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Isotopic signatures of organic matter in sediments of the continental shelf facing the Orinoco Delta: Possible contribution of organic carbon from savannas

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Abstract

The ^{87}Sr, ^{13}C, and ^{15}N isotopic signatures of organic matter in sediments from the continental shelf facing the Orinoco Delta were measured to determine the contribution of sediments transported from the Amazon River by the coastal Guayana current and the sediments transported by the Orinoco River. Box core samples between 60 and 300 m water depth collected along 4 transects located eastwards to the Orinoco Delta were analyzed. Carbon and nitrogen concentrations decreased with depth under water on the shelf, and were strongly correlated indicating homogeneity of organic matter composition. Phosphorus content was also associated to organic matter in most samples, but some of them revealed deposition of P-enriched sediments. The ^{87}Sr/^{86}Sr ratios showed a strong continental signature averaging 0.7117, therefore, limiting the possible carbon and nitrogen sources associated with these sediments to C3 trees, C4 grasses, or freshwater phytoplankton. The δ^{13}C values were relatively high averaging -21‰, above values reported for sediments on the Amapá shelf and the Amazon River in Brazil. Average δ^{13}C values did not differ significantly among transects. High δ^{13}C values point to the influence of organic matter transported from the C4-plants dominated savannas in the northern fringe of the Orinoco River. δ^{15}N values were positive and averaged 5‰, being within the range of values measured in the Marajo island (Amazon River) and the estuary of the Pará River. The δ^{15}N values differed significantly among transects (4.9–5.2‰), lowest values corresponding to the northernmost transect near the coast of Trinidad, and the highest values corresponding to the transect located at the southernmost position.

Keywords: continental shelf; sediments; organic matter; stable isotopes; Orinoco Delta; Amazon River

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1. Introduction

The present sea level was reached in the Caribbean and the northern Atlantic coast towards the middle of the Holocene (6000–3000 years before present) (Warne et al., 2002a,b). During this period the Orinoco River discharged a mass of sediments causing coast progradation and a widening of the deltaic plain filling the eastern Venezuela basin (Fig. 1). At the same time a significant transport of Amazon basin sediments began by the Guayana coastal current that were deposited on the shelf facing the Orinoco Delta and in the Paria Gulf.

The continuous progradation during the Holocene determined a narrowing of the strait between Trinidad

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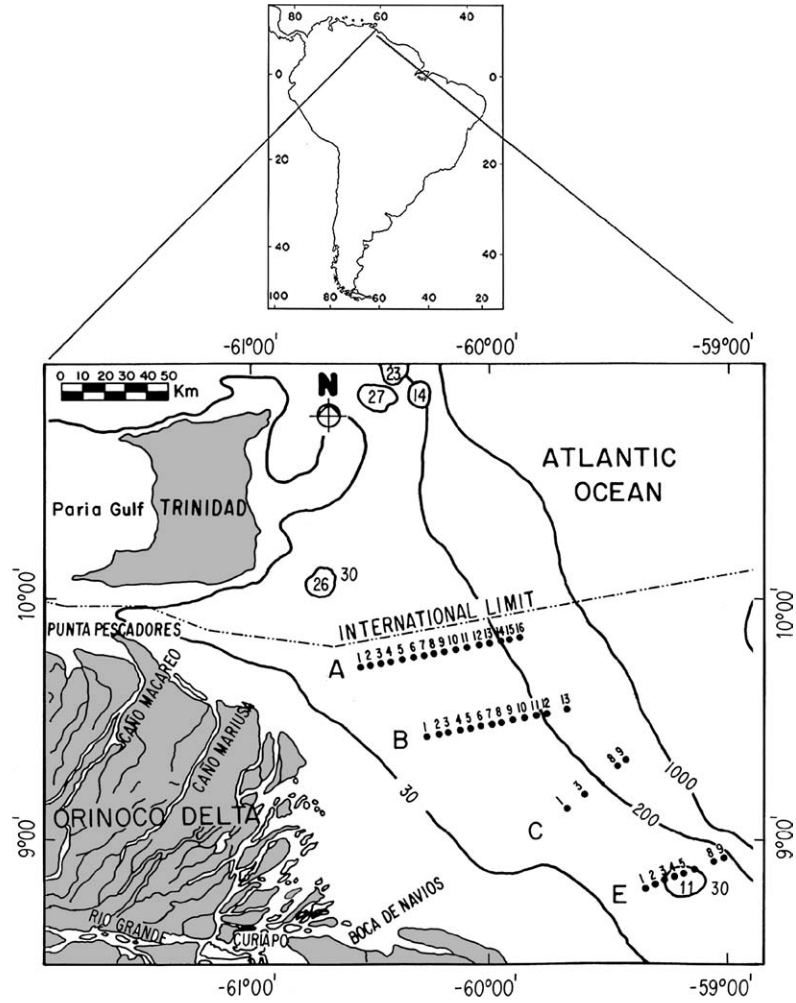

Fig. 1. Location of the sampling points eastwards of the Orinoco Delta. The dots indicate the sampling points, and the numbers on the dots correspond to the samples reported here. The map was slightly modified from an original version produced by PDVSA-Intevep (with permission).

and the continent, which altered hydrodynamics and affected both coast line and continental shelf, resulting in a division of the submarine Orinoco Delta into an Atlantic shelf and the Paria Gulf (Warne et al., 2002a). The mass of sediments carried by the Amazon River into the Atlantic ocean amounts to about 9×10^8 ton/year, while the contribution of the Orinoco amounts only to about 1.5×10^8 ton/year. From the sediment load of the Amazon, about 3×10^8 ton/year are transported northwards along the coast by the Guayana current, from which about 1×10^8 ton/year are deposited on the shelf facing the Orinoco Delta and the Paria Gulf (Allison et al., 1995; Nittrouer et al., 1995).

