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δ^{13}C, δ^{15}N and TOC/TN as indicators of the origin of organic matter in sediment samples from the estuary of a tropical river

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ABSTRACT

The present study aimed to determine the total organic carbon (TOC), total nitrogen (TN), the carbon-nitrogen ratio (TOC/TN), carbon isotope (δ^{13}C), and nitrogen isotope (δ^{15}N) in five sediment cores collected from upstream to downstream of the Rio Serinhaem estuary, State of Bahia, Northeast Brazil, in order to investigate the origin of the deposited organic matter (OM).Significant positive correlation was found between TOC and NT (r_s = 0.75); TOC/TN and TOC (r_s = 0.64); δ^{15}N and TOC (r_s = 0.72); and δ^{15}N and TOC/TN (r_s = 0.63). The values of δ^{13}C and δ^{15}N found are characteristic of terrestrial sources. The TOC/TN ratio confirmed the data found for δ^{13}C and δ^{15}N, which recorded the origin of organic matter from terrestrial C3 type plants. Upstream of the estuary, the highest means of TOC/TN were found (T1 = 36.9 and T2 = 24.4), as reflected by the increase in TOC content or reduction in TN. The OM along the estuary is predominantly from plants with a C3 photosynthetic pattern, indicating that the Serinhaem River estuary is considered a relatively well-preserved environment.

Coastal and estuarine areas are among the most productive, diverse, and economically relevant environments for human society. In addition, they are considered critical locations for the exchange and storage of carbon (C) and nitrogen (N) between lands, rivers, and oceans, playing a major role in the biogeochemical cycling of these elements on a global scale because more than 90% of the carbon buried in the oceans is located in sediments on continental margins (Yu et al., 2010). However, these ecosystems are widely and globally threatened, mainly by anthropogenic activities (Gu et al., 2017; Dang et al., 2018; Da Silva Júnior et al., 2020).

The carbon and nitrogen stored in sediments from coastal environments are a heterogeneous and complex mixture of organic matter (OM) from different sources (marine and freshwater phytoplankton, soil, leaf debris, wastewater, kerogen), which consequently results in materials with diverse characteristics (Li et al., 2016). In addition, the concentrations of organic matter in sediments depend on a number of factors, such as the rate of deposition, the nature of organic sources their flow rates, their preservation potential during transport burial, mineralization and degradation (Sampaio et al., 2010).

Organic matter in aquatic sediments, stable isotope ratios (δ^{13}C and δ^{15}N) and the carbon to nitrogen ratio (TOC/TN) have become increasingly used in OM characterization studies to elucidate the different signatures of sources of organic matter, the processes of transformation of organic carbon (Li et al., 2016; Derrien et al., 2017; Gu et al., 2017; Pastene et al., 2019) and the fate of sedimentary organic matter (Zhang et al., 1997; Wu et al., 2003; Liu et al., 2006; Rumolo et al., 2011; Gao et al., 2012). Such techniques are also used in tracking the extent of discharged sewage in coastal areas (Sampaio et al., 2010). The effectiveness of these parameters is related to the fact that there are differences between the natural abundances of stable carbon isotopes, stable nitrogen isotopes and elemental TOC/TN proportions in organic matter of terrestrial and anthropogenic inputs as well as in situ marine and freshwater inputs (Sampaio et al., 2010; Gao et al., 2012).

In general, terrestrial organic matter, when compared to marine organic matter, has lower values of δ^{13}C and δ^{15}N (Vizzini et al., 2005; Sampaio et al., 2010; Li et al., 2016). Several studies are found in the literature and, consequently, there are many intervals for these variables. For Meyers (1997), δ^{13}C ranging from -35.0 to -25.0‰

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corresponds to values of C3 plants. For river phytoplankton, Gao et al. (2012) cited in their study values of $\delta^{13}C$ ranging from -35.0 to -25.0‰ whereas for marine phytoplankton, Spanó et al. (2014) showed that the values of $\delta^{13}C$ are between -18 and -24‰. For $\delta^{15}N$ values, Gu et al. (2017) mentioned that $\delta^{15}N$ values ranging from -10 to 10‰ correspond to type C3 plants; however, in Gao et al. (2012), these values are approximately around 5‰. In addition, according to Sampaio et al. (2010), a typical sewage effluent can present values of $\delta^{13}C$ in the range of -22.4 to -26.5‰ and values of $\delta^{15}N$ between 1.8 and 3, 8‰, while marine organic matter has values of $\delta\ ^{13}C$ in the range of -18‰ to- 24‰ and $\delta\ ^{15}N$ values between 4‰ and 9‰.

The use of the mass ratio TOC/TN is explained by the difference that exists in the concentrations of carbon and nitrogen in the organic matter produced by the different groups of organisms. The differences are attributed to the structural components of the sources. Vascularized plants have compounds rich in carbon, such as cellulose, while algae are mainly composed of proteins which are rich in nitrogen (Bianchi and Canuel, 2011). TOC/TN values commonly found for seaweed are between 4 and 8, while terrestrial plants have values greater than 12 (Meyers, 1997).

In the present study, total organic carbon (TOC), total nitrogen (TN) and their elemental and isotopic proportions ($\delta^{13}C$ and $\delta^{15}N$) were analyzed in sediment cores from Serinhaem River estuary, located in the Environmental Protection Area (EPA) of Pratigi, Northeast of Brazil, aiming to identify the origin of organic matter in the sediments of the estuary.

The Pratigi EPA, with 856.9 km^2, is located in the Atlantic Forest Domain, in the south of the State of Bahia (Fig. 1), and it is a relatively well-preserved area (Carneiro et al., 2021). The climate of the area is classified as Tropical Rain Forest with no dry season (Bahia, 2014). The great diversity of birds, mammals, reptiles, amphibians, and invertebrate species justify the establishment of the Pratigi EPA among the areas of the highest priority for the conservation of the biodiversity of the Central Corridor of the Atlantic Forest (Oct, 2015).

