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Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico

ELIZABETH S. GORDON* and MIGUEL A. GOÑI

Department of Geological Sciences and Marine Science Program, University of South Carolina, Columbia, SC 29208, USA

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Abstract—Suspended sediments (SS) from the Atchafalaya River (AR) and the Mississippi River and surficial sediment samples from seven shallow cross-shelf transects west of the AR in the northern Gulf of Mexico were examined using elemental (%OC, C/N), isotopic ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$), and terrigenous biomarker analyses. The organic matter (OM) delivered by the AR is isotopically enriched ($\sim -24.5\%$) and relatively degraded, suggesting that soil-derived OM with a C4 signature is the predominant OM source for these SS. The shelf sediments display OC values that generally decrease seaward within each transect and westward, parallel to the coastline. A strong terrigenous C/N (29) signal is observed in sediments deposited close to the mouth of the river, but values along the remainder of the shelf fall within a narrow range (8–13), with no apparent offshore trends. Depleted stable carbon isotope ($\delta^{13}\text{C}$) values typical of C3 plant debris (-27%) are found near the river mouth and become more enriched (-22 to -21%) offshore. The spatial distribution of lignin in shelf sediments mirrors that of OC, with high lignin yields found inshore relative to that found offshore (water depth > 10 m).

The isotopic and biomarker data indicate that at least two types of terrigenous OM are deposited within the study area. Relatively undegraded, C3 plant debris is deposited close to the mouth of the AR, whereas more degraded, isotopically enriched, soil-derived OM appears to be deposited along the remainder of the shelf. An important input from marine carbon is found at the stations offshore from the 10-m isobath. Quantification of the terrigenous component of sedimentary OM is complicated by the heterogeneous composition of the terrigenous end-member. A three-end-member mixing model is therefore required to more accurately evaluate the sources of OM deposited in the study area. The results of the mixing calculation indicate that terrigenous OM (soil-derived OM and vascular plant debris) accounts for $\sim 79\%$ of the OM deposited as inshore sediments and 66% of OM deposited as offshore sediments. Importantly, the abundance of terrigenous OM is 40% higher in inshore sediments and nearly 85% higher in offshore sediments than indicated by a two-end-member mixing model. Such a result highlights the need to reevaluate the inputs and cycling of soil-derived OM in the coastal ocean. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

Organic matter (OM) burial in marine sediments represents the predominant long-term sink in the global biogeochemical cycle of reduced carbon. Deltaic and shelf sediments, which receive large inputs of both autochthonous and allochthonous materials, account for $\sim 90\%$ of organic carbon (OC) burial in the ocean (Bernier, 1982, 1989; Hedges and Keil, 1995). Delineating the processes that affect OM burial in these sediments is therefore essential for a quantitative understanding of the global carbon cycle. Despite its geochemical significance, the mechanisms that control OM burial are still poorly understood. A number of factors that influence the preservation of OM in marine sediments have been proposed, such as sedimentation rate, primary productivity rate, water column depth, oxygen exposure time, OM source, and OM sorption to mineral surfaces (e.g., Emerson and Hedges, 1988; Henrichs, 1992; Aller, 1994; Canfield, 1994; Mayer, 1994; Hedges and Keil, 1995; Hartnett et al., 1998; Hedges et al., 1999). Characterizing the sources of OM delivered to the coastal ocean and defining the processes that affect its ultimate burial may provide better constraints on the mechanisms that underlie OM preservation in the ocean.

A number of techniques have been employed to examine the sources of OM in marine sediments, including bulk measurements (e.g., Gearing et al., 1977; Ruttenberg and Goñi, 1997) and molecular tracers (e.g., Hedges and Parker, 1976; Hedges and Mann, 1979a; Gough et al., 1993; Prahl et al., 1994; Goñi et al., 1998, 2000). A shortcoming of many of these studies is the underlying assumption that a simple two-end-member mixing model in which vascular plant debris is diluted by marine phytoplankton detritus can describe the composition of OM in coastal marine sediments. Such an assumption may have led to an overall underestimate of terrigenous contributions to the OM present in ocean margin sediments. Questions therefore remain regarding the inputs, distribution, and fate of land-derived OM in the ocean (e.g., Hedges et al., 1997).

The study of OM burial in coastal marine sediments is complicated by seasonal and interannual variability in river runoff, primary productivity, and storm-driven sediment resuspension, which affect the input, dispersion, and cycling of sedimentary OM in these coastal environments. Understanding how these factors ultimately control the preservation of OM in coastal seasonal sedimentation requires a multidisciplinary approach and has been the focus of our ongoing work in the northern Gulf of Mexico (Goñi et al., 1998; Allison et al., 2000; Gordon et al., 2001). In this study, we examine the sources of OM delivered to and deposited as surface sediments on the

* Author to whom correspondence should be addressed (gordon@geol.sc.edu).

inner Louisiana shelf, west of the Atchafalaya River (AR). We use elemental, isotopic, and terrigenous biomarker data to evaluate OM origins and to quantify the relative importance of terrigenous and marine OM in these coastal sediments. Specifically, we focus on the analysis of lignin-derived cupric oxide (CuO) oxidation products as a means of tracing the contributions of vascular plant-derived carbon to the OM in shelf sediments. Lignin, a macromolecule uniquely synthesized by vascular plants, has been used as a tracer of terrigenous OM in rivers (Hedges et al., 1986; Goñi et al., 2000; Onstad et al., 2000), estuaries (Goñi and Thomas, 2000), and the coastal and open ocean (e.g., Hedges and Parker, 1976; Hedges and Mann, 1979a; Gough et al., 1993; Prahl et al., 1994; Goñi et al., 1997, 1998). Besides indicating terrigenous provenance, compositional parameters based on the yields of lignin-derived phenols provide qualitative estimates of vegetation sources and of the degradative state of terrigenous OM.

In addition to these lignin-derived products, CuO oxidation yields compounds derived from non-lignin sources that are routinely quantified. These include a suite of *p*-hydroxybenzenes, which are in part derived from the CuO oxidation of aromatic amino acids such as phenylalanine and tyrosine. These compounds have been obtained in high yields from protein-rich samples, such as plankton and bacteria, relative to their recoveries from nitrogen-poor samples, such as vascular plant tissues (Goñi and Hedges, 1992, 1995). Another important category of non-lignin oxidation products includes the benzoic acids, which are derived from non-lignin aromatic biopolymers, such as tannins and aromatic humic substances. These compounds have been obtained from the CuO oxidation of OM sources such as brown macroalgae and in certain vascular plant tissues, such as tree barks (Goñi and Hedges, 1992, 1995). The benzoic acids are also present in relatively high yields in the reaction product suites from highly degraded samples such as soils and humic substances (e.g., Prahl et al., 1994). These non-lignin-derived compounds are used in the present study to further evaluate the provenance of OM present in riverine and coastal sediments from the northern Gulf of Mexico.

2. METHODS

2.1. Study Area

The area of study is the inner Louisiana shelf west of the AR (Fig. 1). The AR is the main distributary of the Mississippi River (MR), branching from the main stem near Simmesport, Louisiana. The Red River flows into the AR below its branch point from the MR, and the Red-Atchafalaya flow is maintained at ~30% of the combined flows of all three rivers. The Mississippi-Atchafalaya river system (MARS) drains ~40% of the continental United States and includes a large portion of North America's grasslands (Fig. 1). The vegetation distribution within the drainage basin includes both C3 and C4 species of grasses, with the C3 grasses dominating the northern latitudes and C4 grasses becoming more abundant in the southern regions (Teeri and Stowe, 1976).

Maximum discharge of the AR typically occurs between January and June, with its peak flow in April. The sediment from the AR (67×10^{12} g y^{-1} , Roberts et al., 1997) is discharged ~150 km west of the Mississippi delta into a system of shallow (1–4 m) bays before export onto the low-gradient continental shelf. Approximately half of the AR sediment load is transported westward along the coast within the Atchafalaya "mud stream" (Wells and Kemp, 1981). The prevailing direction of the mud stream is westward, but strong north and northwesterly winds associated with cold front passages (20–30 events per

year) may temporarily interrupt the direction of this flow such that it is forced southeastward (Walker and Hammack, 2000). Such winter storms also cause the resuspension of bay sediments, which are then flushed onto the inner shelf by the strong north and northwesterly winds (Roberts et al., 1997). Walker and Hammack (2000) estimated that ~12% of the annual AR discharge is flushed from the bay onto the shelf during cold front passages.

The seasonal variability in river discharge and storm-driven resuspension results in the accumulation of flood layers in shelf sediments (Allison et al., 2000). Allison et al. (2000) suggested that flood layers, up to several centimeters thick at inshore locations (<10 m water depth), are deposited between March and April, coincident with high AR discharge and a decrease in storm activity. As a result, the short-term sediment accumulation rates, calculated from ^{7}Be penetration, are 2 to 6 times greater than the long-term ^{210}Pb accumulation rates, a finding that underscores the intensity of sediment reworking in this region.

The distribution of OM in Louisiana shelf sediments follows the pattern of sediment dispersal throughout the study area (Gordon et al., 2001). The short-term OC deposition rates in March and April are higher than long-term OC accumulation rates. However, such seasonal variability in deposition is not reflected in the elemental and isotopic compositions of shelf sediments outside the Atchafalaya delta region, which were found to be comparable during four separate sampling trips (Gordon et al., 2001). In addition to sediment transport processes, OM turnover plays an important role in the OM cycling in the study area. Particulate OM budgets indicate that OM loss, either through remineralization or solubilization, is slightly higher than that produced through primary productivity and results in the burial of only 5% of the combined riverine and marine OM inputs to the study area (Gordon et al., 2001).

2.2. Sample Description

Suspended sediments (SS) were collected from the mouth of the AR in October 1997 and March and April 1998 using the ship's flow-through system (3 m below the water's surface). SS were also collected from a site upstream from the mouth in January 1998. MR SS were collected from two sites (Venice and Vicksburg, Louisiana) during January 1998 (Table 1). After collection, samples were stored in carboys under dark and cool conditions during transport to the laboratory, where the SS were then recovered from the water via settling and centrifugation (3500 rpm for 10 min).

Shelf sediments were collected from several stations located along seven shore-normal transects across the inner Louisiana shelf, adjacent to the mouth of the AR (Fig. 1, Table 2). Surficial sediment samples (0 to 5 cm) were collected in water depths of 5 to 25 m using a Ponar grab sampler during March 1998. At four sites (MI6, WH6, WL1, WH1), surficial samples (0–1 cm) were collected via a 50 × 50 cm box corer. Sediments were refrigerated during transport back to the laboratory, then stored frozen until analysis. All sediment samples were oven dried (55°C), and a portion of the dried sediment was ground to pass a 60-mesh (250 μm) sieve before elemental, isotopic, and biomarker analyses.

2.3. Analytical Methods

2.3.1. Elemental Analysis

OC and total nitrogen (TN) contents were measured on vapor phase-acidified samples (Hedges and Stern, 1984) by high-temperature combustion on a PerkinElmer 2400 elemental analyzer. The average standard deviation of each measurement, determined by replicate analysis of the same sample, was 0.02 wt.%.

