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Variability of Settling Particles Fluxes and Isotopic Composition (δ¹³C and δ¹⁵N) from Material Trapped in Coastal Reefs of Abrolhos Bank, Eastern Brazilian Shelf

Variabilidade Sazonal do Fluxo Vertical de Partículas e Composição Isotópica (δ¹³C e δ¹⁵N) de Material Aprisionado nos Recifes Costeiros do Banco de Abrolhos, Plataforma Leste Brasileira

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Abstract

Elemental and isotopic ratios (C/N, δ^{13} C, δ^{15} N) of sediment samples captured by PVC traps in eight stations along the coastal reefs of the Abrolhos region, Brazil, were analyzed. The study area is characterized by the influence of continental sediments on biogenic sediments. The highest δ^{13} C values were found in the Sebastião Gomes (second shallower station), with average values close to -15‰ in all sampling periods. The isotopic ratio of carbon and nitrogen indicates that the organic matter analyzed has marine origin, with signature features of oceanic regions. The highest C/N ratio average value of 8.29 occurred in Nova Viçosa (the southernmost station and one of the shallowest) during the spring, in other seasons the average value was close to 7 in all periods. Although the values of C/N indicate a significantly marine contribution, δ^{15} N values suggest that N series recycling processes are frequent during the time that the material remained in the environment. The results will provide a baseline for future environmental monitoring and studies on changes in sediment composition in an important set of coastal coral reefs.

Keywords: Sediment traps; Abrolhos; Stable isotopes

Resumo

Foram analisadas as razões elementares e isotópicas (C /N, δ^{13} C, δ^{15} N) de amostras de sedimentos capturadas por armadilhas de PVC em oito estações ao longo dos recifes costeiros da região de Abrolhos, Brasil. A área de estudo é caracterizada pela influência de sedimentos continentais em sedimentos biogênicos. Os maiores valores de δ^{13} C foram encontrados na Sebastião Gomes (segunda estação mais rasa), com valores médios próximos a -15 ‰ em todos os períodos de amostragem. A razão isotópica de carbono e nitrogênio indica que a matéria orgânica analisada tem origem marinha, com características de assinatura das regiões oceânicas. O valor médio da relação C/N mais alta de 8,29 ocorreu em Nova Viçosa (estação mais ao sul e uma das mais rasas) durante a primavera, em outras estações o valor médio foi próximo de 7 em todos os períodos. Embora os valores de C/N indicam uma contribuição significativamente marinha, os valores de δ^{15} N sugerem que os processos de reciclagem do N são frequentes durante o tempo em que o material permaneceu no ambiente. Os resultados fornecerão uma linha de base para o monitoramento ambiental futuro e estudos sobre mudanças na composição de sedimentos em um importante conjunto de recifes de coral costeiros.

Palavras-chave: Armadilhas de sedimento; Abrolhos; Isótopos estáveis



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1 Introduction

Continental shelves and coastal zones are an important system for the production and storage of organic carbon (Hedges & Keil, 1995). The wide variety of marine sources provides a broad spectrum of dissolved, particulate and colloidal materials responsible for organic matter (OM) found in coastal sediments (Goñi et al., 1997; Hedges et al., 1997; Raymond & Bauer, 2001a, 2001b; Sigleo & Macko, 2002). The use of stable isotopes of C and N in studies to identify probable sources of organic matter is widely used to determine the seasonal flows and residence time of these materials in coastal and estuarine environments (Hedges & Parker, 1976; Lucotte et al., 1991). Fry & Sherr (1984) shows that the natural abundance of δ^{13} C carbon isotopes and δ^{15} N nitrogen differ in terrestrial, estuarian, in situ and anthropogenic OM. In marine sediments, the differences can be used to verify the possible sources of OM. This use of stable isotopes to track OM is based on the assumption that stable isotopes are conservative, and that the isotopic composition of OM in natural systems is determined by the physical mixing of the contributing sources (Cifuentes et al., 1989). The simultaneous use of one or more markers is significantly improved in the discrimination of the OM source (Cifuentes et al., 1988). Studies in the last decades documented the isotopic differences of carbon and nitrogen in OM from anthropogenic and natural sources (Sweeney & Kaplan, 1980; Middelburg & Nieuwenhuize, 1998; Struck et al., 2001; Rogers, 2003; Ogrinc et al., 2005). The proposal of combined use of C / N and C and N isotopes is a consensus (Peters et al., 1978; Cifuentes et al., 1988), being a powerful tool to distinguish and quantify the marine OM from terrestrial OM sources (Guo et al., 2004); (ii) to track wastewater from anthropic sources (Rogers, 2003); and (iii) detect denitrification and variations in the past use of nutrients (Voß & Struck, 1997).

