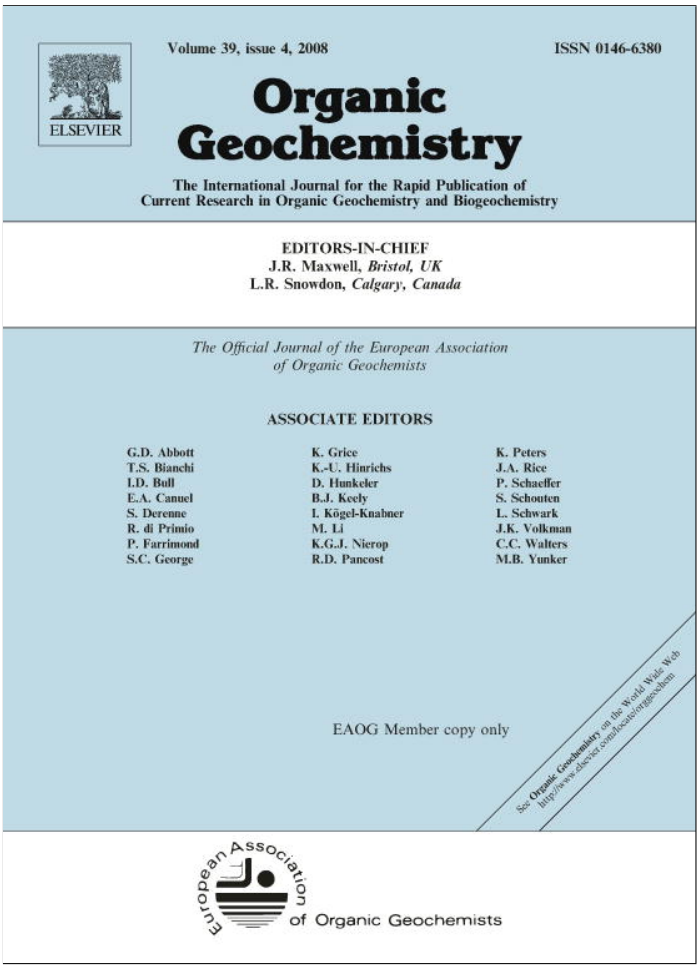

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Organic Geochemistry
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Sources of sedimentary organic matter in the Mississippi River and adjacent Gulf of Mexico as revealed by lipid biomarker and $\delta^{13}C_{TOC}$ analyses

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Received 22 January 2007; received in revised form 7 January 2008; accepted 18 January 2008
Available online 5 February 2008

Abstract

Changes in the organic matter (OM) composition (C/N, $\delta^{13}C_{TOC}$, and lipid biomarker compounds) of surface sediments (0–1 cm) were examined along the dispersal pathway from Mississippi River and marsh/estuarine end members to the adjacent shelf and canyon regions of the Gulf of Mexico. Organic carbon content decreased fourfold from the marsh to the offshore sites, with corresponding changes in organic matter sources. Biomarkers representing allochthonous (higher plant) and autochthonous (algal/plankton/bacteria) sources demonstrated regional differences in the sources of sediment organic matter (SOM). A two end member mixing model using $\delta^{13}C_{TOC}$ indicated that C_3 vascular plant sources comprised ~80% and 50% of the TOC at the river and marsh sites, respectively. However, sources of SOM differed in these regions, with contributions of soil organic matter/terrigenous plant sources dominant in the river ($\delta^{13}C_{TOC} = -25‰$) while marsh plants likely contributed to the enriched signatures found in the marsh sediments ($\delta^{13}C_{TOC} = -18‰$). Allochthonous OM contributions calculated from fatty acid and sterol biomarkers in the river and marsh regions (39–48% and 50–72%, respectively) differed from those determined using $\delta^{13}C_{TOC}$. This was likely due to overlapping $\delta^{13}C_{TOC}$ values for vascular plants and freshwater microalgae and the higher lipid content of the autochthonous sources. Although biomarkers representing terrigenous sources decreased with distance offshore, they comprised approximately 17–34% of the fatty acid and sterols at even the most distal slope and canyon sites, suggesting that these deeper regions could be an important sink for terrigenous carbon. In contrast, the shelf sites were enriched in algal material (60–78% autochthonous OC), with biomarkers for diatoms dominating, suggesting that terrigenous carbon is either diluted in, or bypasses, this region. Results from this study suggest that processes including hydrodynamic sorting, diagenesis, and variations in river flow should be considered in future studies investigating the fate of terrigenous OM in coastal and shelf regions.

1. Introduction

Rivers are the main vectors by which carbon is transferred from land to the coastal ocean thereby providing a key link in the global carbon cycle (Hedges et al., 1997; Richey, 2004 and references therein). In modern marine environments, riverine delivery of organic matter (OM) to continental margins is one of the means by which terrigenous production is preserved, thereby influencing global biogeochemical cycles and the ocean's ability to

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doi:10.1016/j.orggeochem.2008.01.011

sequester atmospheric carbon dioxide. Yet, there remains considerable uncertainty in our ability to adequately quantify carbon exchange from land to the coastal ocean and in our understanding of the processes influencing the fate of terrigenous carbon in coastal sediments (Berner, 1982; Sarmiento and Sundquist, 1992; Hedges and Keil, 1995; Schlünz and Schneider, 2000).

Understanding the fate of organic carbon in the coastal zone is challenging due to uncertainties associated with the processes influencing its supply and preservation. Quantitative budgets are difficult to establish because of natural variations in delivery rates and uncertainties associated with anthropogenic influences (Stallard, 1998; Schlünz and Schneider, 2000; Smith et al., 2001). Seasonal and annual/inter-annual variations in hydrology as well as large events such as storms and hurricanes influence the input, dispersion, and cycling of sediment organic matter in coastal environments, thus making it difficult to trace terrigenous organic matter (Bianchi et al., 2002; Gordon and Goñi, 2003; Allison et al., 2005; Goñi et al., 2006). In addition, recent studies have indicated that processes such as remineralization of riverine organic matter and remobilization may be more important than previously thought (Schlünz and Schneider, 2000; Richey, 2004; Mayorga et al., 2005). Combined with uncertainties related to riverine fluxes and the processing of riverine organic matter, factors controlling OM preservation are still not well understood, including the role of molecular structure, association with organic and inorganic matrices, and influence of depositional conditions (Hedges, 1992; Keil et al., 1997; Wakeham and Canuel, 2005).

Additional challenges arise because river systems vary in their influence on the delivery and burial of organic carbon in coastal sediments (Bianchi et al., 2002 and references therein). Approximately, 85% of the carbon buried in continental margin environments occurs in river dominated ocean margin (RiOMar) systems (Berner, 1982; Hedges and Keil, 1995; McKee, 2003). These RiOMar systems are characterized by large sediment and water inputs from major rivers. In the United States, the Mississippi River is characterized as a RiOMar system. Relative to other major world river systems, the Mississippi River is ranked third in terms of the size of its drainage basin area, seventh in sediment discharge (210×10^6 t yr^{-1}), and seventh in water discharge (530×10^9 m^3 yr^{-1}) (Milliman and Meade, 1983; Meade, 1996; McKee, 2003). Resulting from this high discharge, the adjacent Gulf of Mexico is heavily influenced by OM, nutrients and sediment delivered by the Mississippi River (Hedges and Parker, 1976; Eadie et al., 1994; Trefry et al., 1994). The large inputs of allochthonous (terrigenous) organic carbon delivered from the Mississippi River to the Gulf of Mexico, combined with the effects of the Mississippi River on primary production in the adjacent Gulf of Mexico (Dagg et al., 2004), provide a model system for examining questions about the distribution and fate of allochthonous vs. autochthonous OM delivered to coastal environments.

Previous studies have examined sources of organic matter within the Gulf of Mexico region; however, much of this work has been limited to the shelf region (Hedges and Parker, 1976; Trefry et al., 1994; Bianchi et al., 2002; Mead and Goñi, 2006). Few studies have examined the composition of organic carbon across the coastal margin from the Mississippi River mouth to the shelf, and out to the more distal slope and canyon environments of the Gulf of Mexico. Of these studies, most have relied on lignin, a reliable biomarker for tracing vascular plant derived organic matter (Hedges and Parker, 1976; Goñi et al., 1997, 1998; Bianchi et al., 2002). To augment this body of work, our study characterized the sources of organic carbon across the river to the shelf and deeper slope and canyon regions using several classes of lipid biomarker compounds, as well as C/N and $\delta^{13}C_{TOC}$. Lipid biomarkers provide the ability to distinguish between algal, bacterial and vascular plant sources (Volkman, 1986; Volkman et al., 1998), providing a broader scope of organic carbon source interpretation than lignin alone.

