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Chapter

Stable Carbon and Nitrogen Isotopes in Hydrocarbon and Nitrogenous Nutrient Assessment of S and E Gulf of Mexico Marine Environments: Four Isotope Stories

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Abstract

Stable carbon and nitrogen isotopes were sampled in representative environments of southern and eastern Gulf of Mexico to trace carbon and nitrogen sources and processes affecting them. Sampled sites include a hydrocarbon seep area, a coastal zone influenced by terrestrial discharge, a productive oil field, a coral reef, and a deepwater environment. In Cantarell oil field, $\delta^{13}C$ and $\delta^{15}N$ values of suspended particulate matters, sediments, and benthic organisms show that the principal carbon source to the benthic food web is the downward flux of upper-layer primary production. In the coastal zone, the isotopic terrestrial signature of suspended particles across the low salinity plume indicates that the terrestrial contribution in nearshore waters is progressively diluted by marine organic matter. Hydrocarbon concentrations and $\delta^{13}C$ values from a Bay of Campeche hydrocarbon seep sediment core suggest that the seep contributes to about 72.4% petrogenic carbon to its surface sediment layer. The $\delta^{13}C$ values in corals suggest a carbon source from fixation by zooxanthellae. In the eastern Gulf, organic carbon (C_{org}) and total nitrogen (TN) concentrations and isotopes are indicative of low terrestrial contribution, and the principal long-term nitrogen source to primary producers appears to be nitrate diffusing from the thermocline into the photic zone.

Keywords: carbon-13, nitrogen-15, Bay of Campeche, Gulf of Mexico, oil seep, suspended particles, sediments, coral reef

1. Introduction

The inclusion of stable isotope measurements in environmental studies has proven useful to discern the source and trace the flow and cycling of natural and anthropogenic gaseous, dissolved, and particulate compounds. Biogeochemically relevant stable isotope pairs, such as $^{2}H/^{1}H$, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, and $^{34}S/^{32}S$, actively cycle

between the biotic and abiotic components of ecosystems. These elements are incorporated by organisms into a variety of compounds which are then transformed as they are cycled within the organisms, through the trophic chain and back to the abiotic environ. Although the chemical structure of compounds may be transformed in this flow, the isotopic proportion of an element remains constant or tends to vary in a known proportion, thus providing a means for tracking its source and flow. For example, stable carbon and nitrogen isotopes have been used to trace the source of organic matter into food webs and to establish the trophic structure of ecosystems [1–3]. In general, the stable carbon isotope composition of animals approaches that of its diet, with a small fractionation between them (0.8–1.5‰ [1, 3, 4]), while they are generally about 3‰ enriched in ^{15}N compared to its diet [2, 4, 5].

The mass difference between the light and heavy isotopes is responsible for small changes in the physical properties of an element but is paramount to trace its origin and different physically, chemically, or biologically mediated processes it undergoes [6–8]. This isotopic fractionation (or discrimination), although small, is measurable, and, in a mixture of isotopes of the same element, the lighter isotope (such as ^{12}C) is generally favored in the reaction products, leaving the heavier isotope (^{13}C) in the reactant.

The heavy-to-light isotope ratio of a sample is denoted as

$$R = {}^{m}X/{}_{n_X}$$ (1)

where X is an element with a heavy isotope (m) and a light isotope (n).

The stable isotope ratio of a sample (R_{sa}) is expressed relative to the ratio of a universal standard (R_{std}) by the δ notation and is expressed in per mil units (‰):

$$\delta = \left(R_{sa}/R_{std} - 1 \right) \times 1000$$ (2)

The fractional contribution of two sources (A and B) with different isotopic compositions in a mixture (M) can be estimated from the isotopic composition of each source by isotopic mass balance [8, 9]:
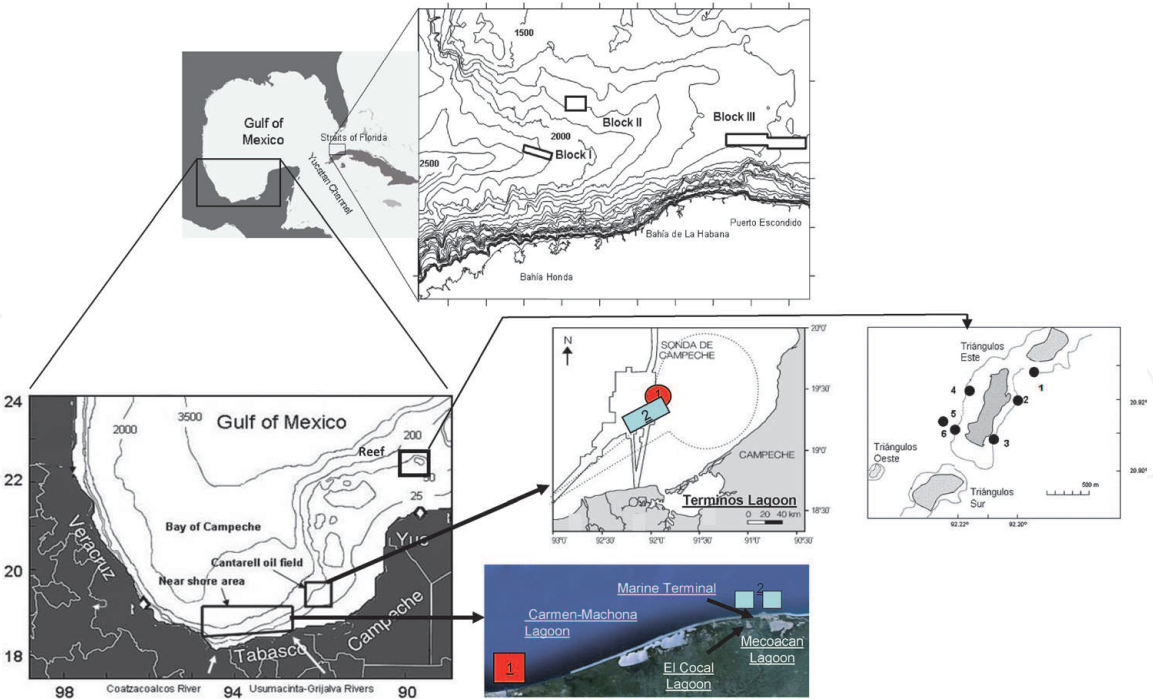
$$\delta_M = f_A \times \delta_A + f_B \times \delta_B$$ (3)

where

$$1 = f_A + f_B$$

The southern and eastern Gulf (S and E Gulf) of Mexico (**Figure 1**) offers contrasting environmental scenarios where stable isotopes can be applied as a tool to discern the origin and flow of organic matter. The principal potential carbon sources to the Bay of Campeche continental shelf, located in the S Gulf, include organic matter deposition from upper-layer primary production, input of terrestrially derived organic matter, oil seeping, and offshore oil extraction. In contrast, organic matter inputs of terrestrial origin in the E Gulf are minor.

In this chapter, carbon and nitrogen sources and flows in these two contrasting Gulf of Mexico regions are traced by means of stable isotopes. Three studies are used here to exemplify the use of stable isotopes in regions with contrasting nutrient and carbon sources. The carbon apportionment is estimated for the Bay of Campeche continental shelf seep. In the Bay of Campeche's Cantarell oil field, the relative contributions of terrigenous, seep, upper-water primary production and anthropogenic carbon and nitrogen sources to the benthic food web are explored. Carbon isotopes in Yucatan shelf coral tissues are used to trace the natural and anthropogenic carbon sources affecting them. Finally, in the E Gulf of Mexico, the

Figure 1.
Southern and Eastern Gulf of Mexico study zones showing the deepwater sampling locations off NW Cuba slope region where sediment samples were collected (upper right panel), Bay of Campeche (middle and lower right panels) and Triangulos Reef in Yucatan Shelf (far right panel). Numbers in the Cantarell oil field region and near shore area depict the two cruises where particles, sediments and benthic organisms were collected. Numbers around Triangulos Reef are sampling sites. Depth contours in meters.

long-term nitrogen sources to primary producers are evaluated using stable nitrogen isotopes of surface sediments.

2. Methodology

Stable carbon and nitrogen isotopes were analyzed in suspended particulate materials collected in the water columns, sediments, and animal matrices. Sample collection, prepping, and analysis for the four case studies are summarized in **Table 1**, details are given below.

2.1 Sampling

Suspended particles were collected in pre-combusted GF/F filters by filtering 2–10 L of seawater with a peristaltic pump, which retained particles with a nominal size of >7 μm. Samples were stored in petri dishes and frozen until analysis. Coastal and shelf benthic organisms and sediments were collected with a box corer or anchor dredge. Sediment cores (25 m long) from the E Gulf were retrieved with a Kullenberg piston corer. The recovered cores were sliced on board into 10 cm sections. Seven of these sections were analyzed in this study. The top 10 cm of the Bay of Campeche continental shelf and coastal sediment core samples were collected with a box corer. Corals and sponges were collected manually. Organisms and sediments were kept at freezing temperatures until analysis.

2.2 Sample treatment

In the laboratory, sediment and filtered particle samples were oven-dried, pulverized, and homogenized to a fine powder in a mortar. Sediment and reef

Matrix	Method of collection	Sample treatment	Isotope analysis	Ancillary data
Seep sediments (^{13}C)	Kullenberg corer	Drying, grinding, acidification, sieving	1, 2	Total hydrocarbons
Macrobenthic organisms (^{13}C, ^{15}N)	Anchor-box dredge	Tissue extraction, rinsing, drying, grinding	1, 2, 3	—
Campeche surface sediments (^{13}C, ^{15}N)	Box corer	Drying, grinding, acidification, sieving	1, 2, 3	Organic carbon, total nitrogen
Suspended seawater particles (^{13}C, ^{15}N)	Seawater filtration	Drying, grinding	1, 2, 4	Organic carbon, total nitrogen
Sponge, algae, and coral tissue (^{13}C)	Collected manually	Drying, grinding, acidification, sieving	1	Polycyclic aromatic hydrocarbons
NW Cuba sediments (^{13}C, ^{15}N)	Box corer	Drying, grinding, acidification, sieving	1, 2	Organic carbon, total nitrogen

1—Sealed tube combustion and a Finnigan MAT-252 stable isotope mass spectrometer (Laboratorio de Geoquímica del Petróleo, Instituto Mexicano del Petróleo). Reported values are averages of 10 replicate runs.
2—Continuous flow in a Europa ANCA-GSL elemental analyzer interfaced to a Europa 20–20 isotope ratio mass spectrometer (Rosenstiel School of Marine Sciences, University of Miami).
3—Sealed tube combustion and a Finnigan MAT-250 stable isotope mass spectrometer (Instituto de Geología, Universidad Nacional Autónoma de México). Reported values are averages of three replicate runs.
4—Continuous flow in a Costech ECS-4010 elemental analyzer interfaced to a Finnigan MAT-252 stable isotope ratio mass spectrometer (Department of Oceanography, Texas A&M University).

