

# An Organic Carbon Budget for the Mississippi River Turbidity Plume and Plume Contributions to Air-sea CO<sub>2</sub> Fluxes and Bottom Water Hypoxia

REBECCA E. GREEN<sup>1,\*</sup>, THOMAS S. BIANCHI<sup>1,†</sup>, MICHAEL J. DAGG<sup>2</sup>, NAN D. WALKER<sup>3</sup>, and GREG A. BREED<sup>4</sup>

<sup>1</sup> *Department of Earth and Environmental Sciences, Tulane University, New Orleans, Louisiana 70118*

<sup>2</sup> *Louisiana Universities Marine Consortium, Chauvin, Louisiana 70344*

<sup>3</sup> *Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, Louisiana 70803*

<sup>4</sup> *Department of Biology, Dalhousie University, Halifax, Nova Scotia B3H 4J1, Canada*

**ABSTRACT:** We investigated seasonal variability in organic carbon (OC) budgets using a physical-biological model for the Mississippi River turbidity plume. Plume volume was calculated from mixed layer depth and area in each of four salinity subregions based on an extensive set of cruise data and satellite-derived suspended sediment distributions. These physical measurements were coupled with an existing food web model to determine seasonally dependent budgets for labile (reactive on time scales of days to weeks) OC in each salinity subregion. Autochthonous gross primary production (GPP) equaled  $1.3 \times 10^{12}$  g C yr<sup>-1</sup> and dominated labile OC inputs (88% of the budget) because riverine OC was assumed mostly refractory (nonreactive). For perspective, riverine OC inputs amounted to  $3.9 \times 10^{12}$  g C yr<sup>-1</sup>, such that physical inputs were 3 times greater than biological inputs to the plume. Annually, microbial respiration (R) accounted for 65% of labile OC losses and net metabolism (GPP - R) for the entire plume was autotrophic, equaling  $5.1 \times 10^{11}$  g C yr<sup>-1</sup>. Smaller losses of labile OC occurred via sedimentation (20%), advection (10%), and export to higher trophic levels (5%). In our present model, annual losses of labile OC are 10% higher than inputs, indicating future improvements are required. Application of our model to estimate air-sea carbon dioxide (CO<sub>2</sub>) fluxes indicated the plume was a net sink of  $2.0 \times 10^9$  mol CO<sub>2</sub> yr<sup>-1</sup>, of which 90% of the total drawdown was from biotic factors. In all seasons, low salinity waters were a source of CO<sub>2</sub> ( $p\text{CO}_2 = 560\text{--}890$   $\mu\text{atm}$ ), and intermediate to high salinity waters were a sink of CO<sub>2</sub> ( $p\text{CO}_2 = 200\text{--}370$   $\mu\text{atm}$ ). Our model was also used to calculate O<sub>2</sub> demand for the development of regional hypoxia, and our spring and early summer budgets indicated that sedimentation of autochthonous OC from the immediate plume contributed 23% of the O<sub>2</sub> demand necessary for establishment of hypoxia in the region.

## Introduction

River-dominated ocean margins (RiOMar) are one of the most important classes of margins, in terms of oceanic influence and human impact (Meybeck 2003). Rivers are the primary interface between terrestrial and oceanic environments and play a central role in linking terrestrial and marine carbon cycles. Annually, rivers transport 1 Gt total carbon to the world's oceans, and a high percentage of global marine organic matter burial (40%) occurs in deltaic environments (Hedges and Kiel 1995). In addition to allochthonous organic carbon (OC) inputs, rates of primary production stimulated on continental shelves by river-borne nutrients are

among the highest in the biosphere (Lohrenz et al. 1990; Turner et al. 1990; Smith and DeMaster 1996). Preliminary evidence shows that large river plumes may be unique in producing more OC than they respire (e.g., Terner et al. 2000), in contrast to marsh-dominated ocean margins or semi-isolated nearshore bodies of water, which tend to be heterotrophic (e.g., Cai et al. 2003). Despite the known importance of RiOMar, the export pathways of OC and the contribution of RiOMar to atmospheric carbon dioxide (CO<sub>2</sub>) drawdown have been inadequately described. Both are of key importance in assessing contributions of coastal ecosystems to large-scale carbon budgets.

The net biological processing of OC by phytoplankton, bacteria, and zooplankton in river plumes is determined by a complex interaction of processes. Physical factors affecting biological OC processing include turbidity effects on light, stratification, residence time, and resuspension (McKee 2003). Chemical factors include delivery of terrestrial

\*Corresponding author; current address: Ocean Sciences Division, Naval Research Laboratory, Stennis Space Center, Mississippi 39529; tele: 228/688-5576; fax: 228/688-4149; e-mail: rgreen@nrlssc.navy.mil

†Current address; Department of Oceanography, Texas A&M University, College Station, Texas 77843-3146.

materials (carbon and nutrients), lability of terrestrial OC, nutrient ratios, flocculation of dissolved organic carbon (DOC), dissolution of particulate organic carbon (POC), and photooxidation. These processes interact with the food web to determine carbon uptake or release by its various compartments, which include autotrophs, bacteria, protozoans, microzooplankton, mesozooplankton, detrital material, and DOC. All of these factors contribute to whether the balance between gross primary production (GPP) and total respiration (R) is net autotrophic ( $GPP > R$ ) or net heterotrophic ( $GPP < R$ ), which determines whether an ecosystem exports or imports carbon. Realistically, net ecosystem metabolism ( $GPP - R$ ) can be difficult to assess because coastal margins are exceptionally heterogeneous and the metabolic balance changes along gradients within a particular ecosystem. Studies in Chesapeake Bay have documented a relationship between the GPP : R balance, salinity, and community size structure, with high net autotrophy occurring only at higher salinities and when GPP was dominated by larger size fractions (Kemp et al. 1997). In the Mississippi River plume, Breed et al. (2004) showed that net autotrophy predominated during most of the year (spring, summer, and fall) at intermediate salinities, corresponding to regions of particularly high GPP. The winter plume was net heterotrophic everywhere and external sources of carbon, such as riverine DOC, were needed to meet respiratory demand (Breed et al. 2004).

The construction of carbon budgets is a necessary step toward understanding coastal carbon cycling and determining the effects of future climatic and anthropogenic changes (e.g., Ver et al. 1999). Organic matter production in autotrophic ecosystems leads to the uptake of  $CO_2$  and plays a key role in the ability of the ocean to compensate for the release of greenhouse gases to the atmosphere by human activities. Based on limited observations, it has been suggested that continental margins are an important sink of  $CO_2$  and may account globally for an air-sea flux of  $0.4 Pg C yr^{-1}$  (Thomas et al. 2004). Such budgets are complicated by variability in net metabolism across coastal ecosystems, with near-shore sites being heterotrophic and sources of  $CO_2$  (Smith and Hollibaugh 1993; Cai et al. 2003), whereas outer shelf areas tend to be autotrophic and sinks of  $CO_2$  (Frankignoulle and Borges 2001). Kemp et al. (1997) proposed that the general global trend of coastal eutrophication will lead to increasing autotrophy in estuaries worldwide. Although this may enhance their role as  $CO_2$  sinks, the increased delivery of inorganic nutrients to many coastal zones has resulted in an increase in hypoxic regions (Diaz 2001), because a fraction of OC sinks from highly productive surface waters to

below the pycnocline where it is consumed by bacteria.

The Mississippi River is the 7th largest in the world by freshwater and sediment flux, drains 41% of the continental United States, and transports 1.2% of the total global input of DOC from rivers to the ocean (van der Leeden et al. 1990; Bianchi et al. 2004). High concentrations of dissolved nitrate from the river ( $>100 \mu mol l^{-1}$ ; Dagg and Whitledge 1991) support significant phytoplankton growth in the Mississippi River plume (Lohrenz et al. 1990, 1999) and one of the U.S.' most productive fisheries. The last 50 yr have marked significant changes in the Mississippi River drainage basin, with increased nutrient delivery from agricultural fertilization leading to a large hypoxic zone on the Louisiana-Texas shelf (Rabalais et al. 1996). Increased rainfall has positively affected chemical weathering, and bicarbonate export in the Mississippi River now accounts for a removal of atmospheric  $CO_2$  of  $1.1 \times 10^{13} g C yr^{-1}$  (Raymond and Cole 2003). As with hypoxia, increased alkalinity export is also linked to agricultural practices. Increases in both nutrient and bicarbonate input to the plume will significantly affect the extent to which the plume is a net sink of atmospheric  $CO_2$  (Cai 2003). Despite the important biogeochemical effects of the Mississippi River plume, only recently have modeling efforts been initiated to quantify OC cycling in the plume across the river-ocean gradient (Breed et al. 2004).

We developed a seasonally and spatially detailed OC budget for the Mississippi River turbidity plume, which originates at Southwest Pass, Louisiana (the largest pass on the bird-foot delta; Fig. 1). The factors controlling carbon cycling in the northwest Gulf of Mexico are highly variable, as evidenced by spatially heterogeneous distributions of primary production, which often differ from other property distributions (i.e., salinity, dissolved inorganic nitrogen [DIN], and chlorophyll *a*; Chen et al. 2000). This indicates the need for regionally-specific carbon budgets that address the unique carbon cycling processes in each particular region. We characterized the immediate plume of the Mississippi River as that associated with suspended sediments, in contrast to the extended plume that is associated with the long-distance spreading of low salinity waters. We characterized the immediate region of the plume because there is a large data set of measurements for this area and it is distinctly identifiable using satellite-derived suspended sediment distributions. Our OC budget was calculated by coupling the physical model that we developed with an existing food web model (Breed et al. 2004). The food web model was used to create OC budgets because it provides an excellent synthesis of data

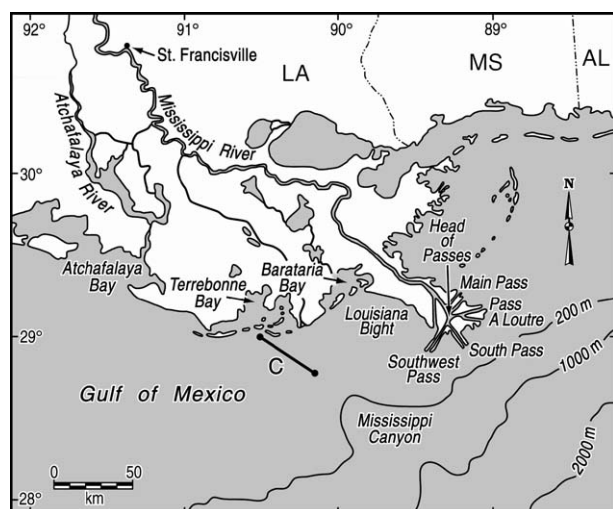


Fig. 1. Schematic map of southeastern Louisiana showing the Mississippi River, the Atchafalaya River, major passes of the Mississippi River through the bird-foot delta, and pertinent water bodies in the northern Gulf of Mexico (modified from Walker et al. 2005).

collected in the plume and makes possible the calculation of OC flows that can not be easily measured, such as total microbial respiration. In addition to presenting the first OC budgets for this plume, we apply these budgets to quantifying turbidity plume contributions to air-sea  $\text{CO}_2$  fluxes and bottom water hypoxia.

## Methods

### PHYSICAL MODEL

Mississippi River plume areas were calculated from satellite-derived suspended sediment distributions based on measurements of the National Oceanic and Atmospheric Administration (NOAA) Advanced Very High Resolution Radiometer (AVHRR). These data were received, processed, and analyzed at the Earth Scan Laboratory, Coastal Studies Institute, Louisiana State University. Pixel size at nadir is  $1.1 \times 1.1$  km. Atmospheric corrections were made to the visible channel of the AVHRR, using the near infrared channel, based on the techniques described by Stumpf and Pennock (1989), Stumpf (1992), and Walker (1996). This technique incorporates corrections for aerosols, glint, downwelling irradiance, and Rayleigh scattering. The AVHRR satellite reflectance measurements were converted to surface suspended sediment concentrations using a nonlinear regression equation developed from sea truth measurements obtained near-simultaneously by helicopter (Walker 1996). Monthly composite images were determined from a database of 142 clear-sky images collected

during 1989–1997 (Walker et al. 1997, 2005). The usual caveat about clear-sky images applies; they occur more often following north winds and clearing skies behind, with many other images hidden by the moisture and clouds that dominate for much of the year. The outer edge of the turbidity plume was defined by the lower limit of suspended sediment detection ( $5 \text{ mg l}^{-1}$ ). In each monthly image, the plume was defined as the region within the  $5 \text{ mg l}^{-1}$  suspended sediment contour, a line drawn west from a point about half way between the river mouth at Southwest Pass and Head of Passes, and a second line drawn southeast from the same point (Fig. 2). Average plume areas and standard deviations for each month were computed using the SeaSpace Terascan software program. All subsequent data analysis was performed using the MATLAB software package (The MathWorks).

Salinity subregion areas and mixed layer depths in each subregion were determined from a large data set of shipboard measurements in the plume. Surface salinities were determined from shipboard Multiple Instrument Data Acquisition System (MIDAS) files, and mixed layer depths were computed from conductivity, temperature, and depth (CTD) profiler measurements. MIDAS and CTD data sets were compiled from 21 cruises conducted from 1989 to 2004 aboard the R/V *Pelican*, N/S *Malcolm Baldrige*, and R/V *Longhorn* (Table 1). Four salinity subregions were defined based on the food web model (0–18, 18–27, 27–32, and 32–34.5; see below), and four seasons were defined (winter: December–February, spring: March–May, summer: June–August, and fall: September–November); the number of cruises was insufficient to compute monthly averages. Data from 3 to 5 cruises were used to create composite surface salinity maps for each season. Contour plots were created of seasonal surface salinities and the percent area in each salinity subregion was computed. To calculate monthly subregion areas, the percent areas in each subregion were assumed constant for all months in a season and were multiplied by the total plume area derived from satellite imagery for each month. Mixed layer depths were calculated using the depth at which vertical changes in density equaled or exceeded a  $0.1 \text{ m}^{-1}$  change from the surface. Seasonal mixed layer depths for each salinity subregion were computed as averages across multiple cruises in a season and multiple data points in each salinity subregion, and from Lohrenz et al. (1999). Monthly plume volumes in each salinity subregion were calculated as the product of the monthly total area (from satellite imagery), the seasonal percent subregion area, and seasonal mixed layer depth.