The sampling points were determined to cover the entire region under study from the upstream to the downstream of the Serinhaem River estuary. Five sediment cores were taken along the Serinhaem River estuary (Fig. 1, Table 1), using a stainless-steel core measuring 1.20 m long and 5 cm diameter. At each location, the sampling core was buried vertically in the sediment, removed, and laid on the vessel. The core was then measured and sectioned in 3 cm intervals. The samples were frozen until they were lyophilized in the laboratory. Owing to the difference in sediment texture, sediment profiles from the five locations had different number of sectioned samples (Table 1). For the determination of total organic carbon (TOC), total nitrogen (TN), particle size

Table 1
Information from sediment cores collected in the Serinhaem estuary. EPA of Pratigi.

Core	UTM Coordinates (m) (WGS84)		Core length (cm)	Number of samples
	X	Y		
T – 1	484,585.272398	8,480,811.5711	43	13
T – 2	485,287.255273	8,481,330.48182	46	14
T – 3	487,511.878745	8,482,827.72368	90	21
T – 4	493,403.265413	8,475,401.66068	60	15
T – 5	498,183.551981	8,470,090.83801	64	18

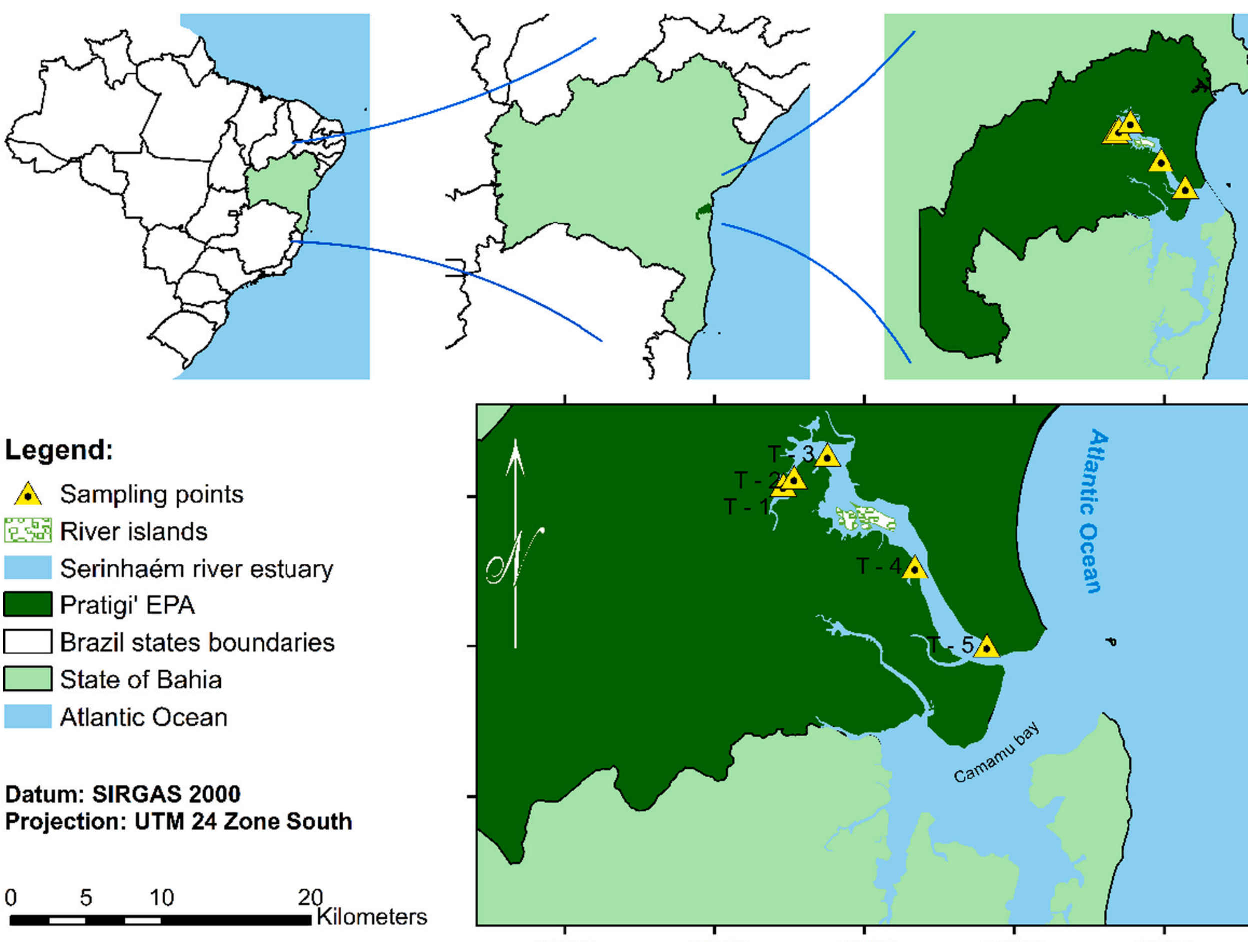

Fig. 1. Location of the Pratigi EPA, Bahia, northeast Brazil, and the five points for collecting sediment cores.

and carbon and nitrogen isotopes ($\delta^{13}C$ and $\delta^{15}N$) in the laboratory, the samples were lyophilized and sieved.

The granulometry analysis was performed following the methodology of Embrapa (2017, adapted). Approximately 3 g of each total lyophilized sample were weighed. They were calcined at 450 °C for 8 h, with subsequent sieving with a 2 mm mesh to quantify the gravel fraction and with a 0.5 mm mesh to quantify the coarse sand fraction (2 - 0.5 mm). The residues were weighed and transferred to Falcon tubes together with a dispersant solution of sodium hexametaphosphate ($(NaPO_3)_6$) at 0.1 mol L^{-1}. The quantification of the sediment particles was carried out in a particle analyzer with laser diffraction (Cilas 1064 model) in the granulometric range of 0.00004 - 0.5 mm, corresponding to the medium sand fractions (0.5 - 0.25 mm), fine sand (0.25 - 0.13 mm), very fine sand (0.13 - 0.063 mm), silt (0.063 - 0.004 mm) and clay (> 0.004 mm). Ternary diagrams (Shepard, 1954; Flemming, 2000) were used to express the granulometric data of the sediment samples.