2.3.2. Stable Carbon Isotopes

Samples were acidified with 1 N HCl to remove inorganic carbon before carbon isotopic measurements. Stable carbon isotope composition of the sedimentary OM was determined by online combustion in a Fisons elemental analyzer interfaced to a VG Optima stable isotope ratio mass spectrometer. The $^{13}\text{C}/^{12}\text{C}$ ratio is expressed in per mil relative to the Pee Dee belemnite standard by the conventional δ nota-

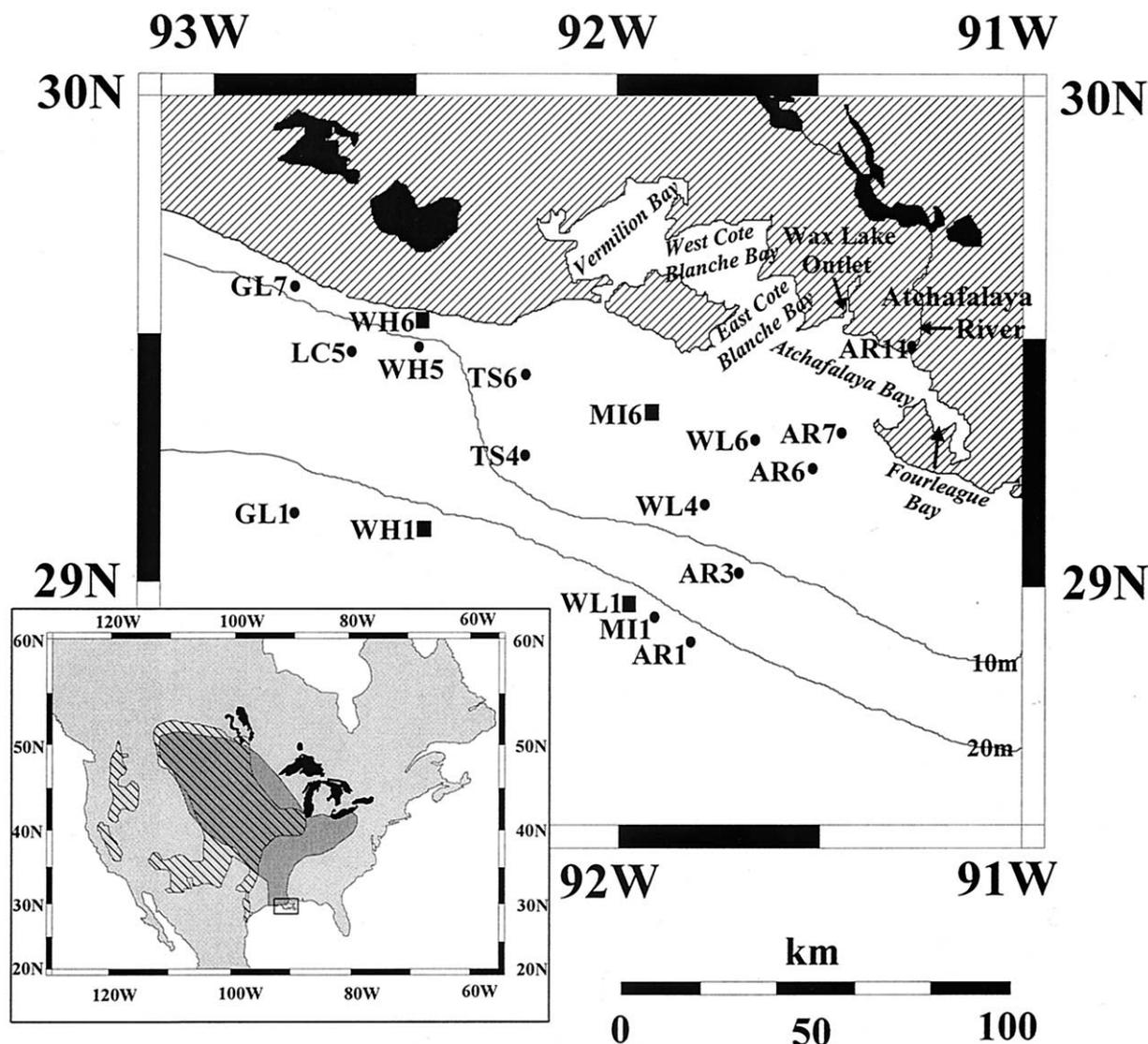


Fig. 1. Map of the study area in the Gulf of Mexico. The dark gray region of North America (inset) represents the Mississippi River watershed, and the hatched area represents the grasslands. Each box core station is indicated by a square symbol, and each grab station is indicated by an enclosed circle. The name of each transect is indicated: AR = Atchafalaya River; WL = Wax Lake; MI = Marsh Island; TS = Trinity Shoal; WH = White Lake; LC = Lake Constance; GL = Grand Lake.

tion. Analytical precision, determined by replicate analysis of the same sample, was 0.3%.

2.3.3. Brunauer-Emmett-Teller (BET) Surface Area

Mineral surface area was determined using a Coulter SA3100 surface area analyzer. Approximately 1 g of unground sediment was out-gassed at 250°C for 1 h under vacuum. Surface area was then determined by a five-point BET multilayer adsorption analysis (Brunauer et al., 1938; Mayer, 1994), which involves five separate injections of a known volume of N₂ gas to the evacuated tube, kept at a constant temperature with liquid N₂. Analytical precision, determined from triplicate analysis of the same sample, was 0.1 m²/g. The accuracy of the Coulter SA3100 was periodically assessed by analyzing alumina powder standards (Coulter Corp.), which showed that measurements had an average error of < 3%. It should be noted that OM was not removed before surface area analyses. The effect of sample pretreatment on its surface area and elemental composition was examined

using a subset of samples from the study area (unpublished data). The results indicated that in addition to removing OM from the mineral surface, peroxide treatment appeared to remove inorganic constituents such as carbonate and silica. The samples in the present study were therefore not treated before surface area determination to avoid introducing experimental error into the surface area measurement.

2.3.4. CuO Oxidation

CuO oxidations were performed using the microwave digestion system described by Goffi and Montgomery (2000). Approximately 400 mg of sediment were oxidized under alkaline (2 N NaOH) conditions with CuO at 150°C for 1.5 h in N₂-pressurized Teflon vessels. A recovery standard composed of ethylvanillin and transcinamic acid was added to each vessel immediately following oxidation. After separating the solid residues by centrifugation, the aqueous hydrolysates were acidified with concentrated HCl to pH 1. The CuO oxidation products were separated from the aqueous phase by thorough extraction

Table 1. River suspended sediment station locations.

Station	ID	Date of sampling	Latitude (°N)	Longitude (°W)	AR discharge, TOS ^a (m ³ /s)	MR discharge, TOS ^b (m ³ /s)
AR mouth	AR11 10/97	29 Oct 97	29.48	91.27	2830	6510
MR, Vicksburg	MVi	28 Jan 98	32.31	90.91	12,120	28,180
AR, Wax Lake	AWL	30 Jan 98	29.70	91.37	11,100	26,420
MR, Venice	MVe	31 Jan 98	29.27	89.35	10,390	24,350
AR mouth	AR11 3/98	06 Mar 98	29.48	91.27	9850	23,390
AR mouth	AR11 4/98	28 Apr 98	29.48	91.27	11,130	25,340

AR = Atchafalaya River; MR = Mississippi River. Discharge data at time of sampling (TOS) obtained from Army Corps of Engineers, New Orleans District (<http://www.mvn.usace.mil.gov>).

^a Discharge measured at Simmesport, Louisiana (30.98°N, 91.80°W), below the divergence from the Mississippi main stem.

^b Discharge measured at Tarbert Landing, Mississippi (31.00°N, 91.62°W).

with ethyl acetate, which was blown to dryness under a continuous N₂ stream and redissolved in pyridine. The extracts were stored frozen until gas chromatography (GC) analysis. Before GC analyses, the CuO oxidation products were derivatized with bis(trimethylsilyl) trifluoroacetamide + 1% trimethylchlorosilane at 60°C for 10 min and injected into an HP6890 GC equipped with a 60-m DB1 column (J&W Scientific) using either on-column or splitless injection. Quantification of CuO reaction products was based on the flame ionization detector response of commercially available high-purity standards, which were analyzed as standard mixtures by the GC (two standard mixtures per day). Compound identification was verified by GC mass spectrometry using a Varian Saturn 2000 ion trap GC mass spectrometer. Using this procedure, the carbon-normalized yields of eight lignin-derived reaction products, including vanillyl (V) phenols (vanillin, acetovanillone, vanillic acid), syringyl (S) phenols (syringaldehyde, acetosyringone, syringic acid), and cinnamyl (C) phenols (*p*-coumaric acid, ferulic acid; Hedges and Mann, 1979b), were estimated. In addition, the yields of *p*-hydroxybenzenes (P) (*p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, *p*-hydroxybenzoic acid) and other benzoic acids (B) (benzoic acid, *m*-hydroxybenzoic acid, 3,5-dihydroxybenzoic acid) that are derived from non-lignin precursors (e.g., Goñi and Hedges, 1995) were quantified. In this paper, the yields of these major reaction product categories are presented, but individual compound data are available upon request.

2.3.5. Radiocarbon Analysis

Radiocarbon analyses were performed at the National Ocean Sciences Accelerator Mass Spectrometry facility at Woods Hole Oceanographic Institution following established procedures (Vogel et al., 1987; McNichol et al., 1992). CO₂ gas, produced by the combustion of sedimentary OC, was converted to graphite via Fe/H₂ catalytic reduction. The graphite was pressed into accelerator mass spectrometry targets and analyzed on the accelerator mass spectrometer. Radiocarbon values are reported as $\Delta^{14}\text{C}$ (‰) and radiocarbon age, according to Stuiver and Polach (1977) and Stuiver (1980).

2.3.6. Statistical Treatment of Data

The propagation of error associated with ratios involving independent variables, such as %OC and %TN, was calculated according to statistical theory (Taylor, 1982). Statistical differences between samples were evaluated using standard *t*-tests. Throughout the paper, statistically significant differences are discussed that are within the 95% confidence interval.

Table 2. Inner Louisiana shelf station locations.

