

Water column processes influencing hypoxia in the northern Gulf of Mexico

Michael Dagg
Louisiana Universities Marine Consortium
8124 Highway 56
Chauvin, LA 70344
mdagg@lumcon.edu

James Ammerman
Institute of Marine and Coastal Sciences
Rutgers University
71 Dudley Road
New Brunswick, NJ 08901

Rainer Amon
Department of Marine Sciences
Texas A and M University at Galveston
5007 Avenue U
Galveston, TX 77551

Wayne Gardner
University of Texas at Austin
Marine Science Institute
750 Channel View Drive
Port Aransas, TX 78373

Rebecca Green
Ocean Sciences Division
Naval Research Laboratory
Stennis Space Center, MS 39529

Steven Lohrenz
Department of Marine Science
University of Southern Mississippi
Stennis Space Center, MS 39529

Running head: Water column processes influencing hypoxia

Abstract

In this review, we use data from field measurements of biogeochemical processes and cycles in the Mississippi River plume and in other shelf regions of the northern Gulf of Mexico to determine plume contributions to coastal hypoxia. We briefly review pertinent findings from these process studies, review recent mechanistic models that synthesize these processes to address hypoxia-related issues, and re-interpret current understanding in the context of these mechanistic models. Some of our conclusions are: both nitrogen and phosphorus are sometimes limiting to phytoplankton growth; respiration is the main fate of fixed carbon in the plume, implying that recycling is the main fate of nitrogen; decreasing the nitrogen loading results in less than 1:1 decrease in sinking organic matter, implying a less than 1:1 decrease in hypoxia; and sedimenting organic matter from the Mississippi River plume can only fuel about 23 % of observed coastal hypoxia, suggesting significant contributions from the Atchafalaya River and, possibly, coastal wetlands. We also identified gaps in our knowledge about controls on hypoxia, and indicated that some re-interpretation of our basic assumptions about this system is required. There are clear needs for improved information on the sources, rates, and locations of organic matter sedimentation; for further investigation of internal biogeochemical processes and cycling; for improved understanding of the rates of oxygen diffusion across the pycnocline; for identification and quantification of other sources of organic matter fueling hypoxia, or other mechanisms by which Mississippi River derived organic matter fuels hypoxia; and for the development of a fully coupled, physical-biogeochemical model.

Introduction:

An extensive zone of bottom water hypoxia, typically $> 15,000 \text{ km}^2$ since 1993, develops in the inner shelf of the northern Gulf of Mexico during most years (Rabalais et al. 2002). Oxygen demand is derived from organic matter input to the bottom layer, and oxygen replacement in the bottom waters is restricted by strong thermohaline stratification. The general consensus is that “hypoxia in the northern Gulf of Mexico is caused primarily by algal production stimulated by excess nitrogen delivered from the Mississippi-Atchafalaya River Basin and seasonal vertical stratification of incoming streamflow and Gulf waters, which restricts replenishment of oxygen from the atmosphere” (CENR 2000, http://toxics.usgs.gov/highlights/new_hypoxia.html).

Recent models (Justić et al. 2002; Scavia et al. 2003; Turner et al. 2005) have utilized statistical relationships between hypoxia and riverine nutrient inputs to the shelf to predict or hindcast hypoxia. These models reinforce the view that nutrient stimulated production from the Mississippi and Atchafalaya Rivers drives the development and maintenance of coastal hypoxia but they do not provide much insight into the detailed mechanisms of nutrient cycling underlying this serious issue. These models have not incorporated the extensive knowledge of biogeochemical processes and cycling that have accumulated over the past two decades of field programs in this region. In this paper, we examine coastal hypoxia from a different perspective, a mechanistic perspective. We briefly review pertinent findings from process studies, review recent mechanistic models that synthesize these processes to address hypoxia-related issues, and re-interpret current understanding in the context of these mechanistic models.

Part A. A summary of important processes.

Nutrients. The open Gulf of Mexico is a permanently stratified, oligotrophic region with low nutrient concentrations in surface waters. Consequently, nutrients from the Mississippi River have a disproportionately large impact on the northern gulf. Dissolved

nutrients in river water are spread as part of the buoyant plume that forms from discharging river water. Nutrients from the Mississippi River don't always contribute to biological production on the Louisiana shelf because wind can move the surface plume offshore and/or eastward as evidenced by occasional entrainment of plume water into the Loop Current and eventual transport through Florida Strait (Ortner et al. 1995). Usually however, a southwesterly or westerly oriented plume of nutrients is evident in the SW Pass region of the Mississippi River delta (Dagg and Breed 2003). Many cruises have been conducted in this region and they typically show that nutrient concentrations, high in river water, diminish rapidly in water discharged from SW Pass. The decrease is predominantly due to two processes: dilution or mixing with oceanic water that has low concentrations of nutrients, and uptake by phytoplankton (Dagg and Breed 2003).

The dominant fate of fixed carbon in the plume, 65% annually, is respiration (Green et al. 2006a) and recycling of plume nitrogen is a major pathway for nitrogen flow (Cotner and Gardner 1993; Gardner et al. 1994). This nitrogen cycling and associated production of organic matter provides an important mechanism for transporting a portion of the river nitrogen load and resultant organic matter production to the shallow regions susceptible to hypoxia development. Primary and secondary productivity, from regenerated nutrients, may lead to particle sinking in shallow, stratified regions, which in turn can contribute to oxygen demand and hypoxia. Any portions of this production that sink below the pycnocline can contribute to development or maintenance of hypoxia. Nitrogen recycling thus is a mechanism for redistributing the production of particulate organic matter derived from riverine nutrients. This redistribution involves both transport and cycling issues.

Nitrate concentrations in the Mississippi River have nearly tripled since 1960 (Turner and Rabalais 1991), consistent with a large increase in nitrogen (N) fertilizer use in the watershed. Phosphorus (P) fertilizer use has also increased since 1960 (Turner and Rabalais 1991), though less than N. Nitrate concentrations in the lower river are usually over 100 μM (Dagg and Whitley 1991; Dagg et al. 2005) and $\text{NO}_x:\text{PO}_4$ ratios typically

range between 20 and 70 (Lohrenz et al. 1999). Total P (TP) and orthophosphate concentrations in the river, which have been measured systematically only since 1974 and 1980, respectively, display no clear temporal trend over that period (Turner and Rabalais 1991; Turner et al. 2006). Since 1960, silicate (Si) concentrations in river water have decreased by ~50% (Turner and Rabalais 1991). As a result of these changes, the ratios of nitrogen, phosphorus, and silica in the Mississippi River have changed considerably (Rabalais et al. 2002). The Total N (TN):TP ratio reached as high as 40:1 by the mid-1980s during the peak of N loading, but has gradually decreased to 20:1 since then (Turner et al. 2006). Silicate to nitrate ratios have reached approximately 1:1 (Rabalais et al. 2002).

Because the receiving, oceanic waters are nutrient poor, phytoplankton production in the plume becomes nutrient limited at some point. Data from a suite of studies assessing nutrient limitation of phytoplankton production (summarized in Rabalais et al. 2002), indicate that either N, P, or Si can limit phytoplankton growth in the system, depending on conditions. N is generally believed to be the main limiting nutrient on an annual basis, due to efficient recycling of P and loss of N to denitrification (Rabalais et al. 2002). N reduction is also the major focus of current hypoxia reduction efforts (USEPA 2001). N limitation appears most common during low flow periods and at higher salinities, particularly during late summer and fall. Si limitation varies more in time and space but is most pronounced in the spring (Dortch and Whitley 1992; Nelson and Dortch 1996). Si limitation impacts only diatoms (Nelson and Dortch 1996; Lohrenz et al. 1999; Rabalais et al. 1999), but diatoms are an important fraction of the biomass of sinking particles (Redalje et al. 1994), so Si dynamics are especially significant for hypoxia.

Though Riley suggested a causal relationship between the high phosphorus and high phytoplankton concentrations around the mouth of the Mississippi River in 1937 (Riley 1937), there was little further attention devoted to P cycling and limitation in this area until the late 1980s. Evidence from nutrient ratios and limited bioassays during the period 1988-1992 showed that P limitation could occur during high flow and at intermediate salinities, especially during spring and early summer (Smith and Hitchcock

1994; Lohrenz et al. 1997; Lohrenz et al. 1999). Measurements of phosphate turnover and alkaline phosphatase activity, a cell-surface enzyme activity induced by P-deficient phytoplankton and bacteria (Hoppe 2003), suggested P limitation in July 1990 but not September 1991 (Ammerman 1992). Additional measurements of high alkaline phosphatase activity near the river plume were made in May of 1992 (Kim 1996) and July of 1993 (Ammerman and Glover 2000), also suggesting P limitation during these periods.

Extensive studies of nutrient concentrations and ratios, alkaline phosphatase activity, nutrient enrichment bioassays, and P turnover times on the Louisiana shelf in March, May, July, and September of 2001 identified P as the limiting nutrient in March, May, and July (Sylvan et al. 2006a). P limitation was particularly strong in May and July, but N limitation was clear by September. P-limitation on the Louisiana shelf followed the river's highest flow period and occurred in both the time period (spring to early summer) and location (mid-salinity waters west of the Mississippi Delta) of highest primary productivity (Lohrenz et al. 1997; Lohrenz et al. 1999). A similar study in July of 2002 also showed strong P-limitation, and additional evidence was provided by the use of a Fast Repetition Rate Fluorometer which showed an increase in the photosynthetic efficiency of phytoplankton incubated with added P (Sylvan et al. 2006b). Thus, under conditions of high discharge, the extent of high N:P ratios is generally larger, suggesting more widespread P limitation. Under lower discharge conditions, the extent of high ratios is smaller, and associated P limitation more spatially restricted.

Because ratios of N, P and Si have changed during the past 50 years, the limiting nutrient has likely shifted also. P limitation is likely more important now because of increased N input from the Mississippi River over the past 50 years (Turner and Rabalais 1991). However, interactions between nutrient concentrations, nutrient ratios, river discharge, plume dynamics, and biological uptake are complex, and it is still not entirely clear what conditions result in N, P or Si being limiting. Nevertheless, primary production stimulated by river nutrients is an important source of organic matter contributing to summer hypoxia (Rabalais et al. 2002) and a better understanding of nutrient limitation

processes is needed, especially if hypoxia reduction is to be accomplished by a reduction in nutrient loading.

Recycling. A major information gap exists in our understanding of the internal dynamics of nitrogen as related to carbon dynamics and hypoxia formation. Fundamental transformation rates of nitrogen, such as nitrification (an O₂ sink), denitrification (a N sink), N-fixation (a N source), and dissimilatory NO₃ reduction to ammonium (DNRA; a N link) have not been sufficiently quantified in this region. The production of chemically-reduced inorganic compounds, such as ammonium and nitrite, resulting from decomposition of organic materials, excretion, or other biogeochemical processes, contributes to total O₂ demand (Pakulski et al. 1995) and supplies nutrients for re-use by phytoplankton. Oxidation of ammonium to nitrite and nitrate may be a significant source of oxygen demand in the water column or at the sediment-water interface. Quantifying the locations and rates of community nitrogen transformations and oxygen consumption is critical to achieving an understanding of hypoxia development. Experimental measurements of these rates at different sites and depths within and outside of the plume are needed to calibrate and verify models describing these processes.

Nitrification, coupled with dissimilatory reduction processes (denitrification and dissimilatory nitrate reduction of ammonium [DNRA]) likely affect oxygen removal in hypoxic regions. Both of these heterotrophic, dissimilatory processes convert oxygen from nitrate to H₂O-oxygen rather than back to oxygen gas (Maier et al. 2000). However, denitrification and DNRA result in different N end products. Nitrogen gas, the end product of denitrification, is biologically inert except for N fixation, whereas NH₄⁺ released from DNRA remains biologically available and could contribute to further O₂ demand if it is transported to zones where O₂ is available for nitrification.