2. Materials and methods

2.1. Sample collection

The average daily water discharge rate for the Mississippi River during the sampling period (14–21 July 2003) was 11,009 m^3 s^{-1} (USGS Tarbert Landing Gauge Station located 340 km upriver from New Orleans). This flow rate is within the expected range for summer, which is characterized by low discharge (i.e., below 14,000 m^3 s^{-1}) (Meade and Parker, 1985; Bianchi et al., 2002). Sediment cores were collected along two transects (Fig. 1). Transect A began within the Mississippi River and proceeded seaward across the continental shelf to the canyon (540 m). Transect B tracked the 50 m

isobath westward. In addition, sites in Barataria Bay (Bara) were sampled to represent estuarine sources. During the cruise, environmental conditions (water depth, salinity, oxygen content and fluorescence (chlorophyll *a*)) were collected from each site using a CTD (conductivity–temperature–depth) sensor (Table 1) and further processed using Seabird Software (SEASOFT – WIN32). At each station, box cores (50 × 50 × 50 cm) were collected, which were subsequently sub-cored onboard the R/V Pelican. Sub-cores were sectioned into 0–1 cm slices for the surface samples and each section was homogenized. Aliquots for lipid, elemental and stable isotope analyses ($\delta^{13}C_{TOC}$) were removed and frozen at −80 °C until further analysis.

In October 2004, three additional box cores were collected at or near the 540 m canyon site (H8, H9, H10). Site H9 was the same location as the 540 m canyon site sampled in July 2003. Three vibracores from marsh sites were also taken. The marsh sites included one interior bay sample at Fisherman's Bay (inner marsh), an open bay sample of the marsh surface (marsh) in Tambour Bay and a mud sample 200 m offshore of Tambour Bay (marsh mud). The 0–1 cm surface interval was collected from each site and freeze dried. All subsequent analyses including lipid, elemental and isotopic measurements utilized the freeze dried sediment.

2.2. Bulk chemical analysis

A sub-sample of wet sediment was dried at 65 °C for several days prior to grinding the sediment for elemental and isotopic analyses. Duplicate analyses were performed for both elemental (total organic carbon (TOC) and total nitrogen (TN)) and stable isotopes ($\delta^{13}C_{TOC}$, $\delta^{15}N$). Dry sediment was weighed (≈20–40 mg) into pre-combusted (4 h at 450 °C) silver capsules and acidified using 10% high purity hydrochloric acid to remove inorganic carbon (Hedges and Stern, 1984). TOC and TN were measured by high temperature com-

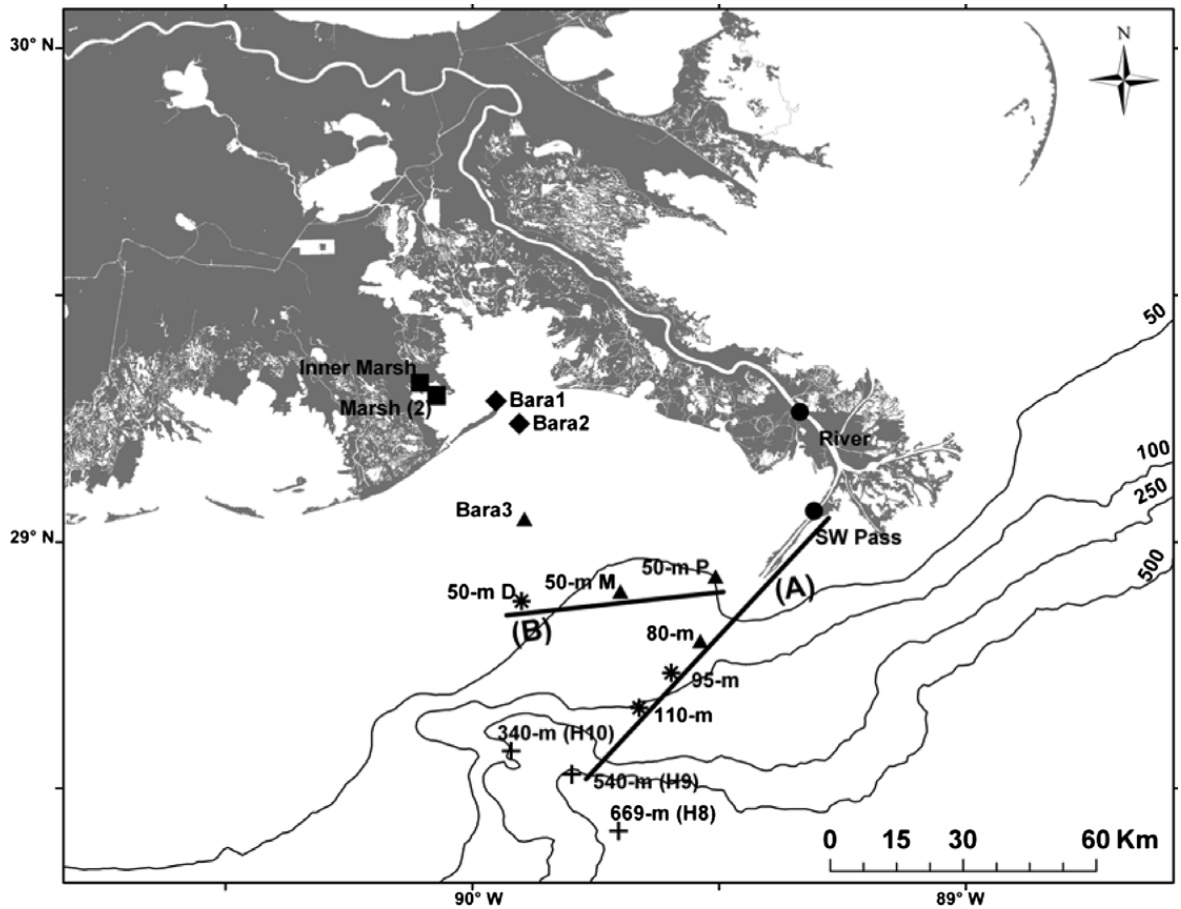

Fig. 1. Locations of surface sediments collected along two transects labeled as (A and B) from the Mississippi River to the Gulf of Mexico during July 2003. Marsh and canyon samples (H8–H10) were collected in October 2004. Sites were grouped by region for data analysis: river (circles), marsh (squares), estuary (diamonds), shelf (triangles), slope (∗), canyon (+) (see Section 2.4).

Table 1
Site information collected during sampling

Region	Station	Latitude °N	Longitude °W	Water depth (m)	Surface salinity	Bottom salinity	Bottom O_2 (mg L^{-1})	Surface fluorescence (mg m^{-3})	Bottom fluorescence (mg m^{-3})
River	River	29 15.7	89 20.1	26	0.2	0.2	7.7	0.21	0.29
	SW Pass	29 3.8	89 18.4	17	0.2	30	6.7	0.31	0.38
	Mean[a]			*21*	*0.2*	*15*	*7.2*	*0.26*	*0.34*
Marsh	Inner Marsh	29 19.3	90 06.3	N/A[b]					
	Marsh	29 17.8	90 04.3						
	Marsh mud	29 17.7	90 04.3						
Estuary	Bara-1	29 17.1	89 57.0	5	15	18	7.1	0.96	0.26
	Bara-2	29 14.3	89 54.2	6	18	21	6.9	0.73	0.67
	Mean[a]			*6*	*17*	*19*	*7.0*	*0.84*	*0.47*
Shelf	Bara-3	29 2.8	89 53.6	27	18	36	6.6	0.73	0.08
	50-m P	28 55.8	89 30.4	46	18	36	7.2	0.51	0.06
	50-m M	28 54.0	89 42.0	59	16	36	7.3	0.68	0.07
	80 m	28 47.9	89 32.3	85	24	36	7.5	0.47	0.06
	Mean			*54*	*19*	*36*	*7.1*	*0.60*	*0.07*
	SD			*24*	*3*	*0.1*	*0.4*	*0.1*	*0.0*
Slope	50-m D	28 52.8	89 54.0	42	20	36	7.1	0.67	0.09
	95 m	28 44.0	89 35.8	94	26	36	7.4	0.20	0.16
	110 m	28 39.8	89 39.7	102	33	36	7.6	0.12	0.29
	Mean			*79*	*26*	*36*	*7.4*	*0.33*	*0.18*
	SD			*33*	*6*	*0.1*	*0.3*	*0.3*	*0.1*
Canyon	540 m	28 31.6	89 47.8	517	34	35	9.4	0.04	0.04
	H8	28 24.8	89 42.2	669	N/A[b]				
	H9	28 31.7	89 47.9	515					
	H10	28 34.5	89 55.2	340					

[a] Standard deviation (SD) of the mean is only reported when $n > 2$.
[b] Hydrographic data were not available for the marsh and October canyon samples.

bustion using a Fisons CHN analyzer (Model EA 1108). Stable isotope analyses ($\delta^{13}C$ and $\delta^{15}N$) were performed using an elemental analyzer interfaced with an isotope ratio mass spectrometer (Europa Scientific Integra) at the University of California-Davis Stable Isotope Facility. Stable isotope values are expressed relative to routine standards, PeeDee Belemnite for $\delta^{13}C$ and atmospheric N_2 for $\delta^{15}N$.

Sediment surface area (SSA) was determined for the 0–1 cm interval collected from each site following the method of Arnarson and Keil (2001). An aliquot of sediment was freeze dried and then heated at 350 °C for 12 h to remove organic matter. The sample was then degassed for >2 h on the Micromeritics Flow Prep 060 sample degas station at 250 °C to remove water. Samples were measured by nitrogen adsorption using a 5 point BET method with the Micromeritics Gemini V Surface area analyzer. Organic carbon was normalized to sediment surface area for each sample (TOC/SSA (mg m^{-2})).