The sediments transported by the Orinoco and Amazon Rivers originate from watersheds with contrasting geology and vegetation. The Amazon River drains the east flanks of the Andes and several million square kilometers of tropical humid lowland forest. The Orinoco drains a watershed including extensive lowland tropical forests, and the Llanos area, covered by savannas dominated by a continuous grass cover and sparsely distributed, fire resistant shrubs and trees. The generalized vegetation map synthesized by Lewis et al. (1995) shows that 65% of the Amazon basin is covered by lowland humid forest, 15% by mixed montane forests, 4% by seasonal forests, and 16% by savanna vegetation (Cerrados). In contrast, 36% of the Orinoco basin is covered by savannas, 51% by lowland humid forests, 7% of mixed montane forests and 6% by seasonal forests (Fig. 2). Additional features of these basins summarized by Lewis et al. (1995) indicate that both rivers have high amplitude of annual change in water-level, which produce extensive flooding and maintain fringing floodplains along the river margins. The fringing floodplain of the Orinoco is concentrated on the northern margin, predominantly covered by savanna vegetation, while in the Amazon basin it occupies both margins covered by tropical forest. Both rivers also have extensive deltaic flood plains.

The contrasting vegetation features of these basins, forests vs. savannas, may be detected through the analysis of the natural abundance of stable isotopes

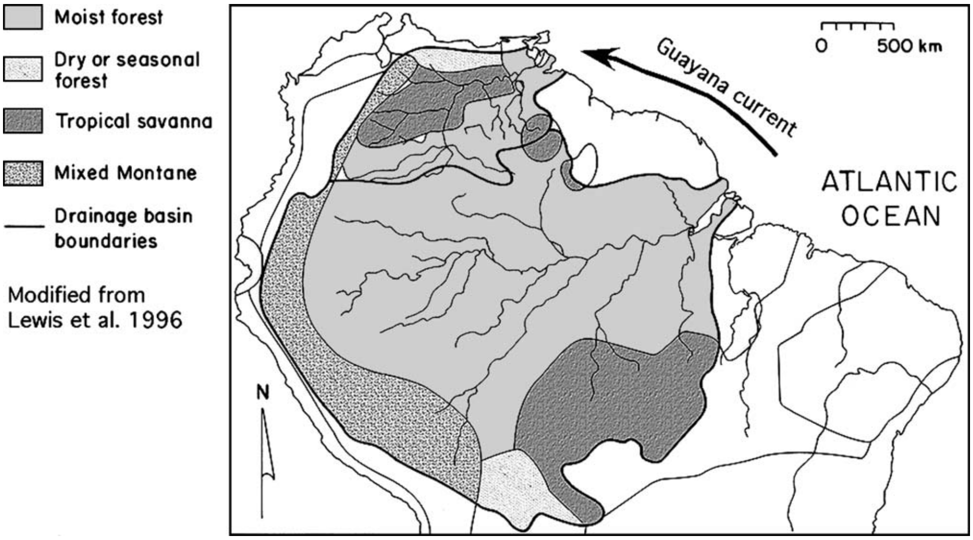

Fig. 2. General map showing the Orinoco and Amazon basins and main vegetation cover. The arrow indicates the direction of the littoral sediment transport from Amazon to Orinoco (Guayana current) (modified from Lewis et al., 1996).

(^{13}C and ^{15}N) in the sediments organic matter. In addition, the contribution of the Roraima formation, one of the oldest geological formations on earth, to the water drained by the Orinoco watershed, may also imprint the sandy sediments transported by the natural abundance of ^{87}Sr. The ^{87}Sr signature would help to differentiate terrestrial and marine sediments, the former showing higher concentrations of this isotope. The development of an off-shore project by PDVSA-Intevep (research institute of the Venezuelan Oil Company) on the Atlantic coast of Venezuela to study the biological and sedimentological features of the continental shelf between Venezuela and the island of Trinidad provided a unique opportunity to test for the presence of these isotopic signatures. Sediments along several transects in the eastern continental shelf of Venezuela were collected (Fig. 1). This paper reports on the strontium, carbon, and nitrogen isotopic signatures of the sediments obtained from sampling points along those transects restricted from 60 to 300 m depth under water.

2. Materials and methods

Sediment samples were collected from the continental shelf facing the Orinoco Delta in October–November 2001, from an oceanographic vessel using a stainless steel box corer of $40 \times 40 \times 20$ cm. Samples were frozen after collection until processed in the laboratory. Forty-two samples were analyzed from the transects A (1–16), B (1–13), C (1–3, 8–9) and E (1–6, 8–9) (see Fig. 1).

To obtain background data on the isotopic signature of organic matter in superficial sediments from the Amazon River basin additional samples were collected from a small boat near the town of Afuá in the Marajo island within the estuary of the Amazon River (2 samples), and the town of Collares within the estuary of the Para River (6 samples), both in Brazil.

