

Organic matter in sediments in the mangrove areas and adjacent continental margins of Brazil: I. Amino acids and hexosamines

Organic carbon
Amino acids
Carbon cycle
Mangroves
Continental margin

Carbone organique
Acides aminés
Cycle du carbone
Mangroves
Marge continentale

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ABSTRACT

The nature of sedimentary organic matter from mangroves and the continental margin of eastern Brazil (8°-24° S) has been investigated in order to obtain information on sources and diagenetic processes. The organic matter content of mangrove sediments is three to four times higher than the maximum content of continental margin sediments. Downslope distribution of organic carbon, nitrogen, amino acids and hexosamines shows an enrichment in water depths between 800 m and 1000 m. The distribution of individual amino acids and hexosamines is highly variable in sedimentary organic matter from mangroves and the continental margin, and the observed compositional differences are mainly due to diagenetic alteration. Organic matter is highly reactive in mangrove sediments and refractory in slope sediments, which suggests that recycled organic matter forms the bulk of the organic matter in upper slope sediments.

From the qualitative differences between organic matter in mangrove sediments and in continental margin sediments it appears that mangrove-derived organic matter is not a significant component of the latter. It is also conceivable that organic matter is retained in mangroves or that it undergoes severe decomposition in coastal waters.

RÉSUMÉ

Matière organique dans les sédiments des mangroves et des marges continentales du Brésil: I. Acides aminés et hexosamines.

La matière organique contenue dans les sédiments des mangroves et de la marge continentale du Brésil, entre 8° et 24° S, a été analysée pour déterminer son origine et les processus de diagénèse. La teneur en matière organique des sédiments est trois à quatre fois plus élevée dans la mangrove que sur la marge continentale. Le carbone et l'azote organiques, les acides aminés et les hexosamines présentent un enrichissement le long de la pente continentale, entre 800 m et 1000 m de profondeur. La répartition des acides aminés et des hexosamines est très variable dans la matière organique sédimentaire des mangroves et de la marge continentale; les différences observées sont dues principalement à des altérations diagénétiques. La matière organique est fortement réactive dans les sédiments des mangroves alors qu'elle est réfractaire dans les sédiments de la pente continentale, ce qui indique que la fraction recyclée constitue l'essentiel de la matière organique des couches sédimentaires supérieures de la pente continentale.

Les différences qualitatives entre la matière organique sédimentaire de la mangrove et celle de la marge continentale montrent que la matière organique

dérivée de la mangrove n'est pas un composant majeur des sédiments de la marge continentale. Il est possible que la matière organique soit retenue dans les mangroves ou qu'elle subisse une décomposition importante dans les eaux côtières.

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INTRODUCTION

Continental margin sediments are important depositories of carbon and associated elements, because of high inputs from both terrestrial and marine sources. It is estimated that about 83% of the organic carbon accumulating in modern marine sediments is buried along continental margins, mainly in deltaic and shelf sediments (Bernier, 1982). Possible increases in the primary productivity of coastal waters due to anthropogenically enhanced nutrient loading suggest that continental margins may be significant as a sink for anthropogenic CO₂ (Walsh, 1991). However, from results of calculations of the riverine flux of suspended sediments to the oceans and the annual carbon burial rate Bernier (1992) concludes that modern marine sediments do not qualify as a sink of anthropogenic CO₂.

In this paper we present results from the continental margin of tropical eastern Brazil (8°-24° S), which is also bordered by dense mangrove vegetation. Mangroves comprise one of the least understood of tropical marine ecosystems (Snedaker, 1984), and quantitative data on the exchange of carbon and nutrients between mangroves, coastal and offshore waters are still insufficient to assess the role of the former as a carbon source or sink on a global scale. The global mangrove area is variously estimated to cover 100 000 km² (Bunt, 1992) or 230 000 km² (Snedaker, 1984) of sheltered coastal intertidal land which is <0.2% of the global land surface area. But as mangroves are among the most productive natural ecosystems on the periphery of continents (Ong, 1982), they might be of particular importance for carbon cycling in tropical and subtropical regions, where they account for approximately 75% of coastal vegetation (Linden and Jernelöv, 1980).

MATERIALS AND METHODS

Study area and objectives

The Brazilian continental margin between 8° S and 24° S (Fig. 1) is characterized by a shallow and narrow shelf (10-30 km wide) except for the Abrolhos region (16°-20° S), where a carbonate platform 250 km wide has developed (Melo *et al.*, 1975). The slope is narrow and steep (Emery and Uchupi, 1984). The hydrographic regime is governed by the southward-directed Brazil Current (Stramma *et al.*, 1990). Upwelling of cold nutrient-rich water leads to enhanced primary productivity south of the river Doce (20° S) and near Cabo Frio (23° S; Summerhayes *et al.*, 1976*b*; Valentin *et al.*, 1987). Primary productivity and river input are low. Broad areas of the shelf are characterized by low organic matter deposition. The suspended matter input from the major rivers (Sao

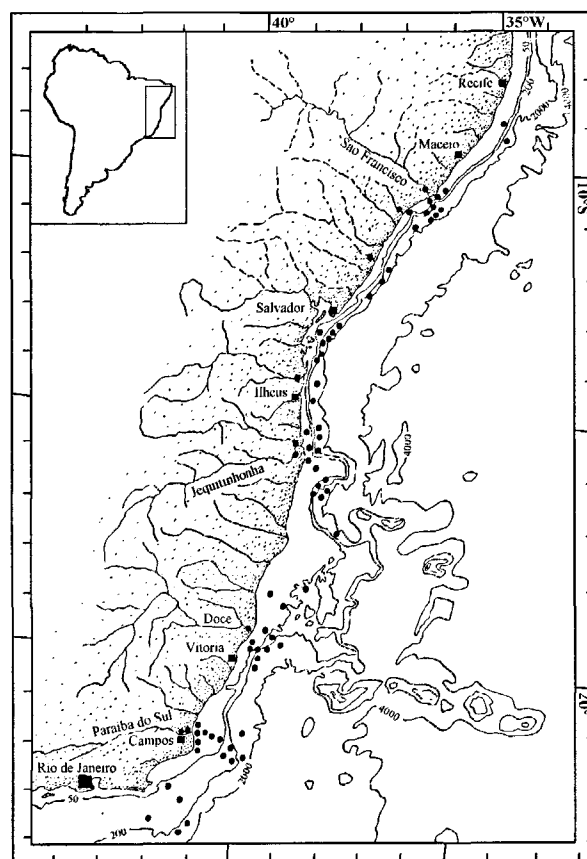


Figure 1

Map of the Brazilian continental margin between 8° S and 24° S including the locations of sediment samples.

