

# Chapter 7

## Modeling River-Induced Phosphorus Limitation in the Context of Coastal Hypoxia

Arnaud Laurent and Katja Fennel

**Abstract** The urban development of coastal areas and the increased use of chemical fertilizers over the last century have led to a worldwide expansion of coastal eutrophication and a significant increase in the occurrence and intensity of human-induced coastal hypoxia. Proportionally, nitrogen load has often increased more severely than phosphorus load and phosphorus limitation became a common seasonal phenomenon in many eutrophic coastal systems. Phosphorus limitation may alter the magnitude, timing, and location of phytoplankton production with potential effects on hypoxia. Yet, because of the difficulty in observing these effects, limited work has been carried out to assess the influence of P limitation on hypoxia. Models are thus useful tools for simulating the effects of river-induced phosphorus limitation on coastal hypoxic systems. Modeling P limitation is important to better understand the processes controlling hypoxia, to improve the predictive skill of hypoxia prediction models, and to design and evaluate nutrient management strategies for hypoxia mitigation. Here, we review the effects of phosphorus limitation on a continuum of coastal hypoxic systems, contrasting the effects of P limitation on systems that are primarily one-dimensional (or “flow-through”) like the Neuse River Estuary versus more dispersive open systems like the Mississippi River plume. We discuss modeling frameworks and techniques that are relevant in this context and summarize recent modeling work that quantitatively assesses the effect of phosphorus limitation on hypoxia development in the Mississippi River plume.

**Keywords** Coastal eutrophication • Biogeochemical model • Phosphorus limitation • Coastal hypoxia • Nutrient load • Hypoxia mitigation

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## 7.1 Introduction

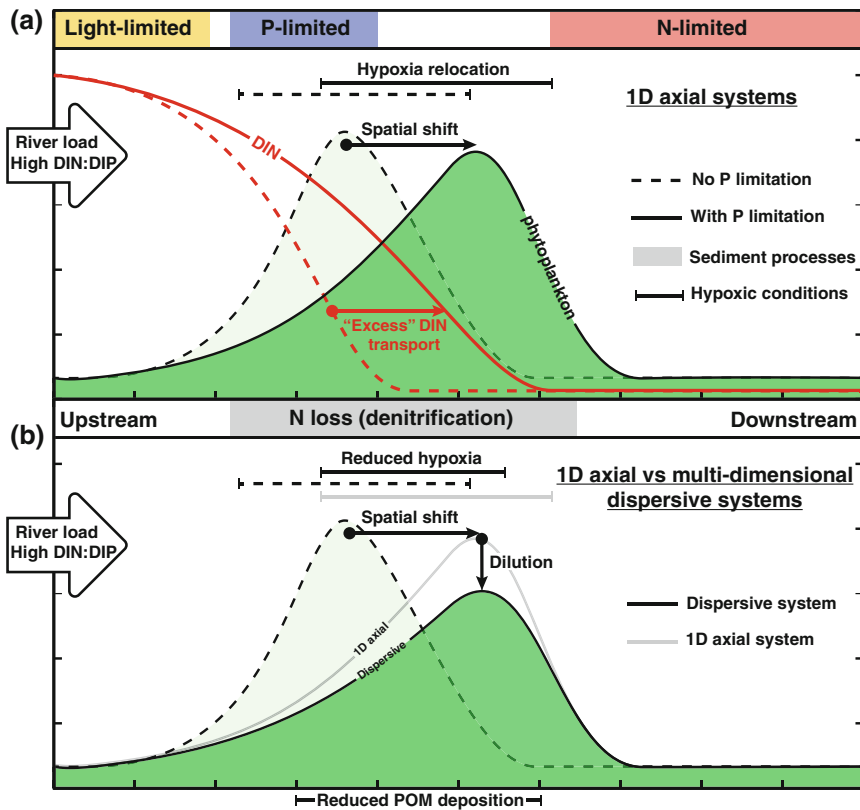
Riverine nitrogen (N) and phosphorus (P) fluxes to the coastal oceans have both increased over the last century due to the development of coastal areas and an increasing use of chemical fertilizers (Zhang et al. 2010). N and P are essential elements for phytoplankton and, for balanced growth, are required approximately in the ratio of 16 N:1P (Redfield et al. 1963). N is typically the limiting element in marine systems because denitrification produces biologically unavailable  $N_2$  resulting in a partial loss of N, while P has no such loss process and is rapidly recycled (Caraco et al. 1990). Increases in river nutrient loads have not necessarily been in the same proportion for N and P because their sources differ. N inputs into watersheds are mainly diffuse and associated with the use of chemical fertilizers (Boesch 2002), whereas P inputs are primarily from point sources related to urban wastewater (Harrison et al. 2010). The stoichiometry of dissolved inorganic N (DIN) and dissolved inorganic P (DIP) in river waters can thus deviate significantly from the Redfield ratio of 16 N:1P. Measures to control nutrient pollution from point sources have been put in place since the 1970s, but the use of chemical fertilizers has increased further since then. This has led to a proportionally larger increase of N loads, altered the N:P stoichiometry such that  $N:P > 16$  in estuarine and river plume waters of many coastal systems (Conley 2000; Scavia and Donnelly 2007; Paerl 2009), and promoted P-limited primary production in otherwise N-limited systems (Howarth and Marino 2006).

P limitation and hypoxia often co-occur in coastal systems because they are both driven by excess nutrient load and eutrophication. A switch from N to P limitation may alter the magnitude, timing, and location of phytoplankton production with a potential effect on hypoxia (Paerl et al. 2004). Yet, limited work has been carried out to assess the influence of P limitation on hypoxia. The paucity of observational evidence for the effects of P limitation on hypoxia results in large part from the effort involved in observing coastal systems at the relevant spatial and temporal scales combined with the inability to manipulate N and P loads at the scale of the whole system. In this context, models are important for simulating the consequences of different resource limitation scenarios and for quantitatively assessing the effects of P limitation on coastal hypoxia.

The objectives of this chapter are to (1) describe the occurrence and effects of P limitation on hypoxic systems, (2) provide an overview of modeling frameworks and techniques that can be used to study river-induced P limitation in the context of coastal hypoxia, and (3) present results from a model investigation for the Mississippi River plume in the northern Gulf of Mexico as a case study of the effect of P limitation on hypoxia. First, we consider how P limitation may influence hypoxia in a one-dimensional flow-through system and then contrast this with a more open and dispersive system. Several examples representing a continuum between these two are provided. We then discuss several modeling frameworks and present recent results from the modeling investigation of Laurent and Fennel (2014) for the Mississippi River plume.