Duplicates of approximately 25 g from each sample were extended on plastic petri dishes and dried in a ventilated oven at 60 °C until constant weight (up to 12 days depending on texture and initial water content). Dried samples were manually disaggregated in a porcelain mortar, and after extraction of visible shells of marine animal the soils were passed through 1.0 mm mesh sieve.

2.1. Total organic carbon, nitrogen and phosphorus

We measured organic matter using an ignition procedure developed by Craft et al. (1991) for estuarine and salt marsh soils. The procedure allows quick determination of organic carbon of numerous samples using loss of weight on ignition (LOI %) at 450 °C, calibrated for carbon with a carbon analyzer:

$$\%\text{Carbon} = (0.4 \times \text{LOI}_{450^\circ}) + \left(0.0025 \times \text{LOI}^2\right);\quad r^2 = 0.99$$

Organic nitrogen was measured using a microKjeldahl procedure (Jackson, 1964). Phosphorus was analyzed following a modified method after Murphy and Riley (1962). The soil subsample was digested in binary acid mixture (4:1 $H_2SO_4/HClO_3$) using V_2O_5 as catalyst, at 180 °C for 45 min or more until the mixture was clear. An aliquot of the digestion is mixed with a molybdate reagent (ammonium molybdate in sulfuric acid + ascorbic acid + potassium antimonyl tartrate), that quickly forms a blue colored compound with PO_4, and is read at 882 nm in a spectrophotometer.

2.2. Analysis of stable isotopes

2.2.1. ^{87}Sr

The sediment samples were processed to eliminate organic matter. About 100 mg of silicate sample was weighted into a Savillex teflon beaker with the addition of 4 ml concentrated HF and about 0.5 ml concentrated HNO_3, both of high purity. After the lid had been slightly screwed on the beaker, it was put onto a hotplate at about 90 °C over night. The following day the lid was then taken off and the solution evaporated to dryness. About 5 ml of 6 M HCl was then added to the residue, the beaker was recovered and put on the hotplate at the same temperature. When the solution had become clear (after a day) it was evaporated to dryness, then redissolved in 0.2 ml 3 M HNO_3 and centrifuged. The solution was then loaded onto ion exchange columns packed with crown ether resin which retains Sr and allows most other elements to pass (Horwitz et al., 1992; Pin et al., 1994). After rinsing out the remaining unwanted elements from the columns, strontium was washed out with high purity water. The collected Sr-fractions were then evaporated to dryness. The isotopic composition of Sr is determined by thermal ionization mass spectrometry (TIMS) and the precision of the TIMS analysis is to be within ±0.01%. The Sr standard used was NBS 987: 0.710258 ± 0.000017.

2.2.2. ^{13}C and ^{15}N

Carbon and nitrogen isotopic analyses were measured at the Southeast Environmental Research Center Stable Isotope Laboratory (SERC, Florida International University) using a standard elemental analyzer isotope ratio mass spectrometer (EA-IRMS) procedures. The EA is used to combust the organic material and to form N_2 and CO_2, which were measured on a Finnigan MAT Delta C IRMS in a continuous flow mode using ultra pure He as a carrier gas. The samples' isotopic ratios (R) are reported in the standard delta notation: $\delta\ (‰) = [(R_{\mathrm{sample}}/R_{\mathrm{standard}})-1]1000$. These stable isotopic results are reported with respect to the international standards of atmospheric nitrogen (AIR, N_2) and Vienna Pee Dee belemnite (V-PDB) for carbon. Analytical reproducibility of this study as based on replicates of internal standards is better than ±0.2‰ for $\delta^{15}N$ and ±0.08‰ for $\delta^{13}C$. Sediment samples were treated with HCl to eliminate carbonates before measurement of carbon isotope ratios.

2.3. Statistical analysis

A one-way analysis of variance was performed to test significance of differences in isotope ratios and concentrations. Linear regression analyses were conducted to test relationships between element concentrations and depth. In both cases we used a JMP statistical software (SAS Institute Inc.).

3. Results

3.1. The $^{87}Sr/^{86}Sr$ ratios

A subset of samples from each transect was analyzed for Sr (Table 1). The average value of the $^{87}Sr/^{86}Sr$ ratios was 0.711772 (±0.001996), well above average ocean water (=0.70918) but similar to average river water (=0.7119) as reported by Jones and Jenkyns (2001). This higher ratio reflects a strong terrestrial contribution, a fact of significance for testing the hypothesis on differences in isotopic composition of organic matter. Two samples reported for the Amazon River averaged 0.7129 (Murthy and Beiser, 1968), within the range of the data reported here for the continental shelf facing the Orinoco Delta.

Differences among transects and samples were substantial, given the precision of this methodology, but more analyses are required for a statistical assessment. Differences were ranked as a relative quotient of sample and ocean water

$$((\text{Sample Sr ratio}/\text{Ocean Water Sr ratio}) - 1)1000$$

They were similar in transects A (3.5–4.0) and B (2.9–3.1), but varied markedly in transects C (1.0–10.2) and E (0.5–2.9). The two samples reported for Amazonian sediments varied from 1.6 to 8.3. These ratios suggest that more samples from both basins should be analyzed to assess differences in the Sr signatures of the tributaries draining geologically contrasting basins such as the Brazil and Guayana shields, the savanna region, and the Andes.

