International Journal of Geosciences, 2020, 11, 393-419
https://www.scirp.org/journal/ijg
ISSN Online: 2156-8367
ISSN Print: 2156-8359

Sedimentary Organic Matter Characterization on a Tropical Continental Shelf in Northeastern Brazil

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How to cite this paper: Barcellos, R.L., Melo, M.C.S.S., Sial, A.N. and Manso, V.A.V. (2020) Sedimentary Organic Matter Characterization on a Tropical Continental Shelf in Northeastern Brazil. *International Journal of Geosciences*, **11**, 393-419.
https://doi.org/10.4236/ijg.2020.116021

Received: May 19, 2020
Accepted: June 26, 2020
Published: June 29, 2020

Abstract

In continental shelf areas works where the focus is Geochemistry are widely relevant, due to the vast complexity and uses of these relief features (social, environmental and economic). On the Brazilian Northeast tropical shelves, with emphasis on the Pernambuco Continental Shelf (PCS), the published studies are limited and have aimed at portions closer to the coastline. The objective of the present work is the description of the characteristics and origin of sedimentary organic matter (SOM) in the inner and middle Pernambuco shelf, defining and classifying the local geochemical sedimentary facies. The sampling stations (136) were collected in the study area, and the grain-size, contents of total organic matter (TOM), calcium carbonate ($CaCO_3$) were analyzed. The samples were processed in an elemental analyzer coupled with a mass spectrometer after the elimination of calcium carbonate. The obtained data were the grain-size, TOM, $CaCO_3$, elemental (C, N) and the stable isotopic ratios of $\delta^{13}C$ e $\delta^{15}N$ of SOM. Based on the measured values of carbon and nitrogen, the C/N ratio, associated to $\delta^{13}C$ e $\delta^{15}N$, is observed that in the PCS predominates an organic matter of marine origin along its entire length: C < 1%, N < 1%, C/N < 5, $\delta^{13}C > -21$ PDB e $\delta^{15}N > 8_{Ar}$. The PCS presents patches of continental origin SOM, associated to the coastal zones adjacent to estuarine systems mouths and covering the paleochannels, which may indicate that this material was carried from the coastal rivers to the offshore areas, possibly by the paleo-valleys that also act as traps of fine sediments and SOM. The statistical analysis indicates the existence of 6 different sedimentary facies and a prevalence of one of them, characterized by poorly-sorted bioclastic sandy-gravel, with low to medium organic contents of marine origin. This indicates that the coastal sedimentary material contributions are low and the local cover is autochthonous of biogenic origin, and deposited according to the surficial topography, morphosedimentary processes and meteoceanographycal conditionings of the study area, typical of moderate hydrodynamic energy environments.

Keywords

Biogenic Sediments, Total Nitrogen, $\delta^{13}C$ Stable Isotopic Ratio, Geochemical Facies, Pernambuco

1. Introduction

The continental shelves could be defined as relief features of the continental margin, whose main characteristic is being the continuity of the continental domain below the seawater level [1] [2]. This physiographical province represents 8.91% of all oceanic basins, although concentrates around 90% of economically important marine resources, as fossil fuels and minerals. Besides this develops the major part of the human activities as transport, artisanal and industrial fishing, tourism, research, and others [3] [4] [5]. In this way is an environment of extreme social, economic and environmental importance, which there is demand of sustainable exploitation in its activities in order to not address any environmental degradation [6]. The continental shelves are dynamic environments, whose extension vary along the geological time and eustatic sea level fluctuations, could even disappear if the regression overcomes the shelf break [5].

The transport and deposition processes associated to those eustatic variations result in the allochthonous and autochthonous sedimentary materials produced on the shelf, being deposited in its surface features or transported according to the local hydrodynamics. In this way the sediments, terrestrial or marine, are products of its predominant nature, where the organic and inorganic particles accumulate bringing with them the historical registers about the environment, by means of textural classification, grain maturity and composition. This marine dynamics is responsible by the complex sedimentary mosaic existing in the shelf, ordering ancient relict and recent materials composition [7] [8] [9].

Among such sedimentary complexity, there's the sedimentary organic matter (SOM) as one of the marine sediments components, which bring information about the biogeochemical interactions between atmosphere, biosphere and geosphere [10]. Besides the hydrodynamics circulation already mentioned, the SOM is influenced mainly by the marine and continental inputs, where its study allows inferences about its sources and origin [11] [12]. The organic contents are correlated to a serial of factors as sedimentary dynamics, water column productivity, microbial consumption taxes, all associated to hydrological and oceanographic conditions [11] [13]. The characterization of organic matter present in the sediments is of extreme importance in environmental studies, since the interpretations of its occurrence represents a great contribution about the cycle—origin, nature and destiny—of this matter in the marine environment, besides the comprehension over the carbon global cycle [14].

The carbon, due to its molecular properties, is an essential element for life, being present in all organisms [15]. The nitrogen, among the essential elements of life (C, P, O, S, N and silicates), presents major abundance in the atmosphere and biosphere [16]. It is also present in the fundamental activities of life, being one of the main nutrients for the marine and terrestrial primary production [17]. The carbon (C) and nitrogen (N) are chemical elements that has more than one isotopic form, and the isotopic natural composition of these elements can be measured, with high accuracy, employing a mass spectrometer [18] [19].

The C/N elemental ratio, according to Saito *et al.*, (1989), presents values possible to correlate with local geological conditions, acting as a geochemical tool for environmental characterization. Reference [20], classify the values < 4 as polychaetes origin organic material. References [11] and [21] classify the C/N ratio according to the intervals: 4 to 7 phytoplankton; 8 to 12 mix between terrestrial and planktonic material; and >20 as terrigenous input from superior plants (C_3).

The stable isotopes use, as natural tracers of organic matter origin is reasoned in the possible differences among its signatures of several sources, between each distinct isotope indicative of material sources/origin. Besides this, these signatures are preserved stable during the mineralization, transport and sediments accumulation [22]. The use of two variables as proxies for SOM characterization leads to a more efficient results, since the indicative values of $\delta^{13}C$ may coincide even from different sources, thus making necessary the use of another variable, such as $\delta^{15}N$ [23]. In the case of $\delta^{15}N$ [24] [25] affirms that such contents cannot be configured as the only parameter, due to the signatures overlapping that a sediment may have according to the interactions of the surroundings. The evaluation of SOM typical isotopic ratios values from shelf environments [11] [21] [26] [27] [28] [29], together with the indicative contents observed in the coastal zone of the study area [30] [31] [32] [33] [34], is observed that the values of $\delta^{13}C > -21.0$ PDB‰ are classified as more enriched in marine material, while the values of $\delta^{13}C < -24.0$ PDB‰ are typical of terrestrial origin.

Researches that deal with marine sedimentology and elemental and isotopic geochemistry are still incipient in the area, and there are no published works that represent the entire extension of Pernambuco Continental Shelf (PCS). There are related works, but limited to small sectors of the shelf, generally along the coast, such as those of [35] [36] [37]. In this way, the present work brings unprecedented data on the distribution, geochemical facies composition, and Sedimentary Organic Matter (SOM) classification, and the origin of inner and middle shelf of Pernambuco State (NE, Brazil), up to the 40 m deep isobath. It aims to classify faciologically the sediments of PCS, as well as to verify the extent of the modern coastal contributions based on the characteristics of SOM.

2. Study Area

The Pernambuco Continental Shelf (PCS) is located at 07˚32' to 08˚55'S parallels and 34˚49' and 35˚09'W meridians. The PCS presents 155 km of length, reaching up to 35 km wide, with a shallow and flattened relief, whose shelf-break rests at an average depth of 65 m [38] [39] [40] [41]. According to [3] subdivision, the present work covers up to the middle shelf, which reaches the 40 m isobath (**Figure 1**).

In general lines, the shelf is composed by Paraíba and Pernambuco marginal sedimentary basins, with dated sediments from Neogen era is also limited by three structural highs and lineaments named from the north to south by: Mamanguape High, Pernambuco Lineament (Recife harbor) and Maragogi High, respectively. The region has "As" climate type according to Köppen Classification (warm and humid), with two marked seasons, rainy from April to September and dry from October to March, 27˚C of average temperature and 2050 mm·yr^{-1} of rainfall [40]-[46].