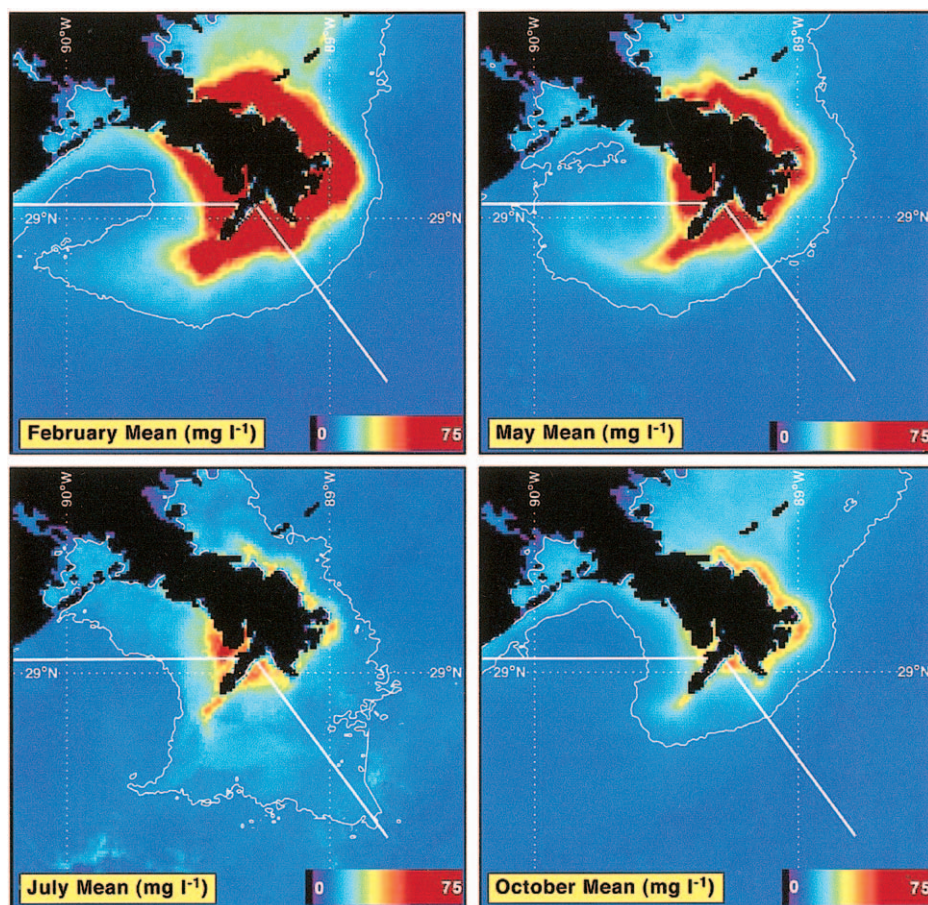


Fig. 2. Composite AVHRR-derived suspended sediment imagery for the Mississippi River turbidity plume showing an example each for winter (February), spring (May), summer (July), and fall (October). The plume is defined as the region between the two straight lines and the  $5 \text{ mg l}^{-1}$  suspended sediment contour (in white).

#### BIOLOGICAL MODEL

We applied an existing food web model for the Mississippi River plume (Breed et al. 2004) to determine seasonal and spatial rates of labile (reactive on time scales of days to weeks) OC cycling. The model of Breed et al. (2004) characterized OC cycling in four salinity regions but did not quantify the size or location of the regions, a requisite to determining plume OC budgets. The model incorporated all possible carbon flows between 8 compartments within the planktonic food web, including 6 living groups of plankton and 2 nonliving components. The living groups were divided into small ( $<8 \mu\text{m}$ ) and large ( $>8 \mu\text{m}$ ) phytoplankton, bacteria, and grazers of 3 size classes, including protozoans ( $<63 \mu\text{m}$ ), microzooplankton ( $63\text{--}200 \mu\text{m}$ ), and mesozooplankton ( $>200 \mu\text{m}$ ). The 2 nonliving compartments were DOC, which supported bacterial growth, and detritus. All compartments were defined for each of

the four salinity subregions (0–18, 18–27, 27–32, and 32–34.5); within each subregion, there were various flows in and out of the system to accommodate riverine DOC input (in subregion 1 only), in situ GPP, respiration, advection, sedimentation, and export to higher trophic levels. A combination of empirical data, collected primarily since 1990 with the start of the Nutrient Enhanced Coastal Ocean Productivity program, and biologically realistic constraints were used in the inverse method to calculate a single best solution for carbon flows between compartments, determined by minimizing the sum of squares of all flows. Mathematical details of the inverse procedure for planktonic food webs can be found in Vézina and Platt (1988) and Vézina (1989).

We made several modifications to this model to include new empirical data that have become available (Table 1). These additions included recent measurements of grazing by microzooplankton (Jochem 2003; Liu and Dagg 2003) and larvaceans

TABLE 1. Cruises from which data was incorporated into our modified food web model and physical model. These data included mixed layer depths, surface salinities, and microzooplankton and mesozooplankton grazing rates. References for the majority of cruises used in the food web model can be found in Breed et al. (2004) and have not been reincluded here. MLD = mixed layer depth (m). LaSER = Louisiana Stimulus for Excellence in Research; NOAA = National Oceanic and Atmospheric Administration; NECOP = Nutrient Enhanced Coastal Ocean Productivity; NSF = National Science Foundation; ONR = Office of Naval Research; NASA = National Aeronautics and Space Administration.

Vessel	Cruise Date	Sponsoring Program	Data Used
RV <i>Pelican</i>	Sep 20–27, 1989	LaSER	MLD, salinity
RV <i>Pelican</i>	April 23–29, 1990	LaSER	MLD, salinity
NS <i>Malcolm Baldrige</i>	July 17–Aug 10, 1990	NOAA/NECOP	MLD, salinity
RV <i>Pelican</i>	Oct 23–29, 1990	LaSER	MLD, salinity
NS <i>Malcolm Baldrige</i>	March 4–17, 1991	NOAA/NECOP	MLD
RV <i>Pelican</i>	Sep 12–18, 1991	NOAA/NECOP	MLD, salinity
RV <i>Pelican</i>	May 5–18, 1992	NOAA/NECOP	MLD
RV <i>Longhorn</i>	May 19–29, 2000	NSF	Microzooplankton grazing
RV <i>Pelican</i>	June 21–28, 2000	ONR	Salinity
RV <i>Pelican</i>	Oct 24–Nov 1, 2000	ONR	Salinity
RV <i>Pelican</i>	April 5–10, 2001	ONR	Salinity
RV <i>Pelican</i>	March 13–16, 2002	NOAA	Salinity
RV <i>Pelican</i>	March 17–24, 2002	NSF	Salinity, microzooplankton and mesozooplankton grazing
RV <i>Pelican</i>	April 24–26, 2002	NOAA	Salinity, mesozooplankton grazing
RV <i>Pelican</i>	May 13–15, 2002	NOAA	Salinity
RV <i>Pelican</i>	June 8–10, 2002	NOAA	Mesozooplankton grazing
RV <i>Pelican</i>	Oct 7–16, 2002	NASA	Salinity
RV <i>Pelican</i>	June 24–30, 2003	NOAA	Salinity
RV <i>Pelican</i>	July 14–21, 2003	NSF	MLD, salinity
RV <i>Pelican</i>	Dec 12–15, 2003	NSF	MLD, salinity
RV <i>Pelican</i>	Aug 9–12, 2004	NOAA	Salinity

(Sato and Dagg unpublished data), which resulted in microzooplankton grazing rates for subregions 1, 2, 3, and 4 of 25, 47, 58, and 27  $\text{mg C m}^{-3} \text{d}^{-1}$  in the winter and 28, 64, 86, and 46  $\text{mg C m}^{-3} \text{d}^{-1}$  in the spring, respectively. We replaced assumed values of mixed layer depth originally used in the model with our calculations of spatially and seasonally dependent depths derived from the physical data described above. Changes in mixed layer depth will affect GPP values (in  $\text{mg C m}^{-3} \text{d}^{-1}$ ) used in the model, because measured values of GPP (in  $\text{mg C m}^{-2} \text{d}^{-1}$ ; Redalje et al. 1994; Lohrenz et al. 1999) are divided by depth. We used the alternative summer model of Breed et al. (2004) as being most characteristic of GPP in the plume under average summer conditions, instead of their original summer model that was from an exceptionally productive summer (Chen et al. 2000). Resulting values of GPP used in the model for subregions 1, 2, 3, and 4 were 65, 138, 30, and 20  $\text{mg C m}^{-3} \text{d}^{-1}$  in winter, 50, 700, 140, and 40  $\text{mg C m}^{-3} \text{d}^{-1}$  in spring, 102, 818, 491, and 120  $\text{mg C m}^{-3} \text{d}^{-1}$  in summer, and 300, 900, 497, and 40  $\text{mg C m}^{-3} \text{d}^{-1}$  in fall, respectively.

#### CALCULATION OF PLUME CARBON BUDGETS

Annual OC budgets were calculated by coupling our physical and biological models. For each salinity subregion, labile OC budgets were constructed by

multiplying carbon flows from the food web model (in  $\text{mg C m}^{-3} \text{d}^{-1}$ ) by plume volume. Monthly budgets (in  $\text{g C mo}^{-1}$ ) were calculated by summing the processes in each of the four subregions, and annual budgets were derived by summing monthly budgets. Most of our focus is on the labile fraction of OC that is readily mineralized, has fast turnover times (days to weeks), and is relevant to food web processes. For a larger scale understanding of plume processes, we incorporated into our annual budget literature values for total riverine DOC ( $3.1 \times 10^{12} \text{ g C yr}^{-1}$ ; Bianchi et al. 2004) and POC ( $8.0 \times 10^{11} \text{ g C yr}^{-1}$ ; Duan and Bianchi unpublished data), burial of POC in sediments, and flocculation of DOC. Burial in shelf sediments was calculated as 30% of terrestrial OC and 15% of marine OC deposited to sediments (McKee et al. 2004). Flocculation of DOC in the Mississippi plume at low salinities was reported to account for <10% of DOC, compared to a range of 5–10% loss of DOC in other rivers (Benner and Opsahl 2001); a 5% loss was assumed in our DOC budget. Modeled estimates of total sedimentation were compared to independent estimates calculated from  $^7\text{Be}$  sedimentation rates (Corbett et al. 2004), average plume area, and a conversion of 1% OC by weight for surface seabed sediments (McKee personal communication). This is a rough comparison because  $^7\text{Be}$  derived rates were seasonally and spatially limited.

Variability in labile OC budgets was determined from uncertainties in physical model parameters. Standard deviations in budgets were calculated using methods of error propagation and the equation

$$\text{OC}_{\text{budget(gC)}} = \text{TotalArea} \times \sum_{i=1}^4 [\text{OC}_{\text{conc(gC m}^{-3})}] \times \text{MLD} \times \text{\%Area}_i \quad (1)$$

where the budget is a sum over all four subregions, and OC concentration is determined from the food web model. Standard deviations for mixed layer depth and total area were included in our analysis (Table 2). Variability in OC concentration caused by mixed layer depth was assumed minor compared to variability in volume and was not considered. We also did not include uncertainties in the percent area of each salinity subregion because there was not enough data to assess its variability, and it is not independent of uncertainties in total area.

#### APPLICATION OF CARBON BUDGETS

Monthly OC budgets were used to estimate the contribution of plume processes to hypoxia in bottom waters along the Louisiana–Texas coast. This analysis involved two steps: calculating the OC demand of the hypoxic zone, and quantifying the OC supply from the turbidity plume to hypoxia. Step 1 was achieved by first calculating the volume of the hypoxic zone. We used an average area of 15,000 km<sup>2</sup> for 1989–2001 (Rabalais et al. 2002) and assumed a thickness for bottom waters of 10 m as in previous models (Bierman et al. 1994; Justić et al. 1997). In reality the thickness of hypoxia varies with the depth of the water column, the location of the pycnocline(s), and the position along the shelf. Based on data for 1990–1994 (Transect C; Rabalais et al. 1999), a thickness of 10 m is likely to be towards the upper end of values observed for hypoxia across the shelf. We also assumed a decrease in dissolved oxygen in bottom waters of 4 mg l<sup>-1</sup>, corresponding to a change from 6 mg l<sup>-1</sup> in winter to 2 mg l<sup>-1</sup> under hypoxic conditions (Turner and Allen 1982). An additional oxygen consumption was calculated based on estimated rates of oxygen replenishment from the surface layer to the bottom layer using eddy diffusivity coefficients (Justić et al. 1997). By applying an O<sub>2</sub> to carbon ratio of 0.288 by weight, we calculated the amount of OC that must be supplied from the upper water column for the onset of bottom water hypoxia to occur. Uncertainty in the OC demand for hypoxia was approximated using a standard deviation for the volume of the hypoxic zone ( $\pm 6.3 \times 10^{10}$  m<sup>3</sup>). This was calculated from the standard deviation for the area ( $\pm 5.1 \times$

10<sup>9</sup> m<sup>2</sup>) and thickness of hypoxia ( $\pm 2.5$  m), the latter determined from a transect south of Terrebone Bay for 1990–1994 (Transect C; Rabalais et al. 1999). Step 2 involved quantifying the plume's OC contribution to bottom waters prior to the last week in July, when the areal size of hypoxia is usually mapped (Rabalais et al. 1999). OC sedimentation from the plume was calculated using our budgets for spring and early summer (March–June). We considered July plume contributions to hypoxia to be zero because river discharge generally flows offshore during this period (Cochrane and Kelly 1986; Salisbury et al. 2004; Walker et al. 2005). The sum contribution of March–June OC sedimentation was then compared to the OC demand for the hypoxic zone.