Francisco, Jequitinhonha, Doce, Paraíba do Sul) of the investigated area is estimated to amount to 10 t km⁻² yr⁻¹ (annual total 28 × 10⁶ t), which is less than 2% of the annual total of South America (Milliman and Meade, 1983). Coastal vegetation is dominated by dense mangroves (*e.g.* Mabeoone and Coutinho, 1970).

Here we present data on the distribution of organic carbon, nitrogen, amino acids and hexosamines in mangrove and continental margin sediments of eastern Brazil (8°-24° S) and discuss their variability. Amino acids, the building blocks of proteins and major components of organic matter in the aquatic environment (*e.g.* Lee, 1988; Parsons *et al.*, 1977), are labile relative to bulk carbon and nitrogen (*e.g.* Henrichs and Farrington, 1987), and constitute a large part of the sedimentary organic matter in the aquatic environment (*e.g.* Degens and Mopper, 1976). The amount and composition of proteinaceous organic matter has been found to provide information on sources and transformation processes (*e.g.* Cowie and Hedges, 1992; Haake *et al.*, 1992; Ittekkot *et al.*, 1984*a, b*; Müller *et al.*, 1986; Whelan,

1977), a matter which is of particular interest for carbon cycling in continental margins where input, turnover and burial of carbon are much higher than in the open ocean (e.g. Berger *et al.*, 1989; Berner, 1982).

Sample collection and preparation

Continental margin sediments were sampled during two cruises with RV *Victor Hensen* within the framework of the German-Brazilian cooperation programme JOPS (Joint Oceanographic Projects) in November/December 1990 and February/March 1991. Mangrove and river sediments were obtained during a land survey in July 1992. Surface sediments of the Paraiba do Sul mangrove area (Fig. 1; 21° 30' S, 41° 10' W) were sampled during low tide. Continental margin sediments were obtained with a box grab. Samples were dried at 40°C.

Analyses

Total carbon and total nitrogen (N) were analyzed by high temperature combustion with a Carlo Erba (Milan, Italy) Elemental Analyzer NA-1500. Inorganic carbon was measured conductometrically with a Wösthoff (Bochum, Germany) Carmhograph 6. Organic carbon (C_{org}) was calculated. Duplicate analyses resulted in a variation of 2.2% of the mean.

Total hydrolyzable amino acids (THAA) and total hydrolyzable hexosamines (THHA) were analyzed with a Pharmacia LKB (Freiburg, Germany) Alpha Plus 4151 Amino Acid Analyzer after hydrolysis with 6 N HCl for 22 h at 110°C. An aliquot of the hydrolysate was evaporated to dryness, and then taken up in distilled water and evaporated to dryness twice again to remove the remaining HCl. The residue was taken up in an acidic buffer solution and an aliquot was injected into the Amino Acid Analyzer. Duplicate analyses resulted in an average variability of 8.2% for THAA and 7.6% for THHA. Average variability of the major individual amino acids and hexosamines lies in the range of 5-15%, while Arg and amino acids present only at a trace level (Met, Orn) varied by 20.5%, 22.9% and 36.9% of the mean, respectively. THHA concentrations were multiplied by a factor of 1.4 to compensate for losses during hydrolysis (Müller *et al.*, 1986). In all, 98 samples were analyzed.

Table 1

Mangrove and continental margin sediments of eastern Brazil subdivided into six groups representing six sediment provinces. Variables used for cluster analysis: carbonate, biogenic opal, N, C_{org} , THAA, THHA, THAA-C, THHA-C, THAA-N, THHA-N, water depth.

Group	Geographical distribution and number of samples
I	Fine-grained sediments from a mangrove area in the Paraiba do Sul river mouth (2 samples)
II	Fine-grained recent siliciclastic sediments from rivers and the inner shelf near river mouths (19 samples)
III	Coarse-grained relict siliciclastic sediments from the inner shelf inbetween river mouths (34 samples)
IV	Coarse-grained carbonate sediments from the outer shelf (12 samples)
V	Coarse-grained carbonate sediments from the continental slope between 13° and 18° S (9 samples)
VI	Fine-grained siliciclastic sediments from the continental slope of the whole area (22 samples)

RESULTS AND DISCUSSION

Bulk components

Based on a cluster analysis of bulk geochemical data and water depth, we have subdivided the samples into six groups representing six sediment provinces (Tab. 1; Jennerjahn, 1994).

Mangrove sediments from the Paraiba do Sul mouth are dark, anoxic and rich in organic matter. They have a biogenic opal content of 4.9%. The shelf is characterized by three types of sediments: (i) fine-grained recent siliciclastic sediments deposited near river mouths, rich in organic matter and labile nitrogen-containing compounds; (ii) coarse-grained relict siliciclastic sediments on the inner shelf, low in organic matter; and (iii) coarse-grained carbonates on the outer shelf, also low in organic matter. While recent and relict siliciclastic shelf sediments have carbonate contents of 10.9% and 15.3% and opal contents of 3.4% and 1.6%, respectively, shelf carbonates (carbonate 83.3%) contain the lowest amount of opal (0.8%) of all sediments investigated.

On the upper slope, fine-grained siliciclastic sediments with a carbonate content of 27.7% and an opal content of 4.0% accumulate (Fig. 2) in morphological traps, the sole exception being the region between Salvador (13° S) and the Abrolhos Bank (18° S). Here, dilution by coarse shelf carbonates transported downslope leads to accumulation on the upper slope of C_{org} -poor sediments which contain 52.3% of carbonate and 2.1% of opal.