3.2. Concentration of carbon, nitrogen and phosphorus

All transects showed a characteristic distribution of element concentration with depth (Fig. 3A–C). The elements analyzed showed a similar pattern of rapid

Table 1
$^{87}Sr/^{86}Sr$ ratios of selected samples from the continental shelf transects

Station	$^{87}Sr/^{86}Sr$ ± st.dev. × 10^6	Sample Sr ratio/ ocean water Sr ratio
A-2	0.712261 ± 18	4.0
A-15	0.711916 ± 14	3.5
B-3	0.711425 ± 20	2.9
B-4	0.711572 ± 26	3.1
C-3	0.710096 ± 17	1.0
C-9	0.716632 ± 16	10.2
E-2	0.711491 ± 15	2.9
E-3	0.710764 ± 16	1.9
E-9	0.709789 ± 12	0.5
Average Orinoco shelf	0.711772	

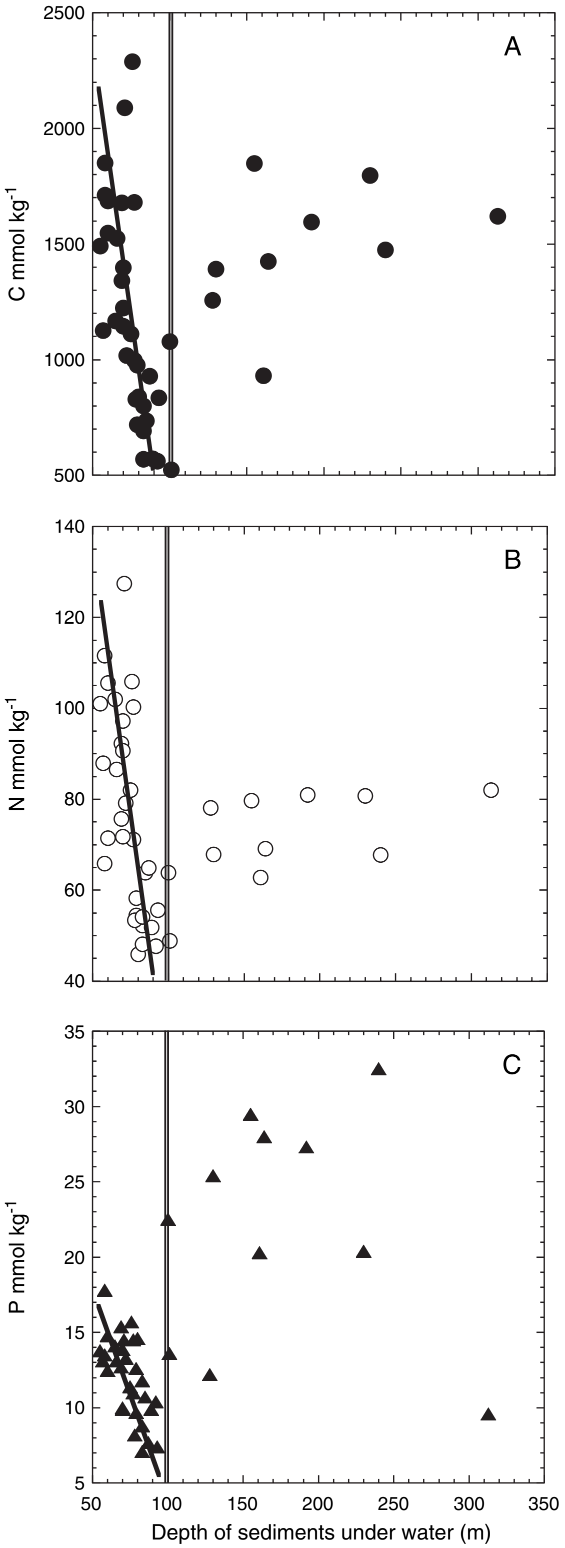

Fig. 3. Vertical distribution of the concentrations of C, N, and P in sediments of the continental shelf. The decrease in concentration between 60 and 93 m was linear and highly significant for all the elements as indicated by the regression analysis. C mmol kg^{-1} = 3327 − 29 m depth; $r^2_{\text{adjusted}} = 0.42$, $p < 0.0001$; N mmol kg^{-1} = 178 − 1.38 m depth; $r^2_{\text{adjusted}} = 0.41$, $p < 0.0001$; P mmol kg^{-1} = 24.17 − 0.164 m depth; $r^2_{\text{adjusted}} = 0.40$, $p < 0.0001$.

concentration reduction in samples from 60 to 93 m depth and increased markedly afterwards. The reduction trend was linear and highly significant (see caption of Fig. 3). Beyond the 100 m water depth sediment concentrations increased but did not show any particular trend. The reduction of C, N and P concentrations occurred within the shelf, the points beyond 100 m water depth are located on the continental slope, where depth increases rapidly with distance from the continent. Average concentration of carbon was significantly smaller in transect B, with <1000 mmol/kg, followed by transect C with 1200 mmol/kg and transects A and E with 1400 mmol/kg sediment (Table 2). Average concentrations of N and P did not differ significantly among transects. The molar ratios C/N differed significantly among transects, but not so the N/P ratios (Table 2).