We also used our monthly OC budgets to calculate the CO<sub>2</sub> flux between plume surface waters and the atmosphere. The surface water concentrations of CO<sub>2</sub> include both an abiotic (solubility) component, determined by the carbon chemistry of the river and marine end members, and a biotic component determined by net ecosystem metabolism. Total dissolved inorganic carbon (DIC) in the plume was determined as:

$$\text{DIC} = \text{DIC}_{\text{abiotic}} + \Delta\text{CO}_{2,\text{biotic}} \quad (2)$$

where  $\Delta\text{CO}_{2,\text{biotic}}$  is calculated from our budget for net ecosystem metabolism and residence time. This calculation for DIC assumes minimal flux of CO<sub>2</sub> between surface and bottom waters, an assumption supported by high riverine freshwater flux and the resulting buoyancy and shear that contribute to vertical separation. Surface water *p*CO<sub>2</sub> values were calculated from total alkalinity (TALK) and DIC values using the CO2SYS software package (Lewis and Wallace 1998), with apparent dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987), the CO<sub>2</sub> solubility coefficient of Weiss (1974), and the sulfate dissociation constant of Dickson (1990). Seasonal silicate and phosphate data were included in the calculations (Lohrenz et al. 1999). Abiotic contributions to *p*CO<sub>2</sub> in each salinity subregion were calculated using TALK and DIC values for the plume calculated along a conservative mixing curve. Monthly riverine values of TALK and pH (on the National Bureau of Standards (NBS) scale) were determined from U.S. Geological Survey data for St. Francisville (Raymond unpublished data), and riverine DIC was calculated using the CO2SYS program (Table 2). The marine end member values for TALK and DIC were assumed equal to the surface water values for the Atlantic Ocean presented in Millero (1996), and the same values were used in all seasons (TALK and DIC of 2.40 and 2.00 mmol kg<sup>-1</sup>, respectively; Cai 2003);

TABLE 2. Plume physical and chemical properties. Certain parameters (i.e., mixed layer depth, % subregion area, mean subregion volume, residence time, and temperature) are presented for each salinity subregion, whereas other parameters (i.e., monthly area, wind speed, pH, total alkalinity [TALK], and dissolved inorganic carbon [DIC]) are presented for each month in a season. The four salinity subregion ranges are 0–18, 18–27, 27–32, and 32–34.5. Standard deviations are in parentheses. No data is indicated by nd.

	Season			
	Winter	Spring	Summer	Fall
Mixed layer depth (m)	2, 5, 15, 10 (nd, 4, 1, 4)	2, 5, 5, 5 (1, 3, 3, 1)	2, 5, 5, 5 (1, 2, 4, nd)	2, 5, 5, 10 (2, 2, 2, 4)
Monthly area ( $10^3$ km <sup>2</sup> )	1.9, 3.1, 2.8 (0.55, 1.0, 0.96)	2.7, 2.0, 2.6 (1.0, 0.87, 0.64)	2.8, 2.1, 2.0 (1.3, 0.55, 0.40)	0.92, 1.0, 1.3 (0.39, 0.61, 0.40)
Subregion area (%)	10, 25, 40, 25	35, 25, 20, 20	15, 45, 20, 20	15, 35, 25, 25
Mean subregion volume (km <sup>3</sup> )	0.52, 3.3, 16, 6.5	1.7, 3.0, 2.4, 2.4	0.69, 5.2, 2.3, 2.3	0.33, 1.9, 1.4, 2.7
Residence time (d)	1, 1.5, 6, 6	1, 1.5, 6, 6	1, 1.5, 6, 6	1, 1.5, 6, 6
Temperature (°C)	9, 16, 17, 20	21, 22, 22, 23	30, 30, 29, 29	23, 24, 25, 25
Wind speed (m s <sup>-1</sup> )	7.0, 7.4, 6.5	7.3, 6.6, 4.5	3.7, 4.4, 4.3	4.7, 7.4, 7.1
Riverine pH	7.74, 7.60, 7.62 (0.37, 0.29, 0.27)	7.66, 7.83, 7.78 (0.19, 0.25, 0.25)	7.72, 7.88, 7.92 (0.22, 0.34, 0.24)	7.84, 7.45, 7.76 (0.31, 0.16, 0.30)
Riverine TALK (mmol kg <sup>-1</sup> )	2.46, 1.93, 1.93 (0.25, 0.47, 0.23)	1.75, 2.10, 2.02 (0.24, 0.28, 0.21)	2.21, 2.48, 2.51 (0.22, 0.24, 0.26)	2.74, 2.37, 2.44 (0.11, 0.37, 0.37)
Riverine DIC (mmol kg <sup>-1</sup> )*	2.55, 2.04, 2.03	1.81, 2.13, 2.06	2.24, 2.48, 2.50	2.77, 2.51, 2.49

\* Calculated using CO2SYS with inputs of riverine pH and TALK.

this is likely an accurate assumption, given current knowledge of plume  $p\text{CO}_2$  (Cai personal communication).

The flux of  $\text{CO}_2$  across the air-sea interface was computed as:

$$\text{Flux}_{\text{CO}_2} = k \times K_{\text{H}}(p\text{CO}_{2,\text{water}} - p\text{CO}_{2,\text{atm}}) \quad (3)$$

where,  $k$  is the gas transfer velocity ( $\text{m d}^{-1}$ ) for  $\text{CO}_2$  and  $K_{\text{H}}$  is the Henry's Law solubility constant of  $\text{CO}_2$ . We used two formulations for the  $k$ -wind speed ( $u$ ) relationship because there is currently no consensus as to which relationship is most appropriate (Frankignoulle and Borges 2001). We applied Liss and Merlivat's (1986) equation  $k = (2.85u - 9.65)(\text{Sc}/660)^{-0.5}$  (relevant for  $3.6 < u \leq 13 \text{ m s}^{-1}$ ) and Wanninkhof's (1992) average wind equation  $k = 0.39u^2(\text{Sc}/660)^{-0.5}$ , where  $\text{Sc}$  is the Schmidt number of  $\text{CO}_2$  in seawater at  $20^\circ\text{C}$ . Values for  $\text{Sc}$  as a function of temperature were computed using a third-order polynomial fit (Wanninkhof 1992). We computed  $\text{CO}_2$  fluxes for both the abiotic and biotic components to quantify the contributions of biological processes to total  $\text{CO}_2$  flux.

There are several factors that affect biotic contributions to DIC, but which are beyond the scope of this work, including contributions from calcifying organisms (Gattuso et al. 1995) and microbial nitrogen cycling (e.g., ammonification, denitrification, and nitrification; Abril and Frankignoulle 2001). Calcifying organisms are not likely to be important contributors to primary production in the plume, given that diatoms dominate numerically, and calcifying organisms such as prymnesiophytes do not become important until outside of the plume (Wawrik and Paul 2004). There are not enough measurements of ammonification, denitrification, and nitrification in the plume to incorporate them into our  $\text{CO}_2$  flux calculations. These processes are likely to be important given measurements of significant nitrification at low and intermediate salinities in spring and summer plume waters (Pakulski et al. 1995; Pakulski et al. 2000).

## Results

### PLUME PHYSICAL PROPERTIES

Seasonal differences in plume spatial structure (Fig. 2) were generally caused by changes in wind stress. Throughout much of the year, winds and Ekman transport cause the plume to flow westward over the shelf (Fig. 2; Cochrane and Kelly 1986; Dinnel and Wiseman 1986). Between October and March, this general pattern is periodically altered by north or northwest winds associated with the passage of continental air masses (DiMego et al. 1976). These wind reversals ( $20\text{--}30 \text{ yr}^{-1}$ ) rapidly alter the direction of the coastal current and river

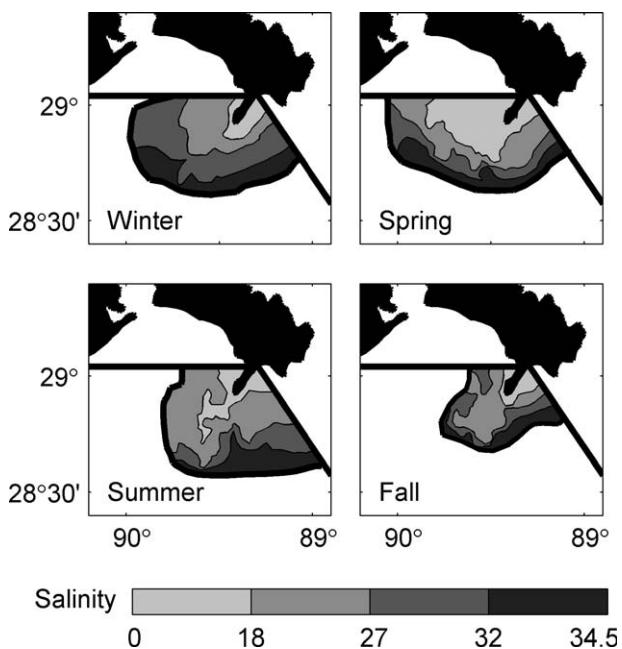


Fig. 3. Surface salinity distributions showing the four subregions defined in the food web model (0–18, 18–27, 27–32, and 32–34.5) in winter, spring, summer, and fall. Salinity distributions were created from a compilation of cruise MIDAS data in months of seasonally average flow. The percent area within each subregion is shown in Table 2.

plumes on the Louisiana shelf (Walker 1996; Walker and Hammack 2000). In July and August westward flow is often interrupted by periods of west winds that induce eastward and southward flow (e.g., Walker et al. 2005). These event scale dynamics are averaged into our monthly images. The average annual plume area was 2,100 km<sup>2</sup> with a maximum area of 3,100 km<sup>2</sup> in January and a minimum area of 920 km<sup>2</sup> in September. These areas are larger than previously presented for the plume because we used a more inclusive plume criterion (5 mg l<sup>-1</sup> suspended sediments versus 10 mg l<sup>-1</sup> in Walker 1996 and 25 mg l<sup>-1</sup> in Walker et al. 2005). A significant relationship was observed between river discharge (m<sup>3</sup> s<sup>-1</sup>) and plume area (km<sup>2</sup>;  $y = 9.67 \times 10^4 x + 5.94 \times 10^8$ ,  $r^2 = 0.63$ ), such that the largest areas were observed in winter and spring months when river discharge was the highest. No significant relationship was observed between plume volume and discharge because seasonal changes in mixed layer depth were associated with factors unrelated to discharge, such as wind stress and the annual temperature cycle. The largest plume volumes were observed in winter months (mean of 26 km<sup>3</sup>) when plume areas and mixed layer depths in salinity subregions 3 and 4 were the largest (Table 2). In spite of seasonal differences in plume temperature, and density, there was little variation between

seasons in mixed layer depth for salinity subregions 1 and 2. There was higher variation in subregions 3 and 4, with the deepest mixed layer depths in winter when wind speed and mixing are highest.

Plume volume in each of the four salinity subregions was an important determinant of plume carbon cycling because rates of biological processes differ between subregions. Surface salinity distributions show that the plume does not consist of neatly formed salinity lobes, but rather that the higher salinity subregions often only exist at the southern edge of the plume (Fig. 3; Rouse 1998). Comparing seasons, subregion 1 generally had the smallest area and volume (Table 2), except in the spring when subregion 1 was largest. This was likely caused by high river discharge and warmer temperatures leading to increased water column stability. Subregion 2 generally had the largest volume, except in winter when subregion 3 had the largest area and volume due to a deep mixed layer depth (15 m) and a high percent area (40%). Over all seasons, the largest plume volumes were observed in subregion 3 in the winter, followed by subregion 2 in the summer. The latter was particularly significant to OC budgets because of high primary production in that subregion (Breed et al. 2004). The percent contribution of subregion 4 to turbidity plume volume was seasonally the most constant of all subregions (c. 23%).