## 7.2 Occurrence of P Limitation in Hypoxic Systems

River-induced P limitation is most often a transient phenomenon that occurs at peak discharge in spring, when N load tends to be particularly high. When primary production is P-limited in estuaries or river plumes, the excess DIN is transported downstream into more saline, N-limited waters where it stimulates primary production (Fig. 7.1a). In other words, the location and timing of DIN uptake are shifted downstream and delayed in time. The spatial shift tends to spread eutrophication over larger regions and into downstream waters compared to a situation where P is not limiting (Paerl et al. 2004). P limitation in the spring is



**Fig. 7.1** Conceptual model showing the spatial effects of river-induced P limitation on DIN concentration, phytoplankton biomass, and hypoxia in one-dimensional flow-through systems (A) and open dispersive systems (B). Resource limitation is indicated at the top. For both flow-through and dispersive systems, N is partly removed by denitrification in the sediment. As an indication, spatial distributions are also represented for systems where P is not limiting (dashed lines)

generally followed by N limitation during the low-discharge season in summer (Conley 2000).

Sediments play an important role in the generation of coastal hypoxia. Particulate organic matter (POM) is deposited and remineralized in the sediments, which consume  $O_2$  in the process. Sediment oxygen consumption (SOC) can be the dominant  $O_2$  sink (Quiñones-Rivera et al. 2010) and thus a significant driver of hypoxia (Fennel et al. 2013; Yu et al. 2015a). A fraction of the deposited N is lost as biologically unavailable  $N_2$  through sediment denitrification, an anaerobic microbial remineralization process that represents a major sink for N in coastal areas (Fennel et al. 2009). P may be adsorbed onto the sediment in oxygenated conditions, but is otherwise released back to the water column as DIP (McManus et al. 1997). This disparity in N and P recycling results in a shift back to N limitation in downstream and offshore waters (Fig. 7.1).

There is currently no consensus on whether P limitation amplifies or weakens hypoxia. P limitation is generally viewed as a mechanism that relocates or spreads hypoxia (Paerl et al. 2004; Scavia and Donnelly 2007) and thereby considered detrimental. Any relocation of primary production due to P limitation will also induce a relocation of  $O_2$  sinks although the detailed mechanisms are nonlinear and thus hard to predict. On the one hand, the decomposition of organic matter in downstream waters should result in higher  $O_2$  consumption rates there and could potentially lead to the development of hypoxic conditions in waters that would be normoxic without P limitation. This is likely the case in one-dimensional flow-through systems like the Neuse River Estuary, which are characterized by strong freshwater-induced stratification and transport akin to a simple translation along their upstream–downstream axis; a shift of primary production along this axis may well result in a linear effect on hypoxia (Fig. 7.1a). On the other hand, P limitation in dispersive open systems, such as river plumes, may reduce the occurrence and magnitude of hypoxia. Excess nutrients in river plumes are being diluted when plumes interact with coastal circulation forced by topography, winds, and tides. In this case, a “downstream” relocation may spread elevated primary production over a larger area while lowering the maxima of primary production in the affected area, in effect “diluting” the imprint of eutrophication (Fig. 7.1b).

Further uncertainty in predicting the effects of P limitation on hypoxia results from its differential effect on sediment-water fluxes of N and P. At low  $O_2$ , N-loss through sediment denitrification is inhibited (Kemp et al. 1990), whereas P is released from the sediments (Ingall and Jahnke 1997). The relative magnitude of these effects is often poorly constrained. Certainly, the  $O_2$  dependence can lead to high sediment-water fluxes of N and P during hypoxic conditions (Conley et al. 2002; Kemp et al. 2005) and result in nonlinear effects of P limitation on hypoxia.

In the following sections, we discuss and compare four prominent examples of hypoxic systems where P limitation has been studied. Their locations are shown in Fig. 7.2.

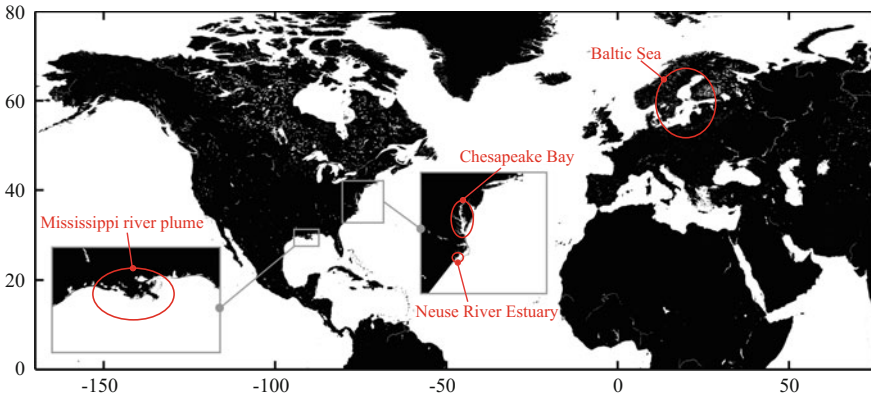


Fig. 7.2 Map showing the location of the four hypoxic systems discussed in Sect. 7.2

### 7.2.1 *Neuse River Estuary*

The Neuse River Estuary is a eutrophic to hypertrophic estuary (Paerl et al. 1998) located on the Atlantic coast of the USA (Fig. 7.2). This shallow estuary ( $\sim 4$  m) has a  $455 \text{ km}^2$  surface area and drains water from a  $16.1 \times 10^3 \text{ km}^2$  watershed (Stow and Borsuk 2000). The estuary discharges into the Pamlico Sound, which is connected to the Atlantic Ocean. N and P loads to this estuary from urban, industrial, and agricultural sources have increased since the 1960s (Stow et al. 2001). Annual total load into the Neuse River Estuary is about  $9.6 \times 10^6 \text{ kg N y}^{-1}$  and  $9.7 \times 10^5 \text{ kg P y}^{-1}$  (1993–2003 average, Burkholder et al. 2006). The increase in nutrient load was followed by the emergence of cyanobacterial blooms in the upstream portion of the estuary and a concomitant increase in bottom-water hypoxia (Paerl et al. 1998, 2004) that can reach over 40% of the estuary's surface area in summer (Buzzelli et al. 2002). The decrease in P loading resulted from a ban of P detergents in the 1980s and represents a “natural” system-wide experiment on the effect of P limitation on a one-dimensional eutrophic flow-through estuary. After the ban came into effect, P limitation developed in the upstream portion of the Neuse River Estuary and led to the downstream transport of excess DIN with a subsequent increase of phytoplankton biomass in mid-estuary waters (Paerl et al. 2004). Evidence for how this affected hypoxia is limited.