The coastal region is bordered by the rivers and derived estuaries of Goiana and Una, together with Capibaribe, Ipojuca, Jaboatão-Pirapama and Sirinhaém, maintain regular water supply, added by the urban outfalls present in these river basins close to the coast [30] [31] [36] [40] [41] [47]. The sea water average temperature is 27.8˚C and the salinity is 33psu, oscillating through the contributions of the mentioned river systems [40] [47] [48]. According to [41], the region presents coastal waters (CW), due to the interactions with terrestrial inputs, although prevailing presence of oceanic warm and salty waters, in this case, the Tropical Water (TW) [47].

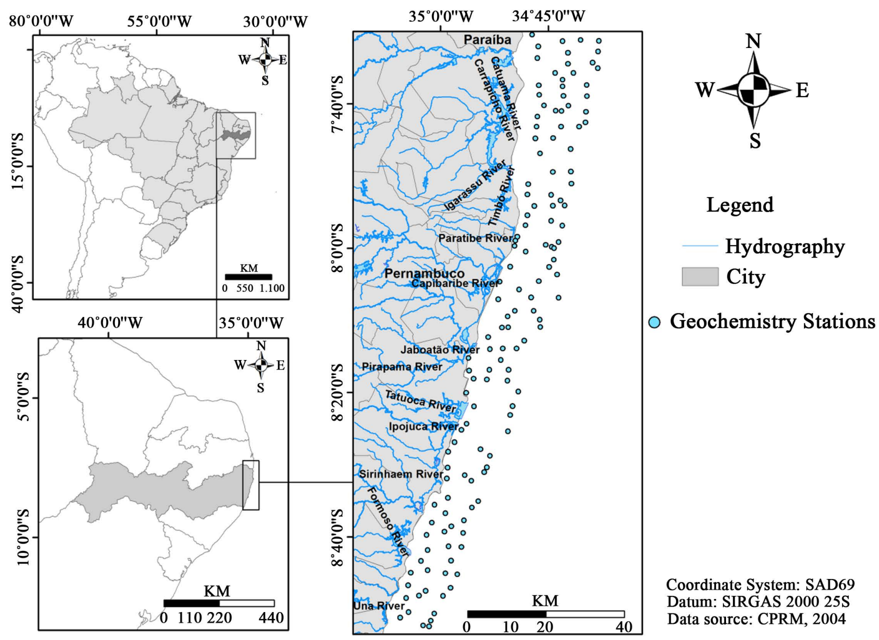

Figure 1. Study area and the sampling stations locations in Pernambuco Continental Shelf (PCS).

Reference [3] classified the PCS based on topography and sediment cover in 3 compartments. First is the inner shelf that extends to the 20 m deep isobath reaching up to 6 km wide and presenting, in general, sandy siliciclastic/biosiliciclastic sediments and smooth relief. However, with irregularities due to the presence of cross-shelf paleo-valleys and beachrocks that serve as substrates for the development of corals and, mainly, calcareous algae. The middle shelf reaches 40 m depth with an average width of 21 km, presenting a gravelly bioclastic character and a much more irregular relief. With the presence of representative waterways and paleovalleys, formed by the shelf exposition and dissection in previous times. The outer shelf, from 40 to 65 m depth, is about 7 km wide and is characterized by erosive features represented by ravines, valleys and crests arranged perpendicular to the coast. It evolved from a subaerial exposed carbonate shelf, when the subsequent sedimentation was not enough to cover it. The outer shelf presents a multiple step break, corresponding to shelf edge terraces, formed by wave abrasion, with associated shelf break (−65 m) and slope canyons.

According to [37] one of the main morphological features of the study area is the presence of lines of beachrocks parallel to the coastline, more prominent in the northern PCS, associated with the Eustatic variations of the Quaternary. Where it can be observed the presence of such formations in different depths (−5, −16, −22, −25, −32 and −45 m) [5], it being able to represent old beaches or waves abrasion terraces associated with periods of sea level stabilization. These features currently act as sequesters of terrigenous material, substrates for algae and protect the coast from waves. The cross-shelf paleo-valleys are also a common feature and have geographical correspondence with modern fluvial-estuarine basins and mouths [5].

3. Methods and Materials

3.1. Grain Size Analysis

Along the study area 136 samples were selected of seabed sediments, collected using a Van Veen grab sampler, sorted by the governmental project "*GRANMAR Brazil*", subproject: "*Mineral potential evaluation of marine granules in Brazilian coastal zone—PE/CE*" of Mineral Resources Research Company of Brazil Geological Survey [49] (**Figure 1**). The surficial sediments were sampled in oceanographic cruises during the 2004 year, covering 2500 km^2 of PCS. The *GRANMAR Brazil* project provided data for the grain-size analysis parameters and bathymetric data of PCS based on 136 points collected in 107 cross-shelf profiles. The profiles were spaced in 1 to 1 nautical mile until 30/40 m depth isobaths, mapping the whole inner shelf and great part of the middle shelf, when it was possible. The gaps between the sampling stations are due to the presence of hard seabed and consequently, the absence of sedimentary cover.

The samples were kept frozen, and later freeze-dried for 48 hours. Grain size was analyzed by a sieving and pipetting method [50], the calcium carbonate ($CaCO_3$) and Total Organic Matter (TOM) contents were determined by the weight difference prior to and after acidification, with 1N HCl and 1 N H_2O_2, respectively [51]. The grain size parameters were employed according to [52] faciological classification diagram and [53] statistical treatment. The textural classification used here was that of [54] [55], based in [56] replacing the term lithoclastic for siliciclastic due to the origin of the particles from rock fragments and silicatic local minerals (mudstones, sandstones and conglomerates), therefore more suitable for the sedimentary cover of the Brazilian northeastern shelf.

3.2. The Elemental (C, N) and Stable Isotopic Ratios ($\delta^{13}C$, $\delta^{15}N$) Analyses

As described in [57], was also performed in this procedure the calcium carbonate elimination with 10% HCl solution [51]. Subsequently the samples were homogenized and macerated. Approximately 500 mg of each sample was weighted in tin capsules on a Metler microanalytical balance, and then closed for packaging using tweezers. The capsules were allocated in the auto sampler for the elemental and isotopic C and N analyses. The analytical processes occurred by the sample automatic combustion (poorly structured) in an elemental EA (*COSTECH*), coupled with a mass spectrometer IRMS (*Thermo Finnigan Delta V Advantage*). The process consisted in the encapsulated samples combustion in chromium oxide (CrO) columns at 1020˚C. Then the material was carried to another column with ionized copper (Cu^{2+}) at 650˚C for N_2 and CO_2 release, which were separated by ion exchange chromatography. The gaseous material was analyzed by mass spectrometer, which the N_2 and CO_2 were previously calibrated with international standards.

The C and N data, expressed in percent (%), were obtained together with the values of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopic ratios values. The samples were burned by oxidation, and the produced gases separated by gas chromatography, purified and carried by a continuous flow of helium. The isotopic ratio values of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) (in parts per thousand) are referred to PDB (Pee Dee Belemnite) and Air (atmospheric air), respectively. The C/N ratios values were obtained, in turn, by the simple division between the contents of each analyzed sample.

3.3. Statistical Analyses

For a better elemental and isotopic data discussion, added with the provided sedimentary composition characteristics, were employed for the statistical analyses of correlation and PCA. The non-parametric correlation coefficient of *Spearman* (*rs*) was used in order to compare how the spatial variability occurs and determine the independent relations between the parameters [58]. The correlation data are presented in **Table 1**.

The Principal Components Analyses (PCA) was performed to obtain the geochemical facies, since it correlates all parameters together. *Primer* 6 was the

Table 1. Spearman (*rs*) correlation coefficient.

	Depth	Gravel (%)	Sand (%)	Mud (%)	TOM (%)	$CaCO_3$	% TOC	% TN	$\delta^{13}C$ PDB‰	$\delta^{15}N$ Air‰
Depth	1.00									
Gravel (%)	−0.17	1.00								
Sand (%)	0.10	−0.67	1.00							
Mud (%)	0.07	−0.33	−0.48	1.00						
TOM (%)	0.04	0.23	−0.45	**0.31**	1.00					
$CaCO_3$	−0.40	0.43	−0.28	−0.16	**0.16**	1.00				
% TOC	−0.03	0.06	−0.05	0.00	0.06	**0.18**	1.00			
% TN	−0.18	−0.01	0.04	−0.03	0.06	0.06	**0.72**	1.00		
$\delta^{13}C$ PDB‰	−0.03	−0.09	0.03	0.05	−0.01	−0.07	0.07	0.30	1.00	
$\delta^{15}N$ Air‰	0.06	0.27	−0.12	−0.15	**0.25**	0.05	**0.22**	**0.28**	**0.26**	1.00

software used and the data was normalized by the function [$\log^{10}(x + 1)$], for a better data elucidation. In this analysis, the parameters N% e o $\delta^{15}N$ Air‰ were not used, since there were few detections in the material, which would result in misinterpretations, due to the absence of nitrogen [59]. Although for facies discussion the data are treated and worked together.