The accumulation of organic carbon (OC) in sediments depends on the supply of OC, the effects of dilution of detrital matter, and the preservation and mineralization in sediments (Hedges & Keil, 1995). Investigations indicated that most OC in sediments from the continental margin are sorbed on surfaces of clay-sized minerals, and thus, preserved from degradation process (Hedges *et al.*, 1997). Changes in $\delta^{15}N$ of sediments may reveal variations in nutrient levels in the water column (Ostrom *et al.*, 1997; Freudenthal *et al.*, 2001). However, early diagenesis also produces changes in the stable isotope signature of N in OM. Two main processes have been proposed to explain these changes in isotopic composition: selective degradation of organic compounds and isotopic fractionation during degradation (Prahl *et al.*, 1997;

Nakatsuka *et al.*, 1997). Isotopic signatures of sedimentary N are affected by biogeochemical processes more than C isotopes (Hoefs, 2009). An apparent increase in δ^{15} N values in marine sediments was observed because of bacterial metabolism or because of digestion by organisms from higher trophic levels (Nakatsuka *et al.*, 1997). The effect of isotopic fractionation associated with early diagenesis of decanted and buried OM seems to have small effects on the isotopic carbon composition (usually \approx 1 ‰). Consequently, the isotopic composition of the resulting sedimentary OM is relatively conserved, and the isotopic signature of the sources largely preserved (Voss *et al.*, 2000).

The objective of the present study is to understand the mass fluxes of particulate material that reaches the coastal reefs of the Abrolhos bank, an important reserve of marine biodiversity, and to characterize $\delta^{13}C$ and $\delta^{15}N$ in the OM, identifying the nature and origin of this material.

2 Study Area

The study area is located in the inner continental shelf of Bahia state, and comprises eight station aligned along the inner reef arc of Abrolhos bank (Figure 1). The stations are located on the top of the coastal reefs, close to the ocean surface. Previous work shows the bimodal characteristic of the coastal current parallel to the coastline of the Abrolhos bank region (Texeira et al., 2013). In studies between 2000 and 2005, these authors define the mean monthly magnitude of the currents varying between 10 and 25 cm/s in the channel that separate the reefs of the continent, with the highest significant mean wave height of 0.4 m and the longest period of 5 s. The tides in the region are semidiurnal, with amplitudes of the main harmonic components equal to 91 and 38 cm. (Teixeira et al., 2013). The driest period occurs between May and October, characterized by S and SE winds with an occurrence of 40%. While the rainy season happens between November and April and is characterized by NE winds with occurrence of 39%.

3 Materials and Methods

In this study was used sediment traps. The traps were made using 60 mm diameter and 35 cm long PVC pipes, which were closed in one of the extremities and fixed vertically with the opening pointing upward. To avoid the loss of sample from the traps, a reduction of 60/40 mm diameter was used and, thus, the trap opening area was 1.25 10⁻³ m² (Figure 1). Ten sediment traps were fixed at each of the eight stations along the coastal reefs of the Abrolhos region, Brazil (Figure 1). After about