Denitrification may be a major N sink, but only a few data on potential rates (Childs et al. 2002) are available for the northern Gulf of Mexico hypoxic region. DNRA rates have not been reported for this region but circumstantial evidence, based on ammonium accumulation (Childs et al. 2002), indicates that DNRA may be important when O₂ levels are low (< 1 mg l⁻¹) in water near the sediment-water interface (i.e. potential

denitrification rates were low and NH_4^+ concentrations were high in these regions). Also in agreement with the DNRA hypothesis, NH_4^+ was released but NO_3^- and NO_2^- were consumed by sediments in benthic incubation chambers (Rowe et al. 2002). Thus, heterotrophic DNRA combined with physical transport and re-nitrification of NH_4^+ in the water column (or sediments) could serve as a pump for O_2 removal and conversion of NO_3^- -oxygen to H_2O -oxygen in hypoxic regions.

Recycling of other important nutrients (P, Si) also occurs and may affect patterns and magnitudes of phytoplankton production and ultimately, the vertical flux of organic matter. There is little information on these processes. P is probably rapidly recycled; plankton on the shelf can utilize DOP (Pakulski et al. 2000) after hydrolysis of the phosphate molecule with alkaline phosphatase or similar enzymes (Hoppe 2003). Limited measurements on the Louisiana shelf show significant DOP concentrations (0.1-0.4 μM) (Kim 1996; Pakulski et al. 2000). High alkaline phosphatase activities are frequently measured on the shelf (Ammerman and Glover 2000; Sylvan et al. 2006a) suggesting that this DOP could be an important P source.

In summary, there are many complex processes involved in recycling of riverine nutrients, and much additional research is needed to understand these processes.

Phytoplankton. Phytoplankton processes in the northern Gulf of Mexico are strongly influenced by the Mississippi River outflow plume. Biological processes within the plume interact in a non-linear manner and are superimposed on a dynamic physical regime that continuously but non-uniformly mixes with receiving waters. Temporal and spatial scales over which various processes occur can be compressed or expanded depending on discharge, season (temperature, light), wind, tide and other factors. Cross-plume differences are significant because processes at the edges and frontal boundaries are different from processes in the plume core. Salinity is only an approximate index of distance from, or time since, discharge. Conceptual models that describe these relationships can be found in Dagg and Breed (2003), Breed et al. (2004) and Green et al.

(2006a). Here, we briefly summarize patterns in phytoplankton processes in different salinity regions of the plume.

In the lower river, concentrations of nutrients are high. High concentrations of dissolved organic matter (D'Sa and Miller, 2003) and suspended particulate matter (Trefry et al. 1994) absorb and scatter light, and strong mixing minimizes exposure of phytoplankton to surface light. Phytoplankton in the lower river grow slowly or not at all (Dagg et al. 2005). Upon discharge, river water forms a buoyant surface plume with dramatic increases in available light. As the river mixes with the coastal water, light is further enhanced by dilution and sinking of large lithogenic particles and particulate organic material (Trefry et al. 1994). Flocculation and aggregation processes also stimulate sinking of materials (Dagg et al. 1996; Breed et al. 2004). Phytoplankton growth and associated carbon uptake increase dramatically (Dagg and Breed 2003).

As mixing of buoyant freshwater and coastal water progresses, phytoplankton growth is no longer constrained by light and, except for temperature, limitations on growth are largely removed. Phytoplankton growth rates approach theoretical maxima in the mid-field region, and can be as high as 3 d^{-1} at summer temperatures of 30°C (Fahnenstiel et al. 1995). Both grazing and dilution by physical mixing tend to reduce phytoplankton concentration, but the growth rates typical of mid-field regions are so high that phytoplankton biomass rapidly accumulates in spite of these loss terms (Lohrenz et al. 1999). Generally, the highest chlorophyll concentrations are seen in the mid-salinity portions of the plume, at salinities in the mid-20s (Lohrenz et al. 1997). These high stocks of phytoplankton are often visible in satellite images. All components of the phytoplankton community have high growth rates (Liu and Dagg 2003) but small phytoplankton experience more grazing mortality in the mid-field than large phytoplankton (Fahnenstiel et al. 1995; Strom and Strom 1996; Liu and Dagg 2003). Large phytoplankton cells are subject to lower grazing mortality in the near- and mid-field regions because of the relatively slow numerical response by their major grazers, the copepods (Liu and Dagg 2003). Consequently, the net growth rate of large phytoplankton is greater than that of small phytoplankton, and large cells, especially diatoms, typically

dominate the phytoplankton community in the mid-field region (Bode and Dortch 1996; Liu and Dagg 2003). High rates of nutrient regeneration are prevalent in these waters (Ammerman 1992; Cotner and Gardner 1993; Gardner et al. 1994; Pakulski et al. 1995; 2000), and regenerated nutrients may contribute significantly to maintaining high rates of phytoplankton production in the mid-field region.

In the far-field plume, nutrient concentrations are greatly reduced because of dilution with ocean water and up-stream utilization by phytoplankton. These low concentrations are limiting to phytoplankton growth, especially to diatoms (Chisholm 1992), and growth rates decrease sharply (Strom and Strom 1996; Liu and Dagg 2003). Grazing on large cells becomes more important (Liu and Dagg 2003). Lower growth rates combined with increased grazing and continued dilution from mixing cause concentrations of larger phytoplankton cells to decrease shortly after nutrient concentrations become limiting. Diatoms however, can still dominate even in the least productive and most offshore regions of the Mississippi River plume (Warwick and Paul 2004) and so it would appear that even quite far offshore, the Mississippi River outflow sometimes influences productivity and phytoplankton community structure. The far-field region eventually transitions into the open ocean end-member, the permanently stratified, oligotrophic Gulf of Mexico where the microbial loop is characteristic (Liu et al. 2004).

In addition to phytoplankton directly related to the immediate discharge plumes from the Mississippi and Atchafalaya Rivers, an extensive coastal band of high chlorophyll is often observed. It is not clear how much of this phytoplankton grew near the delta and become transported along the coast, and how much represents *in situ* production. If this phytoplankton is strongly nutrient limited, it would suggest the former. Chen et al. (2000) suggest both nutrients and chlorophyll are transported along the inner shelf and they attribute the bands of coastal chlorophyll to along-shelf transport and to recycling supported production.

Microbial foodweb. During the last 15 years only a few studies have determined the discharge of dissolved organic carbon (DOC) from the Mississippi and Atchafalaya

Rivers into the northern Gulf of Mexico (Leenheer et al. 1995a; 1995b; Benner and Opsahl 2001; Bianchi et al. 2004). The average DOC concentration near the mouths of the two rivers is ~ 350 μM with the Atchafalaya river having higher concentrations (~ 400 μM) than the Mississippi River at Head of Passes (~ 300 μM) (Pakulski et al. 2000; Chen and Gardner 2004). There is also a qualitative difference in DOM composition between the 2 rivers, indicated by different optical properties of CDOM. These patterns suggest an additional source of DOM in the lower Atchafalaya River (Chen and Gardner 2004, Conmy et al. 2004, Boehme et al. 2005). At this point the number of observations is too small to confirm seasonal patterns and more work is needed to characterize the qualitative differences of DOM in the two rivers. The magnitude of river DOC input is large however, between 2.0 and 3.1 Tg yr⁻¹ are discharged by both rivers (Benner and Opsahl, 2003; Green et al. 2006a) of which about 60% enters the hypoxic region (Dinnel and Wiseman, 1986).

Two important sinks for riverine DOM in the coastal ocean are: a) decomposition by heterotrophic bacteria and b) photooxidation by natural sunlight. The first appears to be of minor importance for hypoxia development because river DOC is largely unavailable to bacteria on time scales of the plume and shelf life of water (weeks to months). Respiration rates in river water are consistently lower than at higher salinities indicating the lower overall lability of Mississippi and Atchafalaya River DOM (Chin-Leo and Benner 1992; Pakulski et al. 1995; Pakulski et al. 2000). An additional indication of the refractory nature of this material comes from a 620-day bacterial decomposition experiment with Mississippi river water that indicated a DOC loss of only 93 μM DOC or 34 % (Hernes and Benner 2003). On a six-month basis, the two rivers introduce a maximum of 0.2 Tg of labile DOC to the hypoxic area. Because bacterial growth efficiency is low (< 10%) in those plumes (Chin-Leo and Benner 1992) only 0.02 Tg C would be converted to biomass which is less than 0.3% of the bacterial carbon demand (7.4 Tg) in the hypoxic region, based on bacterial gross production from Amon and Benner (1998) and bacterial growth efficiencies from Chin-Leo and Benner (1992). There are uncertainties in these calculations because there are few data. For example, the labile contribution from the Atchafalaya River might be greater than the Mississippi River.

Regardless, it is apparent that the direct utilization of river DOM by heterotrophic bacteria is < 1% of the measured bacterial carbon demand and therefore contributes little to hypoxia.

On the other hand, experiments with Mississippi River water indicate as much as 70 – 75 % of lignin phenols, biomarkers for terrestrial-derived organic matter, are photooxidized over a period of 10 – 30 days (Opsahl and Benner 1998; Hernes and Benner 2003). These high rates are consistent with photochemical removal rates of bulk DOC in other rivers (Miller and Zepp 1995; Amon and Benner 1996). According to Miller and Zepp (1995) Mississippi river DOC is remineralized to DIC at a rate of $0.07 \text{ mg C l}^{-1} \text{ d}^{-1}$, indicating that most river DOC will be photochemically converted to DIC within weeks. This would leave a minor fraction for bacterial uptake. DOC that is photooxidized primarily ends up as CO_2 but much of the DON would be converted to NH_4 (Bushaw et al. 1996; Vähätalo and Zepp 2005). These studies suggest that between 10 and 20 % of the recalcitrant river DON could be photoammonified during the course of a summer. Mississippi and Atchafalaya River DON ranges between 10 and 25 μM (Pakulski et al. 2000; Dagg et al. 2005; Duan et al. in press.) indicating a DON import to the hypoxic region of around 0.044 Tg N over a 6 month period. If we assume that 20 % of that DON would be photoammonified during the course of the summer, this would translate to 0.088 Tg ammonia, which is approximately 2 % of the riverine nitrate discharge over the same period and area. Although not usually considered, this NH_4 is an enhancement for phytoplankton production that is (indirectly) derived from riverine nitrogen. NH_4 does not accumulate because concentrations are typically low, possibly indicative of nitrification and rapid uptake. The ratio of DON to DIN in river water varies considerably but a ratio of 0.20 is a reasonable approximation. In summary, riverine DOC does not appear to contribute much to bacterial production in the plume but DON, via photochemical processes, may somewhat enhance riverine DIN inputs.

The largest source of labile DOM for coastal waters is derived from *in situ* (marine) production. Primary production of DOM is poorly understood, with very few direct

measurements (none in the northern GOM). We can derive approximate estimates using indirect approaches:

1. An average estimate for DOC production is 13 % of phytoplankton production (Lee and Henrichs 1993). Phytoplankton production in the Mississippi River plume/hypoxic region of $3 \text{ g C m}^2 \text{ d}^{-1}$ (Lohrenz et al 1999) would yield a DOC production rate of $0.39 \text{ g C m}^2 \text{ d}^{-1}$ or 1.07 Tg C for the hypoxic region and over 6 months.
2. DOC distribution along the salinity gradient is non-conservative showing elevated levels of DOC at mid salinities, especially in the summer (Benner and Opsahl 2001; Dagg et al. submitted). These elevated levels are up to $150 \mu\text{M C}$ above the background levels (conservative mixing line) suggesting DOC production of about 0.45 Tg C over 6 months in the hypoxic region.

Both of those values are minimum estimates because they do not include the rapidly consumed DOM that cycles through the microbial loop within minutes to hours, or the slowly leaching DOM from detritus particles. These estimates are much less than the estimated bacterial C demand (see below) and reflect our poor understanding of C fluxes between primary production and bacteria. The lack of DOM production measurements in this region represents a major gap and should be addressed in future studies.