Table 1.
Summary of sample collection and treatment used to analyze stable carbon and nitrogen isotopes of the different sample matrices.

organisms samples were acidified with 1 N HCl to eliminate the carbonate in the sediment matrix, washed with distilled water, and oven-dried at a temperature of <80°C. The previous studies have shown that acidification can change the δ^{15}N values of the sample (e.g., [10]); however, with this concentration and type of acid, nitrogen isotopes are not significantly fractionated [11]. Organisms were oven-dried overnight at <60°C and then ground in a mortar into a fine powder. Samples analyzed by sealed tube combustion were mixed with copper oxide for carbon isotope analysis, or with elemental copper and copper oxide for simultaneous nitrogen and carbon isotope analyses, and sealed with a torch under vacuum in Pyrex or quartz tubes for carbon and nitrogen isotope analyses, respectively (**Table 1**).

2.3 Sample analysis

Sealed tube samples were combusted at 550°C for carbon isotope analysis and at 900°C when both carbon and nitrogen isotopes were analyzed. The evolved combustion gases (CO_2 and N_2) were separated from the other combustion products by cryogenic distillation and analyzed in either a Finnigan MAT-250 or MAT-252 isotope-ratio mass spectrometer (IRMS). Samples analyzed by a continuous flow were placed inside crucibles in elemental analyzers interfaced to either a Europa 20–20 or a Finnigan MAT-252 IRMS. Runs were calibrated against standards of known isotopic composition and are reported relative to Pee Dee Belemnite (PDB) (or Vienna Pee Dee Belemnite (VPDB) for the Europa 20–20 samples) for carbon and air for nitrogen. The precision of the analyses for the four IRMS that were utilized ranged between ±0.09 and ±0.10‰ for δ^{13}C and ±0.15 and ±0.26‰ for δ^{15}N analyses.

2.4 Ancillary data

Seawater temperature and salinity were measured in situ with a Seabird CTD. Total petroleum hydrocarbons (TPH) in the Bay of Campeche seep and control core samples were analyzed by infrared spectrophotometry as per EPA Method 418.1 [12]. Organic carbon (C_{org}) and total nitrogen (TN) in sediments and C_{org} and N in particles (particulate organic carbon (POC) and particulate nitrogen (PN)) were measured in elemental analyzers, where the carbon is quantified as CO_2 and nitrogen as N_2.

3. Results and discussion

3.1 Carbon apportionment in a bay of Campeche oil seep

Oil seeps are frequent in the S Gulf of Mexico both in the continental slopes [13] and in shallow waters of the Cantarell oil field [14], where major oil exploitation takes place. The volume of seeped oil in the region at any given time can be as high as 46 m^3 [14]. Satellite images of the region have shown that oil seepage between the years 2000 and 2002 appeared in nearly 80% of the analyzed images and area coverage ranged between 0.04 and 207 km^2 with an average of 32 km^2 [15].

The hydrocarbon concentrations and organic matter $\delta^{13}C$ distributions in a sediment core from a borehole drilled in a seep area near to Bay of Campeche's *Akal H* oil rig (92°20′W, 19°20′N) from the Cantarell oil field were compared with those from a nearby reference site (91°40′W, 20°20′N). The two sites lie at approximately 45 m water depth.

The depth distributions of TPH concentrations and $\delta^{13}C$ values in these sediments are given in **Figure 2**. TPH decreased linearly with a depth from 250 to 150 ppm at the reference site, which contrasts to concentrations at the seep site where values increased from 0.1% at 5 m depth to 35% at 20 m [16]. At both locations, $\delta^{13}C$ values showed similar profiles with maxima of −21.9‰ and −20.3‰ at 5 m depth decreasing to −26.5‰ and −22.0‰ at 20 m at the seep and reference sites, respectively.

The near-surface $\delta^{13}C$ values and TPH concentrations are concordant with a common carbon source in the sediment's upper layers of both sites. The topmost layer from the two cores suggests a mixture of organic matter from terrestrial and marine origins, because $\delta^{13}C$ values lie intermediate between values of marine algae (−19 to −16‰) and of C_3 land plants (−27‰) [17–19]. At the seep site, the decrease in the isotopic signature with depth and the concomitant increase of TPH are in clear concordance with a petrogenic hydrocarbon origin in the deep section of the core, in line with the isotopic range of Campeche Sound's oil families [20, 21]. In turn, the $\delta^{13}C$ signature at the reference site agrees with the expected sedimentary organic matter depth distribution from several Gulf of Mexico sites [17, 22].

The relative $\delta^{13}C$ maxima (−22‰ at the reference site and −23‰ at the seep) appear at around 5 m core depth. Below, the $\delta^{13}C$ signal shows that downcore sediments are ^{13}C-depleted to the maximum sampled depth. Several authors have recorded isotopic shifts in the Gulf of Mexico's upper layers of sediment cores [18, 19, 22]. It is generally accepted that downcore $\delta^{13}C$ depletions reflect a terrestrial plant input resulting from a lowering of sea level attributable to the Last Glacial Maximum of the Late Pleistocene (ca. 25,000 B.P.). The upper sediments of different regions of the Gulf of Mexico show $\delta^{13}C$ values on the order of −22 to −18‰ which overlay a thick layer of isotopically lighter values (−23 to −27‰) [17, 23]. In turn, shifts to enriched $\delta^{13}C$ values occur during interglacial periods. The
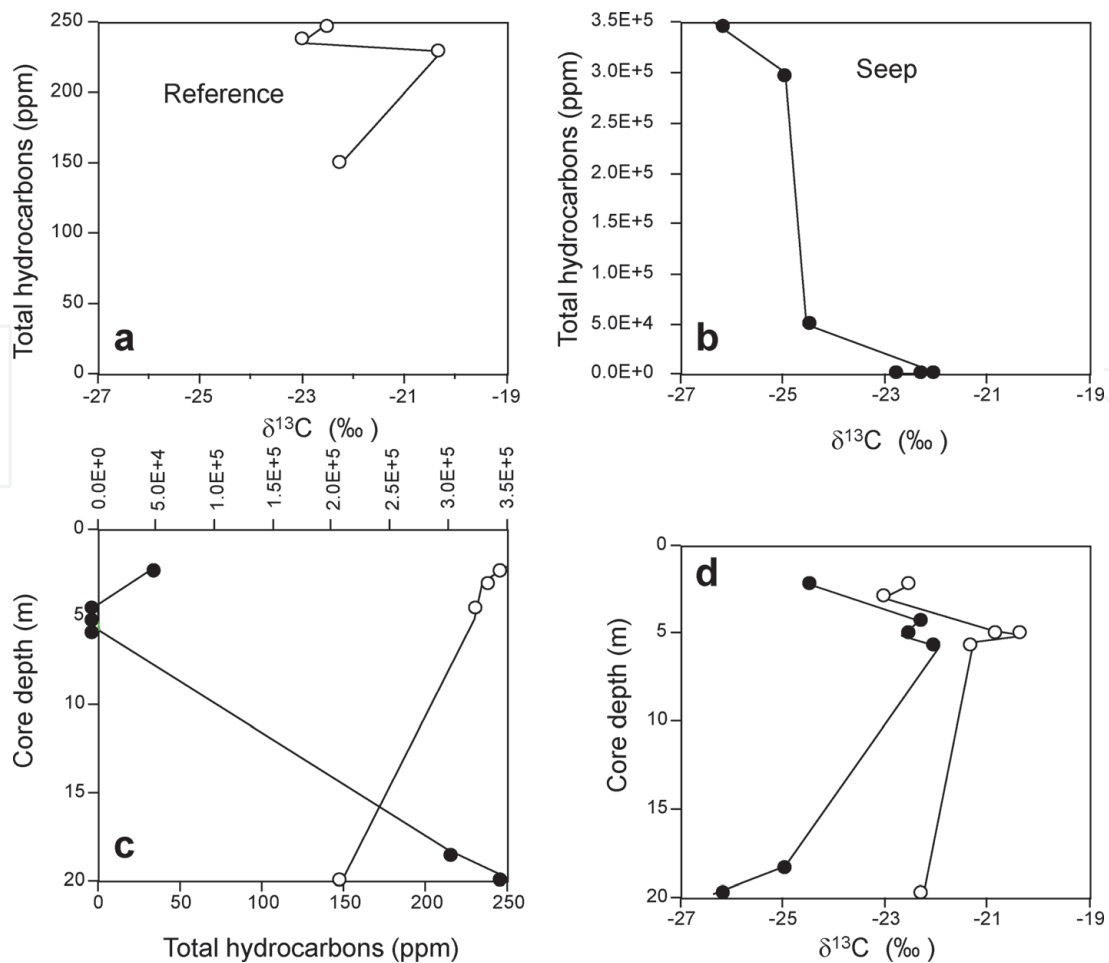
Figure 2.
Upper panel: Total petroleum hydrocarbon concentration vs. δ¹³C composition for (a) reference (opened circles) and (b) seep (closed circles) sites from Bay of Campeche seep region. Lower panel: Depth distribution of (c) total hydrocarbon concentration and (d) δ¹³C values of the reference and seep sites.

magnitudes of these isotopic shifts vary in intensity depending on their location within the Gulf and on prevailing upper-water circulation patterns. Off the Brazos-Trinity Basin and in Pigmy Basin, in the northern Gulf, the isotopic signal varies from −27 to −20‰ as a result of the dominance of terrigenous organic matter during the lowering of sea level [18, 19, 22]. In contrast, this isotopic signal shift is not evident at Ursa Basin, off the Mississippi River delta, where the continuous terrestrial drain overwhelms the isotopically heavier marine signal.

