



Biological effects of Mississippi River nitrogen on the northern gulf of Mexico—a review and synthesis

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Abstract

The Mississippi River currently delivers approximately $1.82 \text{ Tg N year}^{-1}$ ($1.3 \times 10^{11} \text{ mol N year}^{-1}$) to the northern Gulf of Mexico. This large input dominates the biological processes of the region. The “new” nitrogen from the river stimulates high levels of phytoplankton production which in turn support high rates of bacterial production, protozoan and metazoan grazing, and fisheries production. A portion of the particulate organic matter produced in the pelagic food web sinks out of the euphotic zone where it contributes to high rates of oxygen consumption in the bottom waters of the inner shelf, resulting in the development of an extensive zone of hypoxia each summer. In spite of the significance of this river system to the coastal ocean of the northern gulf, we do not have an adequate understanding of the inputs, processing and ultimate fates of river nitrogen. Here we review available literature on this important system and propose a conceptual model showing how biological processes evolve in the river plume between the point of discharge and the point where plume waters are fully diluted by mixing with oceanic water.

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1. Introduction

The continental shelf of the northern Gulf of Mexico is physically and biologically dominated by the Mississippi River. The large input of fresh water contains high concentrations of dissolved nitrate whereas receiving waters of the open Gulf are permanently stratified and depleted of nitrate. In contrast to the continental shelves on the west and east coasts of the US, where upwelling and intrusions of slope water provide the major nutrient inputs, inputs in this system are primarily from the land via the Mississippi River. Furthermore, inputs of dissolved nitrogen have in-

creased dramatically within the past 50 years, contributing to major changes in this coastal ecosystem. The purpose of this paper is to review the effects of this river nitrogen on the biological process of the northern Gulf of Mexico, particularly the continental shelf west of the Mississippi delta where the impacts are the greatest. We then synthesize this information into a conceptual model representing an idealized plume, and make some suggestions about future directions for research in this important system.

2. The Mississippi River

The Mississippi River is one of the world's 10 largest rivers. It is approximately 6260 km in length,

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its average freshwater discharge into the northern Gulf of Mexico is $380 \text{ km}^3 \text{ year}^{-1}$, and its average sediment discharge is $150 \times 10^9 \text{ kg year}^{-1}$ (Meade et al., 1990; Meade, 1995). The magnitude of freshwater discharge is apparent from the distribution of waters with reduced salinity which can sometimes be observed in coastal waters as far west as Port Aransas, TX (Dinnel and Wiseman, 1986) and as far east as Miami, FL (Ortner et al., 1995) (Fig. 1). Additional riverine contributions are made by the major distributary of the Mississippi, the Atchafalaya River, which discharges to the west of the Mississippi River and carries approximately 34% of the total system flow. The drainage basin of the Mississippi–Atchafalaya system includes greater than 40% of the continental US, an area of $3.34 \times 10^6 \text{ km}^2$ (Bernier and Bernier,

1987). Receiving waters originate from the open Gulf of Mexico, a permanently stratified, oligotrophic, subtropical sea (Fig. 1).

Discharge from the Mississippi River delta is from two main channels and numerous smaller distributaries (Fig. 2). On average, discharge is strongest during the spring flood; fall discharge is only about 30% of the springtime high (Fig. 3). Typically, less than 1/3 flows eastward onto the Mississippi/Alabama shelf and most of the water discharging from the delta flows westward (Dinnel and Wiseman, 1986). Mississippi River water is discharged at outer shelf depths because prograded sedimentation over the past 700 years has built a large delta over the shelf (Figs. 1 and 2). At discharge, river water forms a buoyant plume that typically does not interact with the bottom because

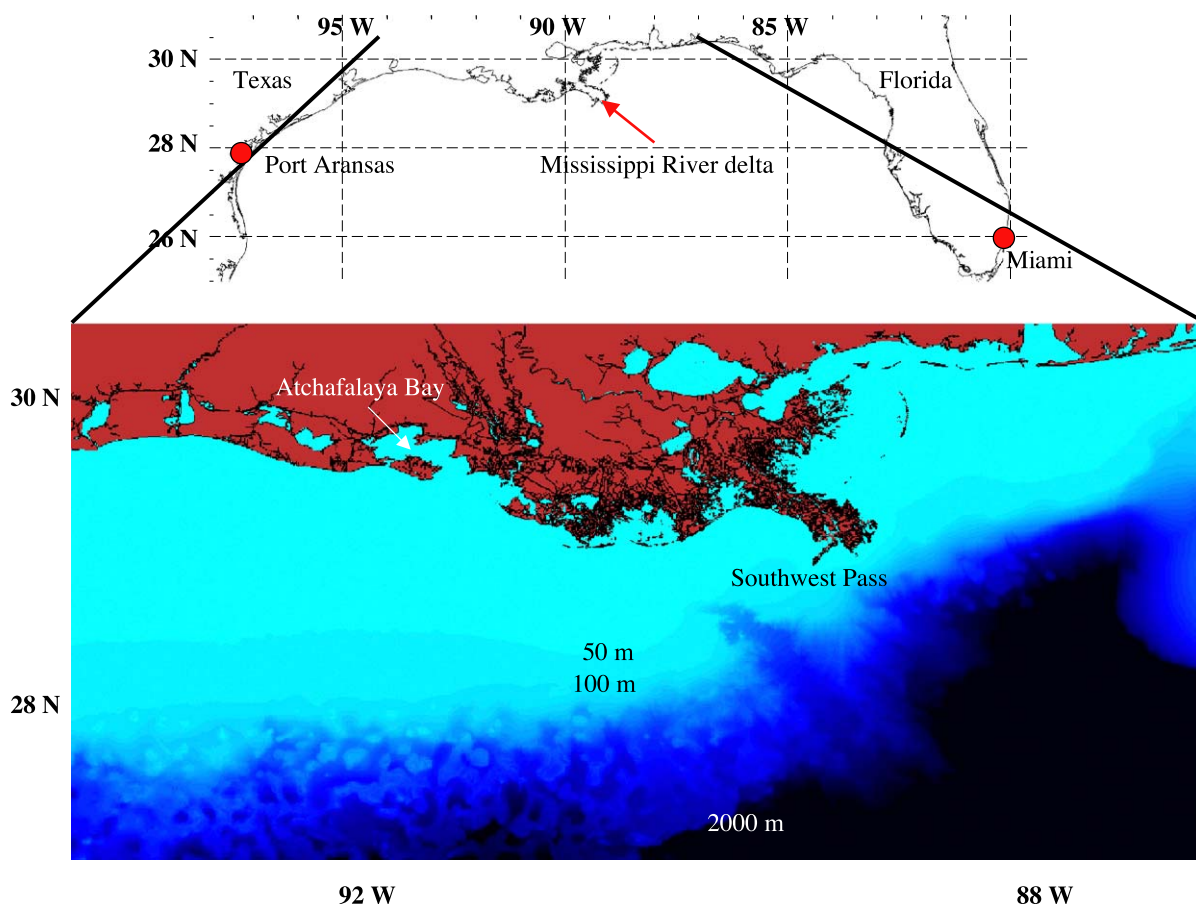


Fig. 1. The northern Gulf of Mexico. The delta of the Mississippi River has built out over much of the shelf during the past 700 years.