2.3. Lipid biomarkers

Sediments were extracted using CH_2Cl_2:CH_3OH (2:1 v/v) using an ASE-200 Accelerated Solvent Extractor (Dionex®) at 80 °C and 1800 psi (2 × 10 min cycles). Frozen sediments were thawed, homogenized and dried with hydromatrix (Varian®) prior to extraction. Surrogate standards including a fatty acid methyl ester (FAME), methyl nonadecanoate (C_{19} FAME), nonadecanol, a wax ester (myristyl arachidate) that yielded a C_{14} alcohol and a C_{20} FAME following saponification, and androstanol were added to each sample prior to extraction. Extracts were partitioned into two phases and the lower organic phase collected. The aqueous phase was back extracted into hexane and the combined organic phases sat over anhydrous Na_2SO_4 overnight to reduce traces of H_2O. The samples were concentrated to 1 ml (Zymark Turbo Vap 500). The weight of each total lipid extract (TLE) was determined gravimetrically using aliquots repre-

senting ~10% of the TLE. A portion of the extract was saponified using 1 N KOH in aqueous methanol (110 °C for 2 h). Neutral and acidic lipids were extracted into hexane from the saponified sample following Canuel and Martens (1993). Fatty acids were converted to methyl esters using BF_3–MeOH. Both fatty acids (as methyl esters) and neutral lipids were separated from other lipid classes by silica gel chromatography following published methods (Canuel and Martens, 1993). Sterols were derivatized to trimethylsilyl (TMS) ethers using BSTFA and acetonitrile by heating at 70 °C for 30 min. Fatty acids (as methyl esters) and alcohols/sterols (as TMS ethers) were analyzed using gas chromatography (GC) (Hewlett–Packard 5890 Series II Plus) with flame ionization detection using a 30 m × 0.32 mm DB5 column (J&W Scientific). Peak areas were quantified relative to internal standards; C_{21} FAME was used for fatty acids and 5(α)H-cholestane for alcohols/sterols. A GC interfaced to a mass selective detector (Hewlett–Packard 6890 GC-MSD) operated in electron impact mode was used to verify the identification of individual compounds using the same conditions as for GC analysis.

Duplicate analyses of four samples (SW Pass, 50 m proximal (50-m P), 50 m mid (50-m M), and 540 canyon) were performed to examine analytical reproducibility. Duplicate sediment aliquots from the same jar were removed for these extractions. Duplicate analyses agreed within ±20% of one another. Duplicate analyses were relatively consistent across the study system, thus results from these sites are presented as the average of the two extractions.

2.4. Data analysis

Biomarker data were analyzed using MiniTab (MiniTab Inc.: release 13.1, 2000) software. Factor analysis, an exploratory multivariate method, was used to identify the dominant factors controlling variance in the data set (Canuel, 2001 and references therein). Prior to factor analysis, the dry weight data (ng g^{-1}) were normalized to correct for differences in concentration (Yunker and Macdonald, 2003; Yunker et al., 2005). Any variables that were undetectable were set to 1 prior to the centred log ratio transformation. For this transformation, the concentration normalized value is divided by the geometric mean and then log transformed (Yunker et al., 2005). Data were then auto-scaled by subtracting the variable mean followed by dividing the variable standard deviation. By taking these initial steps of normalization, the data set was unaffected by negative bias or closure (Yunker et al., 2005). Our initial analysis used 44 variables and 18 observations. Due to the close grouping of various lipid classes (individual long chain fatty acids (LCFAs), long chain alcohols (LCOHs), C_{20} polyunsaturated fatty acids (PUFAs), branched FAs, C_{28}, and C_{30} sterols) the factor analysis was simplified by combining these classes in a subsequent analysis, which consisted of 17 variables (Table 3) and 18 observations (the sites).

Sites were grouped using bathymetry and the scores from the factor analysis to examine regional differences in OM composition. The following site groupings were used to examine regional differences in SOM composition:

(1) River – Mississippi River (River) and Southwest (SW) Pass sites,
(2) Marsh – inner marsh, marsh and marsh mud,
(3) Estuary – Barataria 1 and 2 (Bara-1, Bara-2),
(4) Shelf – Barataria 3 (Bara-3), 50 m mid (50-m M), 50 m proximal (50-m P) and 80 m,
(5) Slope – 50 m distal (50-m D), 95 m, 110 m,
(6) Canyon – 540 m, H8, H9, H10.

Bulk elemental, isotopic, and lipid biomarker data were examined for normality and equal variance between regions. When the data failed to meet these assumptions, as was the case for TOC and TN, non-parametric tests such as the Kruskall–Wallis test were used to examine statistical differences between regions. When data fit a normal distribution, analysis of variance (ANOVA) was used to examine whether there were regional differences in SOM composition. Regression analysis was used to determine relationships between lipid biomarker compounds and to aid in the interpretation of the factor analysis results. Results were deemed significant when $P < 0.05$.

Ratios of lipid biomarker compounds representing terrigenous and marine (algal/plankton) sources were examined. The ratio of terrigenous to aquatic fatty acids (TAR_{FA}) is a measure of the sum of long chain even numbered saturated fatty acids to short chain even numbered saturated fatty acids (Meyers, 1997):

$$TAR_{FA} = \left[\frac{(C_{24} + C_{26} + C_{28})}{(C_{12} + C_{14} + C_{16})}\right]$$

3. Results

3.1. Environmental conditions

Samples were collected over a range of depths from the shallow estuarine sites at 5 m to the Gulf of Mexico Canyon at 669 m depth (Fig. 1, Table 1). The samples represented a salinity range from freshwater (river station: 0.2) to marine values (canyon station: 34) (Table 1). Saline bottom water (Mean = 35 ± 1.9, $n = 9$) existed at all sites except for the river station (0.2) and the Barataria sites (Mean = 19 ± 2.1, $n = 2$). At the time of sampling, bottom water oxygen concentrations were above the level of hypoxia (2 mg l^{-1}) at all sites, ranging from 6.6 mg l^{-1} (Bara-3) to 9.4 mg l^{-1} (540 m). Surface fluorescence varied from 0.04 mg m^{-3} at the canyon site to 0.96 mg m^{-3} at Bara-1 (Table 1).

3.2. Elemental and isotopic measurements

Sediment %TOC and %TN ranged from 1.0% to 7.2% and 0.07% to 0.4%, respectively (Table 2). Although regional differences were not supported statistically, there was a general trend of higher % TOC and % TN for the marsh, inner marsh and Bara-2 samples (4.8% TOC and 0.35% TN), relative to sediments collected from offshore (Shelf mean: 1.6% TOC and 0.19% TN, $n = 4$; Slope mean: 1.4% TOC and 0.17% TN, $n = 3$; Canyon mean: 1.1% TOC and 0.13% TN, $n = 4$). The C/N_a ratio for sediments from the marsh and estuary regions (18, $n = 3$ and 13, $n = 2$, respectively) were significantly higher ($P < 0.001$) than sediments collected from the other regions (10, $n = 13$) (Fig. 2). Marsh samples had the highest C/N_a ratios (18), while the estuarine sites (Bara-1 and -2) had lower and less variable C/N_a ratios (13) (Table 2). Post

Table 2
Sediment characteristics

Region	Station	%TOC	%TN	C/N_a	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	SSA ($m^2\ g^{-1}$)	OC/SSA (mg m^{-2})
River	River	1.7	0.19	11	−25	13	33	0.5
	SW Pass	2.0	0.20	11	−25	12	21	1.0
	Mean[a]	*1.8*	*0.19*	*11*	*−25*	*13*	*27*	*0.7*
Marsh	Inner Marsh	4.3	0.29	17	−18	*2*	12	3.5
	Marsh	7.2	0.40	21	−18	1	8	9.1
	Marsh mud	1.0	0.07	16	−22	−0.3	6	1.6
	Mean	*4.1*	*0.25*	*18*	*−19*	*1*	*9*	*4.7*
	S.D.	*3.1*	*0.17*	*2*	*2*	*1*	*3*	*3.9*
Estuary	Bara-1	1.0	0.09	14	−23	*7*	5	2.0
	Bara-2	3.2	0.29	13	−22	*7*	18	1.8
	Mean[a]	*2.1*	*0.19*	*13*	*−22*	*7*	*12*	*1.9*
Shelf	Bara-3	1.7	0.21	9	−22	11	25	0.7
	50-m P	1.7	0.19	10	−23	11	26	0.6
	50-m M	1.7	0.20	10	−22	11	30	0.5
	80 m	1.5	0.18	10	−22	11	29	0.5
	Mean	*1.6*	*0.20*	*10*	*−22*	*11*	*28*	*0.6*
	SD	*0.1*	*0.02*	*0.5*	*0.6*	*0.3*	*2*	*0.1*
Slope	50-m D	1.4	0.18	9	−22	10	31	0.5
	95 m	1.5	0.17	10	−22	9	34	0.4
	110 m	1.3	0.15	10	−22	10	30	0.4
	Mean	*1.4*	*0.17*	*10*	*−22*	*10*	*32*	*0.4*
	SD	*0.1*	*0.01*	*0.5*	*0.2*	*0.5*	*2*	*0.0*
Canyon	540 m	1.5	0.18	9	−21	10	39	0.4
	H8	1.1	0.14	10	−21	4	NA	NA
	H9	1.1	0.13	11	−22	4	NA	NA
	H10	1.1	0.12	10	−22	4	NA	NA
	Mean	*1.2*	*0.14*	*10*	*−22*	*5*		
	SD	*0.2*	*0.03*	*0.6*	*0.4*	*3*		

[a] Standard deviation of the mean is only reported when $n > 2$.

