

This discussion paper is/has been under review for the journal Biogeosciences (BG).
Please refer to the corresponding final paper in BG if available.

Simulating the effects of phosphorus limitation in the Mississippi and Atchafalaya River plumes

A. Laurent¹, K. Fennel¹, J. Hu², and R. Hetland³

¹Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada

²School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou, China

³Department of Oceanography, Texas A&M University, College Station, Texas, USA

Received: 25 April 2012 – Accepted: 30 April 2012 – Published: 14 May 2012

Correspondence to: A. Laurent (arnaud.laurent@dal.ca)

Published by Copernicus Publications on behalf of the European Geosciences Union.

5625

Abstract

The continental shelf of the northern Gulf of Mexico receives high dissolved inorganic nitrogen and phosphorus loads from the Mississippi and Atchafalaya rivers. The nutrient load results in high primary production in the river plumes and contributes to the development of hypoxia on the Texas-Louisiana shelf in summer. While phytoplankton growth is considered to be typically nitrogen-limited, phosphorus limitation has been observed in this region during periods of peak river discharge in spring and early summer. Here we investigate the presence, spatio-temporal distribution and implications of phosphorus limitation in the plume region using a circulation model of the northern Gulf of Mexico coupled to a multi-nutrient ecosystem model. Results from a 7-yr simulation (2001–2007) compare well with available observations and suggest that phosphorus limitation develops every year between the Mississippi and Atchafalaya deltas. Model simulations show that phosphorus limitation results in a delay and westward shift of a fraction of river-stimulated primary production. The consequence is a reduced flux of particulate organic matter to the sediment near the Mississippi delta, but enhanced fluxes westward in the Atchafalaya and far-field regions. Two discharge scenarios with altered river phosphate concentrations ($\pm 50\%$) reveal a significant variation ($\pm 40\%$ in July) in the spatial extent of phosphorus limitation with changes in phosphate load.

1 Introduction

The Mississippi-Atchafalaya river basin is world's third-largest river basin, over 3.2×10^6 km² in size and constitutes nearly 80 % of the United States freshwater discharge into the Gulf of Mexico (Dunn, 1996). The Mississippi and Atchafalaya rivers, which contribute 2/3 and 1/3 of the discharge respectively, are the main sources of freshwater to the Texas-Louisiana shelf (Fig. 1) and represent about 95 % of its total nitrogen and phosphorus load (Dunn, 1996). Changes in agricultural practices in the Mississippi-Atchafalaya river basin – in particular an increase in the use of fertilizers

5626

– have tripled dissolved inorganic nitrogen concentration (DIN, mainly nitrate (NO_3^-) + nitrite (NO_2^-)) since the 1980s (mostly from 1967 to the early 1980s) in the lower Mississippi River (Turner and Rabalais, 1991; Goolsby et al., 2001). This increase in nutrient load has resulted in eutrophication and high primary production (Turner and Rabalais, 1994; Lohrenz et al., 1997) and contributes to the development of hypoxic bottom waters on the Texas-Louisiana shelf in summer (Rabalais et al., 2002; Greene et al., 2009). Total phosphorus (TP) in the river has also increased, but dissolved inorganic phosphorus (DIP) has decreased since the 1980s (Lohrenz et al., 2008) modifying the stoichiometric balance of nitrogen (N) and phosphorus (P) inputs.

Primary production on the Texas-Louisiana shelf is usually nitrogen-limited during the period of low river flow in late summer and fall (Rabalais et al., 2002), whereas light limitation occurs in late fall and winter and near the river delta (Lohrenz et al., 1999; Fennel et al., 2011). The dissolved inorganic nitrogen to phosphorus ratio (DIN : DIP) in the lower Mississippi River varies seasonally, reaching values well above the Redfield nitrogen-to-phosphorus (N : P) ratio of 16 : 1 during the period of peak discharge in spring and early summer when $\text{DIN} > 100 \text{ mmol m}^{-3}$ (Fig. 2). This can lead to phosphorus limitation of primary production when nutrients are removed in Redfield stoichiometry and phosphate concentrations reach values of less than 0.2 mmol m^{-3} (Dortch and Whitedge, 1992). It has been suggested that TP rather than DIP should be used in the calculation of N : P (Rabalais et al., 2002; Turner et al., 2007), which would indicate near Redfield stoichiometry in the lower Mississippi River. Dissolved organic phosphorus may also be an important source of phosphorus on the Texas-Louisiana shelf (Dagg et al., 2007). However, DIP is the only form of phosphorus that is readily available to phytoplankton. Moreover, the DIN : DIP observations are consistent with physiological measurements and nutrient addition bioassays carried out near the Mississippi delta region (Dortch and Whitedge, 1992; Smith and Hitchcock, 1994) and across the Texas-Louisiana shelf (Sylvan et al., 2006, 2007, 2011; Quigg et al., 2011) which suggest that phosphorus limitation occurs during spring and early summer. This period of phosphorus limitation coincides with the peak in primary production (Lohrenz

5627

et al., 1997) which is thought to contribute to the development of summer hypoxia (Rabalais et al., 2002). Phosphorus limitation may therefore have a significant role in the biogeochemistry of the Texas-Louisiana shelf, leading to a delay in the assimilation of riverine DIN by phytoplankton and the spread of primary production over a larger area on the shelf (Quigg et al., 2011). This would modify the distribution and magnitude of particulate organic matter (POM) fluxes to the sediment and could subsequently affect the development and location of summer hypoxia. Clearly, the effects of phosphorus limitation on the biogeochemistry of the Texas-Louisiana shelf and the consequences of changing DIN : DIP stoichiometry in the Mississippi and Atchafalaya rivers need to be investigated.

Recently, a nitrogen-based model of the lower trophic ecosystem has been coupled to a realistic 3-dimensional circulation model of the northern Gulf of Mexico (Fennel et al., 2011). The model successfully simulates the seasonal cycle and the spatial distribution of nitrate and phytoplankton across the Texas-Louisiana shelf. A 15-yr simulation has provided insights into the temporal and spatial patterns of primary production and phytoplankton loss terms in the region and was used to explain the relationship between primary production and N loads (Fennel et al., 2011). The model does not include DIP and therefore assumes that primary production is limited by light and nitrogen only. Here, we extend the model of Fennel et al. (2011) to explicitly simulate the dynamics of DIP. A 7-yr simulation (2001–2007) is analyzed to assess if and how phosphorus limitation affects the patterns of primary production across the Texas-Louisiana shelf. The results compare well with observations collected during the nutrient limitation studies of Sylvan et al. (2006, 2007, 2011) and Quigg et al. (2011) and corroborate their hypothesis of delayed primary production in the Mississippi delta resulting from phosphorus limitation. This effect is analyzed for several zones across the Texas-Louisiana shelf, and nutrient dynamics in the Mississippi and Atchafalaya River plumes are compared. Finally, sensitivity experiments are presented to study the effect of altered DIP loads on the extent of phosphorus limitation.

5628

2 Model description

2.1 Circulation model

The Regional Ocean Modeling System (ROMS, Shchepetkin and McWilliams, 2005; Haidvogel et al., 2008) was configured to simulate circulation on the northern Gulf of Mexico shelf near the Mississippi and Atchafalaya rivers outflow region. The model grid covers the continental shelf region from 94.6°W to 87.8°W with a variable spatial resolution (Fig. 1). The horizontal resolution varies between ~20 km in the southwestern region and up to 1 km near the Mississippi River delta. The grid has 20 vertical layers with increased resolution near the surface and bottom. The setup and validation of the circulation model is described in detail in Hetland and DiMarco (2008, 2011).