Marine produced DOM is highly labile on short time scales. Applying a relationship between neutral sugar yield and DOC lability (Cowie and Hedges 1984; Skoog and Benner 1997; Amon and Benner 2003) to the hypoxic region and neutral sugar data from Benner and Opsahl (2001) indicates that between 10 and 52% of DOM in the hypoxic region is labile on a time scale of weeks. This is consistent with decomposition experiments with fresh phytoplankton-derived DOM from the region indicating that up to 58 % of the DOM was utilized by bacteria within 3 days (Amon and Benner 1994; 1996).

Integrated gross bacterial production in the Mississippi River plume is high, ranging between about 1.0 and $3.6 \text{ g C m}^{-2} \text{ d}^{-1}$ at intermediate salinities where phytoplankton

production and DOC production are typically highest (Chin-Leo and Benner 1992; Amon and Benner 1998). This mid-salinity maximum was observed during all cruises during which bacterial activity was determined in 1991, 1992, and 1993 (Amon and Benner 1998). DOM supporting this high bacterial production is primarily of marine origin, although riverine DOM may be important in winter (Chin-Leo and Benner 1992). Bacterial production and NH_4 regeneration are tightly coupled in the plume (Dortch and Whittedge 1992; Cotner and Gardner 1993) but bacteria are not the only NH_4 regenerators; approximately 50 % of the total remineralization is attributed to organisms $> 1 \mu\text{m}$ (i.e. not bacteria), consistent with high microzooplankton grazing and NH_4 excretion rates (Chin-Leo and Benner 1992; Cotner and Gardner 1994; Jochem et al. 2004).

Bacterial production appears to have an east-west gradient during the summer months with increasing rates of depth-integrated heterotrophic bacterial production ($\text{mg C m}^{-2} \text{d}^{-1}$, normalized to depth) as you go from east to west (Chin-Leo and Benner 1992). The east-west gradient is mainly driven by rates below the pycnocline. In fact, values above the pycnocline typically decrease from the Mississippi River to the west, while the values below the pycnocline increase (Amon and Benner 1998). Elevated levels in the west could be caused by the input of organic matter from the Atchafalaya River and subsequent accumulation of detritus below the pycnocline.

By decomposing/respiring organic matter, heterotrophic bacteria are the major consumers of dissolved oxygen in the water column, both above and below the pycnocline. Bacterial carbon demand for the $15,000 \text{ km}^2$ hypoxic area over 6 months between mid March and mid September was calculated by Amon and Benner (1998), based on bacterial production and respiration measurements at 60 stations. Applying an average bacterial gross production of $2.7 \text{ g C m}^{-2} \text{d}^{-1}$, the demand was about 7.4 Tg C. Such bacterial carbon demand almost matches the total primary production (8.2 Tg C) in the area over the same period. More studies simultaneously measuring primary production of particulate and dissolved organic matter and bacterial production and respiration are clearly needed.

Fates of phytoplankton and bacterial production.

(a) *lysis.* Viral induced lysis may be an important fate of phytoplankton and bacteria in the Mississippi river plume because high cell concentrations associated with the mid-field region of the plume provide ideal conditions for transmission of marine viruses (Fuhrman 1999). This would have important implications for biogeochemical cycling of nutrients because nitrogen and phosphorus in phytoplankton and microbes destroyed by viruses are primarily shunted to DOM, and are no longer directly available for sinking as intact phytoplankton or for consumption by zooplankton (Wilhelm and Suttle 1999). The frequency of viral infections of bacteria and phytoplankton in the Mississippi River plume is not known.

Salinity induced lysis of river phytoplankton also results in DOM release in the plume. Significant amounts of phytoplankton, up to 23 μg chlorophyll l^{-1} (Dagg et al. 2005), are found in the lower river and it is unlikely that this freshwater phytoplankton maintains its integrity as salinity increases after discharge. On some occasions freshwater phytoplankton may be a large shunt of river nutrients to DOM. During a period of weak winds in June 2003, the freshwater lens from the river spread widely with very little vertical mixing. It appeared that a bloom of freshwater phytoplankton occurred in the low salinity region of the plume (Dagg et al. 2006). Phytoplankton bloomed for a period of about 1-2 days then declined dramatically beginning at salinity < 10 psu. Dagg et al. (2006) concluded this was a bloom of freshwater phytoplankton seeded from the river and salinity stress caused its demise. An increase of DOC concentration > 100 μmol occurred over approximately the same salinity range suggesting it originated from this phytoplankton bloom. In this case, the macronutrients from the river did not stimulate a bloom of marine phytoplankton because nutrients were utilized by the river phytoplankton in the extensive freshwater lens. Salinity induced lysis of this freshwater community released large amounts of DOC that would stimulate the bacterial-driven microbial loop, and river nutrients did not contribute to production of marine phytoplankton that could sink and contribute to hypoxia.

Lysis of marine or freshwater phytoplankton transforms production derived from river nutrients into DOM that in turn stimulates the microbial food web, a pathway that contributes little to direct sinking of organic matter.

(b) Grazing. The major fate of bacterial and phytoplankton production in the ocean is to be grazed (Banse 1992). For the purposes of this paper, grazers are divided into three major categories: the microzooplankton, primarily protozoans; the crustacean mesozooplankton, primarily copepods; and the gelatinous mesozooplankton, primarily pelagic appendicularians or larvaceans. Earlier studies of grazing in the Mississippi River plume and Louisiana shelf area have been reviewed by Dagg and Breed (2003).

The conceptual role of microzooplankton developed in Dagg and Breed (2003) has been supported by recent results (Jochem 2003; Jochem et al. 2004; Liu and Dagg, 2003; Liu et al. 2004; Liu et al. 2005). Microzooplankton account for most of the grazing on bacteria and phytoplankton in the Mississippi River plume and Louisiana shelf.

Micrograzers typically consume half or more of the total daily phytoplankton production, probably consume most of the bacterial production, and may remineralize as much NH_4 as the bacterial population. Protozoans consume all sizes of phytoplankton but usually their grazing is greatest on smaller sizes, $< 20 \mu\text{m}$ (Fahnenstiel et al. 1995).

Phytoplankton growth generally exceeds grazing in the near- and mid-field portions of the plume but grazing often surpasses growth in the far-field, resulting in a decline in phytoplankton stock. Protozoan grazing does not directly result in vertical flux of organic matter from the surface plume because individual protozoan fecal pellets are small and have negligible sinking rates. They may contribute significantly however, if aggregated. The end products of this pathway are mainly respiration of CO_2 for carbon and excretion of NH_4 for nitrogen.

The copepod community usually consumes a much smaller portion of the phytoplankton than the microzooplankton community and does not consume bacteria sized particles at all. However, copepods sometimes consume a significant portion of the daily

phytoplankton production, especially in the far-field when phytoplankton growth is slowed by nutrient limitation. Recent papers (Liu and Dagg 2003; Liu et al. 2005) are generally consistent with the conceptual model developed from earlier studies and presented in Dagg and Breed (2003). Copepods are less able than microzooplankton to consume small cells ($< 5 \mu\text{m}$) and have their major impact on the larger cells. In this way they can help drive the phytoplankton community towards the small cell dominance that typically occurs in the far-field and oligotrophic parts of the system. An important point about copepods is that they produce large, rapidly sinking, fecal pellets, and can contribute significantly to the vertical flux of organic matter. In copepods, about 30 % of the organic matter consumed as food is released as fecal pellets and it takes about 10-20 minutes for food to be processed through the gut. However, in nature a large fraction of copepod fecal pellets is recycled before sinking very far, even though most of the material sinking from the photic zone can be fecal pellets (Aksnes and Wassmann 1993; Sarnelle 1999).

Although ephemeral blooms of doliolids and salps occur on the Louisiana shelf, the most important gelatinous grazers are the larvaceans (Dagg and Breed 2003). In the northern Gulf of Mexico, the larvacean *Oikopleura dioica* feeds non-selectively on particles in the size range of $0.3 - 20 \mu\text{m}$. This size range includes bacteria and a significant fraction of the phytoplankton community. Individual organisms are small ($< 1 \text{ mm}$) but their ability to filter water is greatly enhanced by their secreted gelatinous feeding houses. Each individual removes particles from $1 \text{ to } 5 \text{ L d}^{-1}$ (Sato et al. 2005; Scheinberg and Landry 2005). Gelatinous houses are discarded and a new house is secreted about once hr^{-1} in the northern Gulf of Mexico (Dagg and Brown 2005). Discarded houses, with attached large particles, sink at rates of $> 50 \text{ m}^{-1} \text{ d}^{-1}$ (Alldredge 2005). Also, each individual appendicularian produces large numbers of fecal pellets, approximately 50 h^{-1} in the northern Gulf of Mexico (Dagg and Brown, 2005). These compact pellets sink at speeds of $60 \text{ m}^{-1} \text{ d}^{-1}$ (Dagg and Brown 2005) or $> 100 \text{ m d}^{-1}$ if they contain lithogenic particles (Dagg et al. 1996). In one study larvaceans consumed an average of 20 % of the particles from the upper 5 m of the Mississippi River plume each day. Their compact, fast sinking fecal pellets and discarded gelatinous houses contribute

significantly to vertical OM flux. Recent work (Sato unpublished; Dagg et al. in prep.) suggests larvaceans are even more abundant along the coast than in the Mississippi River plume and they produce large quantities of sinking organic particles in these coastal regions (see below). When abundant, pelagic appendicularians can mediate the rapid vertical transfer of microbial web productivity in the surface layer, which may be only 5 to 15 m thick in the coastal hypoxic region, to the sub-pycnocline layer that becomes hypoxic each summer.

(c) Sinking (sedimentation) Large phytoplankton cells can sink at rates of several m d^{-1} , and aggregates of cells or mixtures of cells and detritus at rates of 10 – 100 m d^{-1} . At these rates, direct sinking of phytoplankton from the most productive layer of the plume, typically only 1-10 m thick, can easily provide a large input of organic matter to the subpycnocline layer that becomes hypoxic. Rapidly sinking (10 - 100 m d^{-1}) fecal pellets provide an additional source of organic matter to the subpycnocline layer.

Large inputs of organic matter to the bottom are associated with the highly productive plume from the Mississippi River birdfoot delta. Vertical flux of organic carbon in various parts of the Mississippi River plume was determined from drifting sediment traps deployed beneath the mixed layer (Redalje et al. 1994). Observed rates were as high as $1.80 \text{ g C m}^{-2} \text{ d}^{-1}$ during spring but rates were lower during other seasons ($0.29 - 0.95 \text{ g C m}^{-2} \text{ d}^{-1}$), and lower away from the immediate plume ($0.18 - 0.40 \text{ g C m}^{-2} \text{ d}^{-1}$) (Redalje et al. 1994). Away from the plume, in a 20 m water column in the middle portion of the hypoxic zone, flux rates measured by moored traps were between 0.50 and $0.60 \text{ g C m}^{-2} \text{ d}^{-1}$ (Qureshi 1995). Data from moored traps in waters this shallow are likely confounded by resuspension and trap concentrating effects so these are probably overestimates.

Another method for estimating organic matter loadings to the hypoxic zone is to estimate bacterial oxygen demand below the pycnocline and apply it to the hypoxic area ($15,000 \text{ km}^2$). Variations of this approach have been done in several papers with broadly similar results. Amon and Benner (1998) calculated that bacterial oxygen consumption alone could reduce the oxygen concentration to hypoxic levels within 1 – 7 weeks during the

summer. Chin-Leo and Benner (1992) calculated that 26 - 56 days of subpycnocline respiration (excluding benthic respiration) could lead to hypoxia. Dortch et al. (2004) included both water and benthic respiration and calculated bottom water oxygen depletion would take about 1 month in the summer. These calculations indicate organic matter sedimentation into the subpycnocline layer is large. However, these calculations of “time to hypoxia” are all underestimates because none included any O₂ replenishment, either vertically through the pycnocline or laterally. Hypoxia development is very sensitive to cross pycnocline exchange (Rowe 2001) and O₂ replenishment must be properly quantified if this type of calculation is used to provide estimates of organic matter loading to the subpycnocline water.