Station	Date	Core interval (cm)	Latitude (°N)	Longitude (°W)	Water depth (m)	Salinity ^a (‰)
AR7	06 Mar 98	0–5	29.31	91.44	6.2	7.3
Atchafalaya delta and bay region						
AR6	06 Mar 98	0–5	29.23	91.52	6.4	18.8
AR11	06 Mar 98	0–5	29.48	91.27	7.2	0.0
Shoal stations						
WL4	07 Mar 98	0–5	29.16	91.78	7.7	29.2
TS4	07 Mar 98	0–5	29.26	92.23	4.8	27.6
Inshore stations						
WL6	07 Mar 98	0–5	29.29	91.66	5.2	20.8
MI6	07 Mar 98	0–1	29.35	91.91	5.3	15.9
TS6	07 Mar 98	0–5	29.43	92.23	7.1	21.1
WH6	07 Mar 98	0–1	29.52	92.48	6.2	11.6
GL7	08 Mar 98	0–5	29.61	92.80	6.7	23.4
Offshore stations						
AR1	06 Mar 98	0–5	28.88	91.82	23.5	34.0
AR3	06 Mar 98	0–5	29.02	91.70	11.8	28.0
WL1	07 Mar 98	0–1	28.95	91.97	22.1	34.4
MI1	07 Mar 98	0–5	28.92	91.91	22.4	34.2
WH1	08 Mar 98	0–1	29.11	92.48	21.7	33.7
WH5	07 Mar 98	0–5	29.48	92.49	10.9	25.9
LC5	08 Mar 98	0–5	29.48	92.66	12.6	30.3
GL1	08 Mar 98	0–5	29.14	92.80	22.8	33.0

Station abbreviations as in Fig. 1.

^a Salinity measured at the bottom of the water column.

Table 3. Elemental and isotopic compositions of river suspended and surficial shelf sediment samples. One standard deviation about the mean is reported in parentheses for samples that were processed in replicate. The standard deviation reported for C/N was calculated on the basis of propagation of error.

Station	%OC salt free	%TN salt free	C/N (atomic)	$\delta^{13}\text{C}$ (‰)	BET SA (m ² /g)	$\Delta^{14}\text{C}$ (‰)	¹⁴ C age (yr before present)
River suspended sediments							
AR11 10/97	1.84	0.20	10.7 (1.0)	-25.0	24.9 (0.7)	-278.4	2570
AR11 3/98	1.43	0.15	11.1 (1.4)	-24.9	38.7	-185.2	1600
AR11 4/98	1.88	0.21	10.4 (1.0)	-23.8	30.4	-244.9	2210
AR, Wax Lake	1.14	0.12	11.1 (2.0)	-24.6	37.4 (0.7)		
MR, Venice	1.68	0.16	12.2 (1.5)	-24.7	30.9		
MR, Vicksburg	1.87	0.16	13.6 (1.7)	-25.0	25.2 (0.7)		
AR SS avg.	1.72	0.19	10.6	-24.6	31.3	-236.2	2127
AR7	5.42	0.22	29.0 (2.7)	-26.9	13.0 (1.1)	-146.0	1220
Atchafalaya delta and bay region							
AR6	1.60	0.18	10.3 (1.2)	-23.4	32.3		
AR11	0.85	0.08	12.2 (3.0)	-23.7	22.1 (1.2)	-236.5	2120
Delta avg.	1.22	0.13	11.3	-23.5	27.2		
Shoal stations							
WL4	0.10	0.02	6.0 (6.2)	-21.2	2.3		
TS4	0.20	0.02	10.2 (9.2)	-21.4	3.1		
Shoal avg.	0.15	0.02	8.1	-21.3	2.7		
Inshore stations							
WL6	1.13	0.11	12.4 (2.3)	-22.4	31.1		
MI6	1.35	0.17	9.1 (1.1)	-22.5	38.0	-203.3	1780
TS6	1.15	0.14	9.4 (1.3)	-22.4	35.1		
WH6	1.28	0.13	11.4 (1.7)	-22.6	44.4	-222.7	1970
GL7	1.18	0.16	8.7 (1.1)	-22.3	46.6	-213.1	1880
Inshore avg.	1.22	0.14	10.2	-22.4	39.0	-213.0	1877
Offshore stations							
AR1	0.84	0.09	10.9 (2.5)	-21.7	23.2	-249.2	2250
AR3	0.89	0.09	11.4 (2.5)	-21.3	20.4		
WL1	0.67	0.10	7.9 (1.6)	-21.2	19.8	-278.3	2570
MI1	0.72	0.10	8.7 (1.8)	-21.3	20.3		
WH1	0.55	0.08	8.0 (2.0)	-21.3	14.5	-252.9	2290
WH5	1.42	0.20	8.4 (0.9)	-22.3	38.0		
LC5	1.05	0.14	8.9 (1.3)	-21.6	n.m.		
GL1	0.31	0.04	9.3 (4.9)	-21.1	11.4	-278.0	2570
Offshore avg.	0.79	0.11	8.9	-21.5	21.2	-264.6	2420

BET SA = surface area determined by the Brunautt-Emmett-Teller method; AR SS = Atchafalaya River suspended sediments; n.m. = not measured.

2.3.7. Principal Components Analysis (PCA)

PCA was performed on the elemental, stable carbon isotopic, and biomarker data. CuO oxidation products were normalized to OC (mg/100 mg OC), and all variables were mean centered before PCA. PCA was performed using XLSTAT, an add-in software package for Microsoft Excel (Addinsoft Corp.).

3. RESULTS

3.1. River SS

The OC content of the SS from the AR mouth varied between 1.4% (March 1998) and 1.9% (October 1997 and April 1998), with an average of 1.7% (Table 3). TN content ranged between 0.15% (March 1998) and 0.21% (October 1997 and April 1998). The MR SS displayed similar values, but lower OC and TN contents were measured in the Wax Lake SS. The resulting atomic carbon-to-nitrogen ratios (C/N) ranged between 10 and 14 for each sample. The stable carbon isotope composition of the SS varied within a narrow range (-24 to -25‰; Table 3). The radiocarbon compositions of the AR mouth SS showed considerable variation, from -185.2 to -278.4‰, with corresponding ¹⁴C ages that ranged between 1600 yr before present (March 1998) and 2570 yr before

present (October 1997). BET surface area also showed a wide range of 25 to 39 m²/g for both AR and MR SS. Such wide ranges highlight the seasonal variability in the delivery of terrigenous OM from the MARS drainage basin.

The CuO oxidation of SS yielded a suite of lignin-derived compounds that include the V, S, and C phenols, as well as non-lignin-derived products such as P and B (Table 4). The carbon-normalized yields of S were the highest (≥ 1.2 mg/100 mg OC) in all SS samples, followed by V yields (≥ 0.9 mg/100 mg OC). C phenols were obtained in much lower yields (0.14 to 0.33 mg/100 mg OC). On average, the combined lignin-derived products (A = S + V + C) accounted for 76% of the CuO products quantified from the river samples. The carbon-normalized yields of the non-lignin-derived CuO products P and B from river SS samples ranged from 0.4 to 0.65 mg/100 mg OC and from 0.37 to 0.49 mg/100 mg OC, respectively.

3.2. Surficial Shelf Sediments

The OC contents of all surficial shelf sediments (Table 3) were lower than the average %OC of AR SS, with the exception of one sample (station AR7). OC contents in shelf sedi-

Table 4. Molecular composition of river suspended and surficial sediment samples. One standard deviation about the mean is reported in parentheses for samples that were processed in replicate.

Station	S (mg/100 mg OC)	V (mg/100 mg OC)	C (mg/100 mg OC)	A (mg/100 mg OC)	B (mg/100 mg OC)	P (mg/100 mg OC)
River suspended sediments						
AR11 10/97	1.43	1.27	0.33	3.03	0.49	0.65
AR11 3/98	1.66	1.38	0.18	3.22	0.48	0.47
AR11 4/98	1.19	0.90	0.14	2.23	0.42	0.46
AR, Wax Lake	1.63	1.38	0.17	3.19	0.46	0.49
MR, Venice	1.31	1.01	0.16	2.47	0.39	0.41
MR, Vicksburg	1.60	1.25	0.19	3.04	0.37	0.40
AR SS avg.	1.43	1.18	0.22	2.82	0.46	0.53
AR7	13.31 (1.77)	11.64 (2.40)	0.32 (0.07)	25.26 (4.25)	0.32 (0.15)	0.65 (0.00)
Atchafalaya delta and bay region						
AR6	1.88	1.78	0.40	4.06	0.36	0.88
AR11	1.50	1.60	0.36	3.45	0.48	0.55
Delta avg.	1.69	1.69	0.38	3.76	0.42	0.72
Shoal stations						
WL4	0.23	0.30	0.04	0.57	0.58	1.39
TS4	0.28	0.24	0.04	0.56	0.22	0.63
Shoal avg.	0.25	0.27	0.04	0.56	0.40	1.01
Inshore stations						
WL6	1.26	1.16	0.32	2.73	0.38	0.92
MI6	1.07 (0.10)	0.89 (0.07)	0.22 (0.04)	2.18 (0.21)	0.45	0.38 (0.10)
TS6	0.79	0.70	0.20	1.69	0.30	0.69
WH6	0.77 (0.03)	0.72 (0.02)	0.20 (0.03)	1.69 (0.08)	0.30	0.30 (0.04)
GL7	0.61	0.61	0.14	1.36	0.34	0.85
Inshore avg.	0.90	0.81	0.22	1.93	0.36	0.63
Offshore stations						
AR1	0.47	0.40	0.08	0.96	0.42	0.33
WL1	0.51 (0.05)	0.43 (0.04)	0.09 (0.02)	1.03 (0.11)	0.37 (0.03)	0.33 (0.08)
MI1	0.57 (0.09)	0.49 (0.05)	0.09 (0.00)	1.14 (0.14)	0.35 (0.06)	0.53 (0.28)
WH1	0.42 (0.02)	0.44 (0.02)	0.11 (0.01)	0.97 (0.05)	0.15 (0.00)	0.34 (0.11)
WH5	0.58	0.53	0.15	1.26	0.44	1.22
LC5	0.44	0.40	0.12	0.96	0.28	0.49
GL1	0.54 (0.08)	0.44 (0.02)	0.09 (0.01)	1.08 (0.11)	0.38 (0.04)	0.86 (0.70)
Offshore avg.	0.50	0.45	0.10	1.06	0.34	0.59

S = syringyl phenols; V = vanillyl phenols; C = cinnamyl phenols; A = sum of syringyl, vanillyl, and cinnamyl phenols; B = benzoic acids; P = p-hydroxybenzenes; AR SS = Atchafalaya River suspended sediments.

ments ranged from 0.1 to 1.4%, with greater %OC at the inshore stations than the offshore stations and generally decreasing seaward within each transect and westward parallel to the coastline. An exception to this trend was seen in the AR transect, where the %OC was low (0.8%) at the mouth of the AR, increased to a maximum of 5.4% ~26 km from the river mouth (station AR7), then decreased seaward. The TN content of all shelf sediments ranged between 0.02 and 0.22%. The nitrogen measured in these sediments appears to be associated with OM (Gordon et al., 2001), so we equate the organic nitrogen content with the measured nitrogen values. The atomic C/N ratios ranged from 10 to 29 along the AR transect. C/N ratios along the rest of the shelf varied between 6 and 12, with most samples exhibiting values that were statistically indistinguishable from the shelf average of 10 (Table 3). Depleted stable carbon isotope values (-27 to -23% ; Table 3) were observed along the Atchafalaya transect, particularly at station AR7. The values along the remainder of the shelf fell within a range of -23 to -20% . The isotopic composition of the shelf sediments were generally more enriched westward along the coast and seaward within each transect.