The model uses a fourth-order scheme for the horizontal advection of tracers and a third-order upwind scheme for the advection of momentum, with conservative parabolic splines to calculate vertical gradients. Vertical mixing is parameterized using the Mellor-Yamada level 2.5 turbulent closure scheme (Mellor and Yamada, 1982; Galperin et al., 1988). Climatologies from the World Ocean Database (Boyer et al., 2005) are used to prescribe temperature and salinity at the open boundaries. Atmospheric forcing is specified using 3-h near-surface winds from the NCEP North American Regional Reanalysis (NARR) high-resolution climate dataset (Mesinger et al., 2006) and surface heat and freshwater flux climatologies of da Silva et al. (1994a,b). Daily freshwater fluxes from the Mississippi and Atchafalaya rivers are based on measurements of freshwater transport by the US Army Corps of Engineers at Tabert Landing and Simmesport, respectively.

2.2 Biological model

The circulation model is coupled to a modified version of the nitrogen cycle model developed by Fennel et al. (2006, 2008). The original model describes the pelagic nitrogen cycle with six compartments representing phytoplankton (Phy), chlorophyll (Chl),

5629

zooplankton (Zoo), nitrate (NO₃), ammonium (NH₄) and detrital particulate organic nitrogen, which is divided into a pool of small detritus (SDet, particles size < 10 μm) that receives losses from phytoplankton and zooplankton and a pool of large detritus (LDet) that represents aggregates of phytoplankton and small detritus. A detailed description, configuration and validation of the nitrogen cycle model for the northern Gulf of Mexico domain is available in Fennel et al. (2011). For this study a dissolved inorganic phosphorus compartment, PO₄, was added to the nitrogen cycle model. It is assumed to represent orthophosphate (hereafter referred as phosphate). The four pathways that control the dynamics of phosphate are uptake for phytoplankton growth, excretion by zooplankton due to feeding and basal metabolism, remineralization of particulate organic matter in the water column, and remineralization of particulate organic matter in the sediment. The release of phosphate from phosphorus sorbed to particulate matter when Mississippi waters enter the Gulf of Mexico (Fox et al., 1985) is not accounted for in the model. A schematic of the modified model structure is given in Fig. 3.

As for ammonium and nitrate, the uptake of phosphate by phytoplankton is assumed to follow Michaelis-Menten dynamics. The rate of nutrient uptake and phytoplankton growth is determined by the most limiting element, N corresponding to DIN = NO₃ + NH₄ or P corresponding to PO₄. The most limiting element is the one with the smaller limitation-factor, L_N or L_P , which are calculated as:

$$L_N = \frac{NO_3}{k_{NO_3} + NO_3} \cdot \frac{1}{1 + NH_4/k_{NH_4}} + \frac{NH_4}{k_{NH_4} + NH_4}, \text{ and} \quad (1)$$

$$L_P = \frac{PO_4}{k_{PO_4} + PO_4} \quad (2)$$

where k_{NO_3} , k_{NH_4} and k_{PO_4} (mmol m⁻³) are the half-saturation concentrations for nitrate, ammonium and phosphate uptake, respectively, and are set to $k_{NO_3} = k_{NH_4} = 0.5$ mmol N m⁻³ and $k_{PO_4} = 0.03$ mmol P m⁻³. The range of observed values for k_{PO_4} is very large (Dortch and Whittedge, 1992). Here, a mid-range value was chosen for k_{PO_4}

5630

that assumes nutrient uptake occurs in Redfield stoichiometry. L_N and L_P are also used to calculate observed nitrogen and phosphorus limitation factors from observations, allowing for a direct comparison between model results and observations.

The specific growth rate of phytoplankton (μ , d^{-1}) is then expressed as a function of light and nutrient limitation as:

$$\mu = \mu(E, T) \cdot \min(L_N, L_P) \quad (3)$$

where $\mu(E, T)$ is the light (E ; Wm^{-2}) and temperature (T ; $^{\circ}C$) limited, nutrient-replete phytoplankton growth rate.

Particulate organic phosphorus is represented by the detritus pools which are assumed to be in Redfield stoichiometry ($N : P = 16$). The formulation and parameterization of excretion and remineralization into phosphate is the same as in the nitrogen cycle model. Excretion of phosphate by zooplankton results from basal metabolism (linear function) and from assimilation of phytoplankton (proportional to assimilation). Water column remineralization of detrital particulate organic matter (small and large pools) into phosphate is a linear function of particulate matter concentration. The time rate of change of phosphate due to biological processes in the water column is:

$$\frac{\partial PO_4}{\partial t} = \frac{1}{N : P} \left(-\mu Phy + l_{BM} Zoo + l_E \frac{Phy^2}{k_P + Phy^2} \beta Zoo + r_S SDet + r_L LDet \right), \quad (4)$$

where l_{BM} (d^{-1}) is the rate of excretion by zooplankton due to basal metabolism, l_E (d^{-1}) is the maximum rate of excretion by zooplankton due to assimilation, k_P ($mmol N m^{-3}$) is the half saturation constant for zooplankton grazing on phytoplankton, β is the zooplankton assimilation efficiency and r_S (d^{-1}) and r_L (d^{-1}) are the remineralization rates of small and large detritus, respectively.

All sinking particulate organic matter (phytoplankton and detritus) is instantaneously remineralized into phosphate when reaching the sediment–water interface at depth

5631

$z = H$. The bottom boundary condition for phosphate at the sediment–water interface is:

$$\frac{\partial PO_4}{\partial t} \Big|_{z=H} = \frac{1}{N : P} \left(\frac{w_{Phy} Phy \Big|_{z=H} + w_{SDet} SDet \Big|_{z=H} + w_{LDet} LDet \Big|_{z=H}}{\Delta z} \right), \quad (5)$$

where w_{Phy} , w_{SDet} and w_{LDet} (md^{-1}) are the sinking velocities of phytoplankton and small and large detritus, respectively, and Δz is the thickness of the bottom layer. This is analogous to the treatment of nitrogen at the bottom, except that a fraction of the particulate organic nitrogen reaching the sediment–water interface is lost through the denitrification pathway (Fennel et al., 2006). All other model parameters are as described in Fennel et al. (2011).

2.3 Simulations

The model was run for the period 2001–2007 using monthly measurements of nutrient loading for the Mississippi and Atchafalaya rivers (Aulenbach et al., 2007). This simulation is referred to as the control run, and its results are compared with observations over the period 2001–2004 from Sylvan et al. (2006, 2007, 2011) and Quigg et al. (2011). The simulation is then compared to one with the original nitrogen-based version of the ecosystem without phosphorus dynamics (Fennel et al., 2011), but otherwise identical forcing, initial and boundary conditions and parameter values (referred to as the N-only simulation). Two additional model runs were carried out to investigate the sensitivity of the system to variations in phosphate load. In these runs, the model setup remains the same as in the control run except that phosphate concentrations in the Mississippi and Atchafalaya rivers are increased or decreased by 50 % compared to the control run. This range of variation has been used in a recent modeling study of the effect of nutrient loading in the Mississippi River plume (Eldridge and Roelke, 2010) and corresponds to the range of variability associated with nutrient reduction strategies and climate change (Eldridge and Roelke, 2010, and references therein).

5632

For model analysis, five geographical zones were defined (Mississippi delta, Mississippi intermediate, Far-field, Atchafalaya delta and Atchafalaya intermediate) and are shown in Fig. 1. The first three sub-regions correspond to an ecological gradient associated with the Mississippi River plume (Rowe and Chapman, 2002; Fennel et al., 2011), while the latter two were defined for the present study to account for the ecological gradient associated with the Atchafalaya River plume.

3 Results

3.1 Surface chlorophyll biomass and phosphate concentration

Simulated and observed surface chlorophyll averaged over the 5 areas defined in Fig. 1 are shown in Fig. 4. Simulated chlorophyll follows a well-defined seasonal cycle in the delta regions and in the Atchafalaya intermediate region, reaching an annual minimum of 2–4 mg m⁻³ during the late fall and winter and an annual maximum of 10–15 mg m⁻³ between June and August (Fig. 4a, b) after the peak river discharge that occurs in late spring (Fig. 2). The amplitude of the annual chlorophyll cycle is smaller in the Mississippi intermediate region (Fig. 4c) and disappears in the far-field region (Fig. 4e) where chlorophyll biomass remains low throughout the year (< 1 mg m⁻³ for most of the time). Overall, chlorophyll decreases westward of the river sources and southward from the Louisiana coast.

