1). Dry sediment (300–800 mg) was hydrolysed with 5 ml KOH solution for 65 min at 190 °C in a microwave system (Anton Paar, Multiwave). The hydrolysate was filtered through a GF/C filter, acidified with 2 N HCl to pH 3 and extracted 7× with 2 ml dichloromethane (DCM) each. After evaporation of the solvent, the extracts were redissolved in 500 µl DCM in an ultrasonic bath. *n*-Hexane (10 ml) was added to precipitate hexane-insoluble compounds. The solution was filtered through a GF/C filter, and the residue was washed 5× with 1 ml *n*-hexane. An aliquot was taken, the solvent was evaporated and, after redissolving the residue in DCM, the sample was trimethylsilylated with MSTFA (*N*-methyl-*N*-trimethylsilyltrifluoroacetamide) at 70 °C for 1 h.

Individual lipids were analysed with a Hewlett Packard 5890 Series II gas chromatograph equipped with a cold injection system (Gerstel, KAS 3), a fused-silica column (DB1, 60 m × 0.25 mm i.d., 0.25 µm film thickness) and He as carrier gas (heating rate of the GC oven: 60 °C for 2 min, 3 °C min^{-1} to 305 °C). The gas chromatograph was coupled to a mass spectrometer (MAT 95Q, Finnigan MAT) operated at 70 eV. Lupeol and sitosterol were identified by comparison with retention times and mass spectra of commercial standards (Aldrich and Roth). All other compound identities were confirmed by comparison of characteristic mass spectral fragments and relative retention times with published data (Betancor et al., 1980; Itoh et al., 1982; Burnouf-Radosevich et al., 1985; Killops and Frewin, 1994; Heinzen et al., 1996). The internal standard (ISTD), 5α-androstan-3β,17β-diol, was added after hydrolysis and used for quantification. The relative biomarker distribution was calculated from the mass percentage contributed by each biomarker to the total content of all five biomarkers (taraxerol, sitosterol, β-amyrin, germanicol and lupeol).

Selected samples were age dated using accelerator mass spectrometry at the Leibniz Laboratory for Radiometric Dating and Stable Isotope Research (University of Kiel, Germany; data in Behling et al., 2001).

For multivariate statistical analysis (Primer 5.0) of the biomarker data we used untransformed biomarker contents (µg/g TOC). Based on the Bray–Curtis Similarity (Bray and Curtis, 1957), group average cluster analysis and multi-dimensional scaling (MDS) were carried out. In addition, we carried out principal component analysis (PCA).

3. Results

3.1. Shallow cores

The sediments in the three shallow cores BDA, FDC and CS predominantly consisted of silt containing 0.9–3.3% TOC (Fig. 2). Two layers in the CS core were rich in OM, 8.6% and 4.5% TOC. The high TOC content of the CS surface sample (0.06 m) can be attributed to remnants of fine root material. TOC contents in the BDA and CS cores were generally lower at greater depth than at the surface (with the exception of one sample in the CS core mentioned above), indicating either diagenetic degradation of OM or changes in primary production and relatively undisturbed sediment deposition. In the FDC core, TOC values were fairly constant over the entire section. Radiocarbon dates indicated a sequential sediment deposition with an age of 1265 ^{14}C yr BP at 1.20 m depth.

For the reconstruction of the Holocene establishment of the current mangrove system, taraxerol, germanicol, lupeol, β-amyrin and sitosterol were chosen. The summed total amounts of all five biomarkers decreased considerably with depth in the BDA core, particularly in the bottom part below 5.50 m (from 255 to 28 µg g^{-1} dry sediment; Fig. 2). In contrast, the biomarker content was more uniform in the second mangrove core, FDC (decrease from 58 to 33 µg g^{-1} with slightly higher values in the middle section; Fig. 2). The content of sitosterol decreased strongly with depth in all cores.

In contrast to the two 'mangrove' cores, the total biomarker content increased with depth in the CS core from the marsh area (from 0.7 to 4.6 mg g^{-1} TOC). The increase was associated with a considerable change in the biomarker pattern, particularly with an increase of the proportion of taraxerol in deeper sediment layers (Fig. 2). In the surface sample, sitosterol contributed >50% to the total biomarkers, whereas the proportion of the mangrove biomarkers germanicol and taraxerol was very low. The most dominant lipid in the surface sample was, however, β-sitostanol (24-ethylcholestan-3β-ol, not quantified). In the bottom part (1.23 m) of the core, the biomarker pattern matched the distribution typical for recent mangrove sediments (see also Fig. 3), with taraxerol dominant (53%) and accompanied by smaller relative amounts of β-amyrin (15%), germanicol (10%) and lupeol (15%). Pollen grains were poorly preserved between 0.30 and 0.65 m core depth. Behling et al. (2001) suggested that these mangrove deposits were exposed and the area was relatively dry with a lower frequency of inundation – the initial formation of a salt marsh. Details of the pollen data in the three shallow cores are given by Behling et al. (2001).