Mineral surface area values were higher at the inshore stations than at the offshore stations (Table 3). Surface area values at the inshore stations were all > 30 m²/g and increased westward along the coast to values at the distal stations that

were greater than those of the river SS. The surface area values at the offshore stations were lower than those inshore and ranged between 10 and 25 m²/g. Stations along the AR transect ranged between 20 and 32 m²/g, except at station AR7 (surface area = 13 m²/g). Anomalously low values were observed at two shelf stations, WL4 and TS4 (~ 3 m²/g), which contained sandy sediment and shell fragments.

The radiocarbon compositions ($\Delta^{14}\text{C}$) of the surficial shelf sediments ranged between -146.4 and -275.2% , with corresponding ¹⁴C ages that ranged between 1220 and 2570 yr before present (Table 3). The youngest age was observed at station AR7, located 26 km from the mouth of the AR, with the remainder of shelf sediments falling within the age range observed for the river SS. The ¹⁴C ages of the offshore sediments were generally greater than those of the inshore stations, but a systematic spatial trend with ¹⁴C age was not apparent.

The yields of the five different CuO product categories from shelf sediments were spatially variable (Table 4), with some notable trends. The combined lignin phenol yields (Λ , mg/100 mg OC) ranged between 0.6 and 25 mg/100 mg OC (Table 4). The lowest values were observed at stations WL4 and TS4, and the highest value was measured at station AR7. The sediments along the remainder of the shelf showed lignin contents between 0.9 and 4.1 mg/100 mg OC, with values decreasing

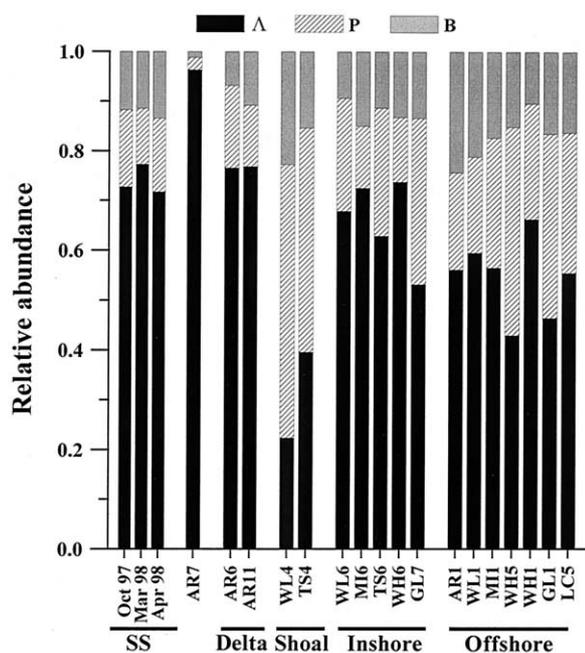


Fig. 2. Relative CuO reaction product abundance. The relative abundance of lignin-derived phenols (shown as Λ , the sum of syringyl, vanillyl, and cinnamyl phenols) and nonlignin CuO products (*p*-hydroxybenzenes and benzoic acids). The station identity is indicated on the x-axis, grouped into river suspended sediments, Atchafalaya delta and bay sediments (AR11 and AR6), shoal (WL4, TS4), inshore (<10 m water depth), and offshore (>10 m water depth) stations. Station AR7 is graphed separately because of its anomalous composition.

westward along the coast and seaward within each transect. Non-lignin P products ranged from 0.3 to 1.4 mg/100 mg OC, with the higher values generally obtained from the stations farther from the river mouth and delta. B yields were lower than P, ranging from 0.2 to 0.6 mg/100 mg OC. The higher B yields were generally measured at the more distal stations relative to those at the river mouth.

The relative abundance of each lignin and non-lignin compound class is illustrated in Figure 2. There is an overall similarity in the compositions of river SS and delta sediments, in which lignin phenols represent ~70 to 75% of the CuO products quantified, with lower contributions from P and B (~5 to 10% each). The compositions of the two inshore stations located immediately to the west of the AR delta (WL6 and MI6) are similar to the compositions of the river samples, with the exception of slightly higher P yields. Despite its proximity to the river mouth, the molecular composition of sediments at AR7 is distinct from river SS. At this location, as expected by the extremely high Λ values, lignin phenols account for an overwhelming 96% of the CuO products. Significantly lower contributions of lignin-derived phenols and higher abundances of non-lignin CuO products characterize the compositions of the remainder of the shelf sediments. Such compositions indicate that lignin-poor OM sources become relatively more important in the locations distal from the river mouth, with the notable exception of WH6 sediments that display a CuO product signature similar to that of river SS and delta sediments.

Among shelf sediments, the composition of WL4 sediments is uniquely characterized by the elevated contributions of P

and, to a lesser extent, B. The sediments at this site were sandy and characterized by very low OC contents and low surface area (Table 3). Other sediments, such as TS4 and GL1, which have similar bulk composition to WL4 (low surface area and low %OC), are characterized by relatively low lignin phenol contributions ($\Lambda = 40$ and 46% of CuO products, respectively). All three of these stations are associated with high-energy regions of the shelf (shoals and sand bars), indicating that both the amount of OC and the composition of the OM are influenced by the hydrodynamic conditions of the sedimentary environment. The remainder of the shelf sediments, both at inshore stations and those offshore from the 10-m isobath, display compositions that are characterized by lower Λ contributions (~60% of total CuO products) and elevated P and B abundances (~35 and 20%, respectively) relative to the river SS and delta surficial sediment samples.

3.3. PCA

PCA has been used in geochemical studies to determine the factors controlling OM composition, particularly in estuarine and coastal environments (e.g., Yunker et al., 1995; Goñi et al., 2000; Canuel, 2001). PCA is similarly used in the present study to elucidate the factors that are primarily responsible for influencing OM composition in the river SS and shelf sediments. Initial PCA of the AR SS and shelf sediments indicated AR7 as a unique sample with strong terrigenous character that projected separately from the rest. To prevent a single sample from biasing the PCA results and to better illustrate the trends of the majority of samples, the PCA was ultimately performed after excluding AR7. The PCA results (Fig. 3) are focused on the first two principal components, which together explain 78% of the variance in the data set. All eight lignin-derived phenols, as well as *p*-hydroxyacetophenone, plot within a tight cluster on the right side of the PCA diagram (Fig. 3a). OC and TN are highly correlated ($r^2 = 0.96$) and plot together in the lower right quadrant of the diagram. Several non-lignin oxidation products, including *m*-Bd and 3,5-Bd, fall within the upper right portion of the diagram in close proximity to the lignin-derived phenols. These compounds have been obtained from the CuO oxidation of brown macroalgae, as well as from terrigenous sources such as plant tissues and humic substances (Goñi and Hedges, 1995). Given the correlation between these compounds and the lignin-derived phenols (Fig. 3a), it seems likely that *m*-Bd and 3,5-Bd are derived from terrigenous rather than marine sources in the present study area.

Two other non-lignin oxidation products, Bd and PI, plot in the upper left quadrant of the PCA diagram. Both compounds have been measured among the CuO oxidation products of amino acids such as phenylalanine and tyrosine (Goñi and Hedges, 1995) and have been shown to be strong tracers of marine OM in coastal sediments (Goñi et al., 2000). The first component thus appears to separate compounds with marine character (negative loadings, left side of plot) from those of terrigenous character (positive loadings, right side of the plot).

The sample PCA plot (Fig. 3b) similarly separates samples by their marine vs. terrigenous character. The river SS project on the right portion of the diagram, indicating strong terrigenous character. Sediment from stations AR6 and AR11 also plot within the terrigenous portion of the diagram, consistent

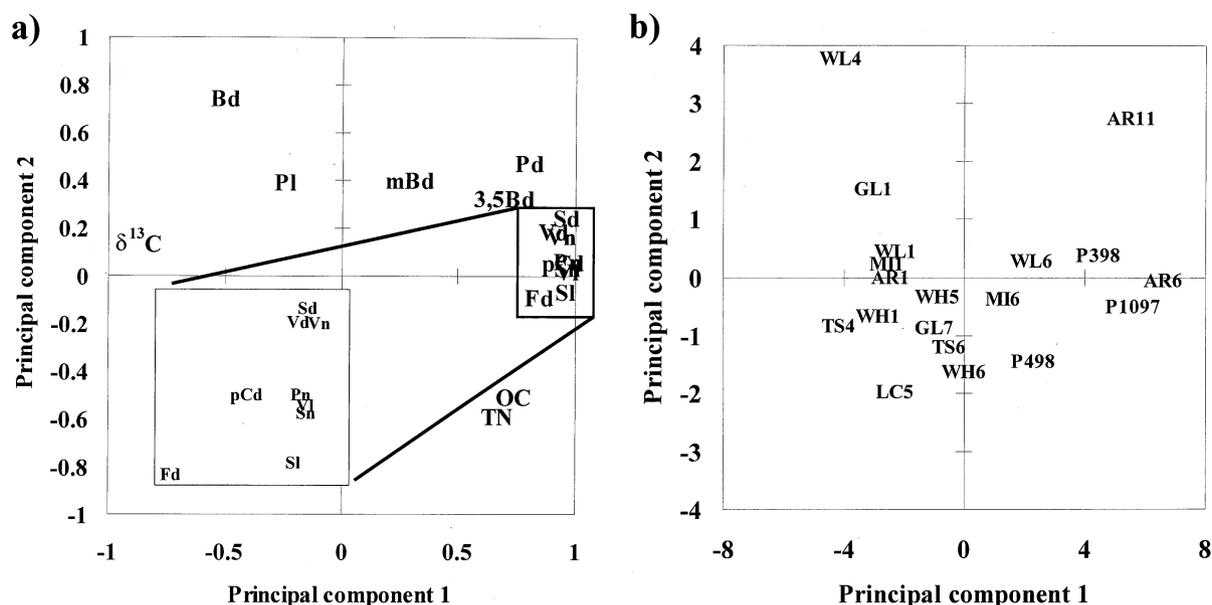


Fig. 3. Principal components diagram. (a) Variable principal components plot. Each variable is indicated on the diagram. The inset is an enlargement of the boxed portion of the plot. (b) Sample principal components plot. The samples are indicated on the diagram.

with their proximity to the AR mouth. The samples located shoreward of the 10-m isobath project in the right portion of the diagram and trend toward the lower left quadrant with increasing distance from the mouth of the river (WL6 through GL7). Such a trend is consistent with the delivery of terrigenous materials to distal, inshore stations by the Atchafalaya mud stream. The samples located seaward of the 10-m isobath, including WL1, MI1, WH1, AR1, LC5, and GL1, along with the shoal stations WL4 and TS4, plot in left quadrant of the diagram. These stations appear to be more strongly influenced by the input of marine carbon than the inshore stations, consistent with the lower abundance of lignin phenols at these sites (Table 4). The composition of sediments deposited at WL4, which plots in the upper left quadrant, is indicative of a strong marine character. The PCA results thus indicate that the inshore stations contain a greater proportion of terrigenous carbon than offshore sediments, which are composed of more marine-derived OM.