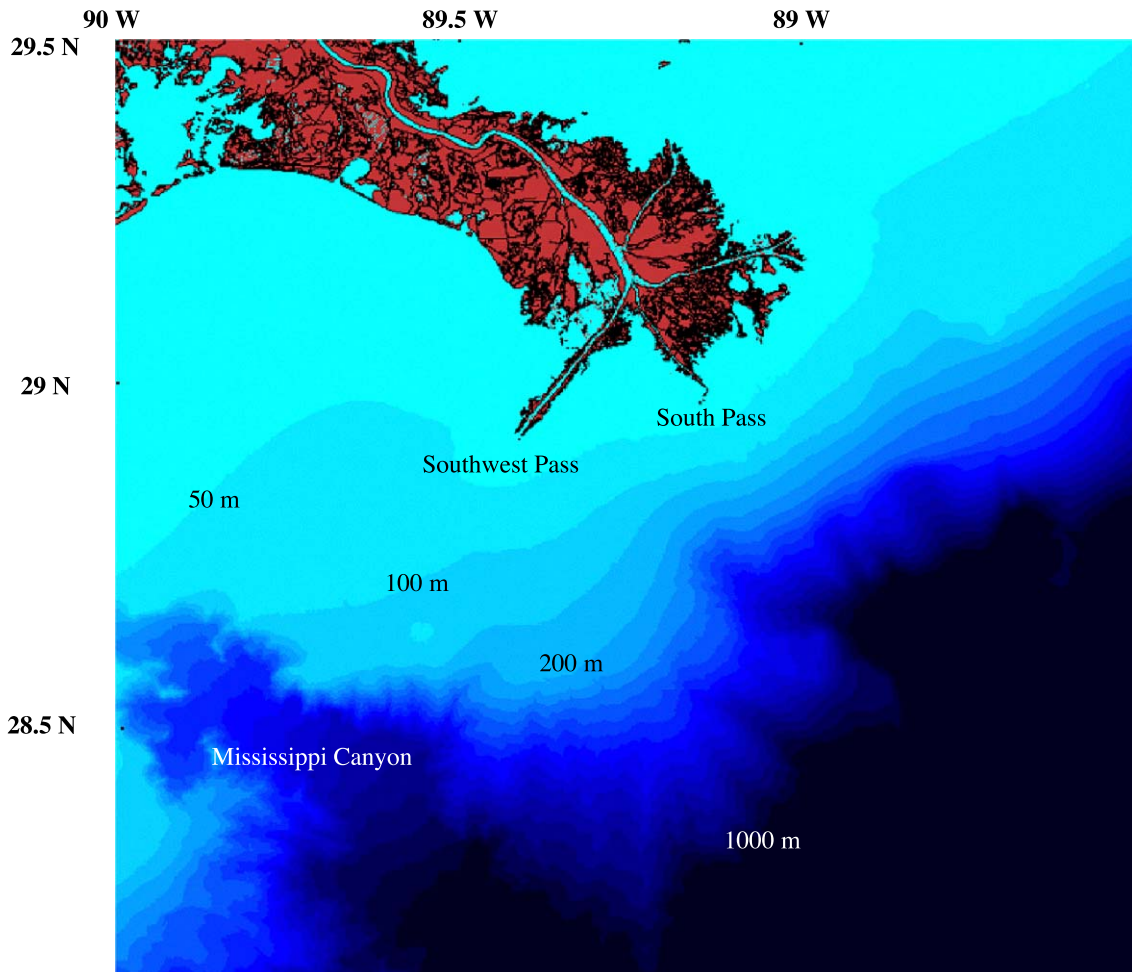


Fig. 2. The Mississippi River delta showing the main discharge channels, South Pass and Southwest Pass.

discharge is in relatively deep water. Mixing of river water by horizontal or vertical entrainment of surface or near-surface ocean water begins immediately downstream of the discharge sites (Garvine, 1982; Wright and Coleman, 1971). Because the amount of discharge is highly seasonal, entrainment zones and plume depths vary seasonally, being nearer the mouth and shallower during low discharge and farther afield and deeper during high discharge. Wind forcing, entrainment, and tidal forces are important in controlling the path and structure of the plumes (Rouse and Coleman, 1976).

There are significant short-term horizontal movements of surface plumes in response to local winds.

Winds are typically from the south or southeast from April to October because the Bermuda High tends to block continental air masses from impacting the northern gulf. From October to April, the regional effect of the Bermuda High is more limited and continental weather systems impact the northern gulf from the northwest (maritime Polar) or from the north (continental Polar or continental Arctic) on time scales of 3–10 days (Henry, 1979). On average, the steady wind regimes ahead of and behind the winter cold fronts change from 3.2 m s^{-1} (southerly component) ahead of the front to 5.5 m s^{-1} (northerly component) behind the front (Fernandez-Partagas and Mooers, 1975). The major change occurs over a distance of

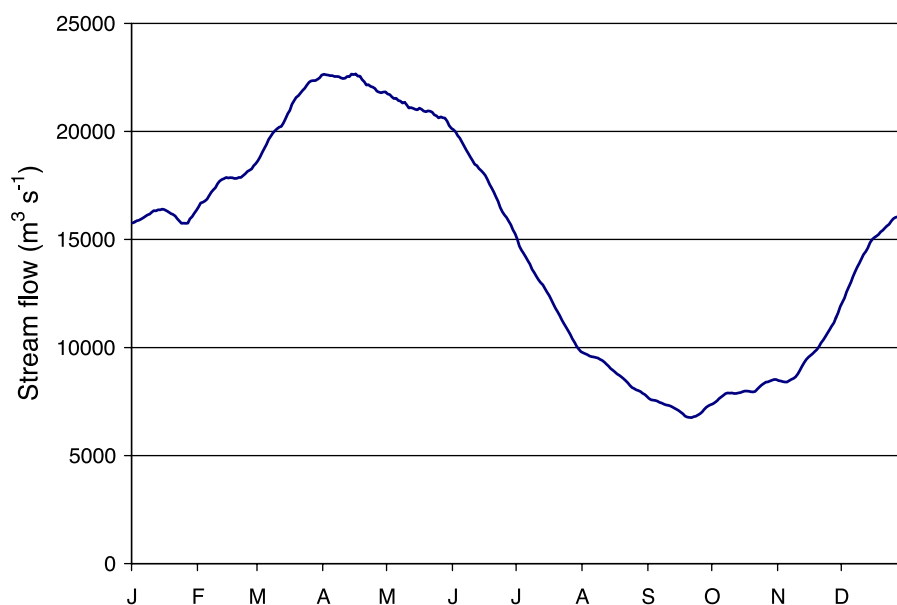


Fig. 3. Mississippi River discharge at Tarbert Landing, MS. This station is below the Mississippi–Atchafalaya branch point. Mean flow is derived from daily averages between 1967 and 2002 data (data from USACE).

about 140 km perpendicular to the front, which corresponds to a time-scale of about 4.5 h. Thus, during the summer, winds favor westward movement of plumes along the shelf whereas during winter, winds periodically tend to push plumes away from the coast. However, prevailing currents have the opposite seasonal effect (Cochrane and Kelly, 1986; Li et al., 1997). During the winter, currents favor a coastally trapped, westward moving plume while summer currents are lax or eastward, tending to detach the plume from the coast and stall westward flow. The combined effects of these opposing forces result in a highly dynamic and unpredictable physical steering regime though rarely is overall flow eastward.

In contrast to the Mississippi, the Atchafalaya River empties into the broad and shallow (~ 1 m deep) Atchafalaya Bay (Fig. 1) where there is minimal horizontal mixing with higher salinity gulf water. Bay salinities are generally <0.5 (all salinities in this paper are expressed on the practical salinity scale and thus are unitless). Atchafalaya River waters discharge at the inner continental shelf some 200 km from the shelf break, isolated from waters of the open gulf. The Atchafalaya plume does not separate from the bottom until it leaves the bay and inner shelf.

Because of vertical mixing in shallow waters, stratification and frontal boundaries offshore of Atchafalaya Bay are generally weaker than offshore of the Mississippi River delta. At the point of discharge, Atchafalaya River water is biogeochemically similar to Mississippi River water but coastal processes affecting Atchafalaya water differ from those of the Mississippi and are not considered further in this paper.

3. Nitrogen inputs

Five large rivers account for 45% of the total river-nitrogen flux into the entire Atlantic Ocean (Nixon et al., 1996). Approximately 85% of this nitrogen flux is from two rivers, the Amazon (54%) and the Mississippi (31%).

The Mississippi River delivers some 1.82 Tg N year⁻¹ (1.3×10^{11} mol year⁻¹) to the northern Gulf of Mexico (Howarth et al., 1996). On a yearly average, Mississippi River dissolved nitrogen is comprised of 53% nitrate, 43% organic nitrogen and 4% ammonium (Turner and Rabalais, 1991). Riverine concentrations of nitrate at Southwest Pass in the

Mississippi delta (Fig. 1) are typically $>100 \mu\text{M}$ (Dagg and Whitley, 1991; Goolsby et al., 1999; Lohrenz et al., 1999). On average, nitrate concentration in the river is positively correlated with freshwater discharge so the flux of nitrate into the gulf follows the seasonal pattern of freshwater discharge (Bratkovitch et al., 1994). This is not the case on shorter time scales.