### 7.2.2 *Chesapeake Bay*

Chesapeake Bay, located about 300 km north of the Neuse River Estuary (Fig. 7.2), is the largest ( $11.5 \times 10^3 \text{ km}^2$ ) and most productive estuary in the USA. This relatively shallow ( $\sim 8$  m with a deep central channel) and partially stratified estuary

drains a  $164.2 \times 10^3 \text{ km}^2$  watershed. Flow is primarily along one axis in Chesapeake Bay but the lower bay is broad with potential for transverse transport and dispersion. Similar to the Neuse River Estuary, Chesapeake Bay has experienced a long-term increase in hypoxia since the 1950s associated with enhanced nutrient loading due to the use of chemical fertilizers and the development of urban areas in the watershed (Hagy et al. 2004; Kemp et al. 2005). Annual total load into Chesapeake Bay is about  $1.5 \times 10^8 \text{ kg N y}^{-1}$  and  $9.6 \times 10^6 \text{ kg P y}^{-1}$  (1990–2012 average, Hirsch et al. 2013). The relatively long residence time for freshwater and nutrients (90–180 days, Kemp et al. 2005) combined with pronounced freshwater stratification that isolates the deeper central channel (20–30 m) results in seasonal hypoxia in the mid-bay, reaching a volume of about  $8 \text{ km}^3$  on average in July (Murphy et al. 2011).

In Chesapeake Bay, resource limitation varies in space and follows a well-defined seasonal cycle controlled by freshwater inputs (Kemp et al. 2005). P limitation develops in the upper section of the bay which receives high N:P river inputs in spring during the peak of freshwater runoff (Fisher et al. 1992, 1999) and is alleviated by remineralized P fluxes from the sediment as waters move downstream (Fisher et al. 1999). The intrusion of N-limited marine waters and the benthic source of P modify nutrient stoichiometry in the lower section of Chesapeake Bay where primary production is typically N-limited. Using N and P load scenarios with a multi-nutrient biogeochemical model, Wang et al. (2016) showed that P load reduction in the upper bay tributaries can be an effective strategy to increase bottom-water  $\text{O}_2$  in the upper bay due to the intensification of P limitation. This suggests a mitigation effect of P limitation on hypoxia. However, direct evidence of the spatial and temporal effects of P limitation on hypoxia is still missing for Chesapeake Bay.

### 7.2.3 *Northern Gulf of Mexico*

The Mississippi–Atchafalaya River Basin is the third largest river basin in the world; it drains a  $3.2 \times 10^6 \text{ km}^2$  watershed and discharges onto the Louisiana shelf through the Mississippi River delta and Atchafalaya Bay. The Mississippi River plume is a dispersive open system controlled by a complex set of interactions with wind forcing, coastal topography, and cross-shore transport associated with eddies (Schiller et al. 2011). As for the previous systems, nutrient loading increased since the 1960s, mainly due to the extensive use of chemical fertilizers, and represents currently an annual total load of about  $1.2 \times 10^9 \text{ kg N y}^{-1}$  and  $1.5 \times 10^8 \text{ kg P y}^{-1}$ . Excess nutrient load results in high primary production (Lohrenz et al. 1997) and recurrent bottom-water hypoxia in summer that extends over  $14.9 \times 10^3 \text{ km}^2$  on average (Obenour et al. 2013). This is the largest hypoxic area in North American coastal waters (Rabalais et al. 2002). Numerous physical processes affect the timing, location, and extent of hypoxia on the Louisiana shelf (Hetland and DiMarco 2008; Wang and Justic 2009; Zhang et al. 2012; Yu et al. 2015a).

On the Louisiana shelf, P limitation occurs during peak discharge in spring and early summer (Sylvan et al. 2006, 2007; Quigg et al. 2011) due to a high N:P ratio in Mississippi River loads. P limitation leads to the downstream (westward) transport of excess N and a subsequent increase of primary production on the western Louisiana shelf (Laurent et al. 2012). Due to a dilution effect, this results in a reduction of hypoxia on the Louisiana shelf (Laurent and Fennel 2014; see details in Sect. 7.4). During the low-discharge season in summer, resource limitation switches back to N limitation because of N-loss through sediment denitrification and mixing with open ocean waters.

### 7.2.4 *Baltic Sea*

The Baltic Sea is the largest brackish water system in the world. It covers a total area of  $381 \times 10^3 \text{ km}^2$  and drains a  $1.6 \times 10^6 \text{ km}^3$  watershed. This relatively deep ( $\sim 55 \text{ m}$ ) semienclosed estuarine system is connected to the North Sea through the Danish Straits, via a series of sills that limit deep-water exchange with the deep and strongly stratified subbasins of the Baltic Sea. The long water residence time of the Baltic Sea (20–30 years) leads to long periods of  $\text{O}_2$  depletion in bottom waters leading to widespread hypoxia in the deep basins (Krauss 2001).

The Baltic Sea has been increasingly affected by anthropogenic eutrophication since the 1960s with a simultaneous increase of hypoxia (Conley et al. 2002, 2011). Currently, the average total N and P loads are about  $7.0 \times 10^8 \text{ kg N y}^{-1}$  and  $0.3 \times 10^8 \text{ kg P y}^{-1}$ , respectively (HELCOM 2013) and are dominated by inputs from major rivers such as the Vistula, Oder, Daugava, Neman, and Neva (Stålnacke et al. 1999). P loads have decreased since the 1980s due to management of point sources (Nausch et al. 1999); hence, one would expect the system to move toward P limitation. Indeed P limitation has been observed but only in nearshore areas such as the Himmerfjärd inlet on the coast of Sweden in spring and early summer following P management measures (Granéli et al. 1990). P limitation rarely occurs in the open waters of the central Baltic Sea due to the efficient release of P from sediments under hypoxic conditions (Eilola et al. 2009). Low  $\text{O}_2$  waters also promote N removal through denitrification when nitrate is available, due to an increased oxic/anoxic interface with increasing hypoxic volume (Vahtera et al. 2007). The resulting low N:P ratio in surface waters of the open Baltic Sea stimulates the development of  $\text{N}_2$ -fixing cyanobacterial blooms (Neumann and Schernewski 2008). These blooms in combination with the external P loads exacerbate bottom-water hypoxia and further increase the internal P load. Despite P load reduction measures, this positive feedback inhibits the recovery of the system from eutrophication (Vahtera et al. 2007).