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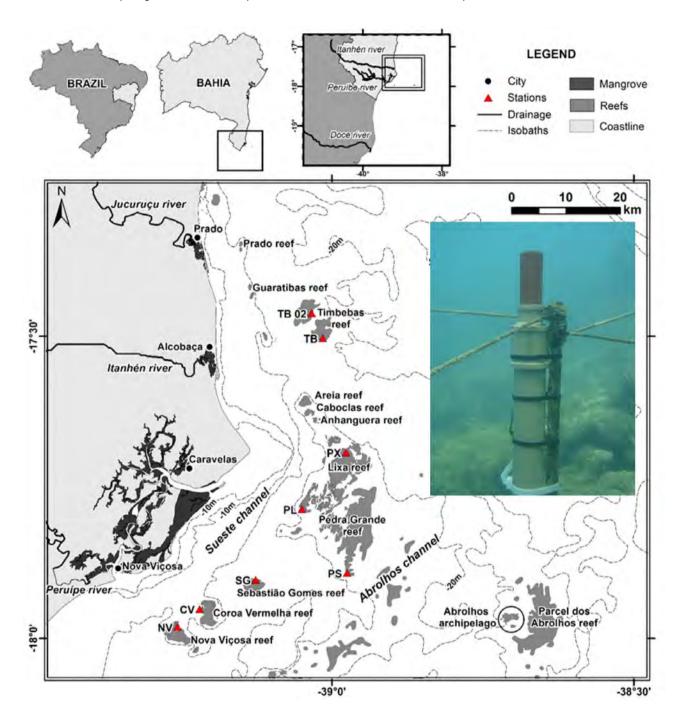


Figure 1 Bathymetry of the study region with station location (big panel), picture of the PVC trap (small panel). Abbreviations indicate the following stations: TB2 – Timbebas north reef, TB – Timbebas south reef; PX – Pedra da Lixa reef; PL – Pedra de Leste reef; PS – South point reef; SG – Sebastião Gomes reef; CV – Coroa Vermelha reef; NV – Nova Viçosa reef.

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three months in the environment, the sediment traps with samples were collected from the reefs. These surveys were performed in March, June, September and December of 2010. Preservative substances were not used in the samples.

The eighty sediment traps (10 at each station) taken in March remained on average for 92 days in the environment, in June, the eighty traps remained for 99 days, in September they were 81 days and in December the traps remained in the environment for 87 days. In the total were collected 320 samples for research. Elemental analysis used an aliquot from every sample collected (n=10) and the fine sediments (silt and clay) were analyzed as follows: For each sample 0.5g were weighed and 10ml of hydrochloric acid (1mol/ L) was added to remove the carbonate. The procedure was repeated in each of the samples until complete removal of the carbonate. After 24 hours the samples were centrifuged, and the supernatant was discarded. The samples were then washed with deionized water and centrifuged again. This procedure was repeated three times before the samples were dried at 50 ° C. After this preparation step, 8mg of each sample were weighed and packed in tin capsule for the elemental analyzes and relation of the organic carbon and nitrogen. For this step, the Costech Elementary Analyzer coupled to a Thermo Finnigan Delta Plus mass spectrometer was used. For calibration, an international standard sediment certified by NIST (National Institute of Standards and Technology), identified by number 1941b, was used, which was submitted to the same treatment procedures of the samples. The results were expressed in ‰ in relation to the international reference standard for carbon isotopes is VPDB, which is shorthand for Vienna Pee Dee Belemnite, for the δ^{13} C, and in relation to the nitrogen isotopes is atmospheric nitrogen, for the δ^{15} N, following the equation:

$$\delta X = \frac{R_{\text{Sample}} - R_{\text{Standart}}}{R_{\text{Standart}}} \times 1000 (\%)$$

where X = C (carbon) or N (nitrogen) and $R = {}^{13}C/{}^{12}C$ for carbon and ${}^{15}N/{}^{14}N$ for nitrogen. Ninety standards were analyzed during measurements. 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 \pm 0.1 ‰, while errors in mass determination were approximately 5%.

The multivariate analysis used the Principal Component Analysis (PCA), to verify the existence of a geochemical gradient between sampling stations. This analysis allows us to rank the responsible factors for the variance of the data and summarize the key trends through its graphical representation in a reduced number of factorial plans (components or axes). The matrix formed with the geochemical data was treated to self-scale the data. After

calculating the similarity by correlation, it was computed the eigenvalues of the dispersion matrix, which measure the variance associated with each principal component. The first axis describes the largest dimension of the multidimensional ellipsoid, while these shafts go through gradually smaller dimensions (Legendre & Legendre, 1984). The multivariate analysis was performed using CANOCO 4.5 software (Leps & Smilauer, 1998).