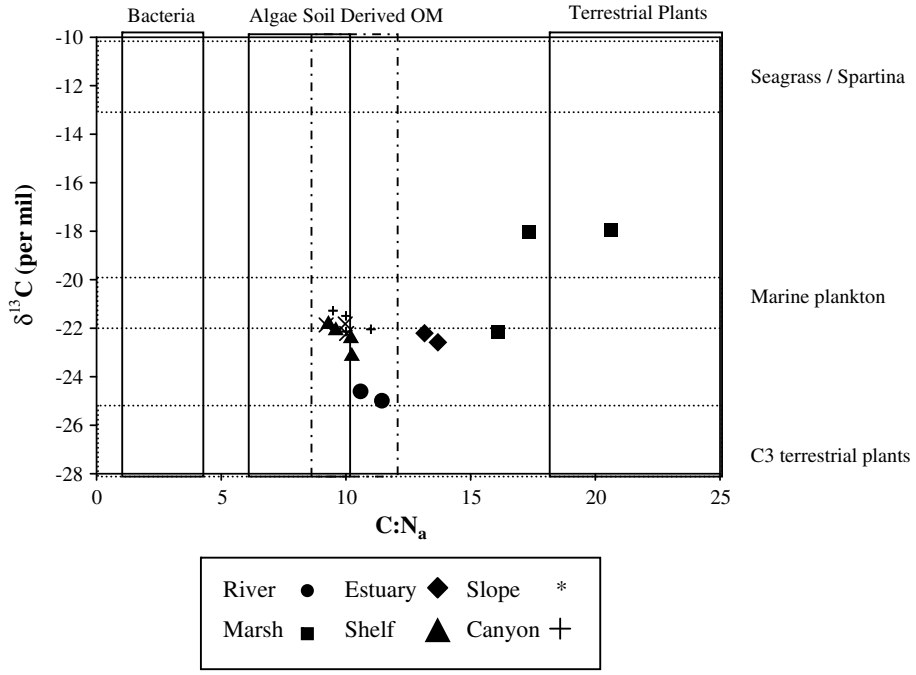

Fig. 2. Property–property plots of $\delta^{13}C$ vs. C/N_a ratios for surface sediments. The symbol types correspond to the regions identified using the bathymetric data and factor analysis (see text).

hoc tests (Fisher comparison test) indicated that the estuary and marsh regions differed from the other regions.

Sediment surface area (SSA) was lower in the marsh region (9 $m^2\ g^{-1}$, $n = 3$) than in the other regions (river: 27 $m^2\ g^{-1}$, $n = 2$; estuary: 12 $m^2\ g^{-1}$, $n = 2$; shelf: 28 $m^2\ g^{-1}$, $n = 4$; slope: 32 $m^2\ g^{-1}$, $n = 3$) ($P < 0.001$) (Table 2). In contrast, the canyon site had the highest SSA (39 $m^2\ g^{-1}$). The marsh and estuary samples had the highest OC/SSA levels (marsh: 4.7 mg m^{-2}, $n = 3$; estuary: 1.9 mg m^{-2}, $n = 2$; river: 0.7 mg m^{-2}, $n = 2$; shelf: 0.6 mg m^{-2}, $n = 4$; slope: 0.4 mg m^{-2}, $n = 3$). Excluding the River site, there was a relationship of decreasing OC/SSA with increasing distance offshore ($r^2 = 0.95$, $n = 11$, $P < 0.0001$).

$\delta^{13}C_{TOC}$ values ranged from −25‰ to −18‰ with the most depleted values at the River and SW Pass sites (−25, $n = 2$) and the most enriched values at the inner marsh and marsh sites (−18, $n = 2$; Table 2; Fig. 2). The shelf and offshore sites had intermediate $\delta^{13}C_{TOC}$ signatures (−21‰ to −22‰). Overall, $\delta^{15}N$ values ranged from −0.3‰ to +14‰, with the marsh samples having the most depleted values (−0.3‰ to 2‰), while the River sites were most enriched (12–3‰). ANOVA indicated significant differences in the isotopic composition of the different regions ($P = 0.003$ for $\delta^{13}C$; $P = 0.001$ for $\delta^{15}N$). $\delta^{13}C_{TOC}$ values for the marsh sediments were enriched relative to the other regions while the river was depleted relative to the other regions ($P < 0.05$; Fisher comparison test). Similarly, $\delta^{15}N$ values for the marsh were enriched relative to the other regions ($P < 0.05$).

3.3. Fatty acid and sterol composition

Total fatty acid (FA) abundance ranged from 30 to 142 μg g^{-1} dry sediment or 1.8 to 8.3 μg mg^{-1}_{TOC} (Fig. 3A). ANOVA indicated significant differences in the carbon normalized abundance of FA between the different regions ($P < 0.008$). The post hoc test found that canyon sediments (6.7 ± 2.2, $n = 4$) were enriched in FA relative to sediments collected from the marsh (2.6 ± 0.7, $n = 3$), river (3.9 ± 0.1, $n = 2$) and slope (3.4 ± 0.7, $n = 3$) regions. FA abundances in the shelf (6.2 ± 1.0, $n = 4$) region were significantly higher than in the marsh and slope regions. FA composition was examined by normalizing the concentration of individual or groups of FA to total FA (% total FA). Overall, saturated FA ($57 \pm 10\%$) were the most abundant class (Fig. 3A), with a dominance of short chain over long chain compounds ($70 \pm 12\%$ vs. $30 \pm 12\%$). On average, monounsaturated FA comprised $27 \pm 7\%$, while polyunsaturated and branched FA made up $8 \pm 3\%$ and $8 \pm 4\%$ of the total FA composition, respectively (Fig. 3A).

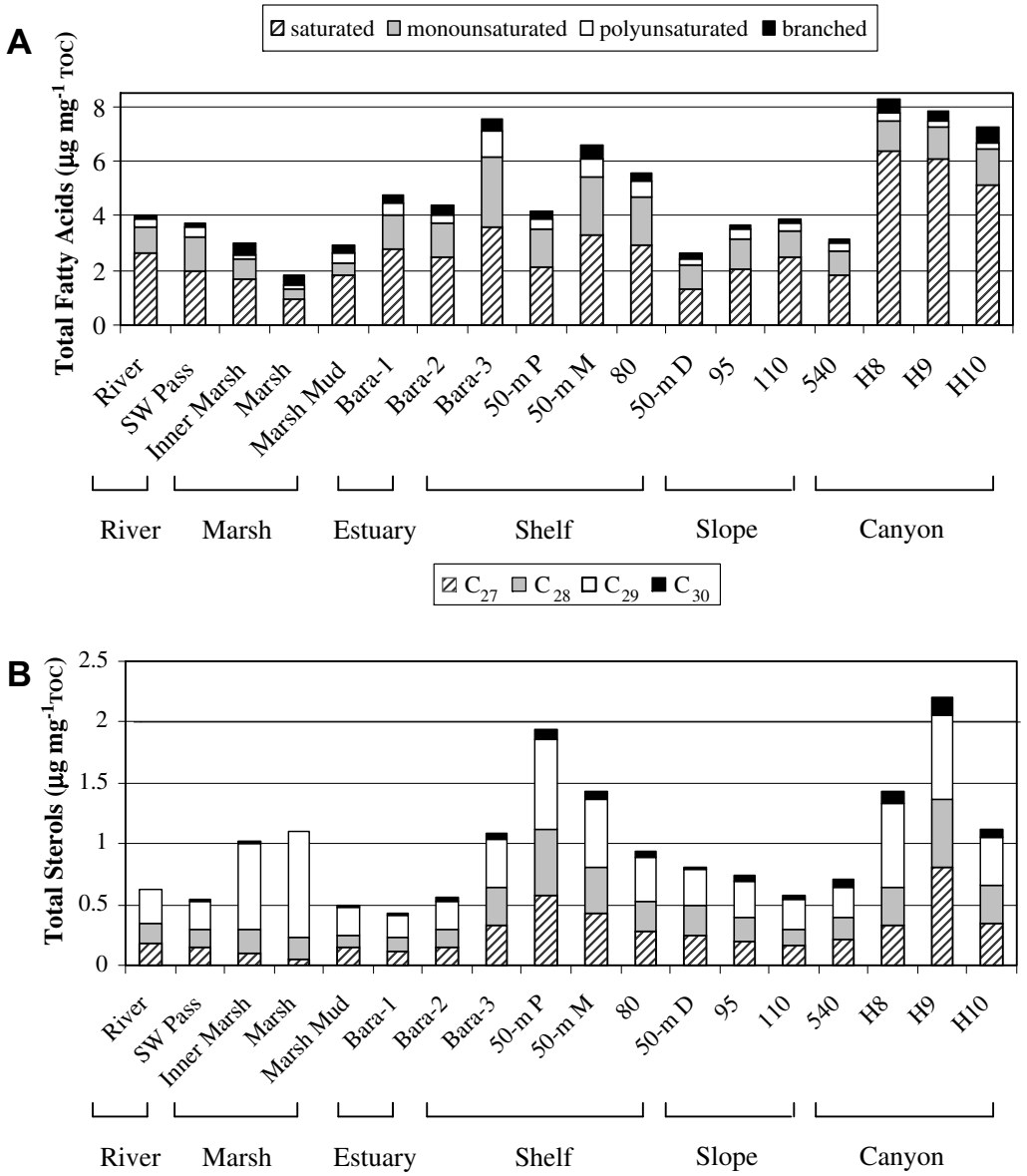

Fig. 3. (A) Total fatty acid abundance (µg mg^{-1}_{TOC} dry sediment) for each site. The fatty acid composition for the site is represented in each bar graph and was calculated by: (percent composition/100 × total fatty acid abundance (µg mg^{-1}_{TOC})). (B) Total sterol abundance (µg mg^{-1}_{TOC} dry sediment) and relative abundance of C_{27}, C_{28} C_{29}, and C_{30} compounds for each site.

