Coupled biogeochemical cycles: eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems

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Nutrient fluxes to coastal areas have risen in recent decades, leading to widespread hypoxia and other ecological damage, particularly from nitrogen (N). Several factors make N more limiting in estuaries and coastal waters than in lakes: desorption (release) of phosphorus (P) bound to clay as salinity increases, lack of planktonic N fixation in most coastal ecosystems, and flux of relatively P-rich, N-poor waters from coastal oceans into estuaries. During eutrophication, biogeochemical feedbacks further increase the supply of N and P, but decrease availability of silica – conditions that can favor the formation and persistence of harmful algal blooms. Given sufficient N inputs, estuaries and coastal marine ecosystems can be driven to P limitation. This switch contributes to greater far-field N pollution; that is, the N moves further and contributes to eutrophication at greater distances. The physical oceanography (extent of stratification, residence time, and so forth) of coastal systems determines their sensitivity to hypoxia, and recent changes in physics have made some ecosystems more sensitive to hypoxia. Coastal hypoxia contributes to ocean acidification, which harms calcifying organisms such as mollusks and some crustaceans.

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Human activity has greatly accelerated the flows of nutrients to estuaries and other coastal marine ecosystems over the past half century, increasing primary production and causing widespread eutrophication (Nixon 1995; NRC 2000; Rabalais 2002). As of the late 1990s, global fluxes in rivers to coastal oceans were some twofold greater for nitrogen (N; Galloway *et al.* 2004; Boyer and Howarth 2008) and two- to threefold greater for phosphorus (P; Howarth *et al.* 1995) than before the Industrial and Agricultural Revolutions. During the past 10 years, in many industrialized countries, P inputs have sharply decreased as a result of improvements in wastewater treatment plants, but N pollution has remained high. The global increase in nutrient fluxes has not been evenly distributed, and some regions have seen much greater changes than others (Figure 1). Two-thirds of the estuaries in the US are degraded as a result of nutrient pollution, which can cause dissolved oxygen depletion (hypoxia and anoxia), loss of critical habitat such as seagrass beds and coral reefs, changes in ecological structure including loss of biodiversity, and increased incidences and duration of harmful algal blooms (HABs; NRC 2000; Bricker *et al.* 2007). Globally, the number and size of anoxic and hypoxic areas ("dead zones") has grown dramatically in recent years (Diaz and Rosenberg 2008). For most of these, low oxygen is a direct result of increased nutrient inputs leading to higher rates of algal production and, subsequently, increased oxygen consumption as the larger supply of organic carbon (C) is respired. In other ecosystems, changes in wind regime and upwelling, rather than nutrient pollution and eutrophication, are the cause of dead zones. In this paper, we highlight some of the complex interactions of biogeochemical cycles that accompany eutrophication, hypoxia, and anoxia.

Primary production in many estuaries and other coastal marine ecosystems in the temperate zone is limited more

In a nutshell:

- Primary production in most temperate estuaries and coastal marine ecosystems is nitrogen (N) limited, although phosphorus (P) also contributes to eutrophication; the input of both nutrients should be managed
- During eutrophication, biogeochemical feedbacks act to further increase the availability of N and P, but to decrease the availability of silica; this positive feedback accelerates eutrophication and hypoxia, and makes harmful algal blooms more likely
- Changes in ocean circulation patterns over recent decades have increased the sensitivity of some estuaries and coastal systems to becoming hypoxic from nutrient pollution
- Decreased levels of dissolved oxygen – low in hypoxic waters and absent in anoxic waters – are associated with elevated carbon dioxide (CO_2) concentrations, which cause acidification and increase the vulnerability of estuaries and coastal systems to continuing perturbations of ocean chemistry from anthropogenic CO_2 emissions into the atmosphere

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by N than by P, and so the increased flows of N to coastal waters are responsible for much of the eutrophication and proliferation of dead zones (NRC 2000). The generality of this statement, however, has been a source of debate for decades (Howarth and Marino 2006). A recent paper by Schindler *et al.* (2008) and a reply by Conley *et al.* (2009) have again brought the argument into public review. Research since the 1950s, and particularly a great body of evidence that has accumulated over the past 30 years, has revealed short-term bioassay evidence for N limitation in estuaries. However, Schindler *et al.* (2008) questioned this coastal marine work; their studies of lakes show that short-term bioassays are not always reliable, and whole-ecosystem experiments provide more robust information on nutrient limitation. Because such experiments in lakes tend to indicate P limitation, and because Schindler *et al.* (2008) were unaware of whole-ecosystem experiments in coastal systems, they hypothesized that many estuaries and other coastal systems are P limited. In fact, whole-ecosystem observations and mesocosm experiments in estuaries, though few in number, have demonstrated N limitation (see Howarth and Marino 2006; Figure 2).