4. Results and Discussion

4.1. Surface Sediments Distribution and Composition

The inner and middle continental shelf region of Pernambuco (PCS) can be characterized as a mixed platform, composed by siliciclastic, carbonate-siliciclastic and carbonate sediment cover ($CaCO_3$ > 50%), and hosts several prominent features such as: banks, beach rocks, coral reefs, paleo-valleys, incised valleys and paleo coastlines. The PCS presents a predominance of sandy-gravelly (between 40% and 60% of samples) bioclastic sediments, poorly sorted with low organic content (predominant TOM < 2%) over the whole studied area. This sedimentology pattern is relatively similar of those observed for Rio Grande do Norte continental shelf [54] [55].

According to the [52] textural diagram classification (**Figure 2**) is possible to observe five sedimentary facies: sand, gravelly-sand, sandy-gravel, mud-sand and mud, with the predominance of gravelly-sand facies in the whole of PCS. The mud facies are present along the coastline, mainly adjacent to the mouths of the following estuarine systems: Goiana, Paratibe, Jaboatão-Pirapama, Ipojuca-Suape and Una, also occurring in a great patch between the Maracaípe e Sirinhaém Rivers, already reported by [35]. While gravelly facies are present both on the inner shelf near to the rivers Goiana, Igarassu (Itamaracá Island), Capibaribe, Pirapama and Ipojuca; and in the middle shelf along the Goiana, Capibaribe, Ipojuca and Formoso rivers areas.

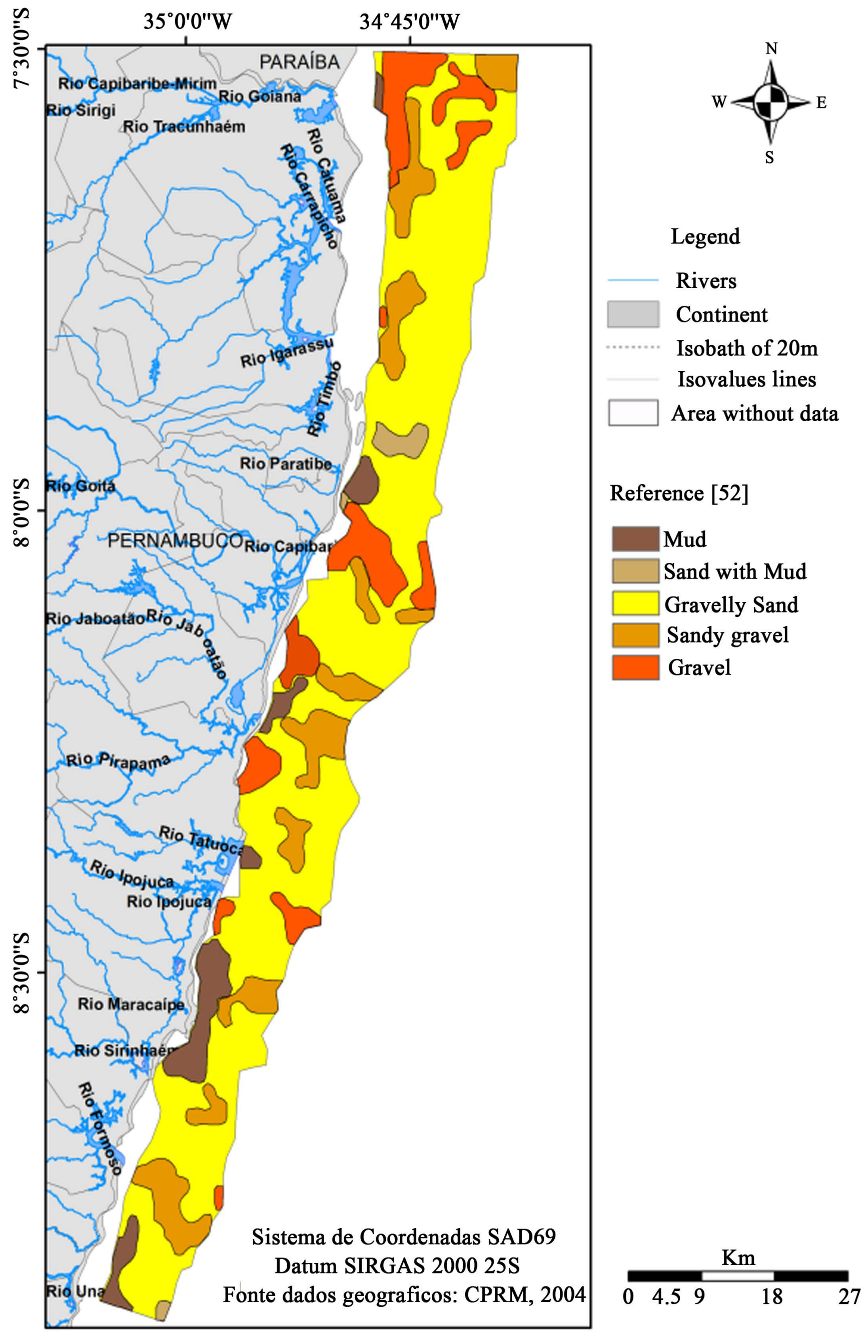

Figure 2. Reference [52] textural classification.

The TOM ranged from 0.20% to 9.30%, with an average of 2.72% and prevailing values between 1.0% and 2.0%, being in general low and typical of exposed continental shelves [60] [61]. The map of TOM (**Figure 3**) presents a spatial distribution pattern where the higher concentrations (>3.0%) occur in the central portion of PCS towards the north, and in the south sector from Maracaípe river until the southern limit of PCS. Patches with contents above 4.0% are present adjacent to the mouths of Capibaribe and Paratibe estuarine systems, as well as in the inner shelf of Goiana river.

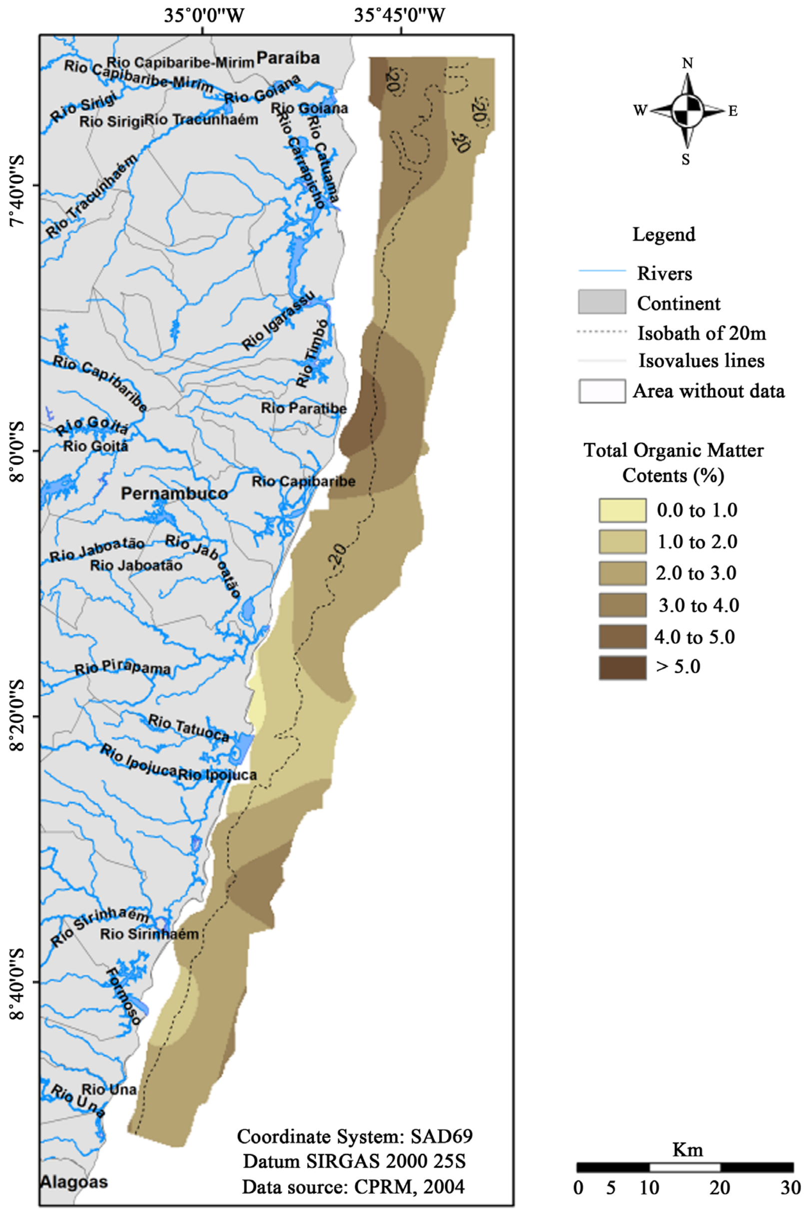

Figure 3. Total Organic Matter (TOM) contents (in %).