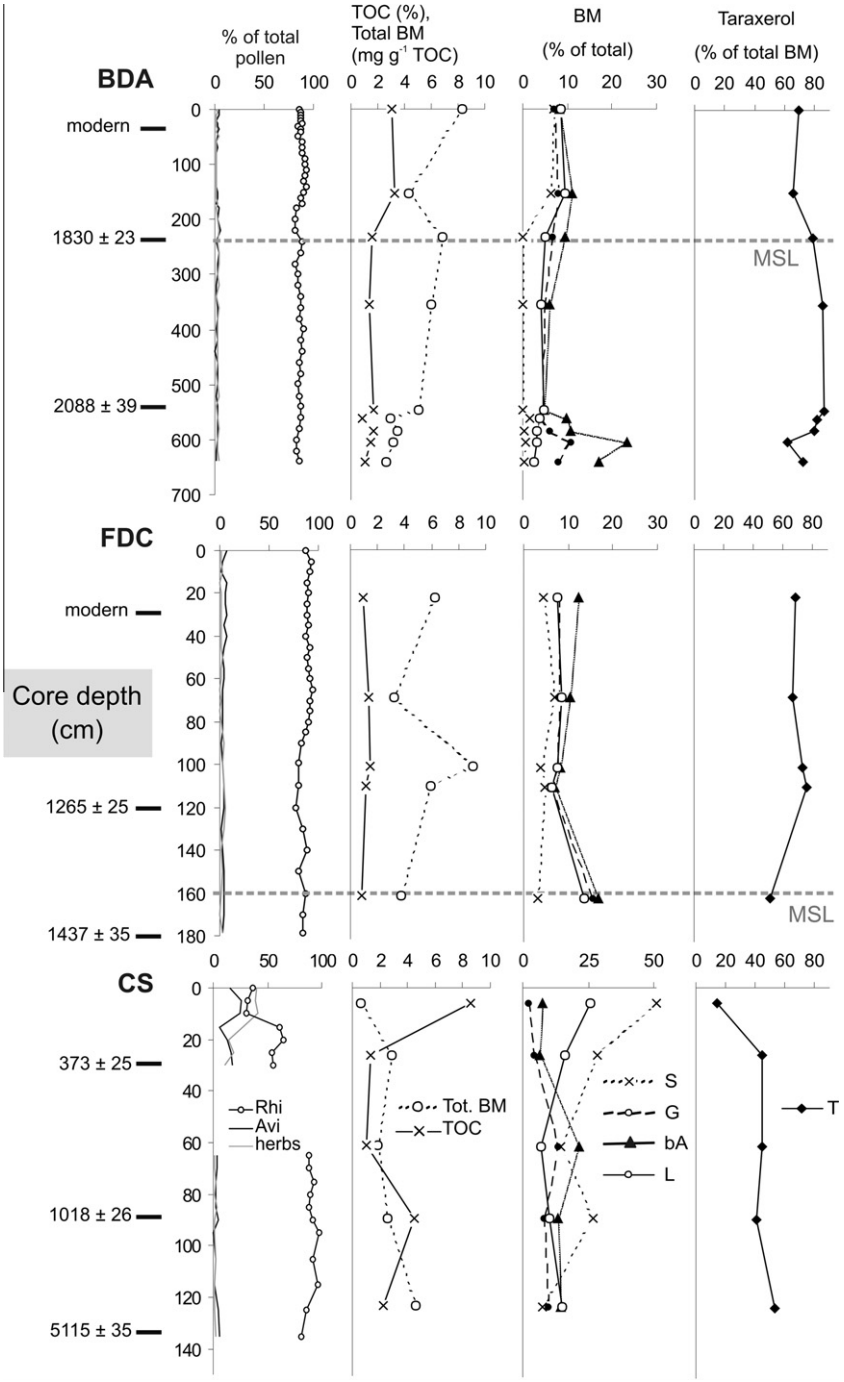

Fig. 2. Shallow core data: Avicennia forest (BDA, Bosque de Avicennia), Salt marsh (CS, Campo Salgado), Tidal creek (FDC, Furo do Chato). ^{14}C age, relative pollen and biomarker distribution, TOC and total biomarker content (total BM). Biomarker distributions are displayed as percentage of the sum of all five selected compounds. T: taraxer-14-en-3β-ol (taraxerol); S: 24-ethylcholest-5-en-3β-ol (sitosterol); bA: olean-12-en-3β-ol (β-amyrin); G: olean-18-en-3β-ol (germanicol); L: lup-20(29)-en-3β-ol (lupeol). Pollen data from Behling et al. (2001). Modern MSL relative to the core depth is indicated with the dashed line (for CS the MSL is 2.7 m below the core bottom).

3.2. Palaeo-cliff, Furo do Taici (RKS-1)

The upper 2–3 m of sediment in the RKS-1 core represented deposits of the current mangrove system. The TOC content decreased in the first 1.90 m depth from 2.1% to 0.2%. In the shallowest sample (0.50 m) the biomarker content was 13 mg g^{-1} TOC (0.27 mg g^{-1} sediment; Fig. 3). The bar chart in Fig. 3 (top left; 0.50 m) shows the typical biomarker distribution in mangrove surface sediments in the study area. The pattern is derived mainly from microbially degraded leaf litter (predominantly *R. mangle*; Koch et al., 2005). From 1.9 m to about 8.5 m, biomarker content was below detection limit. In Fig. 3, we avoided using normalisation to TOC because the low biomarker content would lead to a high variability in the relative biomarker data; selected normalised data are listed in Table 1. Like TOC content, total mangrove pollen continuously decreased in the upper four samples (0.50–1.90 m depth), with *R. mangle*, *A. germinans* and *L. racemosa* contributing 90–97%, 1–6%, and 0–0.3%, respectively, to the pollen count. Below 1.50 m, the sediment colour changed from light to dark grey, which indicated a transition from oxic to suboxic conditions. Greater proportions of fine sand below 2.55 m indicated higher energy conditions.