In all transects, concentrations of C and N were linearly correlated, but the slope of the transect B regression line was 0.0605, compared to 0.304 in transects A and C and 0.0372 in transect D. In the upper panel of Fig. 4 we depicted the regression line of transect B and the regression line corresponding to the other transects (Fig. 4). The differences in C/N ratios of transects A and B are highly significant. It seems that organic matter accumulating in transect B is relatively richer in N than in transect A. Transects C and E occupy intermediate positions. For most samples P concentrations were linearly related to C concentration (lower panel Fig. 4). However, in all transects a few samples stand out of the regression line indicating the presence of organic matter richer in P than the rest. These samples were A13–A16, B13, C8, and E8, all of them collected below 100 m water depth, that is on the continental slope, indicating the more heterogeneous character of the organic matter in this section of the transects.

3.3. Isotopes associated with organic matter, ^{13}C and ^{15}N

The δ^{13}C values showed a quite narrow distribution and averaged −21.03 ± 0.92‰ (1σ). Only one value

Table 2
Average (± standard error) C, N and P concentrations and C/N and N/P ratios

Transects	*n*	C	N	P	C/N	N/P
		mmol/kg				
A	16	1414 (99) a	76.1 (5.1)	17.3 (1.5)	18.7 a	4.9
B	13	908 (110) b	70.7 (5.6)	12.5 (1.7)	12.6 b	5.7
C	5	1249 (177) a,b	71.8 (9.1)	13.5 (2.7)	17.1 a	6.4
E	8	1423 (140) a	82.6 (7.2)	13.5 (2.1)	17.0 a	6.8
ANOVA *p* value		0.007	0.60	0.17	<0.0001	0.09

In parenthesis variation coefficient in %. When $p < 0.05$ numbers in a column followed by the same letter are not statistically different (Tukey HSD test, JMP Statistical Software).

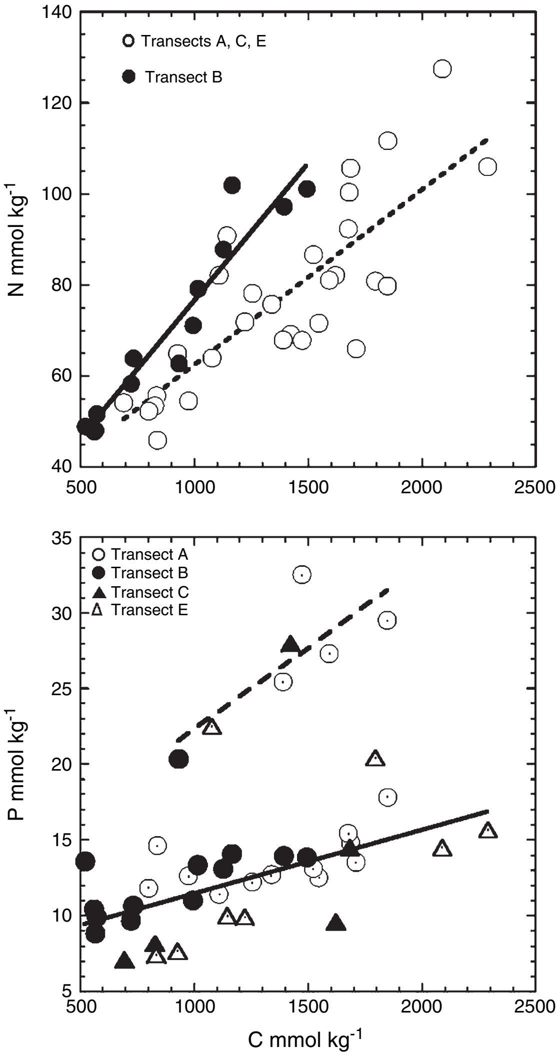

Fig. 4. Relationship between carbon concentration and the concentrations of N and P. In the upper panel the regression lines shown correspond to transect B (closed circles; $n = 13$, $r^2_{adj} = 0.907$, $p < 0.0001$), and the transects A, C and E lumped together (open circles; $n = 29$, $r^2_{adj} = 0.640$, $p < 0.0001$). In the lower panel the solid line corresponds to the general trend ($r^2_{adj} = 0.429$, $p < 0.0001$, $n = 35$), the dashed line corresponds to points beyond 100 m depth ($r^2_{adj} = 0.582$, $p = 0.028$, $n = 7$).

(C9) was out of the main distribution with a value of −25.8‰. There was no regular variation of $\delta^{13}C$ values with depth indicating a rather homogeneous origin of the organic carbon. The average values differed slightly among the transects (Table 3). The more negative values corresponded to transects A and C, but the one-way ANOVA did not reveal significant differences.

The $\delta^{15}N$ values showed a spread pattern between 4.3 and 5.9‰ averaging 5.08 ± 0.28‰ (1σ) and the values of samples below 100 m were slightly more negative than the rest. The average $\delta^{15}N$ values differed significantly among transects (Table 3). The values of transects A and C were slightly, but significantly lower than those of transects B and E.

Table 3
Average (±standard error) relative abundance of ^{13}C and ^{15}N

Transect	n	$\delta^{13}C$ ‰ (VC)	$\delta^{15}N$ ‰ (VC)
A	16	−21.21 (0.21)	4.93 (0.06) b
B	13	−20.90 (0.24)	5.20 (0.07) a
C	5	−21.73 (0.39)	5.04 (0.11) a,b
E	8	−20.47 (0.31)	5.23 (0.10) a
ANOVA p value		0.074	0.018

In parenthesis variation coefficient in %. When $p < 0.05$ numbers in a column followed by the same letter are not statistically different (Tukey HSD test, JMP Statistical Software).