Total sterol concentrations ranged from 5.2 to 78.5 µg g^{-1} dry sediment or 0.5 to 2.3 µg mg^{-1}_{TOC} (Fig. 3B). Total sterol concentrations (µg mg^{-1}_{TOC}) were similar in the canyon (1.4 ± 0.7, $n = 4$) and shelf (1.4 ± 0.5, n= 4) regions. The post hoc test identified that total sterol abundances in the canyon differed from those in the estuary (0.5 ± 0.09, $n = 2$) and river (0.6 ± 0.1, $n = 2$). The C_{29} sterols (24-ethylcholesta-5,22-dien-3β-ol and 24-ethylcholest-5-en-3β-ol) had the greatest abundance averaging $42 \pm 11\%$ (Fig. 3B). 24-Ethylcholest-5-en-3β-ol was the most abundant sterol in almost all samples except for two of the canyon sites where cholest-5-en-3β-ol (cholesterol, a C_{27} sterol) was most abundant. C_{27} and C_{28} sterols comprised $27 \pm 7\%$ and $24 \pm 3\%$, respectively, of the total sterols (Fig. 3B). Cholest-5-en-3β-ol was the second most abundant sterol at the shelf sites and SW Pass, while 24-ethyl-5α(H)-cholestan-3β-ol was the second most abundant sterol in the inner marsh and marsh samples.

3.4. Factor analysis

Together, Factors 1 and 2 explained 66% of the variation in the data. Variables with factor coeffi-

cients, or loadings that were strongly positive on Factor 1 (i.e., >0.8) included 14:0, 16:1ω−7, C_{20} polyunsaturated FA (PUFAs) (Fig. 4A, Table 3). Compounds with the most negative Factor 1 loadings included stigmasterol ($29\Delta^{5,22}$), 24-ethylcholest-5-en-3β-ol (29Δ5), *iso*-C_{14} and C_{16} branched FA, and iso and anteiso C_{15} and C_{17} branched FA (e.g., 14,16 Br. and 15,17 Br.; Fig. 4A). In general, Factor 1, explaining 45% of the variance in the data set, separated the data based on the sources they represented; biomarkers representing autochthonous (plankton and algae) had positive loadings on Factor 1 while biomarkers representing bacteria and allochthonous (vascular plant) sources had negative values (Fig. 4A, Table 3). Linear regression analysis supports this interpretation. C/N_a was inversely related to Factor 1 ($r^2 = 0.67$, $n = 18$; $P < 0.001$). With the exception of 16:0 FA and $29\Delta^{5,22}$ and 29Δ5, Factor 2 tended to separate long chain alcohols (LCOHs) and sterols from FA. 22:6ω−3, 14,16 Br and odd numbered saturated C_{13}–C_{17} FA had the most negative Factor 2 loadings.

Score plots were used to examine relationships between the factors and the sample locations (Fig. 4B). Along Factor 1, the marsh samples were resolved from samples collected from the estuarine and shelf regions. Factor 2 separated the marsh and Bara-1 and Bara-2 samples from the canyon samples. Score plots also helped to validate the site groupings. The estuary region including Bara-1 and Bara-2 grouped closely together within the score plot. The shelf samples including Bara-3, 50-m M, and 80 m also grouped together. Although the 50-m P was not in this grouping, it was still considered part of the shelf sites based on bathymetry. The 50-m D plotted closely to the 95 and 110 sites and thus was grouped with the slope sites. The canyon sites all received positive Factor 2 scores.

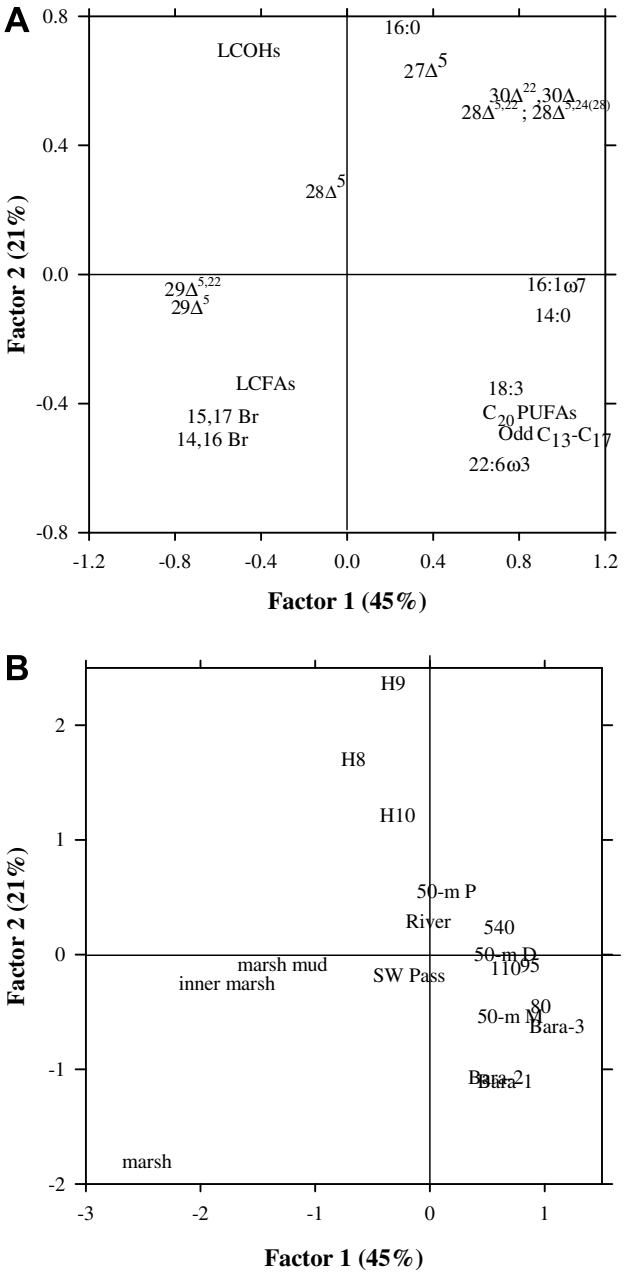

Fig. 4. (A) Results from factor analysis showing loadings for biomarker compounds. Abbreviations and sources for each compound are provided in Table 3. Factor 1 explained 45% of the variance. Biomarkers representing allochthonous (e.g., C_{29} sterols, long chain fatty acids, long chain alcohols) and bacterial sources (15,17 Br and 14,16 Br) had negative values while autochthonous (algal/plankton) sources (PUFAs, C_{28} sterols) had positive loadings. Factor 2 explained 21% of the variance. (B) Factor 1 distinguished between marsh samples and samples collected from estuary (Bara) and shelf/slope regions. Factor 2 provided greater resolution between canyon samples collected in 2004 (H8–H10) from marsh and estuary (Bara-1 and -2) samples.

4. Discussion

4.1. Elemental and isotopic composition of sediment organic matter

Overall, the C/N_a ratios ranged from 9 to 20, indicating that SOM derives from a mixture of microbial and vascular plant sources. C/N_a ratios for surface sediments showed that the marsh region had the highest ratio (18 ± 2.0, $n = 3$) and was unique within the study area (Fig. 2, Table 2). Higher plants are enriched in carbon relative to algae, with C/N_a values ranging from 20 to 500 (Hedges et al., 1997). Hence, the higher C/N_a ratios

Table 3
Variables used in factor analysis and their corresponding sources

Variable	Source[a]
$29\Delta^{5,22}$	Higher plants, freshwater algae
$28\Delta^{5}$	Higher plants, freshwater algae
LCOH	Higher plants
$29\Delta^{5}$	Higher plants, cyanobacteria
16:0	Marine algae
$27\Delta^{5}$	Zooplankton, trace in some algae
$30\Delta^{22}$; 30Δ	Dinoflagellate sterols
$28\Delta^{5,22}$; $28\Delta^{5,24(28)}$	Diatom sterols
LCFA	Higher plants
22:6ω−3	Mainly dinoflagellates
C_{20} PUFAs	Labile algal OM
14:0	Algal
18:3	Algal, some plants
Odd C_{13}–C_{17}	Bacteria
15,17 Br	Bacteria
14,16 Br	Bacteria
16:lω−7	Algal

[a] Source assignments are based on primary literature cited in Section 4.2.

found at the marsh sites are consistent with the accumulation of vascular plant detritus.