Organic matter

Sediments from the mangrove area in the Paraiba do Sul river mouth contain 4.82% C_{org} , 0.42% N, 14.3 mg g⁻¹ THAA and 2.2 mg g⁻¹ THHA (Tab. 2, Fig. 3). Fine-grained recent siliciclastic sediments from rivers and from the shelf near river mouths exhibit C_{org} (1.43%), N (0.14%), THAA (3.7 mg g⁻¹) and THHA (0.7 mg g⁻¹) contents that are high in comparison with all other continental margin sediments. In contrast, coarse relict siliciclastic sediments covering broad areas of the inner shelf between river mouths and coarse carbonates from the outer shelf contain 0.42% and 0.26% C_{org} , 0.04% and 0.06% N, 1.1 mg g⁻¹ and 1.2 mg g⁻¹ THAA, respectively, as well as 0.2 mg g⁻¹ THHA in both cases. Fine-grained siliciclastic sediments from the upper slope are rich in

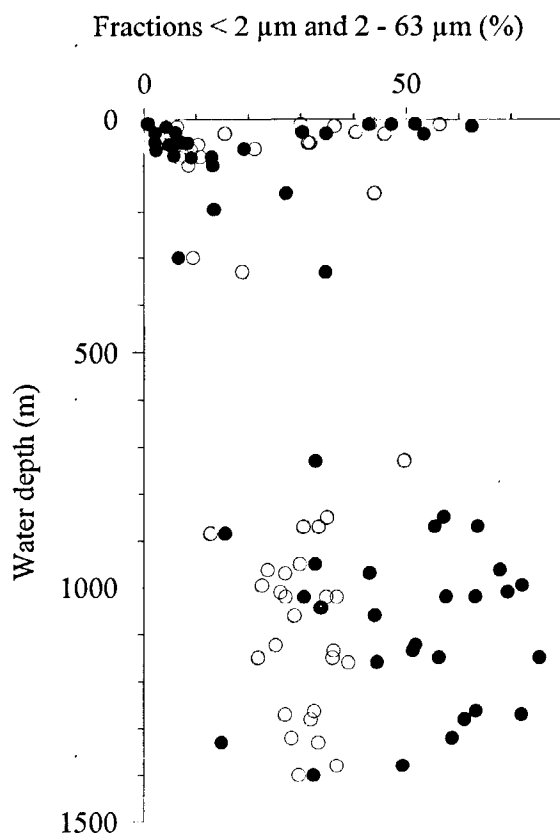


Figure 2

Distribution of grain size fractions $< 2 \mu\text{m}$ (●) and $2-63 \mu\text{m}$ (○) in sediments from the Brazilian continental margin. (Data from Tintnot, 1995).

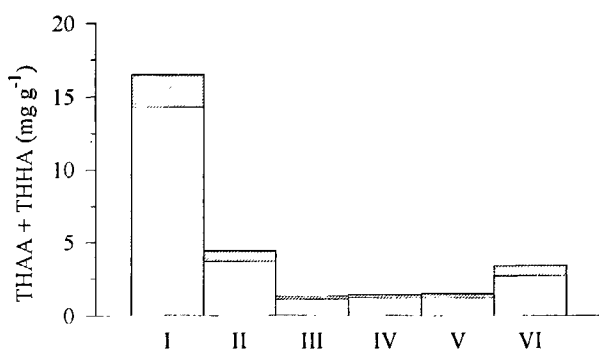


Figure 3

Distribution of THAA (white pattern, mg g^{-1}) and THHA (hatched pattern, mg g^{-1}) in mangrove and continental margin sediments of eastern Brazil (for distribution of groups, see Tab. 1).

C_{org} (1.09%), N (0.14%), THAA (2.7 mg g^{-1}) and THHA (0.7 mg g^{-1}). Carbonate-rich slope sediments from the region between 13° and 18° S, however, are poor in C_{org} (0.51%), N (0.06%), THAA (1.2 mg g^{-1}) and THHA (0.3 mg g^{-1}).

The organic carbon contributed by amino acids and hexosamines is $< 15\%$ in mangrove and recent siliclastic shelf and slope sediments (Fig. 4). Relict siliclastic shelf sediments and shelf carbonates show values of 20% and 30%, respectively. The C/N ratio is highest in mangrove

sediments (11.7) and lowest in shelf carbonates (4.4). Intermediate values were found in all siliclastic sediments (7.8-9.8). Total nitrogen contributed by amino acids and hexosamines is highest in mangrove ($> 50\%$) and lowest in the slope sediments (30%).

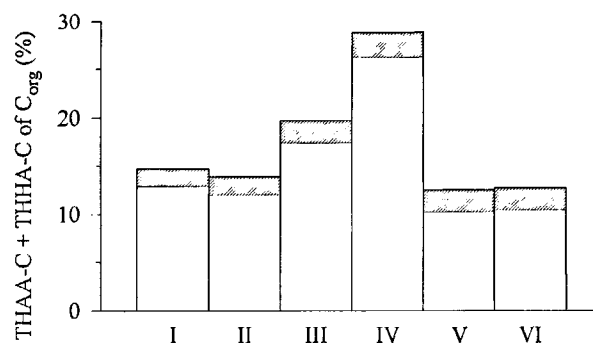


Figure 4

Organic carbon contributed by THAA (white pattern, % of C_{org}) and THHA (hatched pattern, % of C_{org}) in mangrove and continental margin sediments of eastern Brazil (for distribution of groups, see Tab. 1).

Amino acid spectra

Gly, Glu, Asp and Ala are the major amino acids in all spectra and, in general, comprise > 50 mole-% of THAA (51.2-57.5 mole-%) except in mangrove sediments, where they comprise < 50 mole-%. An enrichment in Asp, Gly, β -Ala and γ -Aba is observed from shelf siliclastic to slope sediments. Carbonate sediments from the slope between 13° S and 18° S are enriched in Ser, Gly, β -Ala and γ -Aba. These changes in the amino acid spectra from shelf to slope are similar to changes in amino acid composition resulting from diagenetic alteration as observed in plankton, suspended and sinking particulate matter and surface sediments (e.g. Ittekkot *et al.*, 1984a, b; Müller *et al.*, 1986; Rixen and Haake, 1993).

