Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter of Nova Viçosa–Caravelas estuarine complex, southern Bahia, Brazil

Aplicação de isótopos estáveis de carbono orgânico e nitrogênio e relações C/N como indicadores de fontes de matéria orgânica no complexo estuarino de Nova Viçosa–Caravelas, sul da Bahia, Brasil

Saulo Spano¹, Andre Luiz Belem², Rafael Nunes Doria³, Maria do Rosário Zucchi^{3*}, José Roberto Bispo de Souza³, Alexandre Barreto Costa³, Carlos Alexandre Domingues Lentini³, Antônio Expedito Gomes de Azevedo³

ABSTRACT: This study characterized the elementary ratio and isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N) of surface sediments and suspended solids in surface water of 20 sample points in the estuarine complex of Nova Viçosa–Caravelas, southern Bahia, Brazil. The $\text{d}^{13}\text{C}_{\text{DIC}}$ of the dissolved inorganic carbon (DIC), the $\delta^{18}\text{O}$ and δD and physico-chemical parameters of water was analyzed to estimate the contribution of continental sources, marine and anthropogenic interference in the study area. The area is characterized by the influence of adjacent coastal area through the main channel of Caravelas Estuary entrance and the Peruípe River in Nova Viçosa Estuary, as the main freshwater intake. The highest values of $\delta^{13}\text{C}$ in sediment and DIC in water were found in the Caravelas bar and higher values of total organic carbon and C/N ratio found within the two channels that interconnect the estuaries of Caravelas and Nova Viçosa. The isotope ratios of carbon and nitrogen indicate that the analyzed organic matter has terrestrial origin with strong signature of mangroves, characteristic of estuarine regions. Although the values of C/N indicate an anthropogenic contribution at some sampling points, the $\delta^{15}\text{N}$ found, compared with the literature, suggests that processes of N series cycling in the estuary are sufficient to keep the impact of human activity in the region at low levels. The results may serve as a baseline for future monitoring and environmental studies in estuarine complex of Nova Viçosa–Caravelas.

KEYWORDS: estuarine complex Nova Viçosa–Caravelas; environmental isotopes; sediment and water.

RESUMO: Este estudo caracterizou as razões elementares e isotópicas ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C/N) de sedimentos superficiais e material em suspensão na água superficial em 20 pontos amostrais no complexo estuarino de Nova Viçosa–Caravelas, sul da Bahia, Brasil. Foram analisados o $\delta^{13}\text{C}_{\text{CID}}$ do carbono inorgânico dissolvido (CID), o $\delta^{18}\text{O}$ e δD e parâmetros físico-químicos da água como forma de estimar a contribuição de fontes continentais, marinhas e interferência antrópica na região de estudo. A área é caracterizada pela influência da região costeira adjacente da entrada do canal principal no estuário de Caravelas e pelo rio Peruípe no Estuário Nova Viçosa com o principal aporte fluvial. Os maiores valores de $\delta^{13}\text{C}$ no sedimento e CID da água foram encontrados na barra de Caravelas e maiores valores de carbono orgânico total e relação C/N dentro dos dois canais que interconectam os estuários de Caravelas e Nova Viçosa. A razão isotópica de carbono e nitrogênio indica que a matéria orgânica analisada tem origem terrestre com forte assinatura de mangues, característicos de regiões estuarinas. Embora os valores de C/N indiquem uma contribuição antrópica em alguns pontos, o $\delta^{15}\text{N}$ encontrado e comparado com a literatura sugere que processos de ciclagem da série N no estuário são suficientes para manter o impacto da ação humana na região em níveis baixos. Os resultados obtidos poderão servir de linha base para futuros estudos ambientais e de monitoramento no complexo estuarino de Nova Viçosa–Caravelas.

PALAVRAS-CHAVE: complexo estuarino Nova Viçosa–Caravelas; isótopos ambientais; sedimento e água.

¹Graduate Program in Geology, Centro de Pesquisa em Geofísica e Geologia, Universidade Federal da Bahia - UFBA, Salvador (BA), Brasil. E-mail: spanosaulo@gmail.com

²Departament of Geochemistry, Universidade Federal Fluminense - UFF, Niterói (RJ), Brasil. E-mail: andre_belem@geoq.uff.br

³Graduate Program in Geophysics, Instituto de Física/Centro de Pesquisa em Geofísica e Geologia, Universidade Federal da Bahia - UFBA, Salvador (BA), Brasil. E-mail: mrzucchi@ufba.br; mrdoria@gmail.com; otrebormor@yahoo.com.br; abc@ufba.br; clentini@ufba.br; expedito@ufba.br

*Corresponding author

Manuscrito ID 30038. Recebido em: 02/10/2013. Aprovado em: 24/02/2014

INTRODUCTION

Estuaries are transitional environments between land and ocean, where freshwater originating from land drainage mixes with seawater, creating one of the highest biological productivity areas on the planet (Flemer & Champ 2006). Due to its ecological importance, estuaries provide important services such as food resource, recreation and harbor activities, and act as a gateway from the ocean to the interior (Marques 2009). However, human activities may cause modifications in local water quality and circulation, through hydraulic modification of water ways, resulting in changes of nutrient transport, sediments, and domestic, agricultural or industrial sewage discharge and even in changes in the morphology of the estuarine basin (Levenson 1987).