C/N_a ratios from the River and SW Pass averaged 11 ± 0.6, similar to values of 12 ± 1.3 from previous studies in the lower river (Bianchi et al., 2002). Sources of organic matter in the lower river could include soil derived organic matter from the Mississippi drainage basin, which has a C/N_a ratio between 10 and 13 (Tiessen et al., 1984; Onstad et al., 2000; Gordon and Goñi, 2004). The shelf sites in this study had C/N_a ratios ranging from 9.3 to 10.2, consistent with previous studies that found C/N_a ratios in the shelf and slope regions of the Gulf of Mexico to range between 9.4 and 10.8 (Bianchi et al., 2002; Gordon and Goñi, 2004; Wysocki et al., 2006), indicating a mixture of phytoplankton and allochthonous sources.

$\delta^{13}C_{TOC}$ values ranged from −25‰ to −18‰, similar to those measured in previous studies in the shelf and slope regions (Hedges and Parker, 1976; Bianchi et al., 2002; Gordon and Goñi, 2004). Land derived C_3 plants have $\delta^{13}C_{TOC}$ values of −28‰ to −25‰ while marine plankton range from −22‰ to −19‰ (Hedges et al., 1997). Seagrasses have an isotopic signature of −14‰ to −10‰ (Thayer et al., 1978; Canuel and Martens, 1993) and *Spartina alterniflora*, the dominant macrophyte found in salt marshes in this region, has $\delta^{13}C_{TOC}$ values of −13‰ (Currin et al., 1995; Canuel et al., 1997). When the $\delta^{13}C_{TOC}$ and C/N_a data for surface sediments are examined together (Fig. 2), we find that the marsh region is characterized by enrichments in $\delta^{13}C_{TOC}$ and elevated C/N_a, indicating unique carbon sources to this region. These values are consistent with contributions from marsh macrophytes, seagrasses and/or benthic microalgae ($\delta^{13}C = -15$‰) (Currin et al., 1995). In comparison, $\delta^{13}C_{TOC}$ signatures for the river and SW Pass sites were depleted (−25‰), suggesting contributions from terrigenous C_3 plants and/or freshwater algae. Values for the shelf, slope and canyon sites were intermediate and ranged between −23 and −21‰, similar to marine plankton, but also consistent with a mixture of C_3 and C_4 plant sources (Goñi et al., 1998).

Overall, the C/N_a ratios indicate that the marsh and river regions were enriched in contributions from higher plants; however, the isotopic signatures ($\delta^{13}C_{TOC}$) suggest that the sources of OM to the marsh differ from those to the river region. Our data are consistent with contributions from salt marsh macrophytes like *S. alterniflora* in the marsh region, while contributions from a mixture of C_3 and C_4 plants and soil organic matter are likely more important in the river. In contrast, the elemental and isotopic signatures for organic matter at the shelf, slope and canyon sites were consistent with autochthonous sources or may reflect a mixture of sources including C_3 and C_4 plants as well as plankton (Goñi et al., 1997, 1998). Lipid biomarkers were used to further elucidate OM sources; specifically, these compounds were used to identify the fraction of organic carbon deriving from algal and vascular plant sources.

4.2. Sediment organic matter source assignments

Fatty acids (FA) were grouped to represent potential OM sources as follows: short chain even and odd numbered FA (C_{12}–C_{16}, SCFA) represented contributions from autochthonous (algal + bacterial) sources, branched FA (*iso*- and *anteiso*-C_{15} and C_{17} FA) corresponded to bacterial contributions, polyunsaturated fatty acids (C_{20} and C_{22} PUFA) were attributed to labile plankton derived OM, and long chain even numbered FA (C_{24}–C_{28}, LCFA) represented allochthonous sources (Volkman et al., 1980; Volkman, 1986; Canuel and Martens, 1993; Zimmerman and Canuel, 2001). Sterols representative of autochthonous sources included compounds typically attributed to diatoms and/or other microalgae (e.g., 24-methylcholesta-5,22E-dien-3β-ol and 24-methylcholesta-

5,24(28)-dien-3β-ol: $28\Delta^{5,22}$, and $28\Delta^{5,24(28)}$), sterols known to occur in dinoflagellates (4α,23,24-trimethylcholest-22E-en-3β-ol and 4α,23,24-trimethyl-5α(H)-cholestan-3β-ol: $30\Delta^{22}$ and $30\Delta^{0}$) and cholest-5-en-3β-ol ($27\Delta^{5}$), the major sterol in crustaceans such as zooplankton (Volkman, 1986; Volkman et al., 1998; Killops and Killops, 1993). For this study, we assigned 24-ethylcholesta-5,22E-dien-3β-ol ($29\Delta^{5,22}$) and 24-ethylcholest-5-en-3β-ol ($29\Delta^{5}$), as well as 24-methylcholest-5-en-3β-ol ($28\Delta^{5}$) to allochthonous sources (Volkman, 1986; Volkman et al., 1998). However, it is important to note that these compounds may also occur in some species of algae and cyanobacteria, although they are generally not dominant in these sources (see below).

Biomarkers provide a useful tool for characterizing organic matter sources; however, care must be taken in assigning sources. Ideally, source assignments should be corroborated across compound classes and between biomarker and bulk measurements (Canuel, 2001 and references therein). In this study, $29\Delta^{5}$ contributed 16–43% of total sterols. However, previous studies have indicated that this compound can derive from higher plant sources (Bae and Mercer, 1970; Wannigama et al., 1981; Volkman, 1986) as well as cyanobacteria and algae (Volkman, 1986; Volkman et al., 1998; Canuel and Martens, 1993). Cyanobacteria have been documented in shelf waters of the Gulf of Mexico (Rabalais et al., 1998). To examine the sources of this sterol more closely, the abundance of $28\Delta^{5,22}$, a biomarker for microalgae (particularly, diatoms), was compared to the abundance of $29\Delta^{5,22}$, a biomarker representing vascular plant sources. $29\Delta^{5,22}$ had the most negative score in the factor analysis, which separated terrigenous from algal biomarkers. $29\Delta^{5,22}$ abundances were greater than $28\Delta^{5,22}$ in the river and marsh regions while $28\Delta^{5,22}$ abundances were higher in the shelf and slope regions. Furthermore, $28\Delta^{5,22}$ had a positive relationship ($r^2 = 0.93$, $n = 16$; $P = 0.0001$) with $29\Delta^{5}$ in shelf and slope regions, but not in river and marsh regions. In contrast, $29\Delta^{5,22}$ was positively related ($r^2 = 0.98$, $n = 16$; $P < 0.0001$) to $29\Delta^{5}$ in river and marsh regions, suggesting vascular plant sources for this compound at these sites. These relationships suggest that inputs from cyanobacteria or microalgae other than diatoms may contribute to the concentration of $29\Delta^{5}$ found at shelf and slope regions. Thus, in this study, $29\Delta^{5}$ is derived from both allochthonous and autochthonous contributions but in widely differing amounts depending on the region being examined (Volkman, 1986).

In addition to examining SOM sources for each compound class based on the concentration of individual or groups of biomarkers, we quantified the relative proportion of allochthonous (vascular plant) vs. autochthonous (algal/bacterial) sources using three approaches (Table 4). We calculated the relative proportion of C_3 plants derived from allochthonous vs. autochthonous sources using the bulk $\delta^{13}C_{TOC}$ data and a two end member mixing model where C_3 plants from terrigenous and marine sources were assumed to have $\delta^{13}C_{TOC}$ values of −26‰ and −20‰, respectively (Hedges et al., 1997). These calculations were applied to all regions (river, estuary, shelf, etc.) except for the marsh region samples (inner marsh and marsh) where we used values for end members representing salt marsh plants (−13‰) and C_3 terrigenous plants (−26‰) (Currin et al., 1995; Canuel et al., 1997; Hedges et al., 1997). In addition to using the $\delta^{13}C_{TOC}$ values, we apportioned allochthonous and autochthonous sources using the percent contribution of LCFA and SCFA, TAR_{FA} and the percent contribution of allochthonous and autochthonous sterols (Table 4, Fig. 5).

The proportion of autochthonous and allochthonous sources of organic matter in the river and marsh samples were variable (±22%) both within regions and across the estimates derived from the three approaches ($\delta^{13}C_{TOC}$, fatty acids, and sterols) (Table 4 and Fig. 5). Results from $\delta^{13}C_{TOC}$ and the two end member mixing model indicate that vascular plant sources are elevated within the river and marsh regions (80% and 51%, respectively). In contrast, estimates using FAME suggest lower contributions of vascular plant OM to these regions (39% allochthonous OM for the river and marsh sites, respectively) (Fig. 5A and B). The differences are not surprising given the number of sources and potential overlaps in source assignments, particularly in the river and marsh habitats (Canuel et al., 1995, 1997). An additional factor contributing to the different outcomes from these calculations is that the isotope mixing model likely underestimates riverine algal sources. $\delta^{13}C_{TOC}$ values for riverine algae can vary substantially depending on the isotopic signature of dissolved inorganic carbon (Spiker, 1980; Canuel et al., 1995; Raymond and Bauer, 2001) and overlap with the value we assigned to allochthonous sources. Thus, the proportion of autochthonous and allochthonous sources based