A major portion of this nitrogen is anthropogenic. The large drainage basin of the Mississippi River encompasses an intensive agricultural region of moderate population density. Recently, the net input of dissolved nitrogen to the land within the drainage basin has been estimated to be $2220 \text{ kg N km}^{-2} \text{ year}^{-1}$ (Howarth et al., 1996; Goolsby et al., 1999). This nitrogen comes from fertilizer application ($1840 \text{ kg N km}^{-2} \text{ year}^{-1}$), nitrogen fixation from crops ($1060 \text{ kg N km}^{-2} \text{ year}^{-1}$) and atmospheric deposition of anthropogenic nitrogen ($620 \text{ kg N km}^{-2} \text{ year}^{-1}$). Most of this anthropogenic N-input is subsequently exported as food and feed or lost from the system by volatilization. Smaller amounts are denitrified, lost by manure volatilization or immobilized in the soil (Goolsby et al., 1999). However, approximately 25% of the net anthropogenic input to the drainage basin, $565 \text{ kg N km}^{-2} \text{ year}^{-1}$, is eventually delivered via the Mississippi River system to the coastal zone of the Gulf of Mexico (Howarth et al., 1996).

Concentrations of particulate organic nitrogen (PON) in river water vary between 4 and $25 \mu\text{M}$ (Trefry et al., 1994). PON is well correlated with riverine particulate organic carbon (POC), with an average C/N molar ratio of 8.5. Estimated annual inputs of PON are $2.5 \times 10^{10} \text{ mol year}^{-1}$ (Trefry et al., 1994). The proportion of organic nitrogen in Mississippi River particles is relatively constant at approximately 0.21% except during periods of especially low concentrations of suspended matter when the % N increases sharply. The majority of the variability in terrigenous PON input is associated with variation in the flux of total suspended matter. This can vary as much as an order of magnitude and it is non-linearly associated with freshwater discharge rate. Consequently, the highest inputs of PON typically occur during the winter–spring period of maximum runoff and lowest values generally occur during late-summer and early fall (Trefry et al., 1994).

The importance of other nitrogen inputs to the continental shelf of the northern Gulf of Mexico compared to riverine sources is not well known. Waters of the open Gulf of Mexico are permanently stratified and oligotrophic. The nitracline depth in the open gulf is typically greater than the depth of the shelf break, which is shallow in the northern gulf, approximately 90 m. Consequently slope water intrusions do not usually contain much nitrate and appear not to be an important source of N for the shelf (Li et al., 1997). Generally, shelf-slope exchanges are most likely to result in a net loss of dissolved inorganic and organic materials from the shelf. Exchanges of water are stimulated by occasional intrusions of the Loop Current or its spin-off rings onto the shelf, but these intruding waters usually have low nutrient concentrations. CZCS and SeaWiFS images typically indicate waters transported off the shelf have comparatively higher chlorophyll concentrations. Off-shelf flow can occur in response to cold air outbreaks (Nowlin and Parker, 1974) but this too is likely to result in a net loss of shelf nutrients. Localized coastal upwelling events bring nutrient poor water to the surface and transport nutrient rich coastal water offshore (Dagg, 1988). In addition, the continental shelf of the northern Gulf of Mexico is broad, extending out to $>200 \text{ km}$ in parts. This further reduces potential impact of slope water intrusions over much of the shelf environment.

Atmospheric deposition of DIN is small in comparison to river inputs, equivalent to $0.015 \text{ Tg N year}^{-1}$ or $<1\%$ of the Mississippi River N input (Goolsby et al., 1999).

Overall nitrogen budgets for the shelf between approximately 89.5°W and 97°W indicate that 54–67% of the shelf's nitrogen is contributed by the Mississippi–Atchafalaya River system (Lopez-Veneroni, 1998), further evidence that riverine nitrogen dominates nitrogen supply to this shelf.

4. Pelagic processes

The spatial and temporal scales over which the ecosystem processing of riverine nitrogen occurs are highly variable because of the wide ranges in discharge of river water and its constituents. During periods of low discharge, ecosystem processing of

nitrogen takes place within a more limited spatial range than during high discharge. To facilitate discussion and generalization of these processes, we use the terms near-field, mid-field and far-field, derived approximately from salinity distributions, as a means of defining spatial scale (Table 1). The absolute distance scales of each of these divisions vary widely.

4.1. Suspended sediment

When Mississippi River water reaches the ocean, it immediately forms a buoyant plume that spreads over the receiving ocean waters. This stratification increases light availability to plume waters but high turbidity from suspended sediments restricts light penetration. Within a short distance from discharge, light penetration is enhanced because the suspended lithogenic particles quickly sink out of the surface layer. Larger particles sink directly (Trefry et al.,

1994) and coagulation and aggregation processes enhance the sinking rates of smaller particles (Dagg et al., 1996 and references therein). Concentrations of suspended materials in surface waters at or near the discharge sites vary widely. For example, concentrations at Southwest Pass ranged between 11 mg l^{-1} in September 1975 and 200 mg l^{-1} in April 1983 (Trefry et al., 1992). Regardless of initial concentration, total suspended particulates in surface waters decrease to $<10\%$ of initial values within 5 km of discharge. A decrease to $<3 \text{ mg l}^{-1}$ was observed by 15–30 km in summer/fall 1990 and by 30–70 km in spring 1991 (Trefry et al., 1994). The concentration of suspended matter near the river mouth varies with season and discharge pattern so patterns of light penetration in the near-field plume are also variable (Trefry et al., 1994). Regardless, surface trapping of the river discharge into a shallow plume, combined with flocculation and sinking of suspended sedi-

Table 1

Measured ranges of water properties and ecosystem rates in the Mississippi River plume and adjacent Louisiana shelf

	Near field	Mid field	Far field
Salinity	0–18	18–32	>32
Nitrate (μM) ^a	20–200	0.05–50	0.05–5
Phosphate (μM) ^a	1–6	0.05–4	0.01–1
SPM (mg l^{-1}) ^b	3–200	0.5–20	0.3–6
Chlorophyll ($\mu\text{g l}^{-1}$) ^a % $<8 \mu\text{m}$ ^{c,d,e}	0–5	3–50	0.1–10
	10–80	10–90	60–>99
Phytoplankton growth rate (μ ; day^{-1}) ^{e,f}	0.1–1.5	0.5–2.9	0.1–1
Primary Production ^a ($\text{g-C m}^{-2} \text{ day}^{-1}$) ^a	0–1	0.5–11.5	0.2–3
Bacterial Production ^{g,h,i} ($\text{g-C m}^{-2} \text{ day}^{-1}$)	0.05–1	0.25–2	0.05–0.5
Bacterial Respiration ^{g,h,i} ($\text{g-C m}^{-2} \text{ day}^{-1}$)	0.05–1.5	0.25–3	0.05–0.75
Copepod population ⁱ (Individuals m^{-2}) ⁱ	1×10^4 – 5×10^4	2×10^4 – 5×10^5	1×10^4 – 3×10^5
Copepod Grazing Rate ^{i,j,k} ($\text{g-C m}^{-2} \text{ day}^{-1}$)	0.01–0.175	0.16–0.560	0.092–0.30
Total Mesozoo Grazing (Including Gelatinous) ^j	?	0.16–3.10	0.092–1.3
Microzooplankton Grazing Rate ^{c,k} (day^{-1})	0.2–0.5	0.14–1.12	0.08–1.57
Sedimentation Rate ^d ($\text{g-C m}^{-2} \text{ day}^{-1}$) ^d	0.1–1.2 ^l	0.1–1.80	0.01–0.75
Sedimentation Rate ^d ($\text{g-N m}^{-2} \text{ day}^{-1}$) ^d	?	0.06–0.27	0.03–0.07

McKee et al., unpublished data.

^a Lohrenz et al., 1999.

^b McKee et al., 2003; Trefry et al., 1992.

^c Strom and Strom, 1996.

^d Redalje et al., 1994.

^e Dagg and Powell, unpublished data.

^f Fahnenstiel et al., 1995.

^g Pakulski et al., 2000.

^h Gardner et al., 1994.

ⁱ Benner and Biddanda, 1998; Biddanda unpublished data.

^j Dagg, 1995; Dagg unpublished data.

^k Liu and Dagg, 2003.

^l Primarily terrigenous carbon.

ments, results in a light environment conducive to rapid phytoplankton growth (and associated nitrogen uptake) within several km of river discharge points.