In the central-south portion of PCS are observed contents below 2% in siliciclastic sediments along the Ipojuca-Tatuoca system (Suape Port area), as previously stated by [32] and [62]. In this sector the inner shelf is narrower (3 km width) due to the presence of granitic Sto Agostinho Cape which stands out 2 km offshore from the coastline [63]. The low TOM contents and the lower preservation of the $CaCO_3$, would be indicative of a greater hydrodynamics energy of currents to which this sector is subjected. It may be conditioned by the higher depths (>17 m), very close to the coast, of this portion of the Pernambuco shelf. In fact, [41] state that the hydrodynamics changes according the local seabed morphology, which interferes with the existing flows of the North Brazil Subcurrent.

The $CaCO_3$ contents ranged from 13.0% to 99.6%, with a high average of 80.3%. According to [56] classification adapted by [54], bioclastic and biosiliciclastic sediments ($CaCO_3$ > 50%), predominate in all PCS, especially in its center-north, and southern portion from Maracaípe river towards Una estuary (*APA* "*Costa dos Corais*"). The siliciclastic and silicibioclastic sediments are found in the inner shelf adjacent to Capibaribe/Paratibe, Tatuoca e Maracaípe estuaries and in the middle shelf off Ipojuca-Tatuoca estuaries (Suape Port area).

4.2. Elemental Sedimentary Organic Matter

The total organic carbon (TOC) (Figure 4) ranged from 0.01% to 18.08%, with an average of 1.07%. Values below 1.0% are present in 79.4% of the samples throughout study area. The TOC contents above 1.0% are located on depressed features as paleo-valleys or associated to river mouths adjacencies.

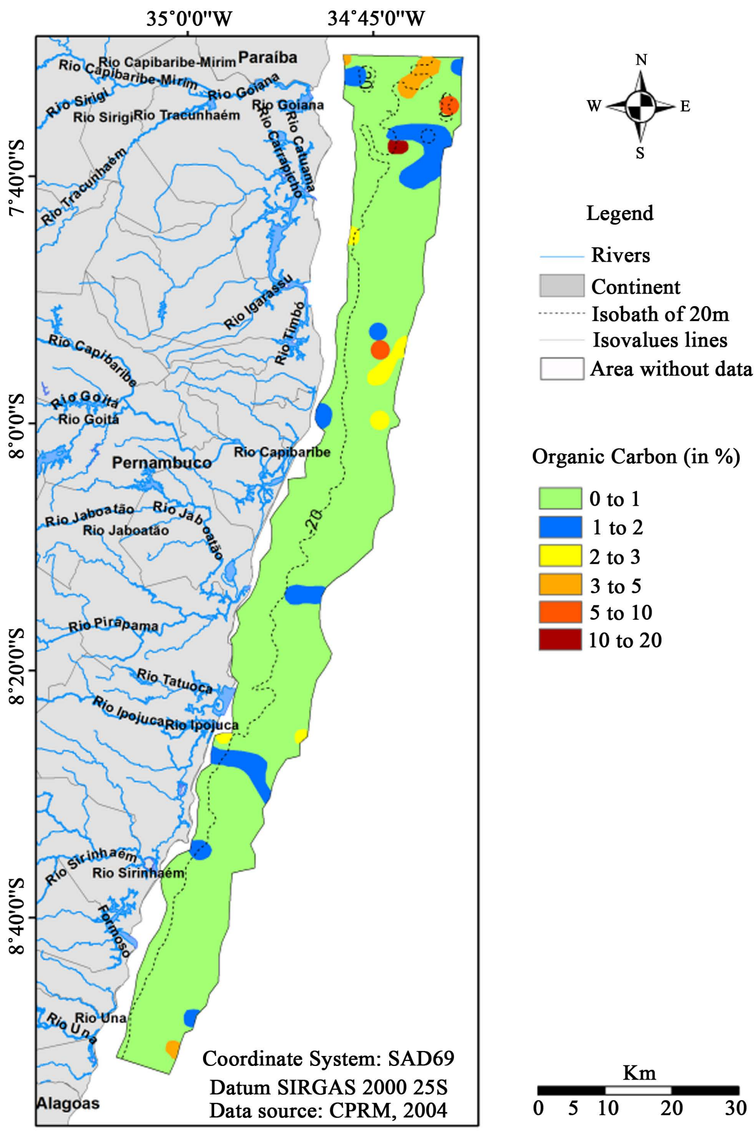

Figure 4. Total Organic Carbon (TOC) contents (in %).

The total nitrogen (TN) values (**Figure 5**) ranged from 0.00% to 3.49%, with average of 1.09%. The TN was detected in only 52.2% of the samples collection. For the 71 samples with detection, in 74.6% the values are below 0.50%. Higher TN contents, analogous to TOC, are associated to the paleochannels, mainly in the most distant areas of the coastline, and are more enriched when compared to other similar shelves [64].

The inputs of carbon in coastal zones are associated to macroalgae, biodeposits and submerged vascularized vegetation decomposition. In the oceans, the material that reaches the bottom is composed of the combination of allocthonous material present in the water column, refractory to microbial decomposition, with the autochthonous biogenic remains. This combination presents values of 0.1% in the coastal zones and 0.1% (marine organisms) until 94.0% (kerogen) in the oceanic regions [10] [60]. According to [60], low TOC contents (<0.50%) are characteristic of most of the ocean basins, particularly of the open seas. The sediments near the coastline, inner seas and continental shelves are generally enriched in TOC, where contents from 0.20% to 0.40% are not uncommon in these areas. According to [64] the TN contents present similar distribution variations, when compared to the TOC, in a range between 0.00% to 2.19%, and the concentrations rising adjacent to coastal areas.

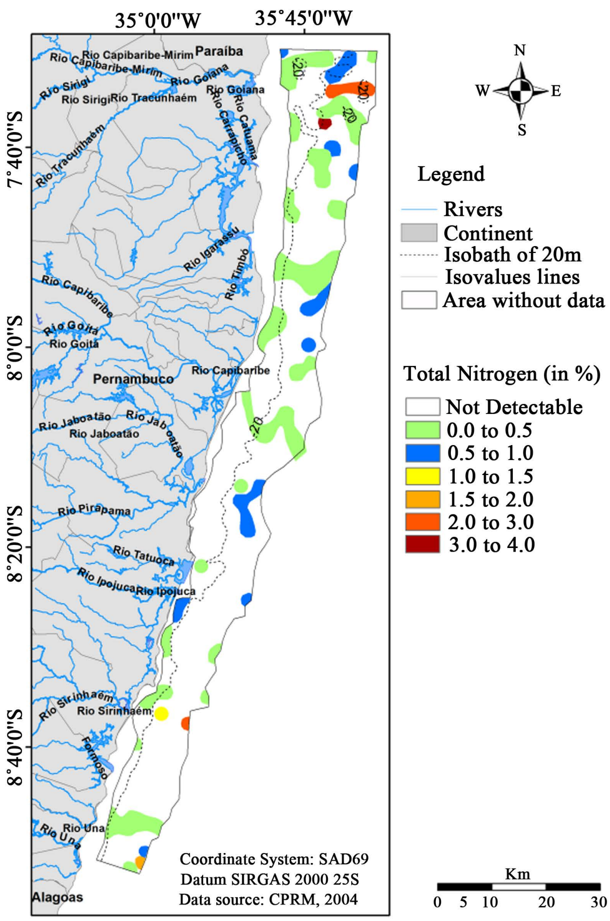

Figure 5. Total Nitrogen (TN) contents (in %).