### **7.2.5 One-Dimensional Flow-Through Versus Dispersive Open Systems**

The effect of P limitation on phytoplankton is similar among the four systems presented above; P limitation displaces their biomass toward downstream waters due to the transport of excess N (Fig. 7.1a). The consequence for hypoxia depends on the system. In one-dimensional systems such as the Neuse River Estuary, hypoxia is thought to respond to P limitation with a displacement or an extension of hypoxic conditions (Fig. 7.1a). On the contrary, in open dispersive systems such as the Mississippi River plume, P limitation dilutes eutrophication and reduces hypoxia (Fig. 7.1b). In intermediate systems, such as Chesapeake Bay, both effects may occur depending on the location and timing of hypoxia. However, these contrasting effects remain speculative due to the limited number of investigations.

The Baltic Sea does not seem to fit in this continuum. It is an unusual system because permanent hypoxia appears to restrict the possibility for P limitation in open waters. This example demonstrates the difference between seasonally and permanent hypoxic systems and illustrates the importance of sediment-water fluxes and recycling in controlling P limitation in eutrophic systems.

## **7.3 Modeling P Limitation in Coastal Hypoxic Systems**

There are primarily three reasons for simulating P limitation in coastal hypoxic systems: (1) to better understand the processes controlling hypoxia, (2) to improve the predictive skill of hypoxia prediction models, and (3) to be better able to evaluate and design nutrient management strategies for hypoxia mitigation. Hereafter, we present an overview of modeling frameworks and strategies that are used to investigate the relationship between coastal hypoxia and nutrient loading. We focus on models that explicitly consider P load and are able to represent P limitation.

### **7.3.1 Statistical Regressions**

Perhaps the simplest approach for assessing the effects of P limitation on hypoxia is through statistical regressions. Statistical regression models have been used to predict hypoxia or bottom O<sub>2</sub> concentration as a function of nutrient loading (Turner et al. 2006; Greene et al. 2009) and physical drivers (Prasad et al. 2011; Forrest et al. 2011; Obenour et al. 2012). Although not strictly a simulation model, this strategy is worth mentioning here because it is a useful tool for assessing the effects of nutrient loading as well as other factors on the development of hypoxia. In this approach, the contribution of N and P loads to hypoxia is inferred from their



statistical weight in the multiple regressions. However, P limitation is not directly represented; hence, this approach does not provide mechanistic insight.

### ***7.3.2 Coupled Physical-Biogeochemical Models***

Biogeochemical models represent the cycling of chemical elements such as C, N, P, or O in an ecosystem due to biotic and abiotic processes. Resource limitation is directly represented in these models; hence, they provide mechanistic insights into the effect of P limitation on hypoxia. The physical framework is also important because nutrient supply, primary production, and freshwater transport are three-dimensional, time-dependent processes that influence the development and location of hypoxia; in addition, vertical stratification is a key driver. Physical-biogeochemical models coupling circulation, physical properties of the water column, and biogeochemistry are therefore essential to study the processes controlling hypoxia in a spatially explicit manner. These models vary in their level of complexity in terms of both their biogeochemistry and physical framework. For instance, biogeochemical models may represent P as DIP only, or may include dissolved organic P (DOP) and the O<sub>2</sub>-dependent P scavenging on detrital POM. Stratification and transport can be represented using coarse resolution box models that parameterize large-scale transport or high-resolution hydrodynamic models that simulate circulation explicitly.

#### **7.3.2.1 Formulations of Limitation by Multiple Nutrients**

Because P limitation is often a transient phenomenon in coastal hypoxic systems, multi-nutrient models that are able to switch between limitation by P and N (and sometimes silicate) are necessary. Several model formulations have been used to represent multi-nutrient limitation in ecosystem models. They can be divided into three general categories (Flynn 2003): (1) simple Monod-type models, (2) more complex cell quota models, and (3) complex mechanistic models that represent internal nutrient pools and feedback processes. Mechanistic models are possibly more realistic in representing the biochemistry of the cell (John and Flynn 2000), but may be over-parameterized due to more unknown parameters, are computationally less efficient, and may be unnecessarily complex for the purpose of simulating the effects of nutrient limitation switches on hypoxia. The quota model, which can include different functional forms of phytoplankton, represents internal nutrient storage. This model type is more efficient and frequently used in ecosystem studies (e.g., Roelke et al. 1999). However, measurements of intracellular nutrient concentrations are scarce, and thus, modeled internal nutrient concentrations cannot be validated against observations. Monod-type models represent nutrient limitation as a direct function of nutrient availability in surrounding waters and assume

balanced growth. They are frequently used in multi-nutrient ecosystem models because of their stability and computational efficiency.

Several multi-nutrient Monod-type functional forms have been proposed (O'Neill et al. 1989). The most commonly used are the minimum and the multiplicative functional forms. The minimum functional form assumes that phytoplankton growth depends on the most limiting nutrient, whereas the multiplicative form assumes co-limitation. The minimum function is frequently used to represent P limitation in biogeochemical models, e.g., to study O<sub>2</sub> dynamics in the Baltic Sea (Neumann et al. 2002; Eilola et al. 2009) and on the Louisiana shelf (Justić and Wang 2014; Laurent and Fennel 2014). These formulations are based on limitation factors  $L_N$  for N ( $L_N = L_{NO_3} + L_{NH_4}$ ) and  $L_P$  for P, calculated as follows:

$$L_{NO_3} = \frac{NO_3}{k_{NO_3} + NO_3} \cdot \frac{1}{1 + NH_4/k_{NH_4}} \quad (7.1)$$

$$L_{NH_4} = \frac{NH_4}{k_{NH_4} + NH_4} \quad (7.2)$$

$$L_P = \frac{DIP}{k_{DIP} + DIP} \quad (7.3)$$

where  $k_{NO_3}$ ,  $k_{NH_4}$ , and  $k_{DIP}$  are the half-saturation constants for nitrate, ammonium, and DIP uptake, respectively. The second factor on the right-hand side of Eq. 7.1 represents ammonium inhibition of nitrate uptake. Quadratic versions of the limiting factors have also been used (Neumann et al. 2002).