Part B. Mechanistic models

Rate measurements of important biological processes in the Mississippi River plume were summarized separately in the previous section. Measurements were made over a wide range of conditions during all seasons, although winter data are sparse. For the Mississippi River plume, all or some of these processes have been synthesized into simple conceptual (non-quantitative) models (e.g. Rowe and Chapman 2002; Dagg and Breed 2003). It is unclear how representative these models are of the Atchafalaya plume region because the physical dynamics of that region are so different from the Mississippi plume. Three sub-models were constructed in Dagg and Breed (2003): one for large phytoplankton (Figure 1), one for small phytoplankton, and one for bacteria. Spatial scales were not set to absolute distances because the absolute scale of the plume varies greatly with the magnitude of discharge. As in Rowe and Chapman (2002), plume processes were separated into near-, mid-, and far-field regions, with each region being approximately defined by a salinity boundary. All processes and stocks were set to a relative scale of magnitude between 0 – 1 and plotted within the context of physical mixing between inflowing river water and receiving oceanic water. These conceptualizations are idealized pictures but they capture the elements of the important biogeochemical cycling within the buoyant plume. All changes in biological properties take place in a physical environment of rapid mixing/dilution of river water with

receiving oceanic water. General water column characteristics of these two conceptual models are similar. The model of Rowe and Chapman (2002) also considered benthic processes whereas Dagg and Breed (2003) did not.

For the purposes of this paper, some important components emphasized in Dagg and Breed (2003) were:

- Growth rate of large and small phytoplankton is initially slow because of light limitation but rapidly increases and reaches maximum rates. At some point in the mid-far field region, growth rates begin to decline because of nutrient limitation.
- Phytoplankton biomass peaks in the mid-field region.
- Microzooplankton grazing closely tracks small phytoplankton biomass, and peaks in the mid-field region. Copepod grazing tracks large phytoplankton biomass less closely and peaks in the far-field.
- Sinking flux from the plume food web, attributed to direct sinking of large phytoplankton and fecal pellets from mesozooplankton, peaks in the mid-field region.
- Labile dissolved organic matter, primarily derived from phytoplankton exudation and small grazers, peaks in the mid-field region and bacterial production closely tracks this DOM.
- NH_4 (recycled nitrogen) is derived from bacteria and microzooplankton but concentrations remain low because of rapid uptake and nitrification.

These conceptualizations provided important understanding of relationships between various biological, chemical and physical processes but quantification of these linkages was still needed. Three quantitative, mechanistic models synthesizing these data have since been constructed.

The response of the planktonic food web in the Mississippi River plume to decreased NO_3 loading was modeled with a nitrogen-phytoplankton-zooplankton (NPZ) ecosystem model (Green et al. 2006b). The nitrogen-based model consisted of 9 compartments

(nitrate, ammonium, labile dissolved organic nitrogen, bacteria, small phytoplankton, diatoms, microzooplankton, mesozooplankton and detritus), and was developed for the spring season when sedimentation of organic matter from plume surface waters is considered important for the development of shelf hypoxia. Parameterization of this NPZ model is based on data synthesized from 20 years of rate measurements in the Mississippi River plume, and on literature derived information about processes coupling various elements of marine food webs. The model was forced by physical parameters specified along the river-ocean salinity gradient, including photosynthetically available radiation (PAR), residence time, light attenuation by dissolved and particulate matter, and mixed layer depth. Verification of model results for a riverine NO_3 concentration of $100 \mu\text{M}$ was achieved using available biological biomass and nutrient data across the salinity gradient. Modeled primary production was validated for different riverine NO_3 inputs by comparison with independently measured data (Figure 2a). The most pertinent point for this paper is that the relationship between NO_3 input and N sedimentation is less than 1:1 (Figure 2b). As NO_3 loadings decline, sedimentation from the plume declines also but at less than a 1:1 ratio. For example, a 30 % decline in NO_3 inputs from the river yielded a 16 % decline in sedimentation, and a 45 % decline in NO_3 yielded a 23 % decline in sedimentation. Nitrogen flow into some other pathways must therefore change by $> 1:1$. Model output indicates the most important pathway or ‘filter’ (Cloern 2001) for this response is microzooplankton grazing. This shift occurs, as all plume processes do, within the context of physical dilution caused by mixing of plume waters rich in NO_3 with receiving oceanic waters depleted in NO_3 . Dilution modifies the NO_3 uptake kinetics by phytoplankton and reduces the ultimate usage of this NO_3 . The overall impacts on coastal hypoxia of these non-linear responses to reductions in NO_3 loading are unclear, and the rates of nitrogen recycling predicted by the model should be verified by additional experimental measurements.

In another modeling study, Breed et al. (2004) divided the Mississippi River plume into 4 regions based on surface salinity and synthesized the processes within each region (Figure 3). Plume region 1 was nearest the mouth of the river and defined by a mean salinity of 10 psu. Regions 2 and 3 had mid salinities of 23 and 29 psu, and region 4 had a

mean salinity of 33 psu. The planktonic ecosystem of each region was divided into 8 compartments representing 6 living groups and 2 non-living groups, dissolved organic carbon and detritus. A carbon budget was constructed for each region. Within each region, there were flows into and out of the system to accommodate sedimentation, sediment resuspension and export to higher trophic levels. Empirical data were used to set the values of trophic flows or to set biologically realistic constraints. A total of 181 potential carbon flows were present in the complete 4-region model for which there were between 51 and 53 equations. The best solution was determined to be the one that minimized the sum of squares of all flows, via an inverse modeling technique. For the purposes of this paper, some important components of the model are:

- Sedimentation peaked in the mid-salinity regions. Sedimentation was equivalent to approximately 10-25 % of phytoplankton production in zones 2 and 3.
- Modeled rates of vertical carbon flux were similar to rates measured by Redalje et al. (1994) for mid-salinity regions in spring, summer and fall but did not match data in winter. Breed et al. (2004) concluded “relating observations of sedimentation to other ecosystem properties remains a problem.”
- In general, the largest flows were in the mid-salinity regions. During spring, summer and fall, these regions were net autotrophic (i.e. they exported organic matter), horizontally and vertically.
- The largest organic carbon sink was respiration, implying the largest organic nitrogen sink was recycling.
- DOC from the river supported significant bacterial production in the winter but not during other seasons. Small variations in the lability of riverine DOC can affect plume trophic flows because the riverine pool of DOC is large.

This analysis provided understanding of the carbon flows within each of the Mississippi River plume regions but could not be used to construct carbon budgets for the system because the size of each region during each season was not known.

A more complete mechanistic model addressing the relationships between nutrient input from the Mississippi River, primary production, sedimentation and hypoxia on the Louisiana shelf was recently completed (Green et al. 2006a). Building on Breed et al. (2004), this model calculated plume volume from mixed layer depth and area of each of the four salinity subregions, as derived from extensive cruise data and from satellite images of suspended sediment distributions (Figure 4). Additional rate measurements from recent cruises further improved the original model of Breed et al. (2004). Combining the food web model for each sub-region with the spatial dimensions of each sub-region allowed determination of the mass of carbon flow in the plume. Although plume dimensions were determined at monthly intervals, actual model runs were done by season because of limitations in process data. For the purposes of this paper, there are several important results from this mechanistic model:

- Autochthonous gross primary production (GPP) equaled 1.3×10^{12} g C yr⁻¹ and dominated labile OC inputs (88% of the budget) because riverine OC was mostly refractory (non-reactive).
- Most biological activity was in salinity regions 2 and 3, and most sedimentation from the plume was in these regions also, with 63 % of total spring and summer sedimentation in region 2 and 28 % in region 3 (Figure 5).
- The overall fates of plume carbon during non-winter periods were to be respired (55-64 %), to sink (19-26 %), to be advected out of the plume (12-16 %) and to be transferred to higher trophic levels (4-5 %). In winter, almost all plume carbon (96%) was respired. Annually, microbial respiration accounted for ~65% of labile OC losses, and smaller losses of labile OC occurred via sedimentation (20%), advection (10%), and export to higher trophic levels (5%).
- Total sedimentation of organic carbon from the Mississippi plume from March to June, the period when hypoxia is established each year, was 1.2×10^{11} g C. By comparison, the organic carbon demand for the entire hypoxic zone was 5.2×10^{11} g C. This demand consisted of 1.7×10^{11} g C required for an oxygen drawdown of 4 mg l⁻¹ within the hypoxic zone, and 3.5×10^{11} g C required to consume oxygen replenished by vertical diffusion (Justić et al. 1997). Therefore,

- sedimentation from the Mississippi plume could directly supply a maximum of 23 % of the organic carbon required for development and maintenance of hypoxia. This is a maximum value because much of this organic matter sedimentation occurs off the shelf and will not serve as fuel for on-shelf oxygen consumption. This indicates additional sources of, and/or controls on, the DIN that determines primary productivity in the more westerly shelf regions must be considered.
- Gross primary production between March and June was 4.9×10^{11} g C. Over the same time period, 1.2×10^{11} g C sedimented out of the plume. By subtraction, 3.7×10^{11} g C or 3.1×10^{10} mol C remained, most of which was respired. By simple stoichiometry, 4.7×10^9 mol N would be available to support ‘recycled’ phytoplankton production outside of the immediate plume.

In summary, more than twenty years of field studies have provided us with a good but still incomplete understanding of biogeochemical processes in the Mississippi River plume and near the Mississippi River delta. Our mechanistic models result from a synthesis of these field studies. This approach contrasts with most previous models that predict the magnitude of hypoxia from statistical or correlative approaches but do not contain a detailed presentation of the underlying processes (Justić et al. 2002; Scavia et al. 2003; Turner et al. 2005). Our models are incomplete in that they do not predict the scale of hypoxia. They do show however, that direct sedimentation of organic matter from the Mississippi River plume is insufficient for the development and maintenance of coastal hypoxia; other processes or sources of organic matter must be considered. In addition, these mechanistic models have identified other important issues requiring further research. These include: a need for better information on the sources, rates, and locations of organic matter sedimentation; a need for better understanding of internal biogeochemical processes contributing to hypoxia; a need for an improved understanding of rates of oxygen diffusion across the pycnocline; and the identification and quantification of other sources of organic matter fueling hypoxia, or other mechanisms by which Mississippi River derived organic matter fuels hypoxia. Some of these issues are preliminarily addressed in the last section of this paper. Overall, the complexity of this system, and the importance of both biological and physical processes in determining the

fates of plume and shelf production, indicates the need for a coupled physical-biological model accompanied by additional rate measurements.

Part C. Gaps and uncertainties

In this section we identify and discuss several gaps and uncertainties in our knowledge of controlling factors for hypoxia in the northern Gulf of Mexico.