Considering that in North America the Last Glacial Maximum ended approximately at 12.5 ky [24], and that a $\delta^{13}C$ maximum was found at 5 m depth, then, using Eq. (3), an average sedimentation rate of 40 cm/ky can roughly be estimated from the depth of this isotopic shift. As shown in **Figure 3**, Gulf of Mexico sedimentation rates vary considerably, from 4 to 11 m/ky off the Mississippi River fan [25, 26], 20–40 cm/ky off Louisiana continental slope, and deep western Gulf of Mexico [26, 27] to 5 cm/ky off NE Gulf's continental shelf [28]. Because Bay of Campeche's continental shelf is near the discharge area of the Coatzacoalcos and the Grijalva-Usumacinta River systems, and the continental shelf is overlain by surface waters of high productivity [29, 30], the calculated sedimentation rate of 40 cm/ky is reasonable and is similar to those estimated for the Gulf of Mexico deep western and northern slope environments [26, 27].

From the $\delta^{13}C$ values of the isotopic maximum depth from the two sites, the relative contribution of seep-derived petrogenic hydrocarbons at that depth can be estimated using the stable isotope-mass balance equation (Eq. (3)). Assuming that the reference site's $\delta^{13}C$ maximum value (−20.3‰) represents the isotopic
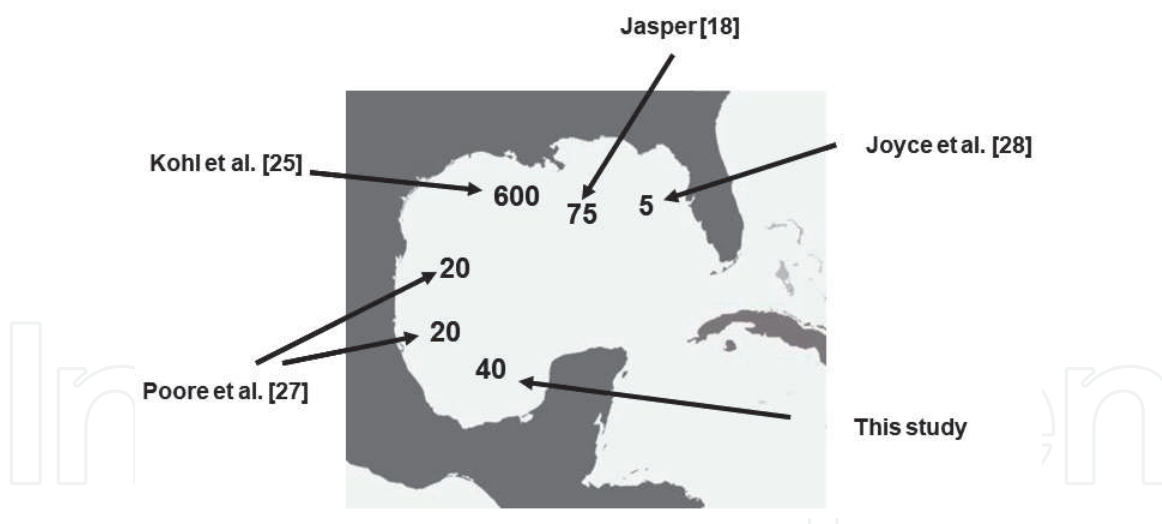
Figure 3.
Estimated sedimentation rate for Bank of Campeche. Also shown are sedimentation rates for several locations of the Gulf of Mexico. Data in cm/ky.

composition of biogenic carbon contribution, and that the $\delta^{13}C$ value at 20 m depth of the seep site (−26.4‰) is entirely petrogenic, then the isotopic composition at the isotopic maximum depth of the seep site (−21.94‰) is constituted by approximately 27.6% biogenic carbon.

Summarizing, the carbon isotope depth profiles were used to distinguish a biogenic hydrocarbon source in the upper layers of the two cores and oil-derived TPH in the deeper sections of the seep site. The carbon isotope distribution with depth also identified the depth of a major paleoclimatic event in the Bay of Campeche, which precluded the input of terrestrial organic matter into the adjacent shelf. Considering the distinct carbon isotope compositions for the two principal carbon sources in these sediments, the oil-derived carbon contribution to the upper sediments of the seep area is estimated at around 72.4%.

3.2 Carbon and nitrogen sources to the benthic food web in the bay of Campeche oil field region

Potential carbon sources to the Bay of Campeche continental shelf and coastal system include in situ primary production, upwelling, terrigenous inputs from rivers, natural seeps, and offshore oil production. In order to discern the carbon and nitrogen sources and infer the benthic trophic structures in the coastal zone and Bay of Campeche's Cantarell oil field region, sediments, suspended particles, and macrobenthic organisms were sampled and analyzed for stable carbon and nitrogen isotopes.

In situ primary production and resulting particle flux can be important sources of organic matter to continental shelf and pelagic sediments. Near-surface water chlorophyll concentrations are relatively high over the Bay of Campeche shelf and decrease offshore [29–31]. According to Hidalgo-González and Alvarez-Borrego [31], the average surface chlorophyll-*a* concentration for the S Gulf of Mexico is 28 mg/m^3, which is more than 2.5 times higher than at the Gulf's open waters. The yearlong upcoast current flowing along this section of the shelf partially explains this increment, because this flow induces upwelling of nutrient-rich subsurface waters [30]. Additionally, the presence of cyclonic rings in the Bay of Campeche resulting from the topographic effect of Campeche Canyon [32] enhances vertical water mass movements which are favorable to primary producers.

Continental drainage is another potential source of organic matter in S Gulf of Mexico. The principal discharge to the region is the Grijalva-Usumacinta River system (the second most important river discharge to the Gulf of Mexico after the Mississippi River), followed by the Coatzacoalcos River. Their flows are seasonally variable with a five- to tenfold oscillation between the highest and lowest runoffs. The presence of drowned land, soil drainage from rainforests, and a series of coastal lagoons, such as the Carmen-Machona Lagoon, underscores the importance of terrestrially derived organic matter flow to the adjacent continental shelf. This input of terrestrial organic matter favors reducing conditions in the deltas and inner shelf sediments of the Coatzacoalcos and Grijalva-Usumacinta Rivers, and thus organic matter tends to be preserved [33]. Off the Coatzacoalcos River, the seasonal convergence of the western downcoast and eastern upcoast coastal currents in the region disperses the supply of terrestrial organic matter to the region [30]. Strong haline and thermal gradients develop off the Coatzacoalcos and Grijalva-Usumacinta River's delta which transport particulate matter from the inner shelf to the shelf break [29].

Another potential organic carbon contributor to the Bay of Campeche is offshore oil exploration and production. Off the Tabasco coast, the Dos Bocas Marine Terminal concentrates the oil produced offshore which in turn is shipped or distributed inland. The produced water (that which is separated from the extracted oil) is partly discharged from the marine terminal to the coastal zone by a submarine diffuser. This partially treated discharged water is usually high in metals and carbon products. Oily and graywater discharges from offshore oil rigs can contribute with organic carbon and nitrogenous nutrients, respectively, to the adjacent environment.

The study zone is localized in the transition zone between the carbonate and terrigenous sediments of the Bay of Campeche continental shelf [34] and spans from nearshore sampling sites off the Coatzacoalcos and Grijalva-Usumacinta Rivers to the 60 m depth isobath in the oil rig zone (**Figure 1**). Results from two cruises to the sampled area are used here to infer the relative importance of the different carbon and nitrogen sources to benthic organisms. In the first cruise, coastal benthic organisms and sediments were collected at three stations off Coatzacoalcos River and Grijalva-Usumacinta deltas and at two stations off Carmen-Machona Lagoon [35]. Samples were also collected 12 nmi due WNW, and 1 nmi off Cocal Lagoon, which is connected to the Carmen-Machona Lagoon System. These samples are used as a coastal reference region. Additionally, continental shelf benthic organisms and sediments were sampled at five locations outside the Cantarell oil rig field at water depths between 38 and 44 m; these samples are used as an offshore reference region.

In a second cruise, sediments and suspended particles of the coastal zone were sampled 1.2 nmi north of the Dos Bocas Marine Terminal discharge zone, at a coastal reference site, inside the Cantarell oil rig field and at two offshore reference regions. Samples were collected at different distances from the discharge points of the marine terminal and oil rigs. **Table 2** summarizes the type of samples collected in each zone.

Figure 4 shows the percentile distribution as boxplots of the $\delta^{13}C$ and $\delta^{15}N$ values in sediments and suspended particles of the coastal and offshore regions. Also shown are the isotopic compositions of potential sources such as particles in oily and graywaters discharged from the oil rigs, in produced water discharged by the Marine Terminal, and the $\delta^{13}C$ average value of Cantarell crude (−27.9‰). The average $\delta^{13}C$ values of oily and produced waters (−27.2 and −26.7‰, respectively) are similar to that of Cantarell oil, because they have a common hydrocarbon source.