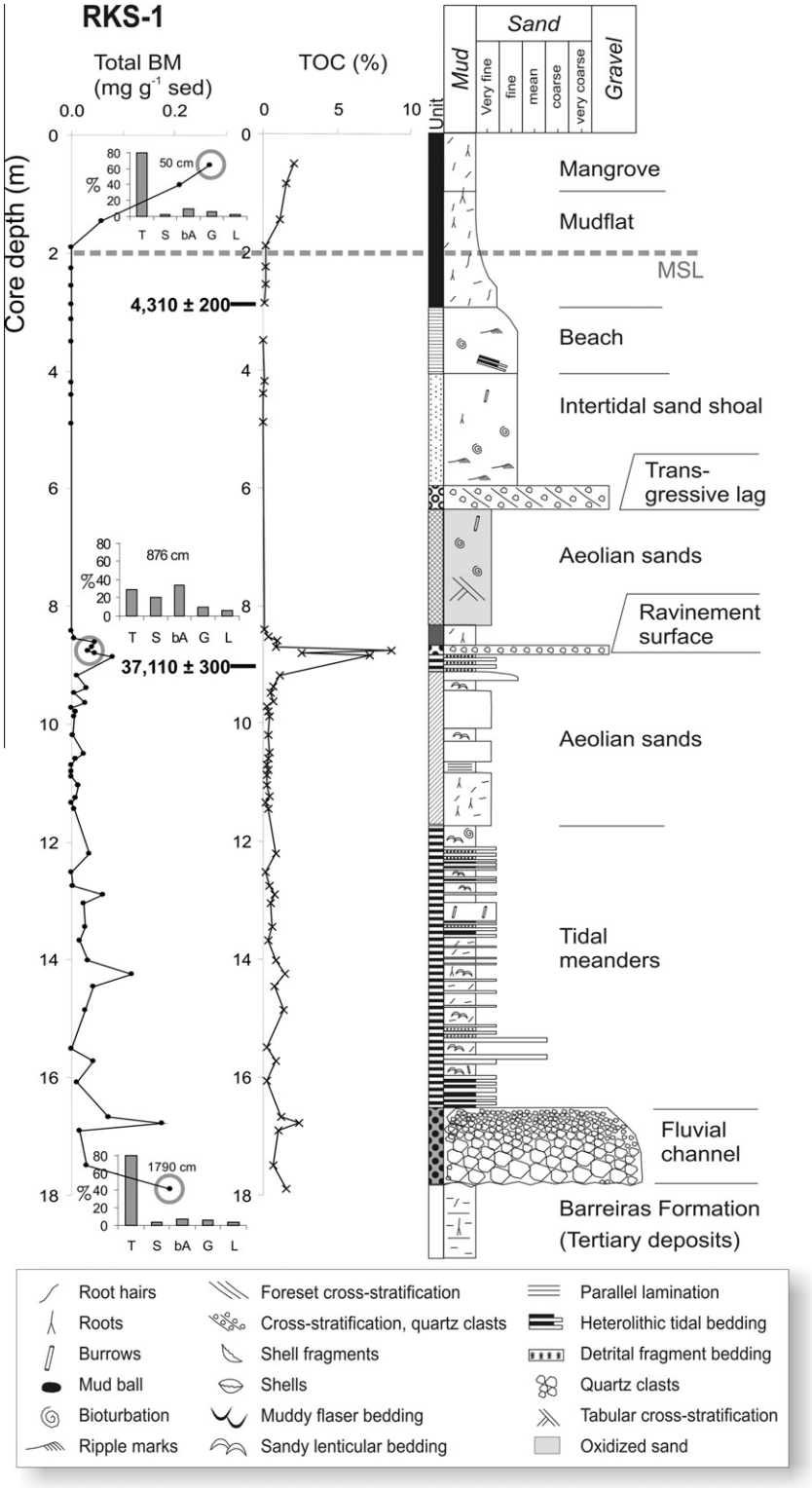

Fig. 3. Core data for RKS-1 (tidal creek, Furo do Taici): sedimentological core description, ^{14}C age, relative pollen distribution, total biomarker content (total BM) and sediment characterisation. Bar charts display the biomarker distribution (BM%) as a percentage of the sum of all five compounds for three samples (marked with circles). T: taraxerol, S: sitosterol, bA: β-amyrin, G: germanicol, L: lupeol. Modern MSL relative to core depth is indicated with the dashed line.

The section between 2.86 and 8.42 m was characterised by a uniform deposition of white fine sand with TOC and biomarker contents near or below detection limit (⩽0.02% TOC), only interrupted by two greenish silt layers at 4.15 and 4.20 m, also with low TOC content (0.06%), and a large, cross-stratified quartz clast layer (6.25–6.55 m). Grain size in this part of the section was homogeneous, but larger than in the top part of the core, indicating an increase in depositional energy. There were no pollen grains along this part of the section, but there were occasional indications of bioturbation and some ripple marks (5.60–6.00 m).

The TOC content in the silt layer below the sand section (8.45–9.38 m) varied between 0.4% at 8.54 m and 8.7% at 8.76 m depth.

Table 1
TOC content (% of g dry sediment), relative biomarker content (% of measured compounds) and total biomarker content of selected samples from RKS cores.

Core	Depth (m)	TOC (%)	Taraxerol (%)	Sitosterol (%)	β-Amyrin (%)	Germanicol (%)	Lupeol (%)	∑Biomarkers (mg g^{-1} TOC^{-1})	∑Biomarkers (mg g^{-1} $sed.^{-1}$)
RKS-1	0.50	2.1	80.4	1.8	9.2	6.1	2.5	13.0	0.27
RKS-1	0.85	1.6	78.3	1.7	10.6	7.6	1.9	13.3	0.21
RKS-1	1.45	1.1	79.8	0.8	12.2	6.3	0.8	5.3	0.06
RKS-1	8.76	8.7	29.5	21.0	33.5	9.7	6.3	0.4	0.03
RKS-1	8.81	2.6	9.2	40.0	10.5	0.9	39.4	4.8	0.04
RKS-1	17.90	1.6	79.9	3.4	7.2	6.1	3.4	11.9	0.19
RKS-2	3.30	1.7	76.6	0.4	12.1	6.9	4.0	13.9	0.23
RKS-2	9.90	1.2	81.2	2.5	6.4	5.9	4.1	5.0	0.06
RKS-3	0.31	1.4	68.9	11.4	7.1	8.7	4.0	3.5	0.05
RKS-3	0.60	0.4	69.4	0.1	16.3	13.3	0.9	16.3	0.06
RKS-3	3.05	1.4	74.8	1.8	9.4	9.1	5.0	11.9	0.17

Pollen grains were not detected despite the high amount of OM. The total content of the five selected biomarkers ranged from 0.4 to 4.8 mg g^{-1} TOC. The sand layer between 8.76 and 8.96 m contained several root fragments characterised by the presence of relatively abundant sitosterol and lupeol (40.0% and 39.4%, respectively) and lower proportions of taraxerol (9.2%), β-amyrin (10.5%) and germanicol (0.9%, Table 1 and bar chart in Fig. 3). Apart from these, 24-ethyl-5α-cholestan-3β-ol, 24-ethylcholestan-3β-ol, 24-ethylcholesta-5,22-dien-3β-ol and triacontanol (*n*-C_{30} alcohol) were found in significant amounts (not quantified). At 8.76 m, the age of the OM was 37,110 ^{14}C yr BP, i.e. near the limit of the radiocarbon method.

From 9.38 to 12.20 m, the sediment was characterised by alternating fine sand and silt layers representing dunes and interdunes. The TOC content never exceeded 0.7% and correlated positively with the presence of finer grain sizes. Some indications of bioturbation and root fragments were found.