One of the modern tools to assess geochemical processes in this environment and to detect anthropic influence is the use of natural stable isotopes as oxygen (O), hydrogen (H), carbon (C) and nitrogen (N), which can carry fingerprints of their hydrologic flows and sedimentary processes, including any anthropogenic modification on the natural system (Zetsche *et al.* 2011).

In the ocean, carbon can be found in the form of dissolved inorganic carbon (DIC), dissolved organic carbon and particulate organic carbon (from phytoplankton, algae, and/or higher plants and detritus). Most of the organic carbon produced is degraded, but the small amount that undergoes deposition may stem from terrestrial organic matter brought by rivers and their tributaries or generated by human intervention. The organic matter in marine sediment reflects the isotopic composition of the source and lets some insights into biogeochemical processes involved in transport and deposition.

Barros *et al.* (2010) used isotopic analysis of the organic fraction of sediments collected in Babitonga Bay, Santa Catarina, Brazil, and found that the organic matter in this location was derived from marine and terrestrial sources with certain influence of urban effluent due to the proximity of the city of Joinville. It was possible to assess the anthropogenic impact in this bay using isotopic fingerprints of particulate organic matter. To understand the influence of natural and anthropogenic processes on the sediment and biogeochemistry process of the estuary-lagoon system of the Itapocu River in Santa Catarina, Fritzen (2007) analyzed the total organic carbon (TOC), total nitrogen, C/N ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. Based on the C/N ratio and $\delta^{13}\text{C}$ values, the author identified the predominant sources of organic matter as mainland and mixed origin tending towards mainland, indicating a tendency of the system to buffer organic matter from external sources. This technique was used by Susanto *et al.* (2012) to trace the organic matter present in the sediment

transported to coral reef areas in Berau, Indonesia, where approximately 10% of the samples had $\delta^{13}\text{C}$ values depleted by more than -23‰ , indicating that most of the sediment was of terrestrial origin. The $\delta^{15}\text{N}$ values indicated that the matter originated in areas with anthropogenic impact and agricultural activities. According to de Andrade (2011), the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N values were used to characterize sources and fate of organic matter in the Passa Vaca River estuary, Salvador-BA, and the results suggested that terrestrial vegetation provided a substantial fraction of the organic matter that was accumulated in the sediment but urbanization around the estuary has changed its natural characteristics, including major ecological damage to the coastal zone. Isotopic analysis is a very robust technique. Elemental analyses, isotope ratios and mass spectrometry were used by Amorim *et al.* (2009) to characterize the surface sediment of a floodplain system of the Amazon River, where the organic matter content of this sediment ranged from 1.7 to 37% of carbon. The $\delta^{13}\text{C}$ and C/N values showed the presence of various sources (terrigenous matter, matter transported by the river and phytoplankton, among others) of the organic matter.

The present study analyzed samples of water, suspended particles and bottom sediments taken from Nova Viçosa–Caravelas estuarine system to trace the origin and fate of the organic matter. Due to its importance for the region, this basic information can be used to assess the anthropic impact coupled with the flow of matter in suspension and in bottom sediment, which can be used to provide baseline data for environmental management of the area.

CHARACTERIZATION OF THE STUDY AREA

The Nova Viçosa ($17^{\circ}54'S$ – $39^{\circ}25'W$) and Caravelas ($17^{\circ}54'S$ – $39^{\circ}25'W$) estuarine system is located in the extreme south of Bahia state and in the continental border of one of the most important coral complex of Brazil, the Abrolhos Bank (Fig. 1). The rivers Macacos and Cupido are key components of the Caravelas Estuary's drainage basin, and the Peruípe is the main river in the Nova Viçosa Estuary's drainage basin. The two estuaries are interconnected by small channels. The mouth of the Caravelas Estuary is formed by the Barra Velha and the Tomba channel. Although there are no records of river discharge in the Caravelas Estuary, it is estimated by regional standards at $4\text{ m}^3/\text{s}$, with a drainage basin of approximately 600 km^2 . According to data from the National Water Agency (*Agência Nacional de Águas* – ANA), the Peruípe River has an average flow ranging from $15\text{ m}^3/\text{s}$ to $30\text{ m}^3/\text{s}$. The drainage basin of the Caravelas Estuary is approximately 600 km^2 , and flow rates range from $3500\text{ m}^3/\text{s}$

inflow at low tide to 3100 m³/s during the flood. Residual transport in the Caravelas Estuary is an inflow of 630 m³/s (Schettini & Miranda 2010).

The main hydrodynamic driving forcing is tidal, with relative contribution of freshwater discharge and wind on the coastal zone. These factors are responsible for the circulation and stratification of the complexes (Schettini & Miranda 2010).

The study area has great ecological importance because it is a transitional environment on the border between mangrove forest, remnants of Atlantic Forest and tourist areas, and because the Caravelas Estuary is the main departure route for ships carrying tourists to visit the Abrolhos Marine Park.