Simulated surface chlorophyll is in good agreement with satellite observations in the Mississippi delta and intermediate regions and the far field region (Fig. 4a, c, e), although the model underestimates chlorophyll biomass during late winter and early spring (Fig. 4a). In the Atchafalaya delta and intermediate regions, which are both directly influenced by the Atchafalaya river inflow, the model systematically underestimates satellite chlorophyll during the first four years of the simulation. This underestimation may be due in part to unresolved processes controlling chlorophyll biomass in this region, and in part to an overestimation of satellite chlorophyll due to colored

5633

dissolved organic matter from wetlands adjacent to Atchafalaya Bay. The model also underestimates the higher annual peak in chlorophyll biomass in the delta regions from 2001 to 2004 (Fig. 4a, b), which is associated with a higher river discharge between April and June (Fig. 2).

The seasonal cycles of phosphate and DIN concentrations are out of phase in the Mississippi River. Phosphate concentration is at its annual maximum in late summer, whereas DIN concentration is at its maximum in spring (Fig. 2). However, their total loads – maximum in spring – are in phase due to the water discharge cycle. Surface phosphate concentrations in the delta regions follow the annual cycle of phosphate load, with annual maximum concentrations of 1–1.5 mmol P m⁻³ for the Mississippi delta region (Fig. 5a) and 2–2.5 mmol P m⁻³ for the Atchafalaya delta region (Fig. 5b) in winter and spring, and with annual minimum concentrations of less than 0.2 mmol P m⁻³ in summer (Fig. 5a, b) after peak discharge and after the annual peak in phytoplankton biomass. A similar seasonal pattern, but of lower magnitude, is found in the intermediate regions (Fig. 5c, d). In the Atchafalaya intermediate region, phosphate concentrations are generally higher than in the Mississippi intermediate region. This difference is important in determining the pattern of phosphorus limitation on the Texas-Louisiana shelf. In the far-field region, phosphate concentrations are low throughout the year, with a minimum in early summer (Fig. 5e), but are usually not entirely depleted.

Simulated phosphate concentrations agree well with observations in the Mississippi and Atchafalaya delta regions and the Atchafalaya intermediate region. In the Mississippi intermediate region, the agreement is excellent in 2001 and with the observations from Sylvan et al. (2006, 2007, 2011) and Lehrter et al. (2009, 2012). The LUMCON observations (Rabalais et al., 1999, 2007) are systematically higher from 2002 onward, but in particular during 2002 (Fig. 5c). This discrepancy may be due to a methodological difference in measurement techniques. The observations of Sylvan et al. (2006, 2007, 2011) are used for the remainder of this manuscript.

3.2 Nutrient limitation on the Texas-Louisiana shelf

Nutrient limitation on the Texas-Louisiana shelf is explored using the limitation factors L_N and L_P (Eqs. 1 and 2). DIN is considered limiting when $L_N < L_P$ or otherwise phosphate. The degree of nutrient limitation is given by the size of the limitation factors, with smaller values indicating stronger limitation and values near 1 indicating weak or no limitation. Nutrient limitation is considered to be significant when $L < 0.75$.

The spatial distribution of nutrient limitation during the eight cruises described by Sylvan et al. (2006, 2007, 2011) and Quigg et al. (2011) is presented in Fig. 6. Data from the first 4 cruises illustrate the seasonal evolution of nutrient limitation during 2001 (Fig. 6a–d). Nutrient limitation is not significant along the Louisiana coast in March ($L > 0.9$). This period corresponds to the beginning of the phytoplankton bloom and high discharge with high nutrient loading from the Mississippi River (Fig. 2). Nutrient concentrations are high but phytoplankton biomass is still close to its annual minimum (Fig. 4). Nutrient limitation is found downstream, mainly from nitrogen in the far-field and from phosphorus in deeper areas south of the Atchafalaya and Terrebonne Bays (Fig. 6a). In May, phosphorus limitation develops at the edge of the Mississippi River plume and near Terrebonne Bay ($L_P \sim 0.5$, Fig. 6b), which corresponds to the Mississippi intermediate region (Fig. 1). This is explained by the high DIN:DIP ratio in the Mississippi River during the preceding discharge period (March–May). Nitrogen limitation ($L_N < 0.2$) occurs in the deeper shelf regions and offshore. Phosphorus limitation is still present in the intermediate region in July and extends even further offshore, reaching maximum strength in the deeper shelf area south of Atchafalaya Bay ($L_P < 0.2$, Fig. 6c). Phosphorus limitation has its maximum extent at this time. With the exception of the Mississippi and Atchafalaya River plumes, which are not nutrient-limited, the entire Texas-Louisiana shelf is nitrogen-limited in September (Fig. 6d).

Similar patterns are found in 2002 (Fig. 6H) and 2004 (Fig. 6e–g). In March 2004, the nearshore areas are not nutrient-limited, except for a region of weak phosphorus limitation ($L_P > 0.75$) south of Terrebonne Bay (Fig. 6e). Nitrogen limitation occurs offshore

5635

at this time. In May 2004, nutrient limitation is well developed with an extended region of phosphorus limitation at moderate levels ($0.6 < L_P < 0.8$) westward of Terrebonne Bay, and a region of strong nitrogen limitation ($L_N < 0.2$) on the deeper shelf and in the far-field. Again, the phosphorus-limited region increases in July 2004, covering the same area as in July 2001. In July 2002, the phosphorus-limited area is smaller than in 2001 and 2004.

The simulated patterns of nutrient limitation agree well with the observations in March (Fig. 6a), July (Fig. 6b) and September 2001 (Fig. 6d), but the model underestimates phosphorus limitation in the Mississippi and Atchafalaya delta regions in May (Fig. 6b) when observed phosphate concentrations are below detection limits ($\text{PO}_4^{3-} < 0.03 \text{ mmol m}^{-3}$). The agreement is also good in 2002 (Fig. 6H) and 2004 (Fig. 6e–g), with some discrepancy in the extent of the phosphorus-limited area, except in July 2004 when the model simulates phosphorus limitation ($L_P > 0.5$) outside Terrebonne Bay in an area of weak nitrogen limitation ($0.6 < L_N < 0.8$, Fig. 6g). The overall spatial and temporal distribution of phosphorus limitation is therefore well represented by the model.

The seasonal cycle and spatial gradient of nutrient limitation over the simulation period is summarized in Fig. 7. In the Mississippi and Atchafalaya delta regions (Fig. 7a, b) DIN and DIP concentrations are always high due to river inflow and thus nutrient limitation is weak ($L > 0.75$). In contrast, nitrogen is almost always strongly limiting in the more oceanic far-field region ($L_N < 0.5$, Fig. 7e). In the Mississippi and Atchafalaya intermediate regions nutrient limitation develops seasonally between June and October (Fig. 7c, d). Westward of Atchafalaya Bay, in the Atchafalaya intermediate region, significant levels of nutrient limitation ($L_N < 0.75$) occur from August to September only (Fig. 7d). In this region, phosphorus limitation is never significant and nutrient limitation did not occur at all in 2001 and 2004. For those two years, June DIN load from the Atchafalaya River was significantly higher (by a factor of 2) than for the other years of the simulation (Fig. 2). This late input of DIN may have alleviated nitrogen limitation

5636

westward of Atchafalaya Bay in summer, resulting in the high annual peak in chlorophyll biomass (Fig. 4d).