Below, between 12.21 and 16.91 m, the sediment consisted of alternating thin (2 cm) silt and sand layers representing tidal meanders. The TOC content correlated positively with silt content and ranged from 0.2% to 2.4%. In the bottom part of the core (17.30–17.90 m), a 20 cm layer of quartz clasts with upwards decreasing grain size indicated changes in deposition dynamics caused by a fluvial channel. The deepest sample at 17.90 m was silty and brownish, and contained several wood and root fragments (Barreiras Formation). The TOC content was 1.6% and mangrove pollen was present in this layer. The lipid distribution was similar to that in the mangrove surface sediment, with taraxerol being the dominant triterpenol, with minor proportions of β-amyrin and germanicol.

3.3. Palaeo-dune (RKS-2) and marsh area (RKS-3)

The RKS-2 and RKS-3 cores consisted mainly of sand, and lipid analysis was only carried out for samples with higher silt content. In RKS-2 the biomarker patterns in the silty layer (2.80–3.39 m; Fig. 4) below the palaeo-dune were similar to those in the mangrove surface sediment (Table 1). In addition, mangrove pollen was detected in this layer, and the TOC content varied between 0.9% and 1.7%. In general, the total selected biomarker content in all non-mangrove layers was lower (1.4–6.1 mg g^{-1} TOC; Table 1) than in mangrove deposits (6.4–13.9 mg g^{-1} TOC).

Core RKS-3 was taken in close vicinity to core CS. The uppermost layer (down to 3.51 m) consisted of silty material with TOC content 0.4–1.7% (Fig. 4). Below 3.51 m, the sediment mainly represented sandy beach and sand shoal deposits with low TOC. Except for sitosterol, all biomarker contents between 0.31 m and 0.60 m depth increased relative to TOC, particularly taraxerol (Table 1). In agreement with the results from the CS core, the top layer (0.31 m) contained relatively high proportions of sitosterol (11.4%) and β-sitostanol (24-ethylcholestan-3β-ol, not quantified). The distribution of biomarkers at 3.05 m resembled that in mangrove surface sediment and was dominated by taraxerol (74.8%), β-amyrin (9.4%) and germanicol (9.1%). The total biomarker content was 11.9 mg g^{-1} TOC. In the RKS-3 core top the mangrove pollen distribution was dominated by Cyperaceae pollen, whereas at 3.51 m depth *R. mangle* and *A. germinans* pollen were most abundant. At this depth, the sediment had an age of 1004 ^{14}C yr BP. Bark remains separated from this sediment sample were dated at 725 ^{14}C yr BP.

The deepest section of core RKS-3 was composed of deposits belonging to the Tertiary "Pirabas" formation (Costa et al., 2002; Rossetti, 2004) and containing remnants of a coral reef that was destroyed in a phase of transgression. It was characterised by high carbonate content, especially in the form of abundant shells and shell fragments, and coarse gravel. TOC content was very low and biomarkers were not detectable.

4. Discussion

4.1. R. mangle biomarkers in core sediments

A major fraction of OM in the surface sediments of the study area is derived from leaf litter. As a result of the methodological challenges only a few studies have reported on the contribution of root biomass to the pool of organic carbon in mangrove sediments. The latest studies estimate a global average mangrove root production of about 44 mol C m^{-2} a^{-1} (Kristensen et al., 2008) vs. ca. 45 mol C m^{-2} a^{-1} of leaf litter production in the study area (1350 g DW m^{-2} a^{-1}, Mehlig, 2001). However, the generally low C/N values in the sediments of the study area suggest that woody tissue, characterised by very high C/N values, did not in general contribute substantially to the sedimentary OM. Nevertheless, decaying roots did cause pronounced local maxima in C/N values and TOC content in the sediment (Dittmar and Lara, 2001).

All mangrove deposits in the cores were characterised by high relative contributions of taraxerol and lower proportions of β-amyrin, germanicol, lupeol and sitosterol. In a previous study in this area, we showed that taraxerol and germanicol are exclusively derived from leaves and roots of the dominant species, *R. mangle* (Koch, 2002; Koch et al., 2003). β-Amyrin was predominant in *R. mangle* leaves but also occurred in lower abundance in *A. germinans* and *L. racemosa* leaves. Lupeol and sitosterol were detected in all three species but the contents were only minor in *R. mangle*. Among the three species, *R. mangle* produces the largest amount of leaf litter with the highest biomarker contents (Koch et al., 2005). As a result of lateral leaf and surface sediment transport by tides, the biomarker signal was similar in all mangrove surface sediments, even in areas dominated by *A. germinans* and *L. racemosa* (Koch et al., 2005).