The wind pattern in the region is influenced by the southern edge of the trade winds. This wind system has two main directions: northeast and east in the spring and summer and southeast during autumn and winter. This pattern is due to cell migration of the South Atlantic Anticyclone to the north in summer and south in winter (Nimer 1989). This region

is also influenced by cold fronts, especially during autumn and winter (Andrade 2004), that cause a new south-south-east component in the atmospheric circulation.

Chaves (1999) found that July and August were the months with the lowest rainfall, whereas November and December showed the highest values, and according to the National Institute of Meteorology (*Instituto Nacional de Meteorologia* – INMET), the annual average precipitation is ~1300 mm/year.

The tidal regime is characterized as meso-tidal, with a maximum height equal to 2.9 m at spring tide and a neap tide of 0.4 m (Barroso 2009). The tide is purely semi-diurnal, with a number of formations equal to 0.12 (Lessa & Cirano 2006). Schettini and Miranda (2010) made an initial characterization of the hydrodynamic flow and transport of suspended particulate matter in the Caravelas Estuary. The authors showed that the estuary was well mixed, weakly stratified and mainly controlled by tidal currents, with a predominance of ebb currents. The behavior of suspended

Figure 1. Location of the samplings in the Nova Viçosa–Caravelas estuarine complex.

particulate matter was modulated by tidal and coastal processes. Freshwater inflow played a secondary role. The Peruípe River acts as an important mechanism of particulate matter transport in the Nova Viçosa portion of the estuarine complex. The average concentration of suspended particulate matter in Caravelas Estuary in the dry period was 8.8 mg/L (neap tide) and 87 mg/L (spring tide), and in the rainy season, the concentrations were 15.3 mg/L (neap tide) and 100 mg/L (spring tide) (Pereira *et al.* 2010). Additionally, the peak concentrations corresponded to periods of reversing tidal currents. The instantaneous flow of suspended particulate matter ranged between -1.97 and 2.58 mg/L.

MATERIALS AND METHODS

Water and sediment samples were collected between 4 and 5 December 2012 during the last quarter moon (neap tide), with low water level at 0.5 m and high water level at 1.5

m at Caravelas bar (see Tab. 1 for each station parameter). A total of 20 stations were located between the Caravelas and Nova Viçosa estuaries with depth ranging from 0.8 m (station #19) and 4.3 m (station #16).

The bottom sediment samples were collected with the aid of a Van Veen grab sampler, placed in previously decontaminated glass containers and kept refrigerated until arrival at the laboratory. In the laboratory, the samples were frozen and stored at -20°C until lyophilization. After lyophilization, the samples were ground to a fine powder through a 140 mesh.

Water samples were collected at a depth of not less than 2 m and were stored in 5 l kegs, fixed with HgCl₂ (mercuric chloride), kept refrigerated until arrival at the laboratory and maintained in this condition until filtering. A fraction of the sample (100 mL) was removed before filtering to perform isotopic analyses of hydrogen, oxygen and DIC. The samples were filtered using a vacuum filtration system with glass-fiber filters (Whatman GF/F 0.60 – 0,70 µm pore

Table 1. Sampling locations with depth, water salinity, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$ and dD for the water and total organic carbon values N, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N ratio for the bottom sediment samples