Asp is significantly correlated with carbonate content (Fig. 5) and hence highest in shelf carbonates. The acidic amino acids Asp and Glu are important for the biochemical and geochemical growth of carbonates (Degens, 1976). Moreover, Carter and Mitterer (1978) found Asp-enriched organic matter to be selectively adsorbed to carbonate surfaces in sediments from Florida Bay. In contrast with the siliclastic sediments, Asp decreases downslope in carbonate sediments. Although a major part of the sediment accumulating in that region is contributed by downslope transport of shelf carbonates rich in Asp, deposition of Asp-poor organic matter derived from other sources gains importance with increasing water depth and distance from the coast.

The aromatic amino acids Tyr and Phe are also higher in mangrove sediments, whereas the non-protein amino acids β -Ala and γ -Aba are lower than in continental margin sediments (Tab. 2). Cowie and Hedges (1992) have shown that vascular plants, phyto- and zooplankton and bacteria contain only trace amounts of the non-protein amino acids β -Ala and γ -Aba which are metabolic products of Asp

Table 2

Geochemical parameters of mangrove and continental margin sediments of eastern Brazil. Numbers given are mean values ± 1 SD. I = mangrove sediments; II = recent siliciclastic shelf sediments; III = relict siliciclastic shelf sediments; IV = recent and relict shelf carbonates; V = slope carbonates; VI = siliciclastic slope sediments. Abbreviations of amino acids and hexosamines: 1. acidic: aspartic acid (Asp), glutamic acid (Glu); 2. neutral: threonine (Thr), serine (Ser), glycine (Gly), alanine (Ala), valine (Val), iso-leucine (Ile), leucine (Leu); 3. basic: histidine (His), ornithine (Orn), lysine (Lys), arginine (Arg); 4. aromatic: tyrosine (Tyr), phenylalanine (Phe); 5. non-protein: β -Alanine (β -Ala), γ -aminobutyric acid (γ -Aba); 6. sulfur-containing: methionine (Met); 7. hexosamines: glucosamine (Glc-NH₂), galactosamine (Gal-NH₂).

Parameter	I	II	III	IV	V	VI
CaCO ₃ (%)	0	10.9 ± 16.1	15.3 ± 17.8	83.3 ± 7.4	52.3 ± 16.7	27.7 ± 9.5
Opal (%)	4.9 ± 0.3	3.4 ± 0.6	1.6 ± 0.8	0.8 ± 0.5	2.1 ± 0.6	4.0 ± 0.7
C _{org} (%)	4.82 ± 0.44	1.43 ± 0.67	0.42 ± 0.30	0.26 ± 0.12	0.51 ± 0.17	1.09 ± 0.23
N (%)	0.42 ± 0.04	0.14 ± 0.05	0.04 ± 0.03	0.06 ± 0.02	0.06 ± 0.02	0.14 ± 0.03
C/N	11.7 ± 0.2	9.8 ± 2.5	9.8 ± 7.5	4.4 ± 2.2	9.0 ± 4.1	7.7 ± 1.0
THAA (mg g ⁻¹)	14.3 ± 1.9	3.7 ± 1.3	1.1 ± 0.8	1.2 ± 0.4	1.2 ± 0.3	2.7 ± 0.6
THHA (mg g ⁻¹)	2.2 ± 0.1	0.7 ± 0.2	0.2 ± 0.2	0.2 ± 0.1	0.3 ± 0.1	0.7 ± 0.1
THAA-C of C _{org} (%)	12.9 ± 0.5	12.0 ± 4.1	17.4 ± 15.6	26.2 ± 13.1	10.2 ± 3.9	10.4 ± 1.7
THHA-C of C _{org} (%)	1.8 ± 0.2	1.9 ± 0.5	2.3 ± 1.7	2.6 ± 1.1	2.3 ± 1.0	2.3 ± 0.4
THAA-N of N (%)	46.7 ± 1.3	35.3 ± 6.6	34.8 ± 13.9	30.3 ± 9.4	25.7 ± 3.5	26.2 ± 4.0
THHA-N of N (%)	4.1 ± 0.5	3.8 ± 0.6	3.7 ± 1.4	2.3 ± 0.6	3.7 ± 0.4	3.9 ± 0.3
THAA acidic (mole-%)	24.4 ± 1.2	25.7 ± 2.1	26.1 ± 3.1	32.7 ± 1.5	30.8 ± 2.7	28.9 ± 1.1
THAA aromatic (mole-%)	5.4 ± 0.3	4.8 ± 0.4	4.9 ± 0.8	4.7 ± 0.4	3.2 ± 0.3	3.1 ± 0.6
THAA non-prot. (mole-%)	2.3 ± 0.3	3.8 ± 1.2	3.2 ± 1.1	2.5 ± 0.9	6.5 ± 1.4	6.2 ± 1.1
THAA/THHA	9.8 ± 1.5	8.0 ± 1.0	10.1 ± 2.9	11.2 ± 2.7	6.0 ± 0.8	5.7 ± 1.0
RI	2.3 ± 0.4	1.3 ± 1.0	1.5 ± 0.9	1.9 ± 0.9	0.5 ± 0.2	0.6 ± 0.3

and Glu (Lee and Cronin, 1982). Ittekkot *et al.* (1984b, 1986) and Müller *et al.* (1986) have used the relative contribution of non-protein amino acids as an indicator of organic matter degradation. Non-protein amino acids increase with decreasing aromatic amino acid contents (Fig. 6). This trend is consistent with previously published amino acid distributions of plankton, bacteria, fungi, higher plants, suspended, sinking and sedimentary organic matter and appears to be independent of organic matter source (Fig. 7). Interestingly, the relationship between aromatic and non-protein amino acids shows different slopes. It is steeper in continental margin sediments than in others, a fact which we attribute to the refractory nature of the organic matter accumulating there.