In the Mississippi intermediate region, significant levels of phosphorus limitation ($L_P < 0.75$) only occur in June and July (Fig. 7c) – also illustrated on the spatial maps presented above (Fig. 6) – following the annual peak discharge. In late spring/early summer, waters transported from the Mississippi delta reach the Mississippi intermediate region where they are depleted in phosphate, initiating a period of phosphorus limitation. It is followed by a period of strong nitrogen limitation between late August and November, when river inflow reaches its annual minimum (Fig. 2). At this time, the region is more influenced by oceanic waters where nitrogen limitation is dominant.

3.3 Effects of phosphorus limitation

The effect of phosphorus limitation on primary production and on the flux of particulate organic matter to the sediment is estimated by comparing the simulation presented above (the control simulation) against the simulation that uses the original nitrogen-based ecosystem model (the N-only simulation).

In both simulations the mean rate of water column-integrated primary production is at its minimum between November and January and at its maximum between May and July on the Texas-Louisiana shelf, with an annual cycle most pronounced in the Atchafalaya regions (Fig. 8b). In the control run, the highest rates of depth-integrated primary production occur in June with an average of $20.6 \text{ mmolNm}^{-2} \text{d}^{-1}$ in the Mississippi delta region and $19.1 \text{ mmolNm}^{-2} \text{d}^{-1}$ in the Atchafalaya intermediate region. Primary production in the Atchafalaya delta region is lower than in the intermediate region due to light limitation near the Atchafalaya River outflow. These rates are lower than previously reported (Lohrenz et al., 1997; Quigg et al., 2011), although the maximum daily rate of primary production – $79.2 \text{ mmolNm}^{-2} \text{d}^{-1}$ in July in the Mississippi delta region – is within the range of primary production reported for the region ($65.4\text{--}144.7 \text{ mmolNm}^{-2} \text{d}^{-1}$, Lohrenz et al., 1990, 1999; Quigg et al., 2011). The comparison between the control and N-only simulations (Fig. 8a) indicates a significant decrease

5637

of primary production due to phosphorus limitation in spring/early summer in the Mississippi delta (–26 % in June) and Mississippi intermediate (–12 % in May) regions, but an increase during summer and early fall in the regions west of Terrebonne Bay – by up to 18 % (intermediate regions) and 27 % (far-field region). In other words, a fraction of the nutrient-stimulated primary production is shifted downstream in space and delayed in time.

This redistribution of primary production influences the depositional flux to the sediment. In the control run, this flux is largest in June and July in the Mississippi delta and in the Atchafalaya delta and intermediate regions, with values of 5.8, 7.2 and $5.4 \text{ mmolNm}^{-2} \text{d}^{-1}$ on average, respectively (Fig. 9b). These values agree with observed depositional fluxes that range between $4.3 \text{ mmolNm}^{-2} \text{d}^{-1}$ and $19.3 \text{ mmolNm}^{-2} \text{d}^{-1}$ at the base of the photic layer in the Mississippi delta region (Redalje et al., 1994). Similar to primary production, the depositional flux is significantly lower in spring and early summer in the control run compared to the N-only simulation (Fig. 9a), mainly in the Mississippi delta (–33 % in June/July) and Mississippi intermediate (–28 % in May) regions, and is higher by up to 30 % in August and September in the regions west of Terrebonne Bay.

3.4 Consequences of altered DIP load

The sensitivity of nutrient limitation patterns to changes in the N : P ratio of the river nutrient load was evaluated by varying river phosphate concentrations by $\pm 50\%$. In these scenarios, the N : P ratio peaks around 38 (for increased phosphate) and 150 (for decreased phosphate). The latter is an order of magnitude higher than the Redfield ratio. Phosphorus limitation is most strongly affected in May and July following the period of maximum nutrient load (Fig. 10a). In the regular simulation, the extent of the phosphorus-limited area increases from an average of $2.14 \times 10^4 \text{ km}^2$ in May to $3.56 \times 10^4 \text{ km}^2$ in July. A 50 % increase in river phosphate concentration significantly reduces the area of phosphorus limitation to $1.31 \times 10^4 \text{ km}^2$ (–39 %) in May and $2.07 \times 10^4 \text{ km}^2$ (–42 %) in July (Fig. 10a). This reduction is compensated by an increase of

5638

the nitrogen-limited area that expands in July (Fig. 10b). Conversely, a 50 % decrease in river phosphate concentration extends the phosphorus-limited area to $3.23 \times 10^4 \text{ km}^2$ (+51 %) in May and $5.29 \times 10^4 \text{ km}^2$ (+48 %) in July (Fig. 10a) and reduces the nitrogen-limited area (Fig. 10b). Phosphorus limitation lasts until September in this case.

5 The interannual variations in river DIN concentrations, in the timing of water discharge and in circulation patterns on the shelf induce significant interannual variability in the extent of phosphorus limitation and its response to altered river phosphate concentrations. When river DIN concentrations are low (2002 and 2003, Fig. 2), the spatial extent of phosphorus limitation is at its minimum and occurs mainly in May with added
10 phosphate (Fig. 10a). In years when DIN load is highest in June (2001 and 2004, Fig. 2), the phosphorus-limited area is at its maximum in July and increases significantly with phosphate reduction (Fig. 10a).

4 Discussion

Nitrogen represents the most important factor limiting phytoplankton growth in the surface waters of the northern Gulf of Mexico (Rabalais et al., 2002), while light limitation
15 due to the presence of suspended terrigenous sediments and chromophoric dissolved organic matter is an important limiting factor in the delta regions of the Mississippi and Atchafalaya rivers (Lohrenz et al., 1990, 1999; Fennel et al., 2011; Quigg et al., 2011). Realistic model simulations presented here demonstrate that in the intermediate salinity region between the light-limited and the nitrogen-limited regions there is a large zone
20 of phosphorus limitation (up to $4.4 \times 10^4 \text{ km}^2$ in size) during the annual peak of primary production between May and July. This result is consistent with the high alkaline phosphatase activity and phosphorus stress measured by Sylvan et al. (2006, 2007, 2011) and Quigg et al. (2011). This spatial succession of light, phosphorus and then nitrogen
25 resource limitation of primary production downstream of the Mississippi River is consistent with and substantiates a framework of resource limitation recently proposed by Quigg et al. (2011) that relates DIN concentration (decreasing downstream of the

5639

Mississippi River) to resource limitation. Significant interannual variability in the timing and intensity of phosphorus limitation (Fig. 7) results from variability in the timing and magnitude of nutrient loads from the Mississippi River. Phosphorus limitation has been suggested to induce a delay in the uptake of nitrogen in the Mississippi River plume
5 (Quigg et al., 2011); an idea that is confirmed by the simulations presented here. The simulations demonstrate how phosphorus limitation alters the distribution of primary production and depositional fluxes on the Texas-Louisiana shelf, spreading the effect of allochthonous nutrient over a larger area. A similar effect has been described for the Baltic Sea (Granéli et al., 1990).

10 The simulation also suggests that phosphorus limitation is more pronounced in the Mississippi intermediate region than in the Atchafalaya intermediate region. In the shallow Atchafalaya delta region bioavailable nitrogen is removed more efficiently by sediment denitrification, which represents 37 % of primary production in June on average, than in the deeper Mississippi delta region where a larger fraction of remineralization
15 occurs in the water column. In the latter denitrification represents only 21 % of primary production in June. Sediment denitrification removes bioavailable nitrogen but does not affect phosphate (Caraco et al., 1990; Blomqvist et al., 2004), resulting in a net decrease in the DIN : DIP ratio and ultimately eliminating phosphorus limitation. In the shallow Atchafalaya regions nutrients remineralized in the sediments are also
20 more readily available to primary producers than in the deeper Mississippi regions. Thus the role of phosphorus limitation varies between the plumes of the Mississippi and Atchafalaya rivers.