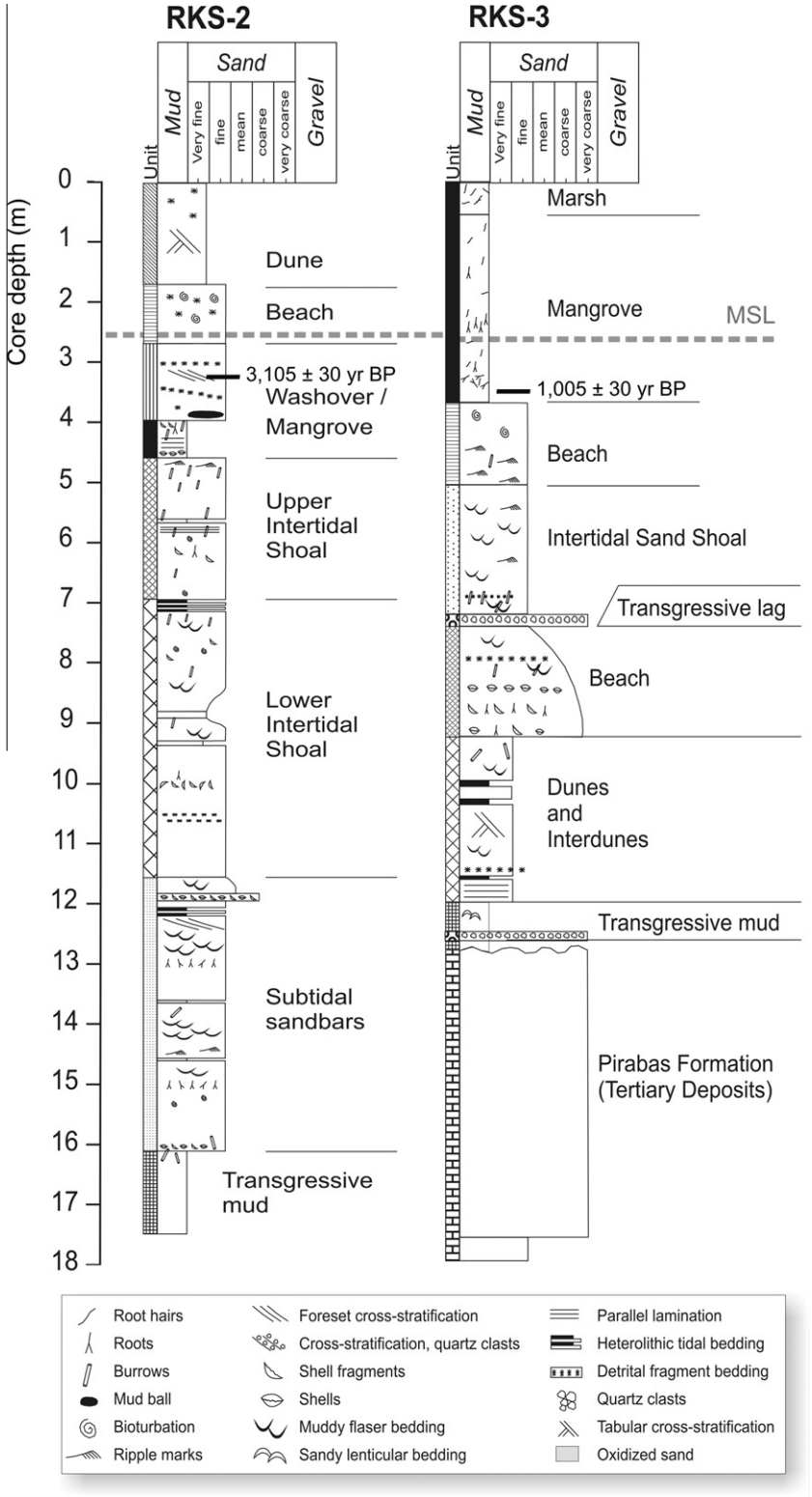

Fig. 4. Core data for RKS-2 (palaeo-dune) and RKS-3 (salt marsh): sedimentological core description and ^{14}C age (BP). Modern MSL relative to the core depth is indicated with the dashed line.

The variability in the relative biomarker pattern was particularly high for samples in which the biomarker content was near or below detection limit. For evaluation of biomarker patterns we therefore focussed on sediments which contained >1% TOC ($n = 40$). Comparing the biomarkers in all samples revealed that germanicol and β-amyrin were correlated linearly with taraxerol, whereas taraxerol neither correlated with lupeol nor with sitosterol (Fig. 5). This suggests that germanicol, β-amyrin and taraxerol have a common source and that they can be considered specific chemotaxonomical biomarkers for *R. mangle* in the study area. Using a set of several biomarkers offers an advantage over applying taraxerol alone, because taraxerol (and both the other compounds)

can potentially be derived from many other higher plant sources (Hegnauer, 1989). Biomarker "fingerprinting" therefore increases the reliability for establishing correct relationships.

The biomarkers were also previously validated in a 3 month microbial incubation experiment (Koch et al., 2005). That study demonstrated that all leaf-derived biomarkers were degraded more rapidly in the sediment than bulk organic carbon. However, the experiment in combination with a quantitative model also revealed that the relative biomarker signature in the sediment predominantly represents *R. mangle* leaf litter. Compared to the other biomarkers, germanicol and β-amyrin showed similar degradation rates, whereas taraxerol was selectively enriched. That finding is confirmed by this study since changes in germanicol and β-amyrin contents in the sediment cores were similar (slope 0.71), whereas the linear correlation of germanicol and β-amyrin with taraxerol showed considerably shallower slopes (0.09 and 0.11, respectively; Fig. 5).

In the upper 1.45 m of RKS-1 (Table 1) biomarker degradation was more than twice as fast as the decay of the bulk of the OM (decrease from 13 to 5.3 mg g^{-1} TOC). Degradation of sitosterol was more efficient than that of triterpenols, resulting in the relative depletion of sitosterol in the upper sediments and confirming previous experimental results on microbial biomarker degradation.

The close correlation of germanicol and β-amyrin with taraxerol (Fig. 5) suggests that the selective relative enrichment of taraxerol happened shortly after deposition, probably within weeks or a few months, and did not proceed in the sediment.

The mangrove deposits were also identified by way of pollen analysis. Comparing surface with older mangrove deposits revealed that the biomarker signatures were relatively invariant. This was consistent with the pollen profiles, which were dominated by *R. mangle* pollen (Fig. 2). The biomarker pattern also resembled results from other mangrove areas with similar species (e.g. Killops and Frewin, 1994; Dodd et al., 1998; Jaffé et al., 2006; Basyuni et al., 2007). Even in the deepest sample of RKS-1 (17.90 m depth), which represented Tertiary (Miocene) sediments, the mangrove biomarker pattern was similar to recent mangrove surface sediments. These Miocene sediments contained mangrove pollen and were part of the Barreiras Formation, which was formed in ancient wetlands such as mangroves and coastal lagoons (Vilas Bôas et al., 2001; Behling and da Costa, 2004). We assume that the residual, refractory proportion of the mangrove biomarkers in the sediment is protected from microbial or photochemical transformation, e.g. to pentacyclic ketones (Volkman et al., 2007) or 3,4-seco-derivatives (Simoneit et al., 2009). This is consistent with similar observations that triterpenols in sediments are diagenetically stable biomolecules (e.g. Versteegh et al., 2004). Barton et al. (1956) already suggested that taraxerol in leaves is ester-bound to functionalised polymers such as cutin. Killops and Frewin (1994) therefore speculated that taraxerol remains largely protected in the leaf matrix and preferentially survives diagenesis within the resistant cuticular matrix.