#### ORGANIC CARBON BUDGET

In our budgets, temporal and spatial variability in labile OC cycling was primarily caused by changes in primary production and respiration. Annually, GPP accounted for the majority of labile OC inputs (88%; Fig. 4) and the largest inputs were generally from salinity subregion 2 and secondarily from subregion 3. The contributions of riverine DOC and POC to the labile pool were assumed small, with assumptions of 3% lability for riverine DOC (Benner and Opsahl 2001) and 10% lability for riverine POC (Duan and Bianchi unpublished data). In the formulation of the food web model, riverine DOC contributes to food web processes in the surface plume but riverine POC does not because it is assumed to sediment near the river mouth. Total labile OC inputs from the plume's food web and riverine sources were  $1.5 \times 10^{12}$  g C yr<sup>-1</sup>. High OC inputs in summer were caused by high rates of GPP and a large plume volume in the most productive region, salinity subregion 2 (Table 2). The lowest OC inputs were observed in winter even though plume volume was large, because rates of GPP were low. Forty-seven percent of annual GPP occurred in summer, 22% in spring, 21% in fall, and 10% in winter. For the nonwinter seasons, the various OC loss pathways were similar, with the highest output to respiration

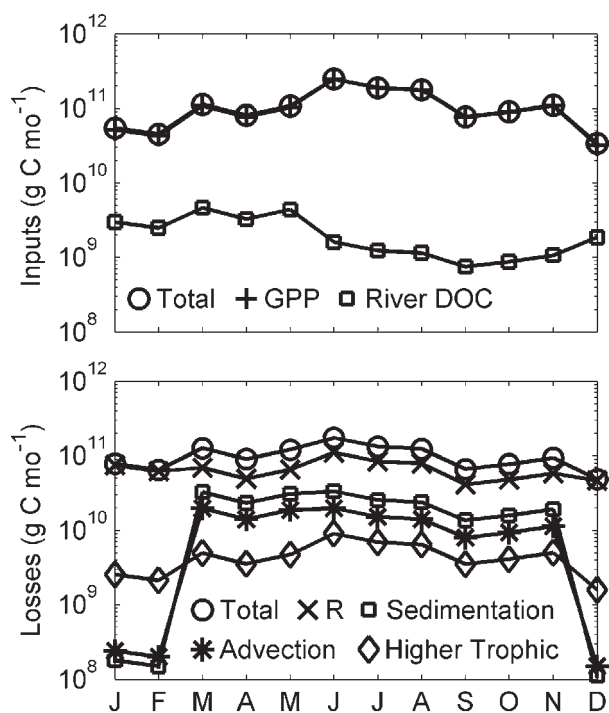


Fig. 4. Monthly budgets for labile OC inputs and outputs associated with the food web model, as a sum over all four salinity subregions. Inputs are from in situ GPP and riverine DOC, and outputs are to total microbial respiration (R), sedimentation, advection, and higher trophic levels. Riverine POC is not represented as an input in panel A, because it is assumed to sediment near the river mouth and to have little effect on food web processes in the surface plume.

(55–64%), followed by sedimentation (19–26%), advection out (12–16%), and transport to higher trophic levels (4–5%; Fig. 4). In winter the majority of OC loss was via respiration (96%), with 3% loss to higher trophic levels and negligible losses to sedimentation and advection out (1%). The percent of GPP exported vertically in the nonwinter seasons ranged from 4% to 67%, depending on salinity, with an average of 27%; the percent was <5% in winter. In the nonwinter seasons, the percentage generally increased with salinity due to the advection of OC from highly productive to less productive subregions (Breed et al. 2004).

Total plume GPP was greater than respiration in all seasons except winter. The general seasonal trends in plume metabolism were similar to those presented in Breed et al. (2004), except that there was more net autotrophy in our results (Fig. 5), with only 4 (of 16) subregions showing net heterotrophy versus 7 subregions in the original model. This difference was caused by the smaller mixed layer depths used in our model, which resulted in higher ratios of GPP : R. Significant spatial variability was observed in net ecosystem metabolism, with near

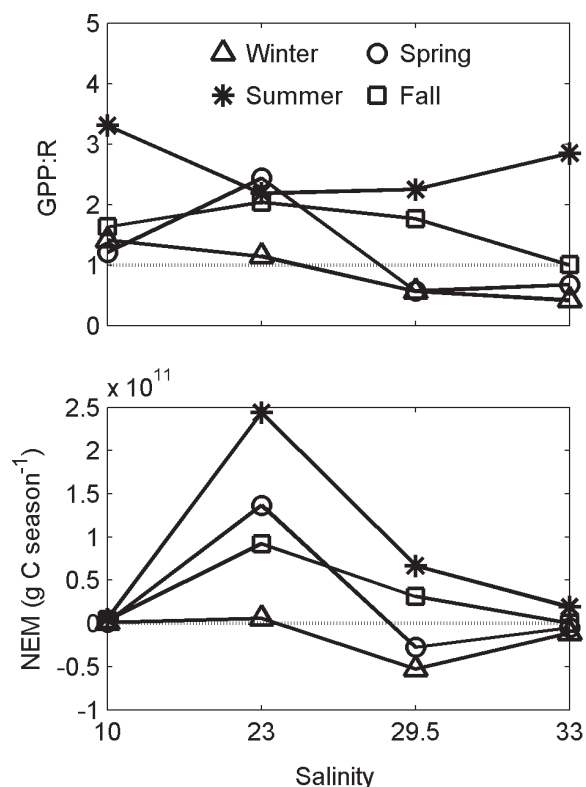


Fig. 5. Plume metabolic balances and budgets as a function of salinity for each season. The budget in each salinity subregion is a sum over the entire subregion plotted at its mean salinity. Total net ecosystem metabolism (NEM) budgets, as a sum over the entire plume, are  $-5.7 \times 10^{10}$  g C in winter,  $1.1 \times 10^{11}$  g C in spring,  $3.4 \times 10^{11}$  g C in summer, and  $1.3 \times 10^{11}$  g C in fall, such that all seasons except winter are net autotrophic.

balance in subregions 1 and 4 in all seasons and large variations in subregions 2 and 3. Annually, the plume was net autotrophic, with average GPP : R ratios of 1.6 and net ecosystem metabolism amounting to  $+5.1 \times 10^{11}$  g C  $\text{yr}^{-1}$ , most of which was contributed by subregion 2.

Total DOC inputs to the Mississippi River turbidity plume were larger than POC inputs. Total POC inputs, from the river and autochthonous GPP, amounted to  $2.1 \times 10^{12}$  g C  $\text{yr}^{-1}$  (Fig. 6). This was less than the total riverine DOC input of  $3.1 \times 10^{12}$  g C  $\text{yr}^{-1}$  but recall that only 3% of this is labile. Biological processing of DOC in the plume was balanced, such that release by phytoplankton, zooplankton, and detritus ( $490 \times 10^9$  g C  $\text{yr}^{-1}$ ) was the same as uptake by bacteria ( $490 \times 10^9$  g C  $\text{yr}^{-1}$ ). There was significant spatial and seasonal variation in net biological processing of DOC. Surplus DOC from biological excretion was generally present in subregions 2 and 3 in the nonwinter seasons, while more DOC was consumed than excreted in all subregions in winter. A net biological input of DOC

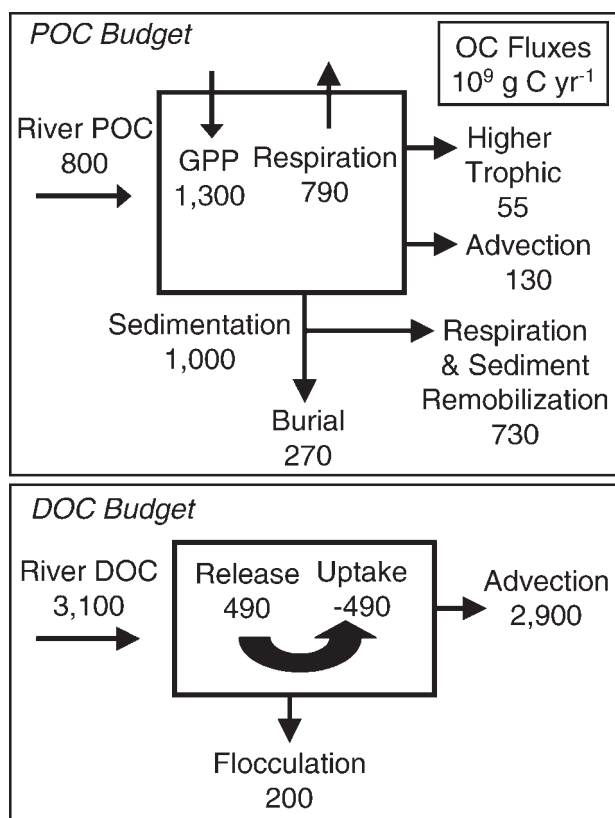


Fig. 6. Annual plume budgets for major fluxes of POC and DOC, including physical forcing via riverine input, sedimentation, and advection out, and biotic processes associated with GPP, respiration, and DOC cycling (exudation and uptake). Aspects of the budget were calculated from literature values, including riverine DOC and POC, burial of POC in sediments, and flocculation of DOC (as discussed in the Methods). The value for OC loss in bottom waters due to respiration and physical sediment remobilization was calculated by difference.

at mid salinities in nonwinter months has previously been documented (Benner and Opsahl 2001). Model results show that phytoplankton, zooplankton, and detritus contributed approximately equally to DOC release in the nonwinter seasons, while zooplankton and detritus were most important in the winter. A small loss of DOC via flocculation was estimated at low salinities ( $2.0 \times 10^{11} \text{ g C yr}^{-1}$ ), though this process needs to be better quantified.

In our budget, the majority of POC is lost to sedimentation and respiration, regardless of its source. The assumption that most riverine POC quickly sediments out of the plume is supported by sediment  $\delta^{13}\text{C}$  measurements, which showed terrestrial OC was restricted to near the river mouth (Turner and Rabalais 1991; Eadie et al. 1994). More recent analyses of lignin-phenol biomarkers have shown that fine-grained, terrestrial organic matter is often transported further to the shelf-break and slope (Bianchi et al. 1997; Goñi et al. 1998), but this

offshore transport likely occurs via lateral movement in the bottom boundary layer, after the material has sedimented. Large terrestrially-derived woody materials typically sediment very quickly near the mouth of the Mississippi River (Bianchi et al. 2002). Our total sedimentation of  $1.0 \times 10^{12} \text{ g C yr}^{-1}$  is generally consistent with  $^7\text{Be}$ -based sedimentation rates that range from  $1 \times 10^{12}$  to  $4 \times 10^{12} \text{ g C yr}^{-1}$ , as calculated from Corbett et al. (2004). Our budgets indicate advection of POC out of the plume in surface waters is minor in comparison to sedimentation which is 8 times greater. The partitioning of this POC in bottom waters between respiration and sediment remobilization is particularly important to resolve given the large amount of OC these processes affect ( $7.3 \times 10^{11} \text{ g C yr}^{-1}$ ). Fluidized and mobile muds on the Louisiana shelf may play an important role in the transport of terrestrially and marine-derived OC to sediments in deeper waters offshore (McKee et al. 2004). Because the role of this mobile mud layer is unquantified, we can not make any determination of the net metabolic balance of the entire ecosystem (surface plus bottom waters).

Seasonal, volume-integrated budgets of labile OC inputs and losses from the physical-biological model did not balance. In winter and spring, OC losses were greater than inputs; in summer and fall, the reverse was the case and inputs were greater than losses. For the annual budget, losses were 10% higher than inputs. One factor likely to contribute to budget imbalance is a lack of data on physical factors, such as residence time, which we assumed was constant among seasons (Table 2). Previous studies have estimated a transit time of 1–2 d from the river mouth through intermediate salinities in nonwinter seasons (Lohrenz et al. 1990; Hitchcock et al. 1997, and references therein), and we have assumed longer residence times at higher salinities outside this fast moving core of the plume. Breed et al. (2004) stated that modeled carbon flows are sensitive to errors in physical mixing parameters. Uncertainty in the plume physical model is an important avenue for future research.

#### VARIABILITY IN OC BUDGETS

Variability in mixed layer depth and plume area were both important contributors to uncertainty in carbon budgets. A standard deviation was determined for annual labile OC inputs from the food web model of  $1.3 \times 10^{12} \pm 0.73 \times 10^{12} \text{ g C yr}^{-1}$  (or  $\pm 56\%$ ). Considering all seasons, uncertainties in mixed layer depth averaged  $\pm 44\%$  of the mean value used in the model (Table 2). This variability is likely caused by differences in wind mixing, occurring temporally throughout a season and spatially throughout a salinity subregion (Fig. 3).

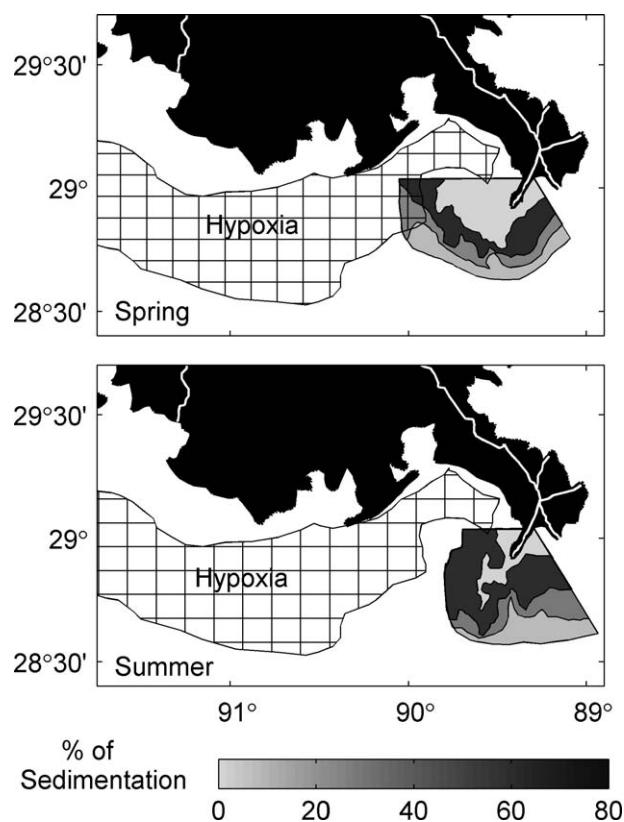


Fig. 7. Maps showing the location of the 1996 hypoxic region (hatched; Rabalais et al. 1999) relative to plume regions of variable sedimentation in the spring and summer. The Atchafalaya River and Bay are located in the upper left-hand corner of each plot. The highest plume sedimentation occurs in salinity subregion 2, accounting for 63% of total plume sedimentation in the spring and summer. On average, lower sedimentation in salinity subregions 1, 3, and 4 in both seasons accounted for 1%, 28%, and 8% of total sedimentation, respectively. The hypoxic zone continues west to about 93.0°W.