It has been speculated that spatial shifts in POM deposition resulting from phosphorus limitation may result in a positive feedback on the development of hypoxic areas
25 (Paerl et al., 2004; Conley et al., 2009). Hypoxic bottom waters are typically found in summer on the Texas-Louisiana shelf (Rabalais et al., 2002), during the peak of phosphorus limitation in surface waters between the Mississippi and Atchafalaya delta regions, which is also the main location of hypoxia (Rabalais and Turner, 2006). Phosphorus limitation may therefore enhance hypoxia in the region westward of Terrebonne

- da Silva, A. M., Young-Molling, C. C., and Levitus, S.: Atlas of surface marine data 1994, Vol. 4, Anomalies of fresh water fluxes, NOAA Atlas NESDIS 9, US Dept. of Commerce, Washington, DC, 1994b. 5629
- Dagg, M., Ammerman, J., Amon, R., Gardner, W., Green, R., and Lohrenz, S.: A review of water column processes influencing hypoxia in the Northern Gulf of Mexico, *Est. Coasts*, 30, 735–752, doi:10.1007/BF02841331, 2007. 5627, 5641
- Dortch, Q. and Whittedge, T. E.: Does nitrogen or silicon limit phytoplankton production in the Mississippi River plume and nearby regions?, *Cont. Shelf Res.*, 12, 1293–1309, doi:10.1016/0278-4343(92)90065-R, 1992. 5627, 5630
- Dunn, D. D.: Trends in nutrient inflows to the Gulf of Mexico from streams draining the conterminous United States, 1972–1993, Water-resour. investigations rep. 96-4113, US Geol Survey, Austin, TX, 1996. 5626
- Dyhrman, S. T., Ammerman, J. W., and Van Mooy, B. A. S.: Microbes and the marine phosphorus cycle, *Oceanography*, 20, 110–116, doi:10.5670/oceanog.2007.54, 2007. 5641
- Eldridge, P. M. and Roelke, D. L.: Origins and scales of hypoxia on the Louisiana shelf: importance of seasonal plankton dynamics and river nutrients and discharge, *Ecol. Model.*, 221, 1028–1042, doi:10.1016/j.ecolmodel.2009.04.054, 2010. 5632
- Fennel, K., Wilkin, J., Levin, J., Moisan, J., O'Reilly, J., and Haidvogel, D.: Nitrogen cycling in the Middle Atlantic Bight: results from a three-dimensional model and implications for the North Atlantic nitrogen budget, *Global Biogeochem. Cy.*, 20, doi:10.1029/2005GB002456, GB3007, 2006. 5629, 5632
- Fennel, K., Wilkin, J., Previdi, M., and Najjar, R.: Denitrification effects on air-sea CO₂ flux in the coastal ocean: Simulations for the northwest North Atlantic, *Geophys. Res. Lett.*, 35, doi:10.1029/2008GL036147, L24608, 2008. 5629
- Fennel, K., Hetland, R., Feng, Y., and DiMarco, S.: A coupled physical-biological model of the Northern Gulf of Mexico shelf: model description, validation and analysis of phytoplankton variability, *Biogeosciences*, 8, 1881–1899, doi:10.5194/bg-8-1881-2011, 2011. 5627, 5628, 5630, 5632, 5633, 5639
- Fox, L. E., Sager, S. L., and Wofsy, S. C.: Factors controlling the concentrations of soluble phosphorus in the Mississippi estuary, *Limnol. Oceanogr.*, 30, 826–832, doi:10.4319/lo.1985.30.4.0826, 1985. 5630

5643

- Galperin, B., Kantha, L. H., Hassid, S., and Rosati, A.: A quasi-equilibrium turbulent energy model for geophysical flows, *J. Atmos. Sci.*, 45, 55–62, doi:10.1175/1520-0469(1988)045<0055:AQETEM>2.0.CO;2, 1988. 5629
- Goolsby, D. A. B., Aulenbach, W. A., Hooper, B. T., and Richard, P.: Nitrogen input to the Gulf of Mexico, *J. Environ. Qual.*, 30, 329–336, doi:10.2134/jeq2001.302329x, 2001. 5627
- Granéli, E., Wallström, K., Larsson, U., Granéli, W., and Elmgren, R.: Nutrient limitation of primary production in the Baltic Sea area, *Ambio*, 19, 142–151, 1990. 5640
- Greene, R. M., Lehrter, J. C., and Hagy III, J. D.: Multiple regression models for hindcasting and forecasting midsummer hypoxia in the Gulf of Mexico, *Ecol. Appl.*, 19, 1161–1175, doi:10.1890/08-0035.1, 2009. 5627
- Haidvogel, D. B., Arango, H., Budgell, W. P., Cornuelle, B. D., Curchitser, E., Lorenzo, E. D., Fennel, K., Geyer, W. R., Hermann, A. J., Lanerolle, L., Levin, J., McWilliams, J. C., Miller, A. J., Moore, A. M., Powell, T. M., Shchepetkin, A. F., Sherwood, C. R., Signell, R. P., Warner, J. C., and Wilkin, J.: Ocean forecasting in terrain-following coordinates: formulation and skill assessment of the Regional Ocean Modeling System, *J. Comput. Phys.*, 227, 3595–3624, doi:10.1016/j.jcp.2007.06.016, 2008. 5629
- Hetland, R. D. and DiMarco, S. F.: How does the character of oxygen demand control the structure of hypoxia on the Texas-Louisiana continental shelf?, *J. Mar. Syst.*, 70, 49–62, doi:10.1016/j.jmarsys.2007.03.002, 2008. 5629
- Hetland, R. D. and DiMarco, S. F.: Skill assessment of a hydrodynamic model of circulation over the Texas-Louisiana continental shelf, *Ocean Model.*, 43–44, 64–76, doi:10.1016/j.ocemod.2011.11.009, 2011. 5629
- Lehrter, J., Murrell, M., and Kurtz, J.: Interactions between freshwater input, light, and phytoplankton dynamics on the Louisiana continental shelf, *Cont. Shelf Res.*, 29, 1861–1872, doi:10.1016/j.csr.2009.07.001, 2009. 5634, 5652
- Lehrter, J., Beddick, D., Devereux, R., Yates, D., and Murrell, M.: Sediment–water fluxes of dissolved inorganic carbon, O₂, nutrients, and N₂ from the hypoxic region of the Louisiana continental shelf, *Biogeochemistry*, 109, 233–252, doi:10.1007/s10533-011-9623-x, 2012. 5634, 5652
- Lohrenz, S. E., Dagg, M. J., and Whittedge, T. E.: Enhanced primary production at the plume/oceanic interface of the Mississippi River, *Cont. Shelf Res.*, 10, 639–664, doi:10.1016/0278-4343(90)90043-L, 1990. 5637, 5639

