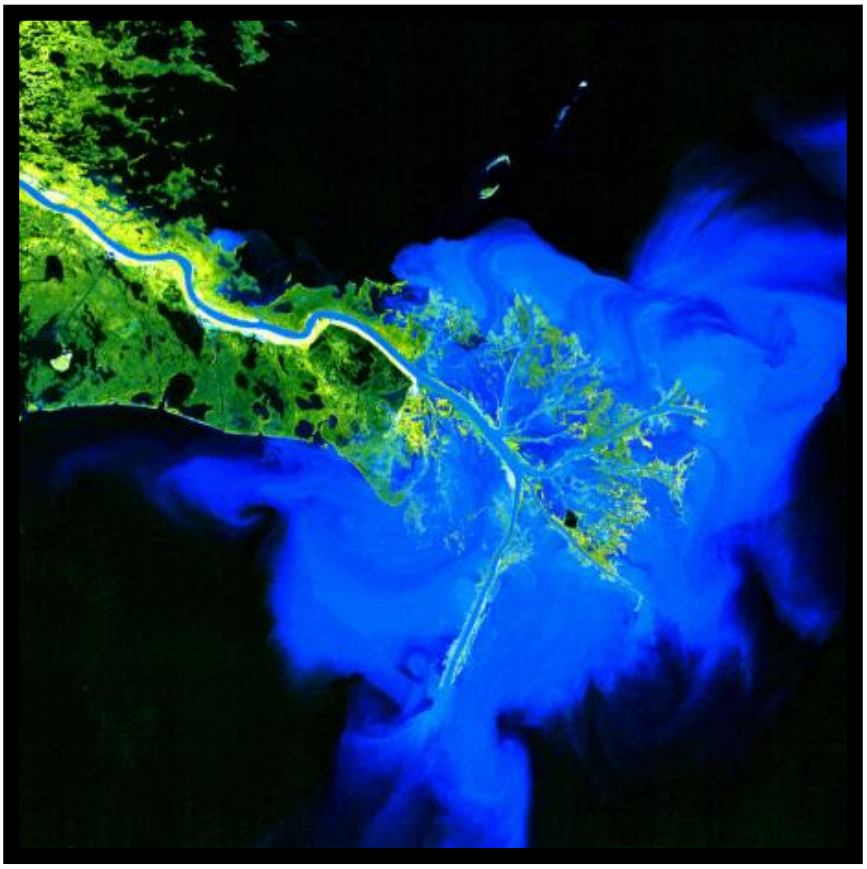
Organic Geochemistry of Sediments in Nearshore Areas of the Mississippi and Atchafalaya Rivers: I. General Organic Characterization

By William H. Orem, Robert J. Rosenbauer, Peter W. Swarzenski, Harry E. Lerch, Margo D. Corum, and Anne L. Bates



Open-File Report 2007-1180

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
DIRK KEMPTHORNE, Secretary

U.S. Geological Survey
Mark D. Myers, Director

U.S. Geological Survey, Reston, Virginia 2007
Revised and reprinted: 2007

For product and ordering information:
World Wide Web: http://www.usgs.gov/pubprod
Telephone: 1-888-ASK-USGS

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment:
World Wide Web: http://www.usgs.gov
Telephone: 1-888-ASK-USGS

Suggested citation:
Orem, W, and others, 2007, Organic geochemistry of sediments in nearshore areas of the Mississippi and Atchafalaya Rivers: I. general organic characterization: U.S. Geological Survey Open-File Report 2007-1180.

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted material contained within this report.

Table of Contents

Page

List of Figures.....3

List of Tables.....4

Conversion Factors.....5

Abstract.....6

I. Introduction.....7

II. Study Area and Sampling.....9

III. Analytical Methods.....14

III.A. Elemental Analysis of Sediments.....14

III.B. Sediment C_1-C_6 Hydrocarbon (Gas) Analysis.....16

IV. Results.....18

IV.A. Elemental Composition of Sediments.....18

IV.B. Hydrocarbon Gases C_1-C_6.....48

V. Discussion.....49

VI. Conclusions.....63

Acknowledgments.....64

References Cited.....65

List of Figures

Fig. 1. Lower Mississippi and Atchafalaya River coring sites, March 2001, oxic and hypoxic coring sites June and September 2002, and June 2003 coring sites. Numbers next to designated sites refer to numbers listed in Table 1.....10

Fig. 2. Multicorer for collection of near surface sediment cores.....15

Fig. 3. Total carbon (% dry wt.) and inorganic carbon (% dry wt.) contents of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....24

Fig. 4. Organic carbon content (% dry wt.) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....25

Fig. 5. Total nitrogen content (% dry wt.) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....26

Fig. 6. Total phosphorus contents (% dry wt.) of sediments from cores collected in the lower Mississippi anf Atchafalaya River estuaries in 2001.....27

Fig. 7. Total sulfur contents (% dry wt.) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....28

Fig. 8. Atomic C/N (organic carbon/total nitrogen) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....29

Fig. 9. Atomic C/P (organic carbon/total phosphorus) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....30

Fig. 10. Atomic N/P (total nitrogen/total phosphorus) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....31
Fig. 11. Atomic C/S (organic carbon/total sulfur) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001..... 32
Fig. 12. Organic elemental data from June 2002 hypoxic-1(●) and oxic-1 (○) sites in the lower Mississippi River system; all results are reported as % dry wt. 44
Fig. 13. Organic elemental atomic ratios from June 2002 hypoxic-1(●) and oxic-1 (○) sites in the lower Mississippi River system..... 45
Fig. 14. Organic elemental data from the lower Mississippi River system for cores collected in September 2002 from the hypoxic-2 site by multicore (●) and vibracore (■), and the oxic-2 site by multicore (○) and vibracore (□);all results are reported as % dry wt..... 46
Fig. 15. Elemental atomic ratios from the lower Mississippi River system for cores collected in September 2002 from the hypoxic-2 site by multicore (●) and vibracore (■), and the oxic-2 site by multicore (○) and vibracore (□).....47
Fig. 16. Organic elemental data from cores MR-J03-3 (○) and MR-J03-5 (●) collected off the lower Mississippi River System; all results are reported as % dry wt..... 50
Fig. 17. Elemental atomic ratios of sediments from cores MR-J03-3 and MR-J03-5 collected off the lower Mississippi River System..... 51
Fig. 18. Free (red) and bound (blue) methane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....54
Fig. 19. Free (red) and bound (blue) ethane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....55
Fig. 20. Free (red) and bound (blue) propane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....56
Fig. 21. Free (red) and bound (blue) butane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....57
Fig. 22. Free (red) and bound (blue) pentane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....58
Fig. 23. Free (red) and bound (blue) hexane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.....59

List of Tables

Table 1. Location and description of coring sites in the lower Mississippi and Achafalaya River estuaries..... 11
Table 2. Elemental C, N, P, and S contents of sediments from 2001 USGS cores in the Mississippi River and Atchafalaya River estuaries.....20
Table 3. Elemental C, N, P, and S contents of sediments from 2002-2003 USGS cores in the lower Mississippi River System.....35
Table 4. Concentrations of C_1 to C_6 hydrocarbon gases in sediments from cores collected in the lower Mississippi and Achafalaya River estuaries.....52
Table 5. Accumulation rates (AR) for total carbon (TC), total nitrogen (TN), and total sulfur (TS) at sites MR-J03-3 and MR-J03-5.....62

Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
Volume		
gallon (gal)	3.785	liter (L)
cubic foot (ft^3)	28.32	liter (L)
Flow rate		
cubic foot per second (ft^3/s)	28.32	liter per second (L/s)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
Mass		
ounce avoirdupois (oz)	28.35	gram (g)
pound avoirdupois (lb)	0.4536	kilogram (kg)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
°F = (1.8×°C) +32
Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:
°C = (°F-32)/1.8
Altitude, as used in this report, refers to distance above the vertical datum.
Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).
Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

SI to Inch/Pound

Multiply	By	To obtain
Length		
meter (m)	3.281	foot (ft)
Volume		
liter (L)	0.2642	gallon (gal)
liter (L)	0.03531	cubic foot (ft^3)
Flow rate		
liter per second (L/s)	0.03531	cubic foot per second (ft^3/s)
liter per second (L/s)	15.85	gallon per minute (gal/min)
Mass		
gram (g)	0.03527	ounce avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

Organic Geochemistry of Sediments in Nearshore Areas of the Mississippi and Atchafalaya Rivers: I. General Organic Characterization

By William H. Orem, Robert J. Rosenbauer, Peter W. Swarzenski, Harry E. Lerch, Margo D. Corum, and Anne L. Bates

Abstract

This report presents results on the general organic characteristics of sediment cores collected from the coastal zone of the Mississippi River system, including distributions of the important nutrient elements (C, N, P, and S). This was part of a larger study conducted from 2001-2005 to examine the delivery of sediment-associated contaminants to the Gulf of Mexico by the Mississippi River system, funded by the USGS Coastal and Marine Geology Program. Companion reports emphasize organic contaminants (Rosenbauer and others, 2006), and metals (Swarzenski and others, 2006). The level of contamination within the deltaic system of the Mississippi River system was determined through the collection of sediment cores from interdistributary bays, and offshore in the Gulf of Mexico, including the zone of hypoxia. Results provide the basis for reconstructing contaminant inventories from which to develop historic perspectives on nutrient loading and hypoxia, and to better understand how sediment-hosted contaminants either directly or indirectly move through biota and ultimately affect ecosystem health.

Concentrations of C, N, P, and S in sediments varied by a factor of 10 between sites, and in down core profiles. Nearshore cores collected in 2001 proved to have erratic downcore C, N, P, and S profiles and sediment deposition rates, suggesting a high energy regime controlled more by variability in river flow rather than by geochemical processes and reactions within the system. These results focused further coring activities further offshore. Atomic C/N ratios suggest that organic matter deposited at all sites is a mix of microbial (algal) and terrestrial (vascular plant) remains, but with algal material dominant. Concentrations of total sulfur in sediments from cores in the zone of hypoxia were often higher than those in nearby zones with oxic water columns. Corresponding atomic C/S ratios were typically lower in sediments from sites in the zone of hypoxia compared to nearby sites with oxic water columns, and thus atomic C/S values may be useful as a proxy for identifying sites impacted by hypoxic conditions in the water column and for examining historical trends in hypoxia. At one site examined in this study, maximum hypoxic conditions were observed in the mid 1960's. The organic elemental composition (C, N, P, and S) of sediments was also used to guide sample selection for contaminant analysis, and to normalize the contaminant data to organic C content of the sediments.

Dissolved hydrocarbon gases in sediments showed a dominance of methane, but identifiable concentrations of ethane and hexane, and trace concentrations of propane, butane, and pentane were also detected. All dissolved gases except hexane were dominated by "bound" gas, gas released only after agitation of the sediment in a blender. Hexane, in contrast was observed mostly as free gas, determined by headspace analysis.

I. Introduction

The Mississippi is one of the Earth's great river systems, ranking seventh worldwide for water discharge (580 km^3 yr^{-1}), and sixth for suspended sediment discharge (200 million metric tons yr^{-1}), (Meade, 1995). The Mississippi River (MR) and its tributaries drain nearly half of the conterminous United States (Spink and others, 1998). Discharge from the Mississippi and Atchafalaya Rivers (the two principal mouths of the Mississippi River system) accounts for about 90% of the freshwater input to the Gulf of Mexico, and is also the major source of sediments, nutrients, and pollutants to the Gulf (Walker, 1996). It is also worth noting that approximately 90% of commercial fisheries in the Gulf of Mexico come from the so-called fertile crescent, the area affected directly by freshwater runoff (including nutrients) from the Mississippi River (Lohrenz and others, 1997). Unlike most of the Earth's other large river systems, however, the Mississippi is highly regulated by manmade structures. About a third of the total flow to the Mississippi River is diverted at the Old River Control Structure into the Atchafalaya River. The construction of dams and reservoirs along the Mississippi/Missouri River system has resulted in substantial decreases in total suspended matter concentrations (Vorosmarty and others, 1997). Levees along the lower Mississippi play a major role in channeling the river and preventing the river mouth from movement within its natural floodplain (Delaney and Craig, 1997). Partly as a result of these various control structures along the MR system, large flood events (e.g. the Missouri River flood of 1993) effectively decrease total suspended matter concentrations in the lower river in subsequent years by scouring and flushing out recently deposited riverbed sediments.

Human activities on land account for 80% or more of marine pollution, and rivers are the major conduits through which contaminants of terrestrial origin are transported to the sea (Meade, 1995; Howarth and others, 2000). Thus, research efforts have focused on the fluvial discharge of global rivers to estuaries and the coastal ocean. Surprisingly, while the Amazon and Yellow Rivers have been systematically studied, the MR system has only recently been comprehensively investigated (Meade, 1995). As a result, research is needed on many aspects of the MR system, such as the role of seasonal storage and resuspension in the off-continent material flux budget (especially nutrients and other pollutants), the interplay between sediment supply, subsidence and wetland loss, and the geographic extent of historic/modern hypoxia (e.g. low levels of dissolved oxygen in surface water, from 1-30% saturation).

Previous work (Meade, 1995) has shown that the Mississippi River system, which drains one of the most industrialized corridors of the world, exhibits surprisingly low concentrations of many dissolved elements. This observation has been found to be generally true for other turbid rivers of the world. In turbid rivers, many contaminants are likely to be associated with suspended sediments, and an accurate assessment of the overall health of such a river is thus incomplete if only dissolved constituents are examined. River-borne contaminants (dissolved and particulate) discharged into the Gulf of Mexico originate from a wide range of natural, industrial, municipal and agricultural inputs. Meade (1995) reports that the combined discharge from industrial and municipal point sources accounts for up to 2 % of the total discharge of the Mississippi River. This delivery of riverine contaminants impacts coastal ecosystem health and productivity, and plays an important role in the formation and intensity of seasonal hypoxic (e.g. low oxygen level) events that occur in the Mississippi Bight.

To address the topic of the delivery of sediment-associated contaminants to the Gulf of Mexico by the Mississippi River system, a study was initiated in 2001 by the USGS Coastal and Marine Geology Program. This study examined organic contaminant deposition and biogeochemical transformations across river-ocean salinity gradients and in recent deltaic sediments. The level of contamination within the deltaic systems was determined through the collection of sediment cores from interdistributary bays, and offshore in the Gulf. Results provide the basis for reconstructing contaminant inventories from which to develop historic perspectives on nutrient loading and hypoxia, and to better understand how sediment-hosted contaminants directly or indirectly move through biota and ultimately affect ecosystem health. Our overall hypothesis is that differential sedimentation of terrigenous, sediment-hosted contaminants in the high energy environment of the lower Atchafalaya and Mississippi Rivers and their respective receiving basins and flood plains can significantly alter the environmental fate and ultimate availability of these constituents. This differential sedimentation is primarily due to the discharge of Atchafalaya River waters into a broad, shallow inner shelf environment, while Mississippi River waters discharge into the Gulf of Mexico, beyond the shelf break (Fig. 1.).

To address the issue of present and historic hypoxia, we are comparing the sediments from sites where the water column is chronically hypoxic to sites that are chronically oxic. Shallow sediment cores provide a window into past hypoxic/anoxic events off the Mississippi River. Specific biomarkers and other redox proxies when combined with radiometric sediment dating (^{210}Pb and ^{137}Cs) will provide historical information of hypoxic events and associated ecosystem shifts. Such a record is invaluable in order to place current hypoxic events into an historical perspective (i.e. the anthropogenic imprint on the extent/duration of hypoxia).

Few datasets of recent sedimentary processes and organic contaminant distributions and loading of the active Mississippi River Delta currently exist. In this report, we address the general organic geochemistry of sediments from inshore and offshore sites. Results include distributions of the important nutrient elements (C,N,P, and S) and other constituents in sediment cores from the inshore and offshore MR (Fig. 1). Other reports emphasize organic contaminants (Rosenbauer and others,, 2007), and metals (Swarzenski and others, 2006). The delta is in a destructive phase of evolution as evidenced by the rapid conversion of wetlands to open marine environs. Sediments deposited in the natural levees and interfluves are now being eroded and contaminants stored in these sediments are potentially being released back into the open coastal/marine environment. Results from this study attempt to fill this information gap.

II. Study Area and Sampling

The main study area includes the lower Mississippi and Atchafalaya River Deltas (Fig. 1). Sediment coring was conducted in 2001, 2002, and 2003 to examine the organic matter composition of sediments. Initial priority was given to sampling and understanding organic matter deposited in fine grained sediments in the study area in the context of sediment-hosted contaminant transport down the Mississippi and Atchafalaya Rivers. A list of all sites sampled for this study is presented in Table 1. Sampling in 2001 focused on five nearshore sites: 2 off the lower Mississippi River and 3 near the mouth of the Atchafalaya River (Fig. 1). From the initial coring effort in 2001, we observed highly irregular and erratic deposition rates in the region closest to the Mississippi and Atchafalaya Rivers (Swarzenski and others, 2006). This indicates a highly energetic and geochemically unpredictable depositional system that is controlled more by the sheer physical energy of flow variability rather than by geochemical processes and reactions within the system. Based on the initial results, our strategy evolved to concentrate on sampling sediments more distant from the MR delta.

During 2002 and 2003, we collected a suite of undisturbed sediment cores that span a wide range of sedimentation rates, degree of hypoxia, total organic carbon concentrations, and variable influences of the MR system (Fig. 1). These cores provide the opportunity to reconstruct organic matter deposition and organic contaminant inventories and time series across transects that should better constrain off-continent material flux and examine the role of water column hypoxia in relation to contaminant bioavailablility and biologic uptake. A mix of short and long cores were collected for organic matter analysis in this

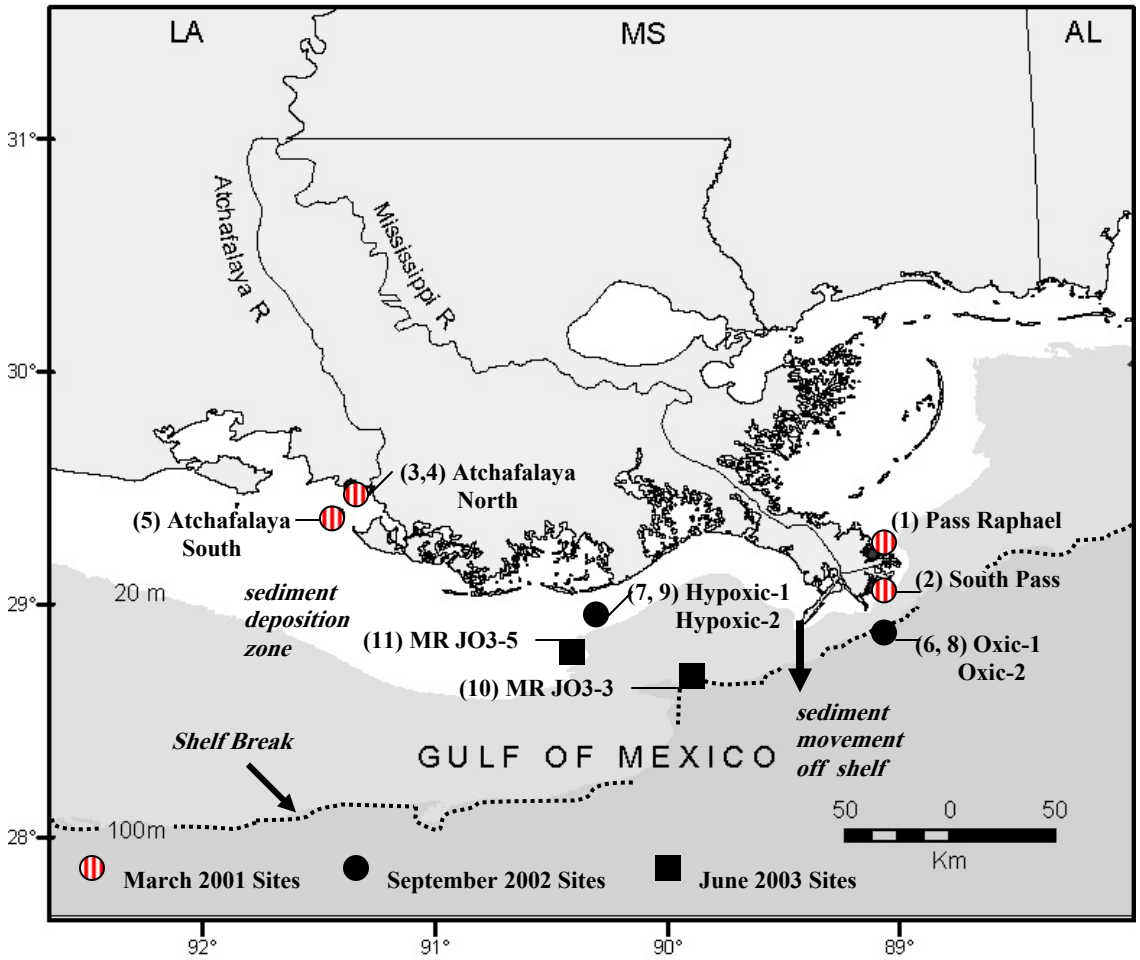


Fig. 1. Map of lower Mississippi and Atchafalaya River showing coring sites, March 2001 , oxic and hypoxic coring sites June and September 2002, and June 2003 coring sites. Numbers next to designated sites refer to numbers listed in Table 1. Note the location of the shelf break near the Mississippi River mouth, facilitating movement of sediment into deep water, compared to large zone of sediment deposition near discharge of Atchafalaya River.