Atchafalaya River. The Atchafalaya River, the major tributary of the Mississippi River, carries 30 % of total system flow but may have a disproportionately large impact on hypoxia because it discharges right at the coast. In contrast, 25 to 50 % of the Mississippi birdfoot discharge goes east and does not contribute to Louisiana shelf productivity or hypoxia (Wiseman et al. 1997; Walker et al. 2005; DiMarco et al. this volume). As a result, both rivers contribute approximately equal volumes of freshwater and associated dissolved and particulate materials to the Louisiana shelf. Also, the Atchafalaya enters the Gulf at about the mid-point of regional hypoxia, such that both E winds in the springtime and W 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. Biogeochemical cycling processes in the Atchafalaya plume are different in several ways from the SW Pass plume (Pakulski et al. 1995; Pakulski et al. 2000). In particular, the two systems have distinct quantities of DOM and are different in terms of their dominant bacterial processes (heterotrophic bacteria, dominant in the Mississippi plume versus nitrifying bacteria, dominant in the Atchafalaya plume (Pakulski et al. 1995; Pakulski et al. 2000)). Research to date indicates high rates of phytoplankton and bacterial production occur in Atchafalaya plume water, in spite of high concentrations of suspended sediments (Dagg 1995; Day et al. 1995). Peak concentrations of nutrients, chlorophyll a and primary productivity along the Louisiana-Texas continental shelf (not including the Mississippi plume) are often associated with the Atchafalaya River plume (Chen et al. 2000). These authors calculated an annual average primary production for coastal waters of the NW Gulf of Mexico of $0.52 \text{ g C m}^{-2} \text{ d}^{-1}$, with the highest values of primary production (up to $3.31 \text{ g C m}^{-2} \text{ d}^{-1}$) occurring on

the Louisiana shelf in coastal waters between Terrebonne Bay and Atchafalaya Bay and further west, suggesting an important contribution from the Atchafalaya River. Lastly, the distribution of coastal hypoxia suggests a significant impact from Atchafalaya River nutrient inputs (Bierman et al. 1994; Rabalais et al. 2002; Scavia et al. 2003).

Nevertheless, our mechanistic understanding of this understudied system remains poor and its contribution to hypoxia cannot be accurately determined at this time. This broad, shallow area is a challenge to study but it is necessary to do so in order to define its importance to hypoxia in this region.

Recycling. The dominant fate of plume carbon, 65% annually, is respiration (Green et al. 2006a). This implies that recycling of plume nitrogen is the major pathway for nitrogen flow in this system. This nitrogen can be transported outside the area of the immediate plume where it can stimulate ‘recycled’ production of phytoplankton. Recycled production provides an important mechanism for keeping a portion of the available nitrogen and organic matter in the water column while plume water is transported to the shallow regions susceptible to hypoxia development. Primary and secondary productivity derived from regenerated nutrients may lead to particles sinking in shallow, stratified regions, which in turn would contribute to oxygen demand and hypoxia. Any portions of this ‘recycled’ production that sink below the pycnocline can contribute to development or maintenance of hypoxia.

For the purposes of this paper, it is necessary to consider the implications of this recycling for hypoxia. What are the mechanisms by which recycled nutrients contribute to hypoxia? It is clear that recycling combined with horizontal transport of surface water is a mechanism for redistributing river nitrogen (and perhaps phosphorus) along the inner shelf. Here, these nutrients can be utilized by the pelagic food web to produce organic matter that may sink below the pycnocline, where its decomposition will consume oxygen.

Recycling processes that occur above the pycnocline fuel additional phytoplankton production. Recycled nutrients can support phytoplankton production numerous times, as

long as the recycling processes take place within the photic zone where nutrients can be taken up by phytoplankton. This mechanism can contribute to the production of phytoplankton (and some bacteria) far from the initial input of nutrients. The rapid uptake of 'new' nutrients combined with the high recycling rates measured in the plume, suggests that recycled production is important over large portions of the inner shelf. However, as long as this recycling is above the pycnocline, the recycled phytoplankton production does not contribute to the sinking flux of organic matter, and therefore does not contribute to the sub-pycnocline oxygen demand. Only if or when the recycled phytoplankton production sinks below the pycnocline can its decomposition (recycling) consume oxygen and contribute to hypoxia.

Furthermore, once recycled production sinks below the pycnocline, it is no longer available to support additional phytoplankton production above the pycnocline. The pycnocline is a barrier to upward nutrient transport in the same way it is a barrier to downward oxygen transport. In the photic zone, nutrients can be recycled many times and support phytoplankton production each time but only once can this production contribute to hypoxia, unless mechanisms exist for returning the nutrients regenerated in the sub-pycnocline water back into the photic zone. Recycling modifies the location of phytoplankton production and presumably also the location of organic matter vertical flux but the magnitude of organic matter sedimentation is not increased by recycling above the pycnocline. Recycled production is not an 'additional source' of organic matter for oxygen consumption below the pycnocline unless these subpycnocline regenerated nutrients are returned to the photic zone and again incorporated into phytoplankton production.

The pycnocline is not an impervious barrier to nutrient diffusion and some exchange occurs. Several physical processes contribute to cross-pycnocline exchanges. This is suggested by variability in the strength and intensity of hypoxia and variation in the cross-pycnocline density gradient (Rowe 2001; DiMarco et al. this volume). The magnitude and variability of this process is not sufficiently known but processes that contribute to upward transport of sub-pycnocline nutrients would simultaneously

contribute to downward transport of oxygen. Furthermore, downward transport of oxygen can sometimes occur without much upward nutrient transport because oxygen gradients are often stronger than nutrient gradients; highest nutrient concentrations are often associated with near-bottom water and gradients near the pycnocline (oxycline) are weak. The magnitude of processes degrading organic matter, removing O₂ and regenerating nutrients in the sub-pycnocline water column versus at the sediment-water interface has not been measured in detail. Sediment oxygen consumption rates have been measured in hypoxic regions (e.g. Miller-Way et al. 1994; Rowe et al. 2002) but rates have not been routinely compared to those in the nepheloid layer or overlying waters. Most studies of water-column nitrogen recycling rates (e.g. Bode and Dortch 1996; Wawrik et al. 2004; Gardner et al. 1994; 1996; 1997) have been done only in surface waters. Nevertheless, to the extent that nutrient re-injection into surface water occurs, with subsequent incorporation into the food web, repeated recycling would repeatedly contribute to hypoxia. A much better quantification of the vertical, cross-pycnocline exchanges of oxygen and nutrients is required (Rowe 2001).

Coastal upwelling is a possible mechanism for returning bottom-water nutrients to the surface. Wind driven upwelling along the Louisiana coast does occur (Dagg 1988) but its spatial extent, frequency and duration have not been documented. It is not possible at this time to quantify the importance of upwelling as a mechanism for supplying nutrients within a hypoxic season. Furthermore, production stimulated by upwelled nutrients must be transported offshore and then settle through the pycnocline to bottom water in order to contribute to hypoxia. A vertically-mixed, coastal boundary layer can support high phytoplankton production but, by definition, this layer is inshore of the stratified water column required for hypoxia development. Wiseman et al. (1997) consider at least part of the Louisiana Coastal Current to be stratified but stratification is not compatible with vertical injection of bottom water nutrients into the surface layer, and the Louisiana Coastal Current is not synonymous with the coastal mixed layer. Event scale deepening of mixing in the Louisiana Coastal Current could occur, associated with increased winds for example, which could lead to cycles of stratification and mixing within this region (DiMarco et al. this volume). These erosion-stratification cycles would also diminish

hypoxia by the same mechanism. Little is known about these potentially important processes but the existence of a band of coastal phytoplankton should not be taken as evidence of upwelling. Autochthonous production from shallow waters along the coastal edge of the hypoxic zone may be derived from the Atchafalaya River. 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).

Coastal wetlands. Louisiana's extensive coastal wetlands could be a significant source of organic matter to the coastal ocean. The "*outwelling hypothesis*" of Odum (1968) suggested that salt marshes transport biologically available organic matter into nearshore waters, enhancing shelf secondary production. While this phenomenon was generally not supported by many earlier studies (Teal 1962; Odum and de la Cruz 1967; Haines 1977), more recent work has shown it may be significant. For example, between 6 and 36% of near-shore DOC off the coast of Georgia originates from coastal salt marshes (Moran et al. 1991). Globally, export of organic carbon from salt marshes ranges from approximately 13 to 328 g DOC m⁻² y⁻¹, and 30 to 140 g POC m⁻² y⁻¹ (Alongi, 1998). Export rates may be higher in Louisiana because of the extreme rates of coastal land loss. Losses have averaged 29.9 miles² yr⁻¹ (77 km² yr⁻¹) in Louisiana over the past 22 yr (Barras et al. 2003). This suggests a potentially significant contribution of POC and DOC to the coastal ocean. Mean organic carbon content of coastal marsh soils is about 0.09 g C cm⁻³ (Hatton et al. 1982), equivalent to 900 g C m⁻² for each cm of depth. Assuming 1 m of soil is lost when marsh is converted to open water yields approximately 70 x 10¹¹ g C yr⁻¹, equivalent to 1.28 g C d⁻¹ for each m² of the hypoxic zone (assumed to be 15,000 km²). This calculation is exclusive of aboveground *Spartina* and other plant production and of porewater DOC. For comparison, annually averaged phytoplankton production on the Louisiana shelf is approximately 0.44 g C m⁻² d⁻¹ (Chen et al. 2000). There are other hints that this may be an important source of OC for Louisiana's coastal ocean. Net metabolism data indicate an external supply of organic matter for estuaries and coastal

regions: Louisiana estuaries are net heterotrophic (Caffrey 2004) and continental shelf waters away from the immediate river plumes are net heterotrophic by an average of $1.3 \text{ g C m}^{-2} \text{ d}^{-1}$ (Lehrter et al. 2006). Higher concentrations of DOM in the Atchafalaya River compared to the Mississippi River are attributed to a wetland contribution, and qualitative differences in DOM between the two rivers support this (Boehme et al. 2004). A wetland contribution to coastal DOM would be independent of phytoplankton production stimulated by river inputs of macronutrients or river DOM. What portion of Louisiana's land loss actually reaches the coastal ocean where it could contribute to coastal food webs is unknown, and the bioavailability of this material is also unknown. The vast magnitude of this pool of organic matter however, justifies further study.

There are preliminary indications that a DOM-fueled microbial foodweb along the coast is productive in the summer (Dagg et al. in prep). In August 2004, high concentrations of DOC and heterotrophic bacteria were observed in coastal regions between the Mississippi and Atchafalaya Rivers. Chlorophyll concentrations in the same region were $< 1 \mu\text{g l}^{-1}$. Larvaceans, consumers of particles $< 20 \mu\text{m}$ including bacteria, were abundant and productive at this time and produced $> 1 \text{ gm C m}^{-2} \text{ d}^{-1}$ of large fast sinking particles in the form of discarded houses and fecal pellets. Even a fraction of this material sinking through the pycnocline would fuel considerable oxygen demand, providing a direct link between coastally derived DOM and hypoxia during a period of low river flow and in regions well away from the river inputs.

Summary:

Over recent decades, field studies have provided us with a good mechanistic understanding of nutrient cycling in the SW Pass plume of the Mississippi River. Recent syntheses of these data, in the form of conceptual and quantitative models, have led to improved understanding of the biogeochemical dynamics and flows within this system. Direct sedimentation of organic matter from the water-column food web of the Mississippi River plume can contribute a maximum of only 23 % of the oxygen demand required for establishment of hypoxia in the spring and early summer. Other probable

sources of organic matter include production stimulated by the Atchafalaya River discharge and recycled production from both rivers. In addition, large amounts of organic matter are lost annually from Louisiana's degrading coastal wetlands and this material may contribute to coastal oxygen demand. There is a need for improved information on the sources, rates, and locations of organic matter sedimentation, for further investigation of biogeochemical processes, for improved understanding of rates of and controls on oxygen diffusion across the pycnocline, and for the identification and quantification of other sources of organic matter fueling hypoxia, or other mechanisms by which Mississippi River derived organic matter fuels hypoxia. Along with empirical studies to address these needs, development of a coupled physical-biological model of the northern Gulf of Mexico should be initiated.

Literature cited.

Aksnes, D.L. and P. Wassmann. 1993. Modeling the significance of zooplankton grazing for export production. *Limnology and Oceanography* 38: 978-985.

Allredge, A. 2005. The contribution of discarded appendicularian houses to the flux of particulate organic carbon from oceanic surface waters, p 309-326. In G. Gorsky, M.J. Youngbluth and D. Deibel (eds.), *Response of marine ecosystems to global change: ecological impact of Appendicularians*. Gordon and Breach .