The TOC, TN, $\delta^{13}C$ and $\delta^{15}N$ contents were analyzed using the methodology adapted from the U.S. Environmental Protection Agency (2002; EPA-NCE/2002 methodology) which consists of decarbonation to eliminate inorganic carbon. Initially, HCl 1 mol L^{-1} was used to eliminate the fraction of inorganic carbon. The sample was placed in a porous boat and weighed on a semi-analytical balance, approximately 1.0 g of the sample. In the chapel, 1 mL aliquots of the HCl mol L^{-1} solution were added to each sample until the reaction ceased. This could be seen when there was no more effervescence of the sample mixture with the acid. Then, after the reaction ceased, the acid could react for 20 min and then the pH of the drained liquid was measured. If the pH of the solution was higher than 7.0, more acid would be added until the pH reached a value below 7, and then the sample washing procedure would be started.

For washing each sample, 1 mL aliquots of hot distilled water were added. Then, the chloride test was performed. A drop of $AgNO_3$ solution (silver chloride) was used in the drained liquid. The absence of chloride was found when the mixture of the liquid with $AgNO_3$ showed transparency. After the elimination of the chloride, when the $AgNO_3$ test was negative, the porous boats with the decarbonated samples were placed on the heating plate with a temperature of around 60 °C to 80 °C for approximately 5 min or until drying. Subsequently, the samples were placed in the oven at 80 °C for 2 h. Subsequently, each sample was taken to the desiccator for 30 min and weighed on a semi-analytical balance. This process was repeated until a constant weight was obtained. Then, 0.1 g of the decarbonated sample was weighed in the tin capsule, using the analytical balance coupled to the elemental carbon analyzer (628 series, LECO).

For the determination of $\delta^{13}C$ and $\delta^{15}N$ concentrations, approximately 8 mg of the decarbonated samples were weighed in tin capsules. The analysis was performed using a Costech elementary analyzer coupled to a Thermo Finnigan Delta Plus mass spectrometer. The isotopic and mass values were referenced in two references certified by the International Atomic Energy Agency (IAEA) (USGS40 and USGS41). The results were expressed in ‰ in relation to the international VPDB (Vienna Pee Dee Belemnite) standard for carbon and to atmospheric nitrogen for nitrogen, following the equation:

$$\delta^{n}X = \left(\frac{R_{sample} - R_{pattern}}{R_{pattern}}\right) \times 1000‰$$

where ^{n}X refers to ^{13}C (carbon) and ^{15}N (nitrogen) and $R = {}^{13}C/{}^{12}C$ for carbon and $^{15}N/^{14}N$ for nitrogen. The accuracy of the analytical preparation and measurement process was approximately 0.1‰. The errors associated with determination of the isotopic values ($\delta^{13}C$ and $\delta^{15}N$) were ± 0.1‰, while errors in mass determination were approximately 5%.

Descriptive statistical analysis was performed and the Spearman's rank correlation was conducted for the data (TOC, TN, TOC/TN, sand, mud, $\delta^{13}C$ and $\delta^{15}N$) because the dataset showed non-normal distribution. Significant correlation was defined as $p \leq 0.05$.

Through the Shepard ternary diagram (Fig. 2.a) it was possible to verify that the sediment samples from the Serinhaém River estuary present predominance of sandy and clayey sand classes. Similar findings were observed from the Fleming ternary diagram (Fig. 2.b). Thus, sand is considered the main indicator for local hydrodynamics. However, only 29.6% of the analyzed samples had a sand content equal to or greater than 75%. Thus, it can be said that the hydrodynamics in the estuary region of the Serinhaém River is a relevant aspect for the dispersion of the sediment and favorable to the distribution of organic and inorganic compounds in the estuary environment of the Serinhaém River.

The sand fraction was predominantly in the five cores (Table 2; Fig. 2). The sand values reached approximately 81% in T4 and the smallest amount of about 62% was noted in the T5 core, in which the highest concentration of mud at 38% was found. The data in the present study agree with those reported by Santos and Nolasco (2017), also on the Serinhaem estuary, which showed the predominance of the medium sand fraction. Other studies in estuaries also exhibit the predominant sand fraction in the respective study environments (Homens et al., 2013; Guimarães et al., 2019).

The TOC levels had a minimum value at T4 (below the limit of quantification of 0.04%) and a maximum value of 7.86% at T1. Analyzing the behavior along with the profile (Fig. 3), it was found that in T1, T2, and T5 the TOC concentrations tend to increase with depth, while in T3 and T4 the values decrease. Table 2 shows the TOC, TN, $\delta^{13}C$, $\delta^{15}N$, C/N, mud and sand values found in the samples evaluated in the five cores.

The values of N had the lowest values in T1, T3, and T4 (below the limit of quantification of 0.10%) and the highest in T1 (0.50%). The vertical profile of TN concentrations in T1, T2, T4, and T5 (Fig. 4) shows that they tend to increase with increasing depth, unlike T3 which tends to decrease. A common behavior of TOC and TN, in all cores, was an increase in concentrations in the depth of approximately 20 cm, however, the values of $\delta^{13}C$ and $\delta^{15}N$ did not change, as shown in Figs. 3 to 7. In addition, from these figures, it is possible to verify that the values of $\delta^{13}C$ and $\delta^{15}N$ remain practically constant in all cores, except for T5, wherein the depth of approximately 25 cm they have lower values of $\delta^{13}C$ and $\delta^{15}N$, indicating that there was a greater contribution of C3 type terrestrial plants in that location. It is noted the T3 core was collected in a more distant place from the vegetation (in the most central part of the estuary), being able to explain its values of TOC and $\delta^{13}C$ practically constant in its vertical profile.

The TOC/TN ratio has been used to investigate the influence of marine and terrestrial organic matter in some ecosystems (Guo et al., 2004; Usui et al., 2006; Gao et al., 2012; Spanó et al., 2014; Gu et al., 2017). In the present study, the values found for the TOC/TN ratio varied greatly among the cores, with 0.11 as the minimum value in T4 and the maximum value of 86 in T1. Higher ratio values of above 20 indicate that the origin of organic matter has its main source from vascular plants, with a C3 type photosynthetic pattern (Saito et al., 1989; Meyers, 1997; Gao et al., 2012) and, although there are some fluctuations throughout the core, they all fall into this pattern. Values like the present study, and attributed to terrestrial plants, were found by Pereira et al. (2006) when studying organic matter at the mouth of the Amazon River, between the states of Pará and Amapá. Gao et al. (2012) when investigating the origin of organic matter in the sediments of Bohai Bay, China, reported TOC/TN values between 10.8 and 42.6, indicating a predominance of terrestrial materials from rivers in the organic matter of surface sediments. When analyzing the vertical profile of the TOC/TN ratio at T1, it was found a variation from 24 to 86, with an average of 37, being the highest among the collected cores.