Based on the Spearman correlation results, it is observed that both parameters (TOC and TN) present a significant correlation (rs = 0.72) (see **Table 1**). The organic carbon is positively associated to $CaCO_3$ contents (rs = 0.18), that according to [65], this positive correlation is an indicator that the organic material present in the samples are from marine origin. In fact, other positive correlations among the studied parameters is also indicative of marine sources for the deposited organic matter found in the majority of Pernambuco continental shelf, ranging from rs = 0.16 to 0.28 highlighted in bold in **Table 1**.

Overall, the carbon and nitrogen contents of PCS present similarity, when compared with the values observed by [30] for the surface sediments of the inner shelf adjacent to Capibaribe estuarine mouth (C < 3%; N < 0.5%), for Goiana river mouth region (C < 1.27%; N < 0.1%) [31], for Jaboatão-Pirapama inner shelf area (C < 8.51%; N < 0.54%) [36], for the mouth of the Formoso river estuary (C < 2%) [66], and in the insular shelf adjacent to Fernando de Noronha Island (C < 3.4% e N < 0.9%) [67]. Some water column values agree with the studied shelf deposits of SOM characteristics, as observed by [33] adjacent to Capibaribe estuarine mouth (C varying from 475 to 975 μM; in the case of nitrogen compounds $N\text{-}NO^2 + N\text{-}NO^3$ from 1.5 to 6.9 μM) and [34] in the estuarine plumes of Capibaribe and Jaboatão rivers (C average < 3.2%, N average < 0.92%). The presented data when compared to the work of [27] is observed that the contents are coherent for a tropical region and for the shelf adjacent for Amazon River the contents are around C < 0.8% and N < 0.2%. In the case of the temperate zone (Gulf of Mexico), the values are slightly higher (C < 1.5% and N < 0.2%), and in the arctic region (Mackenzie River and shelf) the C values reach 17%, prevailing C < 2% and the N is similar to these other climate zones.

When comparing the studies developed by [30] [31] [36] [66] [68] in the line of this research data, is observed that these estuarine regions have major potential for SOM retention than the PCS. The values of inner estuarine portions are higher (C < 9% and N < 1%), decreasing in the shelf direction. Reference [37] described that the positive features of relief (submerged beach-rocks lines) and negative (paleochannels and incised valleys) influence the sedimentary material inputs and deposition in the north PCS. References [69] [70] show that the presence of deeper and depressed areas provide more favorable environment for the deposition of finer materials. This transport mechanism leads the finer sediments to be carried to external shelf areas distant from the coast, allowing the presence of sediments containing C > 10% e N < 4% in the PCS middle shelf.

4.3. Sedimentary Organic Matter Origin

The C/N elemental ratio is a tool widely employed to classify several types of SOM present in aquatic environments [71]. This classification is possible, since the ratio can provide information that allows to indicate, the origin of the SOM, distinguishing the marine and terrestrial sources. According to [72] the organic matter of continental origin may be identified in marine sediments by means of the high values of carbon and low protein contents (<10%), thus resulting in a high C/N ratio (>12), classifying the terrestrial inputs.

The C/N ratio values oscillated between 0.05 and 17.8, with average of 3.5, and in 98.6% of the samples the values are below 6. Based on the classification proposed by [11] [21], autochthonous origin material prevails, of marine origin, and with the presence of continental material carried for deeper shelf portions.

The study carried out in sediments by [30] for Capibaribe estuary mouth area measured C/N values between 4 and >12, [31] for Goiana river inlet observed values of C/N < 13.6 and [36] for the mouth of Jaboatão-Pirapama estuary observed values of C/N < 25.5. Reference [34] for Capibaribe and Jaboatão-Parapama estuarine plumes, observed C/N < 12.8 and <27.9 respectively. Reference [27] classified the material of the Gulf of México and from river Amazon adjacent shelf as biogenic material, composed by proteins (C/N ≈ 5). The values of cited works are similar of those observed in the present study. According to [34] in the water column and [36] in sediments, the values of C/N ratio increase in the rainy season according to the rise of the coastal zone inputs that stimulates the primary production.

The $\delta^{13}C$ contents varied from −31.5 PDB‰ to −14.4 PDB‰, with an average of −21.1 PDB‰ (**Figure 6**). For the 106 samples that the $\delta^{13}C$ were measured, 53.8% are more enriched than −21.0 PDB‰. Based on the classifications proposed by [11] [21] [27] [28] [29] and when compared to the values observed in the coastal zones of the study area by [30] [32] [33] [34] [36] [66] [68], a classification was performed related to SOM origin which is shown in the PCA. There is a marine material prevalence (>−21.0‰ PDB), followed by a wide presence of marine material with continental contributions (between −21.0 PDB‰ and −24.0 PDB‰), with the presence of mixed marine and continental SOM (−24.0 PDB‰ e −26.0 PDB‰), and characteristics of terrestrial origin (<−26.0 PDB‰).

The $\delta^{15}N$, which were measured in 72 samples, ranged from −14.6 Air‰ a 24.6 Air‰, with an average of 5.8 Air‰ and prevailing values of <8 Air‰, in 76.4% of the sampling stations (**Figure 7**). The negative values were located on the paleochannels, one to the north, and the other to the south of the study area. The classification shown in **Figure 7** was established based in the aforementioned literature. By means of this indicator were verified the predominance of mixed material (3 Air‰ to 8 Air‰) and organic material of marine origin (>8 Air‰).

Based on the study developed by [34] [41] for the PCS water masses and the estuarine plumes of Capibaribe and Jaboatão rivers, respectively, is possible to observe that the emissions of SOM regulates the biogeochemical cycles that occur in the coastal zone, mainly in the major primary production periods. Reference [41] shows that due to the meteoceanographic conditions, the local hydrodynamics and the reduced terrestrial inputs, the continental influence do not reach great areas off the coast, being limited to the area immediately adjacent the estuarine mouths. In this way the continental contributions are more expressive

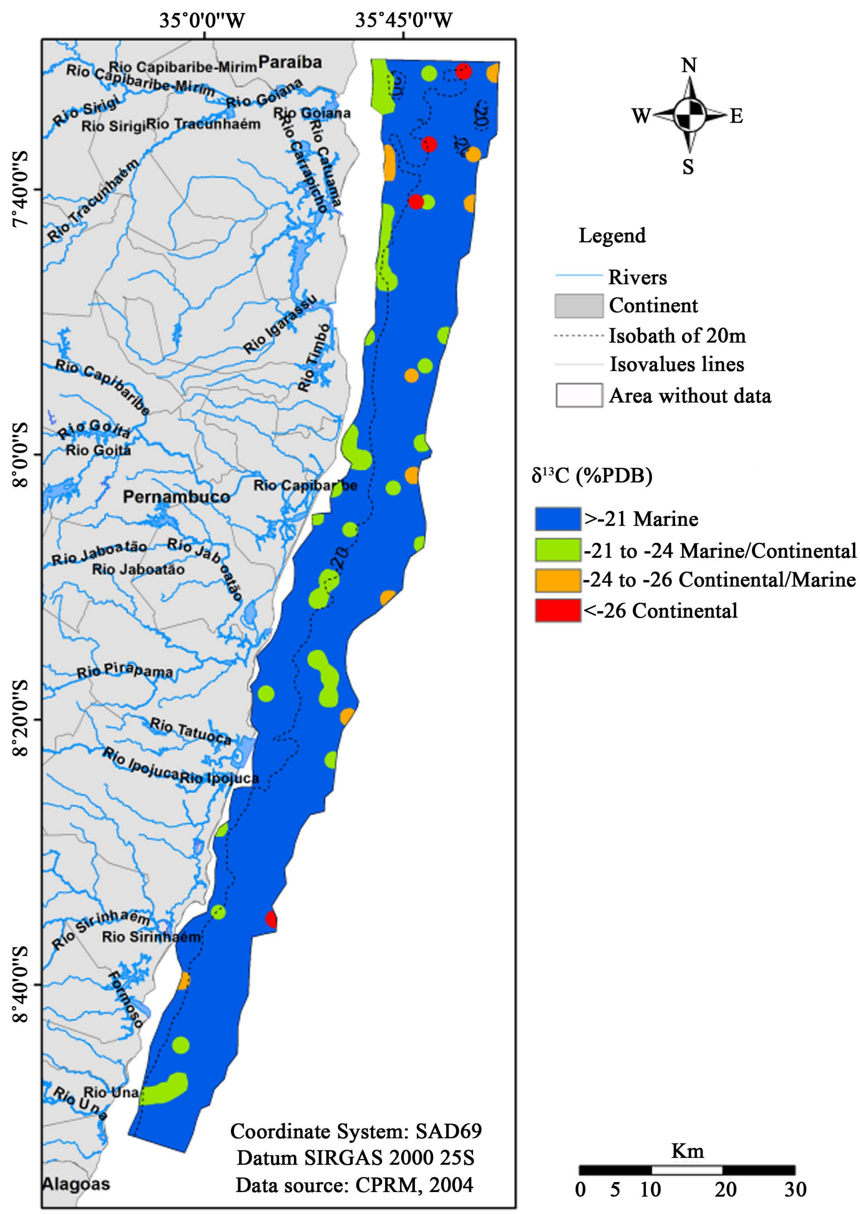

Figure 6. The $\delta^{13}C$ ratio contents in PCS (in PDB‰).

during the rainy period, carrying to the coast the natural origin material together with the SOM from the anthropogenic emissions sources.