4. DISCUSSION

4.2. OM Sources in River SS

4.2.1. AR

To better understand the role of deltaic and shelf environments in the global carbon cycle, it is necessary to delineate the origins of OM supplied to and preserved within coastal marine sediments. The chemical characterization of riverine OM delivered to the study area is a necessary first step toward identifying these sources. The AR SS are isotopically enriched (-24.5‰) relative to SS from other rivers, such as the Columbia (-25.5‰ , Hedges and Mann, 1979a), the Eel (-25.2‰ , Leithold and Hope, 1999), the MacKenzie (-26.5‰ , Ruttenberg and Goñi, 1997) and the Amazon (-27 to -28‰ , Hedges

et al., 1986). Enriched isotopic compositions have also been reported for SS from the MR ($\sim -20\text{‰}$, Ruttenberg and Goñi, 1997) and many of its tributaries (-18.5 to -26.4‰ , Onstad et al., 2000) and have been attributed to the contribution of C4 plant-derived carbon from the MARS drainage basin. C4 plants are more isotopically enriched (average $\delta^{13}\text{C} = -13\text{‰}$) than C3 plants (average $\delta^{13}\text{C} = -27\text{‰}$) because of differences in their respective biosynthetic pathways. C4 grasses, which are abundant in the MARS drainage basin (see Fig. 1; Teeri and Stowe, 1976), likely impart an enriched isotopic signature on the SS of the river system. Careful evaluation of OM sources to shelf sediments that receive potentially significant inputs of this isotopically enriched source is therefore required.

The elemental and isotopic compositions of SS from the MR and its tributaries were also examined by Kendall et al. (2001), who reported more depleted $\delta^{13}\text{C}$ values for the main stem (-24.6 to -26.8‰) and tributaries (-22.6 to -32.1‰) than Onstad et al. (2000). The authors noted the seasonal variability in isotopic composition of the SS and suggested that a greater contribution by plankton to riverine OM occurs during spring and summer than during fall and winter. The authors concluded that nearly 50% of riverine OM is plankton derived, with the remainder composed of terrigenous plant matter, soil OM, and macrophytic material. Such a sizable contribution from river plankton seems unlikely given that productivity in the MR is generally light limited (e.g., Knowlton and Jones, 2000). Further, given that Kendall et al. (2001) suggested that plankton productivity is highest during the period of low river flow, the contribution from riverine plankton to the annual OM load of MARS is likely minimal compared to that from terrigenous OM sources from the drainage basin.

The vegetation sources of terrigenous OM may be qualitatively assessed by examining the relative abundance of the

Table 5. Lignin compositional parameters. One standard deviation about the mean is reported for samples that were processed in replicate, calculated by propagation of error.

Station	S/V	C/V	3,5 Bd/V	Ad/Al _(s)	Ad/Al _(v)
River suspended sediments					
AR11 10/97	1.13	0.26	0.31	0.50	0.54
AR11 3/98	1.20	0.13	0.25	0.40	0.56
AR11 4/98	1.31	0.16	0.35	0.37	0.46
AR, Wax Lake	1.18	0.12	0.24	0.38	0.57
MR, Venice	1.29	0.15	0.28	0.39	0.47
MR, Vicksburg	1.28	0.15	0.21	0.34	0.39
AR SS avg.	1.22	0.18	0.30	0.42	0.52
AR7	1.15 (0.28)	0.03 (0.01)	0.02 (0.01)	0.26 (0.10)	0.24 (0.16)
Atchafalaya delta and bay region					
AR6	1.06	0.22	0.17	0.37	0.42
AR11	0.94	0.22	0.20	0.67	0.61
Delta avg.	0.99	0.22	0.18	0.52	0.52
Shoal stations					
WL4	0.78	0.13	1.06	1.09	0.56
TS4	1.14	0.17	0.47	0.34	0.37
Shoal avg.	0.96	0.15	0.76	0.71	0.47
Inshore stations					
WL6	1.09	0.27	0.21	0.34	0.35
MI6	1.22 (0.15)	0.25 (0.05)	0.27	0.38 (0.09)	0.46 (0.04)
TS6	1.14	0.29	0.26	0.34	0.35
WH6	1.08 (0.05)	0.28 (0.05)	0.27	0.40 (0.05)	0.44 (0.06)
GL7	1.01	0.23	0.37	0.48	0.43
Inshore avg.	1.10	0.26	0.28	0.38	0.40
Offshore stations					
AR1	1.17	0.19	0.58	0.66	0.47
WL1	1.19 (0.17)	0.22 (0.05)	0.47 (0.07)	0.69 (0.21)	0.60 (0.14)
MI1	1.15 (0.22)	0.18 (0.02)	0.41 (0.05)	0.50 (0.09)	0.39 (0.08)
WH1	0.80 (0.27)	0.26 (0.02)	0.05 (0.02)	0.85 (0.19)	0.67 (0.02)
WH5	1.10	0.28	0.57	0.61	0.51
LC5	1.09	0.30	0.45	0.43	0.32
GL1	1.23 (0.18)	0.21 (0.03)	0.44 (0.17)	0.61 (0.03)	0.47 (0.04)
Offshore avg.	1.13	0.23	0.43	0.61	0.49

S = syringyl phenols; V = vanillyl phenols; C = cinnamyl phenols; 3,5-Bd = 3,5-dihydroxybenzoic acid; Sd = syringic acid; Sl = syringaldehyde; Vd = vanillic acid; Vl = vanillin; AR SS = Atchafalaya River suspended sediments Acid: aldehyde ratios (Ad/Al) were calculated as the ratio of Sd/Sl ($Ad/Al_{[s]}$) and the ratio of Vd/Vl ($Ad/Al_{[v]}$).

predominant eight lignin-derived phenols (Table 5). The ratio of S to V phenols (S/V) is used to distinguish angiosperm from gymnosperm plants, while the ratio of C to V phenols (C/V) is used to differentiate between woody and nonwoody plant tissues (Fig. 4). The high S/V ratio (1.2) of the SS indicates a predominant angiosperm source for the lignin exported by the AR, which is consistent with the predominant vegetation covering the grasslands in its drainage basin and agrees with studies of dissolved OM (Opsahl and Benner, 1998) and of SS (Onstad et al., 2000) from the MR and its tributaries. The observed C/V ratios indicate that both woody and nonwoody tissues contribute to the OM of the suspended load. Similar results were reported by Bianchi et al. (2002), who determined that sediments deposited in the lower MR were composed of a mixture of woody and nonwoody angiosperm tissues.

The chemical characterization of the SS indicates that a significant portion of the riverine OM is soil derived. Soil-derived OM has been suggested as an important source for MR SS (Goñi et al., 1997, 1998; Onstad et al., 2000) and for SS from rivers worldwide (Meybeck, 1982). The average C/N ratio of AR SS (11) is lower than terrigenous plant matter (C/N > 20) but is similar to C/N from SS of other world rivers (9–12, Meybeck, 1982). The AR SS are likely comprised of soil-derived OM from the MARS drainage basin, which displays

C/N ratios between 10 and 13 (e.g., Tiessen et al., 1984; Parton et al., 1987). The radiocarbon isotope composition also suggests that a primary source of OM in the SS is soil derived. The ^{14}C ages of the river SS ranged between 1600 and 2570 yr, values that argue against a significant input of recently synthesized vegetation or freshwater phytoplankton. In fact, these data are consistent with the presence of the most recalcitrant pools of soil OM, which are typically associated with mineral material and display turnover times exceeding thousands of years (e.g., Trumbore, 1993; Torn et al., 1997).

In addition to elemental and isotopic evidence, biomarker data support the assertion that OM delivered by the MARS is predominantly soil derived. The elevated acid-to-aldehyde (Ad/Al) ratios of all SS (>0.4; Table 5) indicate that OM from the AR and MR contains relatively degraded lignin. The decay of lignin by terrestrial fungi, which are particularly active in soils, has been shown to increase the Ad/Al ratio of V ($Ad/Al_{[v]}$) and S ($Ad/Al_{[s]}$) phenols. Opsahl and Benner (1995) showed that subaqueous decay of plant tissues can also increase Ad/Al ratios of lignin, but notable increases occurred only after 2 yr of subaqueous decomposition in their study. Given the residence time of OM in soils relative to its transit within the river, the lignin degradation in the present study likely occurred on land. Thus, the elevated Ad/Al ratios of SS are consistent with a

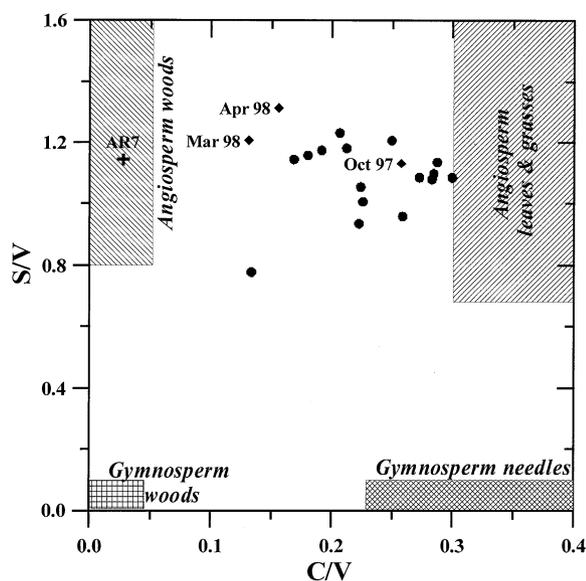


Fig. 4. Syringyl/vanillyl phenol ratio vs. cinnamyl/vanillyl phenol ratio. Typical ranges for woody and nonwoody tissues of both angiosperm and gymnosperm vegetation are indicated. Enclosed circles indicate shelf sediments and diamonds represent Atchafalaya River suspended sediments. Plot labels denote the sampling period for the river samples.

soil-derived OM source. Additional evidence for a soil origin is the elevated yields of 3,5-Bd relative to V phenols obtained in the AR SS samples. Previous studies have shown that high 3,5-Bd/V ratios (0.1–0.4) characterize the CuO product signatures of soil samples from various locations in the United States (e.g., Prah et al., 1994; Jones, 1999). In contrast, relatively undegraded samples, such as vascular plant tissues and soil litter, generally yield 3,5-Bd/V ratios that are < 0.1 (e.g., Goñi, 1992; Jones, 1999). Therefore, elevated values for this ratio have been proposed as a tracer for soil-derived OM (e.g., Prah et al., 1994; Goñi et al., 2000). The 3,5-Bd/V ratios from the samples in the present study ranged between 0.21 and 0.35 (Table 5), which is within the range previously cited for soil-derived OM.