The $\delta^{13}C$ values present the minimum and maximum values at T5, -31.32‰ and -25.40‰, indicating that the main source of organic matter in the study environment is associated with C3 plants. According to Pancost and Boot (2004) and Meyers (1997), terrestrial plants with via

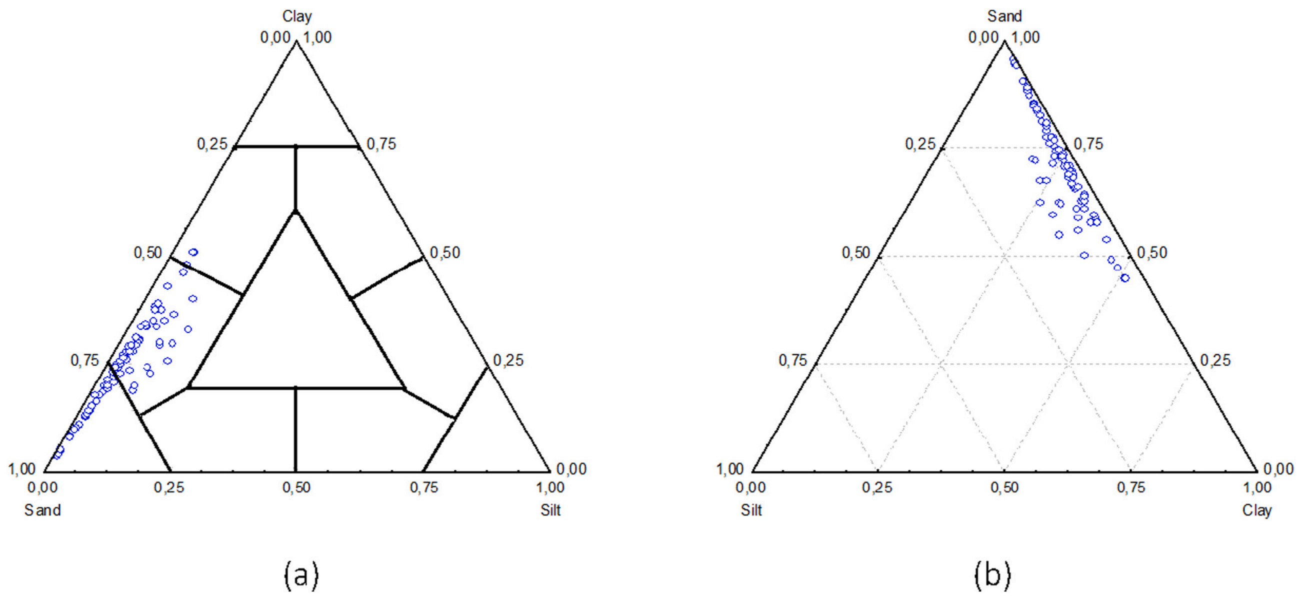

Fig. 2. Ternary diagrams for classifying sediment in the Serinhaem River estuary: (a) Shepard diagram (1954) and (b) Flemming diagram (2000).

Table 2
Values of the means. Minimums. maximums. and standard deviation found in the samples of the five cores (T1 to T5) collected along the estuary of the Serinhaem River. EPA of Pratigi. Bahia State.

Variables		T1	T2	T3	T4	T5
	Min.	4.2	2.4	0.54	<LQ	1.9
	Max.	11.9	9.1	2.76	1.24	5.9
	Mean	7.9	7.0	1.42	0.41	4.2
TOC (%)	SD	2.3	2.3	0.52	0.42	1.2
	Min.	<LQ	0.15	<LQ	<LQ	0.23
	Max.	0.50	0.35	0.26	0.19	0.44
	Mean	0.26	0.28	0.10	0.10	0.34
TN (%)	SD	0.13	0.07	0.05	0.06	0.06
	Min.	24	15.8	5.9	0.1	8.3
	Max.	86	30.8	35.4	24.8	14.3
	Mean	37	24.4	16.9	7.7	12.1
TOC/TN	SD	17	4.3	6.1	8.8	1.5
	Min.	-26.95	-26.65	-26.32	-26.63	-31.3
	Max.	-25.56	-25.81	-25.53	-25.86	-25.4
	Mean	-25.90	-26.30	-25.86	-26.23	-26.4
$\delta^{13}C$ (‰)	SD	0.42	0.28	0.27	0.26	1.6
	Min.	4.42	5.3	-7.6	-5.7	-3.9
	Max.	5.30	1.2	3.4	2.9	3.6
	Mean	4.77	3.9	1.8	-0.9	2.4
$\delta^{15}N$ (‰)	SD	0.30	1.4	2.3	3.0	1.6
	Min.	14.46	17.14	11.68	4.43	25.15
MUD (%)	Max.	44.14	39.08	49.56	41.18	55.24
	Mean	33.69	27.13	28.25	18.35	38.39
	SD	9.81	6.36	10.88	11.97	9.82
	Min.	55.86	60.93	50.43	58.83	44.76
SAND (%)	Max.	85.55	82.85	88.31	95.57	74.85
	Mean	66.30	72.88	71.75	81.65	61.61
	SD	9.81	6.36	10.88	11.97	9.82

Limit of quantification of TOC = 0.04%; Quantification limit of TN = 0.10%.

C3 path have an average value of $\delta^{13}C$ of -27‰, ranging from -22 to -33‰, while for the C4 path it is -9‰ to - 16‰, with an average value of -13‰. This result corroborates whit the values found by Guimarães et al. (2019) when studying the Itapicuru River estuary located in Bahia, northeastern Brazil, as well as by Gao et al. (2012) when studying the Bohai Bay, in China. Both studies indicated organic matter of the studied areas is mainly derived from C3 vascular plants.