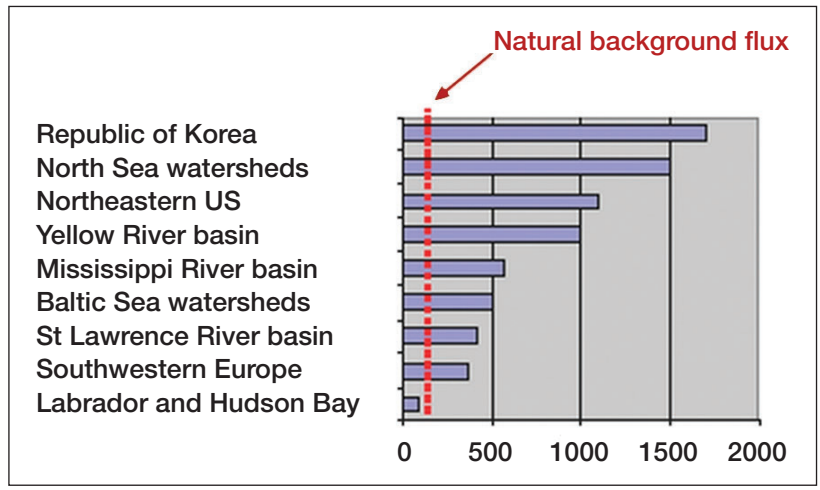

Figure 1. *Average annual flux of nitrogen (N) from the landscape to coastal oceans in rivers for contrasting regions of the world in the temperate zone, expressed per area of watershed (kg N km^{-2} yr^{-1}). The dashed line represents the background flow, absent human activity in the watershed. Reprinted from Howarth (2008).*

Here we focus on the ecosystems in the relatively shallow waters of the continental shelf – namely, estuarine and coastal marine ecosystems – that are most strongly and directly influenced by human-accelerated nutrient inputs from land. We use a broad definition of "estuary" that includes fjords and lagoons whether or not they have riverine freshwater inputs (Wolanski 2007). These types of ecosystems generally have similar biogeochemical responses to nutrient inputs, as long as the salinity is greater than 10–12 parts per thousand (ppt; Howarth and Marino 2006). We emphasize differences in biogeochemical cycles between estuarine and marine ecosystems and lakes. For many decades, water-quality managers in much of North America and Europe focused primarily on P control in both lakes and marine ecosystems, failing to understand the differences in biogeochemical function across these aquatic ecosystem types. We also emphasize temperate ecosystems, because this is where the greatest increase in N pollution has occurred (Boyer and Howarth 2008); in addition, the biogeochemical responses of estuaries and coastal marine ecosystems to nutrient pollution are better studied in temperate regions than in the tropics. The space constraints of this paper prohibit an adequate presentation of tropical systems. Nonetheless, the topic is important, given that nutrient loads in some tropical coastal regions are increasing rapidly, and some evidence suggests these tropical ecosystems may be more sensitive to nutrient pollution than temperate coastal ecosystems are (Corredor *et al.* 1999).

Why is N limitation more likely in estuaries than in lakes?

The relative availability of N and P in an ecosystem determines which nutrient is more limiting: N tends to be limiting when the N:P ratio of nutrients available to primary producers is below the Redfield ratio of 16:1 (molar), the average ratio of these two elements in algae. The ratio of dissolved inorganic concentrations is not a perfect representation of the N:P ratio for availability, resulting from both methodological issues with measuring inorganic P and the faster recycling of organic P (Howarth and Marino 2006). Several biogeochemical mechanisms make N limitation more likely in estuaries than in freshwater lakes. One of these is desorption (release) of inorganic P from clay and silt particles carried to the coastal zone in rivers, as the particles encounter increasing salinity. A great deal of P can be adsorbed to particles in fresh waters, and this bound P often is not available to algae. In seawater, larger numbers of anions (ions with negative charges) compete with phosphate for sorption sites. As a result, phosphate is desorbed from particles and becomes biologically available (Froelich 1988; Howarth *et al.* 1995; Némery and Garnier 2007).

Another important mechanistic difference between freshwater and coastal marine ecosystems regards N fixation by planktonic cyanobacteria. In fresh waters, cyanobacteria commonly bloom and fix N when the availability of N relative to P is low, which helps maintain P limitation of net primary productivity in lakes (Schindler *et al.* 2008). However, N fixation rates are immeasurably low in the water column of almost all estuaries with salinities greater than 8–10 ppt, and the planktonic cyanobacteria capable of N fixation are largely absent (Howarth and Marino 2006; Marino *et al.* 2006; Howarth and Paerl 2008). The lack of planktonic N fixation in estuaries is

Figure 2. *Mesocosms, such as those pictured here on the shore of Narragansett Bay, Rhode Island, have proven very useful in studying nitrogen limitation of primary production and the controls on nitrogen fixation. See* Marino et al. *(2006).*

caused in part by the high levels of sulfate in seawater; these high sulfate levels make assimilation of molybdenum (an element required for N fixation) difficult, thus slowing the potential growth rate of N-fixing cyanobacteria. Slow growth in turn makes cyanobacteria highly vulnerable to grazing by zooplankton and benthic animals (Marino *et al.* 2002, 2006; Chan *et al.* 2006). This is particularly true for heterocystous cyanobacteria, where N fixation occurs only in specialized cells (heterocysts) and is supported by organic C flows from many photosynthetic cells in a long chain. Grazing shortens the length of the chain, reducing the number of photosynthetic cells available for supporting the energy needs of the heterocyst, and thereby greatly reducing N fixation.