It thus appears that mineral-associated soil-derived OM constitutes a substantial fraction of the AR SS. However, the chemical composition of the river SS is not seasonally uniform, as has been observed in other rivers (e.g., Goñi et al., 2000; Masiello and Druffel, 2001). Several parameters highlight the temporal variability in the OM delivered by the AR, particularly %OC, BET surface area, $\Delta^{14}\text{C}$, and lignin content and composition (Tables 3 to 5). For example, the AR SS collected in October 1997 displayed higher C/V and Ad/Al_(v) ratios than other sampling periods, in addition to a greater ^{14}C age, which indicates a greater contribution of degraded, nonwoody lignin, likely associated with soils. The SS collected in March 1998 displayed the highest lignin content of all SS, with comparatively low C/V and Ad/Al_(v) ratios. These data suggest a greater contribution of woody, relatively undegraded plant debris during this sampling period than during October 1997 or April 1998. Floodplain and riverbed erosion processes tied to the different stages of the hydrograph likely account for the observed compositional differences.

4.1.2. Comparison With MR and Its Tributaries

A comparison of the AR to the MR SS from the present study indicates that during the periods sampled, the composition of the suspended load from both rivers was very similar (Tables 3 to 5). The C/N ratios, $\delta^{13}\text{C}$ signatures, and CuO compositions of the OM in the AR and MR SS samples are statistically indistinguishable from each other. In fact, the seasonal variability observed in the AR SS is generally greater than the variability between the AR and MR compositions. On the basis of our collection and analytical methods, these data indicate that both rivers exported similar types of OM during the periods sampled.

A comparison of the SS compositions determined in this study with those reported by Onstad et al. (2000) for SS from the MR and its tributaries, on the other hand, reveals distinct differences. Both the MR and AR SS from the present study are more isotopically depleted and more lignin rich than the values ($\delta^{13}\text{C} \sim -20\text{‰}$; $\Lambda = 1.3 \text{ mg}/100 \text{ mg OC}$) obtained by Onstad et al. (2000) from the main stem of the MR and most of its tributaries, with the exception of the Ohio and Red Rivers. The samples we collected for the present study may contain a higher fraction of lignin-bearing vascular plant debris with a greater contribution of C3 sources than those analyzed by Onstad et al. (2000). Differences in the collection methods used may account for the observed contrasts. Filtration was used to isolate the samples in Onstad's (2000) study (see Canfield, 1997, for details), whereas centrifugation was used to isolate SS in the present study, a difference that may potentially contribute to the differential recovery of the various fractions of the river suspended load (e.g., vascular plant debris, fine clays). An additional explanation may be that the samples were collected under contrasting discharge regimes. Different hydrographic conditions and the seasonal variation in subbasin contribution to the main stem (van der Leeden et al., 1990) may explain the observed compositional differences. Because the analytical techniques of both laboratories are similar and have been satisfactorily compared in the past (e.g., Goñi and Montgomery, 2000), it is unlikely that they contribute to such differences.

4.2. Compositional Heterogeneity of OM Deposited in Shelf Sediments

Overall, it appears that the material delivered by the AR is primarily composed of mineral-associated, soil-derived OM, with an additional contribution from discrete plant fragments. Such compositional heterogeneity is reflected in the shelf sediments. Within our study area, we can differentiate several depositional subenvironments, including the Atchafalaya delta and bay (AR6 and AR11), shoal locations (WL4, TS4), inshore stations ($< 10 \text{ m}$ water depth; WL6, MI6, TS6, WH6, GL7), and offshore stations (AR1, AR3, WL1, MI1, WH1, WH5, LC5, GL1). Consistent differences in the bulk and molecular-level parameters measured (Tables 3 to 5) demonstrate the contrasts in the composition of the OM deposited in each of these regions, which are also highlighted by the PCA results (section 3.3; Fig. 3). For example, the sediments deposited within the Atchafalaya delta and bay region are more isotopically depleted ($\delta^{13}\text{C} = -23.5\text{‰}$) than the majority of shelf

sediments and are more lignin rich ($\Lambda = 3.8$ mg/100 mg OC) than both shelf sediments and river SS (Tables 3 and 4). The elevated lignin content in this region indicates that a substantial proportion of terrigenous OM is deposited at these sites, consistent with their proximity to the river mouth.

In contrast, sediments at the shoal locations, which are areas of high wave energy, are uniquely characterized by low OC and surface area (Table 3) and have low C/N ratios and lignin contents compared to the rest of shelf sediments. Sediments from the inshore region (water depth <10 m) of the shelf are directly influenced by the Atchafalaya mud stream, which typically flows westward within the 10-m isobath (Allison et al., 2000). The OM deposited at these stations is, on average, more isotopically depleted ($\delta^{13}\text{C} = -22.4\%$) and contains higher lignin levels ($\Lambda = 1.9$ mg/100 mg OC) than OM deposited at the offshore stations ($\delta^{13}\text{C} = -21.5\%$; $\Lambda = 1.1$ mg/100 mg OC). Such OM composition is consistent with the delivery of terrigenous material to inshore stations via the mud stream. The radiocarbon composition of shelf sediments is also spatially variable, with a younger ^{14}C age (1877 yr before present) at inshore stations than offshore (2420 yr before present). The greater ^{14}C age of the offshore sediments, along with the greater values for parameters such as 3,5-Bd/V and Ad/Al ratios (Table 5), is consistent with the hydrodynamic sorting and offshore transport of older, more degraded, soil-derived OM.

Station AR7, although located within the geographical vicinity of the delta, is defined as a separate depositional environment because of its unique composition. For example, sediment deposited at AR7 is characterized by the highest C/N ratio (29), most depleted $\delta^{13}\text{C}$ (-27%), and most lignin-rich ($\Lambda = 25$ mg/100 mg OC) OM observed within the study area. Such characteristics, in addition to the low C/V and low Ad/Al ratios measured at this site, indicate the overwhelming deposition of relatively undegraded, woody, C3 plant matter. The ^{14}C composition of this sample (-146%) is more depleted than modern, postbomb values ($\Delta^{14}\text{C} > 0\%$), however, which suggests that older, mineral-associated OM constitutes a portion of the deposited material. This is consistent with the observed characteristics of this sample, which was composed of visible, discrete plant fragments within a mineral matrix. An alternative explanation for the depleted ^{14}C composition is the exposure through sediment resuspension of a relic, peatlike material. Physical separation and ^{14}C dating of the discrete plant fragments in this sample may help differentiate these two potential sources, but this distinction cannot presently be made.

Overall, the deposition of chemically and isotopically distinct terrigenous OM within our study area is consistent with previous studies (Gordon et al., 2001) as well as observations of other river-dominated ocean margins, such as the Eel River shelf (Leithold and Hope, 1999), the Columbia River shelf (Prahl et al., 1994; Keil et al., 1994, 1998), and the Mackenzie River shelf (Goñi et al., 2000). We hypothesize that the contrasts observed among the different depositional subenvironments within the inner Louisiana shelf are predominantly the result of the physical and geological factors that control sediment delivery and reworking in this area (Allison et al., 2000). As previously shown, the delivery of fine sediment to inner shelf via the Atchafalaya mud stream, coupled with the periodic resuspension and mobilization due to storms (Allison et al.,

2000), controls the bulk composition of sedimentary OM along the inner Louisiana shelf (Gordon et al., 2001). Our data suggest that the compositional trends observed across and along the shelf reflect the differential transport and deposition of different types of OM. Understanding the origins, transformations, and fate of these various OM pools is critical to better elucidate the biogeochemical cycles of coastal shelf regions.

4.3. Sources of OM Deposited in Shelf Sediments

4.3.1. Elemental and Stable Carbon Isotopic Constraints

Carbon-to-nitrogen ratios can be used to differentiate the contributions from terrigenous plant matter (C/N = 20–200) and marine phytoplankton (C/N = 6–8; Redfield et al., 1963) in geochemical mixtures, although their application to geochemical samples is limited because of changes during degradation. Such changes include the preferential degradation of nitrogen (e.g., Hedges et al., 1988; Cowie and Hedges, 1996) and the incorporation of nitrogen during humification (e.g., Rice and Hanson, 1984). In the present study, the C/N ratios of the majority of shelf sediment samples fall within a narrow range (8–13), with an average value (C/N = 10) similar to that of the river SS (C/N = 11; Table 3). Although a C/N ratio of 10 is suggestive of a mixture between marine phytoplankton and terrigenous plant matter, these ratios are also consistent with soil-derived OM contributions (Goñi et al., 1998). It is thus conceivable that the shelf sediments contain soil-derived material delivered by the AR SS (see section 4.1). However, because the C/N ratio of soil OM is similar to that of marine detritus, this parameter alone cannot be used to quantitatively estimate OM sources within these surficial sediments.

The stable carbon isotope composition of sedimentary OM provides an additional constraint on OM sources. Depleted $\delta^{13}\text{C}$ values characteristic of C3 plant debris are observed close to the mouth of the AR and decrease to values typical of marine phytoplankton in the offshore and shoal regions (Table 3; Gordon et al., 2001). The values along the shelf are similar to those measured in previous studies (e.g., Hedges and Parker, 1976; Gearing et al., 1977) and were interpreted by those authors as a dilution of terrigenous OM with that derived from marine sources. However, the enriched isotopic signature of river SS, because of the presence of C4 plant-derived OM from the MARS drainage basin, negates such oversimplistic isotopic assessment of OM sources in our study area. For example, roughly equal proportions of C3 and C4 plant-derived matter may render the OM of the river SS isotopically indistinguishable from marine algae (Ruttenberg and Goñi, 1997; Goñi et al., 1998; Onstad et al., 2000). In addition, Goñi et al. (1998) measured the isotopic composition of lignin phenols from Gulf of Mexico sediments and found that a significant portion of these terrigenous biomarkers were relatively enriched in ^{13}C , which is indicative of a C4 origin. The enriched isotopic value of the terrigenous end-member itself therefore confounds the use of stable carbon isotopic compositions alone for source assessment in these shelf sediments.

4.3.2. Biomarker Constraints

Although lignin represents a small fraction of the bulk OM in the sediment samples, its distribution can be used unequivocally

cally to determine the presence of land-derived OM in sediments from our study area. The highest Δ value for shelf sediments, found 26 km from the mouth of the river, is typical of values reported for wood (e.g., Goñi and Hedges, 1992) and is consistent with the elemental and isotopic data from this station that indicate the deposition of discrete C3 plant debris. The lignin contents of the remainder of surficial sediments are similar to those found previously for this shelf region (Hedges and Parker, 1976) but slightly higher than were found for the MR plume and adjacent shelf (Eadie et al., 1994; Bianchi et al., 2002) and along seaward transects from the Mississippi and Atchafalaya deltas (Goñi et al., 1998). Importantly, the surficial sediments at the most distal locations in the present study exhibit elemental and isotopic values that could be interpreted as being characteristic of pure marine carbon. However, these samples have lignin contents approximately one third of the value of the riverine SS samples. This suggests that a significant amount of the OM (~33%) deposited at the most distal station, which is > 100 km from AR mouth, is terrigenous. Such a finding demonstrates how the terrigenous component of marine sediments may be underestimated using elemental and isotopic analyses alone.