Reference [69] stated that the linear depressed features that cross the Pernambuco southern shelf were formed as a result of the Pleistocene sea level fluctuations, with the drowning of the ancient paleo-valleys channels of the rivers. These paleochannels and incised valleys present correspondence with the modern coastal rivers as Formoso River estuarine system. As it is a *starving shelf*, with reduced terrigenous input [73], the PCS paleochannels are preserved by the low sedimentary input that reaches the coast. These negative features, due to the lower hydrodynamic present in them, act as traps of fine sediments [69] [74] [75] [76] [77] [78].

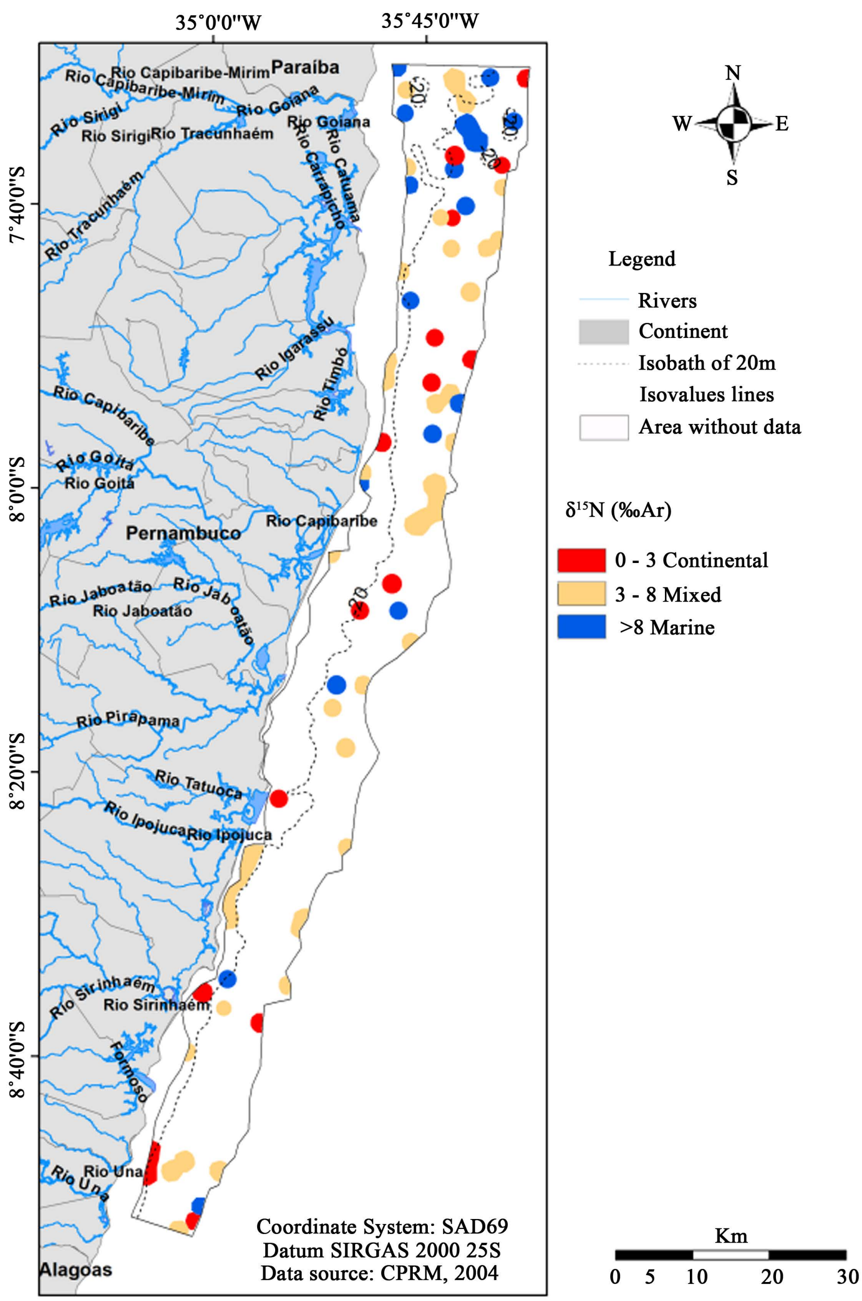

Figure 7. The $\delta^{15}N$ ratio contents in PCS (in AIR‰).

According to these studies, it is inferred that the terrestrial material observed in these channels, are product of the carrying and deposition of the coastal material, which possibly occurred at periods of higher continental contributions. The patches of typical material that would be tracers of SOM of continental origin are spatially associated, according to Figure 2, Figure 3 and Figure 7, of the estuaries of Goiana, Capibaribe and Una rivers, and Igarassu estuarine-lagoonal system. The first three estuaries, excepting the Ipojuca-Tatuoca System, are the larger translittoral rivers of Pernambuco State [40]. These patches of fine sediments with allochthonous SOM occurs mostly in the coastal sampling stations, being directly associated to these water streams inputs. Although these rivers have low average flow (−11 $m^3 \cdot s^{-1}$ to 50 $m^3 \cdot s^{-1}$) [30] [79], they would have the capacity to export terrestrial material, and to print this siliciclastic sedimentation, even if locally, on the inner shelf adjacent to its mouths.

4.4. Geochemical Facies Classification of Pernambuco Shelf

The parameters used in the statistical analysis for the determination of geochemical facies were depth, $\delta^{13}C$ isotopic ratio and the percent of gravel, sand, mud, TOM, $CaCO_3$ and carbon. The nitrogen data, elemental and isotopic, were not included in the analysis for presenting low levels, below the quantity necessary for detection. Thus, the absence of TN and $\delta^{15}N$ data would be considered as geochemical qualified parameters during the execution of the statistical analyses by the software, promoting a false interpretation of the data collection. Although the TN and $\delta^{15}N$ were reconsidered for the description and further detailing of observed geochemical facies.

In this way, 6 facies were obtained, which the two main PCA eigenvectors comprise 48.7% of the total information of the variants (**Table 2**). In **Table 3** is possible to observe that in both components, the depth selected the samples positively, while the gravel and calcium carbonate influenced negatively.

In **Figure 8** are the exposed graphic and the respective eigenvectors.

Based on the PCA, 6 geochemical facies were established (**Table 4**):

- The Facies 1—are samples that varied from siliciclastic to bioclastic, with the predominance of biosiliciclastic, mud to sand granulation, presenting around 5.0% of TOM on average, TN (<0.36%) and TOC below 1.20% with SOM of marine origin ($\delta^{13}C$: −21.2 PDB‰; C/N: 2.9 in average), located around 14 m depth, off the Capibaribe, Sirinhaém e Una estuaries.

Table 2. The PCA eigenvectors.

Principal Components	Autovalues	% Variation	% Cumulative Variation
1	2.07	25.9	25.9
2	1.83	22.8	48.7

Table 3. Principal components calculated by means of the PCA.

Proxies	PC1	PC2
Depth	0.406	0.137
Gravel (%)	−0.532	−0.335
Sand (%)	0.262	−0.359
Mud (%)	0.077	0.564
TOM (%)	−0.284	0.468
$CaCO_3$	−0.564	−0.120
TOC (%)	−0.245	0.312
$\delta^{13}C$ PDB (‰)	0.138	−0.300

Table 4. Geochemical facies description of Pernambuco continental shelf.