Table 4
Proportion of autochthonous and allochthonous sources of SOM

Region	Station	$\delta^{13}C_{TOC}$[a]		Fatty acids[b]			Sterols[c]	
		% Autochthonous	% Allochthonous	% Autochthonous	% Allochthonous	TAR_{FA}	% Autochthonous	% Allochthonous
River	River	23	77	60	40	0.7	54	46
	SW Pass	17	83	63	37	0.5	51	49
	Mean	*20*	*80*	*62*	*39*	*0.6*	*53*	*48*
Marsh	Inner marsh	61	39	55	45	0.6	20	80
	Marsh	62	38	49	51	0.9	11	89
	Marsh mud	30	70	45	55	1.1	52	48
	Mean	*51*	*49*	*50*	*50*	*0.9*	*28*	*72*
	SD	*18*	*18*	*5.0*	*5.0*	*0.3*	*21.5*	*21.5*
Estuary	Bara-1	57	43	68	32	0.4	*62*	38
	Bara-2	63	37	*66*	34	0.4	63	37
	Mean	*60*	*40*	*67*	*33*	*0.4*	*63*	*38*
Shelf	Bara-3	69	31	84	16	0.2	64	36
	50-m P	47	53	77	23	0.3	67	33
	50-m M	65	35	76	24	0.2	70	30
	80 m	60	40	73	27	0.3	*66*	34
	Mean	*60*	*40*	*78*	*23*	*0.2*	*67*	*33*
	SD	*9.6*	*9.6*	*4.7*	*4.7*	*0.1*	*2.5*	*2.5*
Slope	50-m D	69	31	78	22	0.2	*66*	34
	95 m	63	37	70	30	0.4	69	31
	110 m	70	30	*66*	34	0.4	69	31
	Mean	67	33	71	29	0.3	68	32
	SD	3.8	3.8	6.1	6.1	0.1	1.7	1.7
Canyon	540 m	79	21	71	29	0.4	73	27
	H8	75	25	88	12	0.2	58	42
	H9	*66*	34	88	12	0.2	68	32
	H10	64	36	86	14	0.2	67	33
	Mean	*71*	*29*	*83*	*17*	*0.2*	*67*	*34*
	S.D.	*7.2*	*7.2*	*8.2*	*8.2*	*0.1*	*6.2*	*6.2*

[a] Autochthonous and % allochthonous calculated by isotope mass balance (see text for details). Note that % autochthonous represents C_4 marsh plants in marsh region.

[b] % Autochthonous = even- and odd-numbered saturated SCFA (C_{12}–C_{18}) and % allochthonous = even- and odd-numbered saturated LCFA (C_{22}–C_{30}) normalized to total saturated fatty acids; $TAR_{FA} = (C_{24} + C_{26} + C_{28})/(C_{12} + C_{14} + C_{16})$.

[c] % Autochthonous = cholest-5-en-3β-ol, 24-methylcholesta-5,22-dien-3β-ol, 24-methylcholesta-5,24(28)-dien-3β-ol, 4α,23,24 -trimethylcholest-22-en-3β-ol, 24-nor-5α-cholest-22-en-3β-ol, cholesta-5,22-dien-3β-ol, 5α -cholestan-3β-ol, 24-methylcholest-22-en-3β-ol, 23,24-dimethylcholesta-5,22-dien-3β-ol, 4α,23,24-trimethyl-5α (H)-cholestan-3β-ol, 24-norchlolesta-5,22-dien-3β-ol, 5α(H)-cholest-22-en-3β-ol normalized to total sterols analyzed; % Allochthonous = 24-methyl cholest-5-en-3β -ol, 24-ethylcholesta-5,22-dien-3β -ol, 24-ethylcholest-5-en-3β-ol normalized to total sterols analyzed.

on the fatty acid and sterol data may be more reliable in this region. However, the source estimates based on the biomarkers may also be biased by the fact that autochthonous sources are likely enriched in lipid relative to allochthonous sources. Overall, there are pros and cons to each of the approaches ($\delta^{13}C_{TOC}$, fatty acids and sterols) that make it difficult to conclude which estimate of % allochthonous organic matter is most reliable and we advocate a multi-tracer approach is most reliable in these regions.

SOM in the estuary, shelf, slope and canyon regions was dominated by autochthonous sources (60–83%) with a general trend of % autochthonous sources increasing with distance offshore during our study (Table 4 and Fig. 5). Within these offshore regions the levels of variability within and across the three calculations were generally lower (2–10%; Table 4), indicating greater homogeneity in the source composition of the SOM in these regions. Previous studies have shown that these regions are characterized by high primary production (Rabalais

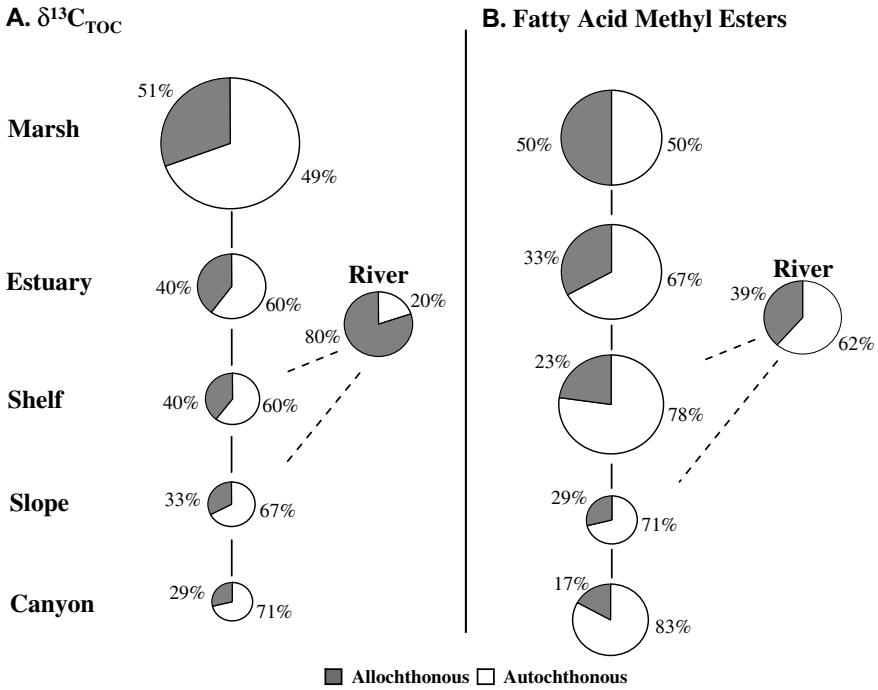

Fig. 5. Autochthonous and allochthonous contributions calculated from $\delta^{13}C$ isotopic mixing model and percent abundance of SCFA and LCFA (see Table 4). The size of the pie represents the %TOC content of surface sediment within regions for the isotopic image (A). For the fatty acid methyl esters (B), the size of the pie is based on total fatty acids (ng g^{-1} dry weight sediment). Hypothesized route of carbon delivery from the marsh and estuarine regions is represented by the solid black lines while dotted lines represent the hypothesized flow path for river organic matter to offshore regions.

et al., 1998; Lohrenz et al., 1999; Dagg et al., 2004). Consistent with these findings, surface fluorescence was highest in estuary and shelf regions during our study (Table 1). Together, these findings support the dominance of autochthonous sources in these regions

Total FA abundance was highest in the inshore regions but decreased by ~50% from the shelf to the slope region (Fig. 5). In contrast, TOC content decreased continuously along the marsh–canyon transect and did not exhibit a dramatic decrease from the shelf to slope regions. Interestingly, total FA (ng g^{-1} dry weight sediment) increased from the slope to canyon, suggesting a preferential accumulation of labile OM in the canyon region. This is consistent with the presence of an active benthic community at this site (Bianchi et al., 2006). Although the proportion of autochthonous sources increased with distance offshore, biomarkers representing vascular plant/soil OM were abundant at even the most distal shelf and canyon regions. The two end member mixing model indicated that 29% of the TOC in the canyon was allochthonous while 17% and 34% of the fatty acid and sterol biomarkers, respectively, were derived from allochthonous sources (Table 4 and Fig. 5). It is important to note that these calculations are conservative because they assume algal/bacterial biomarkers represent *in situ* autochthonous sources. In reality, a portion of the algal material in the slope and canyon regions may be derived from the highly productive plume water on the shelf (Bianchi et al., 2006).

4.3. Terrigenous sources of organic carbon (OC_{terr})

Sites with the most negative Factor 1 scores (marsh) had the highest concentrations of terrigenous plant sterols (μg $mg^{-1}{}_{TOC}$) and were characterized by the highest ratios of TAR_{FA} (Figs. 3 and 4 and Table 4), consistent with contributions from terrigenous (vascular plant) sources. Additionally, the river and SW Pass sites were characterized by moderately negative scores on Factor 1 and high ratios of TAR_{FA}. C/N_a and $\delta^{13}C_{TOC}$ analyses were consistent with higher contributions of vascular plant derived OM to the river and marsh regions although $\delta^{13}C_{TOC}$ signatures revealed differences in the sources of OM (marsh plants vs. terrigenous C_3 plants and/or soil OM). Despite differences in $\delta^{13}C_{TOC}$, both regions are dominated by the same sterols ($29\Delta^5$, $29\Delta^{5,22}$, 27Δ). This is not surprising

because marsh plants and terrigenous plants have similar sterol compositions, while isotopic signatures of these sources differ (Canuel and Martens, 1993; Canuel et al., 1997). Thus the combination of these methods provides insights not possible with each alone.