3.4. C, N, P concentrations and isotope values of sediments from Amazon and Para estuaries

Sediments from the Amazon and Para river estuaries yielded elemental concentrations and isotopic values for a first approximation comparison (Table 4). Compared to the average values of the Orinoco continental shelf carbon concentrations were similar or much lower, while nitrogen concentrations were well above or below them. Phosphorus was much less concentrated, resulting in higher N/P ratios than in the Orinoco Delta. These results are probably associated with large variations in the sand content of the Brazilian samples, but this parameter was not quantified.

The $\delta^{13}C$ values were always more negative than the Orinoco values (Table 4). Only one sample, collected under a community of a Cyperaceae species had values above those characteristic for C3 plants. The $\delta^{15}N$ values were well below the range of the Orinoco Delta values, but we do not have enough samples from the Amazon Delta to undertake a statistical analysis of the differences.

Table 4
C, P, and N concentrations and natural abundance of ^{13}C and ^{15}N in sediments under shallow waters (<5 m) from the Amazon estuary (Afuá town, Island of Marajo) and the Pará estuary (town of Collares)

Sample	C	P	N	C/N	N/P	$\delta^{13}C$	$\delta^{15}N$
	mmol/kg					‰	
Marajo (Amazon) 1	1075	6.1	123	8.7	20.1	−28.5	3.15
Marajo (Amazon) 2	1500	7.9	135	11.1	17.1	−28.5	3.63
Spartina field	167	1.0	36	4.6	35.1	−26.4	3.74
Vegetation free sediments	517	2.9	60	8.6	20.8	−26.4	4.14
Vegetation free sediments	1100	3.8	101	10.9	26.7	−26.4	4.43
Sediment under mangrove	633	2.3	60	10.6	26.0	−26.6	3.58
Sediment around Cyperaceae	500	2.2	53	9.4	24.0	−25.8	3.84
Sediment under Cyperaceae	267	1.5	34	7.9	22.6	−23.1	3.77
Orinoco shelf: 42 points from 4 transects							
Average	1240	14.6	75	16.3	5.7	−21.0	5.09
Standard deviation	446	6.2	20	3.8	1.9	0.9	0.28

4. Discussion

4.1. The $^{87}Sr/^{86}Sr$ ratios

^{87}Sr/^{86}86 ratios have been used to establish the marine vs. terrestrial origin of coastal sediments in several parts of the world because sediments of terrestrial origin are relatively enriched in ^{87}Sr (Murthy and Beiser, 1968; Graustein, 1989).

Our small set of data indicates a strong terrestrial signature and showed a large variability among transects regarding the relative accumulation of the isotope ^{87}Sr. This result supports our argument about the significance of organic matter of terrestrial origin as determinant of the C and N concentrations and their isotopic signatures. However, a more detailed sampling will be required to correlate hydrology with Sr ratios (Graustein, 1989). Palmer and Edmond (1989) analyzed Sr concentration and isotopic ratios in samples from the Orinoco and Amazon basins. They showed that the isotopic signature was related to the geological characteristics of the drainage. In the Andean left bank tributaries of the Orinoco they found that there was a good correlation between the values of the Sr ratio and the inverse of the Sr concentration. This was interpreted as a thorough mixing between waters leaching evaporites with low ^{87}Sr/^{86}Sr ratios and those from more resistant radiogenic silicate rocks. The Sr isotope ratios for the Orinoco and its left bank tributaries ranged from 0.71286 in the Apure River to 0.71911 in the Arauca River, while that of the Orinoco averaged 0.71807. All these values are above the average recorded in the present paper for sediments in the continental shelf, indicating a dilution effect related to the mixture of ocean water with lower Sr ratios. The Amazon values reported by Palmer and Edmond (1989) do not show a clear correlation between Sr concentrations and Sr isotope ratios. This is probably due to the size and geological heterogeneity of the basin. The value reported for the Amazon River at Obidos is slightly lower than our Orinoco average, however, the southern tributaries beyond Obidos, that drain the crystalline Brazilian shield, yielded values well above the Orinoco average (0.717 up to 0.732). In the future Sr isotopic ratios should be measured in the Orinoco tributaries draining the Guayana shield (such as the Caroni, Caura, and Cuchivero Rivers), for a more comprehensive comparison of the Sr concentration vs. Sr isotope ratio relationships.

4.2. The organic matter content and concentrations of N and P

The sediments analyzed here were collected within 30 and 300 m water depth, sampling points being located mostly within the continental shelf (60–100 m depth under water) with a few samples taken from the continental slope down to 300 m depth. The quick reduction of C, N, and P concentrations with depth within the shelf indicates that the amount of organic matter carried in the Orinoco sediments decreases rapidly with the distance from the coast. On the continental slope the concentrations of these elements tend to increase, probably reflecting the contribution from other sediment sources. Deeper waters are probably less turbulent, allowing sedimentation of finer particles. However, we did not analyze enough samples from this area to attempt an explanation for the observed increases.