	Facies	Depth (m)	Gravel (%)	Sand (%)	Mud (%)	TOM (%)	$CaCO_3$	% TN	% TOC	C/N	$\delta^{13}C$ PDB‰	$\delta^{15}N$ AIR‰
1	Average	−13.93	1.04	40.37	58.59	4.94	55.18	0.14	0.58	2.92	−21.22	1.00
	Max.	−7.50	3.94	78.49	88.32	9.20	86.60	0.36	1.20	4.74	−19.44	12.46
	Min.	−20.10	0.00	11.52	17.57	2.40	29.60	0.00	0.04	0.00	−22.54	−14.63
	Standard Dev. ±	4.97	1.55	27.26	28.09	2.07	22.43	0.12	0.36	1.93	1.00	7.54
2	Average	−26.50	0.00	0.00	100.00	3.60	75.33	0.73	0.94	2.34	−19.30	7.11
	Max.	−22.00	0.00	0.00	100.00	6.60	98.60	1.47	1.37	3.70	−17.73	9.18
	Min.	−31.40	0.00	0.00	100.00	2.00	37.20	0.36	0.35	0.24	−21.30	5.20
	Standard Dev. ±	4.71	0.00	0.00	0.00	2.60	33.29	0.64	0.53	1.85	1.82	2.00
3	Average	−22.67	98.63	1.16	0.22	6.15	92.30	0.27	0.79	1.80	−14.80	8.09
	Max.	−9.50	100.00	6.95	1.29	9.00	97.60	0.54	1.86	3.90	0.00	27.64
	Min.	−25.30	91.76	0.00	0.00	4.20	77.40	0.00	0.00	0.00	−25.09	0.00
	Standard Dev. ±	6.45	3.37	2.84	0.53	2.14	7.46	0.23	0.88	1.83	11.63	10.20
4	Average	−19.67	22.73	75.79	1.49	2.41	98.40	2.52	10.44	3.96	−19.52	11.03
	Max.	−10.00	39.63	95.33	2.57	3.40	99.60	3.79	18.08	4.77	−18.14	12.43
	Min.	−28.00	2.10	59.08	0.60	1.80	97.60	0.92	3.39	3.45	−21.81	8.51
	Standard Dev. ±	9.07	19.04	18.29	1.00	0.86	1.06	1.46	7.36	0.71	2.00	2.18
5	Average	−13.63	2.00	96.97	1.03	1.09	32.75	0.07	0.29	0.56	−11.34	1.07
	Max.	−9.30	6.52	99.09	2.48	4.40	62.60	0.55	1.78	3.26	0.00	6.83
	Min.	−19.90	0.00	92.93	0.53	0.20	13.00	0.00	0.00	0.00	−21.94	0.00
	Standard Dev. ±	3.72	1.93	1.90	0.55	1.21	13.39	0.17	0.53	1.25	10.89	2.41
6	Average	−24.95	30.25	65.32	4.43	2.50	86.09	0.22	0.64	1.84	−16,49	2.77
	Max.	−9.90	85.28	95.74	55.10	9.30	99.40	2.46	5.60	17.77	0.00	24.14
	Min.	−37.60	0.91	14.69	−0.49	0.40	30.50	0.00	0.00	0.00	−31.54	−10.96
	Standard Dev. ±	6.25	19.31	19.81	8.93	1.81	13.71	0.39	0.92	2.52	9.19	4.55

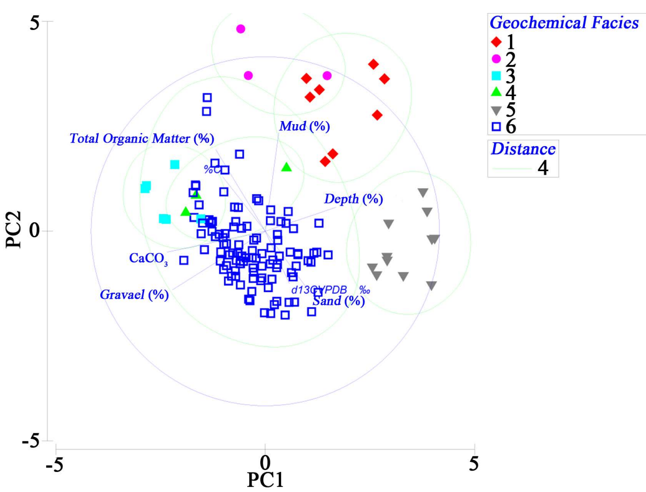

Figure 8. The PCA vectors and graphic representation of studied parameters in the PCS.

- The Facies 2—is composed by bioclastic mud, of marine origin ($\delta^{13}C$: −19.3 PDB‰; C/N: 2.3 in average) with average TOM contents of 3.6%, values of TOC and TN below 1.37% and 1.47%, respectively, located at an average depth of 26 m, off the Sirinhaém river estuary.
- The Facies 3—is formed by bioclastic gravel, with higher average of TOM contents (6.15%), of marine origin ($\delta^{13}C$: −14.8 PDB‰; C/N: 1.8 in average), with TN below 0.54% and TOC < 1.0%. The average depth is 22.7 m, located in the northern PCS.
- The Facies 4—is composed by bioclastic sands with high levels of TOC (10.4% in average) and TN (2.52% in average) in its composition of marine origin ($\delta^{13}C$: −19.5 PDB‰; C/N: 4 in average), limited to a two specific points in PCS, whose high organic contents can be associated with high local biogenic production, located off Goiana estuary in the middle shelf.
- The Facies 5—varies from siliciclastic to silicibioclastic sands, with low TOM contents (1.09% in average), and TOC and TN contents below 0.55% and 1.78% respectively, and SOM of marine origin ($\delta^{13}C$ −11.3 PDB‰; C/N: 0.6 in average). This facies is located mainly adjacent to the Santo Agostinho Cape in the estuarine system of Ipojuca-Tatuoca (Suape Port area) [32], whose granitic rocks of Cabo Granitic Suite [63] would be the main sources of these siliciclastic deposits that occur on the PCS.
- The Facies 6—prevailed over all other facies, being composed by bioclastic sands and gravels, TOM with average of 2.5%, of marine origin ($\delta^{13}C$: −16.5 PDB‰; C/N: 1.8 in average) and, in general, low contents of TOC (0.64% in average) and average values of TN of 0.22%.

This comparatively higher nitrogen average contents compared to carbon, above the C: N ratio of the Redfield relation (106:16) [71], may be the major indicator of local biogenic production in the contribution of organic matter deposited in the surface sediments, in a large part of PCS, see the Facies 6 in **Figure 9**. This proportion of C: N is reflected in the low C/N ratios, indicative of values derived from marine phytoplankton and zooplankton [11] [80], as well as the most enriched contents of $\delta^{13}C$ ratio (−16.5 PDB‰). This factor, added to the low terrestrial coastal supply, gives the predominant character of the PCS, classified as a starving shelf [73], with biogenic sandy-gravel composition, and low to medium organic contents of marine origin.

On the other hand, when the TOM contents are very low due to the moderate to high hydrodynamics of currents in the region, as observed by [41] for PCS and [55] for Rio Grande do Norte shelf, the nitrogen would be more easily recycled in the early stages of oxidation of organic matter after being deposited [81]. This conditioning results in the large number of samples (n = 65) in which the TN was not detected (0.00%).