Region	Suspended particles	Sediments	Macrobenthos
Coastal reference	—	11	6
Marine terminal	33	9	—
Offshore reference	19	9	7
Oil rigs	51	14	—

Table 2.
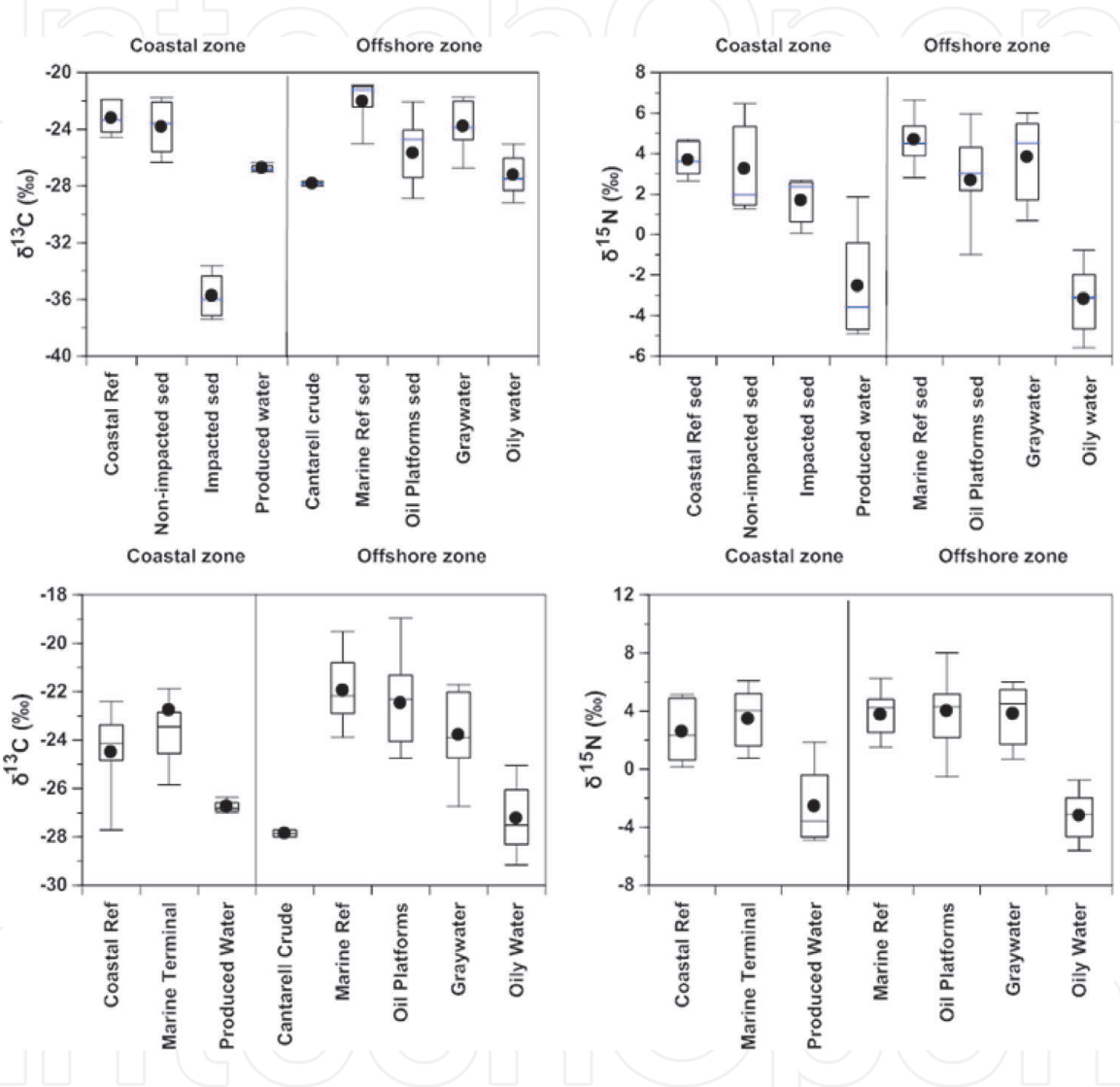*Number of samples collected in the Bay of Campeche coastal, offshore, and seep regions.*

Figure 4.
Box charts of carbon and nitrogen isotopes of marine terminal and costal reference sediments (upper panel) and suspended particles (lower panel) in the coastal zone and marine platform, and reference sediments in the offshore zone. Also shown are the $\delta^{13}C$ and $\delta^{15}N$ values of particles in produced water to the coastal zone, and of oily and grey waters in the offshore zone. The average $\delta^{13}C$ value of Cantarell oil [19] is also depicted. Endmembers denote the 10 and 90 percentiles, and horizontal lines of the box denote 25, 50 and 75% quartiles. Symbol denotes average value.

Because Marine Terminal sediments spanned a wide range of $\delta^{13}C$ values, these were further separated into impacted ^{13}C-depleted sediments (average $\delta^{13}C$ of −35.7‰) and non-impacted sediments whose average $\delta^{13}C$ value (−23.8‰) was similar to the average of the coastal reference zone (−23.3‰). The average $\delta^{13}C$ value of impacted sediments was much lighter than Cantarell oil and oily waters and suggests isotopic fractionation by microbial activity metabolizing carbon discharged in produced waters [36]. The nitrogen isotopic composition of coastal sediments averaged 3.7‰, statistically similar with that of non-impacted sediments. In

contrast, the boxplot of the nitrogen isotope composition of impacted sediments is lighter than that of coastal and non-impacted sediments and suggests a contribution of the lighter $\delta^{15}N$ values from the produced water.

The average carbon isotope composition of offshore sediments ranged from −22.0‰ in the reference zone to −25.7‰ in the oil rig zone, which are heavier than the $\delta^{13}C$ value of Cantarell crude and of the particles discharged with the oily water. The wide spread of $\delta^{13}C$ values for oil rig sediments suggests the input of in situ primary production and hydrocarbons in different proportions. In turn $\delta^{15}N$ values of sedimentary nitrogen mostly ranged between 2 and 5‰, in contrast to the more ^{15}N-depleted discharge of oily waters.

In contrast to the sediments, the $\delta^{13}C$ and $\delta^{15}N$ signatures of suspended particles were statistically similar in the three regions, mostly due to the wide range between maximum and minimum values (**Table 3**). However, histograms of $\delta^{13}C$ values for POC and PN show that the modal $\delta^{13}C$ values in the coastal zone plus marine terminal were generally 1–2‰ lighter than in the Cantarell region (modal values of −25 to −23‰ vs. −23 to −21‰; **Figure 5**). In turn, the distribution of $\delta^{15}N$ values was similar at the two sites, with modal values of $\delta^{15}N$ which were centered at 2 and 5‰, suggesting two principal common nitrogen sources to primary producers in these regions.

The input and fate of terrestrial organic matter into the coastal zone across the coastal plume's salinity gradient at the eastern and western flanks of the oil marine terminal and a river mouth are shown in **Figure 6**. High POC concentrations were

Matrix	Region/ Discharge	$\delta^{13}C$ (‰)		$\delta^{15}N$ (‰)	
		Average	Range	Average	Range
Coastal sediments	River outflow	−23.22 (1.23) [a]	−24.60 to −21.90	3.68 (0.84) [c]	2.60 to 4.70
	Coastal non-impacted	−23.84 (1.98) [b]	−25.82 to −21.74	3.83 (2.29)	2.36 to 6.47
	Coastal impacted	−35.75 (1.72) [a,b]	−37.40 to −33.64	1.11 (0.97) [c]	0.06 to 1.97
Offshore sediments	Offshore reference	−22.01 (1.83) [d]	−25.14 to −20.86	4.69 (1.41) [e]	2.50 to 7.40
	Cantarell oil field	−25.69 (3.12) [d]	−33.87 to −21.10	2.66 (2.63) [e]	−3.17 to 6.22
Coastal particles	Produced water	−26.74 (0.24) [f]	−27.01 to −26.33	−2.26 (2.75) [g,h]	−4.90 to 1.87
	Oily discharge	−27.24 (1.26) [i,j,k]	−29.51 to −24.66	−1.35 (3.39) [l,m,n]	−5.63 to 5.82
	Graywater discharge	−24.27 (3.97) [i]	−37.66 to −21.25	3.83 (2.35) [g,l,o]	0.43 to 8.40
	Coastal zone	−23.74 (1.84) [j]	−29.48 to −21.78	2.36 (2.18) [m,o]	−1.24 to 5.21
	Marine terminal	−23.92 (1.43) [f, k]	−27.40 to −21.74	3.52 (1.97) [h,n]	0.38 to 6.47
Offshore particles	Offshore reference	−21.89 (1.83)	−26.50 to −18.15	3.77 (1.87)	−0.96 to 2.60
	Cantarell oil field	−22.46 (2.61)	−30.38 to −16.33	4.01 (3.32)	−3.17 to 14.82

Superscripts b, i, and o denote significant differences between regions or discharge values (t test, p < 0.05).
Superscripts a, b, c, f, g, h j, k, l, m, and n denote highly significant differences between regions and/or discharge values (t test, p < 0.01).

Table 3.
Basic statistics for stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope values of surface sediments and suspended particles in the river's outflow, coastal zone, oil marine terminal, Cantarell oil field, and reference offshore region. Standard deviations are given in parentheses.
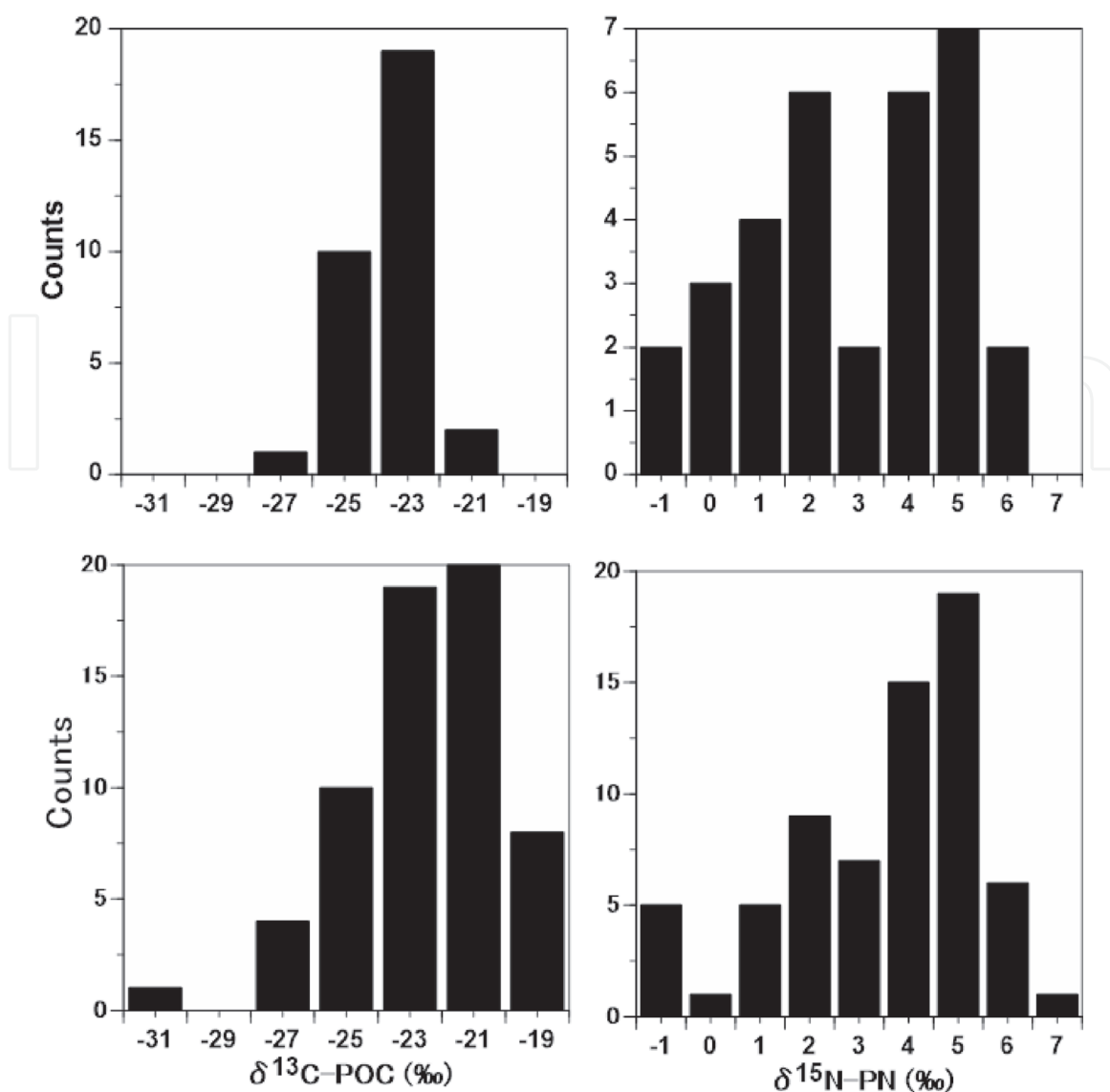
Figure 5.
Histograms of the isotopic composition of particulate organic carbon (δ^{13}C-POC) and particulate nitrogen (δ^{15}N-PN) for the coastal region (upper panel) and Cantarell oil field region (lower panel).