Based on the above, we use the ratio of the relative contributions of aromatic vs. non-protein amino acids (termed hereafter reactivity index (RI)) as an indicator of organic matter reactivity. Fresh organic material contains higher portions of aromatic amino acids and has a higher RI than sedimentary organic matter (Tab. 3). In general, RI is higher in shelf than in slope sediments from the Brazilian continental margin. Among the shelf sediments,

mangrove (RI = 2.3) and carbonate sediments (RI = 1.9) exhibit higher values than recent (RI = 1.3) and relict (RI = 1.5) siliciclastic sediments.

Spatial variability of THAA and THHA distribution and reactivity

Although the RI of mangrove sediments is lower than that found in fresh mangrove leaves (4.7-5.4) or in bacteria (3.4), it is higher there than in the other investigated sediments. Their amino acid spectra do not differ from those of fresh mangrove leaves, phytoplankton, zooplankton and surface particulate matter (*e.g.* Cowie and Hedges, 1992; Lee, 1988; Müller *et al.*, 1986; Tab. 4). One potential source of organic matter are mangrove leaves. Woodroffe *et al.* (1988) and Benner and Hodson (1985) found a 50% decrease of nitrogen in senescent vs. green leaves of several mangrove species. Continuing decomposition of leaves and stems of mangroves on or in the sediment leads to an increase of protein-nitrogen, probably as a result of bacterial colonization (Untawale *et al.*, 1977; Sumitra-Vijayaraghavan *et al.*,

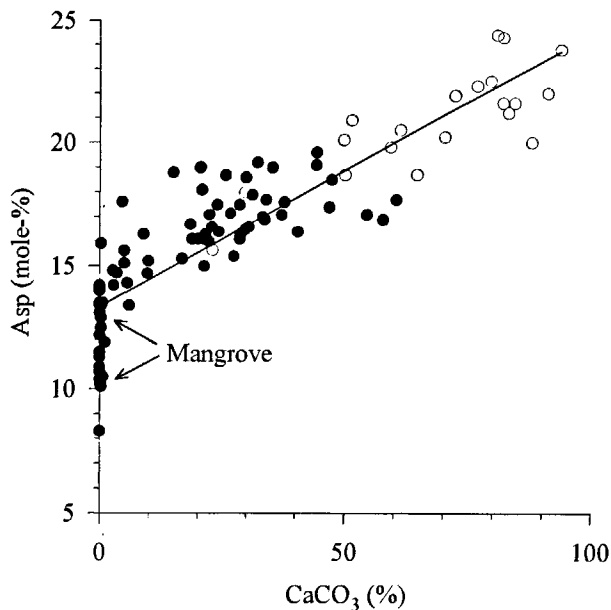


Figure 5

Relative contribution of Asp (mole-%) plotted vs. CaCO_3 content (%) of mangrove (■), siliciclastic (●) and carbonate (○) sediments of eastern Brazil ($Y = 0.11 X + 13.27$, $r = 0.88$, $n = 98$).

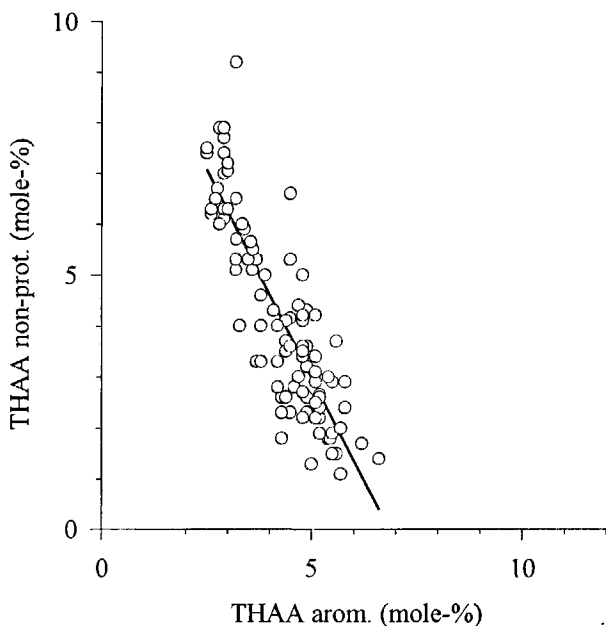


Figure 6

Relative contribution of non-protein THAA (THAA non-prot., mole-%) plotted vs. the relative contribution of aromatic THAA (THAA arom., mole-%) in mangrove and continental margin sediments of eastern Brazil ($Y = -1.63 + 11.14 X$, $r = 0.86$, $n = 98$).

1980; Steinke *et al.*, 1983). Such a rapid loss of organic matter from leaf litter is due to the leaching of water-soluble organic compounds (Twilley, 1985) which are subsequently converted into microbial biomass (Benner *et al.*, 1986). Thus, the observed high reactivity of sedimentary organic matter in the Paraíba do Sul mangrove area may be due to this process. Notwithstanding the high reactivity resulting from microbial biomass, the C/N ratio of 11.7 suggests, however, that the mangrove sediments have a mixed source.

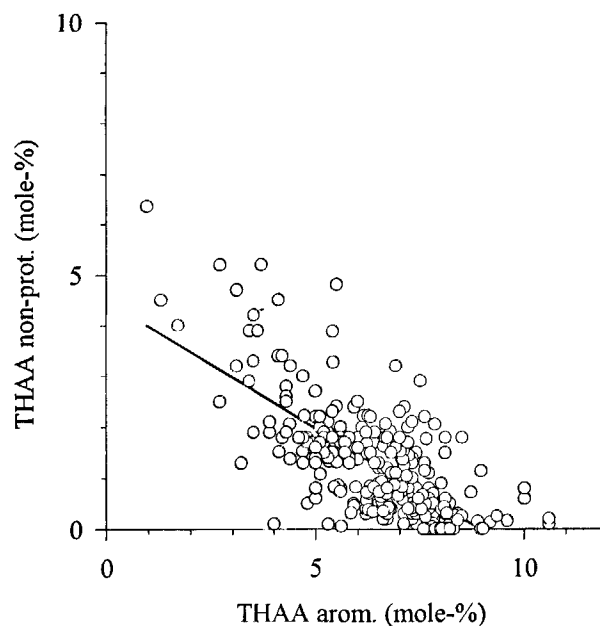


Figure 7

Relative contribution of non-protein THAA (THAA non-prot., mole-%) plotted vs. the relative contribution of aromatic THAA (THAA arom., mole-%) in fungi, bacteria, phyto- and zooplankton, higher plants, suspended and sinking particulate matter and sediments from different areas of the world (for data sources see reference list of Tab. 3; $Y = -0.50 X + 4.49$, $r = 0.71$, $n = 315$).