Despite the low TN detection, in fact, the PCS organic matter is formed mainly by marine algae, and secondarily from marine particulate and dissolved organic carbon (DOC) and traces of freshwater (DOC and POC), according $\delta^{13}C$

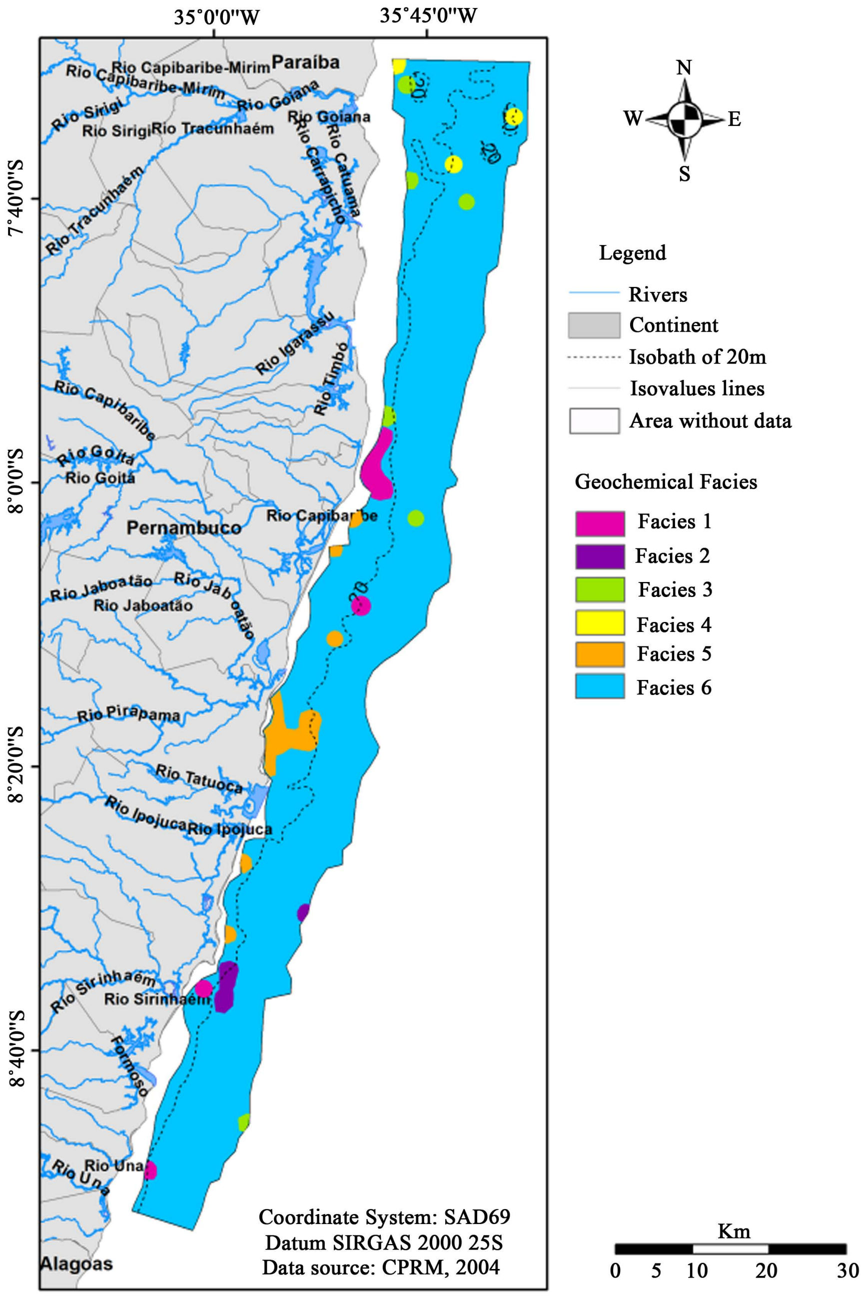

Figure 9. The geochemical Facies in PCS.

versus C/N graphic (**Figure 10**). In the case of the plot of the $\delta^{13}C$ versus $\delta^{15}N$ (**Figure 11**), the surface sediments were also influenced by freshwater phytoplankton, terrestrial superior plants (C_3) and mostly by marine and estuarine organic matter sources.

Observing the facies, it is evident the behavior already mentioned, that the Coastal Water (CW), with terrestrial sediments and organic matter, interacts with the Tropical Water (TA) [41]. In which facies 1 and 5 are more related to estuaries mouths and the associated paleo-valleys, whose mixed and terrestrial contributions can be observed in the studies carried out by [30] [31] [32] [36]

[62] [66] [68]. This demonstrates how the estuarine systems act in the retention of SOM, and in episodes of huge fluvial inputs, could export and reach offshore portions of the shelf. The paleo-valleys would be the natural conducts and connectors of these shelf terrestrial material deposits, as proposed by [69]. References [33] [34] show that the process that occurs in the water column are the result of the relationship between the several activities carried out in the marine environment—discharges of several types of effluents—with the environmental and meteoceanographic variants—precipitation, seasonality, physiography, currents—which result in the deposited material. The facies 6 predominate in whole study area (**Figure 12**). This indicates the large influence of oceanic waters observed by [41] on the Pernambuco Continental Shelf.

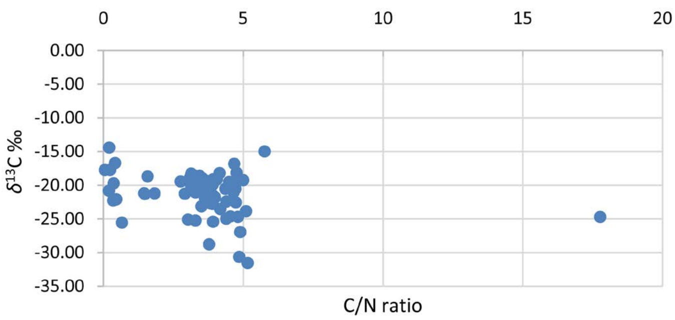

Figure 10. Graphic characterization of SOM sources ($\delta^{13}C \times$ C/N ratio) according to [82].

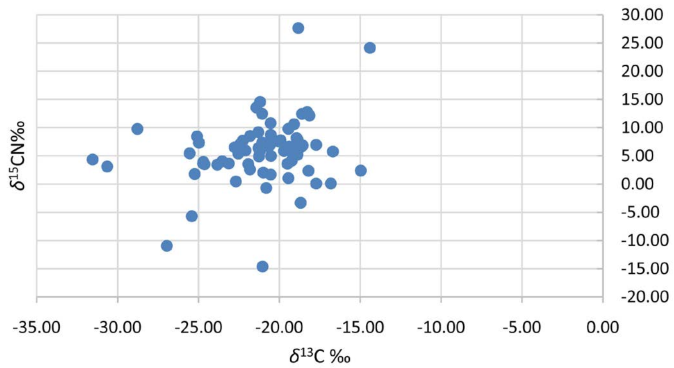

Figure 11. Graphic characterization of SOM sources ($\delta^{13}C \times \delta^{15}N$) according to [82].

Figure 12. Seabed view of geochemical Facies 6 characteristics in the middle shelf off Jaboatão Estuary at 25 m depth (Photography of Ernesto Domingues, 6th June/2018).

5. Conclusions

Based on the data of the present work, it is observed that the inner and middle Pernambuco Continental Shelf (PCS) have a predominance of poorly sorted material of autochthonous bioclastic sandy-gravel origin, with low to medium organic matter contents of marine origin, along its entire length.

The presence of materials of mixed and continental origin is specially located in patches, in the inner shelf region adjacent to the estuarine mouths of Capibaribe, Sirinhaém and Una systems, and off Santo Agostinho Cape (Ipojuca and Tatuoca estuaries). The data shows that due to the factors such as physiography and meteoceanographical conditionings, the terrestrial origin material could be carried to offshore, as from the 20 m isobath.

The facies 6 is the geochemical class that predominates throughout the area, shows an environment with moderate to high hydrodynamic energy, reflected by the poorly sorted bioclastic sandy-gravel cover, with sedimentary organic matter of marine origin.

The facies 2, 3 and 4 are also distributed in patches of muds and gravels of biogenic SOM origin.

Finally, the facies 1 and 5 represent the influence of terrestrial inputs that could bring pollutants and contaminants adsorbed in its composition and the adjacent coastal zones exports for the marine PCS areas. However, it lacks comparative regional studies of sedimentary theme, geochemical and marine geochemistry for further details.

Acknowledgements

The authors of this work thank the Geological Service of Brazil—CPRM, through the project "*Marine Granulates—GRANMAR Pernambuco*", by the sampling expeditions and samples packaging. Our sincere thanks to CAPES for the PhD fellowship support. Our thanks are also indebted to Hortência M. B. de Assis and team (CPRM-PE), Ronaldo G. Bezerra (CPRM-PE), Carlos Fernando de A. Soares Júnior (UFC), Prof. George Satander Sá Freire (UFC) and MsC. Liza Ellen E. Oliveira (UFPE) by the availability of "*in-situ*" collected data, and the partial performed sedimentary analyses. We thank Marine Geology and Geophysical Laboratory (LGGM-UFPE), Geological Oceanography Laboratory (Labogeo-UFPE), for the infrastructure, and support for carrying out the geochemical analyses. Finally, our gratitude to the Prof. Valderez Ferreira from Granite Studies Group—Stable Isotope Laboratory—NEG-LABISE—of University Federal of Pernambuco.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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