associated with low salinity waters and decreased across the salinity gradient to typically lower ocean values, indicating that the relatively high POC concentrations of continental origin decrease as the plume is diluted across the salinity plume.

In contrast, the peak PN concentration at a salinity of 32 suggests a maximum N uptake at optimal inorganic nitrogen and light conditions. Likewise, the low δ^{13}C values of terrestrial particles are concordantly diluted as POC concentrations decrease. Terrestrially derived particles have high C:N molar ratios and low δ^{13}C values, while marine particles approach C:N molar ratios of 6:1 and δ^{13}C values of approx. −23‰. For example, δ^{13}C measurements off the mouth of the Coatzacoalcos River yielded values of −28.5‰ which changed to −23.0‰, indicating a rapid dilution of terrestrially derived organic matter near the river's mouth [37]. These changes have been recorded in other regions of the Gulf of Mexico, such as the Mississippi River plume where both dissolved species [38] and particulate species are diluted [39].

Scatterplots for coastal and Cantarell oil area sediments, benthic organisms, and suspended particles are summarized in **Figure 7**. Also shown is the stable isotope composition of oil from the Cantarell area [20, 21]. Most sedimentary δ^{13}C data points for coastal and shelf regions fall around −22‰ and δ^{15}N values between 3 and 7‰. However, a few coastal samples and one shelf sediment appear to incorporate biogenic methane carbon as suggested by the depleted δ^{13}C values
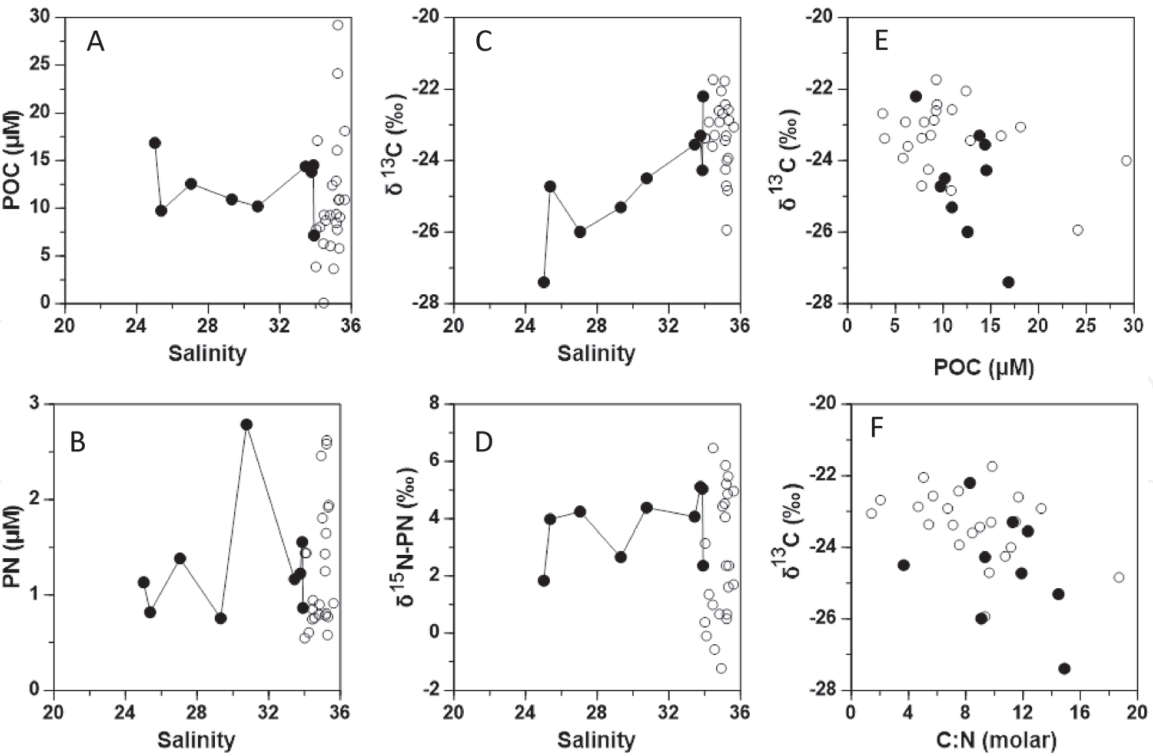
Figure 6.
Salinity vs. parameter scatterplots showing (A) POC, (B) PN, (C) δ¹³C, and (D) δ¹⁵N distributions along the salinity gradient, and (E) δ¹³C vs. POC and (F) δ¹³C vs. C:N molar rations of particulate matter in Bay of Campeche coastal zone. Open circles are high salinity samples, closed symbols are low salinity (<34) samples.
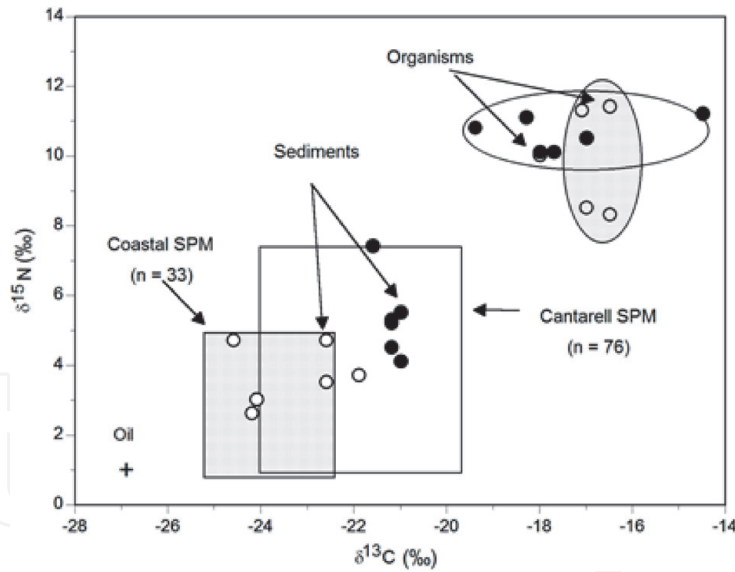

Figure 7.
δ¹⁵N vs. δ¹³C scatterplots of coastal (open circles) and shelf (closed circles) particles (SPM), sediments and benthic organisms of Campeche shelf. The squares enclose the range of isotopic values of suspended particles (not shown) and the cross denotes the isotopic composition of Cantarell oil [20, 21].

between −38 and −34‰. By contrast, the carbon isotope composition of coastal particulate matter ranged between −26 and −22‰. Suspended particles in the shelf area spanned a greater range of δ¹³C and δ¹⁵N values (−26 to −14‰ and −4 to 10‰, respectively). Considering that most particulate matter is composed of auto-trophic organisms, it appears that coastal area and shelf area were constituted by different phytoplankton assemblages. At Dos Bocas Marine Terminal area, the terrestrially derived organic carbon is isotopically lighter than that of the coastal region. POC concentrations decreased along the salinity gradient and increased at

higher salinities. Nitrate concentration decreased somewhat while PN remained constant along the salinity gradient with oscillating isotopic compositions. As shown in the figure, the superposition of carbon and nitrogen isotopes of the water column-suspended particulate matter from nearshore and Cantarell areas with the isotopic values of sediments suggests that the predominant source of sedimentary C_{org} and TN in the Cantarell area is the downward flux of upper-layer production. However, the most negative value ($\delta^{13}C$ of $-38‰$) of some coastal and Cantarell sediment samples suggests the presence of hydrocarbons, particularly off the marine terminal. By contrast, the isotopically lighter carbon in nearshore area particles and sediments reflects a mixture of marine organic matter with that of terrestrially derived origin, principally from the Grijalva-Usumacinta River, which is the most important contributor of terrestrial organic matter to the southern Gulf of Mexico. The predominant coastal current in this sector of the shelf flows westward [30], and, along the coastal plume, numerous smaller discharges would supply additional organic matter of terrestrial origin.

Based on stable isotope analysis, no evidence of seep- or oil-derived carbon in the sampled sediments of the coastal zone and Cantarell area were found. The measured sediment carbon isotope values are also more ^{13}C-enriched than those found at other seep areas, such as in the NW Gulf of Mexico (e.g., -27.5 to $-26.5‰$ [36]) or gas hydrates from southern Gulf of Mexico slope cold seeps [13]. Likewise, $\delta^{13}C$ values for surface sediments sampled in offshore oil rigs of the Cantarell area are significantly lighter (-27.5 to $-26.4‰$ [40]) than those found in this study.