4.2. Transport

Mississippi River water can be transported large distances, depending on wind and discharge level. Based on salinity distribution, Dinnel and Wiseman (1986) suggested that fresh water from the Mississippi River was advected alongshore on the inner shelf to the latitude of the US-Mexico border in approximately 2 months. Under different conditions, Ortner et al. (1995) reported a salinity signal from the Mississippi River off Miami, FL approximately one month after discharge. They also observed slightly elevated concentrations of dissolved organic matter (DOM) and chlorophyll associated with this water but not elevated nitrate, indicating depletion of nitrogenous nutrients is a near- or mid-field process. This is supported by direct observations of nutrient distributions. Elevated concentrations of nitrogenous nutrients associated with river plumes are observed over time and space scales on the order of days and 10–100 km (Dagg and Whitlege, 1991; Hitchcock et al., 1997). Biological responses and associated recycling of “new” nitrogen from the river occurs over larger scales than those of nitrate uptake but observations indicate most biological activity stimulated by inputs of river nitrogen is below detection limits within considerably smaller time and space scales than observable freshwater signals.

4.3. Phytoplankton

Once suspended sediments begin to settle, the surface plume becomes ideal for phytoplankton growth because it is a nutrient-rich and high-light environment (Lohrenz et al., 1990, 1997; Lohrenz et al., 1999). The large input of “new” nitrogen from the Mississippi River into the shelf ecosystem stimulates tremendous blooms of phytoplankton over spatial scales of tens to hundreds of kilometers and time scales of hours to several days (Lohrenz et al., 1990, 1997; Hitchcock et al., 1997). However, mixing diagrams show nitrate sometimes behaves conservatively within the central region of the plume (Hitchcock et al., 1997), indicating the high velocity plume core is

not the major site of N uptake and phytoplankton growth. Instead, frontal boundaries between plume and receiving waters are the regions of most rapid N uptake by phytoplankton (Hitchcock et al., 1997).

There is significant seasonality to the uptake rate of nitrate. During winter and early spring, the nitrate-rich river water spreads farthest before nitrate becomes depleted because discharge is high, concentrations of suspended particulate materials are maximum and water temperatures are coolest. At this time of year, concentrations as high as 20 μM have been observed in surface waters at salinities >25 (Chin-Leo and Benner, 1992) and river nitrate has been observed in surface waters at distances >100 km from discharge sites (Dagg and Whitlege, 1991). By early summer, riverine nitrate distribution is more restricted but can still be observed over significant distances. For example, Pakulski et al. (1995) observed high nitrate concentrations in the river (115 μM) decreased non-conservatively to a still significant level (3 μM) at a surface salinity of 36. During low river flow in the summer and fall however, nitrate is typically gone within a few tens of kilometers from the discharge sites (Dagg and Whitlege, 1991; Hitchcock and Whitlege, 1992; Lohrenz et al., 1999). Chin-Leo and Benner (1992) observed summertime NO_3^- concentrations decreased to levels below detection at surface salinities <25 .

Phytoplankton stock is low in the turbid near-field plume but reaches high levels in the mid-salinity plume region. Chlorophyll concentration at intermediate salinities is commonly $>25 \mu\text{g l}^{-1}$ (Lohrenz et al., 1990, 1999; Redalje et al., 1994). Chlorophyll concentrations decline in the far-field. An analysis of phytoplankton species indicates that blooms in plume waters are comprised primarily of a community of chain-forming diatoms dominated by *Skeletonema costatum* and *Chaetoceros* spp. (Bode and Dortch, 1996).

There is a direct coupling between river inputs of dissolved inorganic nitrogen and the magnitude of phytoplankton production in the delta vicinity (Lohrenz et al., 1997). In general, photic zone rates of integrated phytoplankton production are up to an order of magnitude greater in the mid-field plume region than in far-field shelf waters (Redalje et al., 1994). A seasonal cycle is observed in plume production, with highest rates in summer and lowest rates in

winter (Redalje et al., 1994). In this study, integrated primary production in the mid-field region ranged from a low of $0.40 \text{ g C m}^{-2} \text{ day}^{-1}$ during March to a high of $8.17 \text{ g C m}^{-2} \text{ day}^{-1}$ in summer. Primary production was lower in adjacent shelf (far-field) waters, averaging $0.12 \text{ g C m}^{-2} \text{ day}^{-1}$ in winter and $3.02 \text{ g C m}^{-2} \text{ day}^{-1}$ in summer. Spring and fall rates were intermediate in both regions (Redalje et al., 1994). Lohrenz et al. (1999) reported a similar trend from analysis of an expanded data set that included the Redalje et al. (1994) data. As plume waters are transported away from the mid-field region of peak algal production, rates decline due to nutrient limitation (Redalje et al., 1994; Lohrenz et al., 1999).

Larger cells generally account for a greater fraction of productivity at low and intermediate salinities within the plume. Redalje et al. (1994) showed the $>8 \mu\text{m}$ components of the phytoplankton community were responsible for 34–50% of the integrated phytoplankton production in the mid-field region.

Instantaneous growth rates of phytoplankton agree with the pattern of primary production. Some of the highest reported in situ growth rates of marine phytoplankton, between 2.0 and 3.0 day^{-1} , have been observed in surface waters of the Mississippi plume (Fahnenstiel et al., 1995). Growth rates declined rapidly with depth because of light limitation induced by fine-grained lithogenic materials (Fahnenstiel et al., 1995). Microflagellate and diatom growth rates were not significantly different within mid-field plume waters but at far-field stations diatom growth rates were significantly lower, apparently because of silicate limitation (Fahnenstiel et al., 1995; Dortch and Whitedge, 1992). At locations still farther afield where nutrient concentrations were lower, growth rates of the entire community declined. In nutrient enrichment experiments done at farfield stations on the shelf, small phytoplankton and diatoms had high growth rates (Strom and Strom, 1996).

4.4. Dissolved organic nitrogen

On average, 43% of the dissolved N in the river is in the form of DON (Turner and Rabalais, 1991). It is generally considered refractory and unavailable for rapid utilization by bacteria. This is supported by indications that remineralized organic nitrogen in the Mississippi River plume is primarily of marine rather

than terrestrial origin (Gardner et al., 1994). There is evidence however, that riverine substrates are not entirely refractory and may support some bacterial production (Chin-Leo and Benner, 1992; Benner and Opsahl, 2001). In other regions, photo-oxidation can degrade refractory riverine dissolved organic matter to forms available to bacteria (e.g. Bushaw et al., 1996; Opsahl and Benner, 1998) and that may be the responsible process here also.

Riverine particulate materials may also contribute to the dissolved organic nitrogen pool. Significant amounts of organic matter are dissolved from fluvial particles that are introduced to shelf regions by large rivers, although this tends to occur in the benthos (Keil et al., 1997; Mayer et al., 1998). Recent evidence suggests this pool of organic N may be approximately as large as the inputs of dissolved inorganic nitrogen (Mayer et al., 1998). Little is known about its utilization but if it is primarily a benthic process, it will not have immediate effects on the Mississippi River plume.

4.5. Grazing

Zooplankton grazing is typically the most important immediate fate of marine phytoplankton (Banse, 1992). Three groups dominate zooplankton grazing of phytoplankton in the northern Gulf of Mexico: the protozoa, the gelatinous zooplankton, and the copepods.

Protozoan populations respond quickly when phytoplankton food is abundant. Protozoa are important grazers in the mid-field plume where phytoplankton growth rates are high. In this region, there is close coupling of heterotrophic and autotrophic populations, particularly in the $<20 \mu\text{m}$ size fraction (Bode and Dortch, 1996; Liu and Dagg, 2003), and protozoa consume large numbers of phytoplankton. For example, Fahnenstiel et al. (1995) reported microzooplankton grazing rates on cells $<20 \mu\text{m}$ averaged 82% of algal growth rates, which themselves were very high, during summer. In contrast, no microzooplankton grazing was observed on cells $>20 \mu\text{m}$ (Fahnenstiel et al., 1995), indicating that chain forming diatoms are not subject to the same degree of protozoan grazing mortality as smaller cells in the near- and mid-field regions. In the far-field slightly to the west, phytoplankton growth rates were nutrient limited but still

quite high with rates $>1.0 \text{ day}^{-1}$ measured on several occasions (Strom and Strom, 1996). Here, microzooplankton also consumed significant portions of phytoplankton; the grazing: growth ratio was typically between 0.3 and 0.9 and microzooplankton biomass was correlated with chlorophyll concentration. In contrast to Fahnenstiel et al. (1995), Strom and Strom (1996) observed significant consumption of large diatoms by microzooplankton (heterotrophic dinoflagellates) at some stations. Liu and Dagg (2003) showed microzooplankton grazing rates were low at near-field stations, peaked at intermediate salinities and then declined at their far-field station. Although grazing rates declined in the far-field, phytoplankton growth declined also because of nutrient limitation and, in this area, grazing $>$ growth (Liu and Dagg, 2003). Generally, a large fraction of the nitrogen incorporated into nanophytoplankton, and a smaller fraction of that incorporated into larger phytoplankton, is grazed by protozoans in the plume.