Assuming that the relative biomarker content of the mangrove leaves did not change substantially over time, any deviation from

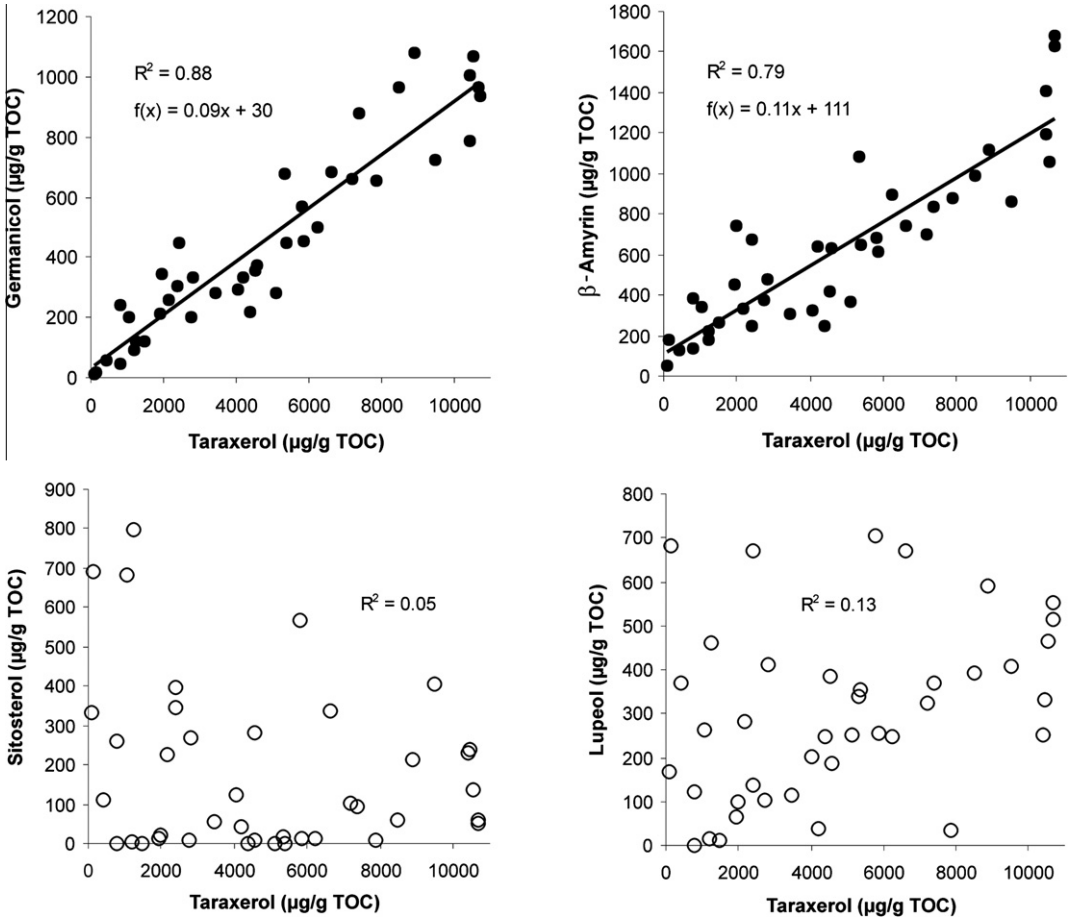

Fig. 5. Correlation of biomarker content (µg/g TOC) in mangrove sediment samples with TOC content > 1%. The three *R. mangle* specific markers were correlated (upper two figures) whereas lupeol and sitosterol did not correlate with taraxerol (lower figures), indicating a source other than *R. mangle*.

the pattern in the cores of this study, such as a relative increase in lupeol or sitosterol, must either be due to an increased contribution by the other two mangrove species *A. germinans* and *L. racemosa* or to marsh vegetation or other allochthonous primary sources such as marine phytoplankton or seagrass. In multivariate cluster analysis (Fig. 6a) and multi-dimensional scaling (MDS, Fig. 6b) of the RKS-1 samples, all mangrove deposits are clearly separated from other sediments. In the cluster dendrogram the *x*-axis represents the degree of similarity; the vertical lines of the branches indicate the similarity value. A similarity value of $S = 100$ would imply that biomarker contents of the samples are identical. Close proximity of data points in the MDS plot represents a high degree of similarity. The validity of the MDS plots can be assessed using the stress value. For two dimensional ordinations, stress values of less than 0.05 give a good representation of analysed data sets (Clarke and Warwick, 1994). The stress value for our MDS analysis was 0.01 and emphasised that the *R. mangle*-derived mangrove deposits are identifiable (e.g. Xu et al., 2007) and that their biomarker patterns clearly differ from other ecotones such as fluvial or mudflat deposits.

Similar results were achieved when only taraxerol was considered. However, PCA revealed that taraxerol, germanicol and β-amyrin contributed equally to the sample variability, so a combination of all three markers as an indicator for *R. mangle* material in the cores provides a higher degree of statistical significance.