An analysis of wind data from the river mouth (NOAA station BURL1) for 1996 showed a similar degree of seasonal variability in wind speed as was observed in mixed layer depth. Monthly uncertainty in satellite-derived plume area averaged  $\pm 34\%$  of the mean (Table 2). Walker (1996) found that the main factors causing day-to-day variability in plume area were wind speed and direction, whereas river discharge mainly determined seasonal and interannual variability. This author showed that the largest winter plumes were observed during strong north winds associated with frontal passages, occurring every 3–10 d. The largest plumes in summer were associated with west winds at low wind speeds. Our criteria for quantifying the extent of the turbidity plume allows for contributions from other passes, located to the north and east of Southwest Pass (e.g., South Pass and Pass a Loutre; Fig. 1). Some of our largest plume measurements show significant

contributions from South Pass sediments advecting to the west around the delta and contributing to the apparent size of the Southwest Pass turbidity plume. During northeast winds, Walker et al. (2005) estimated that 75% of Mississippi River discharge through the bird-foot delta flows onto the Louisiana shelf, due to large contributions from passes on the eastern side of the delta. Variability in our plume area calculations are also contributed to by variability in contributions from surrounding passes on the delta. Our estimates of variability in plume mixed layer depth and area are generally not minimized by considering only a single year from the several years of data that we analyzed; river plume processes are inherently highly dynamic even on short temporal scales. Future assessments of variability in plume carbon budgets should additionally account for uncertainty in biological processes and in percent area in each salinity subregion, uncertainties which we currently do not have the data to constrain.

#### O<sub>2</sub> FLUXES IN BOTTOM WATERS

Plume contributions to mid summer hypoxia were calculated using spring and early summer budgets for OC sedimentation from all 4 subregions. Total sedimentation from March to May and June was  $8.7 \times 10^{10}$  and  $3.3 \times 10^{10}$  g C, respectively, for a sum contribution of  $1.2 \times 10^{11}$  g C ( $\pm 7.3 \times 10^{10}$  g C). In both spring and summer,  $>90\%$  of labile OC sediments originated from mid salinity waters, with subregions 2 and 3 contributing an average of 63% and 28% of total plume sedimentation, respectively (Fig. 7). The Mississippi River turbidity plume is spatially offset from most of the region of hypoxic bottom water but currents in March–June will advect sedimenting material or subpycnocline waters depleted in oxygen (following respiration of sedimenting OC) into the hypoxic zone. The OC demand for the entire hypoxic zone was calculated as a sum of  $1.7 \times 10^{11}$  g C due to a  $4 \text{ mg l}^{-1}$  change in oxygen concentration and  $3.5 \times 10^{11}$  g C due to the vertical diffusion of oxygen (as described in Methods), for a total demand of  $5.2 \times 10^{11}$  g C ( $\pm 2.2 \times 10^{11}$  g C). The turbidity plume's direct contribution is equivalent to 23% ( $\pm 17\%$ ) of this OC demand for the hypoxic zone. Although the spring-summer volume of the plume is only 7% the hypoxic region's volume, it can potentially supply 23% of the OC demand for hypoxia because it contains some of the highest values of primary productivity in the northwest Gulf of Mexico.

Several factors could modify our calculated contribution of the plume to the OC demand of the hypoxic zone. Our estimated contribution could be high if sedimenting particles from plume waters settle to the bottom before reaching the hypoxic

zone. Summertime reversal of currents to eastward flow is sometimes observed as early as June (e.g., Chen et al. 2000; Walker et al. 2005), such that sedimenting OC could be transported to the east, away from the hypoxic zone, even in early summer. Another factor that would cause our estimate to be high is sulfate reduction in anoxic sediments, which would consume OC without consuming oxygen. If this were the case, then some of our sedimenting OC would not be available to contribute to hypoxia. Sulfate reduction on the Louisiana shelf has been implicated as important in the remineralization of OC in sediments (Rowe et al. 2002). Questions remain as to the role of sulfate reduction in determining oxygen consumption in bottom waters on the Louisiana shelf.  $\text{H}_2\text{S}$ , the byproduct of sulfate reduction, has the potential to diffuse into bottom waters and consume oxygen even though sulfate reducing bacteria themselves do not. Complicating this process is the potential effect of high riverine metal inputs, such as iron and manganese, which can immobilize  $\text{H}_2\text{S}$  and convert it into authigenic minerals before it could consume oxygen. Further research is needed to determine the effect of sulfate reduction on oxygen cycling in bottom waters and its effect on regional hypoxia. Our estimated contribution from plume waters would be too low if we have overestimated the size of the hypoxic zone. This would be the case if an average 10 m thickness is indeed at the high end of thickness for hypoxic bottom waters (as noted in Methods). Variability in the diffusive flux of oxygen to the bottom layer could affect our understanding of the importance of plume sedimentation to bottom waters, given the large contribution of this diffusive flux to our oxygen demand calculation (based on eddy diffusivity coefficients of Justić et al. 1997). If there was no downward flux of oxygen, sedimenting OC from the plume would support 71% of the development of hypoxia, indicating that accurate estimates of oxygen diffusion to bottom waters are important.

#### AIR-SEA $\text{CO}_2$ FLUXES

Seasonal differences in  $p\text{CO}_2$  in the plume were determined by both abiotic and biotic processes. Abiotic contributions to  $p\text{CO}_2$  were affected by seasonal changes in water temperature and riverine TALK (Table 2). Winter and spring values of  $p\text{CO}_2$  were lower than in summer and fall because of lower temperatures (Fig. 8). The importance of temperature in determining  $p\text{CO}_2$  is easily visualized at the high salinity end member where constant, seasonally-independent oceanic values of TALK and DIC were assumed, but where  $p\text{CO}_2$  was distinctly lower in winter and spring. Seasonal differences in riverine TALK and DIC also occur,

but play a smaller role than temperature in determining seasonality in  $p\text{CO}_2$ . Bicarbonate dominates alkalinity in the Mississippi River (Raymond and Cole 2003) and is inversely related to river discharge, such that the lowest concentrations are observed in winter and spring. Low winter and spring water temperatures and bicarbonate concentrations were largely responsible for decreased alkalinity, DIC, and  $p\text{CO}_2$  in the river and a net sink of atmospheric  $\text{CO}_2$  in most salinity subregions (Fig. 8). High summer and fall water temperatures and bicarbonate concentrations lead to the plume being a net abiotic source of  $\text{CO}_2$  to the atmosphere. Biotic contributions to  $p\text{CO}_2$  were determined by net plume metabolism. In winter and spring, subregion 3 was characterized by net heterotrophy, which resulted in biotic increases in  $p\text{CO}_2$  (Figs. 5 and 8). In spring (subregion 2) and summer and fall (most salinities), the plume was characterized by net autotrophy, especially at mid salinities, resulting in large biotic decreases in  $p\text{CO}_2$ . In subregion 2 net ecosystem metabolism decreased  $p\text{CO}_2$  by 90  $\mu\text{atm}$  in spring, 130  $\mu\text{atm}$  in summer, and 125  $\mu\text{atm}$  in fall. During the summer and fall, biotic contributions were an important determinant of the direction of air-sea flux, and generally caused subregions 2 and 3 to be net sinks of  $\text{CO}_2$  (Fig. 8). Modeled values of  $p\text{CO}_2$  calculated in fall were similar to empirically measured values (Cai 2003). This comparison lends support to our assumption of minimal  $\text{CO}_2$  flux between surface plume and bottom waters in our  $p\text{CO}_2$  calculations.

Seasonal differences in air-sea  $\text{CO}_2$  fluxes were determined primarily by net ecosystem metabolism, temperature, and wind speed. The absolute magnitude of fluxes (in  $\text{mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) calculated using the Wanninkhof (W; 1992) wind speed formulation were larger by 1.5–2.5 times than fluxes obtained using the Liss and Merlivat (L+M; 1986) formulation, similar to previous findings (Frankignoulle and Borges 2001). Abiotic factors alone lead to the plume being a net  $\text{CO}_2$  sink of  $1.9 \times 10^8 \text{ mol yr}^{-1}$  on average (W:  $1.7 \times 10^7 \text{ mol yr}^{-1}$ ; L+M:  $3.6 \times 10^8 \text{ mol yr}^{-1}$ ), with winter contributing the majority of the drawdown (Fig. 8). Temperature was the most important factor determining abiotic flux differences between seasons, followed by wind speed (Table 2), and lastly by TALK and DIC, which played relatively minor roles, as previously discussed. Air-sea flux budgets amounted to a summed abiotic and biotic sink of  $1.7 \times 10^9 \text{ mol CO}_2 \text{ yr}^{-1}$  (W:  $1.9 \times 10^9 \text{ mol yr}^{-1}$ ; L+M:  $1.4 \times 10^9 \text{ mol yr}^{-1}$ ). Net metabolism contributed 90% of the annual drawdown of  $\text{CO}_2$  in the plume. Areally-integrated budgets of air-sea  $\text{CO}_2$  flux emphasized the large contribution of subregion 2 in the summer. Although the nonwinter seasons contributed all of

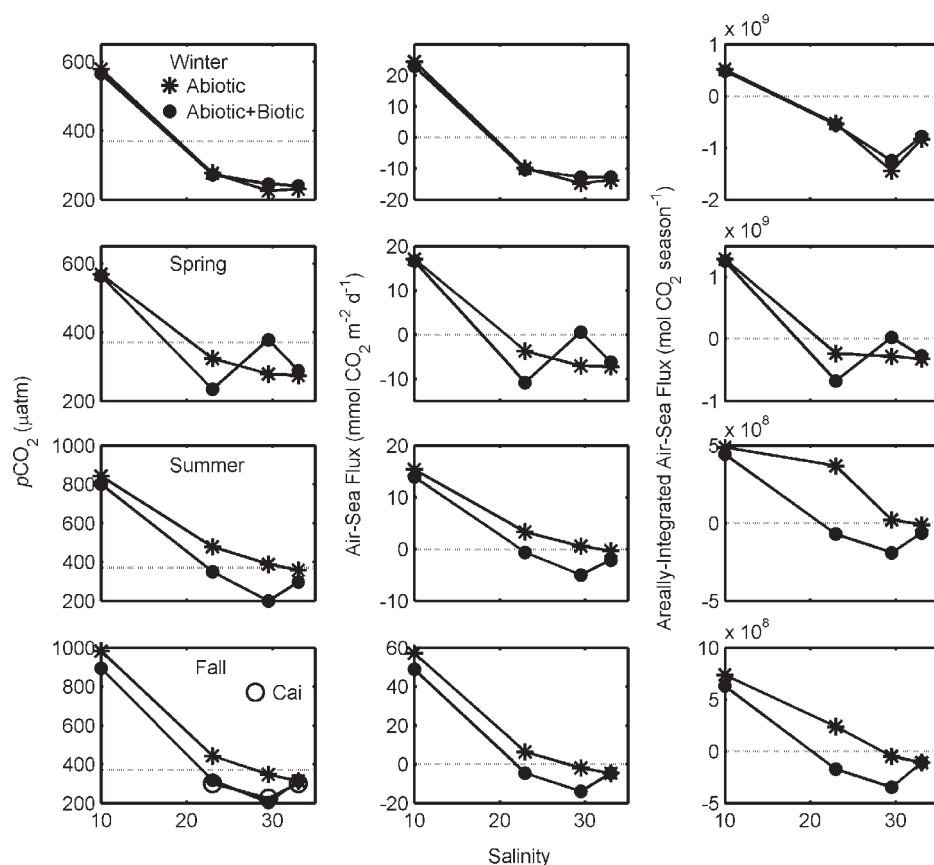


Fig. 8. Abiotic and biotic contributions to  $p\text{CO}_2$  in the plume and air-sea fluxes of  $\text{CO}_2$  in winter, spring, summer, and fall. Atmospheric  $p\text{CO}_2$  values ( $370 \mu\text{atm}$ ) are indicated in the left-hand column (dotted line), and  $p\text{CO}_2$  measurements of Cai (2003) were plotted in Fall for comparison. Note that Cai's (2003) measurements were available for salinities of 23–33, for which they overlapped the abiotic + biotic points. Air-sea fluxes are the average of values obtained using the Liss and Merlivat (1986) and Wanninkhof (1992) wind speed formulations. A line was drawn at zero on all air-sea flux panels, to indicate net direction of  $\text{CO}_2$  flux. Biotic contributions to  $\text{CO}_2$  fluxes were most important in the nonwinter seasons at mid salinities.

the biotic drawdown of  $\text{CO}_2$ , the chemical and physical properties of the winter plume made it an important contributor to  $\text{CO}_2$  drawdown. Total (abiotic + biotic) drawdown from the atmosphere in the winter and fall was  $2.1 \times 10^9$  and  $4.3 \times 10^6$  mol  $\text{CO}_2$ , respectively, whereas spring and summer contributed  $3.3 \times 10^8$  and  $1.2 \times 10^8$  mol  $\text{CO}_2$  to the atmosphere despite high net ecosystem metabolism in summer.