4.3. Carbon and nitrogen isotopic signatures of sediments

In higher plants δ^{13}C values range usually from −10 to −30‰. The main cause for this variation is the photosynthetic metabolism. C3 plants (all trees) growing under full sun exposure have lower values (−24 to −30‰), while C4 plants (tropical grasses and numerous sedge species) have values that range from −10 to −15‰. The range of δ^{15}N values in higher plants is narrower than that of δ^{13}C and varies usually from −5 to +5‰. Plants fixing atmospheric N_2 grown under natural conditions have values around zero or less. The plants using only mineral N from soil (NO_3^- or NH_4^+) have usually positive values. The isotopic analyses were expected to differentiate organic matter in sediments transported from the Amazonian estuary along the Guayana coasts, derived mainly from forest dominated areas (with lower, more negative δ^{13}C values, and possibly more positive δ^{15}N values), from the organic matter transported in Orinoco sediments, presumably influenced by organic matter derived from C_4-dominated vegetation with higher δ^{13}C and lower δ^{15}N values (Medina, 1996; Medina and Izaguirre, 2004).

Natural abundances of ^{13}C and ^{15}N have been successfully used in the investigation of several plant physiological aspects and nutrient cycling in the Amazonian and Orinoco basins. Martinelli et al. (1991) measured the variation in δ^{13}C values in C3- and C4-plants along the Amazon River, and showed large differences among these photosynthetic types. C4-plant values decreased from about −12‰ to −13.5‰, while C3-plant values increased from about −34.5‰ to −30.5‰, from western to eastern Amazon. Differences were explained on the basis of CO_2-recycling and the CO_2-emissions from river water. Martinelli et al. (1992) showed large variations in δ^{15}N values in plant tissues concluding that legumes had usually lower δ^{15}N values than non-legumes indicating N_2-fixation activity. Their study also showed differences in δ^{15}N values among C4-grasses.

Using $\delta^{13}C$ and $\delta^{15}N$ values, Hamilton et al. (1992) found that freshwater phytoplankton and epiphytic algae are the predominant energy sources for many aquatic animals of the Orinoco River. Few species were dependent on organic carbon produced by floating mats of C3- and C4-plants. Pelagic and benthic invertebrates and fishes showed the typical increase in $\delta^{15}N$ value observed in heterotrophs. Phytoplankton samples showed the lowest $\delta^{13}C$ values of these samples ranging from −34 to −36‰.

Forsberg et al. (1993) showed that C4-aquatic macrophytes, that contribute more than 50% of the primary production of the floodplain, are only a minor source of carbon for fishes in the Amazon River (2.5–17.7%). These authors reported average $\delta^{13}C$ values for various plant groups, phytoplankton showed the lowest values (−33.3‰), followed by forest trees (−27.6‰) and C3-macrophytes (−26.2‰), the highest values were measured in C4-macrophytes (−12.8‰).

The values of $\delta^{13}C$ measured in the Orinoco shelf sediments were relatively high (averaging −21‰, see Table 3) compared with organic matter originating either from forests or freshwater phytoplankton. As hypothesized in Section 1, those high values may indicate the influence of particulate organic matter that originated from C4-plants dominated vegetation, in this case, the Orinoco-savannas (Medina, 1996). Sommerfield et al. (1996) conducted carbon isotope analyses on sediments obtained from the continental shelf facing the coast of Amapá, Brazil. The superficial sediment samples were obtained with a method similar to that employed in the Orinoco and the average $\delta^{13}C$ value amounted to −24‰ (Sommerfield et al., 1996; Sommerfield personal communication). These authors documented the carbon isotope distribution of sediments on the Amazon shelf and concluded that the ^{14}C content of modern shelf muds result from the burial of old terrestrial soils carbon (> 5000 years) and atomic bomb ^{14}C enriched marine carbon, implicating that most of the recent riverine particulate carbon is not buried on the shelf. Victoria et al. (1992) measured the carbon isotope composition of Amazon varzea sediments and found a tendency to more negative values of the varzea lakes bottom sediments compared to those sampled along the river channel. The former varied from −18.9 to −32.8‰ and the latter from −19.6 to −28.9‰. The isotopic ratios and concentrations of C and N of the sediments were similar to those of the fine particulate organic matter transported by the river, or produced within the lakes. The distribution of $\delta^{13}C$ values from the Brazilian sites are compared to those reported here in Fig. 5. The standard deviation of the mean increases from 0.9 in the Orinoco shelf up to 1.5 at the Amapá coast, reaching 2.5 and 2.9 within the Amazon River itself indicating that heterogeneity of carbon sources increases towards the Amazon. The sediments from Afua in the Marajo island, and Collares in the Pará estuary, showed the predominance of C3 values, and are comparable to values reported for varzea sediments by Victoria et al. (1992).

Hamilton and Lewis (1992) published few values of $\delta^{13}C$ for superficial sediments in open water areas along the Orinoco River ranging from −26 to −27‰. Those values differed markedly from the signature of coarse debris of the C4-aquatic macrophyte *Paspalum repens* (approximately −12‰). Apparently the predominance of C4-vegetation did not influence the carbon isotope composition of those sediments.