4 Results

Isotopic analysis are shown in Figure 2, the maximum, minimum, average and standard deviation values of $\delta^{15}N$ (‰), $\delta^{13}C$ (‰), total nitrogen (%), total carbon (%) and C/N ratio. C/N ratio during summer was less than 7.0 in TB2, TB and PS and greater than 7.0 in PX, PL, SG, CV and NV. The highest C/N ratio value was 7.8 in SG. During autumn, these values were less than 7.0 in TB2, TB and PX and higher than 7.0 in PL, PS, SG, CV and NV, where the highest value (8.2) was observed. During winter, C/N ratio values were less than 7.0 in TB, PL and PS and greater than 7.0 in TB2, PX, CV and NV. In SG, a C/N ratio of 7.0 was found. The highest value was observed in NV (7.5). Finally, during spring, C/N ratio was less than 7.0 only in PL. In the other stations, C/N ratio was higher than 7.0, with the greatest value (8.3) occurring in NV (Figure 2).

Isotopic analysis results found by previous studies (Souza et al., 2013; Spanó et al., 2014; Ribeiro (unpublished data) in Caravels and Alcobaça mangroves, in Caravelas and Nova Vicosa estuarine channels, in the channel that separates the reef arc from the continent and in coastal reefs are shown in Table 1 and in Figures 2 and 3. Ribeiro (unpublished data) observed δ^{15} N e δ^{13} C values of 2.78 ‰ e -26.44% in Caravelas and 2.12 % and -26.65 % in Alcobaça, respectively. In Caravelas mangrove, Sousa et al. (2013) found δ^{15} N e δ^{13} C values of 1.0 ‰ and -26.90 ‰, respectively. The percentages for total nitrogen and total carbon in mangroves were 0.10% e 0.19% in Caravelas and 1.80% e 3.65% in Alcobaça (Ribeiro, unpublished data). In addition, Sousa et al. (2013) observed for total nitrogen and total carbon 0.25% and 4.50%, respectively, in Caravelas mangroves. These authors also found $\delta^{15}N$ values of 0.70% e 3.10% in the channel that separates the reef from the continent and in the coastal reefs, respectively, while δ^{13} C values were -20.75‰ and -18.33‰ for the same sites. According to Sousa et al. (2013) findings, total nitrogen accounts for 0.10% and 0.14%, whereas total carbon values were 0.85% and 1.12% in the channel and reefs, respectively. Sediment samples captured by the PVC traps exhibited $\delta^{15}N$ and $\delta^{13}C$ mean values of 2.58‰ and -18.2‰. Total nitrogen and total carbon in these samples were 0.39% and 2.83%, respectively.

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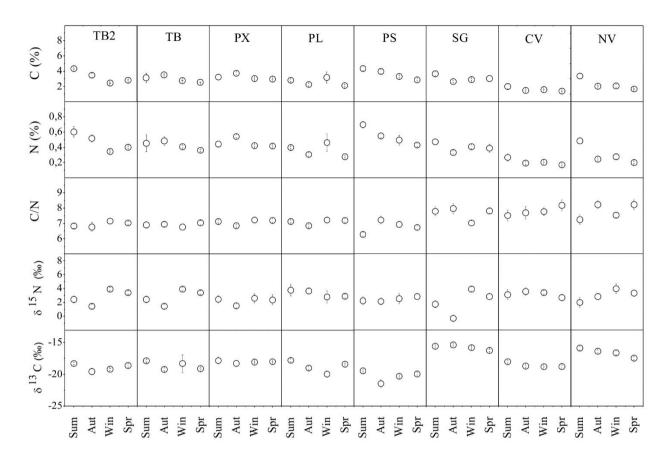


Figure 2 Mean and standard deviation (n=10) of the C/N ratio, $\delta^{15}N$ (%), $\delta^{13}C$ (%), total nitrogen (%) and total carbon (%). Abbreviations indicate the following stations: : TB2 – Timbebas north reef, TB – Timbebas south reef; PX – Pedra da Lixa reef; PL – Pedra de Leste reef; PS – South point reef; SG – Sebastião Gomes reef; CV – Coroa Vermelha reef; NV – Nova Viçosa reef.