The specific phytoplankton growth rate ( $\mu$ ) depends on light ( $E$ ), temperature ( $T$ ), and the nutrient limitation factor such that

$$\mu = \mu_{\max}(E, T) \cdot L_{\text{tot}} \quad (7.4)$$

where  $\mu_{\max}(E, T)$  is the light- and temperature-dependent maximum growth rate of phytoplankton and  $L_{\text{tot}}$  is the nutrient limitation factor ( $0 < L_{\text{tot}} < 1$ ).

The minimum and multiplicative forms of  $L_{\text{tot}}$  are formulated, respectively, as follows:

$$L_{\text{tot}} = \min(L_N, L_P) \quad (7.5)$$

$$L_{\text{tot}} = L_N \cdot L_P \quad (7.6)$$

### 7.3.2.2 Sediment-Water Fluxes

Sediment-water fluxes represent a key aspect of simulating P limitation in hypoxic environments. Nutrient fluxes control the occurrence of P limitation (e.g., Baltic Sea) and its location (e.g., Chesapeake Bay), whereas SOC can be an important sink

for bottom  $O_2$  in eutrophic systems (e.g., Fennel et al. 2013; Yu et al. 2015b). In biogeochemical models, sediment-water fluxes can either be parameterized or mechanistically simulated using a diagenetic model (Fennel et al. 2009). Perhaps the most parsimonious approach is a reflective boundary where SOC, N and P fluxes are proportional to deposited POM (Laurent and Fennel 2014). Simple parameterizations based on observations are used to represent sediment-water fluxes as a function of overlying bottom-water conditions. For example, Fennel et al. (2013) represent SOC as a function of bottom  $O_2$  and temperature based on observed relationships. In this case, nutrient fluxes are a linear function of SOC. More complex parameterizations and representations of P cycling at the sediment-water interface are also used (e.g., Neumann and Schernewski 2008; Eilola et al. 2009; Gustafsson 2012; Justić and Wang 2014). The appropriate level of complexity for these parameterizations depends on the characteristics of the system.

Vertically resolved diagenetic models are the most realistic representation of sediment processes. Yet, they do not necessarily perform better than simple parameterizations of sediment-water fluxes (Wilson et al. 2013). Given their higher computational cost, they are typically used at the expense of physical realism (e.g., Eldridge and Roelke 2010) and simple parameterizations are often preferred. Parameterizations based on diagenetic model results have been proposed as an intermediate solution (Laurent et al. 2016).

### 7.3.2.3 Box Models

Box models have a coarse spatial resolution that reduces hydrodynamics to the large-scale spatial features of the system. For example, a 3-layer box model of the semienclosed Szczecin Lagoon in the southern Baltic Sea was used to describe long-term effects of eutrophication in a coastal system and its response to nutrient management (Humborg et al. 2000). A 4-box, 2-layer circulation framework of the Mississippi River plume was used to study the effects of nutrient loading in the seasonally hypoxic Louisiana shelf (Eldridge and Roelke 2010). This simple transport framework allows for the use of a more complex representation of biogeochemistry, namely the use of a mechanistic diagenetic model to represent realistic sediment-water fluxes, and representation of multiple phytoplankton groups with different nutrient requirements and growth dynamics (Eldridge and Roelke 2010).

An important drawback of the box model framework is its inability to resolve the details of vertical stratification despite its importance in hypoxia formation. For example, in the Mississippi River plume, hypoxic conditions are limited to the relatively thin bottom boundary layer (Wiseman et al. 1997; Fennel et al. 2016). The lack of vertical resolution can be alleviated to some degree by increasing the horizontal resolution (Gustafsson 2012). Nonetheless, the coarse horizontal resolution remains inadequate to represent the spatial effect of P limitation on primary

production (Fig. 7.1), and therefore, box models are limited in their suitability for studying the effect of P limitation on hypoxia.

#### 7.3.2.4 Hydrodynamic Models

High-resolution hydrodynamic models enable the more realistic spatial representation of resource limitation and hypoxia that is often essential for studying the spatial and temporal effects of P limitation on hypoxia in coastal environments. The hydrodynamic models are coupled to biogeochemical models of varying complexities. However, given the computing cost, relatively simple biogeochemical models are often used to represent pelagic processes. This type of framework has been used in large hypoxic systems such as Chesapeake Bay (see Irby et al. 2016 for a model comparison), the Baltic Sea (Eilola et al. 2009), and the northern Gulf of Mexico (Justić and Wang 2014; Laurent and Fennel 2014). Laterally averaged and three-dimensional coarse resolution coupled models have also been used in the Neuse River Estuary (Bales and Robbins 1999; Wool et al. 2003).

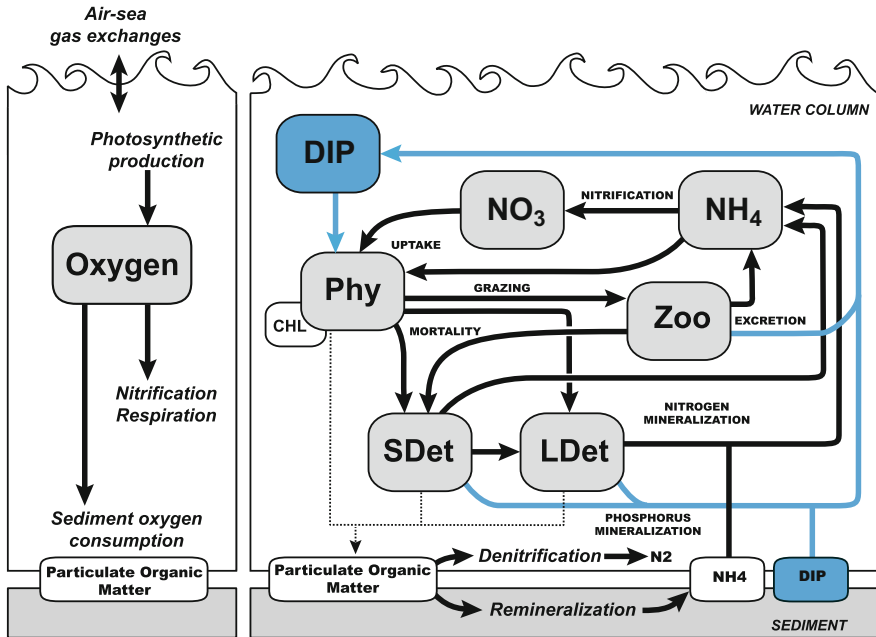
Hereafter, we present an overview of the recent investigations of Laurent and Fennel (2014) that used a coupled hydrodynamic-biogeochemical model of the northern Gulf of Mexico to quantitatively assess the effect of P limitation on hypoxia in a relatively open and dispersive system. Model setup and results are also relevant to other coastal systems where P limitation and hypoxia co-occur.