Alongi, D.M. 1998. *Coastal Ecosystem Processes*. CRC Press, New York

Ammerman, J. W. 1992. Seasonal variation in phosphate turnover in the Mississippi River Plume and the Inner Gulf Shelf: Rapid summer turnover, p. 69-75. *In* T. J. Bright [ed.], *Proceedings of the 1991 NECOP Synthesis Workshop*. Texas A&M Sea Grant.

Ammerman, J. W., and W. B. Glover. 2000. Continuous underway measurement of microbial ectoenzyme activities in aquatic ecosystems. *Marine Ecology-Progress Series* 201: 1-12.

Amon, R.M.W. and R. Benner. 1994. Rapid cycling of high-molecular-weight dissolved organic matter in the ocean. *Nature* 369: 549-552.

Amon, R.M.W. and R. Benner. 1996. Bacterial utilization of different size classes of dissolved organic matter. *Limnology and Oceanography* 41: 41-51.

- Amon, R.M.W and R. Benner. 1998. Seasonal patterns of bacterial abundance and production in the Mississippi River plume and their importance for the fate of enhanced primary production. *Microbial Ecology* 35: 289-300.
- Amon, R.M.W. and R. Benner. 2003. Combined neutral sugars as indicators of the diagenetic state of dissolved organic matter in the Arctic Ocean. *Deep Sea Research I* 50: 151-169.
- Banse, K. 1992. Grazing, temporal changes of phytoplankton concentrations, and the microbial loop in the open sea, p 409-440. In Falkowski, P.G. and Woodhead, A.D. (eds.) *Primary productivity and biogeochemical cycles in the sea*. Plenum, New York.
- Barras, J., S. Beville, D. Britsch, S. Hartley, S. Hawes, J. Johnston, P. Kemp, Q. Kinler, A. Martucci, J. porthouse, D. Reed, K. Roy, S. Sapkota and J. Suhayda. 2003. Historical and projected coastal Louisiana land changes: 1978-2050. USGS Open File Report 03-334, 39 p (Revised January 2004).
- Benner, R. and Opsahl, S. 2001. Molecular indicators of the source and transformations of dissolved organic matter in the Mississippi River plume. *Organic Geochemistry* 32: 597-611.
- Bianchi, T.S., T. Filley, K. Dria and Hatcher, P.G. 2004. Temporal variability in sources of dissolved organic carbon in the lower Mississippi River. *Geochimica et Cosmochimica Acta* 68: 959-967.
- Bierman, V.J., JrS.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.
- Boehme, J., P. Coble, R. Conmy and A. Stovall-Leonard. 2004. Examining CDOM fluorescence variability using principal component analysis: seasonal and regional modeling of three-dimensional fluorescence in the Gulf of Mexico. *Marine Chemistry* 89: 3-14.
- 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.
- Bushaw, K., R.G. Zepp, M.A. Tarr, D. Schulz-Janders, R.A. Bourbonniere, R.E. Hodson, W.L. Miller, D.A. Bronk and M.A. Moran. 1996. Photochemical release of biologically available nitrogen from aquatic dissolved organic matter. *Nature* 381: 404-407.

- Caffrey, J.M. 2004. Factors controlling net ecosystem metabolism in U.S. estuaries. *Estuaries* 27: 90-101.
- Chen, R.F. and G.B. Gardner. 2004. High-resolution measurements of chromophoric dissolved organic matter in the Mississippi and Atchafalaya River plume regions. *Marine Chemistry* 89: 103-125.
- Chen, X., S.E. Lohrenz and D.A. Weisenburg. 2000. Distribution and controlling mechanisms of primary production on the Louisiana-Texas continental shelf. *Journal of Marine Systems*: 25: 179-207.
- Childs C.R., N.N. Rabalais, R.E. Turner and L.M. Proctor. 2002. Sediment denitrification in the Gulf of Mexico zone of hypoxia. *Marine Ecology Progress Series* 240:285-290.
- Chin-Leo, G., and R. Benner. 1992. Enhanced bacterioplankton production and respiration at intermediate salinities in the Mississippi River plume. *Marine Ecology Progress Series* 87: 87-103.
- Chisholm, S. W. 1992. Phytoplankton size, p. 213-237. In P. G. Falkowski and A. D. Woodhead (eds.) *Primary productivity and biogeochemical cycles in the sea*. Plenum Press, New York.
- Cloern, J.E. 2001. Our evolving conceptual model of the coastal eutrophication problem. *Marine Ecology Progress Series* 210: 223 – 253.
- Conmy, R.N., Coble, P.G., Chen, R.F. and Gardner, G.B., 2004. Optical properties of colored dissolved organic matter in the Northern Gulf of Mexico. *Marine Chemistry* 89: 127-144.
- Cotner, J. B. J., and W. S. Gardner. 1993. Heterotrophic bacterial mediation of ammonium and dissolved free amino acid fluxes in the Mississippi River plume. *Marine Ecology Progress Series* 93: 75-87.
- Cowie, G. and J. Hedges. 1994. Biochemical indicators of diagenetic alteration in natural organic matter mixtures. *Nature* 369: 304-307.
- Dagg, M.J. 1988. Physical and biological responses to the passage of a winter storm in the coastal and inner shelf waters of the northern Gulf of Mexico. *Continental Shelf Research* 8: 167-178.
- Dagg, M.J. 1995. Ingestion of phytoplankton by the micro- and meso-zooplankton communities in a productive subtropical estuary. *Journal of Plankton Research* 17: 845-857.

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., T. Bianchi, W. Cai, B.A. McKee and R. Powell. 2006. Fates of dissolved and particulate materials from the Mississippi River immediately after discharge into the northern Gulf of Mexico. *Continental Shelf Research* (submitted).

Dagg, M.J. and G. A. Breed. 2003. Biological effects of Mississippi River nitrogen on the northern Gulf of Mexico – a review and synthesis. *Journal of Marine Systems* 43: 133-152.

Dagg, M.J. and S.L. Brown. 2005. The potential contribution of fecal pellets from the larvacean *Oikopleura dioica* to vertical flux of carbon in a river dominated coastal margin, p. 293-307. In G. Gorsky, M.J. Youngbluth and D. Deibel (eds.), *Response of Marine Ecosystems to Global Change: Ecological Impact of Appendicularians*. Gordon and Breach.

Dagg, M.J., E.P. Green, B.A. McKee and P.B. Ortner. 1996. Biological removal of fine-grained lithogenic particles from a large river plume. *Journal of Marine Research* 54: 149-160.

Dagg, M.J., R. Sato, H. Liu, T. Bianchi, R. Green and R. Powell. 2006. Does the microbial foodweb contribute to bottom water hypoxia in the northern Gulf of Mexico (in prep).

Dagg, M. J., and T. E. Whitedge. 1991. Concentrations of copepod nauplii associated with the nutrient rich plume of the Mississippi River. *Continental Shelf Research* 11: 1409-1423.

Day, J.W., R.R. Twilley, R.F. Shaw, C.J. Madden, B.A. McKee, M.J. Dagg, D.L. Childers, R.C. Rainie and L.J. Rouse. 1995. The influence of Atchafalaya River discharge on Fourleague Bay, Louisiana, USA, p.151-160. In: Dyer, K. (ed.) *Changes in fluxes in estuaries: implications from science to management*. Olsen and Olsen.

DiMarco, S., R. Hetland, S. Howden, S. Murray, N. Walker and W. Wiseman. 2006. Influence of physical oceanographic processes on the distribution and extent of the hypoxic zone (this volume)

Dinnel, S.P. and W.J. Wiseman Jr. 1986. Fresh-water on the Louisiana and Texas Shelf. *Continental Shelf Research* 6:765-784.

Dortch, Q., N.N. Rabalais, R.E. Turner and G.T. Rowe. 2004. Respiration rates and hypoxia on the Louisiana shelf. *Estuaries* 17: 862-872.

Dortch, Q., and T. E. Whitledge. 1992. Does nitrogen or silicon limit phytoplankton production in the Mississippi River plume and nearby regions. *Continental Shelf Research* 12: 1293-1309.

D'Sa, E. J., and R. L. Miller. 2003. Bio-optical properties in waters influenced by the Mississippi River during low flow conditions. *Remote Sensing of the Environment* 84: 538-549.

Duan, S. et al. 2006. Variability in the bulk composition and abundance of dissolved organic matter in the lower Mississippi and Pear Rivers (USA). *Journal of Geophysical Research* (in press).

Fahnenstiel, G. L., M. J. McCormick, G. A. Lang, D. G. Redalje, S. E. Lohrenz, M. Markowitz, B. Wagoner, and H. J. Carrick. 1995. Taxon-specific growth and loss rates for dominant phytoplankton populations from the northern Gulf of Mexico. *Marine Ecology Progress Series* 117: 229-239.

Fuhrman, J.A. 1999. Marine viruses and their biogeochemical and ecological effects. *Nature* 399: 541-548.

Gardner, W.S., R. Benner, R.M.W. Amon, J.B. Cotner, J.F. Cavaletto, and J.R. Johnson 1996. Effects of high molecular weight dissolved organic matter and light on heterotrophic nitrogen dynamics in the Mississippi River plume. *Marine Ecology Progress Series* 133: 287-297.

Gardner W.S., R. Benner, G. Chin-Leo, J.B. Cotner, B.J. Eadie, J.F. Cavaletto, M.B. Lansing. 1994. Mineralization of organic material and bacterial dynamics in Mississippi River plume water. *Estuaries* 17: 816-828.

Gardner, W.S., J.F.Cavaletto, J.B. Cotner, J.R.Johnson. 1997. Effects of natural light on nitrogen cycling rates in the Mississippi River plume. *Limnology and Oceanography* 42: 273-281.

Green, R.E., T.S. Bianchi, M.J. Dagg, N.D. Walker and G.A. Breed. 2006a. An organic carbon budget for the Mississippi River turbidity plume, and plume contributions to air-sea CO₂ fluxes and bottom water hypoxia. *Estuaries* 29:579-597.

Green, R., G. Breed, M. Dagg and S. Lohrenz. 2006b. Modeling planktonic dynamics and response to variable nitrate loading in the Mississippi River plume. *Continental Shelf Research* (submitted).

Haines, E.B. 1977. The origins of detritus in Georgia salt marsh estuaries. *Oikos* 29: 254-260.

Hatton, R., W. Patrick, and R. DeLaune. 1982. Sedimentation, nutrient accumulation, and early diagenesis in Louisiana Barataria Basin coastal marshes, p. 255-267. In: V. Kennedy (ed.), *Estuarine comparisons*. Academic Press, New York.

Hernes, P.J. and R Benner. 2003. Photochemical and microbial degradation of dissolved lignin phenols: implications for the fate of terrigenous dissolved organic matter in marine environments. *Journal of Geophysical Research* 108 doi: 10.1029/2002jc001421.

Hoppe, H. G. 2003. Phosphatase activity in the sea. *Hydrobiologia* 493: 187-200.

Jochem, F. J. 2003. Photo-and heterotrophic pico-and nano-plankton in the Mississippi River plume: distribution and grazing activity. *Journal of Plankton Research* 25: 1201-1214.

Jochem, F.J., M.J. McCarthy and W.S. Gardner. 2004. Microbial ammonium cycling in the Mississippi River plume during the drought spring of 2000. *Journal of Plankton Research* 26: 1265-1275.

Justic, D., N.N. Rabalais, and R.E. Turner. 1997. Impacts of climate change on net productivity of coastal waters: implications for carbon budgets and hypoxia. *Climate Research* 8: 225-237.

Justic, 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.

Kim, J.-S. 1996. Phosphorus limitation in the Mississippi River Plume (MRP) and Louisiana Shelf (LS) during May 1992, p. xii + 64, *Oceanography*. Texas A&M.