For $\delta^{15}N$, the minimum value of -7.59‰ was found in T3 while the maximum value of 5.30‰ was found in T1. Similar values were noted in the literature and attributed to C3 terrestrial plants (Bristow et al., 2013; Gu et al., 2017). The $\delta^{15}N$ values depend on the characteristics of the local nitrogen cycle. Variations in the rate of nitrogen fixation of the atmosphere, mineralization, nitrification and denitrification determine the nitrogen isotopic fractionation (Spanó et al., 2014).

However, only a stable isotope is insufficient to identify the sources of OM due to the complicated contributions in coastal areas. Thus, the representation of diagrams of $\delta^{13}C$ and $\delta^{15}N$, together with the TOC/TN ratio, can be applied to improve source identification (Yu et al., 2010; Li et al., 2016). Therefore, for a better interpretation of the data, a schematic diagram was used (Barros et al., 2010) whose illustrated intervals for $\delta^{13}C$, $\delta^{15}N$ and TOC/TN (Figs. 7 and 8) were based on values found in the literature for the main sources of OM: sewage, mangroves, terrestrial and oceanic origin (Meyers, 1997; Gao et al., 2012; Bristow et al., 2013; Gu et al., 2017; Guimarães et al., 2019). The isotopic values found in the analysis of the cores collected in the Serinhaem River estuary are within ranges similar to those reported in the literature above.

Based on the intervals of $\delta^{13}C$ and $\delta^{15}N$, it is evident from Fig. 8 that all cores are within the values found in mangroves. It can be explained by the presence of mangrove vegetation around the estuary, making the influence of higher C3 plants, since the $\delta^{13}C$ from terrestrial sources are generally more negative than marine sources, especially when the terrestrial sources are from plants that follow the C3 photosynthetic pathway (Barros et al., 2010).

From Fig. 9 showing TOC/TN versus $\delta^{13}C$ ratio, the data also indicate that most samples have a predominantly terrestrial source. However, some T1 and T2 samples exceed these values found in the literature. This may be related to the presence of a large amount of TOC found in these two cores, as well as to the low values of N (Fig. 8), or it may represent a specific organic contribution. It is worth mentioning that T1 and T2, respectively, are the closest points to the city of Ituberá and more upstream in the estuary.

Spearman's rank correlation showed significant positive relationships ($p \leq 0.05$) between TOC and TN; TOC/TN and TOC; $\delta^{15}N$ and TOC; $\delta^{15}N$ and TOC/TN (Table 3). No significant correlations were however noted between sediment granulometry (mud and sand) with the other variables, as the variations in the concentrations of TOC and TN tend to follow the changes in the percentage of finer sediment (silt/clay). Similarly, no significant correlation was observed between mud/sand with the TOC/TN ratio. The composition of the granulometry significantly influences the geochemical behavior of the elements in the sediments (Gu et al., 2017). This is attributed to the higher adsorption ratio

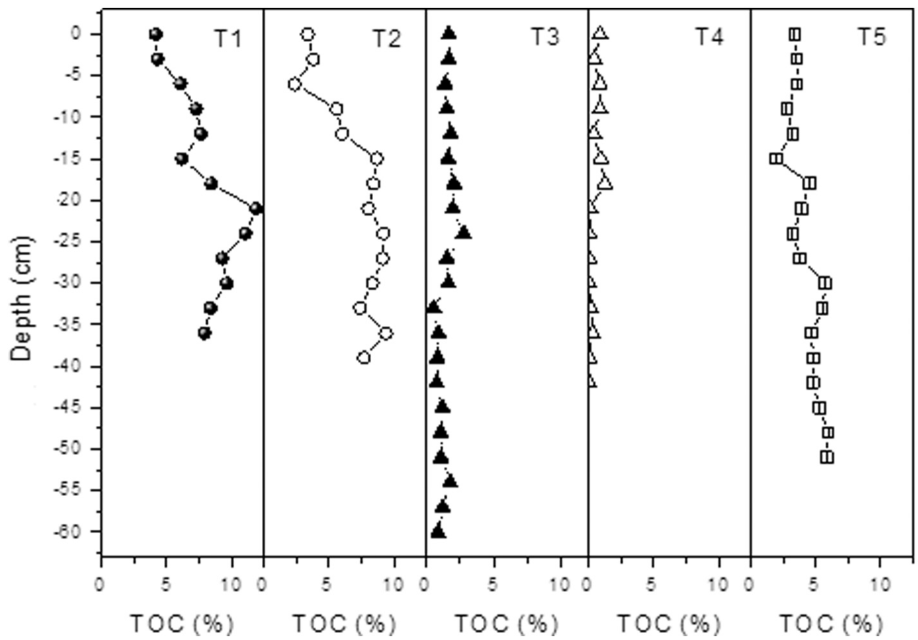

Fig. 3. Vertical profile behavior of total organic carbon (TOC) in the five cores collected in the Serinhaem River estuary, Bahia.

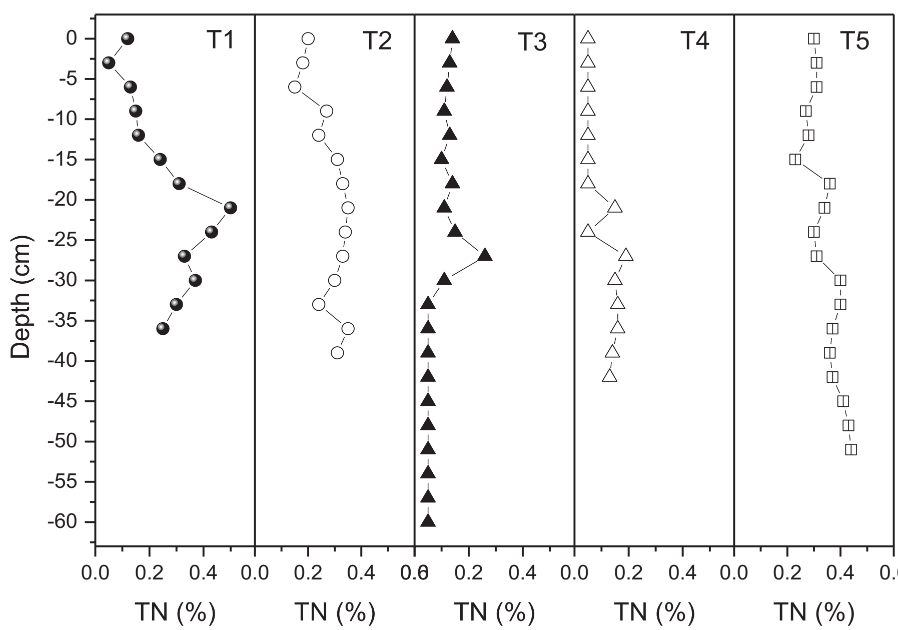

Fig. 4. Vertical profile behavior of total nitrogen (TN) in the five cores collected in the Serinhaem River estuary, Bahia.