Gelatinous zooplankton, primarily larvaceans, salps and doliolids, often form large swarms in coastal regions of the northern Gulf of Mexico. High concentrations of the larvacean, *Oikopleura dioica*, are commonly found in the vicinity of the Mississippi River plume (Dagg, 1995; Dagg et al., 1996) and this organism is an important component of the grazer community. For example, during May 1992 *O. dioica* populations filtered a mean of 20% of the upper 5 m daily at stations within the Mississippi River plume (Dagg et al., 1996). Like protozoans, larvaceans have high rates of population growth. Development time from egg to adult is <1 day at summertime temperatures in the northern Gulf of Mexico (Hopcroft and Roff, 1995) and at maturity each adult can release as many as 400 eggs. *O. dioica* feeds non-selectively on particles in the size range between 0.2 and 20 μm (Bedo et al., 1993), including bacteria, phytoplankton and lithogenic materials. Quantitative impacts of other gelatinous zooplankton have not been directly measured in this region.

The copepod community also consumes significant portions of the phytoplankton stock and productivity in the northern Gulf of Mexico. Depending on the time of year, between 14% and 62% of the daily algal production can be consumed by the copepod community in the mid- or far-field regions (Dagg, 1995). Lithogenic particles are also consumed by copepods

(Turner, 1984) but copepods are inefficient feeders on particles $<2\text{--}3 \mu\text{m}$ and are incapable of ingesting sub-micron sized particles. On the other hand, particles larger than 20 μm , including protozoans, are readily and preferentially consumed by copepods. Copepods grow more slowly than protozoans or gelatinous zooplankton, and their population levels are more closely related to longer-term, seasonal time scales. Liu and Dagg (2003) showed that copepod grazing was small compared to microzooplankton grazing but that copepods enhanced the rate of phytoplankton decline in the far-field, especially the large phytoplankton.

4.6. Higher trophic levels

The northern Gulf of Mexico is a region of high fisheries production; approximately 66% of the total fishery landings for the U.S. Gulf coast are in Louisiana (Chesney et al., 2000). This can be partially attributed to the large flux of “new” nitrogen discharged by the Mississippi River. In other coastal regions, high nitrogen inputs support a short food chain conducive to high trophic transfer from phytoplankton to fish (Runge, 1988; Houde and Rutherford, 1993; Legendre and Rassoulzadegan, 1995) and this appears to be the case for the northern Gulf of Mexico.

The production of copepods, the major food of larval and juvenile stages of many fish species is high in plume-influenced waters (Dagg, 1988; Dagg and Govoni, 1996). Concentrations of copepod developmental stages, especially the early naupliar stages, are high in mid-field plume waters. Winter and spring concentrations are typically between 50 and 100 nauplii l^{-1} and summer concentrations are much higher, sometimes greater than 1000 l^{-1} (Dagg et al., 1987; Dagg and Whitley, 1991; Dagg and Govoni, 1996). Although feeding conditions in regions affected by the large inputs of river nitrogen appear favorable for fish larvae, efforts to measure clear responses in the feeding, growth and recruitment of larval fish have had mixed success (Grimes and Kingsford, 1996), in part because the study regions are so physically dynamic but also because the plume regions offer good feeding opportunities for predators on larval fish (Grimes and Kingsford, 1996). Nevertheless, ichthyoplankton abundance is significantly higher in regions at the

boundary between plume and oceanic water than in adjacent shelf waters (Govoni et al., 1989; Grimes and Finucane, 1991; Govovni, 1997).

4.7. Water-column C&N remineralization

Generally, bacterial production is higher in plume waters than in regions outside the plume. Maximum bacterial abundance and production rate in the northern Gulf of Mexico are observed in plume waters of intermediate salinity (Biddanda et al., 1994; Chin-Leo and Benner, 1992). Abundances and production rates are within the ranges reported for other coastal and estuarine waters. Bacterial production in the near- and mid-field river plume is high, between 5 and 90 $\mu\text{g C l}^{-1} \text{ day}^{-1}$, similar to values reported from estuaries such as Delaware Bay and Chesapeake Bay (Chin-Leo and Benner, 1992).

Riverine (terrestrial) DOC may contribute to bacterial production, especially during the winter when phytoplankton production is low. Chin-Leo and Benner (1992) determined that phytoplankton derived substances supported only 18% of bacterial production during the winter, suggesting that riverine OM supported most bacterial production. During the summer, although bacterial production was higher so was phytoplankton production, and phytoplankton derived materials supported approximately 68% of bacterial production. These measurements were corroborated by Benner and Opsahl (2001) who chemically analyzed DOC across a salinity gradient. They detected higher concentrations of labile substrates in riverine DOM during the winter and lower during the summer. Neutral sugars derived from phytoplankton exudates were a higher fraction of total DOM in intermediate salinity regions of the plume, especially during the summer when they constituted as much as 24% of total DOM.

Bacterial growth and nitrogen regeneration processes are tightly coupled within the river plume in the summer (Cotner and Gardner, 1993; Dortch and Whitlege, 1992). Maximum regeneration rates occur in the surface waters and at intermediate salinities. Cotner and Gardner (1993) developed a conceptual model consistent with other models of plume processes: in the river and the near-field, NH_4 regeneration rates by bacteria are low because of poor substrate conditions, DON is primarily terrestrial in origin because phytoplankton production is low and riverine

DON is refractory; in the mid-field at intermediate salinities, bacterial NH_4 regeneration rates are high because high phytoplankton production and biomass provides plentiful labile material; and in the farfield, phytoplankton production is greatly reduced by nutrient limitation and therefore bacterial regeneration of NH_4 is also greatly reduced.

In spite of a wide range in NH_4 regeneration rates, NH_4 concentrations within the plume are always low. After regeneration, immediate reuptake of NH_4 by both phytoplankton and bacteria is likely responsible for low NH_4 concentrations. In addition, Pakulski et al. (1995) showed that nitrification rates in plume waters are high. Mixing lines of NO_3 vs. salinity showed nonconservative behavior, with depressed NO_3 at low and intermediate salinities. In their experiments, incubations indicated that there was net regeneration of NO_3 at salinities of 18 and 27 and drawdown of NO_3 was all between 0 and 10. They concluded that NO_3 production at intermediate salinities was supported by regenerated NH_4 , and regeneration via bacteria and microzooplankton grazing were both important. Nitrifying bacteria were responsible for more respiration than heterotrophic bacteria at intermediate salinities (Pakulski et al., 1995).

However, bacteria are not always the major remineralizers in the plume. Chin-Leo and Benner (1992) observed that organisms $>1 \mu\text{m}$ (i.e. not bacteria) were responsible for approximately 50% of community respiration in some seasons and regions of the plume. Similarly, Cotner and Gardner (1993) and Gardner et al. (1994) observed that a large fraction of the NH_4 regeneration was by organisms $>1 \mu\text{m}$. This is consistent with the high microzooplankton and mesozooplankton grazing rates reported in mid-field plume waters (Dagg, 1995; Strom and Strom, 1996; Liu and Dagg, in press).

4.8. Sinking

Redalje et al. (1994) simultaneously measured phytoplankton production and vertical particulate flux at the base of the mixed layer during four times of the year in plume (mid-field) and nearby shelf (far-field) waters. Flux was not closely related to production over the annual cycle. In both plume and shelf regions during summer when phytoplankton production m^{-2} is highest, vertical export was equivalent to only 3–9% of

primary production, indicating most production was recycled within the upper water column at that time. In contrast, during late winter when phytoplankton production was lowest, vertical export was large, equivalent to 64–266% of primary production. POC flux in the plume region ranged between $0.29 \text{ g C m}^{-2} \text{ day}^{-1}$ in the summer to $1.80 \text{ g C m}^{-2} \text{ day}^{-1}$ in the spring, with intermediate values (0.95 and $0.69 \text{ g C m}^{-2} \text{ day}^{-1}$) in the winter and fall, respectively. Riverborne suspended POM did not make a significant contribution to trap collected materials; sediment trap δC^{13} values reflected characteristics of marine production (Eadie et al., 1994). PON fluxes showed approximately the same pattern as POC, although the C/N ratio of trap material was lowest (4.8) during the summer period of lowest flux and highest (6.6) during the spring period of highest flux (Redalje et al., 1994). It is not clear why material in the summer, when it presumably contained little fresh phytoplankton, had a higher nitrogen content than in the spring when sinking material was presumably dominated by fresh phytoplankton.