	Point	Longitude	Latitude	Time	Depth (m)	Water Samples				Sediment Samples				
						Salinity	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\delta^{18}\text{O}$ (‰)	dD (‰)	N (%)	C (%)	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)	C/N
4 December 2012	01 (CEC-NV)	039°W 16' 47"	17°S 44' 30"	12:33 PM	4	22.91	-3.9	0.12	5.06	0.169	3.22	1.7	-26.0	19.0
	02 (CEC-NV)	039°W 17' 04"	17°S 45' 31"	01:05 PM	3.5	19.43	-5.3	-0.01	5.03	0.032	0.57	1.5	-25.5	18.0
	03 (CEC-NV)	039°W 16' 58"	17°S 46' 30"	01:53 PM	4	20.06	-6.5	-0.01	4.72	0.047	0.78	2.5	-25.6	16.7
	04 (CEC-NV)	039°W 17' 46"	17°S 46' 51"	02:06 PM low tide	3.3	19.74	-7.0	-0.07	4.30	0.184	4.16	1.1	-27.0	22.6
	05 (CEC-NV)	039°W 18' 07"	17°S 47' 38"	02:21 PM	2.3	19.63	-7.9	-0.03	5.10	0.05	0.84	1.5	-25.9	16.7
	06 (CEC-NV)	039°W 18' 49"	17°S 48' 55"	02:40 PM	2.2	19.12	-9.1	-0.08	5.41	0.089	1.81	0.3	-26.8	20.3
	07 (CENV-C)	039°W 19' 12"	17°S 49' 41"	03:04 PM	3.5	20.46	-6.5	-0.27	4.00	0.042	0.74	3.0	-25.7	17.5
	08 (CENV-C)	039°W 19' 56"	17°S 49' 41"	03:22 PM	3.4	22.15	-4.4	-0.02	3.73	0.135	2.89	3.1	-26.8	21.4
	09 (CENV-C)	039°W 19' 37"	17°S 50' 29"	03:42 PM	3.4	23.40	-2.6	-0.18	3.42	0.094	1.81	2.6	-26.3	19.3
	10 (CENV-C)	039°W 19' 33"	17°S 51' 11"	04:07 PM	2.2	31.08	0.1	0.38	5.96	0.098	1.82	3.5	-25.6	18.5
	11 (CENV-C)	039°W 21' 10"	17°S 51' 24"	04:29 PM	4.2	32.73	0.9	0.60	7.07	0.093	1.60	4.2	-24.8	17.1
	12 (MCENV)	039°W 21' 42"	17°S 52' 32"	04:52 PM high tide	2.2	35.33	1.6	0.93	8.32	0.022	0.23	2.7	-21.6	10.4
5 December 2012	13 (MCENV)	039°W 22' 08"	17°S 52' 43"	07:06 AM high tide	2.5	24.57	-2.6	-0.15	3.49	0.154	1.65	5.4	-23	10.7
	14 (CEC-NV)	039°W 19' 30"	17°S 47' 08"	09:20 AM	3.5	19.86	-8.7	-0.29	3.42	0.033	0.51	3.7	-24.6	15.7
	15 (TCEC)	039°W 16' 04"	17°S 43' 40"	10:11 AM	3.3	21.10	-5.7	-0.11	5.38	0.229	3.76	2.8	-26.1	16.4
	16 (TCEC)	039°W 15' 12"	17°S 42' 25"	10:36 AM	4.3	20.16	-8.5	-0.21	5.14	0.202	3.67	2.5	-26.6	18.1
	17 (MCEC)	039°W 14' 35"	17°S 44' 45"	12:49 PM	1.5	27.20	-2.3	0.33	6.39	0.057	0.68	3.5	-24.4	12.0
	18 (MCEC)	039°W 13' 22"	17°S 45' 05"	01:10 PM	3.2	35.09	1.3	0.69	8.24	0.058	0.84	3.5	-24.4	14.3
	19 (MCEC)	039°W 11' 38"	17°S 44' 35"	01:38 PM	0.8	35.69	1.6	0.85	8.57	0.178	1.89	4.7	-22.7	10.6
	20 (CES)	039°W 10' 19"	17°S 44' 08"	02:05 PM low tide	1.9	36.65	2.6	0.87	8.35	0.142	1.40	4.4	-21.9	9.9

CEC-NV: connection channel between the Caravelas Estuary and Nova Viçosa Estuary; CENV-C: connection channel between the Nova Viçosa Estuary and Caravelas; MCENV: main channel of the Nova Viçosa Estuary; TCEC: tidal channel of Caravelas Estuary; MCEC: main channel of the Caravelas Estuary. CES: Caravelas Estuary shoal. The tide table is relative to Caravelas bar (Source: Brazilian Navy).

size, diameter 47 mm and thickness 0.42 mm), previously calcined in a muffle furnace at 500°C for 5 h. The filters were subsequently frozen and lyophilized to prevent the loss of organic fractions. The physicochemical parameters, pH, salinity and dissolved oxygen, of the samples: were measured *in situ* using a Hi 9828 multiparameter meter by HANNA® instruments.

For the sediment analysis, acid attack was performed with 10 ml of 1 mol/L hydrochloric acid (HCl) on 0.5 g of each sample to remove carbonate. After 24 h, the samples were centrifuged to extract the supernatant liquid, then washed with deionized water and centrifuged three times before being dried at temperatures between 35 and 50°C. For the suspended sediment analysis, samples were prepared using hydrofluoric acid (HF 10%) for the sample filters (Hedges & Stern 1984; Gélinais *et al.* 2001). After treatment, approximately 8 mg of each dry sample was weighed into a tin capsule for elemental analyses of the quantity and isotope ratio of organic carbon and nitrogen using a Costech Elemental Analyzer coupled to a ThermoFinnigan Delta Plus mass spectrometer. The isotopic values were referenced against two references certified by the International Atomic Energy Agency (IAEA) (USGS40 and USGS41).

The isotopic analyses of water were conducted in accordance with the application of the following methodologies: deuterium/hydrogen (D/H) ratio (Brand *et al.* 2000), O^{18}/O^{16} ratio (Epstein & Mayeda 1953) and C^{13}/C^{12} ratio of DIC (Craig 1957). A mass spectrometer of isotopic ratio Finnigan MAT Delta Plus in which they are coupled a Finnigan H-Device Thermo Quest, specific for analyzing the D/H ratio, as well as a Finnigan *Gas Bench II* system for automated online sample preparation, specifically for the analysis of $\delta^{18}O$ and $\delta^{13}C_{DIC}$ (DIC).

For the oxygen-18 analysis, 500 μ L of water was poured into a pressurized container with helium and 0.3% carbon dioxide (Epstein & Mayeda 1953). For the deuterium analysis, 1 ml of water was placed in an oven containing Cr at 850°C (Brand *et al.* 2000). Secondary standards were used in relation to the international VSMOW (Vienna Standard Mean Oceans Waters) standard: PB1 (Salvador distilled sea water) and PB2 (Irecê region well water) for the $\delta^{18}O$ and the δD . For the DIC analysis, 700 μ L of water was placed in a container containing 30 μ L of phosphoric acid pressurized with helium gas, which is released as carbon dioxide (Craig 1957). The standards were measured with solutions of Na_2CO_3 , Li_2CO_3 and secondary standards, measured in relation to solid carbonates of the IAEA NBS 19 standard.