It could be argued that the high $\delta^{13}C$ values may be the result of the contribution of phytoplankton carbon. Indeed, high $\delta^{13}C$ values for phytoplankton of temperate salt marshes have been reported (−21‰, Peterson et al.,

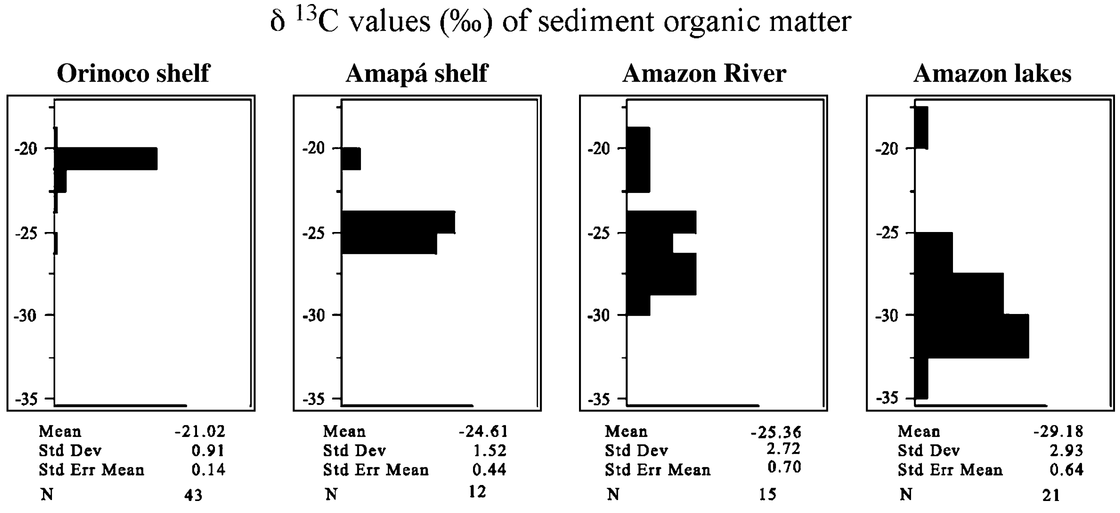

Fig. 5. Comparison of $\delta^{13}C$ values distribution in the Orinoco shelf (present paper), Amapa shelf (Sommerfield et al., 1996, and personal communication), Amazon river varzeas and lake bottoms (Victoria et al., 1992).

1980). However, data for freshwater phytoplankton from the Orinoco (Hamilton and Lewis, 1992) and the Amazon River (Forsberg et al., 1993) indicate values below −30‰ for all the samples analyzed. In addition, Lewis et al. (2001) reported that the net production of phytoplankton calculated over the entire Orinoco floodplain amounts to about 1.6×10^8 kg C y^{-1}, as compared with 1.5×10^{11} kg C y^{-1} transported by the Orinoco River.

The Orinoco transport of particulate organic C amounted to 1641×10^9 kg y^{-1}, and that of particulate N to 209×10^9 kg y^{-1} (Lewis and Saunders, 1989). The C/N ratio calculated on a molar basis from these figures is 9.2, that is, about half that measured in our sediment samples (Table 2). Since there are no evidence of biological changes of those values along the river channel, the different C/N ratios of the sediments can be explained by the contribution of C richer organic matter from sea water, and/or quicker mineralization rate of nitrogen compounds as the sediments are deposited on the shelf.

Particulate P transported by the Orinoco amounted to 0.045×10^9 kg y^{-1}(Lewis and Saunders, 1989), giving a N/P ratio calculated on a molar basis of 10.3, that is, nearly twice as high as the N/P ratios measured in our sediments (Table 2). We hypothesize that this change could be explained by the contribution of P richer organic matter from sea water, or as stated above, that nitrogen compounds are selectively mineralized.

The largest fraction of particulate organic matter transported by the Orinoco probably derives from forests and savannas that are flooded during the high water period, and also from macrophyte vegetation developing along the river channel, particularly within the Delta area itself. In the Amazon River, contribution of organic matter from forests and macrophytes should predominate. We interpret the observed differences in natural abundance of ^{13}C between the Orinoco and Amazon shelves as a result of deposition of particulate organic matter derived from vegetation differing in photosynthetic pathways, the C4-grasses dominating the flooded savannas at the northern fringe of the Orinoco River, and the C4-macrophytes characteristic of both the Amazonian and Orinoco lower basins, and the C3-forests covering the fringe plains of the Amazon River.

We did not find much data on δ^{15}N values from Amazon sediments to compare with those reported here. Our values from Afua and Collares are consistently positive, and lower than the values for the Orinoco shelf. Hamilton and Lewis (1992) reported δ^{15}N values for fringe sediments under free water in the Orinoco with a 3–5‰ range, a little below the values reported here. Their δ^{15}N values for C4-grass are slightly higher than those corresponding to C3-plants. Plankton may be an important source of ^{15}N for the shelf sediments. In temperate salt marshes plankton showed higher δ^{15}N values than a C4-grass (*Spartina alterniflora*) and upland C3 plants (Peterson et al., 1980). Our hypothesis on the relatively lower δ^{15}N values in the Orinoco compared to the Amazon was not supported by the results. Interestingly, Lewis and Saunders (1989) hypothesized that the large values for total N transported by the Orinoco could only be explained by a substantial contribution of biological N_2 fixation. Our values for natural abundance of ^{15}N, however, do not support this assumption. For the tropical systems analyzed here many more measurements of isotopic ratios are required for a precise statement. Analysis of river sediments in both basins are required to detect the kind of relationships between δ^{15}N values of sediments and those of terrestrial, flooded and floating vegetations.

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