The high S/V ratios of all sediments from the study area (>0.75) indicate a predominant angiosperm vegetation source. These results are consistent with the angiosperm signature of AR SS and of surficial sediments from the northern Gulf of Mexico (e.g., Hedges and Parker, 1976; Bianchi et al., 1997, 2002; Goñi et al., 1998). The sediment sample collected at station AR7, which displays a high lignin concentration and a depleted $\delta^{13}\text{C}$, has a low C/V ratio, typical of woody tissue. The remainder of shelf sediments from the present study contain varying amounts of lignin derived from woody and non-woody sources, suggesting that more than one type of terrigenous OM source is deposited along the shelf (Fig. 4). The sediment deposited at station AR7 has Ad/Al ratios (Table 5) that are indicative of relatively undegraded lignin. All the other shelf sediments, on the other hand, display Ad/Al ratios > 0.35 (Table 5), which are characteristic of relatively degraded terrigenous OM. The OM delivered by the AR and deposited outside the Atchafalaya delta thus appears to be degraded in nature, consistent with previous studies (Goñi et al., 1998; Onstad et al., 2000).

4.3.3. Radiocarbon Constraints

The radiocarbon ages of the sedimentary OM provide further evidence for two types of terrigenous OM, with soil-derived OM as the predominant input to the majority of shelf sediments. Goñi et al. (1998) found ^{14}C ages in excess of 2000 yr before present along two transects adjacent to the MR that extended from the shelf to the abyssal plain. The authors concluded that such ages were not consistent with marine plankton as the predominant OM source. Instead, the authors argued that soil-derived OM was a significant component of sediments deposited in those locations. In the present study, the radiocarbon ages of the shelf sediments are in excess of 1200 yr before present, and all but one of the shelf sediments fall within the age range observed for the riverine SS (1600–2600 yr before present). Even with a reservoir correction of 500 yr before present for autochthonous productivity in the Gulf of

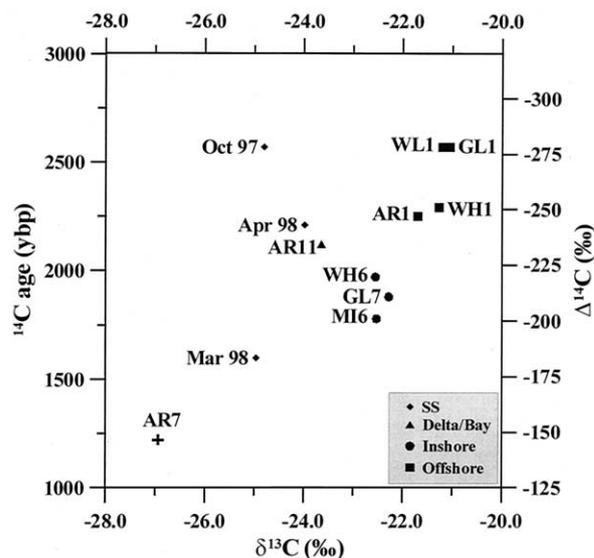


Fig. 5. Radiocarbon isotope composition vs. stable carbon isotope composition. $\Delta^{14}\text{C}$ (‰) is indicated on the right y-axis, while the corresponding ^{14}C age (yr before present) is shown on the left y-axis. Plot labels denote the sampling period for the river suspended sediments (SS) and denote the sampling location for the shelf sediments.

Mexico (Stuiver et al., 1986), the ^{14}C ages of the shelf sediments do not indicate fresh marine phytoplankton as the predominant OM input. Assuming that the ^{14}C ages of the SS mainly reflect a soil-derived OM source, and given that the ages of the shelf sediments are similar to the SS, soil-derived OM must be an important input to the sediments deposited along the inner Louisiana shelf, especially distal from the AR mouth.

The observed relationship between the radiocarbon and stable carbon isotopes (Fig. 5) also illustrates that soil-derived OM is likely responsible for the relatively enriched $\delta^{13}\text{C}$ values of the shelf sediments. If fresh phytoplankton were primarily responsible for the observed $\delta^{13}\text{C}$ values, the expected relationship between these two isotopic tracers would be a modern ^{14}C signature at enriched $\delta^{13}\text{C}$. The opposite trend is observed, however, with more depleted $\Delta^{14}\text{C}$ associated with more enriched $\delta^{13}\text{C}$ values. The older carbon is likely soil derived, and increasing amounts of ^{13}C -enriched soil-derived OM at greater ^{14}C ages explain the observed trend.

Another potential source of ^{13}C -enriched OM to the study area is marsh-derived OM. Chmura et al. (1987) reported enriched isotopic values for salt marshes of coastal Louisiana due to the predominance of the C4 marsh grass *Spartina alterniflora*. The input of fresh *Spartina* debris to the study area is inconsistent with the depleted $\Delta^{14}\text{C}$ observed in these sediments. Erosion of old, marsh sediments, on the other hand, may contribute to the observed isotopic trend (Fig. 5). A significant input of OM from coastal marshes to the study area seems unlikely, however, given that coastal Louisiana is actively subsiding and the marshes likely act as particle sinks (e.g., Hatton et al., 1985). In addition, Nyman et al. (1995) found that marsh particulate OC export is limited because of subsidence. Marsh-derived OM input to the study area therefore seems unlikely but cannot be ruled out.

A potential input of old carbon (i.e., ^{14}C -dead) from hydro-

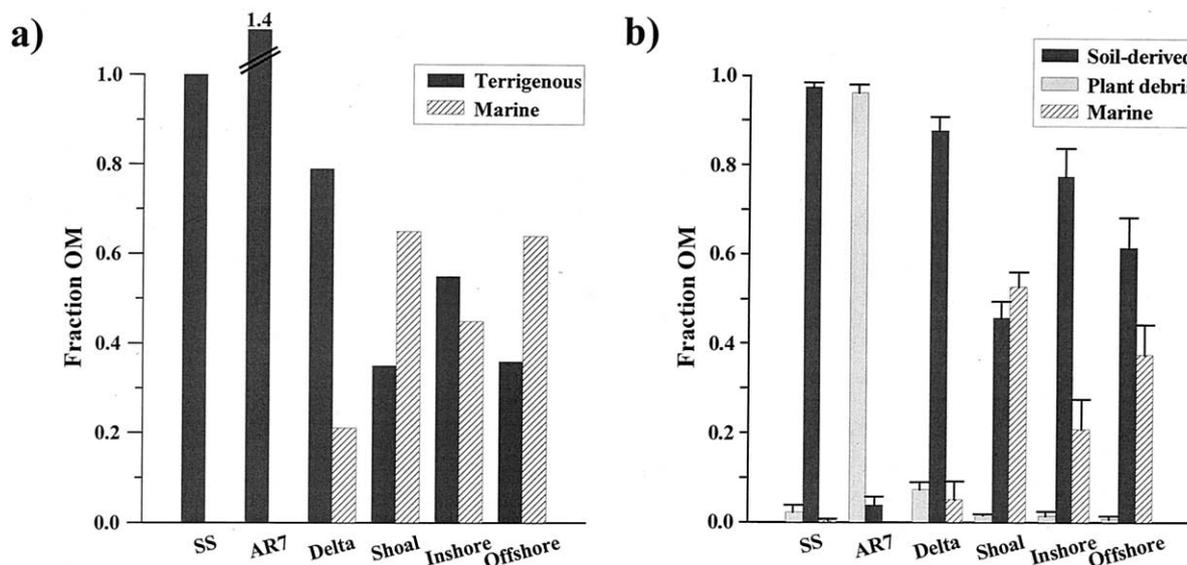


Fig. 6. Fraction of terrigenous organic matter (OM) deposited within the study area. (a) Relative fraction of terrigenous and marine OM calculated by a two-end-member mixing model. (b) Relative fraction of vascular plant debris, soil-derived OM, and marine-derived OM calculated using a three-end-member mixing model. The error bars represent the range in calculated values based on the chosen end-members (see Table 6; Appendix). The fraction of each end-member is shown on the y-axis, and depositional regions, as defined in Figure 2, are indicated on the x-axis.

carbon seeps, which are known to be abundant in the northern Gulf of Mexico slope, and/or from hydrocarbon exploration may also give rise to the older ^{14}C ages of these sediments. Rittenberg and Goñi (1997) reported a depleted stable carbon isotope signature ($\delta^{13}\text{C} = -24.1\text{‰}$) from sediments collected near an oil seep along the Gulf of Mexico slope. Considering the enriched isotopic composition of most shelf sediments, it seems unlikely that fossil hydrocarbons represent a significant fraction of the bulk sedimentary OC in this region. Fossil hydrocarbon input, however, cannot yet be definitively ruled out and may affect the composition of OM in these sediments.

4.4. Quantitative Estimates of Terrigenous OM

A more complete understanding of OM cycling in this coastal marine environment may be gained by the quantitative evaluation of the marine and terrigenous components of the sedimentary OM. Geochemical investigations have historically employed a two-end-member mixing model between marine phytoplankton and isotopically depleted vascular plant debris to quantify the terrigenous component of OM in marine sediments. This two-end-member mixing model was applied to the present study area to quantify the portion of OM considered to be terrigenous in origin (OC_{TERR}), using isotope mass balance (see the Appendix).

The fraction of terrigenous and marine OM deposited within several regions of the study area is illustrated in Figure 6a. The fraction of terrigenous OM is higher at the inshore stations than at the offshore stations, likely because of the influence of the Atchafalaya mud stream on delivering terrigenous OM to the inner Louisiana shelf (Gordon et al., 2001) and the greater dilution by autochthonous productivity at offshore locations. The OM deposited within the delta region of the study area is nearly 80% terrigenous, with a surprising 20% contribution

from algal sources. Such a value for marine-derived OM in deltaic sediments seems unlikely given that phytoplankton growth is believed to be limited within the river plume as a result of high turbidity (e.g., Sklar and Turner, 1981). The OM at station AR7 is calculated to be > 100% terrigenous because of the overwhelming contribution of isotopically depleted C3 plant debris at this location. These two unrealistic OC_{TERR} scenarios indicate that the OM cycling in the present study area is not well represented by this two-end-member mixing model.

The transport and deposition of terrigenous OM is clearly more complex than a simple dilution of river-borne material with increasing amounts of marine detritus. As we have demonstrated, a single, homogenous terrigenous end-member is not representative of the present study area, and we contend that it is likely not representative of marine sediments in general. The deposition at AR7 is best represented by coarse, woody plant fragments of C3 origin, whereas the majority of shelf sediments may be better represented by degraded, soil-derived OM. The deltaic sediments appear to contain a mixture of both OM types. For this reason, a three-end-member mixing model was used to quantify the relative proportions of marine OM, vascular plant debris, and soil-derived OM (see the Appendix).

The contributions of marine-derived, soil-derived, and vascular plant carbon to several depositional regions in the study area are shown in Figure 6b. Nearly 100% of the OM deposited at station AR7 is vascular plant debris. The revised mixing model demonstrates that negligible marine carbon is deposited in deltaic sediments, which is reasonable considering the probable low productivity rates in this turbid region (e.g., Sklar and Turner, 1981). The OM deposited at the shoal stations (WL4 and TS4) is composed of a nearly equal mixture of marine and soil-derived carbon. This is consistent with the greater contribution of P and B, relative to A, at these sites. However, the

Table 6. Organic carbon sources in river suspended and delta/shelf sediments in study area. The sensitivity of the calculation to chosen end-member values is shown. Each depositional region has six results, based on two different marine endmember values and three separate river suspended sediment values. See the Appendix for further explanation.