Sampled macrobenthic organisms in the coastal region consisted mainly of penaeid shrimp, and those from Cantarell included infaunal (polychaetes and sipunculids) and epifaunal (ascidians, echinoderms, and decapods) species. In the two regions, the isotopic compositions of organisms were heavier in carbon and nitrogen than those from sediments and corresponding suspended particles, with $\delta^{13}C$ values oscillating between -19.4 and $-17.0‰$ and $\delta^{15}N$ between 8 and 11‰. Considering that on average there is an increment of 3.5‰ in $\delta^{15}N$ between one trophic level and another [2] and around 1.5‰ in $\delta^{13}C$ [1], then the Cantarell area-sampled specimens are about two trophic levels above primary producers. In the coastal region, the data suggest that the sampled benthic species are two and three trophic levels above producers. These results are in line with a phytoplankton-based benthic trophic chain [41]. In contrast, seep communities derive their carbon sources from isotopically light carbon from oil or gas through chemosynthetic microorganisms, and resulting carbon and nitrogen isotopic values are much lighter, on the order of -60 to $-30‰$ for $\delta^{13}C$ and -17 to 2.5‰ for $\delta^{15}N$ [39, 41].

In summary, the contribution of seep-derived carbon is negligible on a shelf-wide scale for this region. The principal carbon source to benthic organisms in this continental shelf is water column production, with a terrestrial contribution in nearshore waters, which is rapidly diluted as the coastal plume is diluted. It follows that organic carbon derived from the shelf's high primary production overwhelms that from oil seeps and from offshore drilling in this region. However, the sedimentary carbon isotopic composition of the oil terminal suggests the local presence of hydrocarbon-derived organic carbon.

Although stable isotopes are useful tracers of the source and flow of biogeochemically relevant elements in trophic web studies, fractionation processes of nitrogen [2] and even carbon [1, 42], along with mixed diets, may yield an incorrect interpretation of food sources. This problem may be solved by including a third stable isotope (e.g., $^{34}S/^{32}S$, $^{18}O/^{16}O$) which complement the other two [42]. For example, the complementary use of $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ was used to elucidate the complex trophic web of deep-sea hydrothermal vent systems in the southern Gulf of California, where different carbon sources and assimilation processes along

with different sulfide sources (magmatic, biogenic, and photosynthetic) co-occur [43].

3.3 Organic carbon and nitrogen sources to NW Cuba deep-sea sediments

In the E Gulf of Mexico, Cuba's NW sector (**Figure 1**), localized between the Yucatan Channel and the Straits of Florida, is a highly dynamic region. In this region the inflowing Yucatan Current brings in water into the Gulf of Mexico, and the Florida Current transports water from the Gulf out into the Atlantic Ocean via the Gulf Stream. Across the channel near-surface current velocities extend throughout the water column. Low nutrient concentrations in part explain the low surface chlorophyll concentrations reported for the E Gulf of Mexico and Yucatan Channel [44]. As a consequence, atmospheric nitrogen, with a $\delta^{15}N$ near 0‰, is an important potential nitrogen source in this part of the Gulf of Mexico [45]. There is a relatively scarce contribution of terrigenous organic matter input when compared to the N and S Gulf of Mexico, where the Mississippi and the Grijalva-Usumacinta Rivers drain, respectively. Therefore, sediments are dominated by calcareous oozes and marls, although surface sediment magnetic susceptibility distribution for the Gulf of Mexico suggests detrital sediments originating from igneous and metamorphic soils from Cuba depositing off the island's NW continental slope and abyssal plain [46].

Recent search for deep-sea fossil fuels and gas hydrates has renewed interest in the study of deep-sea processes in the Gulf of Mexico [47]. In 2002 a multidisciplinary research group explored the seabed off the northwestern coast of Cuba with the purpose of detecting potential deep-sea hydrocarbon seeping areas [47, 48]. Stable carbon and nitrogen isotopes in surface sediments are used here to detect possible seeping in the area and to infer the relative importance of nitrogen fixation as a source of sedimentary organic matter in the Cuban northwest slope.

During the period of study, upper-water currents in the study zone were on the order of 180 cm/s with an ESE direction, and near-bottom currents reached 40 cm/s (**Figure 8**). The thermocline, which separates the well-mixed upper layer from the stratified deeper waters, was localized at around 75–100 m depth, precluding the vertical advection of subsurface nutrients to upper waters.

Three blocks located in Cuba's exclusive economic zone were explored off the northern slope of Cuba (**Figure 1**). Three samples were collected in Block I, the westernmost site localized 45 km north of the island at a depth of nearly 2200 m. Block II laid at 1800 m depth at 50 km north of the island, and samples were taken at three sites. The easternmost Block III had an elongated surface localized at a depth of 1500 m where six sites were collected. In total, 12 surface samples were subsampled from box-core deployments for carbon and nitrogen stable isotopes and C_{org} and TN analyses.

Figure 9 gives the scatterplots for $\delta^{13}C$, $\delta^{15}N$, C_{org}, TN, and C:N ratios for surface samples from NW Cuba continental slope. C_{org} and TN concentrations were generally low and varied between 0.2 and 0.8% and 0.06 and 0.15%, respectively. Stable isotope values of the organic carbon fraction ranged between −19.1 and −18.5‰, and most $\delta^{15}N$ values varied between 5.4 and 6.4‰ [49]. An analysis of variance for surface C_{org}, TN, and isotope values showed no statistical difference between sites; however, molar C:N ratios were significantly higher at Block II relative to Block III (**Table 4**).

The study zone's C_{org} and TN concentrations are nearly tenfold lower of surface sediments than the southern and northwest Gulf of Mexico [49, 50]. Several factors appear to determine these low C_{org} and TN concentrations. A fraction of water entering through the Yucatan Channel from the Caribbean Sea deviates eastward
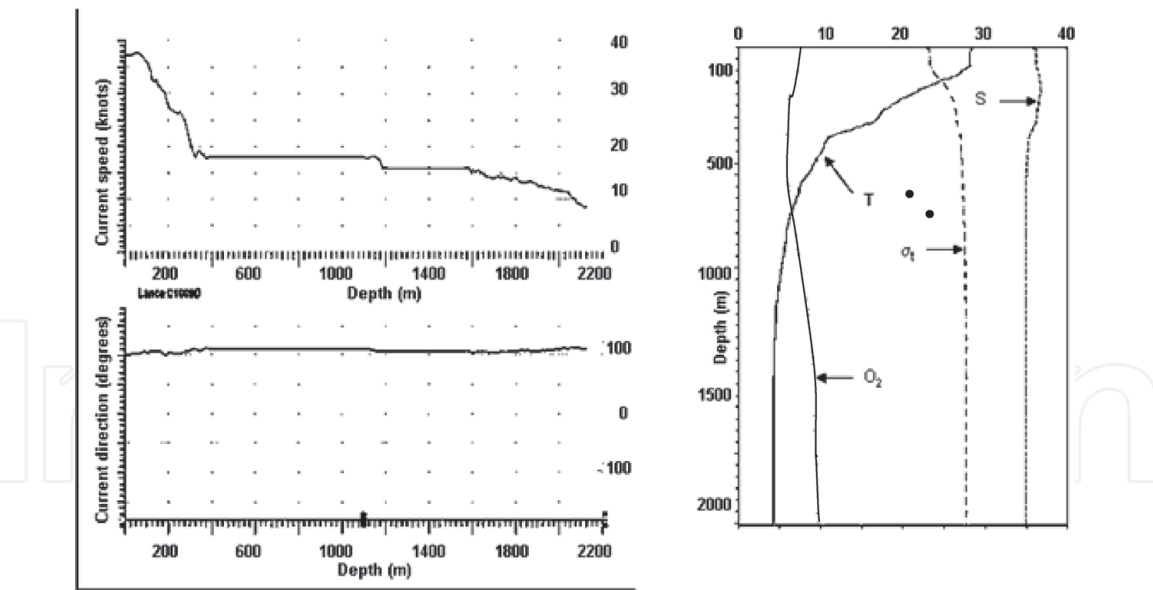
Figure 8.
Representative oceanographic conditions for NW slope of Cuba waters during July 2002. Upper left panel: current velocity (knots) vs. depth (m). Lower left panel: current direction (degrees) vs. depth. Right panel; vertical profiles of temperatures (T, °C), salinity (S, per mile), sigma-t (σ$_t$, (1-density) × 1000) and dissolved oxygen (O$_2$, ml/L).
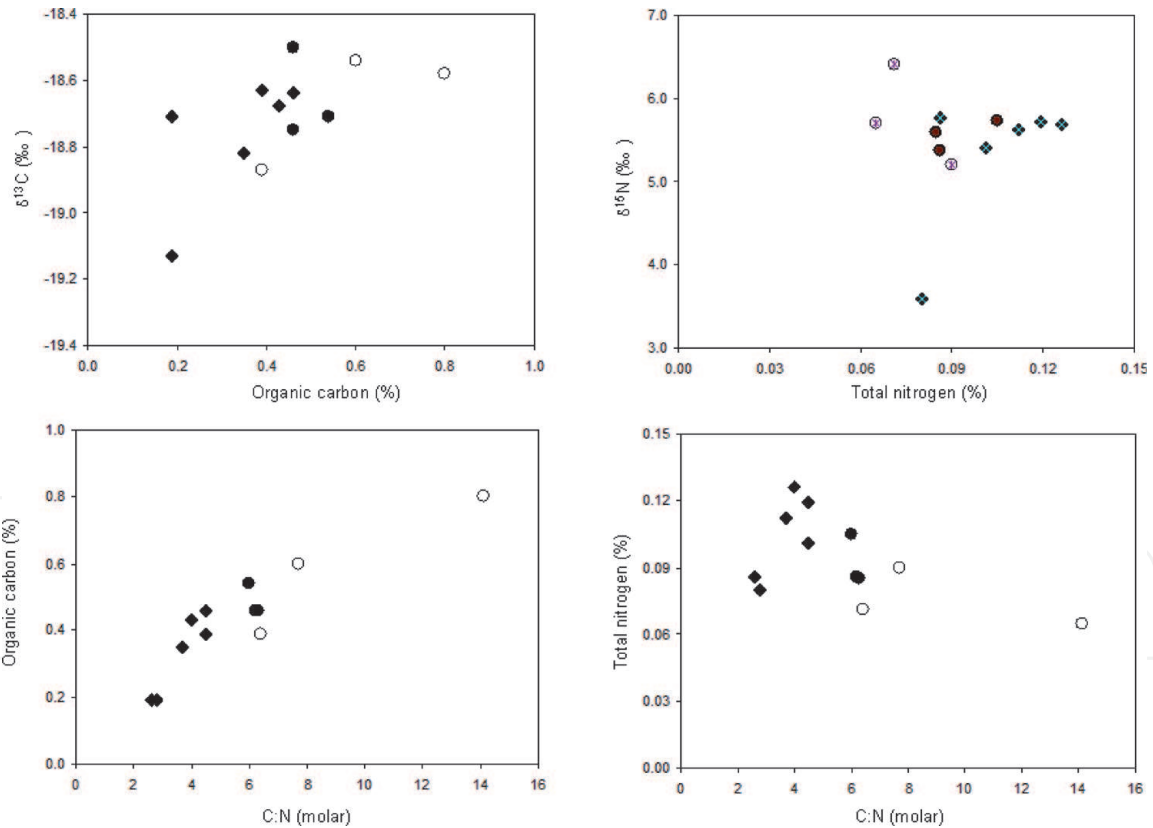