5644

- Lohrenz, S. E., Fahnenstiel, G. L., Redalje, D. G., Lang, G. A., Chen, X., and Dagg, M. J.: Variations in primary production of northern Gulf of Mexico continental shelf waters linked to nutrient inputs from the Mississippi River, *Mar. Ecol. Prog. Ser.*, 155, 45–54, doi:10.3354/meps155045, 1997. 5627, 5637
- 5 Lohrenz, S. E., Fahnenstiel, G. L., Redalje, D. G., Lang, G. A., Dagg, M. J., Whittedge, T. E., and Dortch, Q.: Nutrients, irradiance, and mixing as factors regulating primary production in coastal waters impacted by the Mississippi River plume, *Cont. Shelf Res.*, 19, 1113–1141, doi:10.1016/S0278-4343(99)00012-6, 1999. 5627, 5637, 5639
- Lohrenz, S. E., Redalje, D. G., Cai, W. J., Acker, J., and Dagg, M.: A retrospective analysis of nutrients and phytoplankton productivity in the Mississippi River plume, *Cont. Shelf Res.*, 28, 1466–1475, doi:10.1016/j.csr.2007.06.019, 2008. 5627
- Mellor, G. L. and Yamada, T.: Development of a turbulence closure model for geophysical fluid problems, *Rev. Geophys. Space Phys.*, 20, 851–875, 1982. 5629
- Mesinger, F., DiMego, G., Kalnay, E., Mitchell, K., Shafran, P. C., Ebisuzaki, W., Jovi, D., 15 Woollen, J., Rogers, E., Berbery, E. H., et al.: North American regional reanalysis, *B. Am. Meteorol. Soc.*, 87, 343–360, 2006. 5629
- Paerl, H. W., Valdes, L. M., Joyner, A. R., Piehler, M. F., and Lebo, M. E.: Solving problems resulting from solutions: evolution of a dual nutrient management strategy for the eutrophying Neuse River Estuary, North Carolina, *Environ. Sci. Technol.*, 38, 3068–3073, doi:10.1021/es0352350, 2004. 5640
- 20 Pakulski, J. D., Benner, R., Whittedge, T., Amon, R., Eadie, B., Cifuentes, L., Ammerman, J., and Stockwell, D.: Microbial metabolism and nutrient cycling in the Mississippi and Atchafalaya River plumes, *Est. Coast. Shelf Sci.*, 50, 173–184, doi:10.1006/ecss.1999.0561, 2000. 5641
- Quigg, A., Sylvan, J. B., Gustafson, A. B., Fisher, T. R., Oliver, R. L., Tozzi, S., and Ammerman, J. W.: Going west: nutrient limitation of primary production in the Northern Gulf of Mexico and the importance of the Atchafalaya River, *Aquat. Geochem.*, 17, 519–544, doi:10.1007/s10498-011-9134-3, 2011. 5627, 5628, 5632, 5635, 5637, 5639, 5640, 5641
- 25 Rabalais, N., Turner, R. E., Justić, D., Dortch, Q., and Wiseman, W.: Characterization of Hypoxia. Topic 1 of the integrated assessment of hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program, Decision Analysis Series No. 15, Tech. rep., NOAA, Washington, DC, 1999. 5634, 5652
- 30

5645

- Rabalais, N., Turner, R. E., Dortch, Q., Justić, D., Bierman, V., and Wiseman, W.: Nutrient-enhanced productivity in the northern Gulf of Mexico: past, present and future, *Hydrobiologia*, 475–476, 39–63, doi:10.1023/A:1020388503274, 2002. 5627, 5628, 5639, 5640
- Rabalais, N. N. and Turner, R. E.: Oxygen depletion in the Gulf of Mexico adjacent to the Mississippi River, in: *Past and Present Water Column Anoxia*, edited by Neretin, L. N., vol. 64 of NATO Science Series: IV: Earth and Environmental Sciences, Springer, Netherlands, doi:10.1007/1-4020-4297-3_09, 225–245, 2006. 5640
- 5 Rabalais, N., Turner, R., Gupta, B. S., Boesch, D., Chapman, P., and Murrell, M.: Hypoxia in the northern Gulf of Mexico: does the science support the plan to reduce, mitigate, and control hypoxia?, *Estuar. Coasts*, 30, 753–772, doi:10.1007/BF02841332, 2007. 5634, 5652
- 10 Redalje, D. G., Lohrenz, S. E., and Fahnenstiel, G. L.: The relationship between primary production and the vertical export of particulate organic matter in a river-impacted coastal ecosystem, *Estuar. Coasts*, 17, 829–838, doi:10.2307/1352751, 1994. 5638
- Rowe, G. T. and Chapman, P.: Continental shelf hypoxia: some nagging questions, *Gulf Mexico Sci.*, 20, 153–160, 2002. 5633
- 15 Shchepetkin, A. F. and McWilliams, J. C.: The regional oceanic modeling system (ROMS): a split-explicit, free-surface, topography-following-coordinate oceanic model, *Ocean Model.*, 9, 347–404, doi:10.1016/j.ocemod.2004.08.002, 2005. 5629
- Smith, S. and Hitchcock, G.: Nutrient enrichments and phytoplankton growth in the surface waters of the Louisiana Bight, *Estuar. Coasts*, 17, 740–753, doi:10.2307/1352744, 1994. 5627
- 20 Sundby, B., Gobeil, C., Silverberg, N., and Mucci, A.: The phosphorus cycle in coastal marine sediments, *Limnol. Oceanogr.*, 37, 1129–1145, 1992. 5641
- Sylvan, J., Quigg, A., Tozzi, S., and Ammerman, J.: Mapping phytoplankton community physiology on a river impacted continental shelf: testing a multifaceted approach, *Estuar. Coasts*, 34, 1–14, doi:10.1007/s12237-011-9415-5, 2011. 5627, 5628, 5632, 5634, 5635, 5639, 5652
- 25 Sylvan, J. B., Dortch, Q., Nelson, D. M., Brown, A. F. M., Morrison, W., and Ammerman, J. W.: Phosphorus limits phytoplankton growth on the Louisiana shelf during the period of hypoxia formation, *Environ. Sci. Technol.*, 40, 7548–7553, doi:10.1021/es061417t, 2006. 5627, 5628, 5632, 5634, 5635, 5639, 5652
- 30 Sylvan, J. B., Quigg, A., Tozzi, S., and Ammerman, J. W.: Eutrophication-induced phosphorus limitation in the Mississippi River Plume: evidence from fast repetition rate fluorometry, *Lim-*

5646

ol. *Oceanogr.*, 52, 2679–2685, doi:10.4319/lo.2007.52.6.2679, 2007. 5627, 5628, 5632, 5634, 5635, 5639, 5652

Turner, R., Rabalais, N., Alexander, R., Mclsaac, G., and Howarth, R.: Characterization of nutrient, organic carbon, and sediment loads and concentrations from the Mississippi River into the northern Gulf of Mexico, *Estuar. Coasts*, 30, 773–790, doi:10.1007/BF02841333, 2007. 5627

Turner, R. E. and Rabalais, N. N.: Changes in Mississippi River water quality this century, *Bioscience*, 41, 140–147, 1991. 5627

Turner, R. E. and Rabalais, N. N.: Coastal eutrophication near the Mississippi river delta, *Nature*, 368, 619–621, doi:10.1038/368619a0, 1994. 5627

5647

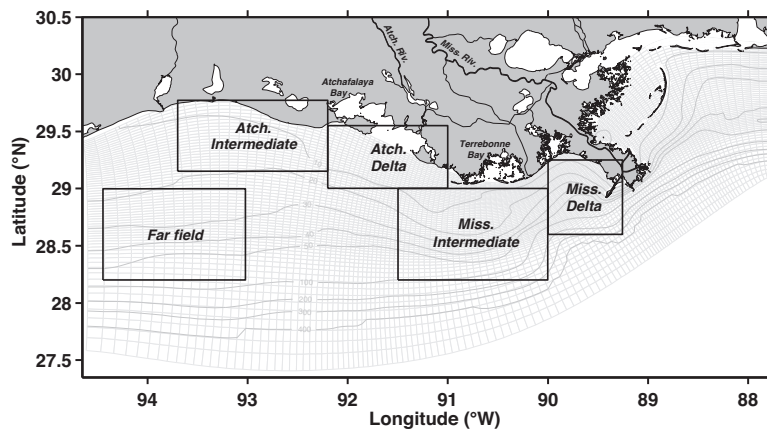


Fig. 1. Model domain, including grid and bathymetry (indicated in meters with the contour lines). The black boxes indicate the location of the five areas used during the analysis.