The results were reported relative to PDB (Pee-Dee Belemnite) calcium carbonate (carbon), atmospheric air (nitrogen) and VSMOW (oxygen and hydrogen):

$$\delta^{\prime\prime} X = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{sample}}} \right) \times 1000\text{‰}$$

where $^nX = ^{13}C$ (carbon), ^{15}N (nitrogen), ^{13}C (carbon), ^{18}O (oxygen) or D (deuterium), $R = ^{13}C/^{12}C$ for carbon, $R = ^{15}N/^{14}N$ for nitrogen, $R = ^{18}O/^{16}O$ for oxygen, and $R = D/{}^1H$ for deuterium. Sample processing and analysis were performed at the Stable Isotope Laboratory, Applied Nuclear Physics Group of Federal University of Bahia (*Universidade Federal da Bahia* – UFBA).

RESULTS AND DISCUSSION

Table 1 shows the values of sampling locations with depth, water salinity, $\delta^{13}C_{DIC}$, $\delta^{18}O$ and δD for the water and TOC values N, $\delta^{13}C$, $\delta^{15}N$ and C/N ratio for the bottom sediment samples. The tide table is relative to Caravelas bar (Source: Brazilian Navy).

The sampling places were named as follows: connection channel between the Caravelas and Nova Viçosa estuaries (01, 02, 03, 04, 05, 06 and 14); connection channel between the estuary of Nova Viçosa and Caravelas (07, 08, 09, 10 and 11); main channel of the Nova Viçosa Estuary (12 and 13); tidal channel of the Caravelas Estuary (15 and 16); main channel of Caravelas Estuary (17, 18 and 19); and the Caravelas Estuary shoal (20).

In the diagram of δD versus $\delta^{18}O$ (Fig. 2) for the water samples, the points are distributed around a straight line of fit ($r = 0.904$) with a much smaller angular coefficient ($\delta D = 4.9\delta^{18}O + 3.7$) than the global meteoric line (GML) ($\delta D = 8.13\delta^{18}O + 10.8$) (Rozanski *et al.* 1993). The fact that this line is below the GML characterizes it as an evaporation line and shows that evaporative processes predominate in

Figure 2. Diagram δD (‰) versus $\delta^{18}O$ (‰) of surface water.

the region; however, isotopic values are very close to zero, varying slightly around this value, showing still some secondary influence of precipitation in the drainage web of the estuarine complex.

DIC values ($\delta^{13}\text{C}_{\text{DIC}}$) in the water increase with salinity, as illustrated in Fig. 3. The analysis of $\delta^{13}\text{C}_{\text{DIC}}$ also permitted identification of sources, where results showed a larger group of samples with negative $\delta^{13}\text{C}_{\text{DIC}}$ (from -10 to -2‰) with clear terrestrial influence and another group, with positive values for $\delta^{13}\text{C}_{\text{DIC}}$ (between 0 and 2‰), corresponding to the points with increasing marine influence, that is, in the mouth, at the shoal and in the main channel of the Caravelas Estuary. This difference reflects the existence of several processes that influence the dissolution of inorganic carbon in the water, due to the mixing characteristic of the estuarine complex.

The isotopic composition of DIC indicates the degree of mixing between biogenic and mineral carbon. The values of $\delta^{13}\text{C}_{\text{DIC}}$ for some rivers of Amazon basin have values between -13.2 and -15.0‰, reflecting the presence of mineral DIC, with mean values for white water tributaries of -17.3‰ and for black water tributaries of -23.4‰ (Martinelli *et al.* 2009). Barros *et al.* (2010) reported isotopic values relating to the composition of $\delta^{13}\text{C}_{\text{DIC}}$ in estuaries along the Brazilian coast ranging between +0.04 and -12.7‰. Negative values of $\delta^{13}\text{C}_{\text{DIC}}$ indicate riverine influence in these stations, in contrast with the clear marine source for positive $\delta^{13}\text{C}_{\text{DIC}}$.

The linear fit shows a good correlation ($R = 0.801$) between TOC and total nitrogen (Fig. 4). From these results, it can be concluded that the nitrogen and carbon in the samples have the same organic origin.

Although point 13 has low salinity, the isotopic values and C/N ratio at this site are characteristic of marine sediment

of the continental platform (Jennerjahn & Ittekkot 1997), with values close to those found at points 19 and 20, that is, the main channel of the Caravelas Estuary and the shoal, which are more external stations with a greater mixture of sea and estuary waters. The water flow in some parts of the channel can lead to remobilization of sedimentary material contributing to an estuarine plume, which can show bulk marine signatures contrasting with low salinity data. Points 4 (connecting channel of Caravelas Estuary–Nova Viçosa), 15 and 16, the tidal channel of Caravelas Estuary, have the highest values of N and TOC, which may reflect the proximity of these points to the city of Caravelas, suggesting anthropic contribution from sewage. These factors can explain the two characteristic C/N groups in the sediment samples.