Figure 9.
*Scatterplots of: (A) δ^{13}C vs. organic carbon concentration, (B) δ^{15}N vs. total nitrogen concentration, (C) organic carbon concentration vs. C:N molar ratios, and (D) total nitrogen concentration vs. C:N molar ratios, in surface sediments from Block I (open circles), Block II (closed circles) and Block III (diamonds). See **Figure 1** for site locations.*

upon entering the Gulf of Mexico, and, because the flow accelerates as it transits through the channel, the thermocline deepens in the eastern side of the current [51], advecting nutrient-impoverished upper waters into the eastern Gulf [44]. Additionally, the northwest side of Cuba does not show a significant input of terrigenous

Variable	SS$_{effect}$[a]	MS$_{effect}$[b]	M$_{error}$[c]	F[d]	p[*]
% C$_{org}$	0.1463	0.0731	0.0176	4.1590	0.0526
% TN	0.0017	0.0008	0.0003	3.2691	0.0857
C:N (molar)	66.1112	33.0558	4.1572	7.9514	0.0103*
δ^{13}C (‰)	0.0365	0.0182	0.0312	0.5833	0.5578
δ^{15}N (‰)	0.4690	0.2345	0.4821	0.4864	0.6301

[a]*Sum of squares between sites (degrees of freedom: 2).*
[b]*Mean square between sites.*
[c]*Mean square of error (degrees of freedom: 9).*
[d]*Fisher test.*
Significant difference ($p < 0.05$).

Table 4.
One-way analysis of variance for organic carbon, total nitrogen, molar C:N ratio, $\delta^{13}C$, and $\delta^{15}N$ in surface sediments from Block I (three samples), Block II (three samples), and Block III (six samples) of northwest slope of Cuba.

material through continental drainage, when compared to the riverine inputs from the northern and southern gulfs. In these nutrient-impoverished surface waters, nitrogen-fixing cyanobacteria have a competitive advantage, and *Trichodesmium* sp. blooms are frequent [44, 51].

The carbon and nitrogen isotopic composition of surface sedimentary organic matter would be similar to that of the overlying euphotic zone if the transit time of particulate organic matter from upper waters to the seafloor is short. In contrast, if particulate organic matter has a longer residence time in the water column, then in situ processes, such as microbial degradation, would transform the isotopic composition acquired in the surface waters by the selective removal of carbon and nitrogen compounds [19, 52]. In this study, the average δ^{13}C value of −18.7‰ in sediments is similar to previously published values for surface water particles from the eastern Gulf of Mexico [35, 44], which suggests a rapid transfer or organic carbon from the upper waters to the sediments. Sedimentary δ^{13}C values further suggest that there was no evidence of extensive hydrocarbon seeping in the studied samples.

Under oligotrophic conditions nutrient limitation in the photic zone precludes nitrogen isotope fractionation, and plankton acquires the isotopic composition of the available nitrate diffusing from below the thermocline [53, 54]. In northwest Gulf of Mexico slope waters, the δ^{15}N composition of nitrate (δ^{15}N$_{average}$ = 5.0‰) and mixed-layer PN (5.5‰) suggests that nitrate diffusing from the thermocline into the photic zone is an important nitrogen source for phytoplankton in that region [39]. If organic matter at the northwest Cuba slope is transferred rapidly from the euphotic zone to the sediments, then the isotopic composition of sedimentary nitrogen (δ^{15}N$_{average}$ = 5.5‰) would be similar to that of upper-water PN. The measured sedimentary nitrogen isotope composition suggests that the principal, long-term nitrogen source to the sediments off the northwest slope of Cuba is nitrate diffusing from the thermocline, which is then deposited in the sediments by large particles with a short residence time in the water column. Surface sediment C:N molar ratios further suggest a predominantly marine origin for organic matter of NW slope of Cuba. Marine-derived organic matter has molar C:N ratios between 4 and 10, which contrast with terrestrially derived matter with ratios above 20, mostly resulting from the abundance of cellulose in its structure [50]. The significantly lower ratios at Block III relative to Block II result from the lowest C$_{org}$ concentrations and highest TN values in the former site which is nearer to the coastline.

3.4 Oil-related baseline levels of a Bank of Campeche coral reef

The high degree of structural complexity and species interdependence renders coral reefs as highly vulnerable ecosystems to natural or anthropogenically induced changes. For example, high mortality has been observed for coral larvae by water-accommodated fraction of fuel oil, dispersed oil, and oil dispersant at concentration levels with an order of magnitude lower than expected concentrations from an oil slick [55].

One of the three reef systems of the Mexican Gulf of Mexico is located in Campeche Bank, off the northwest edge of Yucatan shelf (**Figure 1**). The system is constituted by the emerged reefs Arrecife Alacranes, Cayo Arenas, Cayo Arcas, and Triángulos and by the submerged banks Banco Ingleses and Bajo Obispos [56]. Most of these reefs and banks cover a small area (<20 km^2), with the notable exception of Alacranes which is over 30-fold bigger [56].

Stable carbon isotopes and polycyclic aromatic hydrocarbons (PAHs) were measured in coral, sponge, and algae tissue samples from Triángulos Reef off Campeche Bank (NW of the Yucatan Peninsula) collected in September 2001 at bottom depths ranging between 8 and 19 m. The reef is adjacent to the Bay of Campeche where 80% of the country's crude oil is extracted and a nearby offshore terminal loads petroleum to oil tankers at Cayo Arcas [57]. The purpose of the study was therefore to determine if anthropogenic activity from the nearby offshore oil terminal is detected in this reef system. A second objective was to provide baseline stable isotope and PAH data for the reef systems of that region. Six sponges and six corals (*Montastraea cavernosa*) and two benthic algae samples were collected in the eastern and western flanks of Triángulos Reef at water depths varying between 8 and 18 m. Because the zooxanthellae were not separated from the coral, results represent a mixture of the host tissue and its symbiotic algae [58]. However, previous studies have shown the difference between the δ^{13}C values of algae and its coral hosts is very small when corals derive most of their carbon from their symbionts [59, 60].

Figure 10 shows the stable carbon isotope distribution of the sampled organisms in Triángulos Reef. δ^{13}C values of the corals ranged between $-19.7‰$ and $-14.8‰$,
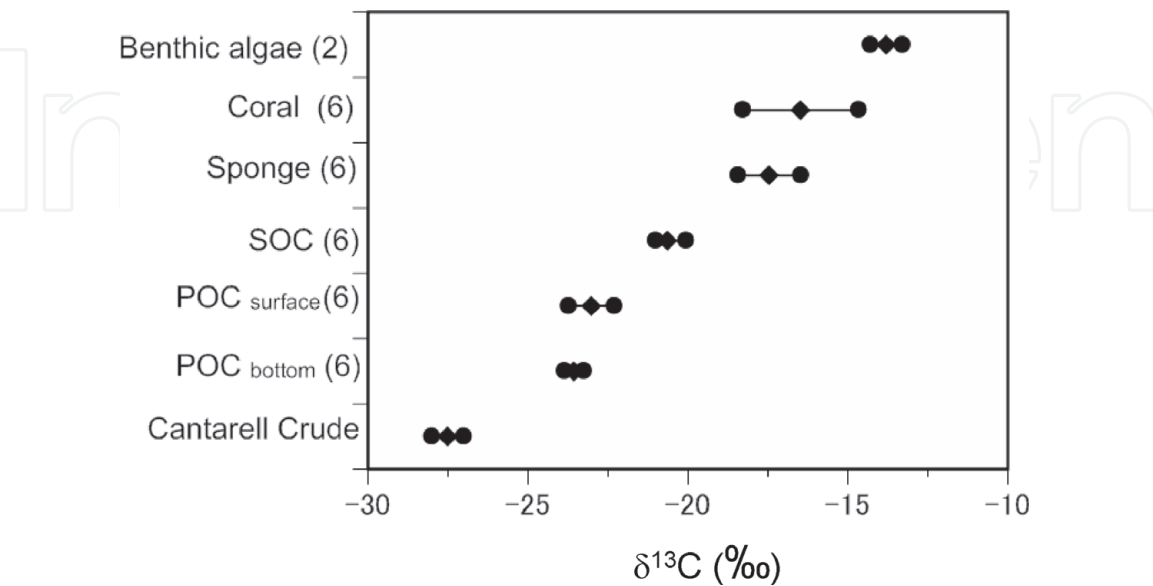

Figure 10.
Stable carbon isotope composition of benthic algae, coral tissue (Montrastrea cavernosa) and sponge tissue form Triángulos Reef collected in September 2001. Also shown are the δ^{13}C values of near-surface particulate and near-bottom organic carbon (POC) and sedimentary organic carbon (SOC) of the region, and of typical Campeche Bank crude [21]. Number of samples are given in parentheses.

with an average value of $-16.5‰$ (standard deviation of $\pm1.8‰$), which is statistically similar to the average in sponge samples of $-17.4‰(\pm1.0)$ (range of -19.0 to $-16.2‰$). In turn, the carbon isotope composition of the two benthic macroalgae samples averaged $-13.8‰$ (±0.5). The isotopic values of these organisms are significantly different from typical crude oil carbon isotope composition of -28 to $-26‰$ of marine siliciclastic and carbonate reservoirs from the Bay of Campeche in the southern Gulf of Mexico [20, 21]. The measured values from our coral samples are similar to those from coral and zooxanthellae (-20.5 to $-13.5‰$ in *Stylophora pistillata*; -19.1 to $.11.9‰$ in *Favia favus*) from the Red Sea [60], coral tissue from two reefs in the western Pacific Ocean (-14.6 to $-12.1‰$ [61]), to $\delta^{13}C$ values between -16.6 and $-12.4‰$ in *Montastrea annularis* from Jamaican reefs [59] and lie within the range for several Indo-Pacific and Caribbean reefs [58]. These data further suggest that the principal carbon source is provided by the zooxanthellae, since these corals are relatively enriched in ^{13}C, in contrast to a ^{13}C-depleted signature when heterotrophic activity by the coral becomes the principal food source [59, 62].