The total area impacted by the river plume varies over time because there are large variations in river discharge. The impacts of the river and its dissolved and particulate constituents on the continental shelf are not only caused by processes operating on a m^{-2} basis but also by the area over which these processes occur. For example, primary production m^{-2} is highest in the summer but the area of high productivity associated with the plume is greatest during the spring when river discharge is at its annual maximum. The spatially integrated productivity resulting from the input of river nitrate may be greater in the spring than the summer, even when higher rates m^{-2} are measured in the summer. This is important to keep in mind when considering riverine impacts on the shelf as a whole. Similarly, the amount of POM sinking to the bottom in the northern Gulf of Mexico is a function of flux m^{-2} and the area over which the flux occurs. In this case however, both components are maximal in the spring and therefore the total amount of POM sinking from the photic zone is greatest in the spring.

5. Benthic processes

Once organic matter reaches the bottom, benthic processes determine how much carbon and nitrogen

are stored, buried, respired, or recycled back into the water column.

5.1. Deposition

Particulate material settling out of the pelagic environment is deposited on the bottom. Deposition of both allochthonous and autochthonous organic carbon, measured by ^{234}Th in the area west of the Mississippi River delta, is between 0.1 and $1.2 \text{ g C m}^{-2} \text{ day}^{-1}$ (McKee and Twilley, 1998), comparable to the direct flux of autochthonous POC measured by sediment traps deployed at the base of the photic zone (Redalje et al., 1994) which ranged between 0.3 and $1.8 \text{ g C m}^{-2} \text{ day}^{-1}$. Redalje et al. (1994) generally observed higher rates of sedimentation in the area they defined as the plume, the mid-range salinities along the mixing gradient. Lower sedimentation rates persisted further to the west, in higher salinity water over the shelf. Redalje et al. (1994) also measured PON sedimentation, which ranged from 0.06 to $0.27 \text{ g N m}^{-2} \text{ day}^{-1}$ in the midfield plume and 0.03 and $0.07 \text{ g N m}^{-2} \text{ day}^{-1}$ over the far-field shelf areas. Considering the similarity between sediment trap and deposition data for POC, it is reasonable to assume that PON deposited on the bottom is in the same range as that measured in sediment traps, although differential remineralization rates for PON and POC may alter this somewhat.

5.2. Resuspension, transport and remineralization

Significant portions of deposited organic matter are resuspended, transported and/or remineralized before burial. McKee and Twilley (1998) estimated that 30% of the organic carbon deposited in the region immediately west of the delta is remineralized within 4 months. It is reasonable to assume at least 30% of sedimented organic nitrogen is also released in the first 4 months in this region. Farther to the west of the immediate deltaic-shelf environment, Rowe et al., 1991 reported average rates of oxygen consumption on the Louisiana shelf equivalent to the remineralization of 70 or $0.2 \text{ g C m}^{-2} \text{ day}^{-1}$. The approximate average primary production in this shelf region is 325 or $0.9 \text{ g C m}^{-2} \text{ day}^{-1}$ (Redalje et al., 1994). Benthic carbon remineralization was thus equivalent to 22% of productivity. These studies suggest benthic recycling

could be a significant source of N for the water column. However, carbon and nitrogen remineralized into the lower water column are unlikely to contribute large quantities of nutrients to the river plume. The plume is buoyant and is separated from the bottom by some distance because discharge is at mid- to outer-shelf depths. Furthermore, the water column on the shelf is typically strongly stratified during most of the late spring, summer and fall, limiting the mixing of nutrients from the deeper water column into the surface layer. Remineralized N from the benthos will mix into the upper water column during late fall and winter when stratification breaks down in shelf waters and water column mixing occurs. Even in winter however, the plume area remains stratified and separated from the bottom, and nutrient inputs from the benthos are unlikely to influence the near- and mid-field regions.

Near bottom or benthic decomposition of organic matter consumes large amounts of oxygen from the bottom waters. Replenishment of bottom water oxygen by diffusion and mixing from the upper waters is restricted in the summer because of temperature and salinity induced stratification. The resulting two-layer system on the shelf effectively seals off the bottom water until fall overturn. Water column stratification combined with high organic matter input to the bottom and high remineralization rates results in the development of bottom water hypoxia during most years. Hypoxia, defined as oxygen concentrations $< 2 \text{ mg l}^{-1}$, typically becomes widespread during summer (Rabalais et al., 1999). Hypoxic waters can be present as early as February and as late as October and persistent, severe hypoxia is typical from mid-May to mid-September (Rabalais et al., 1994). Bottom water hypoxia disappears during the fall as overturn of water on the shelf replenishes oxygen throughout the water column. It is also during this time that regenerated bottom nutrients would be mixed into the upper water column.

Chin-Leo and Benner (1992) estimated 26–56 days are required during the summer for bacteria in waters below the pycnocline to reduce the oxygen concentration from a saturated value to the measured in situ concentration of 0.6 ml l^{-1} . Their rates did not include additional oxygen consumption by organisms $> 1 \text{ } \mu\text{m}$, nor by the benthos. Rowe (2001) provided a more complete analysis of the conditions leading to

bottom water hypoxia but generally observed durations required for hypoxia development were similar to those of Chin-Leo and Benner (1992). Justic et al. (1993) estimated that summertime respiration rates by bottom water and benthos can deplete oxygen in approximately 14–70 days, assuming no oxygen replenishment.

Annual shelf-wide surveys of the distribution of oxygen from the Mississippi River to the Louisiana–Texas border have been made each summer since 1985. Hypoxia was observed in bottom water during each summer survey with the exception of 1988, a summer of exceptionally low freshwater input from the Mississippi River. The area of hypoxia has been as large as $20,000 \text{ km}^2$ (Rabalais et al., 1999). More limited data from earlier years indicate hypoxia occurred at least as early as 1973, and possibly occurred as early as the mid 1960s (Renaud, 1986; Justic et al., 2002). Cores representing the past 100 years of sediment accumulation show increasing concentrations of organic matter. Virtually all of this increase is marine in origin (Eadie et al., 1994). Stable isotope signatures and accumulation patterns of organic carbon in these cores indicate water column productivity has increased significantly since the 1960s, a period that coincides with a doubling of nitrate loading from the Mississippi River. Presence of glauconite, a mineral associated with hypoxia, suggests hypoxia existed but was less common before the 1940s (Nelsen et al., 1994). The foraminifera assemblage from these cores indicates a significant shift in species composition at about the same time, and the more recent community structure is less diverse and more tolerant of low oxygen conditions (Nelsen et al., 1994). Taken together, these data indicate the intensity and areal extent of hypoxia have increased with increased nitrogen loading to the shelf from the Mississippi River (Turner and Rabalais, 1991; Rabalais et al., 1999).

Data also indicate significant variability in the extent and distribution of hypoxia (Wiseman et al., 1997; Rabalais et al., 1999). To date, this variability is not completely predictable. Statistical analysis has shown a significant correlation between river flow and oxygen deficit in bottom water on the inner shelf (Justic et al., 1993). This correlation is phase shifted two months and does not explain all the variability, indicating other factors are also significant. Among

many potentially important processes, the contribution to eutrophication by long-term declines in top-down control has not been explored in this region (Jackson et al., 2001; Daskalov, 2002).

5.3. Denitrification

Limited data indicate denitrification removes a large percentage of the nitrogen that is remineralized in aquatic sediments (Seitzinger and Giblin, 1996; Seitzinger, 1988; Christensen, 1994). In coastal marine sediments, 20–75% of the benthic N efflux is N_2 , and denitrification in estuaries removes an amount of N equivalent to 40–50% of DIN inputs (Seitzinger, 1988). In Fourleague Bay, a shallow estuarine arm of the Atchafalaya River, denitrification was equivalent to 50% of the riverine nitrate entering the estuary (Smith et al., 1985). In the northern Gulf of Mexico to the west of the Mississippi river delta, denitrification rates estimated by Gardner et al. (1993) were consistent with these generalizations (Seitzinger and Giblin, 1996) but Childs et al. (2002) reported denitrification rates on the Louisiana shelf west of the Mississippi river delta were on the low end of those reported for other systems. This process is likely a major sink for nitrogen inputs from the Mississippi River but there are few data.