Table 1. Location and description of coring sites in the lower Mississippi and Achafalaya River estuaries.

Site	Date	Lat.	Long.	Figure	Description
March 2001 Cores					
(1) Mississippi River Pass Raphael Site Core 010314-5	3/14/2001	29 13.014 N	89 07.222 W	2	Brackish water site on east side of delta
(2) Mississippi River South Pass Site Core 010314-6	3/14/2001	29 04.383 N	89 06.933 W	2	Marine site at southern tip of delta
(3) Atchafalaya River North Site 1 Core 010319-1	3/19/2001	29 30.468 N	91 21.630 W	2	Mouth of Atchafalaya River as it enters Achafalaya Bay; western side of a group of barrier islands
(4) Atchafalaya River North Site 2 Core 010320-1	3/20/2001	29 27.402 N	91 20.298 W	2	Close to Atchafalaya River North Site 1, but somewhat further southeast
(5) Atchafalaya River South Site Core 010318-1	3/18/2001	29 23.100 N	91 25.098 W	2	Leeward side of barrier islands separating Atchafalaya Bay from the Gulf of Mexico
June 2002 Cores					
(6) Mississippi River Oxic - 1	6/11/2002	29 20.387 N	89 54.088 W	2	Multicore collected at site in continuously oxic surface water zone.
(7) Mississippi River Hypoxic - 1	6/12/2002	28 56.107 N	90 18.139 W	2	Multicore collected at site in hypoxic surface water zone.

Table 1. Continued.

Site	Date	Lat.	Long.	Figure	Description
September 2002 Cores					
(8) Mississippi River Oxic-2 Core RCE 100_03A	9/17/2002	29 21.984 N	89 55.052 W	2	Multicore collected at site in continuously oxic surface water zone.
(8) MR Oxic - 2 Vibracore Core RCE 101B Orca-2	9/17/2002	29 21.984 N	89 55.052 W	2	Vibracore collected at site in continuously oxic surface water zone.
(9) MR Hypoxic - 2 Multicore Core RCE 102_02A	9/18/2002	28 56.059 N	90 18.257 W	2	Multicore collected at site in hypoxic surface water zone.
(9) MR Hypoxic - 2 Vibracore Core RCE_103B - Hypo2	9/18/2002	28 56.059 N	90 18.257 W	2	Vibracore collected at site in hypoxic surface water zone.
June 2003 Cores					
(10) Mississippi River MR-J-03-3	6/19/2003	28 37.762 N	90 00.620 W	3	Multicore collected from area with oxic water column; water depth 226 m
(11) Mississippi River MR-J-03-5	6/20/2003	28 55.501 N	90 22.501 W	3	Multicore collected from area with hypoxic water column; water depth 23 m.

study. Short multicores (up to 50 cm depth) were collected using an Ocean Instruments, Inc. multi-corer (Fig. 2), to examine processes at the sediment/water interface and changes in deposition during the last century. Longer vibracores, up to 300 cm depth were collected to examine geochemistry over longer time scales. Sediments were extruded in a vertical orientation on shipboard or shortly after return to land. Clean techniques were used during sediment extrusion and sectioning to avoid contamination. Short multicores were sectioned in 1 cm intervals to the bottom of the core, while longer vibracores were sectioned every 2 cm down to 50 cm, and in 5 cm increments below this. Sediment sections were immediately transferred to clean glass jars (I-Chem jars), frozen on dry ice, and shipped frozen back to laboratory facilities (Reston, VA and Menlo Park, CA) for organic geochemical studies.

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

III. Analytical Methods

A. Elemental Analysis of Sediments

Total and organic carbon (TC and OC), total nitrogen (TN), and total sulfur (TS) contents of sediments were determined using a Leco 932 CNS Analyzer (Leco Corporation, St. Joseph, MI, USA). TC, TN, and TS were measured directly, after drying the sediment overnight at 60° C. OC was determined after removal of inorganic carbon (IC), mostly carbonates, which constitutes a variable fraction (0-50%) of the TC content of sediments from these cores. We used an acid vapor method to remove the IC, slightly modified from that of Hedges and Stern (1984) and Yamamuro and Kayanne (1995). Sediment samples (5 to 6 mg) were weighed into prebaked (450° C) silver cups, placed in an acid vapor chamber (dessicator with beakers of concentrated HCl in the bottom), allowed to react for a minimum of 48 hrs, dried (60° C), and analyzed. In addition to samples, blanks and calcium carbonate standards were also placed in the acid vapor chamber. Blanks consisted of a prebaked (450° C) empty silver cup, and were used to monitor organic C contamination during the procedure. Calcium carbonate standards were used to visually determine when the acid vapor treatment was

Fig. 2. Multicorer for collection of near surface sediment cores.

complete, and as a check on the efficiency of the acid vapor treatment. All samples were analyzed at least induplicate. We have used this approach previously to examine TC, OC, IC, TN, and TS concentrations in marine sediments (Orem and others, 1999). Analytical precision (percentage relative standard deviation) was about 2% for TC, 4% for OC and TS, and 3% for TN. IC is reported as the calculated difference between TC and OC (e.g. %TC – %OC = %IC).

Total phosphorus (TP) concentrations in sediments were determined by the method of Aspila and others (1976), slightly modified for work in clastic sediments from the lower MR System. Samples were dried overnight (60° C), cooled to room temperature in a dessicator, weighed, and placed in precleaned (soaked in 10% HCl overnight, rinsed with deionized/distilled water, and baked at 450° C) ceramic crucibles. Generally, 0.4-0.6 g of the sediment was used for TP analysis. Weighed sediment samples were baked at 550° C for 2 hrs., cooled, then transferred into clean plastic centrifuge cones containing 45 ml of 1 M HCl. All plastic and glassware used for TP analysis was cleaned by soaking in 10% HCl overnight, followed by rinsing with deionized/distilled water. The empty crucibles were rinsed with 5 ml of 1 M HCl and the rinse was added to the centrifuge cones for a final volume of 50 ml of 1 M HCl. The samples were extracted in the 1 M HCl for 16 hrs. on a shaker to dissolve the phosphate. An aliquot of each extract was centrifuge-filtered using Millipore ultrafree-CL HVPP low-binding Durapore centrifuge filters (0.45 µm pore size), then neutralized with a 0.1 M NaOH solution, and transferred to plastic test tubes. The filtered aliquots were analyzed for phosphate using the standard phospho-molybdate method (Strickland and Parsons, 1972), and a Brinkman PC900 fiberoptic colorimeter. Analytical precision (percentage relative standard deviation) for the TP analysis is ± 3%.

Elemental ratios (C/N, C/P, N/P, C/S) reported are atomic ratios, calculated after conversion of weights of each parameter to molar units.

B. Sediment C_1-C_6 Hydrocarbon (Gas) Analysis

The concentrations of C_1-C_6 hydrocarbons (methane to hexane) were determined by headspace analysis. Sediments from cores collected at various sites off the Mississippi and Atchafalaya Rivers were sectioned into 4 or 5 cm intervals, and each section transferred to metal cans. Each metal can had a top containing a silicone rubber septum that was secured in a hole in the top with epoxy cement. A small amount of gluteraldehyde was added to the sediment in each can (to retard microbial activity), and the top was secured on the paint can.

Cans containing the sediment were returned to the laboratory in Reston, VA for gas analysis. A known volume of gas (generally 1 ml) in the headspace of the can was extracted using a gas tight syringe and analyzed by gas chromatography with flame ionization detection (GC-FID), using an Aglient 6890N GC equipped with a 30 meter x .32 mm ID Carbonplot column, and a constant hydrogen carrier gas flow of 4ml/min. Analytical conditions for the GC-FID analysis were as follows: (1) initial column temperature of 40° C at injection; (2) ramping to 350°C at 15° C/min.; (3) a final hold at 350 ° C for 5 min. Concentrations of C_1-C_6 hydrocarbon gases were determined using an external standard method, generated using C_1-C_6 gas standards of 100 ppm and 1000 ppm (Supelco). Gas blanks were determined from analysis of degassed water head space. The headspace in each can was analyzed for gaseous hydrocarbons (C1-C6) at least in duplicate. The average gas content from these analyses represents the “free” gas present.

After completion of the “free” gas analysis, the volume of headspace in each can was determined by filling with degassed water, and the contents of each can were transferred to a specially modified stainless steel blender for “bound” gas determination using degassed water. The blender was a commercial product, modified to include a septum that was attached with epoxy cement to a hole in the top of the blender. Degassed water was added to the sample in the blender to adjust the blender headspace to approximately 45 mL. The sediment sample in the blender was homogenized for 5 min. at high speed, and a 1 ml sample of gas in the headspace was removed from the septum in the top of the blender in a gas tight syringe for analysis. Concentrations of “bound” hydrocarbons were determined by GC-FID using the method described for the “free” hydrocarbon analysis. The volume of headspace in the blender was determined for each sample by adding degassed water. The terms “free” and ‘bound” hydrocarbon gas are used operationally here, and imply only ease of extraction, not necessarily the molecular state of the gaseous hydrocarbons in the sediments. After subsampling for “bound” hydrocarbons, the sample was transferred from the blender to a preweighted plastic 500 mL beaker, and dried in oven at 110 C for 48-72 hours. The beaker was then weighed and dry weight of sample determined. Final quantification of the gas content of each sediment sample was calculated using the GC-FID data, the headspace volumes, and the dry weight of each sediment sample (determined following the “bound” hydrocarbon analysis). Concentrations are reported as ppm gas per g sediment (dry weight basis).

IV. Results

A. Elemental Composition of Sediments

2001 coring sites - The elemental composition (TC, OC, IC, TN, TP, TS) of the sediments from cores collected in 2001 from various locations in the lower Mississippi and Atchafalaya River Deltas is presented in Table 2. All TC, OC, IC, TN, TP, and TS concentrations are reported as percent of total sediment on a dry weight basis. Atomic C/N, C/P, C/S, and N/P ratios are also presented in Table 2. Results are plotted in Figs. 3-11. Total C contents in these cores ranged from 0.5% to 5.5%, OC contents from 0.2% to 3.9%, and IC from below detectable levels to 4.5%. The highest total C contents were observed at the surface of the Atchafalaya South site core, but this was primarily inorganic C in composition. Highest organic C contents were observed at the Pass Raphael site in the lower Mississippi River. Downcore variations in total, organic and inorganic C contents were as great or greater than the site to site variations, and downcore profiles were irregular with subsurface maxima common in most of these cores.

TN values range from 0.03% to 0.32% in the 2001 cores from the lower Mississippi and Atchafalaya Rivers (Table 2). The TN data tended to follow the OC data, and the highest total N values were observed at the Pass Raphael site. Downcore profiles for TN generally followed those for OC, and were irregular with depth with numerous subsurface maxima in the cores. TS values ranged from <0.001% to 1.25% in these cores. The highest TS values were observed at the Pass Raphael site (as were TN and OC), and TS values tended to follow those for OC at each core site. TP values ranged from 0.032% to 0.073% in these cores. Highest TP values were observed at the South Pass and Pass Raphael sites. Downcore TP profiles did not resemble those for OC, TN, and TS, suggesting that factors influencing deposition and biogeochemical cycling of P are somewhat different than those for C, N, and S.

Atomic C/N ratios (Table 2 and Fig. 8) range from 7 to 18, but with most values between 8 and 15. Atomic C/N values in the range of 8-15 are usually indicative of a mix of algal and vascular plant material contributing to the organic matter in the sediments (Tissot and Welte, 1984). The Atchafalaya north and south sites had the overall lowest atomic C/N values. The Atchafalaya north 2 site had some of the highest atomic C/N values. This site is near the mouth of the Atchafalaya River and should receive significant riverine discharge of terrestrially derived (vascular plant) organic matter from wetlands along the river and from further upstream. In several of the cores, subsurface maxima in OC content are correlated with maxima in atomic C/N, indicating that these maxima are largely driven by input of terrestrially derived (vascular plant) organic matter.C/N ratios (Table 2 and Fig. 8) range from 7 to 18, but with most values between 8 and 15.

Atomic C/P (Table 2 and Fig. 9) values range from 27 to 167 in these cores, but with most values between 30 and 75. This range of values for atomic C/P is somewhat low for algal- or vascular plant-derived organic matter (e.g. pure algae should have a C/P ratio of 106), suggesting a source of excess P entering the lower Mississippi River Delta area (Tissot and Welte, 1984). The highest atomic C/P values were observed at the Pass Raphael site. This is largely driven by the high OC values, especially over the 10-60 cm depth interval. Atomic N/P ratios ranged from 2.1 to 11.5 (Table 2 and Fig. 10), which are also relatively low relative to atomic N/P values expected for algal- and vascular plant-derived organic matter (Tissot and Welte, 1984). The atomic N/P values also suggest a source of

excess P to these sites. Atomic N/P values were highest at the Pass Raphael site, similar to atomic C/P values. Downcore C/P and N/P values generally follow the OC profiles.

Atomic C/S values (Table 2 and Fig. 11) have a large range of 5.5 to 2480, but with most values between 25 and 100. The lowest atomic C/S values were observed at the South Pass site, and at Pass Raphael above 60 cm. The low atomic C/S values here are largely driven by high TS concentrations. The Atchafalaya sites have generally lower TS concentrations, and higher atomic C/S values. The Pass Raphael site has an unusual atomic C/S vertical profile, with a sharp change at about 60 cm depth.

Oxic/Hypoxic sites – The elemental composition (TC, OC, IC, TN, TP, and TS) and elemental ratios (atomic C/N, C/P, C/S, and N/P) of organic matter in sediments from the hypoxic and oxic sites sampled in June and September 2002 (hypoxic-1 and 2, and oxic-1 and 2 on the map in Fig. 1) are presented in Table 3 and in Figs. 12-15. At the oxic sites, TC concentrations in sediments range from about 1% to 10% in all cores, compared to a range of only 1.6% to 0.9% at the hypoxic sites. Organic C contents ranged from 0.6% to 10% at the oxic sites, and from 0.4% to 1.4% at the hypoxic site. Inorganic C varied from undetectable (<0.01%), up to 0.5% at the hypoxic sites and 0.9% at the oxic sites. Average values for TC, OC, and IC, respectively, for all samples were: 2.76%, 2.56%, and 0.24% at the oxic sites; and 1.08%, 0.721%, and 0.37% at the hypoxic sites. The higher TC and OC content of sediments at the oxic site was driven largely (but not exclusively) by a large maximum in total and organic C (up to 10% TC and OC) in the 25-100 cm depth interval at the oxic site (Fig. 14). The hypoxic site also exhibited an increase in TC and OC over the 25-100 cm depth interval, but the increase was 6-7x smaller than that observed at the oxic site.

TN concentrations in sediments ranged from 0.07% to 0.7% at the oxic sites, and 0.05% to 0.1% at the hypoxic sites (Table 3, Figs. 12 and 14). Average values for TN for all oxic- and hypoxic-1 and 2 samples were: 0.2% at the oxic sites and 0.09% at the hypoxic sites. Downcore profiles for TN paralleled those for OC at both the oxic and hypoxic sites. As with TC and OC, the higher TN content of sediments at the oxic sites was largely, but not exclusively, due to the large increase in organic matter deposited in the 25-100 cm depth interval at the oxic sites.

In contrast to carbon and nitrogen, TP values were comparable at the oxic and hypoxic sites: range of 0.03% to 0.07% at the oxic sites (average for all samples, 0.05%); and a range of 0.05% to 0.07% at the hypoxic sites (average for all samples, 0.06%), (Table 3). The downcore profile for TP did not exhibit the large maximum in the 25-100 cm interval that was observed for TC, OC and TN (Figs. 12 and 14).

TS concentrations in sediments ranged from 0.1% to 3% at the oxic sites, and from 0.03% to 1.5% at the hypoxic sites (Table 3). Average TS concentrations for all samples were about 0.7% at the oxic site and about 0.4% at the hypoxic site. Sediments from hypoxic sites would be expected to have higher TS concentrations relative to oxic sites, assuming comparable organic matter contents. This was observed at the hypoxic 1 and oxic

Table 2. Elemental composition (% dry wt.) of sediments from 2001 USGS cores in the Mississippi and Atchafalaya River estuaries: total C (TC), organic C (OC), inorganic C (IC), total N (TN), total P (TP), total S (TS) and atomic C/N, C/P, C/S, and N/P ratios.

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
Mississippi River	0-2	2.11	1.88	0.23	0.184	0.0733	0.191	11.9	66.1	26.3	5.55
Pass Raphael Site	2-4	1.38	0.951	0.43	0.131	0.0609	0.178	8.46	40.3	14.3	4.76
Core 010314-5	4-6	0.955	0.586	0.37	0.080	0.0443	0.286	8.54	34.1	5.47	3.99
	6-8	1.64	1.28	0.36	0.140	0.0543	0.444	10.7	60.8	7.70	5.70
	8-10	2.81	2.46	0.36	0.249	0.0576	0.932	11.5	110	7.05	9.56
	10-12	2.18	1.98	0.20	0.194	0.0581	0.765	11.9	87.9	6.91	7.38
	12-14	1.80	1.68	0.12	0.178	0.0642	0.424	11.0	67.5	10.6	6.13
	14-16	1.93	1.80	0.13	0.186	0.0716	0.470	11.3	64.8	10.2	5.74
	16-18	1.91	1.77	0.14	0.183	0.0719	0.434	11.3	63.5	10.9	6.79
	18-20	1.88	1.72	0.16	0.186	0.0678	0.532	10.8	65.4	8.63	6.07
	20-25	2.22	2.08	0.14	0.193	0.0784	0.526	12.6	68.4	10.6	5.44
	25-30	2.05	1.99	0.06	0.197	0.0701	0.654	11.8	73.2	8.12	6.21
	30-35	2.32	2.19	0.13	0.211	0.0599	0.834	12.1	94.3	7.01	7.79
	35-40	3.18	3.03	0.15	0.265	0.0628	1.15	13.3	124	7.03	9.33
	40-45	3.61	3.48	0.13	0.288	0.0621	1.06	14.1	144	8.76	10.2
	45-50	3.76	3.94	0.00	0.316	0.0607	1.25	14.5	167	8.41	11.5
	50-60	1.31	1.17	0.14	0.117	0.0537	0.447	11.7	56.2	6.99	4.82
	60-70	0.774	0.638	0.14	0.064	0.0502	0.021	11.6	32.8	81.1	2.82
	70-80	0.809	0.588	0.22	0.061	0.0523	0.015	11.2	29.0	105	2.58
	80-90	1.03	0.838	0.20	0.090	0.0549	0.054	10.8	39.4	41.4	3.62
	90-100	0.925	0.773	0.15	0.064	0.0536	0.026	14.1	37.2	79.4	2.64
	100-106	0.870	0.644	0.23	0.055	0.0543	0.062	13.6	30.6	27.7	2.24
Mississippi River	0-2	1.90	1.52	0.38	0.158	0.0644	0.199	11.2	60.7	20.4	5.42
South Pass Site	2-4	2.00	1.58	0.42	0.167	0.0630	0.196	11.0	64.7	21.5	5.86
Core 010314-6	4-6	2.32	1.74	0.58	0.208	0.0769	0.226	9.76	58.3	20.6	5.98
	6-8	2.09	1.56	0.53	0.180	0.0666	0.236	10.1	60.4	17.6	5.98