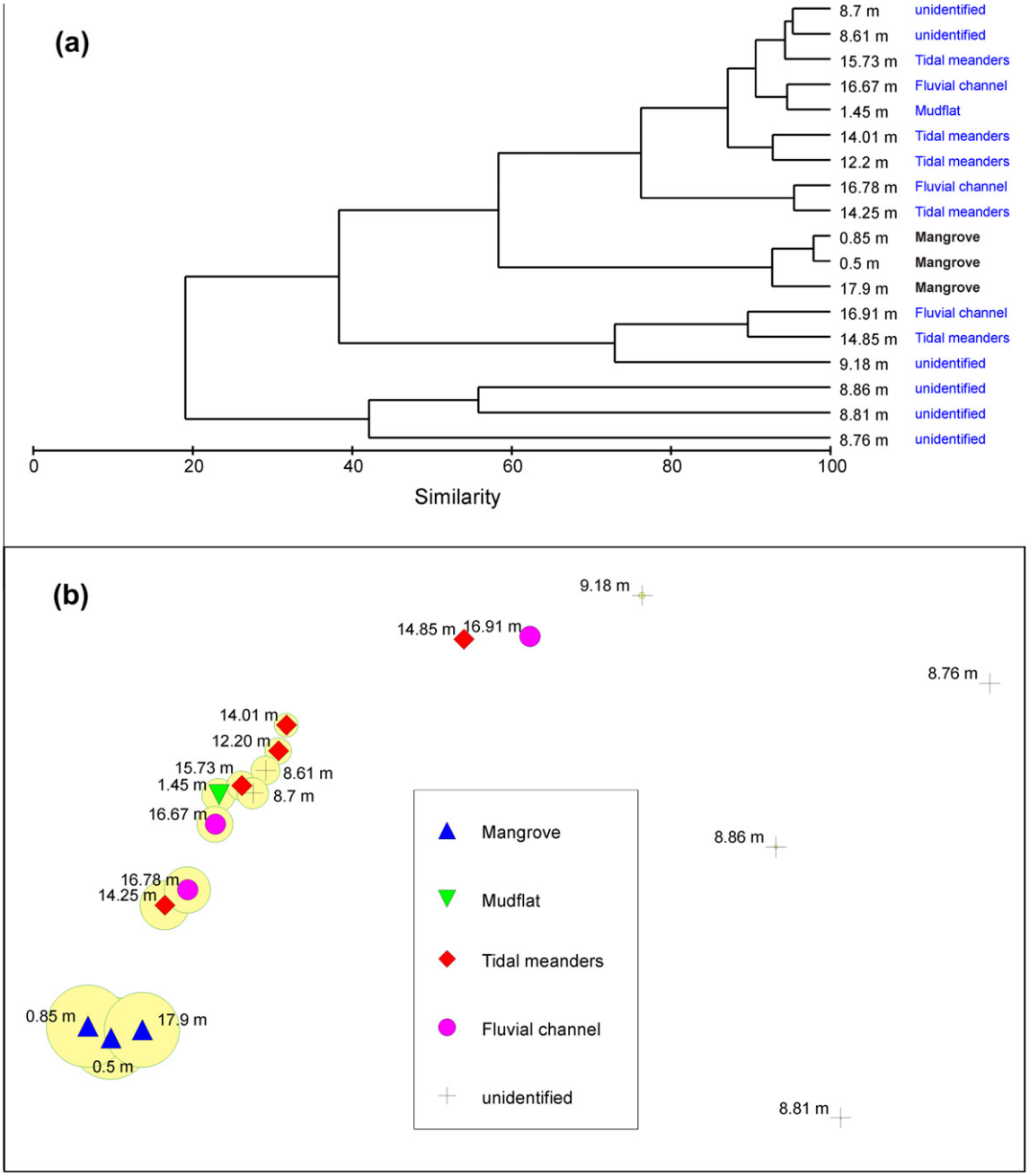

Fig. 6. (a) Multivariate cluster analysis (Bray–Curtis similarity, Bray and Curtis, 1957) and (b) multi-dimensional scaling (MDS) based on biomarker contents (μg/g TOC) in the RKS-1 core sediments with TOC content > 1%. Taraxerol content is represented by bubble size. Mangrove deposits differed from fluvial, mudflat and tidal meander sediments. Samples in the interval 8.61–8.86 m were categorised as unidentified because the origin could not be verified by way of the biomarkers.

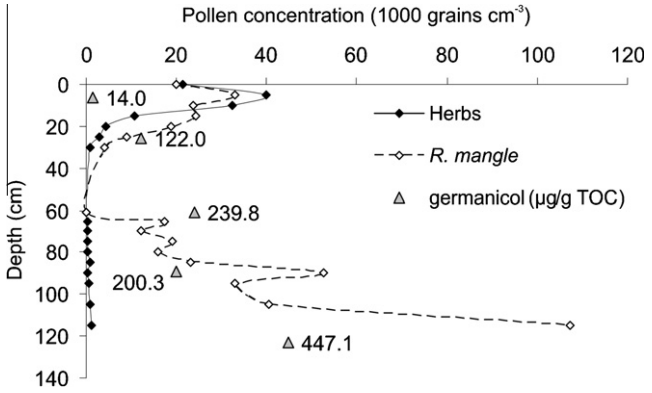

Fig. 7. Absolute mangrove and herbaceous pollen counts and germanicol content, normalised to TOC, in the shallow salt marsh (CS) sediment core.

4.2. Species transition: validation of biomarkers from pollen analysis

In the marsh area (cores CS and RKS-3) biomarker data and pollen analysis (Behling et al., 2001) indicated a transition from mangrove to marsh vegetation (Table 1, Figs. 2 and 4). In the top section of these cores, abundant sitosterol, sitostanol, as well as Cyperaceae and Poaceae pollen, reflected the influence of the recent marsh vegetation (Koch et al., 2003). In deeper sediments, *R. mangle* represented up to 95% of total pollen, herbaceous pollen was relatively scarce (1–3%) and the biomarkers showed the typical mangrove pattern.

Although the vegetation in the CS location was dominated by herbaceous plants, *R. mangle* pollen content was high in the surface sediment as well. This can be explained by high pollen production of this species in neighbouring areas and import via wind drift (Behling et al., 2001). In contrast to *R. mangle* pollen, germanicol and taraxerol content was lowest in the surface sediment and increased with depth (Fig. 7). For this special case, we conclude that the biomarker signatures in the sediment sequence provide a better resolution of the actual vegetation structure and more appropriately describe the origin of the OM.

In general, the biomarker and pollen data showed that both techniques are suitable for tracking the succession in the CS and RKS-3 cores and for distinguishing between mangrove and marsh sediments. However, taraxerol and *R. mangle* pollen were not correlated in our analysis (Fig. 8), as occurred in an earlier study by Versteegh et al. (2004). The low correlation coefficient suggests that there is neither a linear relationship between the relative proportions nor between the contents of taraxerol and *R. mangle* pollen in the sediment. The correlation between pollen and taraxerol contents is potentially biased by (i) different transport mechanisms (wind/tidal drift), (ii) different degradation regimes, (iii) non-linear relationship between pollen and biomarker production, (iv) additional sources for taraxerol, or (v) successional changes in biomarker and pollen production. All of these factors obviously also hinder the important step of calculating quantitative estimates for palaeoproductivity.

4.3. Reconstruction of palaeoenvironment

Radiocarbon analysis of the shallow sediment cores showed that the mangrove deposits accumulated continuously, suggesting that the influence of bioturbation on the sediment succession was low (Behling et al., 2001). Relatively constant TOC values in the FDC core were attributed to a change in subsoil productivity or a change in the degree of degradation. Since the biomarker patterns were quite similar, a change in the degradation regime (e.g. by a change in nutrient or oxygen availability) compared to the other cores is the most likely reason for constant TOC values in this core.