## 7.4 The Mississippi River Plume Case Study

### 7.4.1 Model Description

The model simulates circulation and biogeochemistry with the Regional Ocean Modeling System (ROMS, Haidvogel et al. 2008). The circulation model is described in Hetland and DiMarco (2008, 2012). The biogeochemical model aims at a parsimonious representation of the N and P cycles (Fig. 7.3). It is based on the N-cycle model of Fennel et al. (2006, 2008), which was extended to include DIP (Laurent et al. 2012) and O<sub>2</sub> (Fennel et al. 2013).

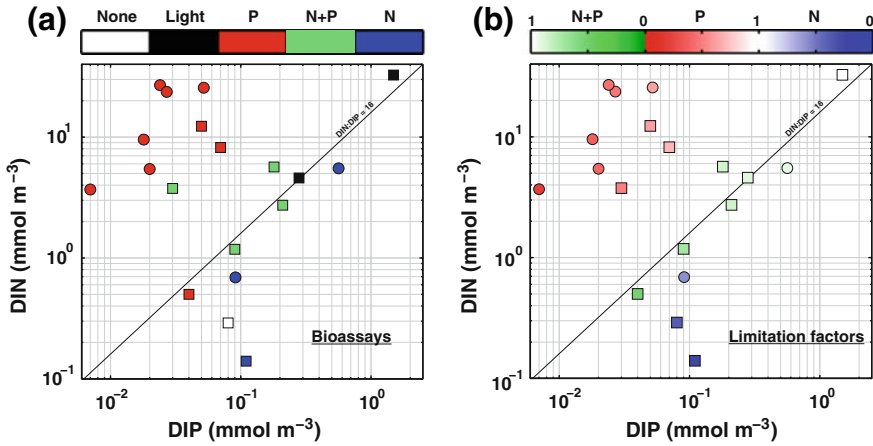
In the model, phytoplankton growth is limited by either DIN or DIP according to the multi-nutrient formulation described by Eqs. 7.1–7.4. Nutrient limitation factors inferred from inorganic nutrient measurements on the Louisiana shelf compare well with their corresponding nutrient addition bioassays (Fig. 7.4), indicating that the formulation of resource limitation in the model is appropriate. DIN and DIP sources are the Mississippi and Atchafalaya rivers (see locations in Fig. 7.5) and remineralization of POM in the water column and in the sediment. The sediment-water interface is represented as a reflective boundary with a preferential return of DIP to



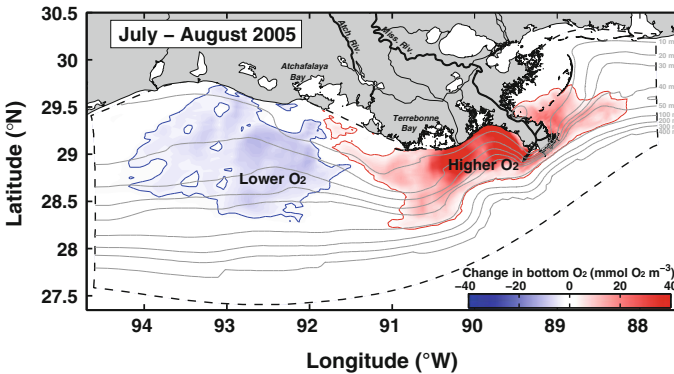
**Fig. 7.3** Schematic of the biogeochemical model used in Laurent and Fennel (2014). The state variables are phytoplankton (Phy), zooplankton (Zoo), slow-sinking small detritus (SDet), fast-sinking large detritus (LDet), nitrate (NO<sub>3</sub>), ammonium (NH<sub>4</sub>), DIP, and O<sub>2</sub>. The dynamics of O<sub>2</sub> is coupled with the production and respiration of organic matter via the sources and sinks indicated in the left panel. Figure from Laurent and Fennel (2014) subject to a CC-BY 4.0 license

the water column due to denitrification in the sediment. Slowly sinking phytoplankton (Phy) and suspended detritus (SDet) coagulate into fast-sinking large detritus (LDet) as a function of their concentration according to  $\tau \cdot (SDet + Phy)^2$  where  $\tau$  is the coagulation rate. Sources and sinks of O<sub>2</sub> are associated with the N-cycle (Fig. 7.3) as follows: In the water column, O<sub>2</sub> is produced by photosynthesis, lost through nitrification and respiration, and exchanged with the atmosphere at the air-sea interface; O<sub>2</sub> is lost at the sediment-water interface due to sediment oxygen consumption (Fennel et al. 2008, 2013). The model does not consider O<sub>2</sub> feedbacks on sediment denitrification and on the P cycle because these processes are not well constrained for the Louisiana shelf and because bottom-water O<sub>2</sub> is generally well-above anoxic conditions where nonlinearities are expected to become important.

Two types of simulations are used by Laurent and Fennel (2014) to quantify the effects of P limitation: (1) In a baseline simulation, the multi-nutrient version of the model with N and P cycling (as illustrated in Fig. 7.3) is used. In this simulation, either N or P can limit primary production. (2) In an additional, single-nutrient simulation, only the N-cycle version of the model is used (here, DIP is disabled, but all other processes and model forcing are identical to the baseline simulation).