Table 2. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
Mississippi River	8-10	2.65	2.00	0.65	0.187	0.0659	0.279	12.5	78.3	19.1	6.27
South Pass Site	10-12	1.37	1.03	0.34	0.118	0.0616	0.170	10.2	43.1	16.2	4.24
Core 010314-6	12-14	2.60	2.11	0.49	0.234	0.0688	0.305	10.5	79.1	18.5	7.52
	14-16	2.03	1.59	0.44	0.164	0.0690	0.208	11.3	59.4	20.4	5.26
	16-18	2.07	1.61	0.46	0.179	0.0672	0.194	10.5	61.8	22.2	5.89
	18-20	2.23	1.69	0.54	0.151	0.0654	0.222	13.0	66.6	20.3	5.10
	20-25	1.86	1.52	0.35	0.158	0.0659	0.201	11.2	59.5	20.2	5.30
	25-30	2.25	1.78	0.47	0.217	0.0686	0.296	9.56	66.9	16.0	7.00
	30-35	2.39	2.10	0.29	0.240	0.0692	0.303	10.2	78.2	18.5	7.67
	35-40	2.19	1.68	0.51	0.171	0.0589	0.291	11.4	73.6	15.4	6.42
	40-45	1.26	0.873	0.39	0.106	0.0635	0.183	9.60	35.4	12.7	3.69
	45-50	2.06	1.47	0.59	0.166	0.0646	0.252	10.3	58.6	15.6	5.68
	50-60	1.56	1.04	0.52	0.143	0.0640	0.218	8.48	41.9	12.7	4.94
	60-70	1.62	1.19	0.43	0.175	0.0660	0.227	7.93	46.5	14.0	5.86
	70-74	2.43	2.06	0.37	0.227	0.0663	0.267	10.6	80.1	20.6	7.57
Atchafalaya River	0-2	1.57	1.26	0.31	0.138	0.0634	0.080	10.6	51.2	42.0	4.81
North Site	2-4	1.06	0.721	0.34	0.090	0.0528	0.034	9.34	35.2	56.6	3.77
Core 010319-1	4-6	1.01	0.727	0.28	0.093	0.0529	0.028	9.12	35.4	69.3	3.89
	6-8	1.45	1.10	0.35	0.135	0.0526	0.080	9.50	53.9	36.7	5.68
	8-10	1.78	1.45	0.33	0.173	0.0597	0.126	9.77	62.6	30.7	6.41
	10-12	1.34	1.09	0.24	0.127	0.0538	0.068	10.0	52.2	42.8	5.22
	12-14	1.07	0.806	0.26	0.098	0.0521	0.042	9.59	39.9	51.2	4.16
	14-16	0.85	0.594	0.26	0.078	0.0511	0.046	8.88	30.0	34.5	3.38
	16-18	1.21	0.986	0.23	0.114	0.0626	0.071	10.1	40.6	37.1	4.03
	18-20	0.806	0.619	0.19	0.072	0.0508	0.020	10.0	31.4	82.6	3.13
	20-25	0.800	0.511	0.29	0.060	0.0457	0.056	9.93	28.8	24.4	2.90

Table 2. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
Atchafalaya River	25-30	0.855	0.625	0.23	0.079	0.0494	0.026	9.23	32.6	64.2	3.54
North Site	30-35	0.753	0.536	0.22	0.064	0.0426	0.071	9.77	32.4	20.2	3.32
Core 010319-1	35-40	0.502	0.325	0.18	0.046	0.0362	<0.001	8.24	23.2	>868	2.81
	40-45	0.808	0.596	0.21	0.083	0.0537	<0.001	8.37	28.6	>1590	3.42
	45-50	0.855	0.613	0.24	0.060	0.0465	<0.001	11.9	34.0	>1640	2.85
	50-60	1.07	0.807	0.26	0.100	0.0532	<0.001	9.41	39.1	>2150	4.16
	60-70	1.28	1.03	0.25	0.120	0.0548	0.024	10.0	48.5	114	4.84
Archafalaya River	0-2	1.74	0.719	1.03	0.088	0.0597	0.062	9.53	31.0	31.0	3.26
North Site 2	2-4	0.998	0.719	0.28	0.046	0.0480	0.041	18.2	38.6	46.8	2.12
Core 010320-1	4-6	0.785	0.369	0.42	0.045	0.0322	0.024	9.56	29.6	41.0	3.09
	6-8	0.675	0.441	0.23	0.041	0.0389	0.026	12.5	29.2	45.3	2.33
	8-10	0.754	0.401	0.35	0.041	0.0392	0.031	11.4	26.4	34.5	2.31
	10-12	1.11	0.891	0.22	0.081	0.0499	0.036	12.8	46.0	66.1	3.59
	12-14	1.13	0.723	0.41	0.082	0.0464	0.030	10.3	40.2	64.3	3.91
	14-16	0.508	0.206	0.30	0.032	0.0322	0.014	7.51	16.5	39.3	2.20
	16-18	0.734	0.471	0.26	0.045	0.0382	0.024	12.2	31.8	52.4	2.60
	18-20	0.934	0.804	0.13	0.062	0.0458	0.042	15.1	45.3	51.1	2.99
	20-25	1.09	0.874	0.22	0.070	0.0501	0.034	14.6	45.0	68.6	3.09
	25-30	1.08	1.05	0.03	0.096	0.0540	0.044	12.8	50.1	63.7	3.93
	30-35	1.10	1.09	0.01	0.100	0.0557	0.046	12.7	50.5	63.3	3.97
	35-40	1.29	1.33	0	0.127	0.0571	0.084	12.2	60.1	42.3	4.92
	40-45	1.38	1.48	0	0.140	0.0641	0.074	12.3	59.5	53.4	4.83
	45-50	1.19	1.17	0.02	0.093	0.0519	0.082	14.7	58.1	38.1	3.96
	50-60	1.10	0.940	0.16	0.094	0.0521	0.047	11.7	46.5	53.4	3.99
	60-70	0.991	0.579	0.41	0.096	0.0548	0.046	7.03	27.2	33.6	3.87

Table 2. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
Archafalaya River	70-80	0.978	0.619	0.36	0.078	0.0480	0.044	9.25	33.2	37.6	3.59
North Site 2	80-90	1.17	0.891	0.28	0.099	0.0533	0.037	13.8	43.1	64.3	4.11
Core 010320-1											
Atchafalaya River	0-2	3.41	1.08	2.33	0.100	0.0418	0.086	12.6	46.6	33.5	3.70
South Site	2-4	4.63	0.918	3.71	0.092	0.0375	0.032	11.6	49.3	76.6	4.24
Core 010318-1	4-6	5.51	1.01	4.50	0.087	0.0362	0.016	13.5	80.9	168	5.97
	6-8	5.02	0.856	4.16	0.072	0.0383	0.009	13.9	56.7	254	4.09
	8-10	4.62	0.931	3.69	0.085	0.0431	0.001	12.8	61.2	2480	4.79
	10-12	2.39	0.840	1.55	0.111	0.0568	0.146	8.82	43.4	15.4	4.92
	12-14	1.73	1.02	0.71	0.122	0.0581	0.143	9.75	56.7	19.0	5.81
	14-16	1.79	1.06	0.73	0.129	0.0580	0.210	9.58	84.9	13.5	8.86
	16-18	2.14	0.940	1.20	0.120	0.0544	0.144	9.14	63.4	17.4	6.95
	18-20	2.75	1.03	1.70	0.124	0.0560	0.097	9.69	58.0	28.3	5.99
	20-25	1.61	1.27	0.34	0.152	0.0618	0.134	9.74	65.4	25.3	6.71
	25-30	1.45	1.13	0.31	0.140	0.0616	0.124	9.41	54.0	24.3	5.73
	30-35	1.45	1.15	0.30	0.140	0.0614	0.135	9.58	53.2	22.7	5.56
	35-40	1.39	1.06	0.33	0.139	0.0633	0.131	8.89	47.9	21.6	5.38
	40-45	1.45	1.18	0.28	0.159	0.0613	0.144	8.65	47.5	21.9	5.48
	45-50	1.54	1.21	0.33	0.155	0.0621	0.167	9.10	60.1	19.3	6.60
	50-60	1.59	1.33	0.26	0.178	0.0648	0.167	8.71	65.8	21.3	7.55
	60-70	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	70-80	1.55	1.21	0.33	0.163	0.0644	0.130	8.66	65.0	24.8	7.51
	80-85	1.49	1.18	0.32	0.159	0.0641	0.129	8.65	57.1	24.4	6.60
	85-bt	1.56	1.25	0.30	0.175	nd	0.156	8.33	nd	21.4	nd

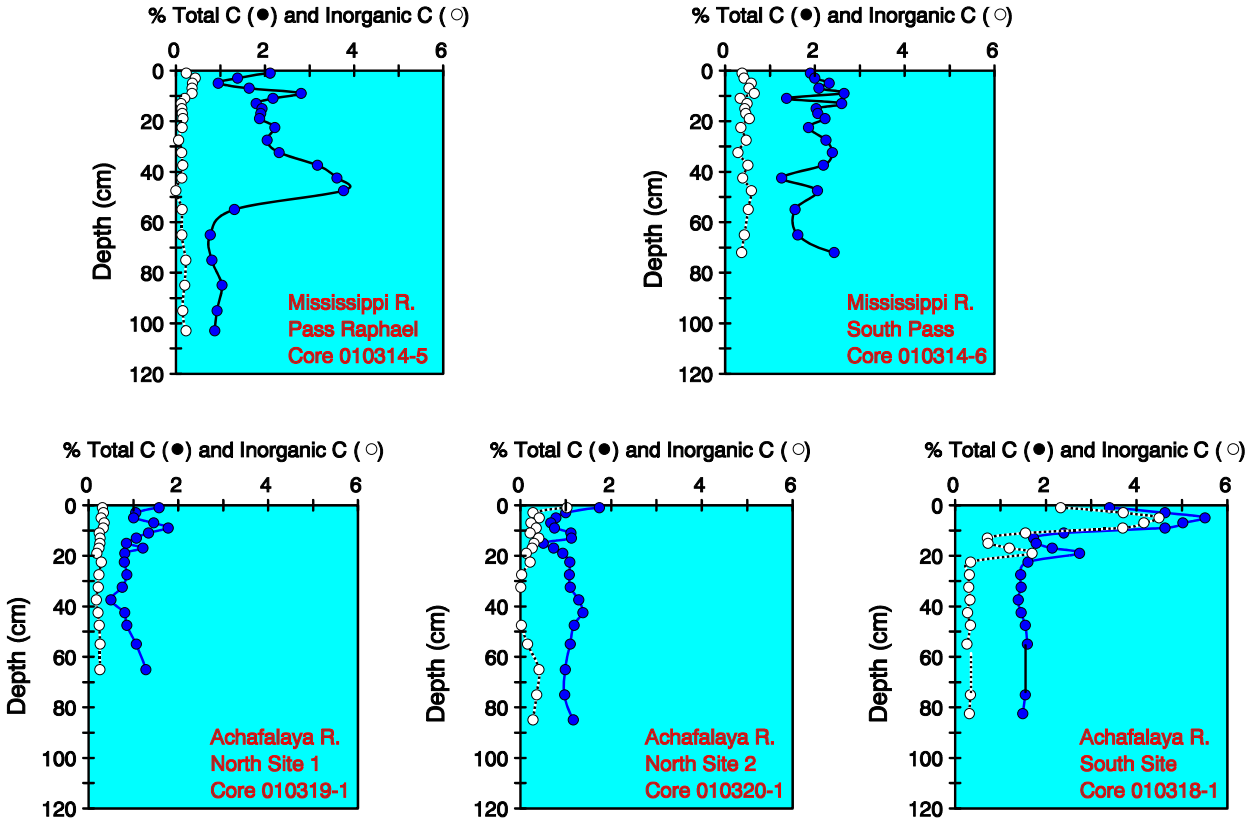


Fig. 3. Total carbon (% dry wt.) and inorganic carbon (% dry wt.) contents of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

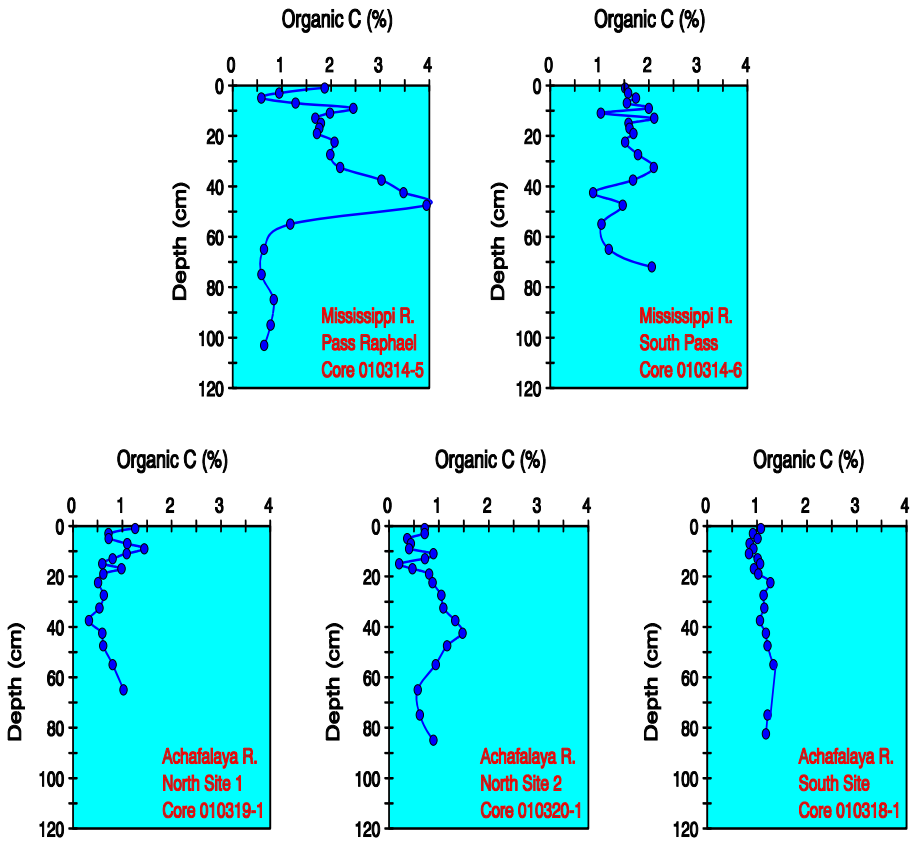


Fig. 4. Organic carbon content (% dry wt.) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

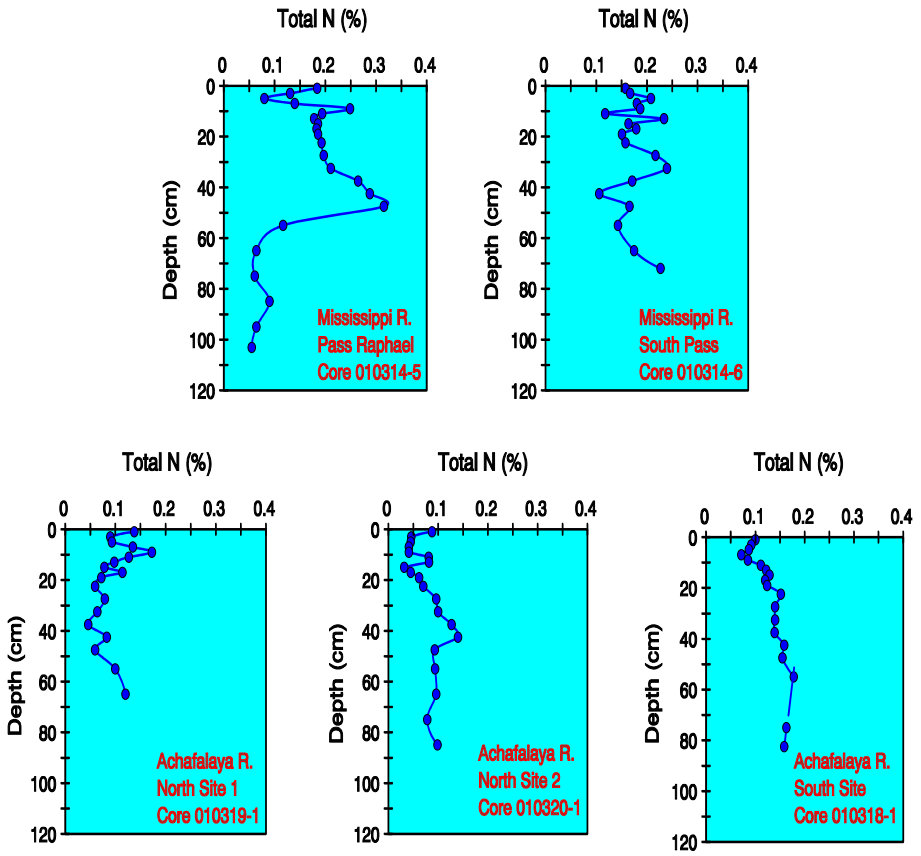


Fig. 5. Total nitrogen content (% dry wt.) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

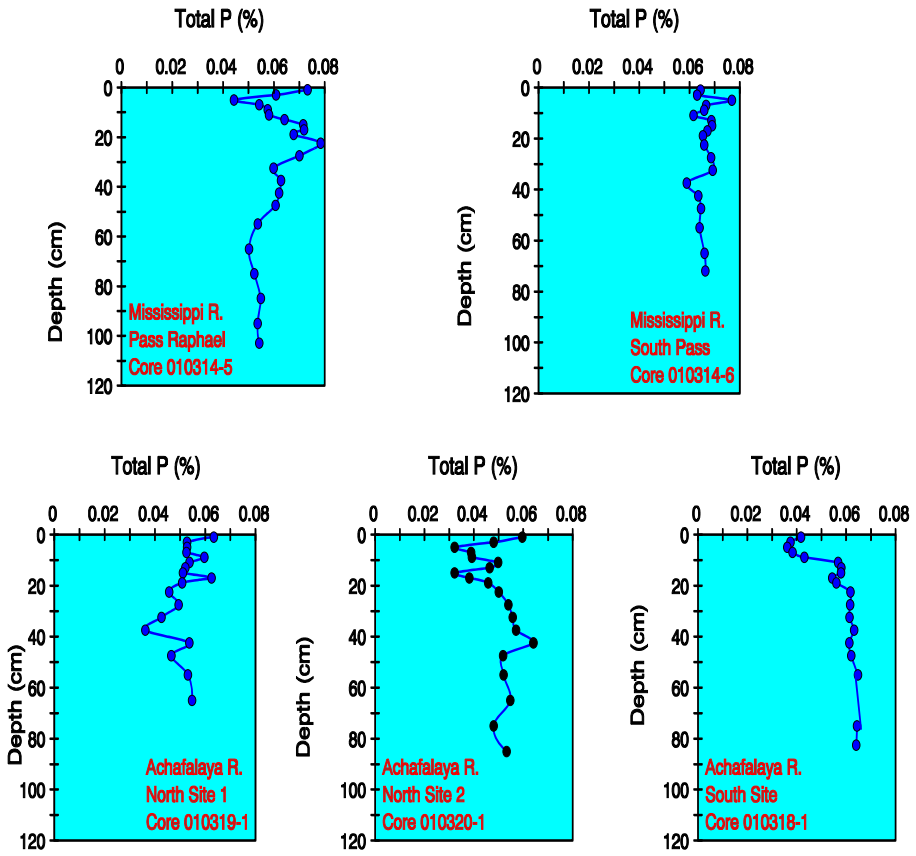


Fig. 6. Total phosphorus contents (% dry wt.) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

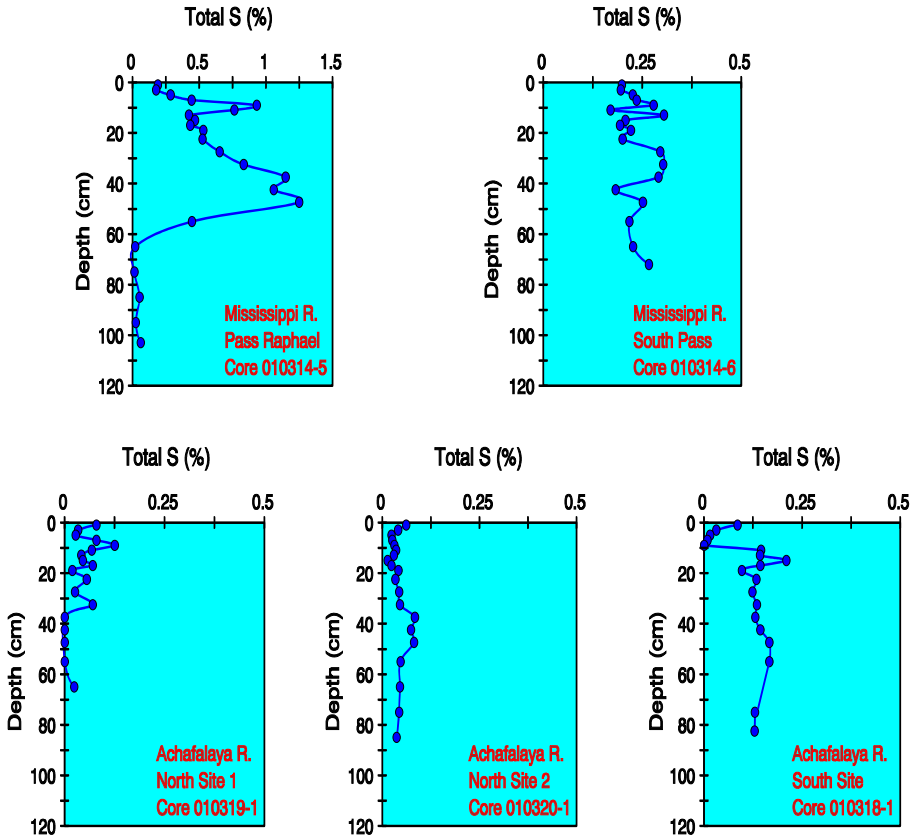


Fig. 7. Total sulfur contents (% dry wt.) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001 (note different scale for Pass Raphael site).