## Discussion

### COMPARISON OF MISSISSIPPI RIVER TURBIDITY PLUME OC BUDGET TO PREVIOUS STUDIES

Despite differences in physical characteristics, there are remarkable similarities between the OC budgets for the Mississippi River turbidity plume and pelagic waters of Chesapeake Bay. These two systems represent classic examples of a deltaic, salt-wedge extended estuary in the case of the Mississippi plume and a coastal plain, partially-mixed

estuary in the case of Chesapeake Bay, both of which receive large inputs of inorganic nutrients from agricultural runoff and wastewater discharges. The similarity of their OC budgets allows for a good comparison of the different processes controlling carbon cycling in the two systems. Area-normalized GPP is similar for the plume ( $1.3 \times 10^{12}$  g C  $\text{yr}^{-1} / 2.1 \times 10^9 \text{ m}^2 = 619 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) and Chesapeake Bay ( $2.4 \times 10^{12}$  g C  $\text{yr}^{-1} / 3.5 \times 10^9 \text{ m}^2 = 686 \text{ g C m}^{-2} \text{ yr}^{-1}$ ; Kemp et al. 1997), and similar summer rates of GPP are observed in the mid and lower Chesapeake Bay and at intermediate salinities in the plume ( $5 \text{ g C m}^{-2} \text{ d}^{-1}$ ). Respiration is the largest OC sink in both ecosystems, accounting for a mean total loss of 61% in the plume and 85% in Chesapeake Bay, versus 52–87% in numerous other coastal ecosystems (Kemp et al. 1997). We suggest that some combination of riverine nutrient inputs and physical factors, such as residence time, for the Mississippi plume and Chesapeake Bay result in their having similar annual GPP rates. Riverine

loading of total OC and DIN are 14 times higher in the Mississippi plume ( $3.9 \times 10^{12}$  g C yr<sup>-1</sup> and  $9.4 \times 10^{11}$  g N yr<sup>-1</sup>, respectively; Dagg et al. 2004) than in Chesapeake Bay ( $2.9 \times 10^{11}$  g C yr<sup>-1</sup> and  $6.1 \times 10^{10}$  g N yr<sup>-1</sup>, respectively; Kemp et al. 1997). In contrast to nutrients, residence times are higher in Chesapeake Bay, on the order of months (Boynton et al. 1995), versus several days in the Mississippi plume. Short residence times and a single point source of nutrients in the plume restrict high GPP to a narrow band of intermediate salinities, as phytoplankton growth is limited by light at low salinities and nutrients at high salinities. Longer residence times and multiple nutrient sources in the Chesapeake Bay result in nonlimiting DIN concentrations in surface waters throughout the bay and high summer GPP in both the mid and lower Bays (91% of the total pelagic area). These two different scenarios result in the dominance of physical total OC fluxes (i.e., fluxes associated with water transport) in the Mississippi plume (Fig. 6), versus the dominance of biological fluxes in Chesapeake Bay, such that the ratio of physical to biological total OC inputs was 3 in the Mississippi plume and only 0.07 in Chesapeake Bay.

Net metabolic autotrophy in the Mississippi plume is well explained by the predominance of high inorganic nutrient loading relative to total OC loading. For various coastal regions, Kemp et al. (1997) proposed that net ecosystem metabolism is related to the source of nutrient inputs, such that: ecosystems receiving most of their nutrients from terrestrial organic matter are generally heterotrophic and demonstrate an inverse relationship between metabolism and GPP (Smith and Hollibaugh 1993; Caffrey 2004), and ecosystems under high inorganic nutrient loading tend to be autotrophic and demonstrate a positive relationship between metabolism and GPP (e.g., Kemp et al. 1997). The Mississippi River turbidity plume distinctly falls into the latter category, with the river delivering very high dissolved inorganic nutrients ( $>100 \mu\text{mol l}^{-1}$  dissolved nitrate; Dagg and Whitledge 1991), associated with high population development and agricultural activity in the drainage basin. The DIN : total OC loading ratio for the plume is ca. 0.2, which is the same as the ratio for the highly net autotrophic Chesapeake Bay, though net ecosystem metabolism for the Mississippi plume is much higher (240 versus  $\sim 100$  g C m<sup>-2</sup> yr<sup>-1</sup>). When just the labile fraction of total OC is considered for the Mississippi plume, then the DIN : total OC loading ratio is higher (8); a consideration which is certainly relevant to the comparison of loading ratios and net ecosystem metabolism across ecosystems. The relationship between nutrient loading and metabolism suggests that other temperate river plumes with

high riverine DIN concentrations, such as the Changjiang and the Huange, may also be net autotrophic.

The percentage of primary production that is vertically exported from surface waters of the Mississippi River turbidity plume, as in other regions of the northwest Gulf of Mexico, is highly variable. Our calculated values ranged from 0% to 67%, depending on season and salinity. Using primary productivity and sediment trap measurements, Redalje et al. (1994) showed that 4–140% of production was lost to POC vertical flux in the immediate plume. We compared our spring and summer ratios with those of Redalje et al. for the unique locations where their measurements were made, salinity subregion 3 in spring and subregion 2 in summer. Our value in the spring for subregion 3 of 64% compared well with Redalje et al.'s value of 50% in the same salinity subregion. Our summer value for subregion 2 of 11% was consistent with Redalje et al.'s measured values of 3–9%. At least two factors contributed to higher spring compared to summer ratios, including higher grazing in the summer by both microzooplankton and mesozooplankton and higher advection of OC through the surface plume in spring than in summer. We calculated that  $590 \text{ mg C m}^{-3} \text{ d}^{-1}$  was advected into subregion 3 in the spring, whereas only  $70 \text{ mg C m}^{-3} \text{ d}^{-1}$  was advected into subregion 2 in the summer, substantially affecting the amount of OC available for sedimentation. Several previous studies of hypoxia on the Louisiana shelf have assumed that 50% of primary production is exported below the pycnocline, independent of season (Rabalais et al. 1991; Justić et al. 1997; Scavia et al. 2003). For a station in the core of the hypoxic zone (where several of these models are based) a rough estimate of the fraction of production exported from surface waters was highly variable and ranged from 10% to 200% (references in Rabalais et al. 1996). More data are required on this important ratio and the factors that control it in different parts of the river plume and across the Louisiana shelf, if we are to accurately predict the contributions of pelagic OC production to bottom water hypoxia.

#### DISTINCT SOURCES OF OC TO BOTTOM WATERS OF THE HYPOXIC ZONE

Due to the large extent of the hypoxic zone ( $\sim 15,000 \text{ km}^2$ ) and dynamic shelf currents, sedimenting organic matter to bottom waters will originate from a diversity of overlying surface waters. These various overlying waters have different biological and physical controlling factors, indicating the need for regionally-specific OC budgets that can incorporate the particular dynamics of each

region. We have calculated the unique contribution to hypoxia from one source of organic matter to bottom waters, the turbidity plume of the Mississippi River, which we calculated could supply  $\sim 23\%$  of the OC demand for the hypoxic zone. Our budget of GPP for the plume accounts for 5–10% of annual autochthonous production for the entire Louisiana–Texas shelf (140,000 km<sup>2</sup>; Chen et al. 2000). Primary productivity in the immediate region of the Mississippi River delta has previously been shown to be correlated with riverine nitrate + nitrite flux, whereas productivity to the west of this region was not correlated with riverine nutrient flux (Lohrenz et al. 1997). This suggests additional nonriverine sources of and controls on DIN, which determine primary productivity in these more westerly shelf regions. In the following, we will consider other possible sources of labile organic matter to bottom waters along the Louisiana coast, which include autochthonous sources from the Mississippi and Atchafalaya Rivers and coastal wetlands and allochthonous sources from in situ production by marine phytoplankton, of which the Mississippi River turbidity plume is an example.

Allochthonous inputs of organic matter are a potential contributor to hypoxia. There is debate over whether direct inputs of riverine OC contribute to hypoxia, depending on assumptions related to OC lability and losses during transport to the hypoxic zone (Carey et al. 1999; Rabalais et al. 2002). Riverine POC is a mixture of labile phytoplankton biomass, which accounts for on average 8% of total POC and as high as 20% when phytoplankton biomass is high (Dagg et al. 2005; Duan and Bianchi unpublished data), and more refractory (on a time scale of tens to hundreds of years) terrestrial material from soil organic matter and vascular plant detritus. If we assume that most riverine POC settles near the river mouth, riverine POC is 10% labile (on the time scale of several months), and 25% of it is transported to the hypoxic zone, the resultant contribution is only  $2 \times 10^{10}$  g C yr<sup>-1</sup>, equivalent to only 4% of the carbon demand of the hypoxic zone. This rough estimate suggests that direct riverine inputs of POC are not an important contributor to hypoxia, but also highlights uncertainties in current estimates of riverine contributions. Another large uncertainty is the fraction of riverine DOC that is labile. We have used values of 2–4%, consistent with empirical evidence, but small changes in the lability of this large pool of OC could result in significant enhancements to the microbial loop component of the food web. As in our model results, this component of the food web (i.e., bacteria and micrograzers) is generally not considered a significant contributor to sinking material (Legendre and

Michaud 1998). There are other autochthonous sources of OC along the coast that need to be assessed. Barataria Bay was shown to be an active source of DOC ( $4.28 \times 10^{10}$  g C yr<sup>-1</sup>; references in Guo et al. 1999) and POC (Bianchi unpublished data) injection onto the adjacent shelf (Fig. 1). Interpretation of sediment  $\delta^{13}\text{C}$  measurements can be confounded by mixing of the distinct signatures of phytoplankton ( $-18\text{‰}$  to  $-22\text{‰}$ ), terrestrial C<sub>4</sub> plants ( $-11\text{‰}$ ), and terrestrial C<sub>3</sub> plants ( $-28\text{‰}$  to  $-30\text{‰}$ ). This problem can be addressed through compound-specific work, such as in Wysocki et al.'s (2005) findings using lignin-specific isotope analyses, which showed that 50–60% of total OC in sediments of the eastern Louisiana shelf is from terrestrial sources, of both riverine and marsh origin. Their work showed high terrestrial contributions near the Mississippi River mouth followed by a decrease in values and an increase again near Terrebonne Bay. As with riverine inputs of OC, the lability of marsh-derived material is not well known and would benefit from better constraint through bioassay techniques (Servais et al. 1989).

Autochthonous production from shallow waters along the coastal edge of the hypoxic zone, including the Atchafalaya River plume, are likely an important source of OC to bottom waters in the hypoxic zone. This coastal band of shallow water has high nutrient and chlorophyll contents (Sklar and Turner 1981; Chen et al. 2000), and is often distinctly separated from the Mississippi River turbidity plume by a region of low nutrients and chlorophyll, as seen in both in situ (Bode and Dortch 1996; Liu and Dagg 2003) and satellite-derived measurements (Müller-Karger et al. 1991; Walker et al. 2005). The Atchafalaya River plume enters the northwest Gulf through a wide, shallow embayment to the west of our study site and discharges 30% of the water from the Mississippi River system (Fig. 1). The Atchafalaya enters the Gulf at about the mid point of regional hypoxia, such that both east winds in the springtime and west winds in the summertime force the Atchafalaya River plume over the hypoxic zone, in contrast to the more seasonal contributions from the Mississippi River plume. Chen et al. (2000) showed that peak concentrations of nutrients and chlorophyll *a* and rates of primary productivity along the Louisiana–Texas continental shelf (not including the Mississippi plume) are often associated with the Atchafalaya River plume. For their study region, these authors calculated an annual average primary production for coastal waters of the northwest Gulf of Mexico of  $0.52$  g C m<sup>-2</sup> d<sup>-1</sup>, with the highest values of primary production (up to  $3.31$  g C m<sup>-2</sup> d<sup>-1</sup>) occurring on the Louisiana shelf in coastal waters between Terrebonne and Atchafalaya Bays and further west.

Nutrients required to support this coastal production may come from the Atchafalaya River, nutrient regeneration in the extended plume of the Mississippi River, coastal marshes and bays such as Barataria and Terrebonne, and upwelling of nutrient-rich bottom waters. Given the likely importance of shallow coastal areas, a more mechanistic understanding of the supply of nutrients to these regions and the subsequent delivery of organic matter to bottom water is clearly needed.

In contrast to previous models, we quantified the unique contribution of sedimentation from the Mississippi River turbidity plume to bottom waters. Previous numerical models developed to study hypoxia include a two-box, oxygen flux model (Justić et al. 1997, 2002) and 3-dimensional (Bierman et al. 1994) and 1-dimensional mass balance models (Scavia et al. 2003). Justić et al. (2002) simulated oxygen dynamics for one location off the Louisiana coast, situated to the west of the Mississippi plume in the hypoxic zone. Bierman et al. (1994) simulated summer steady-state, phytoplankton-nutrient-oxygen dynamics for the entire Louisiana inner shelf using a coarse, 21-segment spatial grid. In their model, the entire region of our study was represented by two grid segments, for which near-river chlorophyll concentrations were not well represented by their model results. Their model represented summer conditions of net eastward flow along the shelf, such that the Atchafalaya River but not flow from the Mississippi River delta had the greatest effect on shelf processes; bottom water oxygen concentrations were well simulated under this scenario, suggesting the Atchafalaya River plume as a source of OC for shelf hypoxia. Scavia et al. (2003) modeled the Mississippi and Atchafalaya Rivers as point nutrient sources, using their total nitrogen loads as surrogates for organic matter load below the pycnocline, and assumed a constant westward flow from both sources. Taken together, the following regions have been modeled in relation to hypoxia in the northwest Gulf of Mexico: the Mississippi River turbidity plume (our study), a station south of Terrebonne Bay (Justić et al. model), and a coarse spatial grid of the Louisiana coast (Bierman et al. model); the Scavia et al. model is not particularly region specific regarding the details of organic matter cycling. Shallow coastal regions, such as the Atchafalaya River discharge, have never been modeled because these regions are too shallow for standard oceanographic sampling. Future research should focus on the specific pathways of OC transformation in near-shore shelf regions, with special emphasis on food web (bacteria-phytoplankton-grazer) interactions and other processes that control the fate of OC in a dynamic, river-influenced coastal shelf environment.