of finer particles, with a grain size of <63 μm (silt and clay), which have a larger surface area that provides good binding sites for organic matter (Meyers, 1994; Gao et al., 2012; Gu et al., 2017; Guimarães et al., 2019). Thus, it is evident that "the grain size effect" is not an important factor that influences the distribution of organic carbon and stable isotopes in sediments collected from the core samples.

In the present study, TOC data correlate significantly and positively with TN data. According to Rumolo et al. (2011), this positive correlation suggests that the levels of inorganic nitrogen were insignificant for the composition of the TN and that it is formed mainly by its organic part (organic nitrogen). Li et al. (2016) corroborated the same idea, when finding the correlation between TN and TOC, as they stated that when this occurs, it suggests that most of the sedimentary nitrogen is of organic origin. Similar behavior was found by Carreira et al. (2002) when studying the Guanabara Bay in southeast Brazil and Vilhena et al. (2018) when studying two coastal areas in the northwest of the state of Pará, Brazil.

The values of the TOC/TN ratio have a significant positive relationship with the TOC concentrations which indicates that the variation of the TOC/TN ratios at the sampling locations is controlled by the TOC concentrations (Gao et al., 2012). The concentration of TN seems to have no influence on the distribution of the TOC/TN ratio, as there is no significant relationship between them (Gao et al., 2012). Considering that the TOC/TN ratio strongly reflects the sources of OM, it is expected that there is a significant negative correlation between the $\delta^{13}C$ and TOC/TN relationship, i.e., OM with a high TOC/TN ratio has lighter $\delta^{13}C$ value (Wu et al., 2003; Gao et al., 2012). However, it is shown in Table 3 that in the present study, the TOC/TN ratios have no $\delta^{13}C$ relationship

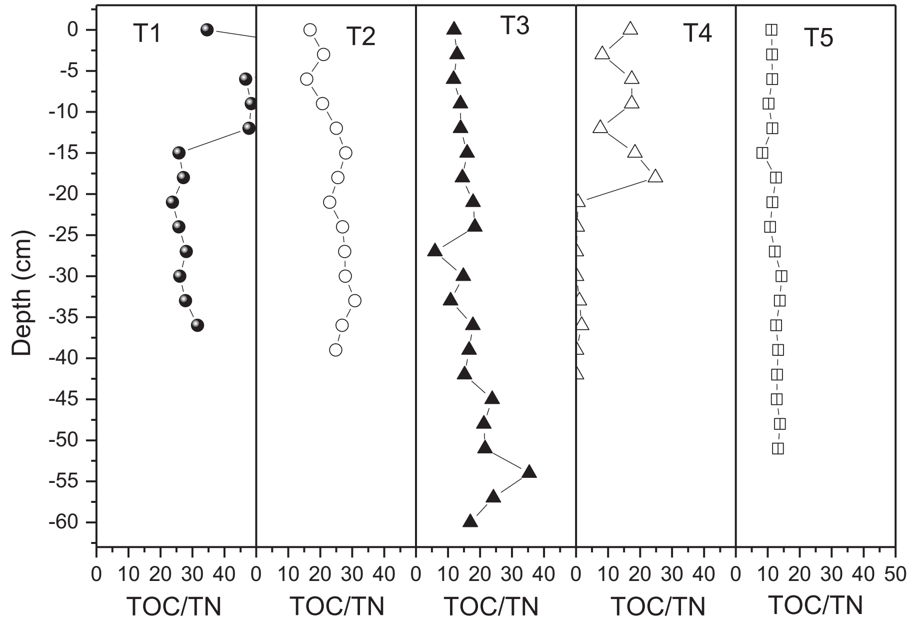

Fig. 5. Vertical profile behavior of the TOC/TN ratio in the five cores collected in the Serinhaem River estuary, Bahia.

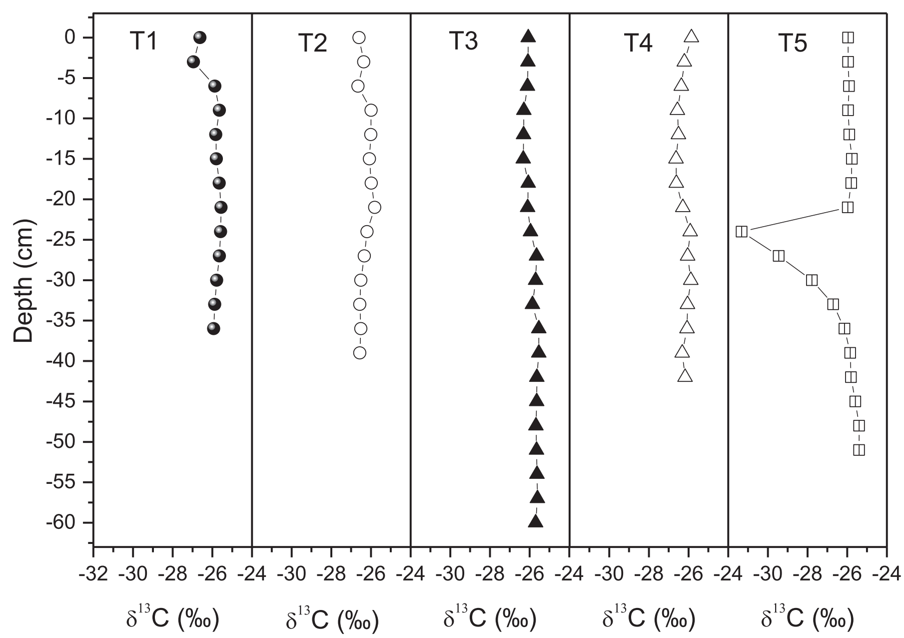

Fig. 6. Vertical profile behavior of $\delta^{13}C$ in the five cores collected in the Serinhaem River estuary, Bahia.