Literature	Region	N(%)	OC(%)	δ ¹⁵ N (‰)	δ ¹³ C (‰)	C/N
This work	Stations shown in Fig. 1	0,39	2,54	2,58	-18,20	7,3
(Souza et al., 2016)	Todos os Santos bay	0,20	1,21	5,09	-18,02	6,3
(Spano <i>et al.</i> , 2014)	Est. channel Caravelas	0,10	1,90	1,43	-26,10	18,9
	Est. channel Nova Viçosa	0,09	1,77	3,28	-25,84	18,8
(Souza <i>et al.</i> , 2013)	Caravelas mangrove	0,25	4,50	1,00	-26,90	18,3
	Abrolhos channel	0,10	0,85	0,70	-20,75	9,5
	Reefs	0,14	1,12	3,10	-18,33	8,0
(Ribeiro, unpublished data)	Caravelas mangrove	0,10	1,80	2,78	-26,44	17,7
	Alcobaça mangrove	0,19	3,65	2,12	-26,65	19,0

Table 1 δ^{15} N, δ^{13} C, nitrogen, organic carbon and C/N ratio mean values of the sediment captured by the traps compared to literature. Est. = Estuarine

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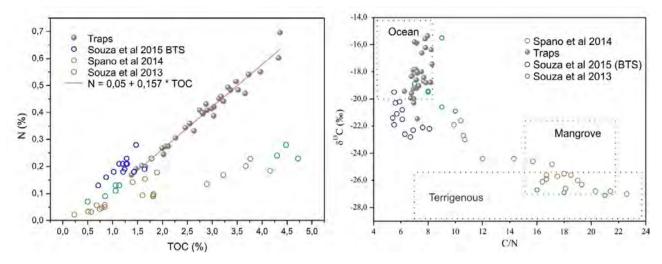


Figure 3 In the right panel δ^{13} C (‰) *versus* C/N ratio compared to those found by previous studies for the same area and for Todos os Santos bay (TSB). The polygons are based on Carreira *et al.* (2002); Goñi *et al.* (2003); Barros *et al.* (2010); Kumara (2011). In the left panel total Organic Carbon (%) versus total nitrogen (%) in the sediment samples collected by the traps (this study), estuarine samples from Abrolhos region (Souza *et al.*, 2013), and samples from Todos os Santos bay (Souza *et al.*, 2017).

Regarding C/N ratio, Ribeiro (unpublished data) observed mean values of 19.0 and 17.7 in Alcobaça and Caravelas mangroves. Sousa et al. (2003) found C/N ratios of 18.3 in Caravelas mangrove, 9.5 in the channel that separates the reef from the continent, and 8.0 in the coastal reefs. According to Spanó et al. (2014) the C/N ratio in the estuarine channel from Caravelas to Nova Viçosa was 18.9, while in the estuarine channel from Nova Viçosa to Caravelas this value was 18.8. The C/N ratio in the sediment captured by the traps in the reefs was 7.3. C/N ratio values ranged from 6.27 in PS during summer to 8.29 in NV. These values indicate OM from marine origin according to Saito and Matsumoto (1989), as these values are in between 5 and 7, or close to 7. Also following the criterion established by Stein (1991), who considers values less than 10 as a signature of marine source, the sediment sampled can be considered as of marine origin. Hence, all sediment captured by the traps can be classified as derived from marine sources.

When compared to previous studies in the same region (Souza *et al.*, 2013) and in the Todos os Santos bay (Souza *et al.*, 2017), the C/N ratio show similar values (Figure 3). However, most part of the OM can possibly be related to the trapping procedure, what is evident in the total carbon and total nitrogen values, which are twice higher than those found by Souza *et al.*, (2013). Furthermore, isotopic values of the sediment sampled are similar to values described in literature (Carreira *et al.*, 2002; Goñi *et al.*, 2003; Barros *et al.*, 2010; Kumara, 2011) (Figure 3).

Hence, this suggests a marine origin to the sediment samples analyzed.