#### THE MISSISSIPPI RIVER TURBIDITY PLUME AS A SINK OF ATMOSPHERIC CO<sub>2</sub>

A gradient in CO<sub>2</sub> cycling was observed in the plume from terrestrially-dominated, low salinity waters as net sources of CO<sub>2</sub> to higher salinity waters as net sinks of CO<sub>2</sub>. The fluxes of CO<sub>2</sub> in mid to high salinity plume waters are similar to those previously observed in European continental shelf waters. An extensive study of the North Atlantic European Shelf, covering all four seasons, showed that the shelf was a significant net sink of CO<sub>2</sub> (Frankignoulle and Borges 2001). For the Gulf of Biscay and the North Sea, values of  $p\text{CO}_2$  and fluxes were in the ranges of 200–400  $\mu\text{atm}$  and +4 to  $-70 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ , respectively, which are in the same range as our values for the Mississippi plume (Fig. 8). Low salinity plume waters are highly influenced by terrestrial inputs and are a net source of CO<sub>2</sub>, as has been observed in other terrestrially-dominated systems. Extremely high  $p\text{CO}_2$  values, in the range of 1,000–8,000  $\mu\text{atm}$ , have been observed in several estuaries, including the Scheldt (Frankignoulle et al. 1996a) and Loire (Abril et al. 2003), as well as marsh-dominated coastal waters (e.g., Cai et al. 2003). Similar to the Mississippi plume, a gradient from low salinity waters as a source of CO<sub>2</sub> to higher salinity waters as a sink of CO<sub>2</sub>, contributed to by in situ primary production, has been observed in the Scheldt (Borges and Frankignoulle 2002) and Elbe River plumes (Brasse et al. 2002).

We have identified the Mississippi plume as a net sink of atmospheric CO<sub>2</sub> by accounting for an annual cycle of riverine inputs and net metabolism. Human activities release 7.7 Gt C yr<sup>-1</sup> to the atmosphere, of which the ocean supports significant uptake, behaving as a sink of 2.0 Gt C yr<sup>-1</sup> (Sarmiento and Gruber 2002). Fluxes in the coastal ocean are not explicitly considered in the global ocean budget because of significant temporal and spatial variability in physical and biological processes, including the production, respiration, and export of OC and inputs of inorganic carbon from rivers and coastal upwellings. An overriding question is whether the continental shelves are net autotrophic or heterotrophic, especially given differences observed between nearshore and outer shelf regions (Gattuso et al. 1998). Our CO<sub>2</sub> budgets for the Mississippi River turbidity plume are preliminary, and future work should focus on clarifying certain of our assumptions, including TALK and DIC variability in the high salinity end member, the contribution of microbial processes such as ammonification, nitrification, and denitrification to changes in TALK (e.g., Abril and Frankignoulle 2001), and the use of other gas transfer-

wind formulations (e.g., Wanninkhof and McGillis 1999). Despite these uncertainties, our findings contribute to an understanding of variability in air-sea CO<sub>2</sub> fluxes in a river-dominated ocean margin that is highly affected by anthropogenic disturbance. We have shown that the Mississippi plume is a net sink of CO<sub>2</sub> due to a combination of abiotic and biotic factors resulting in net autotrophy. Air-sea flux budgets resulted in a total sink for the turbidity plume of  $2.0 \times 10^9$  mol CO<sub>2</sub> yr<sup>-1</sup>, of which 90% of the total drawdown was from biotic factors. Our results are based on a detailed model of plume chemistry, physical structure, and trophic interactions and match empirical *p*CO<sub>2</sub> measurements collected in the fall (Cai 2003).

Evidence from previous studies shows that river plumes significantly affect CO<sub>2</sub> cycling at larger scales by the spreading of fresher waters by the prevailing surface circulation (Frankignoulle et al. 1996b; Kumar et al. 1996; Terson et al. 2000). Using Coastal Zone Color Scanner climatologies, Terson et al. (2000) showed that the Amazon River plume was a net sink of CO<sub>2</sub> more than 2,000 km from shore, making the western equatorial Atlantic Ocean a net sink of CO<sub>2</sub>, in contrast to the central and eastern parts of the equatorial belt. For the Mississippi plume, we showed that high salinity plume waters were a net sink of CO<sub>2</sub> in all seasons (*p*CO<sub>2</sub> = 240–310 μatm; Fig. 8). Given that Mississippi River plume waters advect much farther than we have considered here (Müller-Karger et al. 1991; Walker et al. 2005), future studies using advances in remote sensing will likely show the importance of the extended plume as a larger sink of CO<sub>2</sub> than we have calculated in the current study.

#### ACKNOWLEDGMENTS

Financial support for this research was provided by Tulane University's Center for Bioenvironmental Research, the Louisiana Board of Regents, NOAA Grant No. NA160A2672 (LEAG) to M. J. Dagg, NASA/LEQSF (2001-04) to T. S. Bianchi, and NASA Cooperative Agreement #NCC13-0300102-5-22059-8300 to N. D. Walker. We thank Adele Babin for processing AVHRR imagery and Pete Raymond for providing U.S. Geological Survey pH and alkalinity data. We also thank Robert Chen, Jim Dorrance, Bernie Gardner, Gary Hitchcock, and Brent McKee for cruise underway data, and Steve Lohrenz for mixed layer depth data. Michele Frankignoulle provided helpful comments on our CO<sub>2</sub> flux calculations. The manuscript was improved by insightful comments from Stephen Smith and an anonymous reviewer.

#### LITERATURE CITED

- ABRIL, G., H. ETCHEBER, B. DELILLE, M. FRANKIGNOULLE, AND A. V. BORGES. 2003. Carbonate dissolution in the turbid and eutrophic Loire estuary. *Marine Ecology Progress Series* 259:129–138.
- ABRIL, G. AND M. FRANKIGNOULLE. 2001. Nitrogen-alkalinity interactions in the highly polluted Scheldt Basin (Belgium). *Water Resources* 35:844–850.
- BENNER, R. AND S. OPSAHL. 2001. Molecular indicators of the sources and transformations of dissolved organic matter in the Mississippi River plume. *Organic Geochemistry* 32:597–611.
- BIANCHI, T. S., T. FILLEY, K. DRIA, AND P. HATCHER. 2004. Temporal variability in sources of dissolved organic carbon in the lower Mississippi River. *Geochimica et Cosmochimica Acta* 68:959–967.
- BIANCHI, T. S., C. D. LAMBERT, P. H. SANTSCHI, AND L. GUO. 1997. Sources and transport of land-derived particulate and dissolved organic matter in the Gulf of Mexico (Texas shelf/slope): The use of lignin-phenols and loliolides as biomarkers. *Organic Geochemistry* 27:65–78.
- BIANCHI, T. S., S. MITRA, AND B. MCKEE. 2002. Sources of terrestrially-derived carbon in the lower Mississippi River and Louisiana shelf: Implications for differential sedimentation and transport at the coastal margin. *Marine Chemistry* 77:211–223.
- BIERMAN, JR., V. J., S. C. HINZ, D.-W. ZHU, W. J. WISEMAN JR., N. N. RABALAIS, AND R. E. TURNER. 1994. A preliminary mass balance model of primary productivity and dissolved oxygen in the Mississippi River plume/inner Gulf Shelf region. *Estuaries* 17: 886–899.
- BODE, A. AND Q. DORTCH. 1996. Uptake and regeneration of inorganic nitrogen in coastal waters influenced by the Mississippi River: Spatial and seasonal variations. *Journal of Plankton Research* 18:2251–2268.
- BORGES, A. V. AND M. FRANKIGNOULLE. 2002. Distribution and air-water exchange of carbon dioxide in the Scheldt plume off the Belgian coast. *Biogeochemistry* 59:41–67.
- BOYNTON, W. R., J. H. GARBER, R. SUMMERS, AND W. M. KEMP. 1995. Inputs, transformations and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. *Estuaries* 18: 285–314.
- BRASSE, S., M. NELLEN, R. SEIFERT, AND W. MICHAELIS. 2002. The carbon dioxide system in the Elbe estuary. *Biogeochemistry* 59:25–40.
- BREED, G. A., G. A. JACKSON, AND T. L. RICHARDSON. 2004. Sedimentation, carbon export and food web structure in the Mississippi River plume described by inverse analysis. *Marine Ecology Progress Series* 278:35–51.
- CAI, W.-J. 2003. Riverine inorganic carbon flux and rate of biological uptake in the Mississippi River plume. *Geophysical Research Letters* 30. [doi:10.1029/2002GL016312].
- CAI, W.-J., Z. A. WANG, AND Y. WANG. 2003. The role of marsh-dominated heterotrophic continental margins in transport of CO<sub>2</sub> between the atmosphere, the land-sea interface and the ocean. *Geophysical Research Letters* 30. [doi:10.1029/2003GL017633].
- CAFFREY, J. M. 2004. Factors controlling net ecosystem metabolism in U.S. estuaries. *Estuaries* 27:90–101.
- CAREY, A. E., J. R. PENNOCK, J. C. LEHRTER, W. B. LYONS, W. W. SCHROEDER, AND J.-C. BONZONGO. 1999. The role of the Mississippi River in Gulf of Mexico hypoxia. Environmental Institute Publication Number 70, prepared for The Fertilizer Institute by The University of Alabama, Tuscaloosa, Alabama.
- CHEN, X., S. E. LOHRENZ, AND D. A. WIESENBERG. 2000. Distribution and controlling mechanisms of primary production on the Louisiana-Texas continental shelf. *Journal of Marine Systems* 25:179–207.
- COCHRANE, J. D. AND F. J. KELLY. 1986. Low frequency circulation on the Texas-Louisiana continental shelf. *Journal of Geophysical Research* 91:645–659.
- CORBETT, D. R., B. MCKEE, AND D. DUNCAN. 2004. An evaluation of mobile mud dynamics in the Mississippi River deltaic region. *Marine Geology* 209:91–112.
- DAGG, M., R. BENNER, S. LOHRENZ, AND D. LAWRENCE. 2004. Transformation of dissolved and particulate materials on continental shelves influenced by large rivers: Plume processes. *Continental Shelf Research* 24:833–858.
- DAGG, M. J., T. S. BIANCHI, G. A. BREED, W.-J. CAI, S. DUAN, H. LIU, B. A. MCKEE, R. T. POWELL, AND C. M. STEWART. 2005. Biogeochemical characteristics of the lower Mississippi River, USA, during June 2003. *Estuaries* 28:664–674.