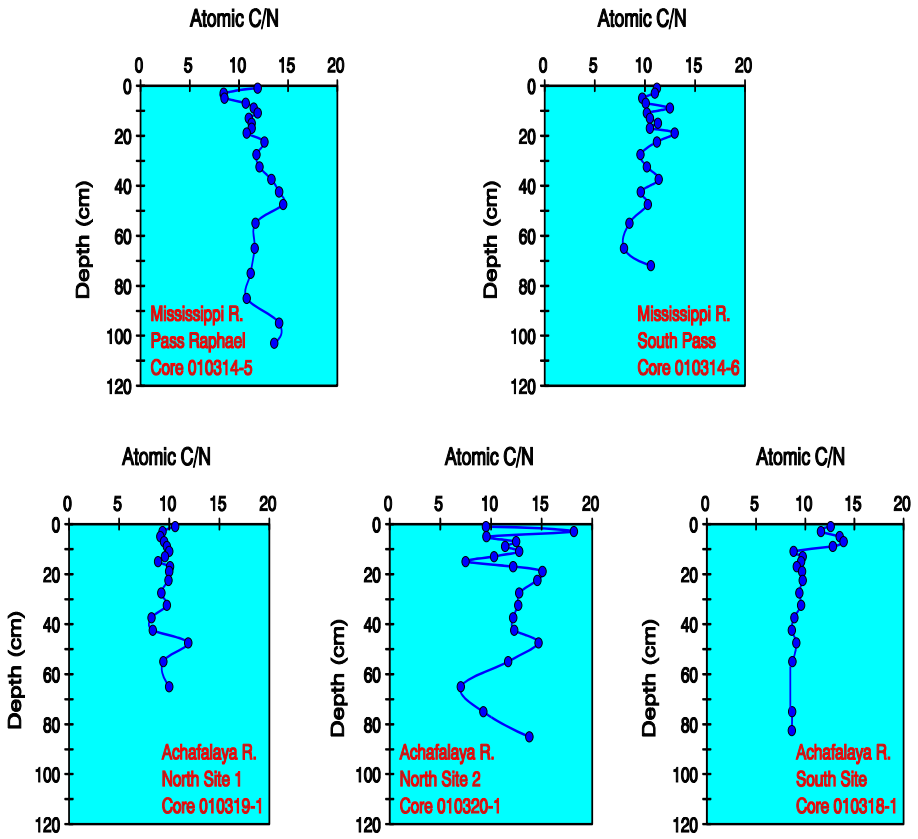


Fig. 8. Atomic C/N (organic carbon/total nitrogen) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

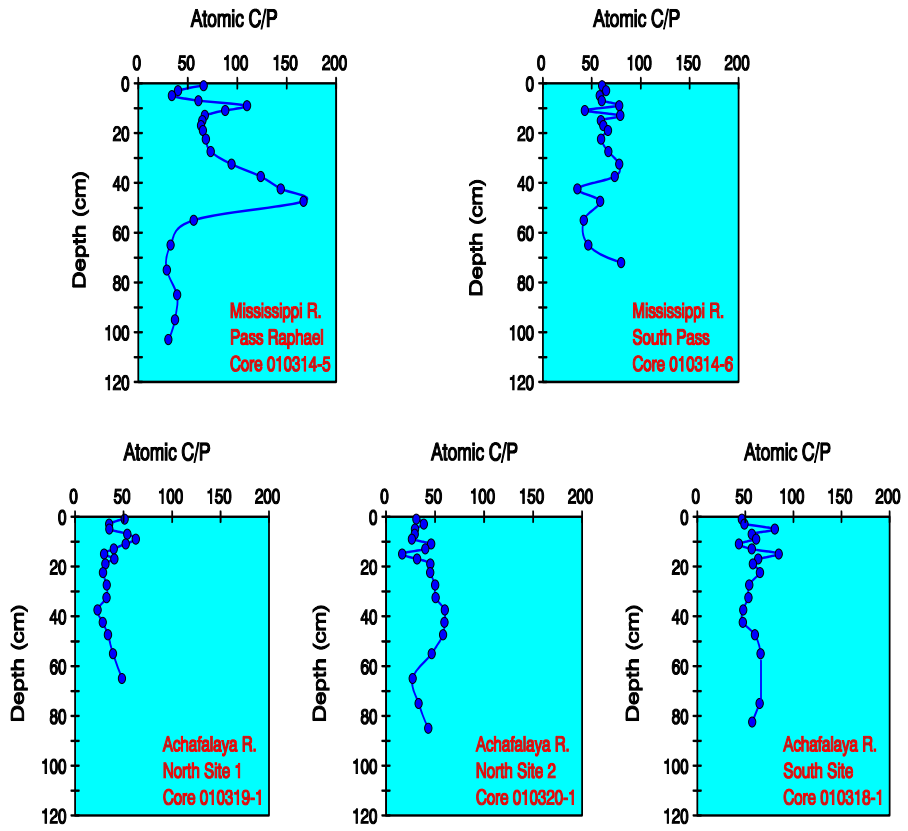


Fig. 9. Atomic C/P (organic carbon/total phosphorus) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

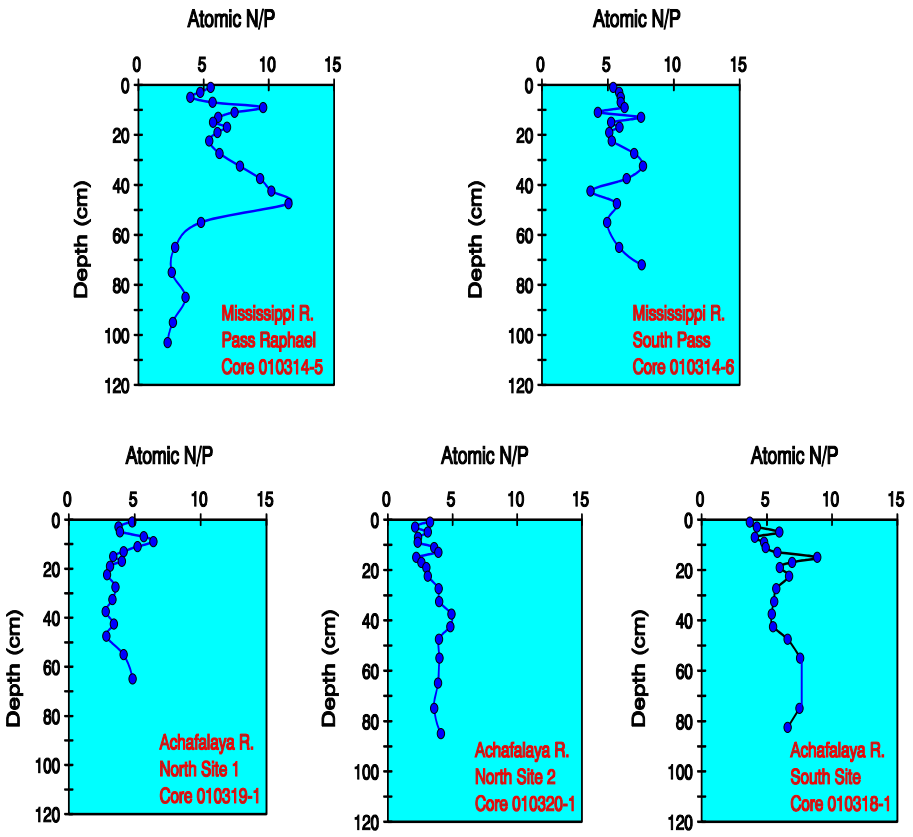


Fig. 10. Atomic N/P (total nitrogen/total phosphorus) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

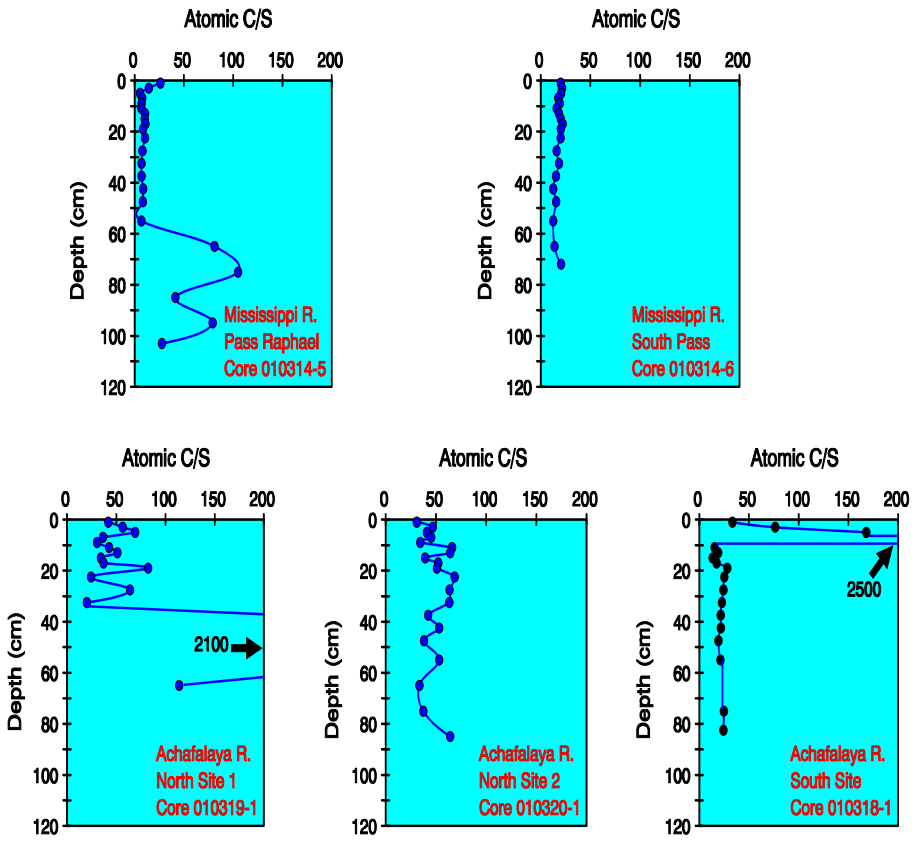


Fig. 11. Atomic C/S (organic carbon/total sulfur) of sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

1 sites (Fig. 12). Sediments at the oxic 2 site, however, had much higher TS concentrations compared to hypoxic 2, reflecting the generally higher organic C contents in the oxic 2 sediments (Fig. 14). Downcore profiles of TS generally paralleled those for C and N at all oxic and hypoxic sites.

Overall atomic C/N and C/P values were relatively low at both the oxic and hypoxic sites, reflecting greater deposition of microbially-derived (algal) organic matter in these sediments. Atomic C/N, C/P, and N/P values were generally higher at the oxic coring sites (Oxic-1 and -2), compared to the hypoxic coring sites (Hypoxic-1 and -2), (Figs. 13 and 15). This is consistent with a greater proportion of terrestrially-derived organic matter at the oxic sites, though deposition of algal material still dominated at the oxic sites. The range of atomic C/N, C/P, and N/P values were: 2-23, 30-829, and 3-49, respectively in sediments from the oxic sites, and 6-14, 21-61, and 2-5, respectively in sediments from the hypoxic sites. Average atomic C/N, C/P, and N/P values were: 12.5, 168, and 11.8, respectively in sediments from the oxic sites, and 9.7, 32, and 3.4 in sediments from the hypoxic sites. Significant changes in downcore atomic C/N, C/P, and N/P values (maxima and minima in the vertical profiles) at all sites, largely reflect changes in organic carbon deposition over time.

Atomic C/S values ranged from 3.5 to 23 in sediments from oxic site cores, and from 1.3 to 75 in sediments from the hypoxic cores. Average atomic C/S values were 9.9 for all oxic site samples, and 12.8 for all hypoxic site samples. The shallow multicore samples (@ 0-30 cm) had average atomic C/S values of 10.5 at the oxic sites and 7.0 at the hypoxic sites. Lower atomic C/S values were anticipated in sediments from the hypoxic sites, reflecting possible microbial sulfate reduction in the water column and additional deposition of metal sulfides in sediments. This was certainly the case at the hypoxic 1 versus oxic 1 sites (Fig. 13). Lower atomic C/S values were also observed at oxic 2 compared to hypoxic 2 (Fig. 15). However, comparison of atomic C/S values at the oxic 2 and hypoxic 2 sites was complicated by a large difference in organic carbon contents between the two locations. The downcore atomic C/S profiles were very irregular at the oxic 2 and hypoxic 2 sites. Atomic C/S values showed an overall decrease with depth at the oxic 2 and hypoxic 2 sites, probably reflecting both biodegradation of OC and buildup of metal sulfides in the sediments from microbial sulfate reduction.

June 2003 core sites – Elemental C,N,S data and atomic C/N and C/S ratios for sediments from cores MR-J03-3 and MR-J03-5 (location map in Fig. 1) are presented in Table 3 and plotted in Figs. 16 and 17. Core MR-J03-5 is located near the 2002 hypoxic-1 and 2 core sites (Table 1, Fig. 1), and is considered to be in the zone of hypoxia in the Gulf of Mexico near the Mississippi River delta (Rabalais and others, 2001 and 2002). Core MR-J03-3 is located further offshore, and is considered to have an oxic water column. Only TC was determined in these cores. Sediment concentrations of TC have a tight range of 1.4% to 1.7% (average for all samples of 1.44%) in core MR-J03-3, and a somewhat larger range of 0.6% to 1.7% (average for all samples of 1.13%) in core MR-J03-5. TC concentrations in the MR-J03-3 core were similar to those in the oxic-1 core (Fig 12), but different from those in the oxic-2 core, which had a pronounced maximum in TC beginning at about 25 cm depth (Fig. 14). Core MR-J03-5 had TC concentrations similar to those in the the hypoxic-1 and 2 cores. The downcore profile of TC in core MR-J03-3 is relatively constant, with a slight peak at about 3 cm, and several other minor peaks downcore. Core MR-J03-5 has a much more variable downcore profile, with a maximum TC value at about 3 cm, and a minimum at about 7 cm. Below 3 cm, core MR-J03-3 had higher TC concentrations compared to core MR-J03-5.

TN concentrations ranged from 0.13% to 0.22% (average for all samples of 0.17%) in core MR-J03-3, and from 0.05% to 0.19% (average for all samples of 0.09%) in core MR-J03-5. As with TC, concentrations of TN in sediments from core MR-J03-3 were similar to those in the oxic-1 core, but lower than those in oxic-2. This was primarily due to the large maximum in TC and TN in the 25-100 cm increment in the oxic-2 core. The MR-J03-5 core has sedimentary TN concentrations similar to those at hypoxic-1 and 2. Downcore profiles of TN parallel those for TC in both the MR-J03-3 and -5 cores.

In contrast to TC and TN, which are higher in the MR-J03-03 core, TS values were distinctly higher in the MR-J03-5 core compared to the MR-J03-3 core. TS concentrations ranged from 0.16% to 0.58% in the MR-J03-5 core (average for all samples of 0.31%), compared to 0.16% to 0.24% in the MR-J03-3 core (average for all samples of 0.20%). The downcore profile of TS in the MR-J03-3 core resembled that for TC and TN, whereas the downcore profile for TS in the MR-J03-5 core was distinctly different from

Table 3. Elemental composition (% dry wt.) of sediments from 2002-2003 USGS cores in the lower Mississippi River estuary: total C (TC), organic C (OC), inorganic C (IC), total N (TN), total P (TP), total S (TS), and atomic C/N, C/P, C/S, and N/P ratios.

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
Oxic 1 Multicore	0-1	1.77	1.18	0.59	0.157	0.0630	0.349	8.76	48.3	9.02	5.51
	1-2	1.22	0.816	0.40	0.118	0.0490	0.196	8.06	42.9	11.1	5.32
	2-3	1.59	0.974	0.62	0.145	0.0476	0.262	7.83	52.8	9.92	6.74
	3-4	2.12	1.67	0.45	0.177	0.0497	0.409	11.0	86.6	10.9	7.88
	4-5	2.11	1.61	0.50	0.185	0.0501	0.507	10.1	82.9	8.48	8.16
	5-6	1.99	1.68	0.31	0.181	0.0546	0.448	10.8	79.3	10.0	7.33
	6-7	1.80	1.53	0.27	0.179	0.0475	0.531	9.97	83.1	7.69	8.33
	7-8	1.81	1.48	0.33	0.168	0.0497	0.505	10.3	76.8	7.82	7.47
	8-9	1.61	1.41	0.20	0.165	0.0484	0.476	9.96	75.1	7.91	7.54
	9-10	1.86	1.69	0.17	0.180	0.0480	0.498	10.9	90.8	9.06	8.29
	10-11	1.74	1.55	0.19	0.177	0.0463	0.557	10.2	86.3	7.43	8.45
	11-12	2.00	1.80	0.20	0.198	0.0471	0.643	10.6	98.6	7.47	9.30
	12-13	1.69	1.45	0.24	0.169	0.0489	0.535	10.0	76.5	7.23	7.64
	13-14	1.74	1.53	0.21	0.166	0.0505	0.801	10.7	78.1	5.10	7.27
	14-15	1.73	1.46	0.27	0.173	0.0484	0.788	9.84	77.8	4.94	7.90
	15-16	1.80	1.61	0.19	0.187	0.0484	0.867	10.0	85.8	4.96	8.54
	16-17	1.78	1.47	0.31	0.183	0.0468	0.825	9.37	81.0	4.76	8.65
	17-18	1.70	1.50	0.20	0.198	0.0478	0.759	8.83	80.9	5.28	9.16
	18-19	1.82	1.55	0.27	0.209	0.0501	0.718	8.65	79.8	5.76	9.22
	19-20	2.11	1.73	0.38	0.262	0.0524	0.778	7.70	85.1	5.94	11.0
	20-21	3.15	3.23	0	0.391	0.0568	0.979	9.63	147	8.81	15.2
	21-22	2.06	1.72	0.34	0.360	0.0499	0.768	5.57	88.9	5.98	16.0
	22-23	1.26	0.991	0.27	0.316	0.0480	0.647	3.66	53.2	4.09	14.6
	23-24	1.02	0.717	0.30	0.376	0.0473	0.499	2.22	39.1	3.84	17.6
	24-25	1.05	0.793	0.26	0.457	0.0499	0.503	2.02	41.0	4.21	20.2

Table 3. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
Oxic-2 Multicore	0-1	1.95	1.67	0.28	0.195	0.0660	0.268	9.99	65.2	16.6	6.53
	1-2	1.44	1.08	0.36	0.135	0.0547	0.233	9.33	50.9	12.4	5.46
	2-3	1.94	1.39	0.55	0.158	0.0550	0.312	10.2	65.2	11.9	6.35
	3-4	2.00	1.54	0.46	0.174	0.0522	0.364	10.3	76.1	11.3	7.37
	4-5	2.47	1.81	0.66	0.181	0.0566	0.301	11.7	82.5	16.0	7.07
	5-6	2.20	1.96	0.24	0.186	0.0650	0.392	12.3	77.8	13.3	6.33
	6-7	2.26	1.86	0.40	0.191	0.0564	0.383	11.4	85.0	13.0	7.49
	7-8	2.53	1.92	0.61	0.195	0.0525	0.356	11.5	94.3	14.4	8.21
	8-9	2.19	1.83	0.36	0.179	0.0517	0.360	11.9	91.3	13.6	7.66
	9-10	2.24	1.76	0.48	0.185	0.0545	0.433	11.1	83.3	10.8	7.51
	10-11	2.50	2.02	0.48	0.171	0.0565	0.363	13.8	92.2	14.8	6.69
	11-12	1.58	0.920	0.66	0.102	0.0529	0.134	10.5	44.8	18.3	4.26
	12-13	1.90	0.960	0.94	0.102	0.0487	0.110	11.0	50.8	23.3	4.63
	13-14	2.35	2.34	0.01	0.175	0.0438	0.480	15.6	138	13.0	8.84
	14-15	2.54	2.42	0.12	0.181	0.0444	0.630	15.6	140	10.2	9.01
	15-16	2.17	2.18	0	0.172	0.0449	0.505	14.8	125	11.5	8.47
	16-17	2.45	2.26	0.19	0.208	0.0483	0.660	12.7	121	9.14	9.52
	17-18	3.00	2.83	0.17	0.217	0.0455	0.948	15.2	160	7.97	10.5
	18-19	3.50	3.38	0.12	0.241	0.0422	1.06	16.4	206	8.51	12.6
	19-20	3.72	3.74	0	0.257	0.0389	0.924	17.0	248	10.8	14.6
	20-21	3.01	3.01	0	0.206	0.0393	0.821	17.0	198	9.79	11.6
	21-22	2.97	3.36	0	0.206	0.0401	0.902	19.0	216	9.94	11.4
	22-23	2.44	2.44	0	0.180	0.0419	0.923	15.8	150	7.06	9.50
	23-24	3.81	4.08	0	0.247	0.0399	1.20	19.3	264	9.08	13.7
	24-25	3.52	3.56	0	0.248	0.0393	1.17	16.7	234	8.12	14.0
	25-26	3.96	4.13	0	0.267	0.0400	1.19	18.0	266	9.26	14.8
	26-27	3.42	3.52	0	0.236	0.0404	1.05	17.4	225	8.95	12.9