5.4. Burial

In the region immediately west of the Mississippi River delta, burial rates of organic carbon are between 25–300 $g\ C\ m^{-2}\ year^{-1}$ (Eadie et al., 1994; McKee and Twilley, 1998). Assuming a C/N ratio of 6 such as might be expected from fresh sinking phytoplankton, this is equivalent to 4.2–50 $g\ N\ m^{-2}\ year^{-1}$ (Redalje et al., 1994) but assuming a more conservative C/N ratio of 9 such as that present in riverine POM, the range would be 2.8–33 $g\ N\ m^{-2}\ year^{-1}$. If remineralization rates in sediment organic matter are higher for N than they are for C, these burial estimates for N should be lowered. Highest rates of burial are found in the vicinity of Southwest Pass and rates generally decrease with distance from the river mouth (McKee and Twilley, 1998).

In the immediate vicinity of riverine discharge, up to 70% of carbon (and presumably also nitrogen) burial is from terrestrial sources. This component

decreases to <5% at farfield sites (McKee and Twilley, 1998), where marine carbon dominates burial. Burial rates of organic carbon, and presumably also nitrogen, have increased since 1930 but the increase is attributable primarily to marine carbon, not terrestrial carbon (Eadie et al., 1994). Higher rates of flux to the bottom are due to greater water column productivity supported by increased NO_3 loading. Eadie et al. (1994) demonstrate there has been a linear relationship between increased NO_3 loading and increased organic carbon burial since 1950.

6. Synthesis

Here we develop a preliminary conceptual model of the biological responses within the river plume. Data are limited for some elements of our conceptualization. Spatial scales are loosely defined in terms of near-field where salinity is low, intermediate or mid-field where salinities are approximately 18–32, and farfield where salinities are generally >32 (Table 1). The absolute spatial scales and the association of a particular process with a specific salinity range vary with the magnitude of freshwater discharge and other factors that are not fully understood. The biological processes within the plume interact in a nonlinear manner and are superimposed on a highly dynamic physical regime that continuously but nonuniformly mixes with receiving waters. Scales of distance or time can be compressed or expanded depending on discharge, wind, tide and other factors. Crossplume 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. Our model is therefore a simplified picture of processes within an idealized plume. We believe the elements of our conceptual model are representatives of plume processes but recognize that any empirical analysis or survey of the plume is unlikely to show such orderly patterns.

6.1. Conceptual model of plume water evolution

Our model of plume processes is summarized in the three panels of Fig. 4. Fig. 4a,b shows processes relating to small phytoplankton cells and large phy-

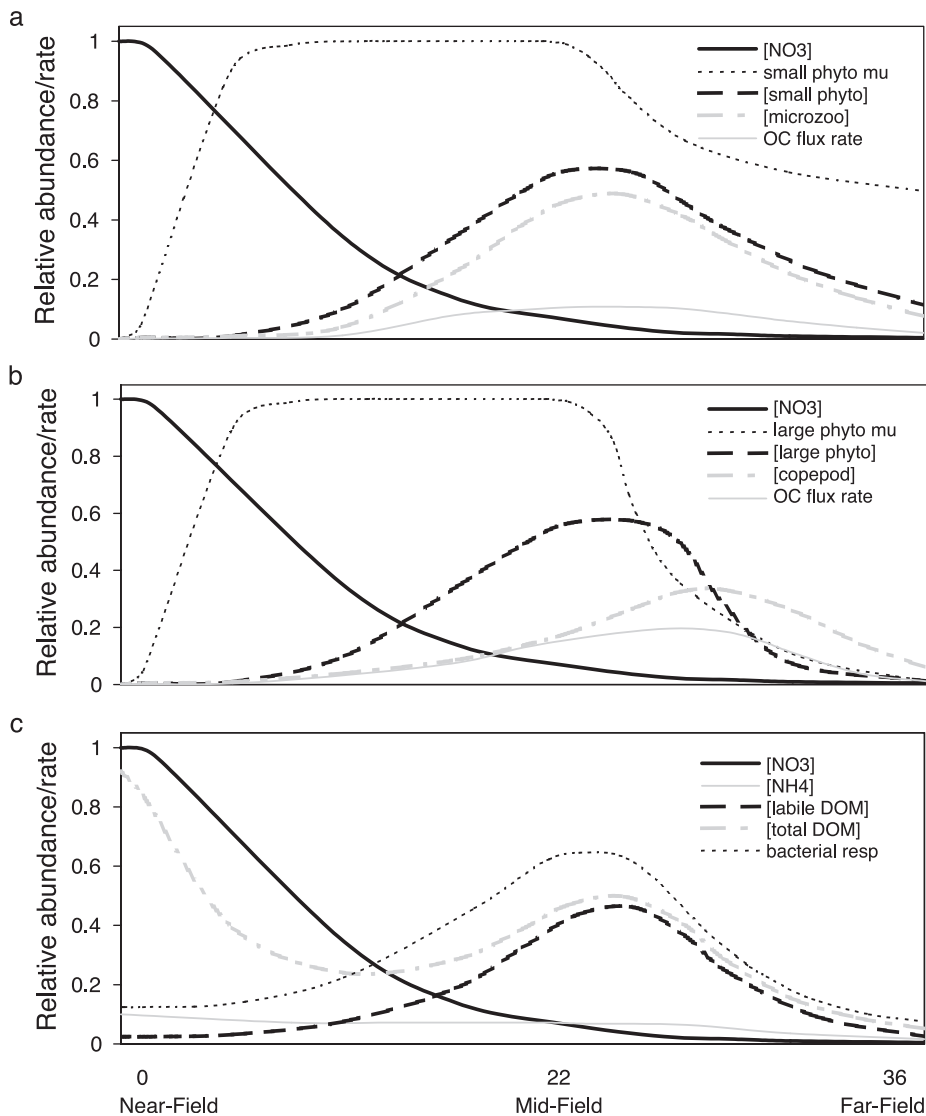


Fig. 4. Conceptual biological model of the Mississippi River plume as it mixes with shelf water. The model conceptualizes the gross scale dynamics of the plankton community. The Y-axis is presented on a relative scale, with one representing maximal rate or highest concentration; the X-axis is the salinity gradient of the river plume, beginning at 0 at the river mouth and ending at 36. Separate models are presented for (a) small phytoplankton ($< 10 \mu\text{m}$), (b) large phytoplankton ($> 10 \mu\text{m}$), and (c) bacteria. The models for large and small phytoplankton are most strongly linked by grazing on microzooplankton by mesozooplankton. The microbial loop and bacterial nitrogen recycling are linked to both models through grazing of bacteria by microzooplankton and reuptake of bacterially liberated DIN by phytoplankton. Legends: [NO₃] = nitrate concentration; small phyto mu = growth rate of small phytoplankton; [small phyto] = small phytoplankton concentration; [microzoo] = microzooplankton concentration; OC flux rate = organic carbon sedimentation rate from the ecosystem derived from small (a) or large (b) phytoplankton production; large phyto mu = growth rate of large phytoplankton; [large phyto] = concentration of large phytoplankton; [copepod] = copepod concentration; [NH₄] = ammonium concentration; [labile DOM] = labile dissolved organic matter concentration; [total DOM] = total dissolved organic matter concentration; bacterial resp = bacterial respiration rate.

toplankton cells respectively, and Fig. 4c describes bacterial processes.

In the river prior to discharge, nitrate concentration is usually over 100 μM but high concentrations of suspended particulate matter absorb and scatter light, and mixing minimizes the time any phytoplankton cell will be in a surface, lighted environment. Phytoplankton in the lower river grow slowly or not at all, and chlorophyll concentration (an index of phytoplankton biomass) is low.