- DAGG, M. J. AND T. E. WHITLEGE. 1991. Concentrations of copepod nauplii associated with the nutrient-rich plume of the Mississippi River. *Continental Shelf Research* 17:845–857.
- DIÁZ, R. J. 2001. Overview of hypoxia around the world. *Journal of Environmental Quality* 30:275–81.
- DICKSON, A. G. 1990. Standard potential of the reaction:  $\text{AgCl(s)} + \frac{1}{2}\text{H}_2\text{(g)} = \text{Ag(s)} + \text{HCl(aq)}$ , and the standard acidity constant of the ion  $\text{HSO}_4^-$  in synthetic seawater from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* 22:113–127.
- DICKSON, A. G. AND F. J. MILLERO. 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep Sea Research* 34:1733–1743.
- DIMEGO, G. J., L. F. BOSART, AND G. W. ENDERSEN. 1976. An examination of the frequency and mean conditions surrounding frontal incursions into the Gulf of Mexico and Caribbean Sea. *Monthly Weather Review* 104:709–718.
- DINNEL, S. P. AND W. J. WISEMAN. 1986. Freshwater on the Louisiana and Texas shelf. *Continental Shelf Research* 6:765–784.
- EADIE, B. J., B. A. MCKEE, M. B. LANSING, J. A. ROBBINS, S. METZ, AND J. H. TREFRY. 1994. Records of nutrient-enriched coastal ocean productivity in sediments from the Louisiana continental shelf. *Estuaries* 17:754–765.
- FRANKIGNOULLE, M. AND A. V. BORGES. 2001. European continental shelf as a significant sink for atmospheric carbon dioxide. *Global Biogeochemical Cycles* 15:569–576.
- FRANKIGNOULLE, M., I. BOURGE, C. CANON, AND P. DAUBY. 1996b. Distribution of surface seawater partial  $\text{CO}_2$  pressure in the English Channel and in the Southern Bight of the North Sea. *Continental Shelf Research* 16:381–395.
- FRANKIGNOULLE, M., I. BOURGE, AND R. WOLLAST. 1996a. Atmospheric  $\text{CO}_2$  fluxes in a highly polluted estuary (The Scheldt). *Limnology and Oceanography* 41:365–369.
- GATTUSO, J.-P., M. FRANKIGNOULLE, AND R. WOLLAST. 1998. Carbon and carbonate metabolism in coastal aquatic ecosystems. *Annual Review of Ecology and Systematics* 29:405–434.
- GATTUSO, J.-P., M. PICHON, AND M. FRANKIGNOULLE. 1995. Biological control of air-sea  $\text{CO}_2$  fluxes: Effect of photosynthetic and calcifying marine organisms and ecosystems. *Marine Ecology Progress Series* 129:307–312.
- GOÑI, M. A., K. C. RUTTENBERG, AND T. I. EGLINTON. 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochimica et Cosmochimica Acta* 62:3055–3075.
- GUO, L., P. H. SANTSCHI, AND T. S. BIANCHI. 1999. Dissolved organic matter in estuaries of the Gulf of Mexico, p. 269–299. In T. S. Bianchi, J. R. Pennock, and R. R. Twilley (eds.), *Biogeochemistry of Gulf of Mexico Estuaries*. Wiley, New York.
- HEDGES, J. I. AND R. G. KIEL. 1995. Sedimentary organic matter preservation: An assessment and speculative synthesis. *Marine Chemistry* 49:81–115.
- HITCHCOCK, G. L., W. J. WISEMAN JR., W. C. BOICOURT, A. J. MARIANO, N. WALKER, T. A. NELSON, AND E. RYAN. 1997. Property fields in an effluent plume of the Mississippi River. *Journal of Marine Systems* 12:109–126.
- JOCHEM, F. J. 2003. Photo- and heterotrophic pico- and nanoplankton in the Mississippi River plume: Distribution and grazing activity. *Journal of Plankton Research* 25:1201–1214.
- JUSTIĆ, D., N. N. RABALAIS, AND R. E. TURNER. 1997. Impacts of climate change on net productivity of coastal waters: Implication for carbon budgets and hypoxia. *Climate Research* 8:225–237.
- JUSTIĆ, D., N. N. RABALAIS, AND R. E. TURNER. 2002. Modeling the impacts of decadal changes in riverine nutrient fluxes on coastal eutrophication near the Mississippi River Delta. *Ecological Modeling* 152:33–46.
- KEMP, W. M., E. M. SMITH, M. MARVIN-DIPASQUALE, AND W. R. BOYNTON. 1997. Organic carbon balance and net ecosystem metabolism in Chesapeake Bay. *Marine Ecology Progress Series* 150:229–248.
- KUMAR, M. D., S. W. A. NAQVI, M. D. GEORGE, AND D. A. JAYAKUMAR. 1996. A sink for atmospheric carbon dioxide in the northeast Indian Ocean. *Journal of Geophysical Research* 101:18121–18125.
- LEGENDRE, L. AND J. MICHAUD. 1998. Flux of biogenic carbon in oceans: Size-dependent regulation by pelagic food webs. *Marine Ecology Progress Series* 164:1–11.
- LEWIS, E. AND D. W. R. WALLACE. 1998. Program developed for  $\text{CO}_2$  system calculations. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee.
- LISS, P. S. AND L. MERLIVAT. 1986. Air-sea gas exchange rates: Introduction and synthesis, p. 113–127. In P. Buat-Menard (ed.), *The Role of Air-Sea Exchange in Geochemical Cycling*. Reidel, Dordrecht.
- LIU, H. AND M. J. DAGG. 2003. Interactions between nutrients, phytoplankton growth, and grazing by micro- and meso-zooplankton in the plume of the Mississippi River. *Marine Ecology Progress Series* 258:31–42.
- LOHRENTZ, S. E., M. J. DAGG, AND T. E. WHITLEGE. 1990. Enhanced primary production at the plume/oceanic interface of the Mississippi River. *Continental Shelf Research* 10:639–664.
- LOHRENTZ, S. E., G. L. FAHNENSTIEL, D. G. REDALJE, G. A. LANG, X. CHEN, AND M. J. DAGG. 1997. Variations in primary production of northern Gulf of Mexico continental shelf waters linked to nutrient inputs from the Mississippi River. *Marine Ecology Progress Series* 155:45–54.
- LOHRENTZ, S. E., G. L. FAHNENSTIEL, D. G. REDALJE, G. A. LANG, M. J. DAGG, T. E. WHITLEGE, AND Q. DORTCH. 1999. Nutrients, irradiance, and mixing as factors regulating primary production in coastal waters impacted by the Mississippi River plume. *Continental Shelf Research* 19:1113–1141.
- MCKEE, B. A. 2003. RiOMar: The Transport, Transformation and Fate of Carbon in River-dominated Ocean Margins. Report of the RiOMar Workshop, 1–3 November 2001. Tulane University, New Orleans, Louisiana.
- MCKEE, B. A., R. C. ALLER, M. A. ALLISON, T. S. BIANCHI, AND G. C. KINEKE. 2004. Transport and transformation of dissolved and particulate materials on continental margins influenced by major rivers: Benthic boundary layer and seabed processes. *Continental Shelf Research* 24:899–926.
- MEHRBACH, C., C. H. CULBERSON, J. E. HAWLEY, AND R. M. PYTKOWICZ. 1973. Measurements of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography* 18:897–907.
- MEYBECK, M. 2003. Global analysis of river systems: From Earth system controls to Anthropocene syndromes. *Philosophical Transactions of the Royal Society of London B* 358:1935–1955. [doi:10.1098/rstb.2003.1379].
- MILLERO, F. J. 1996. *Chemical Oceanography*, 2nd edition. CRC Press, Boca Raton, Florida.
- MÜLLER-KARGER, F. E., J. J. WALSH, R. H. EVANS, AND M. B. MEYERS. 1991. On the seasonal phytoplankton concentration and sea surface temperature cycles of the Gulf of Mexico as determined by satellites. *Journal of Geophysical Research* 96:12645–12665.
- PAKULSKI, J. D., R. BENNER, R. AMON, B. EADIE, AND T. WHITLEGE. 1995. Community metabolism and nutrient cycling in the Mississippi River plume: Evidence for intense nitrification at intermediate salinities. *Marine Ecology Progress Series* 117:207–218.
- PAKULSKI, J. D., R. BENNER, T. WHITLEGE, R. AMON, B. EADIE, L. CIFUENTES, J. AMMERMAN, AND D. STOCKWELL. 2000. Microbial metabolism and nutrient cycling in the Mississippi and Atchafalaya River plume. *Estuarine Coastal and Shelf Science* 50:173–184.
- RABALAIS, N. N., R. E. TURNER, D. JUSTIĆ, Q. DORTCH, AND W. J. WISEMAN JR. 1999. Characterization of hypoxia: Topic 1 Report for the Integrated Assessment of Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 15, NOAA Coastal Ocean Program, Silver Springs, Maryland.
- RABALAIS, N. N., R. E. TURNER, D. JUSTIĆ, Q. DORTCH, W. J. WISEMAN JR., AND B. K. SEN GUPTA. 1996. Nutrient changes in the

- Mississippi River and system responses on the adjacent continental shelf. *Estuaries* 19:387–407.
- RABALAIS, N. N., R. E. TURNER, AND W. J. WISEMAN JR. 2002. Hypoxia in the Gulf of Mexico, a.k.a. "The Dead Zone." *Annual Review of Ecology and Systematics* 33:235–263.
- RABALAIS, N. N., R. E. TURNER, W. J. WISEMAN, AND D. F. BOESCH. 1991. A brief summary of hypoxia on the northern Gulf of Mexico continental shelf: 1985–1988, p. 35–47. *In* R. V. Tyson and T. H. Pearson (eds.), *Modern and Ancient Continental Shelf Anoxia*. Geological Society Special Publication No. 58, London, U.K.
- RAYMOND, P. A. AND J. J. COLE. 2003. Increase in the export of alkalinity from North America's largest river. *Science* 301:88–91.
- REDALJE, D. G., S. E. LOHRENZ, AND G. L. FAHNENSTIEL. 1994. The relationship between primary production and the vertical export of particulate organic matter in a river-impacted coastal ecosystem. *Estuaries* 17:829–836.
- ROUSE, L. J. 1998. An observational study of the Mississippi-Atchafalaya coastal plume: Final Report, OCS Study MMS 98-0040. U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, Louisiana.
- ROWE, G. T., M. E. CRUZ-KAEGI, J. W. MORSE, G. S. BOLAND, AND E. G. ESCOBAR BRIONES. 2002. Sediment community metabolism associated with continental shelf hypoxia, northern Gulf of Mexico. *Estuaries* 25:1097–1106.
- SALISBURY, J. E., J. W. CAMPBELL, E. LINDNER, L. D. MEEKER, F. E. MÜLLER-KARGER, AND C. J. VÖRÖSMARTY. 2004. On the seasonal correlation of surface particle fields with wind stress and Mississippi discharge in the northern Gulf of Mexico. *Deep-Sea Research II* 51:1187–1203.
- SARMIENTO, J. L. AND N. GRUBER. 2002. Sinks for anthropogenic carbon. *Physics Today* 55:30–36.
- SCAVIA, D., N. N. RABALAIS, R. E. TURNER, D. JUSTIĆ, AND W. J. WISEMAN, JR. 2003. Predicting the response of Gulf of Mexico hypoxia to variations in Mississippi River nitrogen load. *Limnology and Oceanography* 48:951–956.
- SERVAIS, P., A. ANZIL, AND C. VENTRESQUE. 1989. Simple method for determination of biodegradable dissolved organic carbon in water. *Applied Environmental Microbiology* 55:2732–2734.
- SKLAR, F. H. AND R. E. TURNER. 1981. Characteristics of phytoplankton production off Barataria Bay in an area influenced by the Mississippi River. *Contributions in Marine Science* 24:93–106.
- SMITH, S. V. AND J. T. HOLLIBAUGH. 1993. Coastal metabolism and the oceanic organic carbon balance. *Review of Geophysics* 31:75–89.
- SMITH, JR., W. O. AND D. J. DEMASTER. 1996. Phytoplankton biomass and productivity in the Amazon River plume: Correlation with seasonal river discharge. *Continental Shelf Research* 16:291–319.
- STUMPF, R. P. 1992. Remote sensing of water quality in coastal waters, p. 293–305. *In* Proceedings of the First Thematic Conference on Remote Sensing for Marine and Coastal Environments. Society of Photo-Optical Instrumentation Engineers, Ann Arbor, Michigan.
- STUMPF, R. P. AND J. R. PENNOCK. 1989. Calibration of a general optical equation for remote sensing of suspended sediments in a moderately turbid estuary. *Journal of Geophysical Research* 94: 14363–14371.
- TERNON, J. F., C. OUDOT, A. DESSIER, AND D. DIVERRES. 2000. A seasonal tropical sink for atmospheric CO<sub>2</sub> in the Atlantic ocean: The role of the Amazon River discharge. *Marine Chemistry* 68:183–201.
- THOMAS, H., Y. BOZEC, K. ELKALAY, AND H. J. W. DE BAAR. 2004. Enhanced open ocean storage of CO<sub>2</sub> from shelf sea pumping. *Science* 304:1005–1008.
- TURNER, R. E. AND R. L. ALLEN. 1982. Bottom water oxygen concentration in the Mississippi River Delta Bight. *Contributions in Marine Science* 25:161–172.
- TURNER, R. E. AND N. N. RABALAIS. 1991. Changes in the Mississippi River water quality this century—Implications for coastal food webs. *BioScience* 41:140–147.
- TURNER, R. E., N. N. RABALAIS, AND Z. N. ZHANG. 1990. Phytoplankton biomass, production and growth limitation on the Huanghe (Yellow River) continental shelf. *Continental Shelf Research* 10:545–571.
- VAN DER LEEDEN, F., F. L. TROISE, AND D. K. TODD. 1990. *The Water Encyclopedia*, 2nd edition. Lewis, Boca Raton, Florida.
- VER, L. M., F. T. MAACKENZIE, AND A. LERMAN. 1999. Carbon cycle in the coastal zone: Effects of global perturbations and change in the past three centuries. *Chemical Geology* 159:283–304.
- VÉZINA, A. F. 1989. Construction of flow networks using inverse methods, p. 62–81. *In* F. Wulff, J. G. Field, and K. H. Mann (eds.), *Network Analysis in Marine Ecology*. Springer, New York.
- VÉZINA, A. F. AND T. PLATT. 1988. Food web dynamics in the ocean. I. Best-estimates of flow networks using inverse methods. *Marine Ecology Progress Series* 42:269–287.
- WALKER, N. D. 1996. Satellite assessment of Mississippi River plume variability: Causes and predictability. *Remote Sensing Research* 58:21–35.
- WALKER, N. D. AND A. B. HAMMACK. 2000. Impacts of winter storms on circulation and sediment transport: Atchafalaya-Vermilion Bay region, Louisiana. *Journal of Coastal Research* 16:996–1010.
- WALKER, N. D., A. B. HAMMACK, AND L. J. ROUSE. 1997. Predictability of Oceanic and Atmospheric Conditions off the Mississippi Delta: A Field Manual, Louisiana Applied Oil Spill Research and Development Program, OSRADP Technical Report Series 97-011, (CD distribution). Baton Rouge, Louisiana.
- WALKER, N. D., W. J. WISEMAN, L. J. ROUSE, AND A. BABIN. 2005. Effects of river discharge, wind stress, and slope eddies on circulation and the satellite-observed structure of the Mississippi River plume. *Journal of Coastal Research* 21:1228–1244.
- WANNINKHOF, R. 1992. Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research* 97:7373–7382.
- WANNINKHOF, R. AND W. R. MCGILLIS. 1999. A cubic relationship between air-sea CO<sub>2</sub> exchange and wind speed. *Geophysical Research Letters* 26:1889–1892.
- WAWRIK, B. AND J. H. PAUL. 2004. Phytoplankton community structure and productivity along the axis of the Mississippi River plume in oligotrophic Gulf of Mexico waters. *Aquatic Microbial Ecology* 35:185–196.
- WEISS, R. F. 1974. Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Marine Chemistry* 2:203–15.
- WISEMAN, JR., W. J., S. P. MURRAY, J. M. BANE, AND M. W. TUBMAN. 1982. Temperature and salinity variability within the Louisiana Bight. *Contributions in Marine Science* 25:109–120.
- WYSOCKI, L. A., T. S. BIANCHI, AND T. R. FILLEY. 2005. Sources of organic carbon to a river-dominated coastal shelf: The use of chemical biomarkers to track inputs to sediments. *Eos Transactions AGU* 86(18), Joint Assembly Supplement, Abstract OS23A-14. New Orleans, Louisiana.

#### SOURCES OF UNPUBLISHED MATERIALS

- BIANCHI, T. S. unpublished data. Tulane University, New Orleans, Louisiana 70118.
- CAI, W.-J. personal communication. University of Georgia, Athens, Georgia 30602.
- DUAN, S. AND T. S. BIANCHI. unpublished data. Tulane University, New Orleans, Louisiana 70118.
- MCKEE, B. personal communication. Tulane University, New Orleans, Louisiana 70118.
- RAYMOND, P. unpublished data. Yale University, New Haven, Connecticut 06520-8106.
- SATO, R. AND M. J. DAGG. unpublished data. Louisiana Universities Marine Consortium, Chauvin, Louisiana 70344.

Received, July 13, 2005  
 Revised, November 30, 2005  
 Accepted, February 28, 2006