Table 3. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
Oxic-2 Multicore	27-28	4.00	3.99	0.01	0.268	0.0409	1.00	17.4	252	10.6	14.5
	28-29	5.43	5.99	0	0.323	0.0411	0.923	21.6	376	17.3	17.4
	29-30	6.61	6.71	0	0.366	0.0378	0.898	21.4	458	19.9	21.4
	30-31	6.02	6.67	0	0.343	0.0346	0.803	22.7	497	22.2	21.9
	31-32	8.61	8.53	0.08	0.461	0.0345	1.20	21.6	638	19.0	29.5
	32-33	9.63	10.1	0	0.516	0.0314	1.46	22.8	829	18.5	36.3
Oxic-2 Vibracore	5-10	2.27	2.04	0.23	0.201	0.0493	0.638	11.8	107	8.53	9.02
	10-15	3.21	3.02	0.19	0.236	0.0380	1.89	14.9	205	4.26	13.7
	15-20	3.67	3.94	0	0.268	0.0286	2.96	17.1	355	3.55	20.7
	25-30	3.53	3.79	0	0.265	0.0425	2.28	16.7	230	4.44	13.8
	50-55	9.84	10.2	0	0.718	0.0330	2.08	16.6	797	13.1	48.1
	75-80	10.25	10.3	0	0.743	0.0333	2.48	16.2	798	11.1	49.3
	100-105	1.01	0.852	0.16	0.070	0.0463	0.339	14.2	47.4	6.71	3.34
	125-130	1.27	0.658	0.61	0.074	0.0560	0.491	10.4	30.3	3.58	2.92
	150-155	1.06	0.807	0.25	0.104	0.0552	0.474	9.05	37.7	4.54	4.17
	175-180	1.15	0.822	0.33	0.085	0.0565	0.417	11.3	37.5	5.26	3.33
	200-205	1.36	0.833	0.53	0.106	0.0630	0.583	9.16	34.1	3.81	3.72
	225-230	1.24	0.860	0.38	0.105	0.0618	0.173	9.55	35.9	13.3	3.76
	250-255	1.08	0.983	0.10	0.112	0.0581	0.339	10.2	43.6	7.74	4.26
Hypoxic-1 Multicore	0-1	1.09	0.619	0.47	0.112	0.0548	0.332	6.44	29.1	4.98	4.52
	1-2	0.981	0.622	0.36	0.111	0.0550	0.398	6.53	29.2	4.17	4.46
	2-3	1.11	0.708	0.40	0.135	0.0560	0.402	6.12	32.6	4.70	5.33
	3-4	1.08	0.700	0.38	0.106	0.0503	0.360	7.70	35.9	5.19	4.66
	4-5	1.01	0.581	0.43	0.100	0.0571	0.288	6.78	26.2	5.38	3.87
	5-6	1.09	0.630	0.46	0.110	0.0551	0.505	6.68	29.5	3.33	4.41

Table 3. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
Hypoxic-1 Multicore	6-7	1.21	0.737	0.47	0.131	0.0544	0.646	6.56	34.9	3.04	5.32
	7-8	1.11	0.650	0.46	0.106	0.0548	0.837	7.15	30.6	2.07	4.28
	8-9	1.16	0.738	0.42	0.117	0.0545	0.981	7.36	34.9	2.01	4.75
	9-10	1.19	0.741	0.45	0.108	0.0531	0.995	8.00	36.0	1.99	4.50
	10-11	1.16	0.719	0.44	0.113	0.0558	0.986	7.42	33.2	1.95	4.48
	11-12	1.18	0.787	0.39	0.113	0.0546	1.46	8.12	37.2	1.44	4.58
	12-13	1.22	0.801	0.42	0.119	0.0562	1.04	7.85	36.8	2.06	4.68
	13-14	1.62	1.13	0.49	0.128	0.0545	1.09	10.3	53.5	2.77	5.19
	14-15	1.45	0.943	0.51	0.103	0.0538	0.888	10.7	45.2	2.83	4.23
	15-16	0.931	0.496	0.44	0.074	0.0537	0.639	7.82	23.8	2.07	3.05
	16-17	0.917	0.454	0.46	0.084	0.0546	0.943	6.30	21.4	1.28	3.40
	17-18	0.979	0.546	0.43	0.088	0.0546	1.10	7.24	25.8	1.32	3.56
	18-19	1.05	0.633	0.42	0.098	0.0522	1.34	7.53	31.3	1.26	4.15
Hypoxic-2 Multicore	0-1	1.09	0.748	0.34	0.091	0.0653	0.184	9.58	29.5	10.8	3.08
	1-2	1.04	0.730	0.31	0.094	0.0630	0.157	9.06	29.9	12.4	3.30
	2-3	1.06	0.629	0.43	0.082	0.0612	0.262	8.94	26.5	6.41	2.96
	3-4	1.03	0.635	0.40	0.073	0.0590	0.267	10.1	27.8	6.35	2.74
	4-5	1.08	0.622	0.46	0.070	0.0590	0.235	10.4	27.2	7.06	2.62
	5-6	1.04	0.614	0.43	0.068	0.0593	0.231	10.5	26.7	7.09	2.54
	6-7	1.01	0.551	0.46	0.057	0.0586	0.178	11.3	24.2	8.26	2.15
	7-8	1.00	0.556	0.44	0.068	0.0587	0.163	9.54	24.4	9.10	2.56
	8-9	0.967	0.576	0.39	0.059	0.0588	0.175	11.4	25.3	8.78	2.22
	9-10	0.992	0.551	0.44	0.060	0.0588	0.151	10.7	24.2	9.74	2.26
	10-11	0.997	0.541	0.46	0.065	0.0593	0.174	9.71	23.5	8.30	2.42
	11-12	1.02	0.550	0.47	0.065	0.0589	0.170	9.87	24.1	8.64	2.44
	12-13	0.985	0.553	0.43	0.060	0.0611	0.155	10.7	23.3	9.52	2.17
	13-14	0.993	0.544	0.45	0.059	0.0601	0.145	10.8	23.3	10.0	2.17

Table 3. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
Hypoxic-2 Multicore	14-15	0.986	0.547	0.44	0.060	0.0576	0.125	10.6	24.5	11.7	2.30
	15-16	1.01	0.545	0.46	0.062	0.0598	0.126	10.2	23.5	11.5	2.29
	16-17	0.992	0.548	0.44	0.062	0.0598	0.134	10.3	23.6	10.9	2.29
	17-18	1.00	0.537	0.46	0.063	0.0608	0.138	9.94	22.8	10.4	2.29
	18-19	1.00	0.555	0.44	0.063	0.0611	0.104	10.3	23.4	14.2	2.28
	19-20	1.01	0.564	0.45	0.065	0.0610	0.124	10.1	23.8	12.1	2.35
	20-21	0.997	0.543	0.45	0.061	0.0592	0.129	10.4	23.6	11.2	2.28
	21-22	0.990	0.560	0.43	0.059	0.0602	0.127	11.1	24.0	11.8	2.17
	22-23	0.969	0.537	0.43	0.063	0.0589	0.093	9.94	23.5	15.4	2.36
	23-24	0.969	0.541	0.43	0.063	0.0555	0.129	10.0	25.1	11.2	2.51
	24-25	1.04	0.562	0.48	0.066	0.0642	0.145	9.93	22.6	10.3	2.27
	25-26	1.26	0.774	0.49	0.090	0.0662	0.220	10.0	30.2	9.39	3.01
Hypoxic-2 Vibracore	5-10	1.00	0.799	0.20	0.085	0.0555	0.108	11.0	37.1	19.7	3.39
	10-15	1.03	0.842	0.19	0.086	0.0587	0.108	11.4	37.0	20.8	3.24
	15-20	0.965	0.798	0.17	0.066	0.0580	0.091	14.1	35.5	23.4	2.52
	20-25	1.04	0.866	0.17	0.082	0.0625	0.121	12.3	35.7	19.1	2.90
	25-30	1.18	1.06	0.12	0.103	0.0577	0.165	12.0	47.4	17.1	3.95
	50-55	1.40	1.15	0.25	0.118	0.0624	0.238	11.4	47.5	12.9	4.18
	75-80	1.23	1.08	0.15	0.120	0.0616	0.284	10.5	45.2	10.2	4.31
	100-105	1.16	1.36	0	0.117	0.0589	0.066	13.6	59.5	55.0	4.39
	125-130	0.878	0.924	0	0.084	0.0549	0.033	12.8	43.4	74.7	3.38
	150-155	0.930	0.994	0	0.106	0.0596	0.069	10.9	43.0	38.4	3.93
	175-180	1.28	1.12	0.16	0.107	0.0598	0.099	12.2	48.3	30.2	3.96
	200-205	1.28	1.09	0.19	0.120	0.0593	0.095	10.6	47.4	30.6	4.47
	225-230	1.18	1.32	0.14	0.126	0.0556	0.154	12.2	61.2	22.9	5.01

Table 3. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
MRJ03-3A	0-1	1.54	nd	nd	0.216	nd	0.162	8.31*	nd	25.4*	nd
	1-2	1.47	nd	nd	0.170	nd	0.200	10.1*	nd	19.6*	nd
	2-3	1.68	nd	nd	0.133	nd	0.196	14.7*	nd	22.9*	nd
	3-4	1.54	nd	nd	0.169	nd	0.174	10.6*	nd	23.6*	nd
	4-5	1.48	nd	nd	0.173	nd	0.169	9.98*	nd	23.4*	nd
	5-6	1.46	nd	nd	0.175	nd	0.164	9.73*	nd	23.8*	nd
	6-7	1.46	nd	nd	0.173	nd	0.173	9.84*	nd	22.5*	nd
	7-8	1.44	nd	nd	0.171	nd	0.168	9.82*	nd	22.9*	nd
	8-9	1.48	nd	nd	0.177	nd	0.176	9.75*	nd	22.4*	nd
	9-10	1.52	nd	nd	0.166	nd	0.171	10.7*	nd	23.7*	nd
	10-11	1.62	nd	nd	0.158	nd	0.174	12.0*	nd	24.8*	nd
	11-12	1.51	nd	nd	0.160	nd	0.184	11.0*	nd	21.9*	nd
	12-13	1.44	nd	nd	0.159	nd	0.179	10.6*	nd	21.5*	nd
	13-14	1.56	nd	nd	0.159	nd	0.177	11.4*	nd	23.5*	nd
	14-15	1.45	nd	nd	0.158	nd	0.171	10.7*	nd	22.6*	nd
	15-16	1.49	nd	nd	0.159	nd	0.169	10.9*	nd	23.5*	nd
	16-17	1.48	nd	nd	0.156	nd	0.178	11.1*	nd	22.2*	nd
	17-18	1.47	nd	nd	0.158	nd	0.188	10.8*	nd	20.9*	nd
	18-19	1.47	nd	nd	0.157	nd	0.189	10.9*	nd	20.8*	nd
	19-20	1.48	nd	nd	0.192	nd	0.212	8.99*	nd	18.6*	nd
	20-21	1.50	nd	nd	0.173	nd	0.210	10.1*	nd	19.1*	nd
	21-22	1.38	nd	nd	0.164	nd	0.198	9.81*	nd	18.6*	nd
	22-23	1.37	nd	nd	0.163	nd	0.211	9.80*	nd	17.3*	nd
	23-24	1.40	nd	nd	0.164	nd	0.193	9.95*	nd	19.4*	nd
	24-25	1.40	nd	nd	0.170	nd	0.198	9.60*	nd	18,9*	nd
	25-26	1.39	nd	nd	0.168	nd	0.215	9.65*	nd	17.2*	nd
	26-27	1.40	nd	nd	0.170	nd	0.228	9.60*	nd	16.4*	nd

Table 3. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
MRJ03-3A	27-28	1.39	nd	nd	0.166	nd	0.215	9.76*	nd	!7.2*	nd
	28-29	1.39	nd	nd	0.172	nd	0.233	9.42*	nd	15.9*	nd
	29-30	1.38	nd	nd	0.173	nd	0.229	9.30*	nd	16.1*	nd
	30-31	1.39	nd	nd	0.171	nd	0.217	9.48*	nd	17.1*	nd
	31-32	1.40	nd	nd	0.179	nd	0.210	9.12*	nd	17.8*	nd
	32-33	1.39	nd	nd	0.178	nd	0.220	9.11*	nd	16.9*	nd
	33-34	1.38	nd	nd	0.178	nd	0.220	9.04*	nd	16.7*	nd
	34-35	1.41	nd	nd	0.179	nd	0.213	9.18*	nd	17.7*	nd
	35-36	1.36	nd	nd	0.177	nd	0.213	8.96*	nd	17.0*	nd
	36-37	1.40	nd	nd	0.183	nd	0.210	8.92*	nd	17.8*	nd
	37-38	1.48	nd	nd	0.175	nd	0.206	9.86*	nd	19.2*	nd
	38-39	1.37	nd	nd	0.178	nd	0.205	8.98*	nd	17.8*	nd
	39-40	1.44	nd	nd	0.190	nd	0.242	8.84*	nd	15.9*	nd
	40-41	1.40	nd	nd	0.175	nd	0.225	9.33*	nd	16.6*	nd
	41-42	1.36	nd	nd	0.176	nd	0.218	9.01*	nd	16.6*	nd
	42-43	1.37	nd	nd	0.178	nd	0.216	8.98*	nd	16.9*	nd
	43-44	1.36	nd	nd	0.176	nd	0.195	9.01*	nd	18.6*	nd
	44-45	1.39	nd	nd	0.180	nd	0.213	9.00*	nd	17.4*	nd
	45-46	1.40	nd	nd	0.177	nd	0.199	9.22*	nd	18.8*	nd
	46-47	1.37	nd	nd	0.178	nd	0.203	8.98*	nd	18.0*	nd
MRJ03-5A	0-1	1.47	nd	nd	0.164	nd	0.346	10.4*	nd	11.3*	nd
	1-2	1.63	nd	nd	0.188	nd	0.378	10.1*	nd	11.5*	nd
	2-3	1.71	nd	nd	0.162	nd	0.320	12.3*	nd	14.3*	nd
	3-4	1.62	nd	nd	0.151	nd	0.343	12.5*	nd	12.6*	nd
	4-5	0.895	nd	nd	0.070	nd	0.202	14.9*	nd	11.8*	nd

Table 3. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
MRJ03-5A	5-6	0.841	nd	nd	0.077	nd	0.204	12.7*	nd	11.0*	nd
	6-7	0.641	nd	nd	0.051	nd	0.164	14.6*	nd	10.4*	nd
	7-8	0.919	nd	nd	0.064	nd	0.286	16.7*	nd	8.58*	nd
	8-9	1.08	nd	nd	0.063	nd	0.535	20.0*	nd	5.39*	nd
	9-10	1.22	nd	nd	0.089	nd	0.544	16.0*	nd	5.99*	nd
	10-11	1.18	nd	nd	0.110	nd	0.448	12.5*	nd	7.03*	nd
	11-12	1.28	nd	nd	0.084	nd	0.579	17.8*	nd	5.90*	nd
	12-13	0.969	nd	nd	0.081	nd	0.470	14.0*	nd	5.50*	nd
	13-14	1.06	nd	nd	0.151	nd	0.356	8.19*	nd	7.95*	nd
	14-15	1.10	nd	nd	0.057	nd	0.331	22.5*	nd	8.87*	nd
	15-16	0.867	nd	nd	0.065	nd	0.300	15.6*	nd	7.71*	nd
	16-17	1.54	nd	nd	0.050	nd	0.307	35.9*	nd	13.4*	nd
	17-18	0.972	nd	nd	0.085	nd	0.289	13.3*	nd	8.98*	nd
	18-19	1.06	nd	nd	0.098	nd	0.266	12.6*	nd	10.6*	nd
	19-20	1.07	nd	nd	0.070	nd	0.218	17.8*	nd	13.1*	nd
	20-21	0.936	nd	nd	0.040	nd	0.194	27.3*	nd	12.9*	nd
	21-22	1.04	nd	nd	0.087	nd	0.220	13.9*	nd	12.6*	nd
	22-23	1.25	nd	nd	0.049	nd	0.163	29.7*	nd	20.5*	nd
	23-24	1.05	nd	nd	0.059	nd	0.236	20.8*	nd	11.9*	nd
	24-25	0.939	nd	nd	0.089	nd	0.291	12.3*	nd	8.61*	nd
	25-26	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	26-27	1.08	nd	nd	0.072	nd	0.202	17.5*	nd	14.3*	nd
	27-28	1.54	nd	nd	0.125	nd	0.378	14.4*	nd	10.9*	nd
	28-29	0.924	nd	nd	0.081	nd	0.144	13.3*	nd	17.1*	nd
	29-30	1.02	nd	nd	0.180	nd	0.267	6.61*	nd	10.2*	nd
	30-31	1.16	nd	nd	0.064	nd	0.323	21.1*	nd	9.59*	nd

Table 3. Continued

Sample	Depth (cm)	TC (%)	OC (%)	IC (%)	TN (%)	TP (%)	TS (%)	C/N (Atomic)	C/P (Atomic)	C/S (Atomic)	N/P (Atomic)
MRJ03-5A	31-32	0.986	nd	nd	0.032	nd	0.216	35.9*	nd	12.2*	nd
	32-33	1.10	nd	nd	0.126	nd	0.251	10.2*	nd	11.7*	nd

* Ratio calculated using TC rather than OC

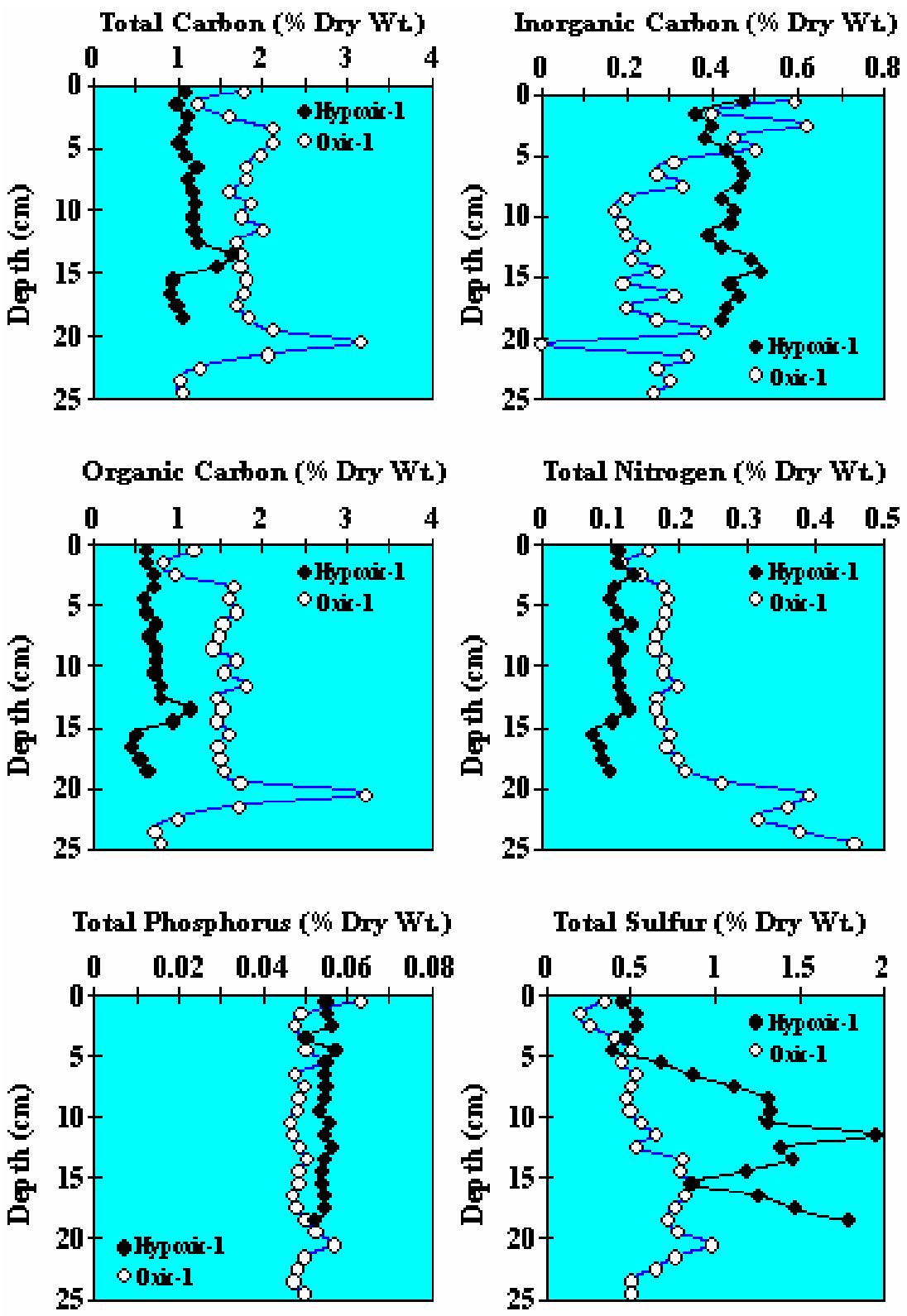


Fig. 12. Organic elemental data from June 2002 hypoxic-1(●) and oxic-1 (○) sites in the lower Mississippi River system; all results are reported on a dry weight basis.