The C/N ratio has been used to assess the relative influence of marine and terrestrial organic matter in some ecosystems (Guo *et al.* 2004; Usui *et al.* 2006). Saito *et al.* (1989) suggested that a ratio greater than 20 indicates terrestrial origin, and a value between 5 and 7 indicates marine origin. Stein (1991) indicated that values lower than 10 are related to marine origin, and values close to 10 represent marine and terrestrial contributions to the sediment. Other values are reported in the literature for mangrove sediment, river sediment and continental shelf sediment with C/N values of 18.3 ± 3.4 , 17.6 ± 10.8 and 8.7 ± 3.9 , respectively (Jennerjahn & Ittekkot 1997).

The C/N ratio has a minimum value of 9.9 at point 20, a maximum of 22.6 at point 4 and an average value of 16.3 for the whole channel, considering all the sampling points. The results show a transition region tending to values more characteristic of terrigenous sediment.

The comparative ranges of different sources of the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N values are from Kumara (2011), Goñi *et al.* (2003), Barros *et al.* (2010), Carreira *et al.* (2002) (Figs.

Figure 3. $\delta^{13}\text{C}_{\text{DIC}}$ (‰) versus salinity of the surface water.

Figure 4. Total Organic Carbon (%) versus total nitrogen (%) in the studied bottom sediment.

5 and 6). The isotopic values found in the analyses of the Nova Viçosa–Caravelas Estuary are within ranges similar to those reported in the above literature.

Although the isotopic values and C/N found in some samples indicated anthropic sources, nitrogen isotope values in the range quoted by Carreira *et al.* (2002) for domestic effluent or sewage were not observed in the Nova Viçosa–Caravelas Estuary, suggesting that some nitrogen cycling in the estuary may lead to differential N fractionation.

In contrast with terrestrial and anthropic signatures, marine sediments reflect the isotopic composition of its carbon source. The main source is phytoplankton in the ocean (-18 to -24‰), and in coastal areas, in addition to phytoplankton, terrestrial matter carried by rivers contributes to the sediment (Martinelli *et al.* 2009). Deines (1980) produced a classification of carbon isotope values in marine sediment with a bimodal distribution, one with heavier values between -10 and -19‰ and the other with values between -20 and -30‰ , with values more frequently in the lighter area between -23 and -25‰ . The mean value of $\delta^{15}\text{N}$ in the leaves of the trees in Brazilian forest areas near to the ocean is $3.13 \pm 1.73\text{‰}$ (Martinelli *et al.* 2009). $\delta^{15}\text{N}$ values depend on the characteristics of the local nitrogen cycle. Variations in the nitrogen fixation rate from the atmosphere, mineralization, nitrification and denitrification determine the isotopic fractionation of nitrogen (Högberg 1997). In this case study, the mean value for $\delta^{15}\text{N}$ was $2.9 \pm 1.3\text{‰}$, suggestive of the influence of higher plants, as were the carbon isotopic values. In the literature regarding the composition of total organic matter in estuaries along the Brazilian coast, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values ranging from -21.7 to -26.2‰ and from $+9.2$ to -0.1‰ , respectively, have been reported (Barros *et al.* 2010). Based on this classification, the values found in this study indicate a mixture of sources. Regarding the particulate

organic matter samples, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ characteristics are similar to those of the bottom sediment taken from the same stations, despite the isotopic values being slightly different due to biogeochemical processes linked with the sedimentation processes. Samples of the particulate matter at stations 12 and 20 seem to differ, mainly in the $\delta^{13}\text{C}$ values, from the samples collected at stations 1, 6 and 16. This difference in behavior may be due to greater oceanic influence at stations 12 and 20 than at the other sites.

The results obtained for the suspended sediment in this work range from -27.14 to -22.44 , indicating a mixture of sources provided by the estuarine dynamics, including phytoplankton and aquatic and terrestrial plants as main sources, the latter being included due to the soil erosion processes of the drainage basin.

CONCLUSIONS

The C/N ratios obtained for bottom sediment in Nova Viçosa–Caravelas estuarine complex showed a mean value of 16.3, which indicates the influence of terrigenous and mangrove organic matter. Points 15 and 16 had the highest values of both TOC and N due to their proximity to the city of Caravelas, that is, these sites may experience anthropic influence.

Regarding $\delta^{13}\text{C}_{\text{DIC}}$, negative land-related values were observed (between -10 and -2‰), and positive marine-related values for $\delta^{13}\text{C}_{\text{DIC}}$ (between 0 and 2‰) shows the ocean influence at the mouth of the estuary.

The $\delta^{13}\text{C}$ sediment analysis yielded results consistent with other studies performed on the Brazilian coast, indicating matter of terrestrial origin mixed with sewage. However, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ classification of the organic matter in

Figure 5. $\delta^{13}\text{C}$ (‰) versus C/N in the bottom sediments.