5648

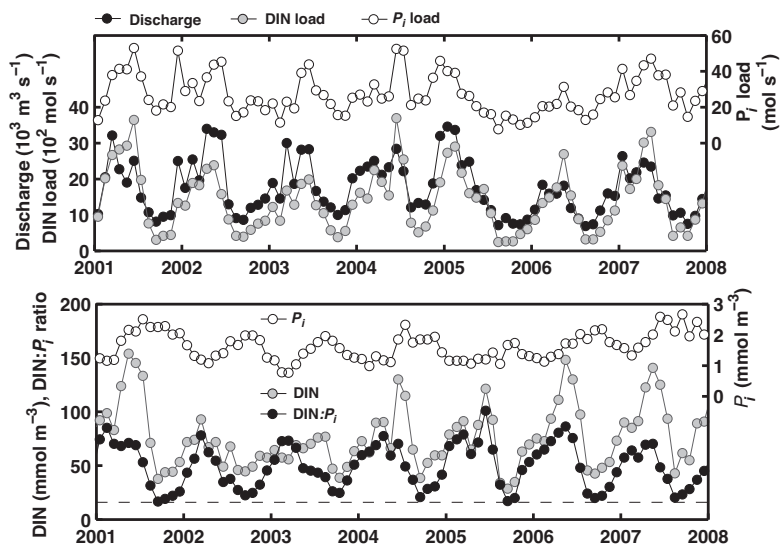


Fig. 2. Mississippi River forcing. Upper panel: freshwater discharge and nutrient loads. Lower panel: Nutrient concentrations and DIN : DIP ratio.

5649

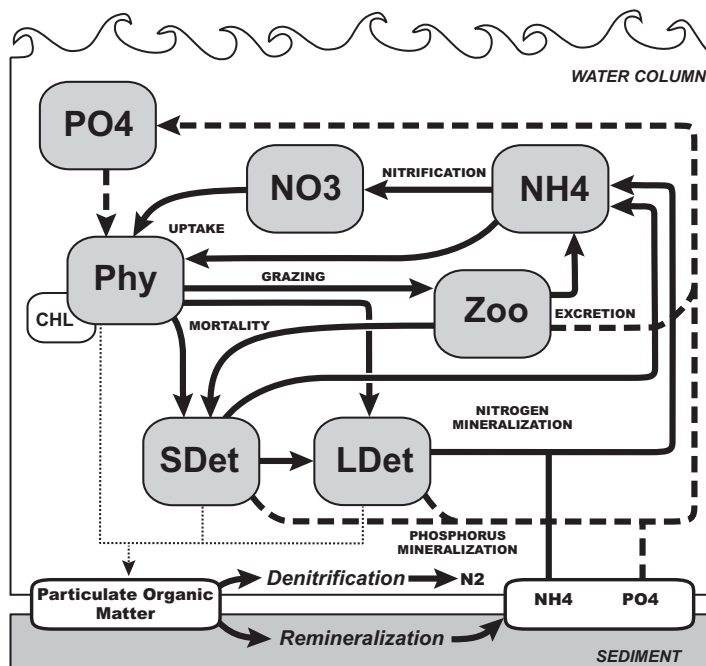


Fig. 3. Schematic of the ecosystem model. Dark arrows indicate ecosystem processes, thick dashed arrows represent the processes associated with phosphate (and were added to the nitrogen-based model). Thin dotted arrows represent the sinking of organic material. At the sediment–water interface, sedimenting particulate organic matter is instantly remineralized into ammonium and phosphate. Part of the particulate organic nitrogen is lost to nitrogen gas (N₂) through denitrification.

5650

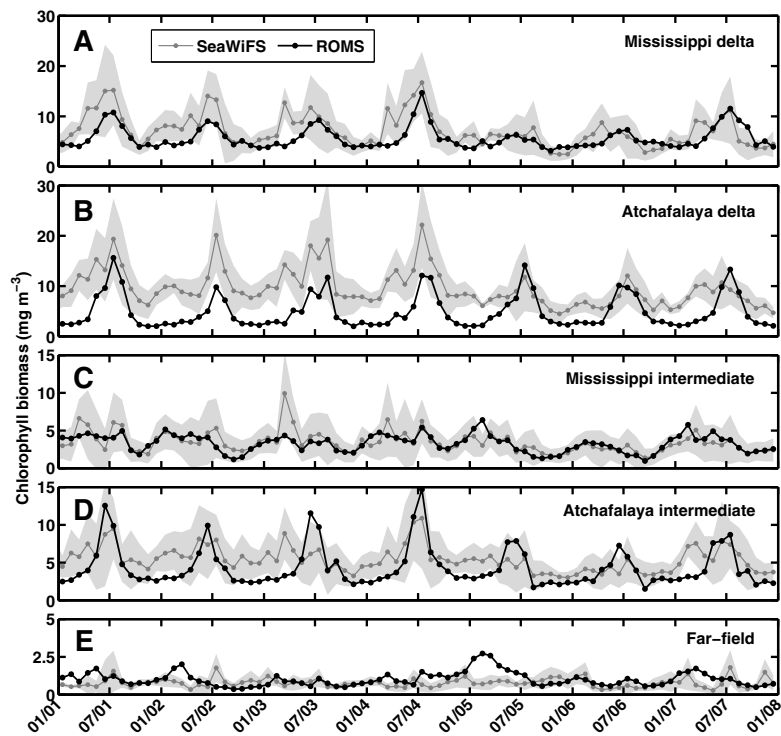


Fig. 4. Comparison between simulated (black lines) and observed (grey lines) monthly averaged surface chlorophyll biomasses for the five regions shown in Fig. 1. The grey area represents one standard deviation of the observations.

5651

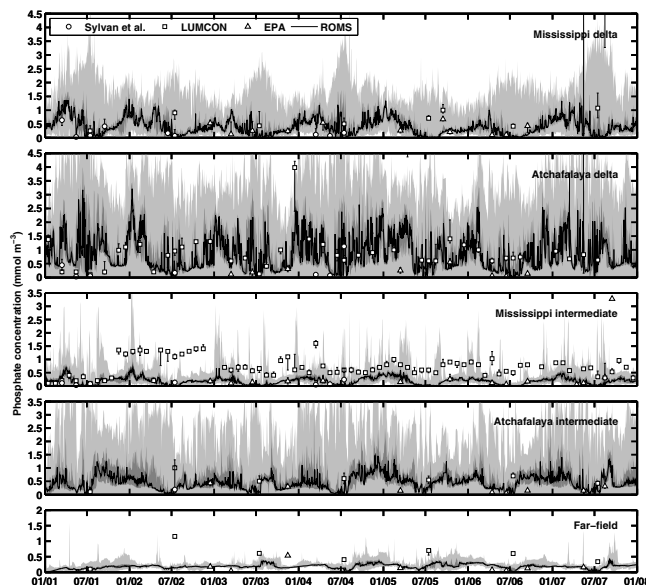


Fig. 5. Time series of simulated surface phosphate concentrations averaged over the five regions in Fig. 1, including the median (black line), the range between the 25th and 75th percentile (dark grey area) and the range between the minimum and maximum value (light grey area). Also shown are observations from Sylvan et al. (2006, 2007, 2011, circles), LUMCON (Rabalais et al., 1999, 2007, squares) and EPA (Lehrter et al., 2009, 2012, triangles). Observations are averaged by month with error bars indicating the range between the 25th and 75th percentile.

5652

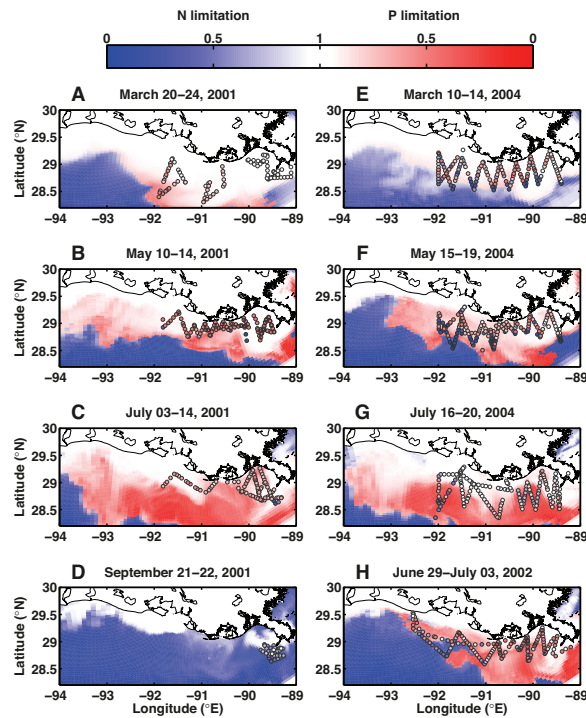


Fig. 6. Simulated (colour maps) and observed (circles) nutrient limitation on the Texas-Louisiana shelf in March, May, July and September 2001 (**A–D**), in March, May and July 2004 (**E–G**) and in June–July 2002 (**H**). The colour-coded scale corresponds to L_N (blue) and L_P (red), whereas nutrient limitation does not occur in the white region.