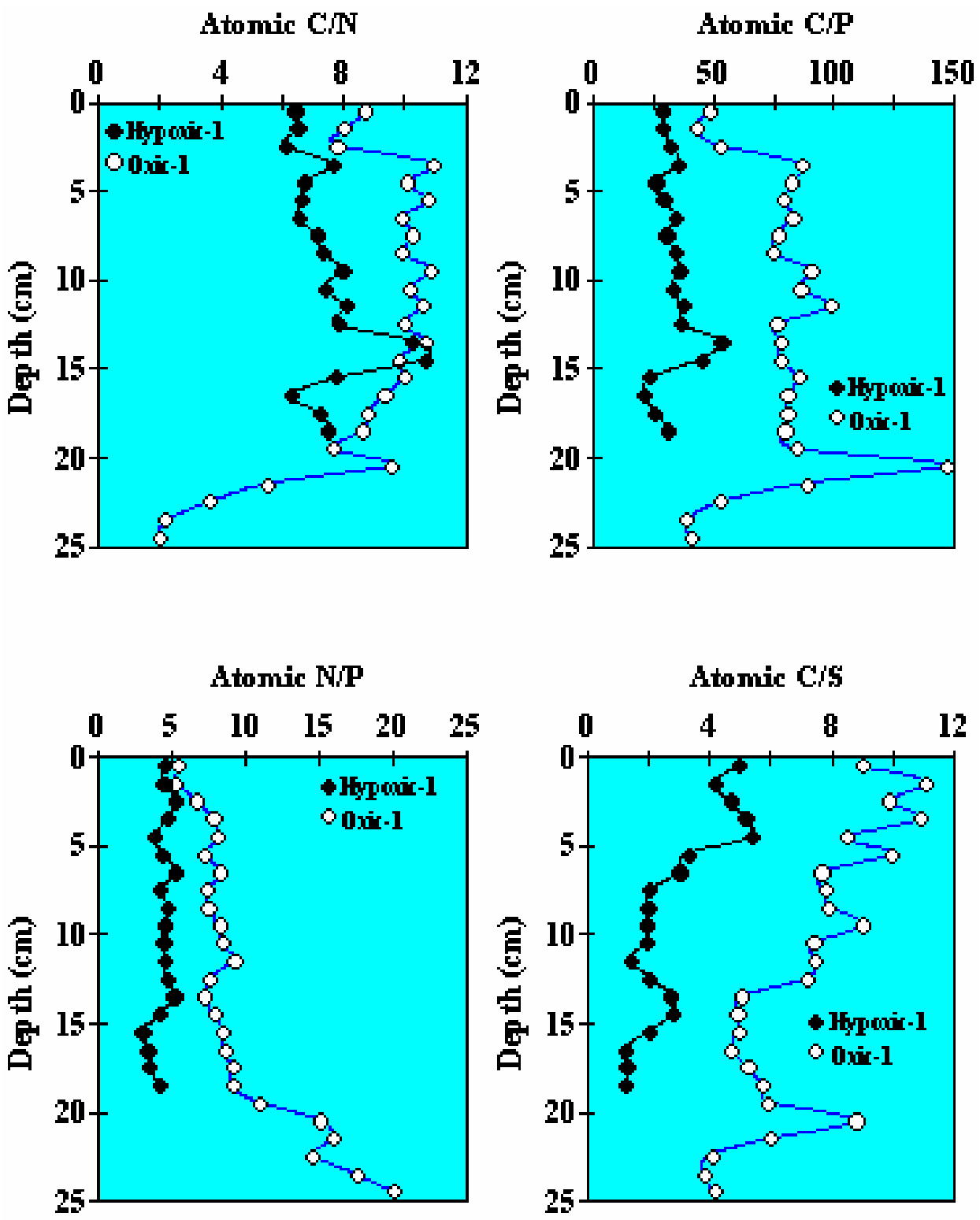


Fig. 13. Organic elemental atomic ratios from June 2002 hypoxic-1(●) and oxic-1 (○) sites in the lower Mississippi River system.

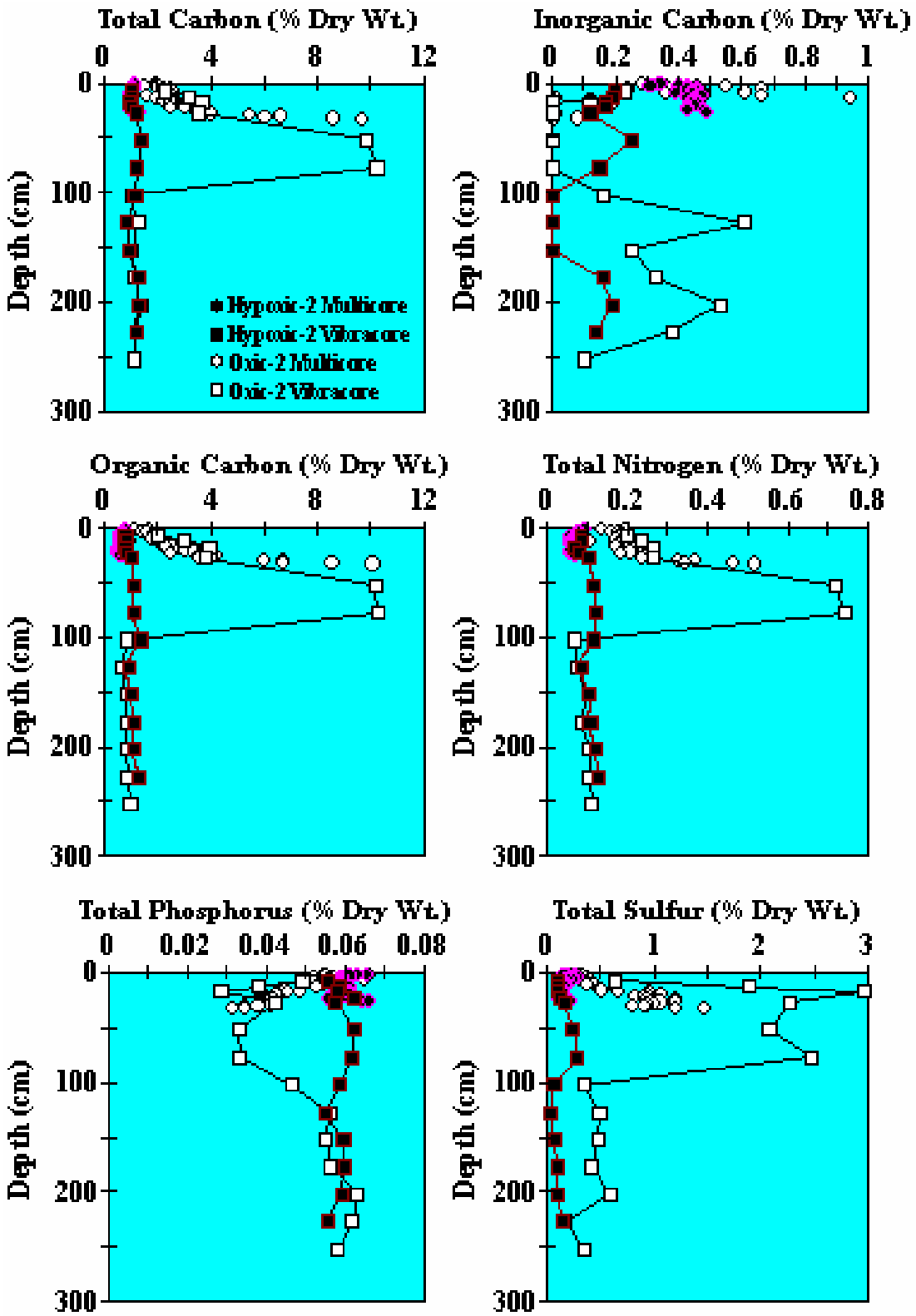


Fig. 14. Organic elemental data from the lower Mississippi River system for cores collected in September 2002 from the hypoxic-2 site by multicore (●) and vibracore (■), and the oxic-2 site by multicore (○) and vibracore (□). All results are on a dry weight basis.

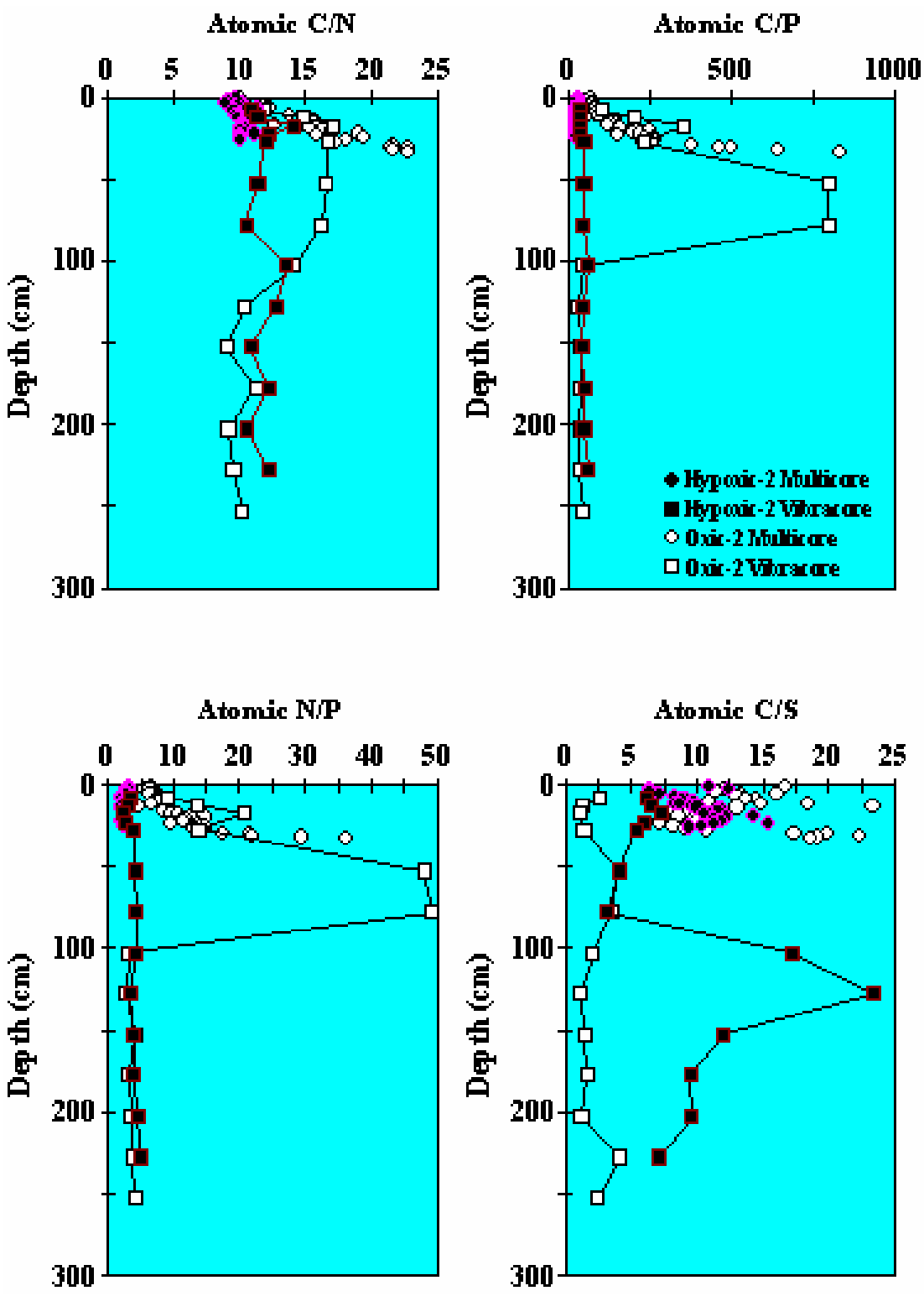


Fig. 15. Elemental atomic ratios from the lower Mississippi River system for cores collected in September 2002 from the hypoxic-2 site by multicore (●) and vibracore (■), and the oxic-2 site by multicore (○) and vibracore (□). All results are on a dry weight basis.

that for TC and TN. In particular, the MR-J03-5 core exhibited pronounced maxima in TS from 0-4 cm, and especially in the 7-20 cm interval.

The high TS values and the downcore peaks in TS in the MR-J03-05 core are also evident in the elemental C/S plot (Fig. 17). Atomic C/S values average 10.8 for all samples in the MR-J03-5 core, compared to an average atomic C/S of 19.7 for the MR-J03-3 core. The lower atomic C/S values in the MR-J03-5 core compared to MR-J03-3 core, reflect the position of the former in the general zone of hypoxia. Atomic C/S values ranged from 16-25 for all sediment samples from the MR-J03-3 core, and 5-20 in sediments from the MR-J03-5 core. The downcore atomic C/S profile in the MR-J03-5 core shows a minimum in atomic C/S centered about 10 cm depth, reflecting elevated TS values. In contrast, the MR-J03-3 core shows a gradual decline in atomic C/S with depth, but with no major excursions. At depths below about 25 cm, atomic C/S values in cores MR-J03-3 and -5 approach each other, but with the values in the MR-J03-5 core still generally lower.

Atomic C/N values were higher overall at the MR-J03-5 site than the MR-J03-3 site. Average atomic C/N values for all samples were 9.87 and 16.7 for the MR-J03-3 and -5 cores, respectively. The MR-J03-3 core had a relatively smooth downcore atomic C/N profile, with perhaps a slight decline in atomic C/N with depth. The downcore atomic C/N profile in the MR-J03-5 core, in contrast, had an irregular downcore profile with a great degree of variability in atomic C/N. The higher atomic C/N values at the MR-J03-5 site probably reflect greater input of terrestrial organic matter to the sediments at this more inshore site (Fig. 1), and the irregularity in the profile reflects changing discharge patterns in the lower Mississippi River system.

C. Hydrocarbon Gases (C_1-C_6)

Concentrations of hydrocarbon gases (C_1-C_6) were determined in the 2001 cores, and results are presented in Table 4 and in Figs. 18-23. Methane (C_1) dominates the hydrocarbon gas distributions in all cores, generally accounting for >90% of the total hydrocarbon gases present. Ethane, propane, and hexane have significant concentrations in most cores, while butane and pentane are undetectable in many core intervals. Concentration ranges (dry wt. basis) for total hydrocarbons ("bound" plus "free") are as follows: methane (C_1) 8 to 11,689 ppm/g sediment , ethane (C_2) 0.05 to 1.39 ppm/g sediment, propane (C_3) <0.01 to 0.52 ppm/g sediment, butane (C_4) <0.01 to 0.24 ppm/g sediment, pentane (C_5) <0.01 to 1.06 ppm/g sediment, and hexane (C_6) <0.01 to 5.29 ppm/g sediment. The highest hydrocarbon gas concentrations (mostly methane) were observed at the Atchafalaya South site, and the lowest at Pass Raphael.

"Bound" hydrocarbons constitute a significant fraction of the total hydrocarbon gases in most sediments. Butane and pentane detected in these samples was all present as "bound" gas. The percentage of "bound" methane was variable, and ranged from <3% to >99% of the total, but was more often the dominant form of methane in these samples, except at the Atchafalaya River South site. Ethane and propane were also present primarily as "bound" gas. In contrast, hexane in most samples is present as 'free" gas.

The vertical profiles of methane, the overwhelmingly dominant hydrocarbon gas, generally show increasing concentration with depth. This is most apparent at the Atchafalaya South site, where concentrations of methane sharply increase below 20 cm. In contrast, ethane, propane, and hexane concentrations generally increase with depth. Too little data is available for butane and propane to delineate vertical concentration trends.

V. Discussion

Results from this study provide information on the general organic characteristics of sediments from coastal Louisiana off the Mississippi and Atchafalaya River systems, including spatial and downcore distributions of the important organic elements: C, N, P, and S. These data are useful in interpreting the relative proportions of autochthonous and allochthonous organic matter being deposited in this region, nutrient loading stimulating algal production in the coastal zone, and the presence of hypoxic conditions. In addition to this direct utility, results are used in interpreting and normalizing organic contaminant data obtained as part of this study, and reported elsewhere (Rosenbauer and others, 2007).

Our initial work in 2001 focused on sites directly off the mouths of the Mississippi and Atchafalaya Rivers. However, these nearshore sites proved to have erratic deposition rates suggesting a high energy regime controlled more by variability in river flow rather than by geochemical processes and reactions within

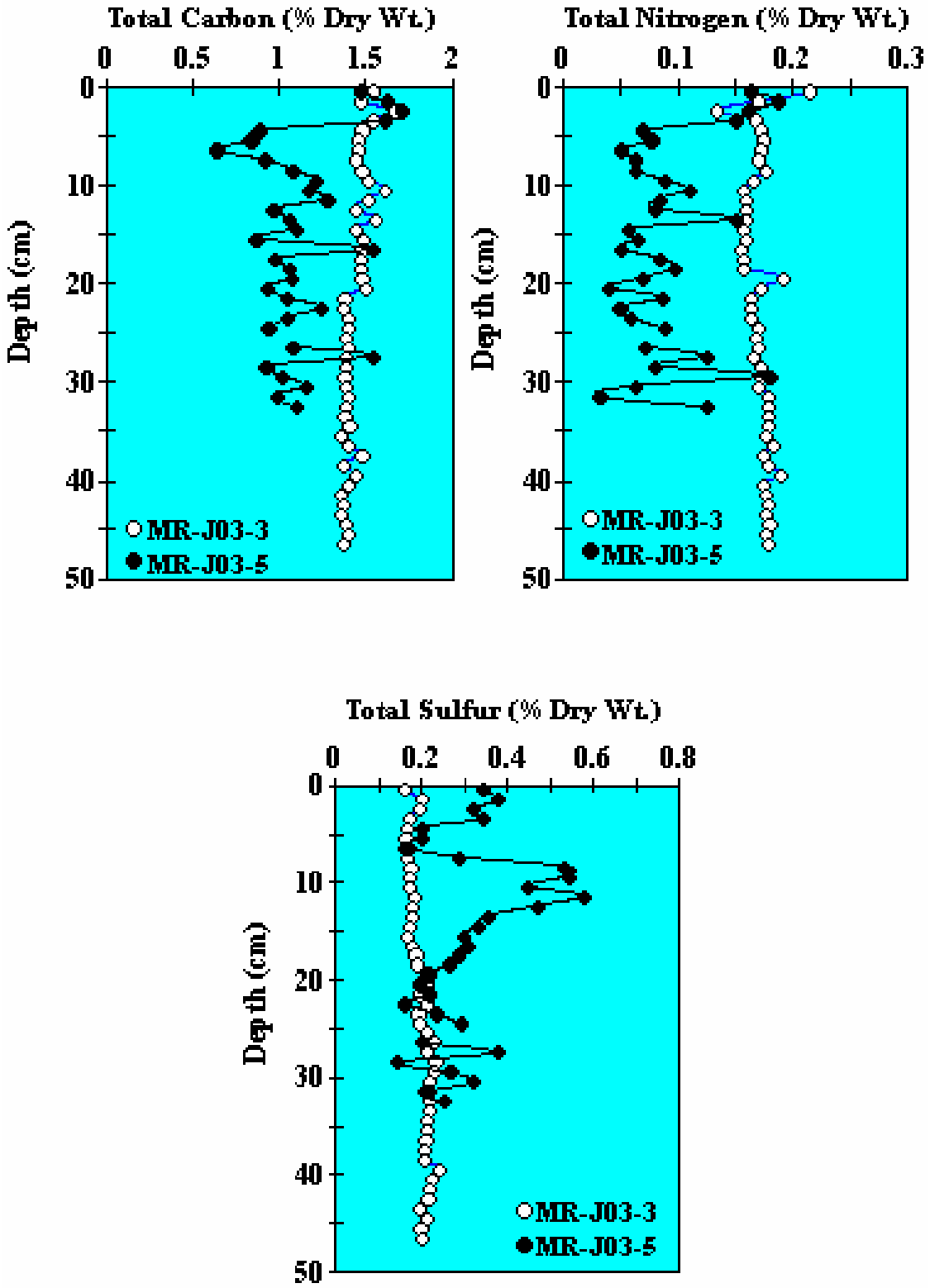


Fig. 16. Organic elemental data from cores MR-J03-3 (○) and MR-J03-5 (●) collected off the lower Mississippi River System. Results are reported as % on a dry weight basis.