Lee, C. and M. Henrichs. 1993. How the nature of dissolved organic matter might effect the analysis of dissolved organic carbon. *Marine Chemistry* 41: 105-120.

Leenheer, J.A., L.B. Barber, C.E. Rostad and T.I. Noyes. 1995. Data on natural organic substances in dissolved, colloidal, and suspended-silt and -clay, and bed-sediment phases in the Mississippi River and some of its tributaries, 1991-1992. *Water-Resources Investigations Report, 94-4191*: p 47, US Geological Survey, Denver, CO.

Leenheer, J.A., Noyes, T.I. and Brown, P.A., 1995. Data on natural organic substances in dissolved, colloidal, and suspended-silt and -clay, and bed-sediment phases in the Mississippi River and some of its tributaries, 1987-1990. *Water-Resources investigations report, 93-4204*: p 71. US Geological Survey, Denver, CO.

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.

Lehrter, J.C., M.M. Murrell, J.D. Hagy, R.S. Stanley, J.G. Campbell and R.M. Greene. 2006. Primary production, respiration, and net ecosystem metabolism on the Louisiana continental shelf adjacent to the Mississippi and Atchafalaya Rivers. American Society of Limnology and Oceanography, Victoria, Canada. June 4-9, 2006. (Abstract).

Liu, H. and M.J. Dagg. 2003. Interactions between nutrients, phytoplankton growth, and micro- and meso-zooplankton grazing in the plume of the Mississippi River. *Marine Ecology Progress Series* 258: 31-42.

Liu, H., M.J. Dagg, L. Campbell and J. Urban-Rich. 2004. Picophytoplankton and bacterioplankton in the Mississippi River plume and its adjacent waters. *Estuaries* 27: 147-156.

Liu, H., M.J. Dagg, C-J. Wu and K-P. Chiang. 2005. Mesozooplankton consumption of microplankton in the Mississippi River plume, with special emphasis on planktonic ciliates. *Marine Ecology Progress Series* 286: 133-144.

Lohrenz, S.E., G.L. Fahnenstiel, D.G. Redalje, G.A. Lang, X.G. 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.

Lohrenz, S.E., G.L. Fahnenstiel, D.G. Redalje, G.A. Lang, M.J. Dagg, T.E. Whitledge 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.

Maier, R.M., I.L. Pepper and C.P. Gerba. 2000. *Environmental Microbiology*. Academic Press. San Diego

Miller, W. and R. Zepp. 1995. Photochemical production of dissolved inorganic carbon from terrestrial organic matter: Significance to the oceanic organic carbon cycle. *Geophysical Research Letters* 22: 417-420.

Miller-Way, T., G.S. Boland, G.T. Rowe and R.R. Twilley. 1994. Sediment oxygen consumption and benthic nutrient fluxes on the Louisiana Continental Shelf: A methodological comparison. *Estuaries* 17:809-815

Moran, M.A., R.J. Wicks and R.E. Hodson. 1991. Export of dissolved organic matter from a mangrove swamp ecosystem: evidence from natural fluorescence, dissolved lignin phenols, and bacterial secondary production. *Marine Ecology Progress Series* 76: 175-184.

Muller-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.

- Nelson, D. M., and Q. Dortch. 1996. Silicic acid depletion and silicon limitation in the plume of the Mississippi River: Evidence from kinetic studies in spring and summer. *Marine Ecology Progress Series* 136: 163-178.
- Odum, E.P. 1968. A research challenge: evaluating the productivity of coastal and estuarine water. *Proceedings of the 2nd Sea Grant Conference, Graduate School of Oceanography, University of Rhode Island.*
- Odum, E. P., and A.A. de la Cruz. 1967. Particulate organic detritus in a Georgia salt marsh-estuarine ecosystem, p. 383–388. In Lauff, G.H., (ed.), *Estuaries*, American Association for the Advancement of Science, Washington, D.C.
- Opsahl, S. and R. Benner. 1998. Photochemical reactivity of dissolved lignin in river and ocean waters. *Limnology and Oceanography* 43: 1297-1304.
- Ortner, P.B., T.N. Lee, P.J. Milne, R.G. Zika, M.E. Clarke, G.P. Podesta, P.K. Swart, P.A. Tester, L.A. Atkinson, and W.R. Johnson. Mississippi River flood waters that reached the Gulf Stream. *Journal of Geophysical Research* 100(C7): 13595 – 13601.
- Pakulski, J., R. Benner, R. Amon, B. Eadie and T. Whittedge. 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. Whittedge, R. Amon, B. Eadie, L. Cifuentes, J. Ammerman and D. Stockwell. 2000. Microbial metabolism and nutrient cycling in the Mississippi and Atchafalaya River plumes. *Estuarine, Coastal and Shelf Science*, 50: 173-184.
- Rabalais, N. N., R. E. Turner, Q. Dortch, D. Justic, V. J. Bierman, and W. J. Wiseman. 2002. Nutrient-enhanced productivity in the northern Gulf of Mexico: past, present and future. *Hydrobiologia* 475: 39-63.
- 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.
- 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: 829-838.
- Riley, G. A. 1937. The significance of the Mississippi River drainage for biological conditions in the northern Gulf of Mexico. *Journal of Marine Research* 1: 70-74.
- Rowe, G.T. 2001. Seasonal hypoxia in the bottom water off the Mississippi River Delta. *Journal of Environmental Quality* 30: 281-290.

Rowe, G.T. and P. Chapman. 2002. Continental shelf hypoxia: some nagging questions. *Gulf of Mexico Science* 20: 153-160.

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.

Sarnelle, O. 1999. Zooplankton effects on vertical particulate flux: testable models and experimental results. *Limnology and Oceanography* 44: 357-370.

Sato, R., Y. Tanaka and T. Ishimaru. 2005. Clearance and ingestion rates of three appendicularian species, *Oikopleura longicauda*, *O. rufescens* and *O. fusiformis*, p. 189-205. In G. Gorsky, M.J. Youngbluth and D. Deibel (eds.), *Response of Marine Ecosystems to Global Change: Ecological Impact of Appendicularians*. Gordon and Breach.

Scavia, D., N.N. Rabalais, R.E. Turner, D. Justic 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.

Scheinberg, R.D. and M.R. Landry. 2005. Clearance rates and efficiencies of *Oikopleura fusiformis* on the natural prey assemblage of a subtropical coastal ecosystem, p 207-223. In G. Gorsky, M.J. Youngbluth and D. Deibel (eds.), *Response of Marine Ecosystems to Global Change: Ecological Impact of Appendicularians*. Gordon and Breach

Sklar, F.H. and R.E. Turner. 1981. Characteristics of phytoplankton production off Barataria Bay in an area influenced by the Mississippi River. *Contributions to Marine Science* 24: 93-106.

Skoog, A. and Benner, R. 1997. Aldoses in various size fractions of marine organic matter: implications for carbon cycling. *Limnology and Oceanography* 42: 1803-1813.

Smith, S. M., and G. L. Hitchcock. 1994. Nutrient Enrichments and phytoplankton growth in the surface waters of the Louisiana Bight. *Estuaries* 17: 740-753.

Strom, S. L., and M. W. Strom. 1996. Microplankton growth, grazing, and community structure in the northern Gulf of Mexico. *Marine Ecology Progress Series* 130: 229-240.

Sylvan, J. B., Q. Dortch, D. M. Nelson, A. F. M. Brown, W. Morrison, and J. W. Ammerman. 2006a. Phosphorus limits phytoplankton growth on the Louisiana shelf during the period of hypoxia formation. *Environmental. Science and Technology* (submitted).

Sylvan, J. B., A. Quigg, S. Tozzi, and J. W. Ammerman. 2006b. Eutrophication induced phosphorus limitation in the Mississippi River Plume: Evidence from fast repetition rate fluorometry. *Limnology and Oceanography* (submitted).

- Teal, J.M. 1962. Energy flow in the salt marsh ecosystem of Georgia. *Ecology* 42: 614-624.
- Trefry, J. H., S. Metz, T. A. Nelsen, R. P. Trocine, and B. J. Eadie. 1994. Transport of particulate organic carbon by the Mississippi River and its fate in the Gulf of Mexico. *Estuaries* 17: 839-849.
- Turner, R. E., and N. N. Rabalais. 1991. Changes in Mississippi River water-quality this century. *Bioscience* 41: 140-147.
- Turner, R. E., N. N. Rabalais, and D. Justic. 2006. Predicting summer hypoxia in the northern Gulf of Mexico: Riverine N, P, and Si loading. *Marine Pollution Bulletin* 52: 139-148.
- Turner, R.E., N.N. Rabalais, E.M. Swenson, M. Kasprzak and T. Romaine. 2005. Summer hypoxia in the northern Gulf of Mexico and prediction from 1978 to 1995. *Marine Environmental Research* 59: 65-77.
- USEPA. 2001. Action Plan for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico, 2001. Mississippi River/Gulf of Mexico Watershed Nutrient Task Force.
- Vähätalo, A.V. and Zepp, R.G., 2005. Photochemical mineralization of dissolved organic nitrogen to ammonium in the Baltic Sea. *Environmental Science Technology* 39: 6985-6992.
- Walker, N.D., W.J. Wiseman, L.J. Rouse, and A. Babin. 2005 Effects of river discharge, wind stress, and slope eddies on circulation of the Mississippi River plume. *Journal of Coastal Research* 21:1228-1244.
- Warwik, 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.
- Warwick B., J.H. Paul, D.A. Bronk, D. John and M.Gray. 2004. High rates of ammonium recycling drive phytoplankton productivity in the offshore Mississippi River plume. *Aquatic Microbial Ecology* 35:175-184
- Wilhelm, S.W. and C. A. Suttle. 1999. Viruses and nutrient cycles in the sea. *Bioscience* 49: 781-788.
- Wiseman, W.J., N.N. Rabalais, R.E. Turner, S.P. Dinnell and A. MacNaughton. 1997. Seasonal and interannual variability within the Louisiana coastal current: stratification and hypoxia. *Journal of Marine Systems* 12: 237-248.

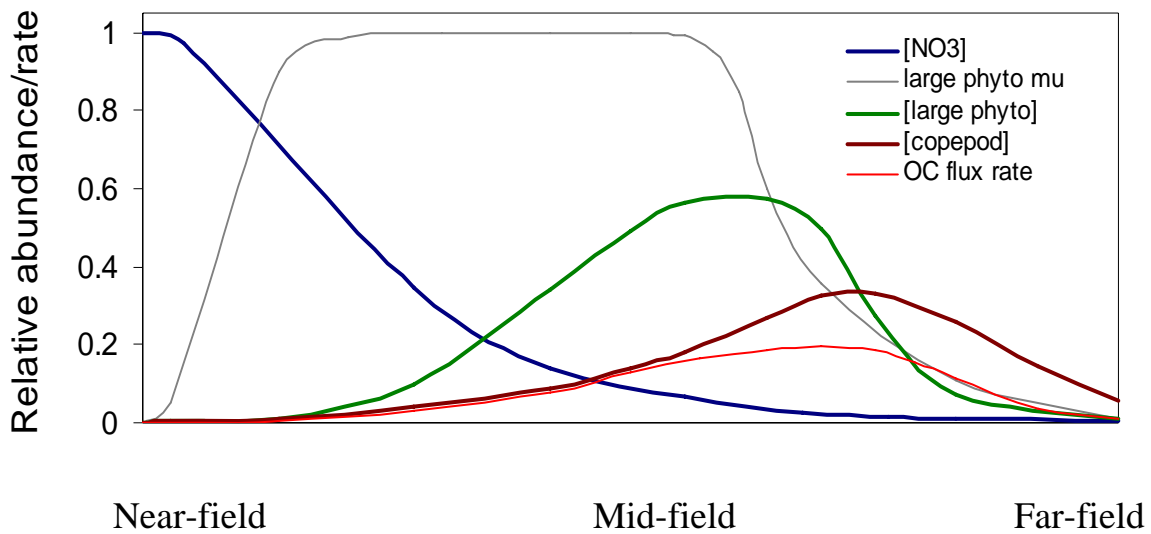


Figure 1. Conceptual model of the Mississippi River Plume as it mixes with shelf waters. The y-axis represents the stock or process on a relative scale from 0 to 1, with 1 being maximum. The X-axis represents the salinity gradient from the river mouth on the left to the oceanic regime on the right. This model is for large phytoplankton; others (not shown) are for small phytoplankton and for bacteria. Legend: ‘[NO3]’ is NO₃ concentration, decreased from river concentration by dilution/mixing with NO₃ depleted oceanic water and by biogeochemical use; ‘large phyto mu’ is the growth rate of large phytoplankton (diatoms), initially low because of light limitation, then maximum until nutrients begin to become limiting, then declining; ‘[large phyto]’ is the stock or biomass of large phytoplankton, initially small but increasing rapidly to a maximum in the mid-field because of high growth rates and low loss rates, then declining because growth rate slows and losses due to grazing, sinking, and dilution increase; ‘[copepod]’ is the stock of relatively slow growing mesozooplankton grazers that feed primarily on large phytoplankton; and ‘OC flux’ is the sinking of phytoplankton and fecal pellets from the water column to the sub-pycnocline region beneath the plume (from Dagg and Breed, 2003).