Possible sources are mangrove leaf litter and refractory organic matter introduced from the rivers. In general, leaf litter is a major component of the organic matter deposited in mangroves (Woodroffe, 1985).

The highest amounts of C_{org} , N, THAA and THHA, as well as the enrichment of non-protein amino acids and the low RI in recent siliciclastic shelf sediments, can again be attributed to a mixed source: primary productivity in estuaries, recycled organic matter from the shelf and terrestrial organic matter introduced by rivers.

In contrast, relict siliciclastic shelf sediments contain small amounts of C_{org} , N, THAA and THHA, but the organic matter deposited is less refractory than that of the recent siliciclastic shelf sediments, as indicated by the low non-protein amino acid content and the higher RI. While protein-nitrogen content is comparable to that of the organic matter of recent siliciclastic shelf sediments, protein-carbon content is much higher, which suggests a lower contribution of terrestrial carbon in relict siliciclastic shelf sediments. Also, these characteristics suggest a marine origin for the organic matter of the relict siliciclastic sediments from the inner shelf between river mouths. Their high reactivity may originate from a thin film of fresh primary produced organic matter which has been found to cover redistributed coarse-grained lithogenic matter recycled numerous times (Summerhayes *et al.*, 1975).

The lowest C_{org} , N, THAA and THHA contents are found in the carbonate shelf sediments. The low C/N ratio (4.4), despite low contributions from amino acids, is similar to those observed by Müller (1977) in deep sea sediments. He concluded that C/N ratios in sediments with a C_{org} content

of <0.3% are largely affected by inorganic nitrogen sorbed to clay minerals. The low protein-nitrogen contribution to total N in carbonate shelf sediments corroborates these findings.

Although siliciclastic sediments from the continental slope contain fairly high amounts of C_{org}, N, THAA and THHA (Tab. 2), the lowest amounts of protein-carbon and -nitrogen measured, the lowest RI and the large portion of non-protein amino acids exhibit the refractory nature of the organic matter.

Downslope variability of THAA and THHA distribution and reactivity

C_{org}, N, amino acid and hexosamine contents are highest in sediments of the Brazilian continental margin in water depths between 800 and 1000 m (Fig. 8). Minimum C_{org}, N, THAA and THHA values were found in sediments from

just below the shelfbreak, whereas maximum values were found on the upper slope. Midslope accumulation of carbon is a common feature of the continental slopes of the world (e.g. Biscaye and Anderson, 1994; Paropkari *et al.*, 1992; Pedersen *et al.*, 1992; Premuzic *et al.*, 1982). The very low RI of slope sediments is comparable to that of deep-sea sediments (Tab. 3). Its conservative behaviour with water depth (Fig. 9) and the refractory nature of the deposited organic matter suggest that it is recycled material.

Clay mineralogy provides further evidence of downslope transport of riverborne sediments (Tintelnot, 1995), mainly through submarine canyons of the major rivers (Summerhayes *et al.*, 1976a). In particular, in the São Francisco canyon, high amounts of river-derived illite were found down to a water depth of 1280 m. The depletion of carbonate and Asp in these canyon sediments compared to the rest of the slope sediments also suggests deposition of riverborne material.

Table 3

Organic matter characteristics and RI of organic material from land and the aquatic environment. Metres refer to water depth. References: * = This paper; 1 = Cowie and Hedges (1992); 2 = Cruz and Poe (1975); 3 = Burdige and Martens (1988); 4 = Strahlendorff (1988); 5 = Kemp and Mudrochova (1973); 6 = Dave *et al.* (1988); 7 = Müller *et al.* (1986); 8 = Ittekkot *et al.* (1984a); 9 = Ittekkot *et al.* (1984b); 10 = Honjo *et al.* (1982); 11 = Bartsch (1993); 12 = Whelan (1977); 13 = Rosenfeld (1979); 14 = Kawahata and Ishizuka (1993); 15 = Chen *et al.* (1977); 16 = Sowden *et al.* (1977).

Material	C _{org} (%)	C/N	THAA-C of C _{org} (%)	THAA arom. (mole-%)	RI	Ref.
Higher plants						
<i>Avicennia schaueriana</i> leaves, fresh	42.2	19.5	6.8	8.4	4.7	*
<i>Avicennia schaueriana</i> leaves, senescent	42.3	41.8	3.2	7.6	3.5	*
<i>Rhizophora mangle</i> leaves, fresh	45.4	33.6	5.2	8.1	5.4	*
<i>Rhizophora mangle</i> leaves, senescent	44.2	62.0	2.6	8.1	4.5	*
Vascular plants	46.0	53.4	–	6.1	4.7	1
<i>Juncus roemerianus</i> lives	–	–	–	6.1	–	2
<i>Spartina cynosuroides</i> live	–	–	–	5.5	–	2
<i>Scirpus americanus</i> live	–	–	–	5.2	–	2
<i>Distichlis spicata</i> live	–	–	–	6.0	–	2
Macrophytes	33.8	12.9	–	5.7	30.2	1
<i>Spartina alterniflora</i> leaves	34.7	19.3	8.9	5.8	3.6	3
<i>Zostera manna</i> leaves	30.6	20.7	10.0	6.6	18.9	3
<i>Haoloduli wrightii</i> leaves	26.6	13.8	14.0	7.2	18.0	3
Water						
North Sea, 5 m	–	–	–	7.9	29.0	4
North Sea, 5 m above seafloor	–	–	–	6.9	18.7	4
Plankton, microorganisms						
Phytoplankton (marine)	24.3	5.7	–	5.9	6.1	1
<i>Phaeocystis glubosa</i>	–	–	–	8.2	–	4
<i>Coscinodiscus granii</i>	–	–	–	9.0	–	4
<i>Biddulphia aurita</i>	–	–	–	4.0	–	4
Zooplankton (marine)	31.4	4.2	–	5.1	4.2	1
<i>Calanus finmarchicus</i>	–	–	–	7.1	–	4
Zooplankton (freshwater)	50.3	4.4	–	9.2	–	5
Bacteria	38.6	3.9	–	5.4	3.4	1
Fungi	39.8	6.9	–	5.6	7.6	1
<i>Enteromorpha flexuosa</i>	–	–	–	6.8	4.6	6
<i>Enteromorpha tubulosa</i>	–	–	–	5.0	5.6	6
Suspended particulate matter						
TSM, S-Atlantic, subantarctic sector	41.5	4.5	–	8.7	87.0	7
TSM, S-Atlantic, antarctic sector	12.4	5.3	–	8.0	–	7
TSM, Lake Ontario (freshwater)	–	–	–	8.2	–	5
TSM, North-Sea, 5 m water depth	25.4	6.6	–	7.8	14.8	4
TSM, North Sea, 5 m above seafloor	21.3	8.0	–	6.8	9.8	4