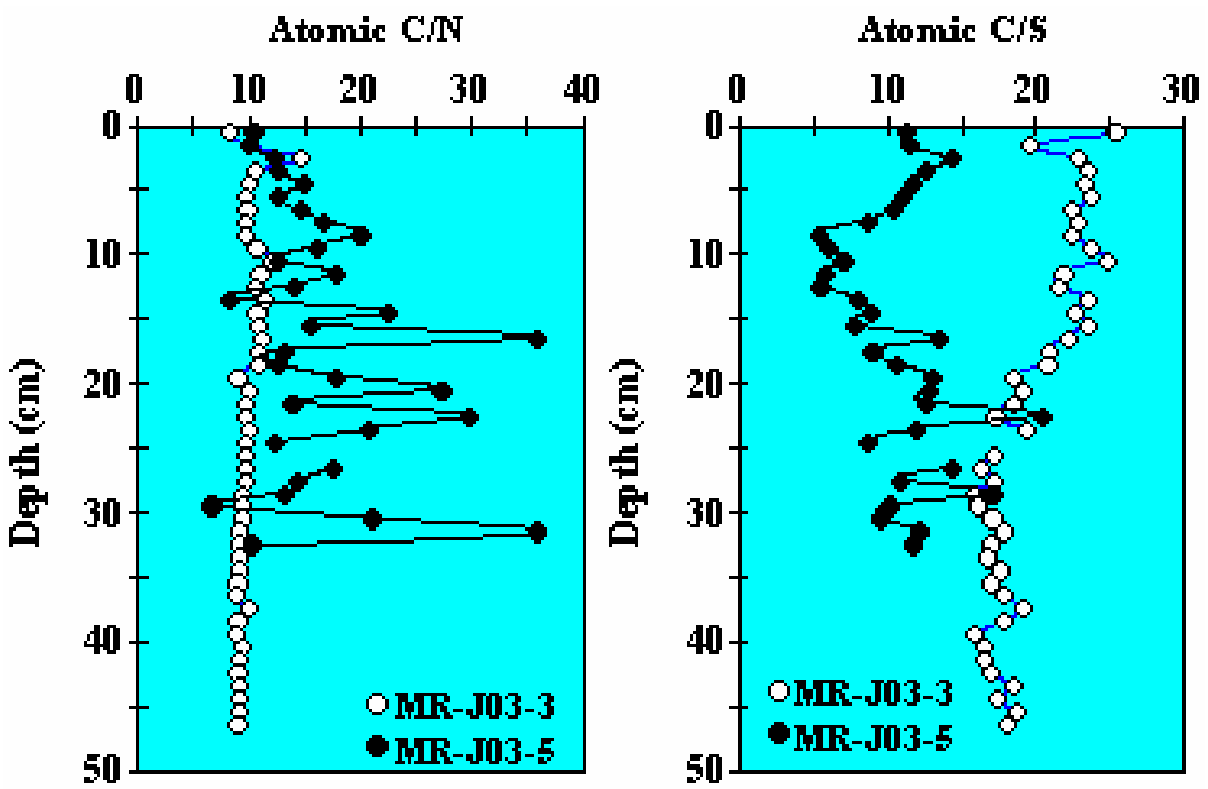


Fig. 17. Elemental atomic ratios of sediments from cores MR-J03-3 and MR-J03-5 collected off the lower Mississippi River System.

Table 4. Concentrations of C1 to C6 hydrocarbons in sediments from cores collected in the lower Mississippi and Achafalaya River estuaries, in ppm gas/g sediment (dry wt.) as free (FR), bound (BD), and total (TOT) gas.

Sample	Depth	Methane (C1)			Ethane (C2)			Propane (C3)			Butane (C4)			Pentane (C5)			Hexane (C6)		
	(cm)	FR	BD	TOT	FR	BD	TOT	FR	BD	TOT	FR	BD	TOT	FR	BD	TOT	FR	BD	TOT
Mississippi River	0-4	37.5	47.1	84.6	0.22	0.86	1.08	0.14	0.38	0.52	0.00	0.14	0.14	0.00	0.00	0.00	0.06	0.00	0.06
Pass Raphael Site	4-8	115	63.6	179	0.30	1.09	1.39	0.18	0.00	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Core 010314-5	8-12	11.3	38.3	49.6	0.10	0.53	0.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.11	0.25	2.36
	12-16	4.37	12.1	16.5	0.00	0.52	0.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.41	0.3	3.71
	16-20	16.2	15.3	31.5	0.15	0.46	0.61	0.00	0.36	0.36	0.00	0.00	0.00	0.00	0.00	0.00	2.58	0.32	2.9
	20-25	11.2	8.50	19.7	0.62	0.54	1.16	0.00	0.37	0.37	0.00	0.00	0.00	0.00	0.00	0.00	5.12	0.17	5.29
	25-30	5.42	65.3	70.7	0.16	0.35	0.51	0.00	0.40	0.40	0.00	0.11	0.11	0.00	0.00	0.00	0.82	1.05	1.87
	30-35	6.99	64.2	71.2	0.14	0.24	0.38	0.00	0.18	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.00	0.13
	35-40	10.5	68.3	78.8	0.00	0.41	0.41	0.00	0.13	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.28
	40-45	1.92	60.0	61.9	0.00	0.18	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00	0.11
	45-50	2.34	55.9	58.2	0.00	0.19	0.19	0.00	0.09	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.05
Mississippi River	0-4	13.0	57.2	70.2	0.00	0.25	0.25	0.00	0.19	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.12
South Pass Site	4-8	27.3	63.7	91.0	0.05	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.72	0.82
Core 010314-6	8-12	34.8	95.4	130	0.13	0.20	0.33	0.06	0.23	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.85	0.96
	12-16	51.0	66.2	117	0.05	0.14	0.19	0.05	0.27	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.06
	16-20	116	70.8	187	0.24	0.15	0.39	0.09	0.21	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.51	0.95	1.46
	20-25	51.3	63.1	114	0.00	0.08	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.12
	25-30	2.91	56.3	59.2	0.00	0.17	0.17	0.00	0.08	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.07	0.23
	30-35	31.2	118	149	0.00	0.10	0.10	0.00	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.07	0.25
	35-40	25.2	156	181	0.00	0.12	0.12	0.00	0.05	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.20	0.29
	40-45	173	308	481	0.05	0.08	0.13	0.00	0.04	0.04	0.00	0.02	0.02	0.00	0.00	0.00	0.05	0.17	0.22
	45-50	119	1890	2010	0.02	0.11	0.13	0.00	0.11	0.11	0.00	0.05	0.05	0.00	0.00	0.00	0.03	0.18	0.21
Atchafalaya River	0-5	11.3	93.5	105	0.00	0.79	0.79	0.00	0.33	0.33	0.00	0.14	0.14	0.00	1.06	1.06	0.12	0.04	0.16
North Site 1	5-10	3.20	211	214	0.12	0.7	0.82	0.00	0.34	0.34	0.00	0.13	0.13	0.00	0.07	0.07	0.07	0.04	0.11
Core 010319-1	10-15	8.43	499	507	0.06	0.52	0.58	0.00	0.25	0.25	0.00	0.11	0.11	0.00	0.05	0.05	0.10	0.00	0.10
	15-20	16.6	818	835	0.00	0.33	0.33	0.00	0.21	0.21	0.00	0.11	0.11	0.00	0.00	0.00	0.10	0.00	0.10
	20-25	8.34	1090	1100	0.07	0.91	0.98	0.00	0.44	0.44	0.00	0.18	0.18	0.00	0.08	0.08	0.04	0.04	0.08

Table 4 Continued

Sample	Depth	Methane (C1)			Ethane (C2)			Propane (C3)			Butane (C4)			Pentane (C5)			Hexane (C6)		
	(cm)	FR	BD	TOT	FR	BD	TOT	FR	BD	TOT	FR	BD	TOT	FR	BD	TOT	FR	BD	TOT
Atchafalaya River	25-30	68.5	2070	2140	0.08	0.84	0.92	0.00	0.39	0.39	0.00	0.17	0.17	0.00	0.06	0.06	0.06	0.03	0.09
North Site 1	30-35	22.9	1600	1620	0.00	0.42	0.42	0.00	0.22	0.22	0.00	0.08	0.08	0.00	0.00	0.00	0.08	0.00	0.08
Core 010319-1	35-38	24.1	1580	1607	0.19	0.56	0.75	0.00	0.15	0.15	0.00	0.07	0.07	0.00	0.00	0.00	0.06	0.00	0.06
Atchafalaya River	0-5	8.14	26.9	35.0	0.00	1.30	1.30	0.00	0.46	0.46	0.00	0.24	0.24	0.00	0.00	0.00	0.00	0.00	0.00
South Site	5-10	8.42	20.0	28.4	0.00	0.88	0.88	0.10	0.34	0.44	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.04	0.12
Core 010318-1	10-15	1.58	6.67	8.23	0.00	0.48	0.48	0.00	0.19	0.19	0.00	0.07	0.07	0.00	0.00	0.00	0.00	0.00	0.00
	15-20	11.4	5.08	16.5	0.00	0.20	0.20	0.05	0.12	0.17	0.00	0.00	0.00	0.00	0.00	0.00	1.03	0.00	1.03
	20-25	207	21.8	229	0.00	0.37	0.37	0.00	0.18	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00	0.39
	25-30	4150	121	4270	0.16	0.40	0.56	0.12	0.14	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.46
	30-40	5780	3580	9360	0.05	0.81	0.86	0.00	0.25	0.25	0.00	0.10	0.10	0.00	0.00	0.00	0.00	0.03	0.03
	40-50	5000	6680	11700	0.08	0.29	0.37	0.00	0.13	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	50-60	4350	7200	11500	0.00	0.33	0.33	0.00	0.15	0.15	0.00	0.00	0.00	0.00	0.00	0.00	2.36	0.07	2.43
	60-70	6160	2760	8920	0.07	0.13	0.20	0.00	0.09	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	70-80	4280	4140	8420	0.00	0.46	0.46	0.00	0.16	0.16	0.00	0.08	0.08	0.00	0.00	0.00	0.00	0.00	0.00

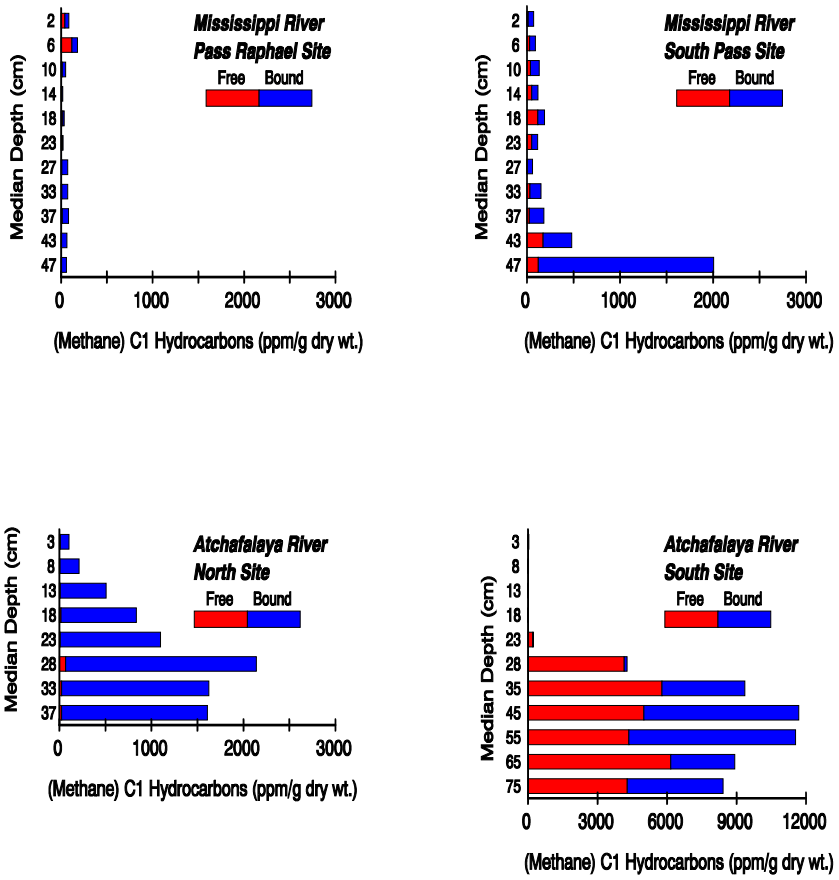


Fig. 18. Free (red) and bound (blue) methane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

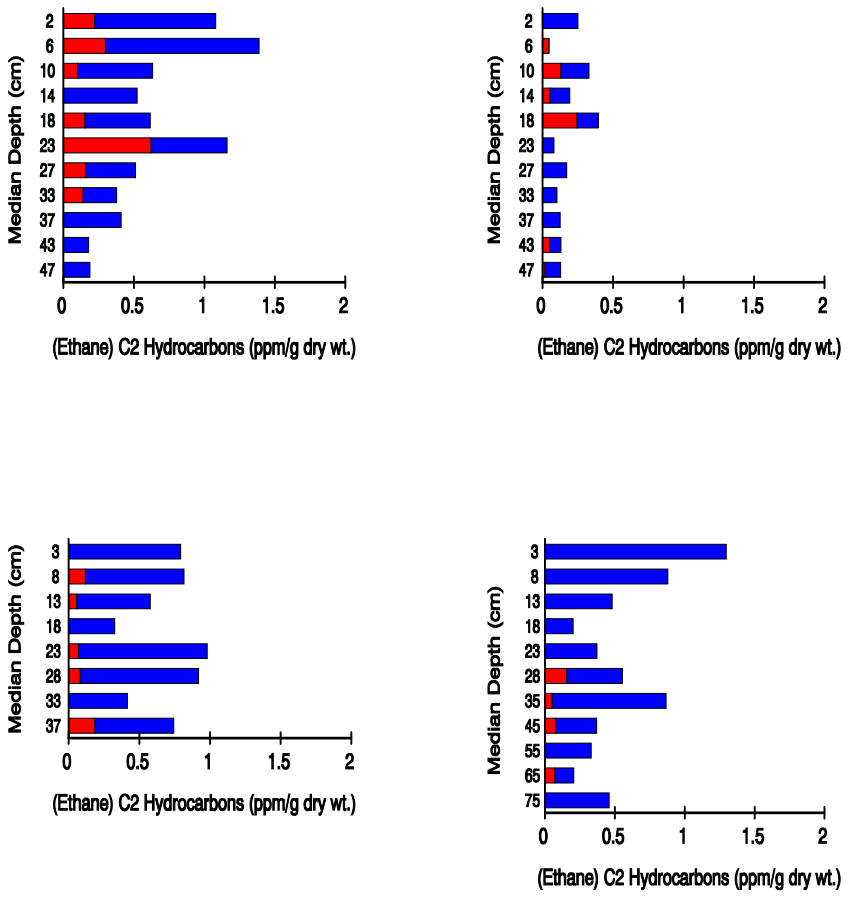


Fig. 19. Free (red) and bound (blue) ethane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

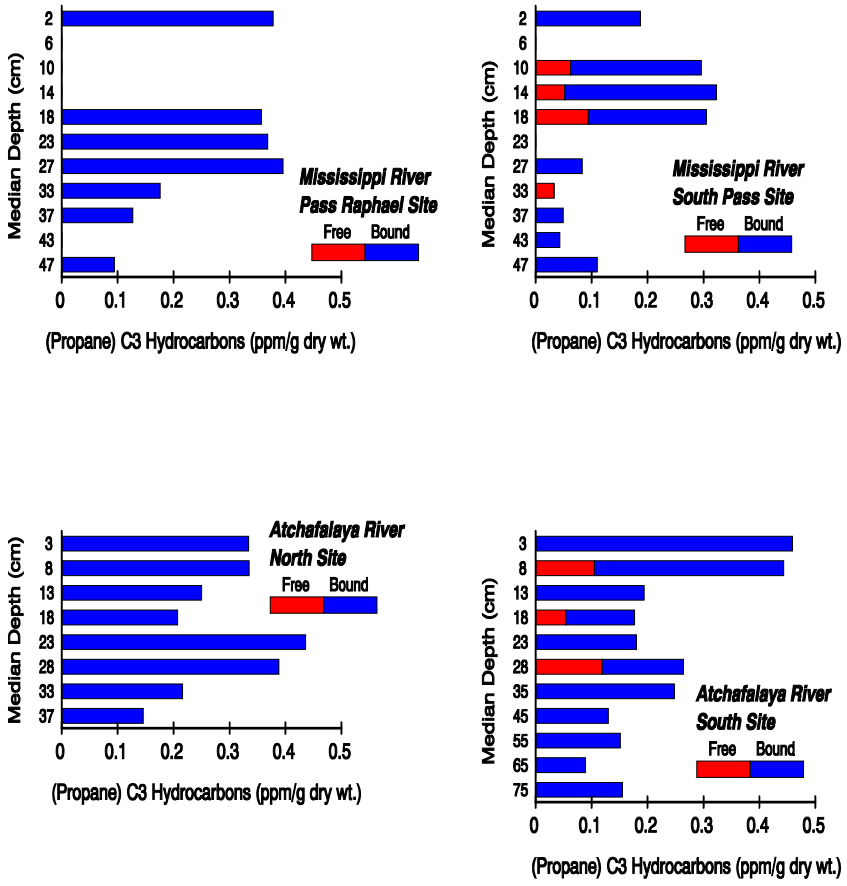


Fig. 20. Free (red) and bound (blue) propane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya river estuaries in 2001.

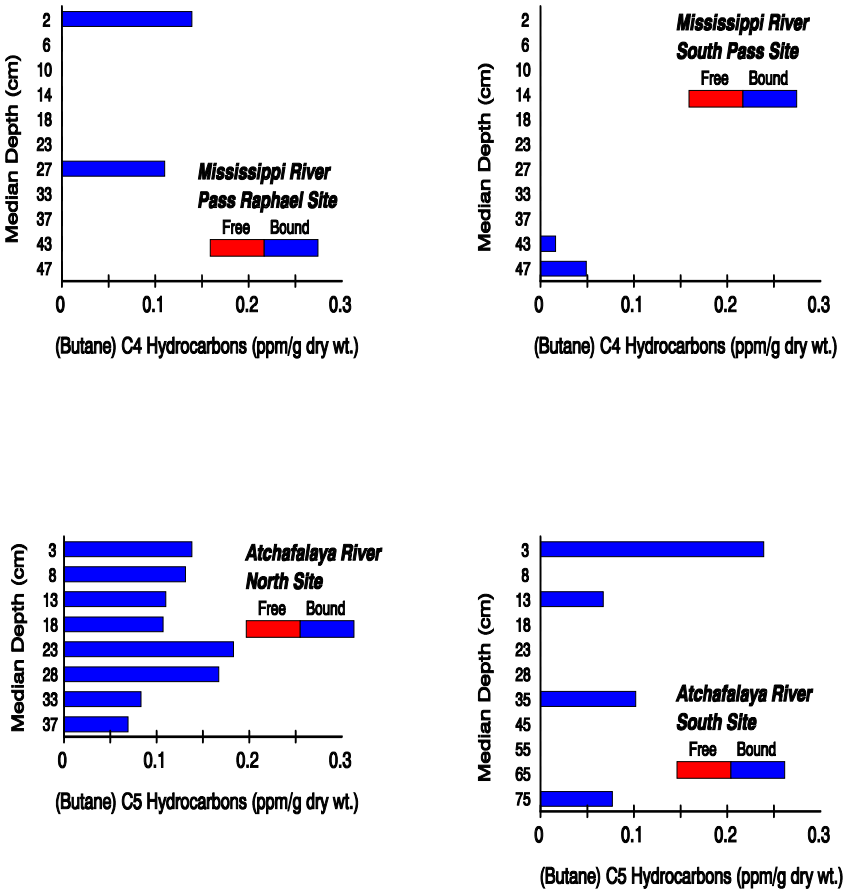


Fig. 21. Free (red) and bound (blue) butane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

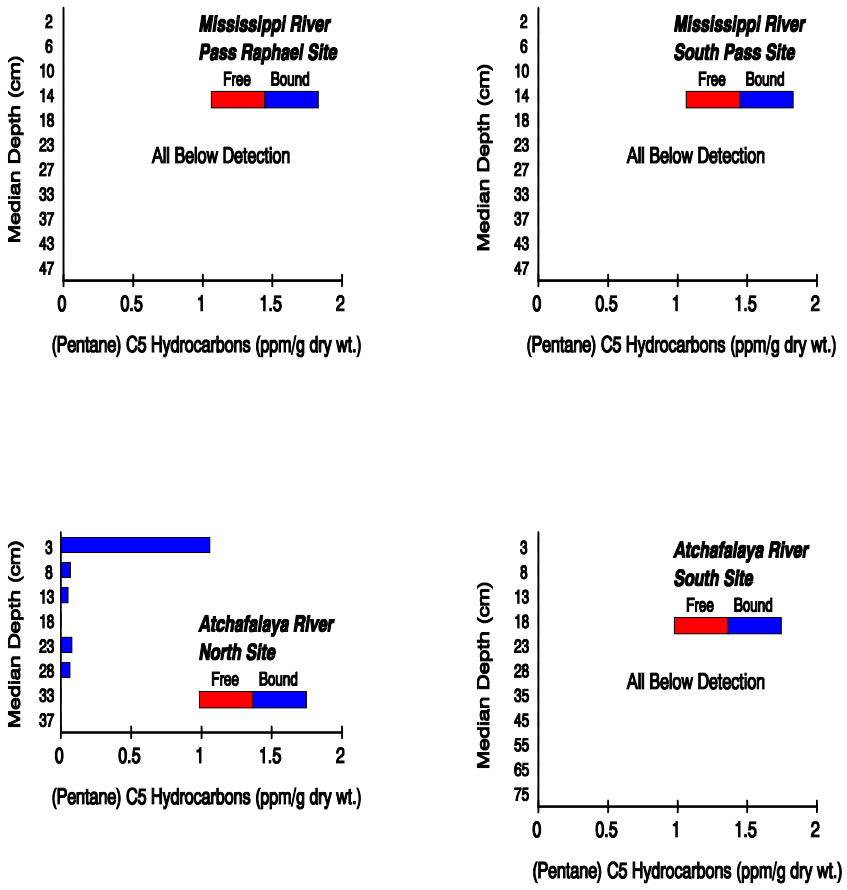


Fig. 22. Free (red) and bound (blue) pentane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalyaa River estuaries in 2001.