($r_s = 0.08$). This must be attributed to the fact that during the sediment diagenesis, the TOC/TN ratio can be altered by the selective degradation of the organic matter components. Commonly, TOC/TN ratios tend to decrease over time due to the release of CO_2 or CH_4 because of the decomposition processes (e.g., autolysis, leaching and microbial mineralization) of organic matter (Wu et al., 2003; Gao et al., 2012), as well as preserving ammonia and adding nitrogen associated with microorganisms (Gao et al., 2012). Pastene et al. (2019) also found a significant negative correlation between TOC/ TN and $\delta^{13}C$ and attributed this to a mixture of different types of OM in the study area.

It is worth mentioning that the TOC/TN ratios decrease during the organic matter decomposition processes if particulate nitrogen in the form of bacterial biomass is added as protein to the organic matter pool, as well as if terrestrial remains of nitrogen poor macrophytes, during the process decomposition, present the production of nitrogen greater than the release of plant material (Müller, 1977; Müller and Mathesius, 1999). According to Müller (1977), in addition to the direct diagenetic effects, changes in the TOC/TN ratio also depend on the connection of organic material to clay minerals. OM not bound to clay minerals in marine sediments shows a tendency for higher rates of decrease in TOC/ TN ratios than OM linked to clay minerals, because, when bounded, it is "protected" against microbial decomposition, in which during the process nitrogen is preferably released. Also, according to Müller (1977), the fraction of inorganic nitrogen is composed mainly of ammonium, which is bound to clay minerals. Depending on the shape of the clay minerals, some sediments may have a lesser capacity to bind to organic nitrogen.

A significant positive correlation ($r_s = 0.63$) was found between

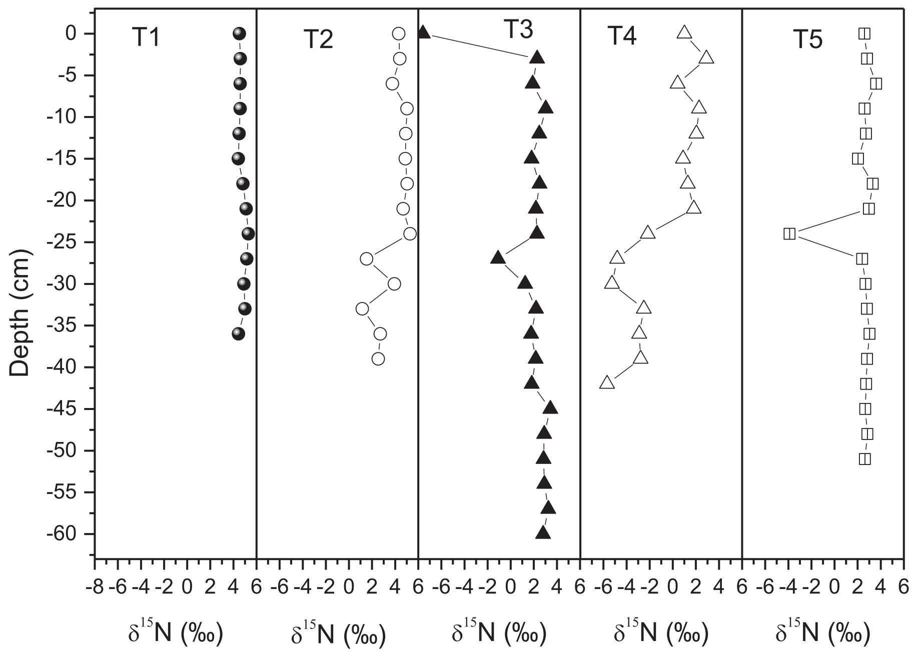

Fig. 7. Vertical profile $\delta^{15}N$ vertical behavior in the five cores collected in the Serinhaem River estuary, Bahia.

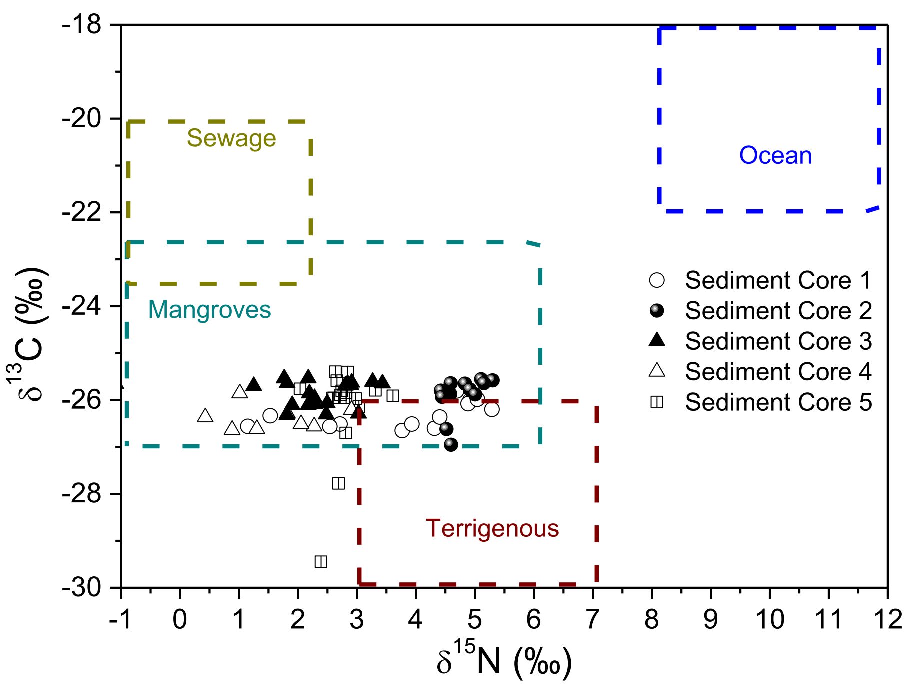

Fig. 8. $\delta^{13}C$ versus $\delta^{15}N$ for the samples from the five cores collected along the Serinhaem River estuary.