PAHs (organic compounds with two or more fused aromatic rings) have different sources in the marine environment [63]. Oil-derived PAHs account for about 20% of total hydrocarbons in crude oil and are complex mixtures of two to eight rings although naphthalene and its alkylated homologs are usually present at higher concentrations since, in crude oil, PAH concentrations usually decrease with increasing molecular weight [63]. Other PAH sources to the environment include pyrolysis of organic matter which generates high-molecular-weight PAH [64] and microbial and plant biosyntheses [63].

Table 5 gives concentrations of individual and total PAH concentrations (ΣPAH) in coral and sponge samples from this study and for three potential hydrocarbon sources in the region [57]. ΣPAH averaged 4.5 ppb in coral and 11.7 ppb in sponge (excluding the eastern flank sample with 147.4 ppb). These results suggest a relatively pristine environment, similar to PAH concentrations in reef organisms from Micronesia [65], where Σ_{16}PAH for sponges and corals varied between 7 and 722 ppb. PAH concentrations of this study are also low than those from the Red Sea coast, where Σ_{16}PAH in corals was two to three orders of magnitude higher [66]. Compared to coral samples, measurable PAHs in sponge samples reflect their relatively high lipid content and limited PAH-metabolizing capabilities [65]. Except for measurable concentrations of naphthalene and its alkylated homologs, most individual PAH concentrations in coral samples were present below the detection or quantitation limits (**Table 5**). In contrast, three of the six sponge samples showed concentrations around 5 ppb of benzo(*b*)fluoranthene, three had phenanthrene near the detection limit, one sample had 4 ppb fluorine, and the significantly higher PAH concentrations of the sponge collected in the eastern flank (station 6) result from high values of alkylated naphthalenes. Individual PAH distributions suggest an oil-derived origin, where low-molecular-weight PAH and its alkylated homologs predominate [63, 66]. In contrast, the lack of high-molecular-weight PAHs indicates the absence of these compounds from pyrogenic sources.

One month before this study, Cram et al. [57] measured individual PAHs in sediments from Triángulos Reef and nearby Cayo Arcas. These authors also analyzed the PAH composition from Cayo Arcas and Cantarell crude oils and from the ship's fuel oil. They detected measurable PAHs in only 7 of the 71 sediment samples in Cayo Arcas with concentrations between 3 and 28 ppm, and, of the 6 individual PAHs they detected, only pyrene and benzo(*b*)fluoranthene were also found in the sponge samples from the present study (**Table 5**). Tracing the source of oil in the reef's sediments, Cram et al. [57] suggest a pyrolytic origin of PAHs where high-molecular-weight hydrocarbons (4–6 rings) predominate. Another potential source

Sample	Site	Reef sector	δ^{13}C (‰)	Naphthalene	2-Methylnaphthalene	1-Methylnaphthalene	2,6-Dimethylnaphthalene	Acenaphthene	Fluorene	Dibenzothiophene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(b)pyrene	Benzo(a)pyrene	Perylene	Indene(1,2,3,cd)pyrene	Benzo(g,h,i)perylene	ΣPAH
Coral	1	NE	−15.40	—	2.4	1.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3.8
	2	NE	−19.69	—	2.0	1.4	—	—	1.2	—	—	—	—	—	—	—	—	—	—	—	—	—	1.0	5.6
	3	W	−14.76	1.8	4.7	3.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	9.5
	4	SE	−17.09	—	1.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.5
	5	W	−15.21	—	2.2	1.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3.5
	6	W	−16.67	—	2.0	1.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3.1
Sponge	0			—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	1	NE	−16.96	—	2.4	—	2.2	—	—	—	—	—	—	—	—	—	4.2	—	—	—	—	—	—	8.8
	2	NE	−17.58	2.7	4.6	2.9	3.4	—	—	—	2.3	—	—	—	—	—	5.8	—	—	—	—	—	—	21.7
	3	W	−19.03	—	3.0	2.0	2.3	—	—	—	—	—	—	—	—	—	5.2	—	—	—	—	—	—	12.5
	4	SE	−17.98	—	1.3	—	1.2	—	—	—	2.3	—	1.7	1.3	—	—	—	—	—	—	—	—	—	7.8
	5	W	−16.24	—	2.4	1.6	2.2	—	—	—	1.5	—	—	—	—	—	—	—	—	—	—	—	—	7.7
	6	W	−16.89	29.0	58.0	33.0	19.0	—	4.0	1.6	2.8	—	—	—	—	—	—	—	—	—	—	—	—	147.4
Crude oils[57]	CN		N.A.	137.0	N.A.	N.A.	N.A.	97.0	81.0	N.A.	93.0	121.0	17.0	50.0	50.0	17.0	16.0	14.0	N.A.	—	N.A.	N.A.	—	745..0
	CA		N.A.	39.3	N.A.	N.A.	N.A.	70.0	107.8	N.A.	45.5	273.0	128.7	264.8	—	—	—	—	N.A.	—	N.A.	N.A.	—	1001.6

Sample	Site	Reef sector	δ¹³C (‰)	PAH (µg/kg)																				
				Naphthalene	2-Methylnaphthalene	1-Methylnaphthalene	2,6-Dimethylnaphthalene	Acenaphthene	Fluorene	Dibenzothiophene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(b)pyrene	Benzo(a)pyrene	Perylene	Indene(1,2,3,cd)pyrene	Benzo(g,h,i)perylene	ΣPAH
Fuel oil[57]			N.A.	208.6	N.A.	N.A.	N.A.	199.1	454.4	N.A.	111.8	127.3	77.3	—	—	—	—	—	N.A.	—	N.A.	N.A.	—	1772.1
Sfc water				**9.8**	—	—	—	—	—	—	**7.9**	—	8.0	7.9	—	—	—	—	—	—	—	—	—	—
Cayo Arcas sediments[57]			N.A.	—	N.A.	N.A.	N.A.	—	—	N.A.	—	P	—	P	P	P	P	—	N.A.	P	N.A.	N.A.	—	—

Concentrations in bold are present below the limit of quantitation. Also given are the PAH composition of Cantarell crude oil (CN), Cayo Arcas crude oil (CA), and fuel oil from the sampling ship as reported by Cram et al. [57]. Organisms and sediments were collected in September 2001. Surface water samples were collected in September 2010. N.A., not analyzed; P, present but not quantified.

Table 5.
*Stable carbon isotope values, polycyclic aromatic hydrocarbons (PAHs), and naphthalene-alkylated homolog concentrations (wet weight) in coral (*Montastraea cavernosa*) and sponge samples from Triángulos reef.*

of hydrocarbons appears to be ballast water from the relatively intense ship traffic in the region [57]. Our data, especially the sponge sample from station 6, suggest that a potential source of these compounds in the reef could be the crude oils from the region or discharged ballast waters from oil tankers. The relatively higher solubility of low-molecular-weight PAHs can explain their incorporation into the reef's food web.

In summary, the δ^{13}C values measured in corals suggest a carbon source from fixation by zooxanthellae. This implies that Triángulos Reef is not under evident stress, because corals expel these algae under unfavorable conditions. In such a case, the isotopic composition of the coral would resemble that of heterotrophic activity, such as feeding from zooplankton. Additionally, most PAHs measured in corals were below the detection limit, while the few individual PAHs detected in sponges and corals (mostly low-molecular-weight PAHs) suggest the presence of oil-derived compounds from either Cantarell oil field or Cayo Arcas marine terminal.

4. Conclusions

Stable carbon and nitrogen isotopes from anthropogenically impacted and relatively pristine marine environments in these studies show its usefulness in tracing the sources and flows of these elements in the environment. These studies spanned Gulf of Mexico coastal, shelf, and deep-sea regions, where isotopes were analyzed in surface and subsurface sediments, marine particles, and marine organisms. Ancillary data provided additional information on several biogeochemical issues.

In Bay of Campeche's Cantarell oil field sediments, hydrocarbon seeping was traced at different depths of a sediment core, which showed a distinct δ^{13}C oil-related signature relative to a nearby reference site. At 20 m core depth, the ^{13}C-depleted seep sediments were associated with high total hydrocarbon concentrations indicating the vertical migration of oil. In the seep and reference cores, a δ^{13}C maximum (−19‰) is concordant with the onset of the recent interglacial period (10,000 years B.P.).

In another study in this region, carbon and nitrogen isotopes in suspended particles, surface sediments, and macrobenthic organisms from the coastal zone and in the Cantarell oil field were used to trace the sources of organic matter to the benthic community. Results show that marine-derived organic matter is the principal carbon source to Bay of Campeche sediments, with an additional terrestrial contribution in the nearshore region. This implies that, on a shelf-wide scale, coastal discharge, oil extraction, and seeping have no direct effect to the benthic food web.

Carbon and nitrogen stable isotopes measured in surface sediments from the northwest slope of Cuba, along with C:N ratios and C_{org} and TN concentrations, traced the sources of sedimentary organic matter as marine derived. Surface sediment δ^{15}N values suggest that nitrate diffusing from the thermocline, and not nitrogen fixation, is the principal long-term nitrogen source to primary producers in the upper waters. In addition, a comparison with reported δ^{15}N and δ^{13}C values in the region suggests that organic matter flux from the surface ocean to the sediments is fast, most likely as sinking particles.

In Triángulos Reef, the stable carbon isotope composition of corals and sponges suggests that this ecosystem is not under evident stress, because the δ^{13}C signal would then change to that of a heterotrophic-based carbon source. PAH concentrations suggest a relatively pristine environment, although the individual PAH distribution, with relatively high concentrations of naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, and 2,6-dimethylnaphthalene, indicates some impact from petrogenic sources.

Acknowledgements

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