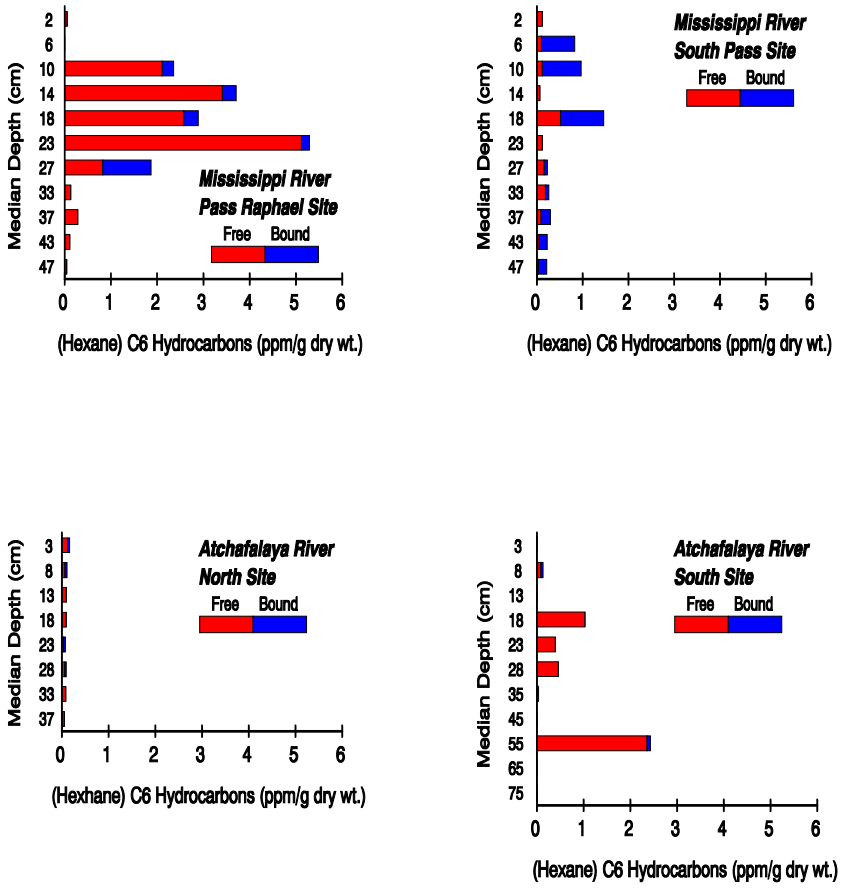


Fig. 23. Free (red) and bound (blue) hexane concentrations (ppm/g dry wt.) in sediments from cores collected in the lower Mississippi and Atchafalaya River estuaries in 2001.

the system. Elemental organic analyses, and hydrocarbon gas studies also indicated erratic conditions, with possible seasonal removal and redeposition of sediment in the upper 10-20 cm at the 2001 sites. Vertical profiles of C, N, P, and S are often very erratic in the upper 20 cm of sediment (upper 50 cm at Pass Raphael site), (Figs. 3-7). Methane concentrations are near zero in the upper sections of the 2001 cores (except at the Atchafalaya North site), before increasing suddenly at depths between 20 and 50 cm (Fig. 16). These results support the idea of rapid sediment deposition and removal by strong currents in the upper portions of these sediments.

Ratios of the elemental composition of organic matter in sediments (atomic C/N, C/P, and N/P) are frequently useful in distinguishing the source of organic matter to sediments (Macko and others, 1993; Tissot and Welte, 1984). At most sites from this study, atomic C/N values did not usually exceed 15, and in many instances were <10. Atomic C/N values in this range suggest a mix of autochthonous (algal) and allochthonous (terrestrially-derived) sources of organic matter being deposited in the sediments, but with autochthonous sources dominating. Atomic C/P and N/P ratios are also relatively low overall (generally <100 and 10, respectively), again suggestive of the dominance of autochthonous organic matter. This conclusion is consistent with previous work on organic matter in sediments from the offshore Mississippi River system (Goni and others, 1998). This result is somewhat surprising considering the proximity of the Mississippi and Atchafalaya River deltas to the offshore sampling sites, and the expected transport of terrestrially derived organic matter down the river. However, much of the authochthonous organic matter derived from the river discharge may be carried further offshore. In addition, the river system discharges dissolved nutrient elements into the nearshore area, which may stimulate algal productivity here.

Delivery of excess nutrients (especially N) from the Mississippi River system, and stratification of the water column related to climatic conditions and seasonal changes in freshwater discharge from the Mississippi River system are thought to be the main factors responsible for the development of hypoxic conditions in the coastal Gulf of Mexico near the Mississippi and Atchafalaya River deltas (Justic and others, 1995; Wiseman and others, 1997). A large focus of the sampling effort in this study was coring in this hypoxic zone (sites Hypoxic-1 and 2, and MR-J03-05), and nearby areas that were considered to have had oxic conditions in the water column (sites Oxic-1 and 2, and MR-J03-3), (see Table 1, and Fig. 1). Atomic C/S values of sediments may be useful as an indicator of anoxic and hypoxic conditions in aquatic systems (Cornwell and Sampou, 1995). Hypoxic or anoxic conditions in the water column in marine environments may allow anaerobic microbial processes such as sulfate reduction to occur. The reactive sulfide produced as a byproduct of microbial sulfate reduction may then react with iron and precipitate iron sulfide minerals to the underlying sediments. This “extra” metal sulfide delivered to sediments in zones with anoxic/hypoxic water columns increases sedimentary sulfur concentrations, and results in lower atomic C/S values in the sediments. We observed elevated TS concentrations and low atomic C/S values at Hypoxic-1 compared to Oxic-1, and at MR-J03-5 compared to MR-J03-3, confirming that our Hypoxic-1 and MR-J03-5 sites were indeed located in the zone of hypoxia. We did not observe higher sedimentary TS or lower atomic C/S at the Hypoxic-2 compared to Oxic-2, suggesting that the Hypoxic-2 site, while located in the general zone of hypoxia, was not hypoxic. This may reflect some degree of patchiness in the overall zone of hypoxia in this region. Results do suggest that TS concentrations and atomic C/S values may be useful indicators of hypoxia in the overlying waters, and downcore variations in TS and atomic C/S may provide historical context to hypoxia in a given region.

In regard to historical context, the TS and atomic C/S data from the MR-J03-5 core (Figs. 16 and 17) indicate a peak in hypoxia, indicated by a maximum in TS and a minimum in atomic C/S, centered at about 10 cm depth. Sedimentation rates and sediment mass accumulation rates for this and other sites in this study were determined using vertical distributions of $^{239,240}Pu$, ^{137}Cs, and $^{210}Pb_{ex}$ (= $^{210}Pb_{tot} - ^{226}Ra$), (Swarzenski and others, 2006). The linear sedimentation rate for hypoxic site MR-J03-5 was determined as: 0.26 cm yr^{-1} (^{210}Pb-based) to 0.36 cm yr^{-1} ($^{239,.240}Pu$ peak-based); much slower than that at oxic site MR-J03-3: 1.24 cm yr^{-1} (210Pb-based) to 0.99 cm yr^{-1} ($^{239,240}Pu$ peak-based). The estimated sedimentation rates at MR-J03-5 place the peak in hypoxia (based on TS and atomic C/S ratios) at this site in the mid 1960's. Atomic C/S values actually increased (increasing oxic conditions) between the mid 1960's and about 1990, before decreasing again in years since about 1990. Above about 22 cm (e.g. since about 1920 in the MR-JO3-5 core), atomic C/S values at the hypoxic MR-J03-5 site have been significantly lower than those at the oxic MR-J03-3 site. Sedimentation rates were not available for the Hypoxic-1 core, although this site also had a minimum in atomic C/S values at a depth of 10-20 cm, with increasing values toward the surface (Fig. 13).

Mass accumulation rates of sediments from sites MR-J03-3 and MR-J03-5 (Fig. 1) were also determined by Swarzenski and others (2006): 0.87 g cm^{-2} yr^{-1} (^{210}Pb-based) to 0.69 ($^{239,240}Pu$ peak-based) at MR-J03-3, and 0.30 g cm^{-2} yr^{-1} (^{210}Pb-based) to 0.38 g cm^{-2} yr^{-1} ($^{239,240}Pu$ peak-based) at MR-J03-5. Average values for TC, TN, and TS in these cores were: 1.44%, 0.171%, and 0.198%, respectively at MR-J03-3, and 1.13%, 0.092%, and 0.305%, respectively at MR-J03-5. These values allow average accumulation rates for TC, TN, and TS to be calculated at these sites; results of these calculations are shown in Table 5. Accumulation of TC, TN, and TS were all higher at MR-J03-3, reflecting the much higher mass accumulation rates at this site, which is located along the Mississippi River Canyon and may receive direct sediment discharge funneled down the canyon (Coleman and others, 1981; Penland and Boyd, 1981). Despite higher TS concentrations at MR-J03-5, the MR-J03-3 site has slightly higher overall TS accumulation due to the much higher mass of sediment accumulated here.

Results of hydrocarbon gas analysis of sediments from the 2001 cores show that methane is the dominant hydrocarbon gas. Total concentrations of the different hydrocarbon gases in sediments from this study were comparable to those determined in other nearshore coastal sediments (Martens and Berner, 1977; Claypool and Kvenvolden, 1983; Judd, 2004). Ratios of $C_1/C_2 + C_3$ have been used to distinguish biogenic from thermogenic gas, with biogenic gas having values >1,000 and thermogenic gas having values <100 (Bernard and others, 1977 and 1978; Fleischer and others 2001). The $C_1/C_2 + C_3$ ratio in these sediments ranges from about 10 to >20,000, suggesting both biogenic and thermogenic gas is present (Anderson and Bryant, 1990; Bouma and Roberts, 1990). However, microbial methane utilization may be skewing the $C_1/C_2 + C_3$ values in some samples giving the gas composition the appearance of being thermogenic (Oremland, 1981; Orphan and others, 2001)

Table 5. Accumulation rates (AR) for total carbon (TC), total nitrogen (TN), and total sulfur (TS) at sites MR-J03-3 and MR-J03-5.

Site	TC AR (^{210}Pb) (mgC cm^{-2}yr^{-1})	TC AR (^{239,240}Pu) (mgC cm^{-2}yr^{-1})	TN AR (^{210}Pb) (mgN cm^{-2}yr^{-1})	TN AR (^{239,240}Pu) (mgN cm^{-2}yr^{-1})	TS AR (^{210}Pb) (mgS cm^{-2}yr^{-1})	TS AR (^{239,240}Pu) (mgS cm^{-2}yr^{-1})
MR-J03-3	12.5	9.9	1.5	1.2	1.7	1.4
MR-J03-5	3.4	4.3	0.3	0.3	0.9	1.2

VI. Conclusions

This report presents results of general organic analysis of sediments from a series of cores collected in the offshore Mississippi River system, including: organic elemental analysis (C, N, P, and S) and hydrocarbon gas analysis. Results of organic contaminants, trace element distributions, and radiochemical dating of the same sediment cores are presented elsewhere (Rosenbauer and others, 2007; Swarzenski and others, 2006).

Concentrations of C, N, P, and S in sediments varied by a factor of 10 between sites, and in down core profiles. Nearshore cores collected in 2001 proved to have erratic downcore C, N, P, and S profiles and sediment deposition rates, suggesting a high energy regime controlled more by variability in river flow rather than by geochemical processes and reactions within the system. These results focused further coring activities further offshore. Atomic C/N results suggest that organic matter deposited at all sites is a mix of microbial (algal) and terrestrial (vascular plant) remains, but with algal material dominant. Concentrations of total sulfur in sediments from cores in the zone of hypoxia were often higher than those in nearby zones with oxic water columns. Corresponding atomic C/S ratios were typically lower in sediments from sites in the zone of hypoxia compared to nearby sites with oxic water columns, and atomic C/S values may be useful as a proxy for identifying sites impacted by hypoxic conditions in the water column and for examining historical trends in hypoxia. At one site examined in this study, maximum hypoxic conditions were determined to have occurred in the mid 1960's, based on analysis of atomic C/S values in a dated core. The organic elemental composition (C, N, P, and S) of sediments was also used to guide sample selection for contaminant analysis, and to normalize the contaminant data to organic C content of the sediments.

Dissolved hydrocarbon gases in sediments showed a dominance of methane, but identifiable concentrations of ethane and hexane, and trace concentrations of propane, butane,.and pentane were also detected. All dissolved gases except hexane were dominated by "bound" gas, gas released only after agitation of the sediment in a blender. Hexane, in contrast was observed mostly as free gas, determined by headspace analysis.

Acknowledgments

Funding for this project was provided by the U.S. Geological Survey, Coastal and Marine Geology Program (John Haines, Program Coordinator). Several colleagues participated in the collection and sectioning of cores during various cruises for this study, we especially acknowledge Marci Marot, Chris Reich, Brian Kindinger, Nancy Dewitt, and Marissa Beck for their assistance. The captain and crew of the R/V Longhorn and Steve Rabalais (Louisiana Universities Marine Consortium) provided essential logistical support. Curtis Palmer and Sandra Neuzil (USGS, Reston, VA) provided helpful reviews that greatly improved the quality of this report.

References Cited

Anderson A.L., and Bryant W.R. (1990) Gassy sediment occurrence and properties: Northern Gulf of Mexico. Geo-Marine Letters 10: 209-220.

Aspila K.I., Agemian H., and Chau, A.S.Y., 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. The Analyst, 101, 187-197.

Bernard R.B., Brooks J.M., and Sackett W.M. (1977) A geochemical model for characterizing hydrocarbon gas sources in marine sediments. In: Proceedings of Offshore Technology Conference OTC 2934, OTC, Houston, TX, pp.435-438.

Bernard B., Brooks J., and Sackett W. (1978) Light hydrocarbons in recent Texas continental shelf and slope sediments. J. Geophys. Res. 83C: 4053-4061.

Bouma A.H., and Roberts H.H. (1990) Northern Gulf of Mexico continental slope. Geo-Marine Letters 10: 177-181.

Claypool G.E., and Kvenvolden K.A. (1983) Methane and other hydrocarbon gases in marine sediments. Ann. Rev. Earth and Planetary Sci. 11: 299-327.

Coleman J.M., Prior D.B., and Adams C.E., Jr. (1981) Erosional furrows on continental shelf edge, Mississippi delta region. Geo-Marine Letters 1: 11-15.

Cornwell J.C., and Sampou P.A. (1995) Environmental controls on iron sulfide mineral formation in a coastal plain estuary. In: Geochemical Transformations of Sedimentary Sulfur (M.A. Vairavamurthy, and A.A. Schoonen, eds.), ACS Symposium Series 612, American Chemical Society, Washington, DC, pp. 224-242.

Delaney R. L., and Craig M.R. (1997) Longitudinal changes in Mississippi River floodplain structure. Onalaska (WI). US Geological Survey. Project Status Report 62 No. PSR 97-02. Upper Mississippi River Long Term Resource Monitoring Program.

Fleischer P., Orsi T.H., Richardson M.D., and Anderson A.L. (2001) Distribution of free gas in marine sediments: a global overview. Geo-Marine Lett. 21: 103-122.

Goni M.A., Ruttenberg K.C., and Eglinton T.I. (1998) A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. Geochim. Cosmochim. Acta 62: 3055-3075.

Hedges J.L., and Stern J.H. (1984) Carbon and nitrogen determinations of carbonate-containing solids. Limnol. Oceanogr. 29: 657-663.

Howarth R., Anderson D., Cloern J., Elfring C., Hopkinson C., Lapointe B., Malone T., Marcus N., McGlathery K., Sharpley A., and Walker D. (2000) Nutrient Pollution of Coastal Rivers, Bays, and Seas, Issues in Ecology No. 7, Ecological Society of America, Washington, DC, 16 pp.

Judd A.G. (2004) Natural seabed gas seeps as sources of atmospheric methane. Environmental Geology 46: 988-996.

Justic D., Rabalais N.N., Turner R.E. (1995) Stoichiometric nutrient balance and origin of coastal eutrophication. Marine Pollution Bulletin 30: 41-46.

Lohrenz S.E., Fahnenstiel G.L., Redalje D.G., Lang G.A., Chen X., and Dagg M.J. (1997) Variations in primary production of northern Gulf of Mexico continental shelf waters linked to nutrient inputs from the Mississippi River. Mar. Ecol. Prog. Ser. 155: 45-54.

Macko S.A., Engel M.H., and Parker P.L. (1993) Early diagenesis of organic matter in sediments: assessment of mechanisms and preservation and preservation by the use of isotopic molecular approaches. In: Organic Geochemistry, Principles and Applications (Engel M.H. and Macko S.M., eds.), Plenum Press, NY, pp. 211-224.

Martens C.S., and Berner R.A. (1977) Interstitial water chemistry of anoxic Long Island Sound sediments: I. dissolved gases. Limnol. Oceanogr. 22: 10-24.

Meade R.H. (1995) Contaminants in the Mississippi River, 1987-1992. U.S. Geological Survey Circular 1133, pp. 140.

Orem W.H., Holmes C.W., Kendall C., Lerch H.E., Bates A.L., Silva S.R., Boylan A., Corum M., and Hedgman C. (1999) Geochemistry of Florida Bay sediments: nutrient history at five sites in eastern and central Florida Bay. J. Coastal Res. 15: 1055-1071.

Oremland R.S. (1981) Microbial Formation of Ethane in Anoxic Estuarine Sediments. Appl Environ Microbiol. 42: 122-129.

Orphan V.J., Hinrichs K.-U., Ussler W. III, Paull C.K., Taylor L.T., Sylva S.P., Hayes J.M., and Delong E.F. (2001) Comparative analysis of methane-oxidizing Archaea and sulfate-reducing bacteria in anoxic marine sediments. Appl. Environ. Microbiol. 67: 1922-1934.

Penland S., and Boyd R. (1981) Shoreline Changes on the Louisiana Barrier Coast. Oceans 13: 209-219.

Rabalais N.N., Turner R.E., and Wiseman W.J. Jr. (2001) Hypoxia in the Gulf of Mexico. J. Environ. Qual. 30: 320-329.

Rabalais N.N., Turner R.E., and Wiseman W.J. Jr. (2002) Gulf of Mexico Hypoxia, a.k.a. “the dead zone”. Annu. Rev. Ecol. Syst. 33:235–263.

Rosenbauer R.J., Orem W.H., Swarzenski P.W., Hostettler F.D., Dougherty J., and Lerch H.E. (2007). Organic geochemistry of sediments in nearshore areas of the Mississippi and Atchafalaya Rivers: II. Organic contamination and composition. U.S. Geological Survey, Open-File Report, in preparation.

Spink A., Sparks R. E., van Oorschot M., and Verhoeven J.T.A. (1998) Nutrient dynamics of large river floodplains. Reg. Rivers: Res. & Management 14: 203-216.

Strickland J.D.H., and Parson T.R. (1972) A Practical Handbook of Seawater Analysis. Fisheries Research Board of Canada, Ottawa, 310 pp.

Swarzenski P.W., Baskaran M., Rosenbauer R.J., and Orem W.H. (2006) Historical trace element distribution in sediments from the Mississippi River delta. Estuaries and Coasts 29: 1–14.

Tissot B.P., and Welte D.H. (1984) Petroleum Formation and Occurrence. Springer-Verlag, NY, 699 pp.

Vorosmarty C.J., Sharma K.P., Fekete B.M., Copeland A.H., Holden J., Marble J., and Lough J.A. (1997) The storage and aging of continental runoff in larger reservoir systems of the world. Ambio. 26:210-219.

Walker N.D. (1996) Satellite assessment of Mississippi River plume variability: causes and predictability. Remote Sens. Environ. 58:21-35

Wiseman W. J., Rabalais N. N., Turner R. E., Daniel S. P., and MacNaughton A. (1997) Seasonal and inter-annual variability within the Louisiana coastal current: stratification and hypoxia. Journal of Marine Systems 12: 237-248.

Yamamuro M., and Kayanne H. (1995) Rapid direct determination of organic carbon and nitrogen in carbonate-bearing sediments with a Yanaco MT-5 CHN analyzer. Limnol. Oceanogr. 40: 1001-1005.