5 Discussion

The marine sediment reflects the isotopic composition of its carbon source. In the ocean, the main source of carbon is the phytoplankton (-18% to -24%) and in the coastal region there is also the contribution from the continental sediment brought by the rivers (Martinelli et al., 2009). Deines (1980) classified the carbon isotopic values in marine sediments and obtained a bimodal distribution, where one mode has heavier values, between -10 and -19‰, and a lighter mode with values between -20 and -30‰, being the most frequent values contained by the lighter mode and raging from -23 to -25‰. The sediment samples exhibited values higher than -20 ‰, except in PS during autumn (-21.46 \pm 0.64‰) and winter (-20.21 \pm 0.27 ‰). Moreover, PS was the station where the lowest values were found. The heaviest values were observed in SG, with the greatest values during autumn (-15.24 \pm 0.34‰) and the lowest during spring (-16.22 \pm 0.18%). These results indicate that the sediment collected by the traps is of marine source, as most of the carbon isotopic values are around -18 % (Table 1).

The mass of suspended particulate OM showed different values depending on the season. This is probably related to wind regime in the region. Segal *et al.* (2008) observed a considerable increase in the amount of sediment

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captured by PVC traps in PL and PS. These authors found that the amount of sediment collected doubles from summer to winter and suggest that this pattern is related to the wind regime. Dutra et al. (2004) results for PL, PX and PS indicate that south-quadrant winds cause the resuspension of the sediment deposited in the bottom, and thus large amount of sediment captured by the traps during spring. In summer, when north-quadrant winds are dominant, the lowest amount of sediment collected was found. This is in good agreement with previous studies (Segal, 2003; Dutra et al., 2004; Segal et al., 2008). On the other hand, the highest amount of material captured by the traps was observed during winter and spring in four of eight stations, while in the other four stations the highest values were found during autumn, which is different from Dutra et al. (2004) and Segal et al. (2008). During spring, high values in the southern portion of the study area were also observed by Segal et al. (2008). The highest mean value in SG was approximately 30 times greater than the lowest mean value in TB2 during spring. Similar values were observed by Segal (2003) in coastal reefs of the Abrolhos bank during winter and spring.

The $\delta^{15}N$ values vary in accordance with the local nitrogen cycle. The variation of the nitrogen fixation rate processes from atmosphere, mineralization, nitrification and denitrification determine the isotopic fractionation of nitrogen (Högberg, 1997). According to Martinelli et al. (2009), δ¹⁵N values in leaves from Brazilian forests near to the ocean are $3.13\pm1.73\%$. In the sediment samples, $\delta^{15}N$ values ranged from -0.49 ± 0.35 in SG during summer to 3.69 ± 0.21 % in NV during winter. The highest values in TB, TB2, PX, SG, CV and NV occurred during winter. In PL and PS the highest values were found during summer and spring, respectively. On the other hand, the lowest values occurred during summer in TB2, SG and NV, during autumn in TB, PX and PS, and during winter in PL and CV. Due to δ^{15} N values variability, it is not possible to categorically determine the origin of the sediment, thus, being necessary the interpretation of C/N ratio results.

Total nitrogen means values exhibited variations among stations and in all sampling periods. The station

with the highest percentage was PS during summer (0.70 \pm 0.04%), while the lowest values was observed in CV during spring (0.17 \pm 0.01%). Total nitrogen highest values occurred in TB2, PS, SG, CV and NV during summer, in TB and PX during autumn and in PL during winter. However, the lowest values were observed in TB, PX, PL, PS, CV and NV during spring, in SG during autumn and in TB2 during winter. As can be seen in Figure 2 and 3, C/N ratio values indicate a blend between the components. Concerning the particulate OM, the pattern relative to δ^{13} C e o δ^{15} N are similar to that described in previous studies in the region (e.g., Sousa et al., 2013 and Spanó et al., 2014). In addition, Souza et al., (2013) found, in the reef region, δ^{13} C and C/N ratio values close to those observed in the present study. According to Barros et.al. (2010), δ^{13} C and δ^{15} N values relative to total OM composition in estuaries along the Brazilian coast ranges from -21.7 to -26.2% and from +9.2 a -0.1‰, respectively. Isotopic analysis of the sediment indicates δ^{13} C values higher than -21.5%, what suggests that the sediment is of marine origin, while $\delta^{15}N$ values were between -0.5 and 4.0%, which are similar to values observed in estuarine sediment.