Previous studies have found greater allochthonous contributions inshore by the Mississippi River mouth (Hedges and Parker, 1976; Gearing et al., 1977; Bianchi et al., 1997; Goñi et al., 1998; Gordon and Goñi, 2004; Mead and Goñi, 2006). Early studies suggested that allochthonous organic carbon (OC_{terr}) was deposited on the inner continental shelf of the Gulf of Mexico and that little of this organic carbon was transported to the outer shelf or slope (Hedges and Parker, 1976; Gearing et al., 1977). More recent investigations have shown that OC_{terr}, particularly those fractions associated with fine grained sediments, may be delivered to outer continental shelf and slope regions (Prahl and Muehlhausen, 1989; Goñi et al., 1997, 1998; Gordon and Goñi, 2004). Using lignin oxidation products and radiocarbon data, Goñi et al. showed that C_3 and C_4 plant materials of "old" radiocarbon ages were transported to shelf and slope regions (Goñi et al., 1997, 1998). This OC_{terr} likely derives from soils in the watershed of the Mississippi River. Consistent with the study by Goñi et al., Bianchi et al. (1997) found non-woody angiosperms were the dominant form of vascular plant material transported to sediments in deeper regions of the Gulf of Mexico (i.e., Texas shelf).

Our biomarker results provide further support for offshore delivery of OC_{terr} (Fig. 5). The slope and canyon regions including 50-m D, 95 m, 110 m and 540 m canyon were characterized by fine grained sediments with high sediment surface area (Table 2) and have signatures consistent with contributions from allochthonous sources (Figs. 3 and 5). The likely mechanism for transporting OC_{terr} to these offshore regions is hydrodynamic sorting, the process by which organic rich material associated with finer grained sediments is carried further offshore (Keil et al., 1994, 1998). On the Washington coast, Prahl and colleagues showed that highly degraded, fine grained terrestrial material was transported offshore to the slope regions due to hydrodynamic sorting (Prahl, 1985; Prahl et al., 1992). Using lignin phenols, Bianchi et al. (2002) found that hydrodynamic sorting removed large woody particles of angiosperm origin, reducing the amount of coarser terrigenous material carried out to the Gulf of Mexico slope. More recently, Gordon and Goñi (2004) also found that hydrodynamic sorting controlled the fate of terrestrial organic matter in the Northern Gulf of Mexico.

4.4. Aquatic (algal/plankton) sources of SOM

The deltaic margin within the Gulf of Mexico region is characterized by high productivity due to the influence of the Mississippi River (Lohrenz et al., 1990, 1994). Previous studies have found high productivity ($>10\ g\ C\ m^{-2}\ d^{-1}$) within the shelf region of the Gulf of Mexico during summer months (July–August 1990) (Lohrenz et al., 1999). Bara-3, 50-m M, 50-m P, and 80 m are located within the shelf region (24–85 m deep), with salinity values ranging from 16 to 23, where high primary productivity occurs (Lohrenz et al., 1999). These sites grouped together in our factor analysis and had the highest concentrations ($\mu g\ mg^{-1}$ OC) of SCFA and algal sterols. Low ratios of TAR_{FA} also indicate that the dominant sources for these sites were likely algal/bacterial in origin.

In our study, average surface water fluorescence ($0.12 \pm 0.08\ mg\ m^{-3}$) for the slope and canyon sites (95, 110, 540 m) was lower than for sites located on the shelf (Bara-3, 50-m P, 50-m M) ($0.64 \pm 0.12\ mg\ m^{-3}$), indicating lower contributions from algal production in the slope/canyon regions during the sampling period (Table 1). However, algal material from the highly productive shelf and river regions may be transported to the deeper, offshore regions (Bianchi et al., 2006). Average concentrations of plankton sterols (shelf: $504 \pm 172\ ng\ mg^{-1}$ TOC; slope: $274 \pm 40\ ng\ mg^{-1}$ TOC) and SCFAs (shelf: $1762 \pm 396\ ng\ mg^{-1}$ TOC; slope: $903 \pm 183\ ng\ mg^{-1}$ TOC) were lower in slope vs. shelf sediments. These distributions could reflect increased effects of diagenesis, resulting in selective degradation of the plankton lipids. At offshore sites, the sediment accumulation rates are lower than at the shelf sites ($0.39\ cm\ yr^{-1}$ for the canyon and $5.9\ cm\ yr^{-1}$ for 50-m P (Allison et al., 2007), allowing increased oxygen exposure and more time for degradation to occur in the surfacemost oxygenated sediments (Hedges et al., 1999). There is also more bioturbation at the 540 m canyon site, evidenced by abundant worm tubes and macrofauna (Bianchi et al., 2006), also promoting decomposition of labile organic matter.

Only one other study in the Gulf of Mexico region has used lipid biomarker compounds to

investigate OM sources. Mead and Goñi (2006) used lipids in their investigation of pre (March 2001)- and post (October 2002)-hurricane effects on SOM off the Atchafalaya River. Based on total characterizable lipids, Mead and Goñi (2006) found zooplankton ($C_{27\Delta}{}^{5}$) and dinoflagellates to be important sources of sterols in the surface sediment samples they investigated. Diatom sterols were less abundant. In contrast, our results indicate diatoms dominated the algal material farther west where our sediments were collected. Diatom sterols had a positive relationship with 16:1ω−7 ($r^2 = 0.81$, $n = 18$; $P < 0.00001$), a fatty acid proxy for algal and bacterial material (Perry et al., 1979; Killops and Killops, 1993). Diatom sterols were also positively related to PUFAs ($r^2 = 0.6$, $n = 18$; $P = 0.0004$), indicating that diatom production contributed to the higher concentration of fresh OM (PUFAs) in the surface sediments. Wysocki et al. (2006) found diatoms made up > 80% of phytoplankton community in surface waters along the Louisiana shelf during the spring 2000 sampling season. They also found that much of the phytodetritus in surface sediment was diatom in origin (Wysocki et al., 2006).

Cyanobacteria are known to be an important source of primary production in the Gulf of Mexico (Rabalais et al., 1998). However, because of their small cell size, they may be more effectively consumed and/or decomposed in the water column rather than being delivered to the sediments. It has been suggested in previous studies in oceanic regions that food webs consisting of larger plankton, specifically diatoms, may attribute disproportionately to the export of OC out of surface waters (Buesseler, 1998). Previous studies in the Gulf of Mexico region have shown that much of the *in situ* productivity associated with the Mississippi River plume that supports carbon flux is comprised of diatoms (Lohrenz et al., 1999), consistent with our results.

In addition to spatial variability in SOM sources to the Gulf of Mexico, we found evidence for temporal variability. The canyon samples collected in 2003 (540 m) and October 2004 (H8, H9, H10) differed in composition indicating temporal changes in the delivery and storage of algal/plankton OM. Samples H8, H9, and H10 were collected one month following Hurricane Ivan. During our 2003 sampling, the presence of labile algal biomarkers and ^{7}Be inventories (Bianchi et al., 2006) suggested recent accumulation. Interestingly, PUFAs were less abundant in 2004 than in 2003 while sterol biomarkers showed the opposite trend. Because of the low rate of production in the surface waters of the offshore region, the algal biomarkers collected in 2004 appear to be more refractory (sterols and 16:0 FA) relative to those collected in 2003 (PUFAs) suggesting they may derive from redistribution of sediments from productive shelf/plume regions (Bianchi et al., 2006). In addition to the high concentrations of algal biomarker compounds in the 2004 canyon samples, terrigenous plant biomarkers were also elevated compared to the other slope sites within this region, further illustrating the seasonal and inter-annual variation that occurs within the system.

5. Summary

Utilizing lipid biomarker compounds, $\delta^{13}C_{TOC}$ and C/N ratios, this study provided baseline information for characterizing the sources of organic matter associated with recently deposited sediments in the Mississippi River–Gulf of Mexico region. Sources were quantified using both a two end member $\delta^{13}C_{TOC}$ isotopic mixing model and by partitioning autochthonous and allochthonous sources using fatty acid and sterol biomarkers. Our results show allochthonous material from the Mississippi River is delivered throughout the shelf to the canyon region. Additionally, diatom production from the productive shelf region is delivered to the canyon. This supplies the canyon with fresh OM as evidenced by an active benthic community in 2003. However, the region is physically dynamic and processes such as hydrodynamic sorting and sediment redistribution play important roles in transport of OM to offshore regions. By further elucidating OC sources within this region, carbon budgets for river dominated ocean margins can be improved. Future research inspired by this project should include analysis of seasonal changes in organic material accumulation, as well as a more thorough examination of non-steady state processes and the role of episodic events.

Acknowledgements

We thank our collaborators Tom Bianchi, Stuart Wakeham, Mead Allison, and Brent McKee for their assistance during sample collection and insights they contributed to our interpretation of the data. We also thank the crew of the *R.V. Pelican,*

lab groups of Drs. Allison, McKee and Bianchi for sampling assistance while on the cruise and Troy Sampere for further sample and data assistance. This work constituted a portion of E.J. Waterson's M.S. thesis and benefited from comments provided by Rebecca Dickhut, Hugh Ducklow, and John Milliman. We thank Tom Bianchi and Stuart Wakeham for comments on the original manuscript as well as Mark Yunker, John Volkman and an anonymous reviewer for their contributions to improving this manuscript. This research was supported by NSF grant OCE-0223295 to E.A.C. Additional support was provided by the Virginia Institute of Marine Science. This paper is Contribution 2908 of the Virginia Institute of Marine Science, The College of William and Mary.

Associate Editor—**John K. Volkman**

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