Table 3 (continued)

Material	C _{org} (%)	C/N	THAA-C of C _{org} (%)	THAA arom. (mole-%)	RI	Ref.
Sinking particulate matter (sediment traps)						
S-Atlantic, Drake Passage, 965 m	2.9	5.6	—	6.6	15.3	7
S-Atlantic, Drake Passage, 2540 m	2.8	6.6	—	6.6	11.9	7
Sargasso Sea, 3200 m	5.1	—	12.3	4.7	2.1	8
Panama Basin, 667 m, Aug-Dec. 1979	11.0	9.6	16.6	8.2	6.8	9, 10
Panama Basin, 1268 m, Aug-Dec. 1979	8.6	8.8	8.8	8.0	3.6	9, 10
Panama Basin, 2869 m, Aug-Dec. 1979	6.9	9.9	14.8	8.0	8.9	9, 10
Panama Basin, 3769 m, Aug-Dec. 1979	5.2	9.1	21.0	5.8	4.5	9, 10
Panama Basin, 3791 m, Aug-Dec. 1979	5.9	11.2	21.0	5.5	2.3	9, 10
Panama Basin, 890 m, Feb.-Nov. 1980	—	—	—	6.8	7.1	9
Panama Basin, 2590 m, Dec. 1979-July 1980	—	—	—	7.1	5.7	9
Panama Basin, 3560 m, Dec. 1979-July 1980	—	—	—	5.3	4.0	9
Northern Bay of Bengal, 782 m, Nov. 1987-Oct. 1988	7.3	7.9	19.5	7.2	5.1	11
Northern Bay of Bengal, 1759 m, Nov. 1987-Oct. 1988	5.2	8.5	14.1	6.5	2.8	11
Central Bay of Bengal, 928 m, Nov. 1987-Oct. 1988	7.7	8.1	17.8	7.2	4.8	11
Central Bay of Bengal, 2255 m, Nov. 1987-Oct. 1988	5.8	8.4	14.5	6.9	4.1	11
Southern Bay of Bengal, 1029 m, Nov. 1987-Oct. 1988	7.0	7.6	18.0	7.7	7.7	11
Southern Bay of Bengal, 2995 m, Nov. 1987-Oct. 1988	5.5	8.2	13.3	7.0	4.7	11
Surface sediments (marine)						
Mangroves, Brazil	4.8	11.7	12.9	5.4	2.3	*
Recent siliciclastic shelf, Brazil	1.4	9.8	12.0	4.8	1.3	*
Relict siliciclastic shelf, Brazil	0.4	9.8	17.4	4.9	1.5	*
Carbonate shelf, Brazil	0.3	4.4	26.2	4.7	1.9	*
Siliciclastic slope, Brazil	1.0	7.8	10.3	3.1	0.5	*
Carbonate slope, Brazil	0.5	9.0	10.2	3.2	0.5	*
Siliciclastic slope, upwelling, Brazil	1.4	7.2	10.7	3.0	0.5	*
Atlantic (30°N, 60°W), 5454 m	0.4	5.0	—	0.5	<0.1	12
Cape Lookout Bight, N. Carolina, USA, 8 m	—	—	15.0	5.8	3.6	3
Florida Bay, USA, Mangrove, anoxic	—	—	—	3.8	—	13
Long Island Sound, USA, anoxic	—	—	—	5.1	—	13
North Sea	0.6	—	—	4.8	2.4	4
Panama Basin (1°N, 84°W), 3450 m	—	—	—	1.0	0.2	14
Panama Basin (5°N, 85°W), 3911 m	1.7	9.9	8.5	1.4	0.4	9, 10
Surface sediments (freshwater)						
Lake Ontario, 225 m	5.2	—	—	5.2	—	5
Sedimentary humic acids, Lake Ontario	51.2	8.6	—	6.6	—	5
Sedimentary fulvic acids, Lake Ontario	36.9	5.7	—	6.0	—	5
Soils						
				(wt.-%)		
Podsollic soil	—	—	—	3.5	—	15
Soil from arctic climate zone	—	—	—	4.2	—	16
Soil from cool temperate climate zone	—	—	—	3.4	—	16
Soil from subtropical climate zone	—	—	—	3.8	—	16
Soil from tropical climate zone	—	—	—	2.8	—	16

Mangrove-derived organic carbon in coastal sediments

Although the coastline of the investigated area is covered by dense mangroves which mostly grow in sheltered areas in river mouths (e.g. Bittencourt *et al.*, 1982; Dominguez and Barbosa, 1994; Mabesoone and Coutinho, 1970), carbon export from mangroves is not necessarily linked to river discharge. Export of carbon and nutrients from mangroves can occur in particulate or dissolved form and mainly depends on the tidal amplitude (e.g. Boto and Bunt, 1981; Gong and Ong, 1990; Rezende *et al.*, 1990; Robertson and Daniel, 1989; Twilley, 1985; Woodroffe *et al.*, 1988). In general, it is confined to shallow coastal waters (Wattayakorn *et al.*, 1990; Wolanski *et al.*, 1990).

Lacerda (1992) estimated global carbon export from mangroves to be of the order of $35\text{--}50 \times 10^{12} \text{ g yr}^{-1}$.