Sedimentary region	OC _{MAR} (%)	OC _{SOIL} (%)	OC _{VP} (%)
River suspended sediments			
MR SS, marine = -19.5‰	0	96	4
MR SS, marine = -21.5‰	0	97	3
AR SS, marine = -19.5‰	1	99	0
AR SS, marine = -21.5‰	1	99	0
Kendall MR SS, marine = -19.5‰	0	97	3
Kendall MR SS, marine = -21.5‰	0	97	3
AR7			
MR SS, marine = -19.5‰	0	4	96
MR SS, marine = -21.5‰	0	5	95
AR SS, marine = -19.5‰	0	4	96
AR SS, marine = -21.5‰	0	4	96
Kendall MR SS, marine = -19.5‰	0	5	95
Kendall MR SS, marine = -21.5‰	0	5	95
Delta sediments			
MR SS, marine = -19.5‰	5	86	9
MR SS, marine = -21.5‰	6	86	8
AR SS, marine = -19.5‰	9	86	5
AR SS, marine = -21.5‰	10	85	5
Kendall MR SS, marine = -19.5‰	0	92	8
Kendall MR SS, marine = -21.5‰	0	92	8
Shoals			
MR SS, marine = -19.5‰	53	46	1
MR SS, marine = -21.5‰	53	45	2
AR SS, marine = -19.5‰	56	43	1
AR SS, marine = -21.5‰	57	41	2
Kendall MR SS, marine = -19.5‰	49	50	1
Kendall MR SS, marine = -21.5‰	48	50	2
Inshore sediments			
MR SS, marine = -19.5‰	21	77	2
MR SS, marine = -21.5‰	25	73	2
AR SS, marine = -19.5‰	25	75	0
AR SS, marine = -21.5‰	29	71	0
Kendall MR SS, marine = -19.5‰	12	86	2
Kendall MR SS, marine = -21.5‰	14	84	2
Offshore sediments			
MR SS, marine = -19.5‰	34	65	1
MR SS, marine = -21.5‰	42	57	1
AR SS, marine = -19.5‰	40	60	0
AR SS, marine = -21.5‰	47	53	0
Kendall MR SS, marine = -19.5‰	27	72	1
Kendall MR SS, marine = -21.5‰	35	64	1

OC = organic carbon; MAR = marine; SOIL = soil-derived; VP = vascular plant; AR SS = Atchafalaya River suspended sediments; MR SS = Mississippi River suspended sediments, reported by Onstad et al. (2000); Kendall MR SS = MR SS based on values reported by Kendall et al. (2001). The end-members and calculations are described in detail in the Appendix.

unusual characteristics of these samples, with low surface area, low OC content, and C/N ratios lower than the marine end-member, may give rise to unreliable estimates. The importance of the mud stream in delivering soil-derived OM to the inshore stations (<10 m water depth) is apparent, with soil-derived OM accounting for ~80% of the deposited carbon and marine-derived OM accounting for the remainder. The average contribution of vascular plant debris is negligible at the inshore and offshore sites. Overall, the soil-derived OM signal predominates the majority of shelf sediments (65–77%), with a greater percentage of marine OM in offshore sediments (34%) than at inshore stations (21%). Such a trend is consistent with the lower concentrations of lignin products and higher yields of non-lignin oxidation compounds measured in offshore sediments (Table 4).

The sensitivity of the mixing model to the chosen end-

member compositions was examined by defining the soil-derived OM end-member by two additional compositions and by varying the isotopic composition of the marine end-member (see the Appendix). The result of such calculations (Fig. 6b; Table 6) reveals that the contribution from each OM source is dependent upon the end-member composition, as has been observed by previous investigators (e.g., Prahl et al., 1994; Goñi et al., 2000). The sensitivity of the calculation to the isotopic composition of the marine end-member is most apparent in the offshore sediments, with the marine contribution increasing from its initial value of 34% ($\delta^{13}\text{C}_{\text{MAR}} = -19.5\text{‰}$) to 42% ($\delta^{13}\text{C}_{\text{MAR}} = -21.5\text{‰}$). The contribution of marine carbon is also greater in the inshore sediments (25%, $\delta^{13}\text{C}_{\text{MAR}} = -21.5\text{‰}$) than the original result (21%, $\delta^{13}\text{C}_{\text{MAR}} = -19.5\text{‰}$). The portion of marine carbon at each other site is minimally affected by the marine isotopic value. The chemical

composition of the soil-derived OM end-member, on the other hand, has a measurable effect on the contribution of marine and terrigenous carbon deposited within each environment (Table 6). Despite the variability based on the chosen end-member, the overall result of the mixing model is unchanged: a significant amount of terrigenous carbon is deposited within the study area, even at the offshore locations.

An important result of the mixing model is the greater calculated abundance of terrigenous OM in the majority of shelf sediments with the three-end-member mixing model than with the conventional two-end-member approach. The estimates of terrigenous carbon abundance (soil-derived OM plus vascular plant carbon) are ~40% higher in inshore sediments and nearly 85% higher in offshore sediments with the three-end-member than with the two-end-member model. This calculation clearly demonstrates the need for a reevaluation of terrigenous carbon in marine sediments given the contribution from two distinct terrigenous OM sources.

5. CONCLUSIONS

1. The composition of the SS of the AR vary seasonally but generally contain isotopically enriched OM that reflects the contribution from C4 grasses in the MARS drainage basin. The OM is relatively aged and degraded and is likely derived from soils of the drainage basin.
2. The terrigenous OM deposited on the inner Louisiana shelf is compositionally heterogeneous, with contributions from both discrete plant debris and soil-derived OM. Fresh vascular plant debris with a C3 isotopic signature appears to be deposited close to the mouth of the AR. In contrast, the vast majority of the terrigenous OM deposited on the AR shelf is composed of relatively degraded, isotopically enriched, soil-derived OM, which is transported westward along the coastline within the Atchafalaya mud stream and across the shelf during sediment resuspension events.
3. Autochthonous productivity is an important contributor to the OM deposited at stations seaward of the 10-m isobath, which display elevated levels of non-lignin CuO oxidation products.
4. Quantification of terrigenous OM in these coastal sediments is complex because of the heterogeneous composition of the terrigenous end-member itself. The quantification of carbon sources using a three-end-member mixing model demonstrates the variability of OM deposition in coastal sediments and highlights the need for well-constrained end-members.
5. The comparison of the two-end-member and three-end-member mixing models reveals that the two-end-member model that is typically employed in geochemical studies underestimates the amount of terrigenous OM deposited in the present study area by 40 to 85%. The results clearly demonstrate that the two-end-member mixing model may have led to the underestimate of the terrigenous carbon content of marine sediments in general, and highlights the need for a reassessment of terrigenous OM burial, with particular emphasis on the role of soil-derived OM.

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We dedicate this paper to the memory of John I. Hedges, our friend and mentor, who with his work and perseverance set a standard of excellence for many geochemists and oceanographers. This dedication is most fitting because John's career started with the analyses of stable carbon and lignin compositions of sediments from this area. We feel lucky to have had the honor of knowing him. He will be missed and remembered.

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APPENDIX

The two-end-member mixing model used to quantify the terrigenous component of deposited carbon (OC_{TERR}) via isotope mass balance is as follows:

$$\%OC_{TERR} = \frac{(\delta^{13}C_{sample} - \delta^{13}C_{marine})}{(\delta^{13}C_{riverine} - \delta^{13}C_{marine})}$$

where $\delta^{13}C_{sample}$ is the measured isotopic composition at each station (Table 3), $\delta^{13}C_{marine}$ is a published isotopic value for marine plankton from the Louisiana shelf (-19.5‰ ; Eadie et al., 1994), and $\delta^{13}C_{riverine}$ is the average isotopic composition of AR SS (-24.6‰).

The three-end-member mixing model was based on a system of three equations, as follows:

$$\delta^{13}C_{MAR} \times OC_{MAR} + \delta^{13}C_{SOIL} \times OC_{SOIL} + \delta^{13}C_{VP} \times OC_{VP} = \delta^{13}C_{sample}$$

$$\Lambda_{MAR} \times OC_{MAR} + \Lambda_{SOIL} \times OC_{SOIL} + \Lambda_{VP} \times OC_{VP} = \Lambda_{sample}$$

$$N/C_{MAR} \times OC_{MAR} + N/C_{SOIL} \times OC_{SOIL} + 0.033 \times OC_{VP} = N/C_{sample}$$

where OC_{MAR} is the portion of OC that is marine derived, OC_{SOIL} is the portion of OC that is soil derived, and OC_{VP} is the portion of OC derived from vascular plant debris. The marine end-member values were chosen on the basis of a published isotope value (-19.5‰ ; Eadie et al., 1994), a lignin content of zero, and a N/C ratio based on the Redfield ratio (C/N = 6.6; Redfield et al., 1963). The soil-derived OM end-member is defined on the basis of the average chemical composition (C/N = 10.7; $\delta^{13}C = -22.2\text{‰}$; $\Lambda = 1.39$ mg/100 mg OC) of the SS from MR tributaries reported by Onstad et al. (2000). The vascular plant end-member is based on typical values for C3 plant matter, with a substantial woody component (C/N = 30; $\delta^{13}C = -27\text{‰}$; $\Lambda = 26$ mg/100 mg OC). Such values were chosen to encompass those observed within the study area, particularly of the sample collected at station AR7, which was composed of discrete plant fragments. Unlike the two-end-member mixing approach, in which mass balance is used as a constraint on the calculation, this three-end-member approach uses three variables and does not include mass balance in the initial calculation. As a result, the contribution from the three end-members did not always sum to 100%. In these cases, the individual percentages were “normalized” to their sum to achieve mass balance.

The sensitivity of the mixing model to the chosen end-member compositions was examined by defining the soil-derived OM end-member by two additional compositions and by varying the isotopic composition of the marine end-member. The soil-derived OM end-member, initially defined by the composition of SS of MR tributaries (Onstad et al., 2000), was also defined (1) by the chemical composition of the SS from the AR mouth measured in the present study (C/N = 10.6; $\delta^{13}C = -24.6\text{‰}$; $\Lambda = 2.86$ mg/100 mg OC) and (2) by the composition of MR tributary SS reported by Kendall et al. (2001), the average of which (C/N = 8.4; $\delta^{13}C = -25.1\text{‰}$) was more nitrogen rich and more isotopically depleted than those reported in Onstad et al.'s (2000) study. Kendall et al. (2001) did not determine the biomarker composition of the SS, so the lignin value was defined to be that measured by Onstad et al. (2000). The isotopic composition of the marine end-member, initially defined as -19.5‰ , was also assigned a value of -21.5‰ (Fry and Wainright, 1991).