The geochemical data obtained were subjected to multivariate evaluation through the principal components analysis (PCA). According to this evaluation, the first principal component explained 46% of the total variance while the second component explained 20% of the total variance, reaching 66% of the cumulative total variance, as shown in Figure 4.

Spatial variability was mainly due to the bathymetric gradient. According to the PCA graphs, it was possible to observe a shift of the samples of PL, PS, TB and TB2 stations towards positive values of PCA (Figure 4), justified by greater depth and high concentrations of the $\delta^{15}N$ (‰), $\delta^{13}C$ (‰), total nitrogen (%) and total carbon (%), relative to the other sampling stations. The distribution of SG, CV and NV samples were related to the higher concentrations of terrigenous sediment, C/N ratio and flow that presented shift towards a negative value of PCA.

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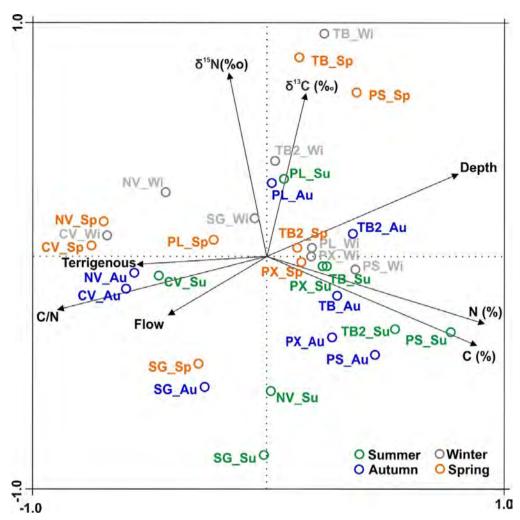


Figure 4 Principal component analysis performed to geochemical variables (C/N ratio, $\delta^{15}N$ (‰), $\delta^{13}C$ (‰), total nitrogen (%) and total carbon (%), flow and terrigenous in the sediment samples collected by the traps from Abrolhos region. Abbreviations indicate the following stations: : TB2 – Timbebas north reef, TB – Timbebas south reef; PX – Pedra da Lixa reef; PL – Pedra de Leste reef; PS – South point reef ; SG – Sebastião Gomes reef; CV – Coroa Vermelha reef; and NV – Nova Viçosa reef. Su – summer, Au – autumn, Wi – winter and Sp – spring

6 Conclusions

The amount of sediment captured by the traps varied in accordance with the oceanographic conditions in each sampling period, where dynamic forcing, winds and waves were responsible for resuspension of particles from the bottom to water column. The seasonality relative to the amount of sediment captured by the traps sediment are not observed considering neither the isotopes ¹³C and ¹⁵N, nor the C/N ratio.

According to the results found by the present work, there is no difference regarding the origin of the material captured by the PVC traps during the year 2010. The differences found are only relative to the amount of sediment, but not to composition. This marine source

generates sediment to the system year-round, with local dynamics playing a role in making this material available to the environment. Hence, the variability observed is relative to the different dynamics (winds and waves) throughout the year.

With regard to the ecosystems in the Abrolhos region, δ^{13} C values lower than 20‰, which were found in the suspended particulate matter of Abrolhos Bank coastal reefs, and higher than 25‰, which were observed in the sediment collected in the Nova Viçosa and Caravelas estuarine channels (Spanó *et al.*, 2014), indicate distinct signatures, *i.e.*, different sources of the material made available to these ecosystems. The same pattern was found for C/N ratio, where values lower than 10 were observed in the reefs, and values higher than 15 occurred in mangroves

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(Spanó *et al.*, 2014). This, therefore, confirms that the sediment in these areas are of different sources.

According to the PCA analysis, it was possible to observe a shift of the samples of PL, PS, TB and TB2 stations towards positive values, justified by greater depth and high concentrations of the $\delta^{15}N$ (%), $\delta^{13}C$ (%), total nitrogen (%) and total carbon (%), relative to the other sampling stations, while the distribution of CV, SG and NV samples were related to the higher concentrations of terrigenous, C/N ratio and flow that presented shift towards a negative values of PCA.

7 References

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