Figure 6. $\delta^{13}\text{C}$ versus $\delta^{15}\text{N}$ for the studied bottom sediment and suspended particulate matter(s).

the sediment shows that these values are really intermediate between these two sources, with a great tendency towards terrigenous and mangrove sources but not characteristic of sewage according to other literature data (Carreira *et al.* 2002), despite the fact that there are two cities very close to Nova Viçosa-Caravelas estuarine complex. These results suggest that the biogeochemical processes inherent to the estuarine environment are playing an important role in cycling organic matter of urban origin.

Particulate organic matter in the water exhibited similar behavior to the matter removed from the bottom at the same stations. This result also indicates that the organic matter that reaches the channel due to the drainage bowl is not carried far and is soon deposited at the bottom. Even near the Caravelas and Nova Viçosa shoals, the values found are also characteristic of a terrigenous rather than marine source, which is interpreted as the result of estuarine hydrodynamics. Typical values of organic matter of marine origin are found in the mouth of the Caravelas Estuary, showing residual transport from the sea to the mainland at this point. The drainage basin and the material comprising the channel banks make a large contribution to the deposited

matter along the innermost part of the channel. Regarding bottom sediment, the data show that the points with the highest values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are located near the town of Caravelas. In the central region of the channel, lower values for these parameters are found, most likely influenced by vegetation and the contribution of matter from the rivers.

The environmental classification based on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of organic matter in sediments and suspended matter collected in this work shows that values vary between terrigenous (characteristic of mangroves) and marine ranges, giving a baseline for future monitoring work in this important estuarine complex.

ACKNOWLEDGMENTS

The authors would like to thank the Coordination for the Improvement of Higher Level Personnel (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – CAPES) for granting the support during the Master's course at Universidade Federal da Bahia and the valuable comments of the reviewers.

REFERENCES

- Andrade K.M. 2004. *Comportamento dos sistemas frontais sobre a América do Sul [Behavior of frontal systems over South America]*. Instituto Nacional de Pesquisas Espaciais, São José dos Campos, Master's Dissertation, 155 p.
- Amorim M.A., Moreira-Turcq P.F., Turcq B.J., Cordeiro R.C. 2009. Origem e dinâmica da deposição dos sedimentos superficiais na Várzea do Lago Grande de Curuai, Pará, Brasil [Origin and dynamics of sediment deposition in the Lago Grande de Curuai floodplain, Pará, Brazil]. *Acta Amazonica*, **39**(1):155-162.
- Barros G.V., Martinelli L.A., Oliveira Novais T.M., Ometto J.P., Zuppi G.M. 2010. Stable isotopes of bulk organic matter to trace carbon and nitrogen dynamics in an estuarine ecosystem in Babitonga Bay (Santa Catarina, Brazil). *Science of the Total Environment*, **408**:2226-2232.
- Barroso C.P. 2009. Dinâmica de bancos e pontais arenosos associados a desembocadura do estuário de Caravelas, BA [Dynamics of banks and sandy spits associated with the mouth of the Caravelas estuary, BA]. Universidade de São Paulo, São Paulo-SP, Master's Dissertation.
- Brand W.A., Avak H., Seedorf R., Hofmann D., Conradi T. 2000. New methods for fully automated isotope ratio determination from hydrogen at the natural abundance level. *Geophysical Prospecting*, **28**:967-976.
- Carreira R., Wagener A.L.R., Readman J.W., Fileman T.W., Macko S.A., Veiga A. 2002. Changes in the sedimentary organic carbon pool of a fertilized tropical estuary, Guanabara Bay, Brazil: An elemental, isotopic and molecular marker approach. *Marine Chemistry*, **79**:207-227.
- Chaves R. 1999. Variabilidade da precipitação na região sul do nordeste e sua associação com padrões atmosféricos [Rainfall variability in a southern northeast region and its association with atmospheric patterns]. Instituto Nacional de Pesquisas Espaciais, São José dos Campos-SP, Master's Dissertation.
- Craig H. 1957. Isotope standards for carbon and oxygen and connection factors for mass spectrometric analysis of carbon dioxide. *Geochimica et Cosmochimica Acta*, **12**:133-149.
- Epstein S. & Mayeda T. 1953. Variations of ^{18}O content of waters from natural sources. *Geochimica et Cosmochimica Acta*, **4**:213-221.
- De Andrade C.L.N. 2011. Biogeoquímica do ambiente estuarino do rio Passa Vaca em área urbana de Salvador, BA [Biogeochemistry of the estuarine environment of Passa Vaca River in the urban area of Salvador, BA]. Universidade Federal da Bahia, Salvador-Ba, Master's Dissertation.
- Deines P. 1980. The isotopic composition of reduced organic carbon. In: P. Fritz & J.C.H. Fontes (eds.), *Handbook of Environmental Isotope Geochemistry*. Elsevier Scientific Publishing Company, Amsterdam, vol. 1, p. 329-406.
- Flemer D.A. & Champ M.A. 2006. What is future fate of estuaries given nutrient over-enrichment, freshwater diversion and low flows? *Marine Pollution Bulletin*, **52**:247-258.
- Fritzen L.B. 2007. Composição, origem e grau de enriquecimento do material orgânico sedimentar no setor norte do sistema estuarino-lagunar do rio Itapocu, SC [Composition, origin and degree of enrichment of sedimentary organic matter in the northern sector of the Itapocu River lagoon-estuarine system, SC]. Universidade Federal de Santa Catarina, Florianópolis-SC, Master's Dissertation.
- Gélinas Y., Baldock J.A., Hedges J.I. 2001. Demineralization of marine and freshwater sediments for CP/MAS ^{13}C NMR analysis. *Organic Geochemistry*, **32**:677-693.
- Goñi M.A., Teixeira M.J., Perkey D.W. 2003. Sources and distribution of organic matter in a river-dominated estuary (Winyah Bay, SC, USA). *Estuarine, Coastal and Shelf Science*, **57**:1023-1048.