TOC/TN and $\delta^{15}N$. Liu et al. (2006) also reported that in the intertidal sediments of the Yangtze estuary, China, heavier values of $\delta^{15}N$ were found where the TOC/TN ratios were higher, and the authors attributed this relationship to the result of the diagenesis of organic matter. Vilhena et al. (2018) observed the same behavior in Guanabara Bay, southeast Brazil. Isotopic nitrogen compositions can be easily modified by a series of complex biogeochemical processes at some time scales. Dynamic nitrogen cycling is subject to the effects of the kinetic isotopic fraction, especially during biogenic transformation and recycling of dissolved and particulate nitrogen compounds (Gao et al., 2012). If only small changes in the TOC/TN ratio occur, it suggests that organic carbon and nitrogen are mineralized or preserved to the same extent (Müller, 1977; Müller and Mathesius, 1999).

Although $\delta^{13}C$ and $\delta^{15}N$ of sediments can be modified by microbial rearrangement, the isotopic fractionation specifically associated with initial diagenesis is negligible and the isotopic composition of the sedimentary organic matter is quite conservative, mirroring the isotopic signatures of the sources (Di Leonardo et al., 2009). It is important to remember that unlike the TOC/TN ratios, the $\delta^{13}C$ values are not significantly influenced by the grain size of the sediment, making them useful in the reconstruction of past sources of organic matter in places with histories of changes in deposition conditions (Meyers, 1994).

This work has an important contribution in relation to the knowledge of processes that occurred in this environment through the analyses of

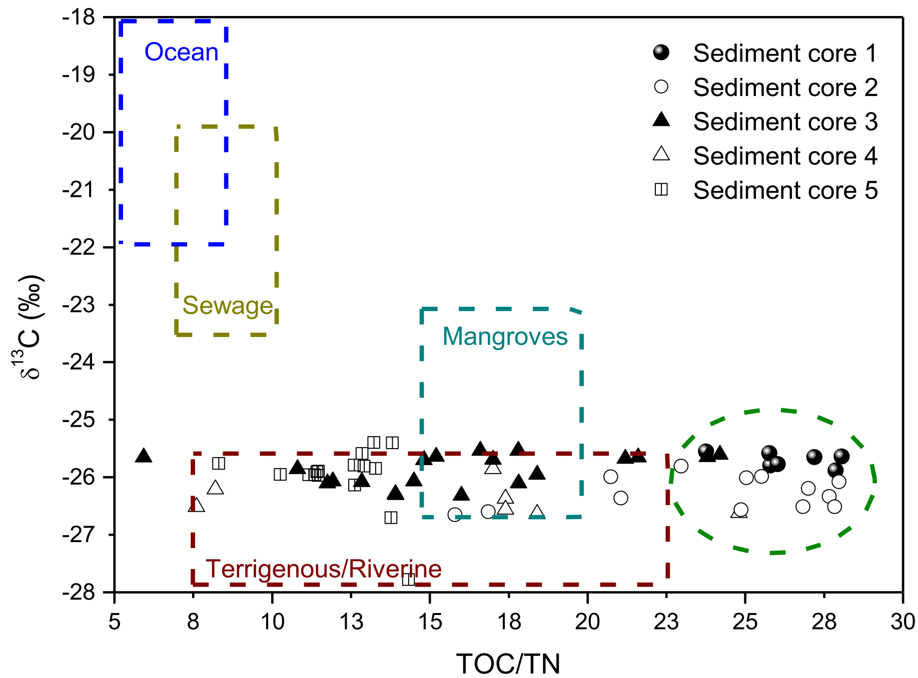

Fig. 9. $\delta^{13}C$ versus TOC/TN for samples from the five cores collected along the Serinhaem River estuary.

Table 3
Spearman's correlation coefficient for the samples from the five cores collected in the Serinhaem River estuary. EPA of Pratigi. (Values in bold: $p \leq 0.05$).

	TOC	TN	TOC/TN	Sand	MUD	$\delta^{13}C$	$\delta^{15}N$
TOC							
TN	**0.75**						
TOC/TN	**0.64**	0.03					
Sand	-0.39	-0.35	-0.10				
MUD	0.39	0.35	0.10	-1.00			
$\delta^{13}C$	0.07	0.07	0.08	0.06	0.06		
$\delta^{15}N$	**0.72**	0.39	0.63	-0.16	0.16	0.22	

TOC, TN, $\delta^{13}C$, and $\delta^{15}N$ along with the studied sediment profiles. The TOC/TN ratios obtained for the five cores collected in the Serinhaem River estuary located in the Pratigi EPA, Bahia, presented values that indicate the influence of organic matter specifically of higher plants with type C3 photosynthetic pattern. Both $\delta^{13}C$ and $\delta^{15}N$ values in the sediment profiles were also related to plants with type C3 photosynthetic pattern from terrestrial sources and from mangroves along the estuary. The analysis, $\delta^{13}C$, and $\delta^{15}N$ in estuarine sediments showed results consistent with other studies carried out in estuaries in Bahia, indicating a terrestrial origin, which can be justified by the presence of mangrove vegetation around the estuary. The points with the highest values of TOC and TN occurred close to the city of Ituberá; however, the TOC/TN, $\delta^{13}C$ and $\delta^{15}N$ ratios do not indicate anthropogenic contribution. Hence, even though the city of Ituberá is remarkably close to the Serinhaem River estuary, the present findings suggest that the biochemical processes inherent to the estuarine environment play a more important role in the cycle of organic matter than human interference.

CRediT authorship contribution statement

As recommended, the description of the authors' contribution to the scientific production submitted for evaluation follows.

Luanna Maia Carneiro: Conceptualization, Formal Analysis, Writing - Original draft preparation, Experimentation, Validation.

Maria do Rosário Zucchi: Visualization, Data Curation, Writing, Reviewing and Editing.

Taise Bomfim de Jesus: Data Curation, Project coordinator.

Jucelino Balbino da Silva Júnior: Conceptualization, Reviewing and Editing, Data Curation.

Gisele Mara Hadlich: Conceptualization, Writing, Reviewing and Editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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