Upon discharge, river water forms a buoyant plume that spreads over the receiving waters, immediately and dramatically altering the light environment. In the near-field plume, light is further enhanced by direct sinking of the large lithogenic particles and much of the particulate organic material. Flocculation and aggregation processes also stimulate sinking of materials from the surface. Light penetration increases dramatically, stimulating growth of marine phytoplankton. At this point, riverine nitrate has only been minimally diluted and irradiance increases enough to support phytoplankton growth. In the mid-field plume region, neither light nor nutrients are limiting, and except for temperature, physical and nutrient limitations on phytoplankton growth are all but gone. Phytoplankton growth rate often approaches the theoretical maximum in the mid-field region, and can be as high as 2 or 3 day^{-1} . For simplicity, we have assumed that both large and small phytoplankton have approximately the same maximum growth rate on a relative scale (Fig. 4a and b). Thus, the initial response of both large and small phytoplankton is a rapid increase in growth rate and both categories are assumed to maintain maximum growth rates in the surface plume until moving into far-field regions where nutrients become limiting and growth rates decline.

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 accumulates in spite of these loss terms. Small phytoplankton experience more grazing mortality at lower salinities than large phytoplankton because they are primarily grazed by microzooplankton, organisms that numerically respond more rapidly than the slower growing copepods and large protists that graze larger phytoplankton. Microzooplankton populations closely follow the increase in biomass of small phytoplankton (Fig. 4a), grazing a

significant proportion of the small phytoplankton in the near- and mid-field regions. In addition, larvae (not shown in Fig. 4), organisms that can grow and numerically respond at even higher rates than protozoans, can have a large grazing impact on small cells in the mid-field region. Large phytoplankton cells are subject to lower grazing mortality in the near- and mid-field regions because of the relatively slow numerical response by copepods. Consequently, the net growth rate of large phytoplankton is greater than that of small phytoplankton, and large cells, especially diatoms, dominate the phytoplankton community in these regions.

At the transition between mid- and far-field regions, nitrate concentration has been greatly reduced by dilution and uptake by phytoplankton. Bacteria may also take up nitrate, further reducing the DIN pool. These low concentrations are limiting to phytoplankton growth, especially to diatoms (Chisholm, 1992), and growth rates decrease sharply. In addition, populations of copepods have increased and grazing on large cells becomes important (Fig. 4b). Lower growth rates combined with increased grazing by copepods and continued dilution from mixing cause concentrations of larger phytoplankton cells to decrease shortly after nutrient concentrations become limiting. Large cells are also subject to loss by direct settling and this might be enhanced when nutrient limitation begins to affect cell physiology and buoyancy regulation. In contrast, small cells sink slowly or not at all. Consequently, stocks of large cells decrease rapidly after reaching peak levels in mid-field regions (Fig. 4b).

As nutrient limitation begins, growth of small phytoplankton declines less rapidly than that of large cells because of their larger surface-to-volume ratio and a greater ability to utilize recycled NH_4 and low concentrations of NO_3 (Chisholm, 1992). However, growth of small phytoplankton does slow. Microzooplankton grazing, a function primarily of prey concentration rather than prey growth rate, continues. Lower growth rates, grazing mortality and continuous dilution result in decreasing concentrations of small phytoplankton. Copepods (Fig. 4b) consume microzooplankton as well as large phytoplankton, which may relax microzooplankton grazing on small phytoplankton. This cascade effect may further slow the rate of decline by small cells relative to large cells,

although the stocks of both categories are in decline. Small cells become a greater fraction of the total phytoplankton biomass as plume waters transit from mid- to far-field regions because their stocks do not decline as rapidly as large cells.

Microzooplankton abundance in the mid-field (Fig. 4a) increases exponentially, closely tracking their small phytoplankton prey. Microzooplankton populations decline with the reduction of small phytoplankton populations in the far-field (Fig. 4a) and the increase in populations of their copepod predators (Fig. 4b). As with all processes in this system, continuous dilution by physical mixing contributes to changes in the concentrations of microzooplankton.

At conditions of the oligotrophic, open ocean end-member (salinity of 36), populations of microzooplankton grazers and small phytoplankton are tightly coupled, and stocks of both are low. After copepod populations peak in the mid- and far-field regions, they decline, primarily due to dilution and predation induced mortality. At conditions of the oligotrophic, open ocean end-member, copepod populations are small and involved in the food web primarily as grazers of microzooplankton and the few large phytoplankton cells remaining in the system.

Bacteria contribute significantly to carbon and nitrogen cycling in plume waters (Fig. 4c). In the near-field, the pool of riverine DOM is mainly refractory and supports relatively little bacterial activity. The labile fraction of DOM increases with salinity for three reasons. First, some of the refractory material flocculates and settles out in the near-field region. Second, some of the refractory DOM from the river is photo-oxidized to labile forms in the near- and mid-field regions. Third, labile excretions from the phytoplankton and other components of the marine food web increase dramatically in the mid-field region. Labile DOM can be produced by exudation from phytoplankton, or by dissolving detritus and zooplankton fecal pellets (usually bacterially mediated), or it can come from zooplankton excretions, living and dead bacterial cells, and a range of organisms at higher trophic levels. Labile DOM concentrations peak in highly productive mid-salinity regions of the plume.

Bacterial respiration and production follow changes in labile DOM concentrations. Rates are relatively low in river water and in the near-field plume, peak in the mid-field region where highest

concentrations of labile DOC and DON occur, and decline again in the farfield plume after phytoplankton and microzooplankton derived DOM has been diluted by mixing and removed by bacterial uptake (Fig. 4c). Consumption of bacteria by microzooplankton and larvaceans may be an important recycling pathway for carbon and nitrogen and an important link between the microbial loop and the classical nutrient-phytoplankton–zooplankton food web.

Some DON consumed by bacteria is released as NH_4 where biologically available nitrogen is abundant. Grazer excretion is an additional source of NH_4 . When grazing is intense and zooplankton concentrations high, this source might be greater than the amount released by bacteria, especially in the far-field where NO_3 is limiting and bacteria are less likely to excrete NH_4 . Free NH_4 is quickly taken up by phytoplankton and/or bacteria, which results in concentrations of NH_4 being low and essentially constant along the entire plume. The degree of competition for NH_4 between bacteria and phytoplankton is unclear but NH_4 turnover rates are high.

Bacteria also nitrify NH_4 in the plume, oxidizing it to NO_3 . This process has only been detected in mid-salinity surface waters where NO_3 concentration is high. Nitrification is probably not common in the far-field where DIN and DON concentrations are low, and it does not appear to occur in the near-field. Given the lack of data, it is unclear how nitrification in surface waters impacts nitrogen cycling overall.

The most important gaps in our understanding of nitrogen cycling in the Mississippi River plume are probably associated with various bacterial processes.

In the near-field, sediment flux from the river plume is dominated by lithogenic materials and terrestrial derived POM. After settling, organic coatings may desorb from particulate material and contribute to DON but little is known about this process or about its contribution to the nitrogen dynamics of the shelf. PON flux in mid-field regions is dominated by marine production. Flux rates increase greatly in this region because of high biological production. Direct flux from large phytoplankton declines in far-field regions as the concentrations of large cells decline, but fecal pellets, molts, and other exudates from mesozooplankton continue to produce a significant flux of organic material. This results in the long gradual decline in OM sedimentation shown in Fig. 4b.

Organic sedimentation generated by small phytoplankton cells tends to track the small cell concentrations more closely. However, flux from these cells is small because (a) small cells have low sinking rates and (b) protozoan grazers produce small pellets that have low sinking rates. Most flux from this part of the food web is derived from larvaceans, organisms that graze small cells and produce relatively large compact pellets with high sinking rates.

Organic matter flux from the photic zone is a highly variable fraction of mixed layer primary production and is highly dependent upon the activity of grazers, bacteria, and other organisms. At times, especially in the spring, large amounts of organic matter sink from the plume into the bottom layer. Much of this POM is dissolved before reaching the bottom, and most is dissolved before it is permanently buried. DON and DOC released from sinking particles are utilized by bacteria just as in the surface plume. During periods of strong physical stratification, the oxygen demand from decomposition of OM leads to hypoxia in bottom water and benthos over broad areas of the inner shelf. Because of hypoxia, denitrification should be enhanced in both the hypoxic bottom water and in the benthos. Residual organic N is buried.

We emphasize that this conceptual model is an idealization of plume processes. Some sections of our model are speculative because there are few data. The most important gaps in our understanding of nitrogen cycling in the Mississippi River plume are probably associated with various bacterial processes but other significant gaps exist. Most important however, is the primitive understanding of the time and space scales of these processes and how these processes interact. These scales and interactions are tied to the physical conditions of the plume and are therefore dependent on discharge as well as local factors such as wind, currents and tides. A predictive capability of how drainage basin processes affect nitrogen cycling in the Mississippi River plume will require extensive empirical studies and coupled physical–biological modeling efforts.

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