**Fig. 7.4** Results of resource limitation bioassays as a function of initial (ambient) nutrient concentration. **A** Original results. **B** Nutrient limitation factors calculated from initial DIN and DIP concentrations using Eqs. 7.1–7.4 (co-limitation is assumed if  $|L_N - L_P| < 0.1$ ). Filled squares and circles indicate bioassays from Sylvan et al. (2006) and Quigg et al. (2011), respectively. Phytoplankton in the bioassays was light-limited (black), P-limited (blue), N- and P-limited (green), and N-limited (red). In original bioassays indicating no limitation (white, left panel), phytoplankton did not respond to added nutrient or light (see references for details)

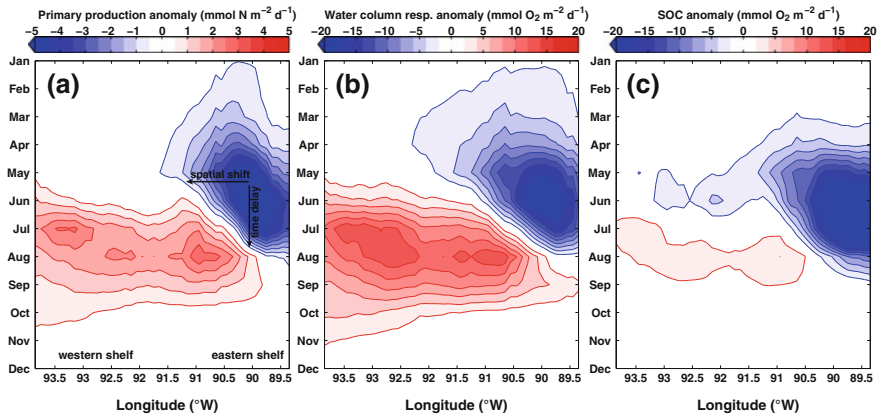


**Fig. 7.5** Results from Laurent and Fennel (2014) showing average change in *bottom*  $\text{O}_2$  concentration due to P limitation in July and August 2005 on the Louisiana shelf. Positive values (red) indicate an increase in  $\text{O}_2$  concentration. Red and blue isolines indicate  $-3$  and  $+3$   $\text{mmol O}_2 \text{ m}^{-3}$ , respectively. The effect of P limitation on *bottom*  $\text{O}_2$  was calculated daily in the *bottom* layer of each grid cell as the difference between  $\text{O}_2$  concentration from the baseline and the N-only simulations. Shown is the average difference in July and August 2005

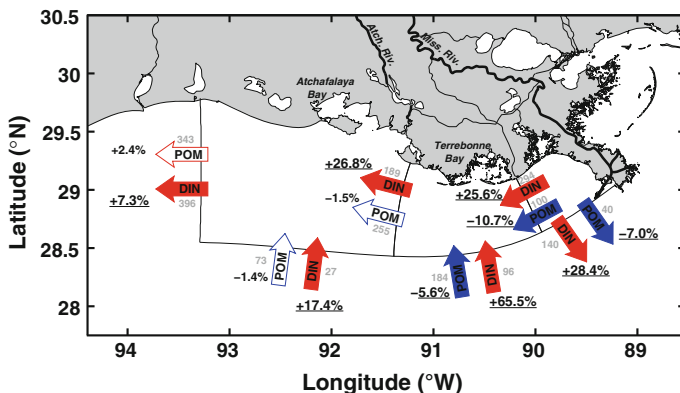
Differences between the N-only and the baseline simulations are due to the absence of P limitation in the former and illustrate the effect of P limitation on the system.

### 7.4.2 Spatial/Temporal Shift in Primary Production

The model successfully simulates resource limitation on the Louisiana shelf, namely the development of P limitation between March and July and the switch back to N limitation in September. P limitation results in excess DIN that is transported downstream (i.e., westward) between March and July, where it fuels primary production in otherwise N-limited waters (Laurent et al. 2012). This induces a time delay and a westward relocation of a fraction of primary production (Fig. 7.6a). Here, we quantify this relocation using the simulations described in Laurent and Fennel (2014), in terms of the change in horizontal transport of POM and DIN across the boundaries of three boxes representing the western, mid-, and eastern Louisiana shelf (Fig. 7.7). With P limitation, the following changes in transport occur: (1) Less primary production occurs on the eastern shelf resulting in a smaller transport of POM westward and across the shelf break into the open Gulf of Mexico, (2) Westward transport of DIN is larger, and (3) Transport of DIN across the shelf break is larger (Fig. 7.7). Offshore transport of DIN across the shelf break is larger near the Mississippi delta, but more of this DIN is recirculated onto the mid- and western shelf. On average, 34 and 26% more DIN is transported westward into the mid- and western shelf boxes, respectively. POM and DIN fluxes further west onto the Texas shelf also increase slightly (Fig. 7.7).



**Fig. 7.6** Results from Laurent and Fennel (2014) showing spatial and temporal changes in water column integrated primary production (A), water column respiration (B), and SOC (C) due to P limitation on the Louisiana shelf. Values represent monthly and latitudinal averages for the Louisiana shelf ( $z \leq 50$  m). Latitudinal averages were obtained by averaging over the shelf (from the coast to the 50 m isobath) for each  $0.1^\circ$  longitude bin. Shown is the difference between the baseline and the N-only simulations



**Fig. 7.7** Changes in average POM and DIN transport over the Louisiana shelf due to P limitation. Transport is calculated from the simulations of Laurent and Fennel (2014) for three boxes representative of the shelf, their boundaries shown with a *thin black line*. The southern boundaries follow the 50-m isobath. *Arrows* indicate the direction of the transport and their color an increase (red), a decrease (blue), or a small change (white) due to P limitation (also indicated in percent). The gray number beside each *arrow* indicates the magnitude of the transport (in  $10^3 \text{ mmol N s}^{-1}$ )

### 7.4.3 The Dilution Effect

Laurent and Fennel (2014) have shown that P limitation reduces the size of the July–August hypoxic area by an average of 29%. In their simulation, changes in bottom-water  $\text{O}_2$  are asymmetric over the Louisiana shelf with a significant increase on the eastern shelf, but only a small decrease on the western shelf (Fig. 7.5). Two additive effects explain this spatial asymmetry: the westward shift of organic matter respiration against the backdrop of weakening vertical stratification and the net shift of respiration from the sediments to the water column.

The intensity of the simulated water column stratification varies along the freshwater gradient of the Mississippi River plume (e.g., Hetland and DiMarco 2008; Zhang et al. 2012; Laurent and Fennel 2014). Simulated water column stratification is strongest on the eastern shelf, especially in summer when upwelling-favorable winds pile up freshwater near the Mississippi delta (Zhang et al. 2012). Stratification intensity decreases toward the western shelf, away from the Mississippi River delta (Hetland and DiMarco 2008). Since simulated bottom  $\text{O}_2$  concentration is highly correlated with stratification intensity on the Louisiana shelf (Fennel et al. 2013), a westward shift in organic matter respiration results in a reduction of hypoxia (Laurent and Fennel 2014).