5653

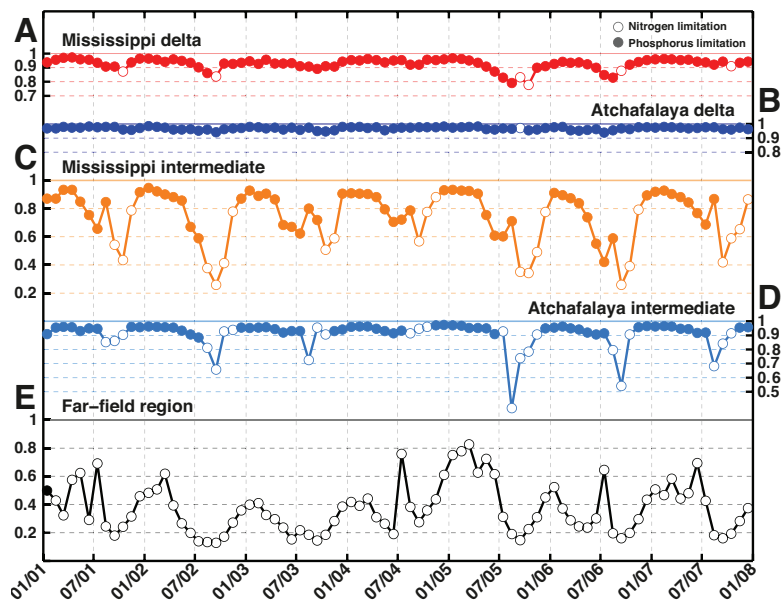


Fig. 7. Times series of monthly mean, area-averaged type and magnitude of nutrient limitation for the five regions described in Fig. 1. Open circles represent nitrogen limitation (L_N) and closed circles phosphorus limitation (L_P).

5654

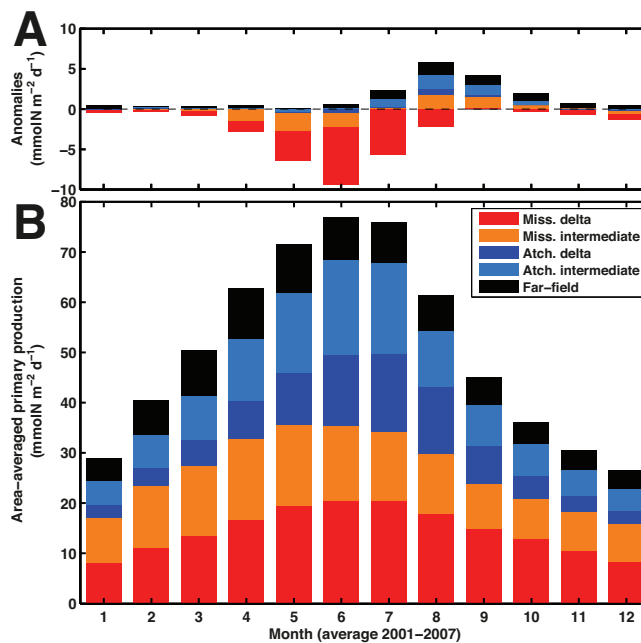


Fig. 8. Annual cycle of water column-integrated primary production for the five regions shown in Fig. 1. **(A)** Anomalies calculated by subtracting results from the control run (with phosphate) from results of the nitrogen-only model. Positive values indicate an enhancement of primary production in the control run. **(B)** Primary production in the control run. Monthly means were calculated for the period 2001–2007.

5655

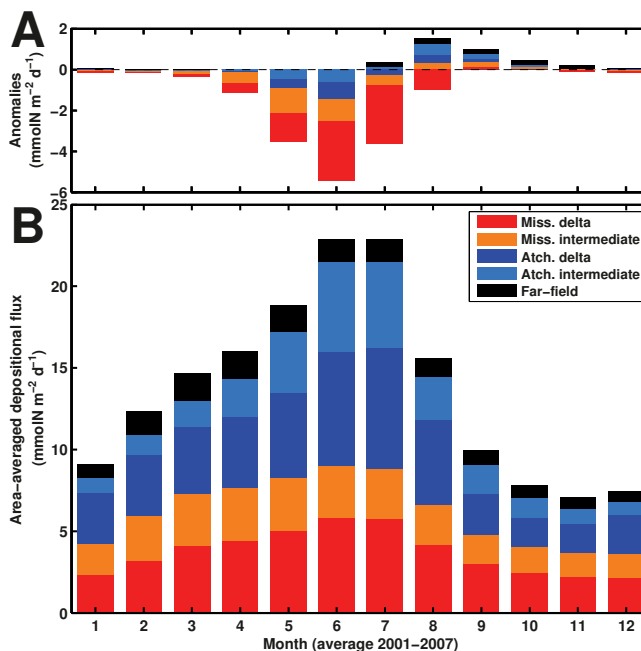


Fig. 9. Annual cycle of depositional flux at the sediment–water interface for the five regions shown in Fig. 1. **(A)** Anomalies calculated by subtracting results from the control run (with phosphate) from the results of the nitrogen-only model. Positive values indicate an enhancement of depositional flux in the control run. **(B)** Depositional flux at the sediment–water interface in the control run. Monthly means were calculated for the period 2001–2007.

5656

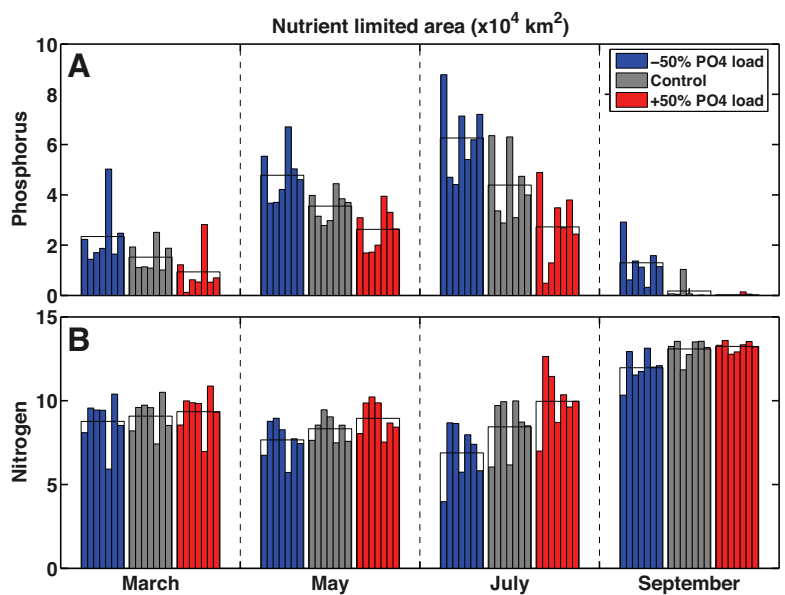


Fig. 10. Total area of surface phosphorus (**A**) and nitrogen (**B**) limitation ($L < 0.75$) in March, May, July and September for the control simulation (grey) and for the model experiments with increased (red) and decreased (blue) phosphate. Filled bars indicate the monthly average for each year (from left to right, 2001–2007) and open bars indicate the average calculated over the whole simulation. Total model area is $14.6 \times 10^4 \text{ km}^2$.