- Guo L., Tanaka T., Wang D., Tanaka N., Murata A. 2004. Distributions, speciation and stable isotope composition of organic matter in the southeastern Bering Sea. *Marine Chemistry*, **91**:211-226.
- Hedges J.I. & Stern J.H. 1984. Carbon and nitrogen determinations of carbonate-containing solids. *Limnology and Oceanography*, **29**:657-663.
- Högberg P. 1997. ^{15}N natural abundance in soil-plant systems. Tansley Review No. 95. *New Phytologist*, **137**:179-203.
- Jennerjahn T.C. & Ittekkot V. 1997. Organic matter in sediments in the mangrove areas and adjacent continental margins of Brazil. I. Amino acids and hexosamines. *Oceanologica Acta*, **20**:359-369.
- Lessa G.C. & Cirano M. 2006. On the circulation of a coastal channel within the Abrolhos coral-reef system - Southern Bahia (17° 40' S). *Journal of Coastal Research*, **1**:450-453.
- Levenson H. 1987. Estuaries and coastal waters need help. *Environmental Science & Technology*, **21**:1052-1054.
- Marques J.C. 2009. *Ecological Indicators for Coastal and Estuarine Environmental Assessment: A User Guide*. WIT Press, UK, 183 p.
- Martinelli L.P., Ometto J.P.H.B., Ferraz E.S., Victoria R.L., Camargo P.B., Moreira M.Z. 2009. *Desvendando Questões Ambientais com Isótopos Estáveis [Unraveling Environmental Issues with Stable Isotopes]*. Oficina de Textos, São Paulo.
- Kumara M.P. 2011. *The Impacts of Tree Density on the Physical and Biological Characteristics of Planted Mangrove Stands in Sri Lanka*. A thesis submitted in partial fulfilment of the requirements of Edinburgh Napier University, for the award of Doctor of Philosophy. Edinburgh Napier University, School of Lifesciences, Edinburgh, Scotland, Thesis.
- Nimer E. 1989. *Climatologia do Brasil (Brazilian Climatology)*. Secretaria de Planejamento da Presidência da República, Fundação Instituto Brasileiro de Geografia e Estatística, Diretoria de Geociências, Departamento de Recursos Naturais e Estudos Ambientais, Rio de Janeiro.
- Pereira M.D., Siegle E., Miranda L.B., Schettini C.A.F. 2010. Hidrodinâmica e transporte de material particulado em suspensão em um estuário dominado por maré: estuário de Caravelas (BA) [Hydrodynamics and transport of suspended particulate matter in a tide-dominated estuary: Caravelas estuary (BA)]. *Revista Brasileira de Geofísica*, **28**(3):427-444.
- Saito Y., Nishimura A., Matsumoto E. 1989. Transgressive sand sheet covering the shelf and upper slope off Sendai, Northeast Japan. *Marine Geology*, **89**:245-258.
- Schettini C.A.F. & Miranda L.B. 2010. Circulation and suspended particulate matter transport in a tidally dominated estuary: Caravelas estuary, Bahia, Brazil. *Brazilian Journal of Oceanography*, **58**(1):1-11.
- Stein R. 1991. Accumulation of organic carbon in marine sediments. Results from the deep sea drilling project/ocean drilling program. *Lecture Notes in Earth Sciences*, **34**:217.
- Susanto H.A., Yoneda M., Komoda M., Hoike H. 2012. Assessment of sediment organic matter transportation using stable isotope analysis. *Proceedings of the 12th International Coral Reef Symposium*, Cairns, Australia, 9-13 July 2012.
- Rozanski K., Araguás-Araguás L., Gonfiantini R. 1993. Isotopic patterns in modern global precipitation. In: P.K. Swart, K.C. Lohmann, J. McKenzie, S. Savin (ed.) *Climate Change in Continental Isotopic Records*. Geophysical Monograph Series, 78, AGU, Washington, DC, p. 1-36.
- Usui T., Nagao S., Yamamoto M., Suzuki K., Kudo I., Montani S., Noda A., Minagawa M. 2006. Distribution and sources of organic matter in surficial sediments on the shelf and slope off Tokachi, western North Pacific, inferred from C and N stable isotopes and C/N ratios. *Marine Chemistry*, **98**:241-259.
- Zetsche E., Thornton B., Midwood A.J., Witte U. 2011. Utilisation of different carbon sources in a shallow estuary identified through stable isotope techniques. *Continental Shelf Research*, **31**(7-8):832-840.