In addition, the simulations suggest that P limitation leads to a redistribution of respiration between sediment and water column (Fig. 7.6b, c). The westward shift of primary production occurs on a broadening shelf, thus spreading primary production over a larger area and essentially diluting phytoplankton and detritus (Fig. 7.6a). Smaller concentrations of phytoplankton and suspended detritus (even

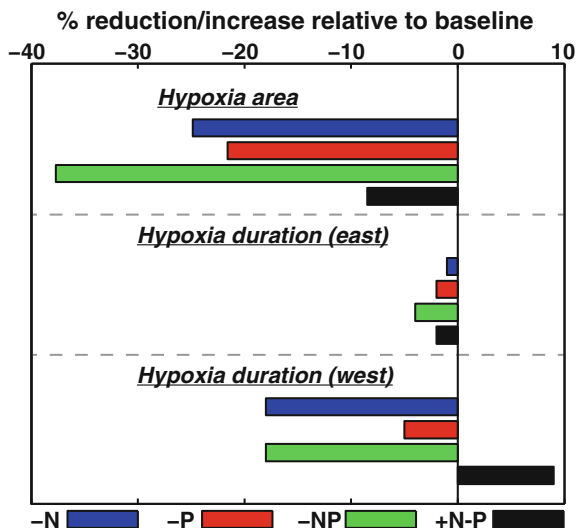


if present over a larger area) reduce coagulation into fast-sinking, larger detritus; hence, more organic matter is respired in the water column and less in the sediment when P limitation is present. This leads to an asymmetric effect of P limitation on respiration between the eastern and the western Louisiana shelf (Fig. 7.6b, c). Observations and simulations show that hypoxia mainly occurs within the bottom boundary layer (BBL) on the Louisiana shelf (i.e., within less than 5 m above the bottom; see Fennel et al. 2016). In this layer, SOC is the main O<sub>2</sub> sink and therefore controls hypoxia development on the Louisiana shelf (Fennel et al. 2013; Yu et al. 2015b). The net shift of respiration from sediments to the water column due to P limitation reduces respiration within the bottom boundary layer and therefore the overall extent of hypoxia (Laurent and Fennel 2014).

### 7.4.4 Hypoxia Remediation Strategies

Four nutrient reduction scenarios were tested in Laurent and Fennel (2014) to assess their effect on summer hypoxia: a 50% decrease of river DIN load (−N), a 50% decrease of river DIP load (−P), a 50% decrease of river DIN and DIP loads (−NP), and a 50% increase in river DIN load with a simultaneous 50% reduction of river DIP load (+N−P). The dual N and P load reduction (−NP) maximizes the decrease in hypoxia size and duration (Fig. 7.8). Decreasing N load only (−N) reduces hypoxia on the western shelf but the hypoxic area is larger than with a dual nutrient reduction. Reducing P only (−P) reduces the hypoxic area but not hypoxia duration on the western shelf. Finally, decreasing P but with a simultaneous increase of N

**Fig. 7.8** Results from the nutrient load experiments of Laurent and Fennel (2014) showing the relative change in summer 2004 hypoxic area and hypoxia duration at an eastern and western shelf station, associated with a modification in nutrient river load as follows: −50% DIN (−N), −50% DIP (−P), −50% nutrients (−NP), and +50% DIN, −50% DIP (+N−P)



(stronger P limitation) leads to a small reduction of the hypoxic area, but also to a longer duration of hypoxic conditions on the western shelf (Fig. 7.8). A dual N and P load reduction strategy is therefore recommended to mitigate hypoxia on the Louisiana shelf.

## 7.5 Conclusions and Recommendations

River-induced P limitation is a common phenomenon in coastal hypoxic systems. Although consideration of P limitation is of direct relevance for hypoxia mitigation through nutrient load reduction, there is still limited direct evidence for the effect of P limitation on hypoxia. Models are invaluable tools because they allow one to simulate system-wide N and P load manipulations that are necessary to quantitatively assess the effects of resource limitation. This was illustrated by the recent modeling investigation of the Mississippi River plume (Laurent and Fennel 2014). This type of coupled hydrodynamic-biogeochemical model is most suitable to examine the effect of P limitation on hypoxia because it represents limitation by multiple resources and hypoxia within a realistic spatial and physical setting. This is essential in this context, and similar investigations should be conducted in other P-limited coastal hypoxic systems.

Based on the general understanding of P limitation and the results of the Mississippi River plume study, we were able to distinguish between two types of hypoxic systems: one-dimensional flow-through and open dispersive systems, illustrated by the conceptual model in Fig. 7.1. One-dimensional systems such as estuaries may respond linearly to P limitation with a downstream relocation of hypoxia. More open and dispersive systems such as river plumes likely have a nonlinear response to P limitation because stratification weakens downstream where phytoplankton biomass is relocated and the dilution of biomass over the shelf reduces depositional flux, and subsequently hypoxia. Intermediate systems such as large estuaries may respond differently to P limitation depending on the timing and location of hypoxia. The different effect of P limitation on this continuum of systems needs to be considered with regard to hypoxia mitigation strategies.

Further investigations that compare the effect of P limitation on hypoxia across these various types of systems are needed to confirm our conceptual model. The Neuse River Estuary is a good candidate for studying the effect of P limitation on one-dimensional systems because both resource limitation and hypoxia were previously investigated there. A relatively simple biogeochemical model should be sufficient to simulate resource limitation in this system. Chesapeake Bay is a good candidate for intermediate systems. Sediment-water feedbacks such as the inhibition of denitrification at low  $O_2$  may need to be considered in Chesapeake Bay (or similar intermediate systems), given the relatively long residence time of the deep waters. Wang et al. (2016) simulated the effect of N and P load reduction on bottom-water  $O_2$  in Chesapeake Bay and concluded that increased P limitation associated with P load reduction has a positive effect on bottom-water  $O_2$  where P

limitation occurs. A follow-up study is necessary to characterize the direct effect of P limitation on the timing, location, and intensity of hypoxia in this intermediate system. Model frameworks should be designed carefully in open dispersive systems and include the essential processes influencing hypoxia development. For example, coagulation and sediment remineralization were necessary to simulate the response to P limitation in the Mississippi River plume. It was also important to represent the spatial variation in stratification over the Louisiana shelf. Essential processes vary among systems, and therefore, local characteristics should be taken into account during model development.

Simulated river-induced P limitation in this continuum from one-dimensional flow-through to open dispersive systems will significantly improve our conceptual understanding of resource limitation in the context of coastal hypoxia and will help design and improve nutrient load reduction strategies to mitigate river-induced hypoxia.

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