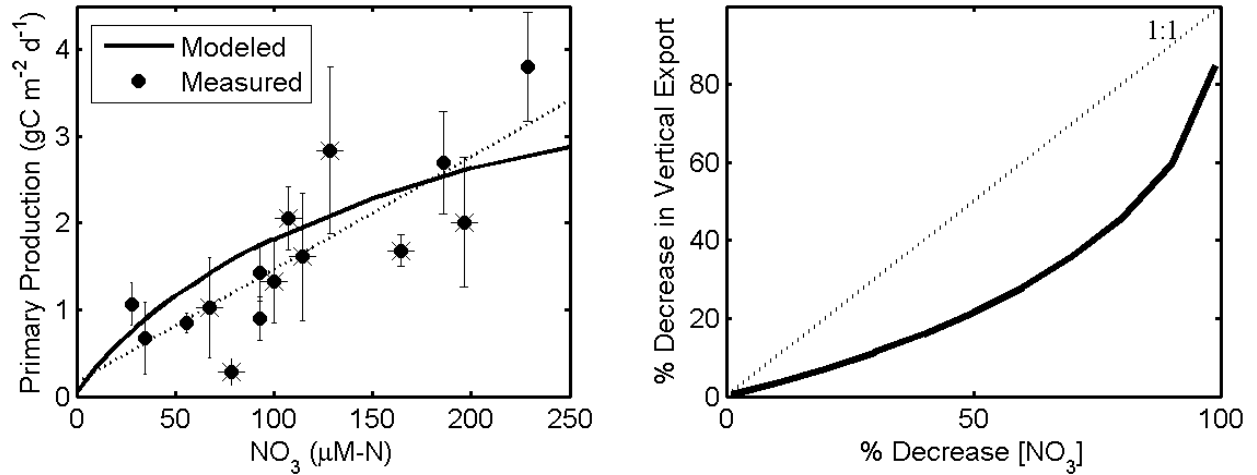


Figure 2a (left panel). Plume primary production as a function of riverine NO₃ input for the spring period. Modeled values of primary production were calculated as an average over intermediate to high salinities (>15), the region in which most measurements were made. Primary productivity measurements are an average of data collected around the delta in multiple years and seasons (Lohrenz *et al.*, 1997); spring (March – May) measurements are indicated by asterisks. A linear fit to measured values is indicated by the dashed line ($R^2 = 0.68$), and error bars on measured values indicate ± 1 SE.

Figure 2b (right panel). Changes in vertical PON export as a function of changes in riverine NO₃ loading (below 112 μM; the long-term riverine mean). Modeled values of vertical export were calculated as an average over intermediate to high salinities (>15). The effect of changing NO₃ loading on sedimentation is not a 1:1 relationship, indicating that ‘filters’ (Cloern 2001) exist between NO₃ inputs and the sedimentation response. Figure 2. from Green et al (2006b)

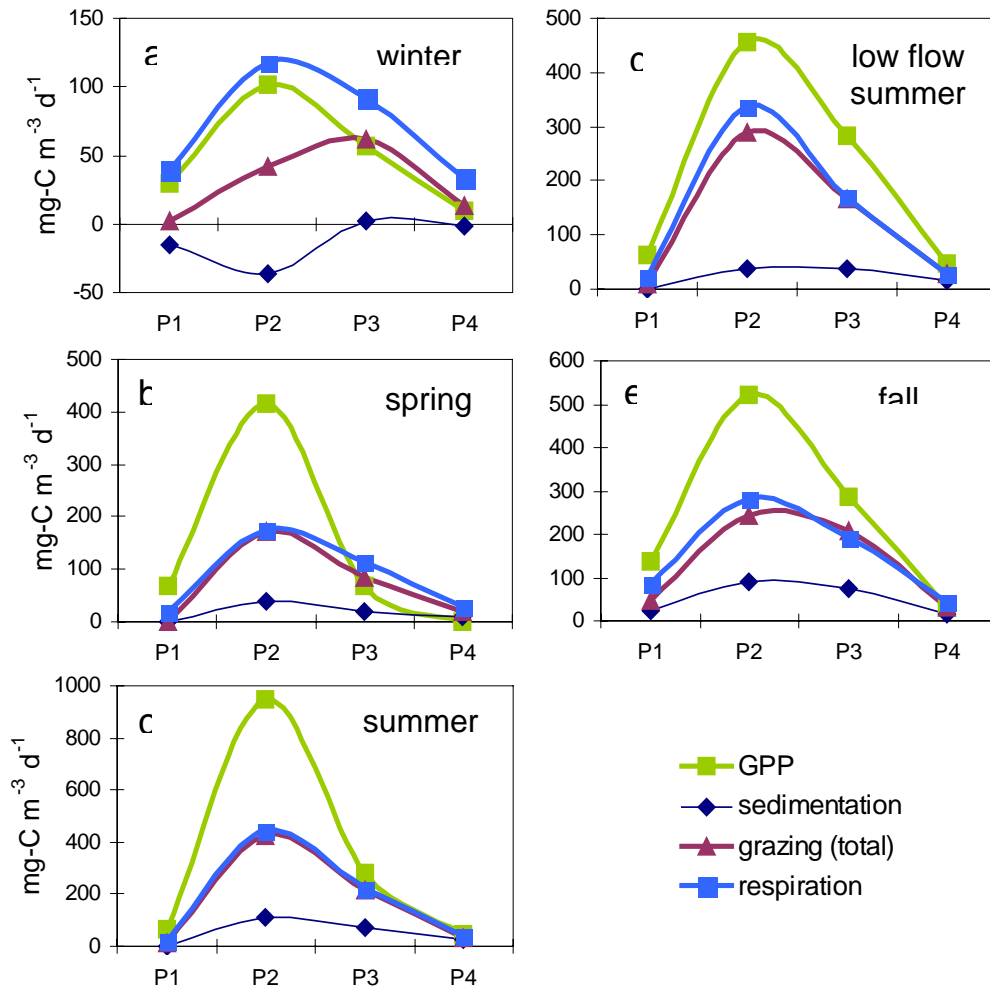


Figure 3. Summary of results of the inverse model of processes in the Mississippi River plume (from Breed et al. 2004). Note different scales during different seasons. The mid-salinity regions, P2 and P3, but especially P2, have the most activity, including the highest sedimentation rates. Sedimentation (vertical flux) tracks phytoplankton production (GPP) fairly well but is not the primary fate, equaling approximately 10-25 % of PP in zones 2 and 3 where most of the sinking flux occurs.

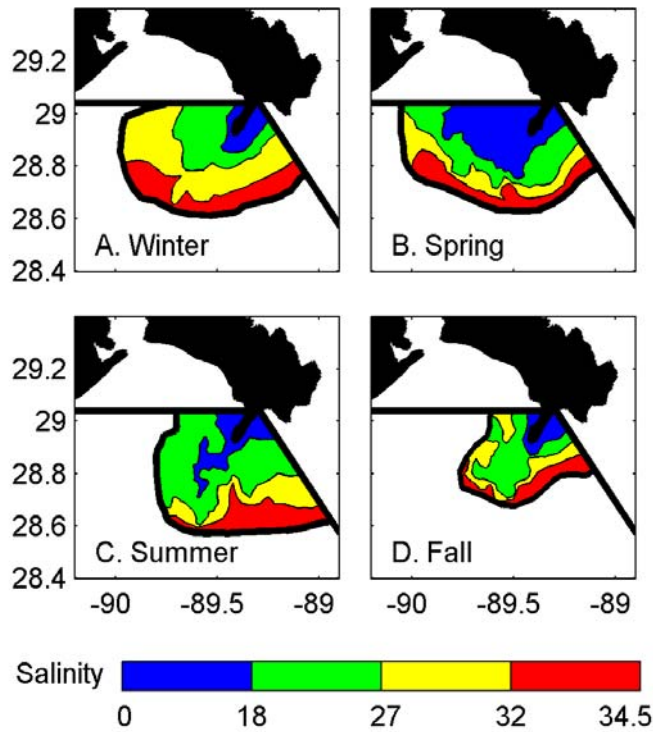


Figure 4. Surface salinity distributions showing the four subregions defined in a carbon budget model of the Mississippi River plume (from Green et al 2006a). Regions were identified from surface salinity derived from underway maps produced from multiple cruises, and from suspended sediment distribution derived from satellite imagery.

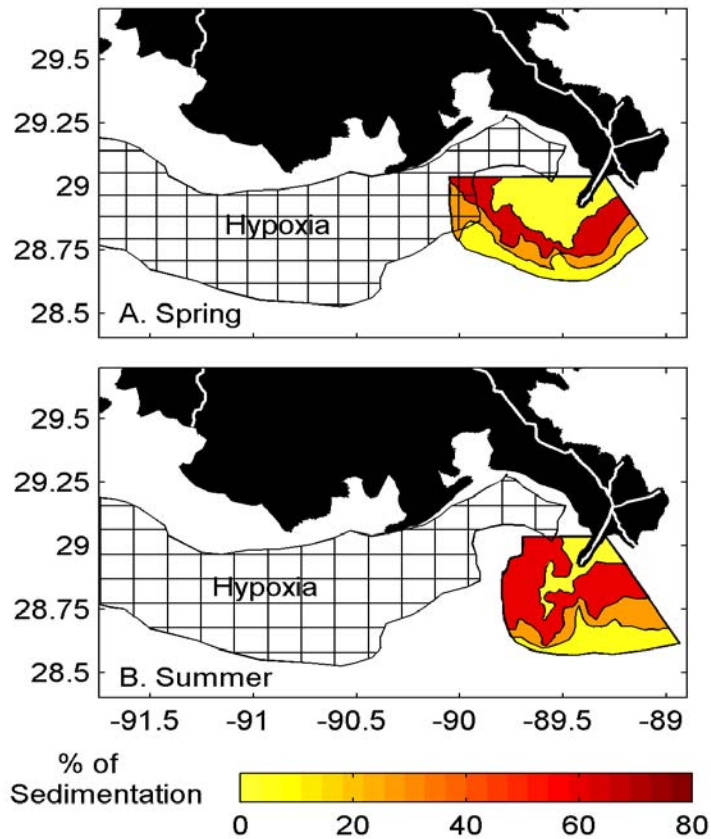


Figure 5. The 1996 hypoxic region relative to sedimentation of organic matter from the Mississippi River plume (from Green et al. 2006a). Spring and early summer organic matter sedimentation from the plume can contribute a maximum of 23 % of the O_2 demand necessary for establishment of hypoxia, assuming all sedimented organic matter is transported into the region that develops hypoxic conditions.