This is about 9.5–13.5% of the total input of terrestrial organic carbon to the ocean by rivers, which is calculated to be $370 \times 10^{12} \text{ g yr}^{-1}$ (POC $172 \times 10^{12} \text{ g yr}^{-1}$, DOC $198 \times 10^{12} \text{ g yr}^{-1}$; Meybeck, 1993). Mangrove-derived carbon might account for 12.6–18.0% of the total input of terrestrial organic carbon to tropical and subtropical seas (Lacerda, 1992), where it could be an important component of continental margin sediments. In the case of Brazil, however, the contribution of mangrove-derived particulate carbon to the continental margin sediments appears to be negligible. The C_{org}-content of mangrove sediments is three to four times higher than that of C_{org}-rich continental margin sediments, and higher by one order of magnitude than that of C_{org}-poor continental margin sediments. Sedimentary organic matter is highly reactive in mangroves, as compared to continental margin sediments

Table 4

Amino acid composition of mangrove sediments, fresh leaves of *Avicennia schaueriana* and *Rhizophora mangle*, phytoplankton and zooplankton (data from Cowie and Hedges, 1992) and total suspended matter from the subantarctic South Atlantic (data from Müller et al., 1986).

Amino acid	Mangrove sediments, Paraiba do Sul (mole-%)	Fresh leaf of <i>Avicennia schaueriana</i> (mole-%)	Fresh leaf of <i>Rhizophora mangle</i> (mole-%)	Phyto-plankton (mole-%)	Zoo-plankton (mole-%)	TSM, subantarctic S-Atlantic (mole-%)
Asp	11.6	9.0	10.6	7.9-15.1	8.9-13.3	9.5
Thr	7.2	6.4	6.3	4.6-5.8	3.8-5.3	5.1
Ser	7.5	6.9	7.0	2.7-5.7	3.3-4.9	5.8
Glu	12.9	12.9	11.8	9.8-20.8	12.4-19.9	12.0
Gly	14.6	10.7	10.4	8.4-12.0	10.1-13.2	8.9
Ala	10.8	8.5	8.8	7.2-13.0	10.4-11.7	10.6
Val	6.6	6.9	6.6	5.5-7.3	4.7-6.8	7.3
Met	1.1	1.9	1.1	1.4-2.4	1.2-2.3	2.6
Ile	4.2	5.7	5.5	4.1-5.4	3.5-5.2	5.3
Leu	6.8	10.2	9.7	6.0-8.8	6.6-7.9	9.6
Tyr	1.9	3.3	3.1	2.1-3.1	1.6-3.6	4.2
Phe	3.6	5.2	5.0	1.6-4.3	2.4-2.8	4.5
β -Ala	1.4	0.1	0.1	<0.1-1.0	0-0.9	0.1
γ -Ala	0.9	1.7	1.4	0.3-0.8	0.3-1.2	0
His	1.5	1.7	2.3	0.8-1.8	0.5-2.0	2.4
Orn	0.5	0.3	0.2	0-1.9	0.2-2.7	0
Lys	4.4	4.3	5.8	5.0-15.2	7.7-11.7	7.6
Arg	2.9	4.3	4.4	2.3-5.5	2.7-5.5	4.4

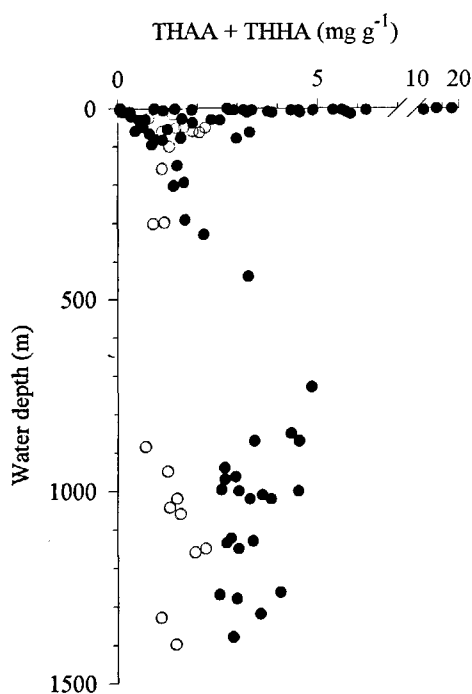


Figure 8

Distribution of THAA + THHA (mg g^{-1}) in mangrove and continental margin sediments. ● = mangrove and siliciclastic sediments, ○ = carbonate sediments.

where it is extremely refractory (Tab. 3). This suggests that mangrove carbon introduced into coastal waters is degraded rapidly and deposited in the coastal zone or else retained in the mangrove areas. Given the small carbon inventory of sediments in broad areas of the shelf with high C_{org} contents near river mouths, only the latter hypothesis seems to be probable, implying that mangroves act as a sink for organic carbon in the investigated area.

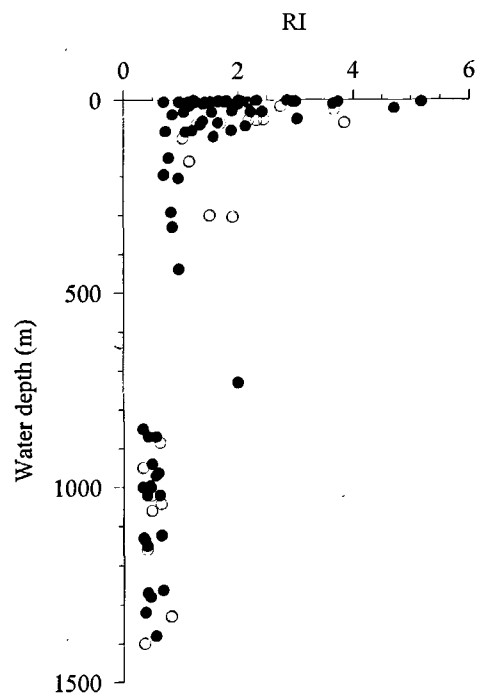


Figure 9

RI of organic matter in mangrove and continental margin sediments. ● = mangrove and siliciclastic sediments, ○ = carbonate sediments.

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