The oldest evidence for Holocene mangroves on the Rio Caeté peninsula is dated at 5100 ^{14}C yr BP at the topographically elevated CS site (2.7 m above MSL), where it was replaced at ca. 420 ^{14}C yr BP by the current salt marsh vegetation (Cohen et al., 2005). The data from the RKS cores extend this picture. Earliest Holocene mangrove remains were found around 4300 ^{14}C yr BP at Furo do Taici (RKS-1, 2.0 m above MSL) and at 1000 yr BP at Campo Salgado (RKS-3, 2.7 m above MSL). At location RKS-2 (2.6 m above MSL) the mangroves were first established around 3100 ^{14}C yr BP and were later covered by dunes. Below these deposits marine and fluvial sands predominated, indicating a higher relative sea level and regular inundation in the salt marsh (RKS-3) and palaeo-dune area (RKS-2). A regression period allowed the first mangroves to become established.

The depth and age of the oldest mangrove deposits at the CS and RKS-3 sites differed strongly, even though both cores were taken in close proximity to each other and at similar elevation (ca. 2.7 m above MSL). A possible explanation may be the existence of a palaeo-channel which was rapidly filled with sediment after being cut off from water supply.

In the RKS-1 core we found an OM-rich sediment layer (8.76–8.81 m; up to 8% TOC) for which an age of 37,110 ^{14}C yr BP was determined. The origin of this material could not be unequivocally

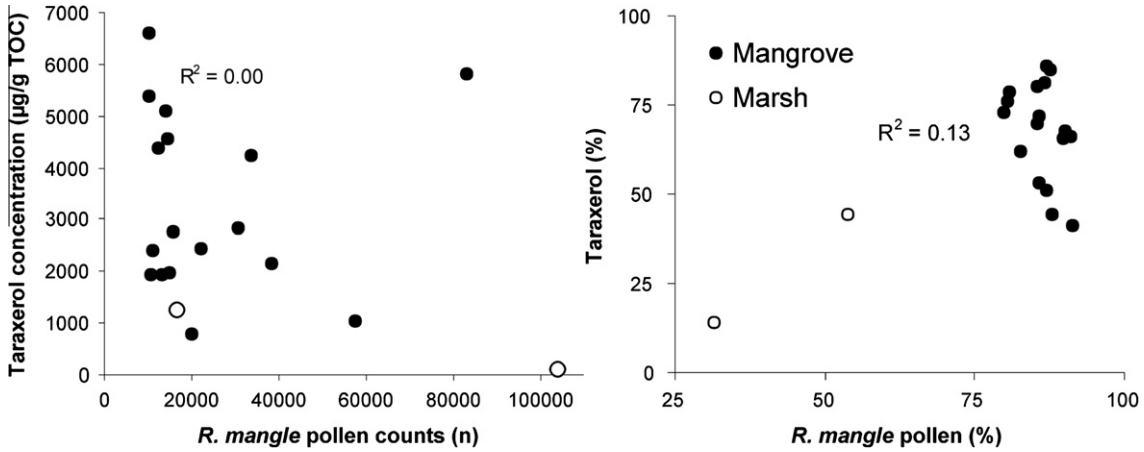

Fig. 8. Correlation of taraxerol and *R. mangle* pollen contents (left) and relative content (right) in mangrove (black dots) and marsh sediments (circles). Coefficient of determination was calculated for mangrove sediments. The marsh samples refer to the upper two samples in the CS core (compare Fig. 7).

assigned. Stratigraphic information suggested sediment deposition in an intertidal shoal. The biomarker analysis showed a higher relative content of β-amyrin and sitosterol (Fig. 3), highly dissimilar to mangrove deposits, which led to a separate cluster in the statistical analysis (Fig. 6). The contribution of β-amyrin suggests a terrestrial rather than a marine origin and sitosterol probably derives from herbaceous species.

Generally, our data confirm the results from earlier studies (Behling et al., 2001; Cohen et al., 2005) and indicate that within the past 5100 yr the relative sea level in the Caeté Estuary was never higher than at present. However, it must be considered that mangroves grow at different elevations in the tidal zone so that the use of mangrove remnants as a palaeo-sea level indicator involves a methodological range of possible error of ca. 1–1.5 m. Nevertheless, according to Behling and da Costa (2001), lake Crispim (Pará, Brazil), located next to the modern coastline with an elevation of 1 m above MSL (Fig. 1), was never flooded within the last 7600 yr. Similar results were found by Vital and Stattegger (2000). For the mouth of the Amazon the authors assumed a relative sea level similar to the present one since 6000 yr BP.

In the sample from the Barreiras group (late Tertiary, RKS-1, 17.90 m core depth) the typical mangrove lipid biomarker distribution was detected. The occurrence of mangrove material in the Barreiras deposits is supported by earlier geological and palynological studies (Behling and da Costa, 2004) and demonstrates the enormous preservation potential of the selected biomarkers. In offshore samples of the African shelf, Versteegh et al. (2004) also identified taraxerol, which persisted for 1.2 million yr. After deposition and an initial, rapid and selective microbial degradation of the plant material, the relative pattern of the chosen biomarkers persisted for 2 million yr or more in the sediments.

5. Conclusions

Comparing microbially reworked surface sediments with deeper mangrove deposits, it was demonstrated that relative biomarker distributions remain largely unchanged, resisting degradation on timescales of millions of years and are suitable for identifying mangrove remains in ancient sedimentary OM. Biomarkers and ^{14}C data for cores RKS-1 to 3 confirm that the recent mangrove system in the Caeté Estuary is not older than 5100 yr and that a transition from mangrove to marsh vegetation in the current marsh area occurred around 420 yr BP.

Taraxerol was repeatedly detected in marine sediments and was shown to originate from mangroves. The combination of several biomarkers and multivariate analyses provides a more reliable tool for the identification of mangrove-derived organic matter than a single biomarker and should strengthen the application for the reconstruction of palaeoenvironments. A future aim would be to reconstruct primary productivity. For our study, production data and biomarker contents of leaf litter, together with microbial decay rates in the sediment of the study area, are available. However, the biomarker content was too variable to reliably reconstruct mangrove leaf litter production. Changes in the degradation regime are probably the most important issue hindering a productivity assessment.

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