A third difference between estuaries and freshwater lakes is the supply of nutrients. Both lakes and estuaries receive nutrients from their watersheds and upstream ecosystems, but estuaries also receive nutrients from "downstream" coastal ocean waters through reverse estuarine flow that mixes with fresher waters moving downstream. For those regions that have a relatively wide continental shelf – such as Western Europe, the Atlantic coast of North America, and the coast of China – the coastal waters have a low N:P ratio caused by high rates of denitrification found on continental shelves (Galloway *et al.* 2004; Fennel *et al.* 2006). As a result, the relative nutrient inputs to estuaries from these coastal waters are greater for P than for N. For instance, Chesapeake Bay receives an estimated 25% of its entire P load but almost none of its N inputs from the coastal ocean (Boynton and Kemp 1995; Nixon *et al.* 1996). Recently, Li *et al.* (in press) demonstrated that the Yangtze River estuary remains N limited – despite a very large increase in the N load of the Yangtze River – because of a large flux of P from adjacent ocean waters, where the N:P ratio of dissolved nutrients is low.

Eutrophication-driven changes in nutrient cycles

During eutrophication, biogeochemical feedbacks in bottom sediments can increase the availability of both N and P (Conley *et al.* 2007; Vahtera *et al.* 2007; Kemp *et al.* 2009). In most estuaries, even when not eutrophic, oxygen penetrates only a few millimeters into the surface sediments due to high rates of oxygen consumption. The burrows of animals, however – particularly those of species that pump water through the burrow in the process called "bio-irrigation" – increase the effective surface area. The oxygen penetrates the sediment across the burrow walls, as well as across the surface of the sediment. As a result, throughout the burrowing depth, sediments are a complex maze of highly reducing zones intermixed with more oxidized zones. The maze is an ideal structure for nitrification – the oxidation of ammonium to nitrate – to coexist in nearly the same space with denitrification – the reduction of nitrate to N_2 gas. This coupled nitrification–denitrification often removes a substantial portion of the N load from an estuary (Seitzinger 1988).

As estuaries become more eutrophic, the bottom waters can become hypoxic or anoxic. Even when waters remain oxygenated, eutrophication increases the inputs of organic C to bottom sediments, sulfate reduction rates increase, and the sediments become more reducing with higher concentrations of sulfides. Sustained bottom-water anoxia can result in the complete loss of animals in bottom sediments. Hypoxia and/or more sulfide-rich sediments can result in changes in the composition of the benthic fauna, with species that burrow and irrigate to substantial depths in the sediments being replaced by others less effective at irrigating the sediments (Rosenberg 2001; Middelburg and Levin 2009). A positive feedback results, with yet higher sulfide concentrations and more reducing sediments, because less oxygen is pumped by animals. The threshold oxygen level varies greatly with different benthic species, but major faunal shifts often occur even at oxygen levels above those usually used to designate hypoxia (2 mg L^{-1}; Vaquer-Sunyer and Duarte 2008).

The changes in animal species composition, oxygen fluxes, and sulfide levels in sediments that accompany eutrophication have three consequences for N cycling (Figure 3). First, nitrification slows greatly, as a result of lower oxygen availability and sulfide inhibition of nitrifying bacteria (Joye and Hollibaugh 1995). Consequently, denitrification also slows, as the nitrate supply decreases. Second, the higher sulfide levels seem to favor another process that competes with denitrification for nitrate: the dissimilatory nitrate reduction to ammonium, or DNRA

(An and Gardner 2002; Burgin and Hamilton 2007). Third, the process of anaerobic ammonium oxidation (anammox) to N_2 gas slows or stops as sulfide concentrations rise (Thamdrup and Dalsgaard 2002). All three of these trends result in more N being conserved in the estuary and less being converted to N_2 gas. Thus, this positive feedback on N biogeochemistry leads to a non-linear increase in further primary production and eutrophication.

Eutrophication also creates a positive feedback of increasing P supply. Due to changes in the sulfur (S) and iron (Fe) cycles, P storage in many sediments decreases and P flux to the water increases. As C inputs increase and oxygen inputs to the sediment decrease, sulfate reduction becomes increasingly important in sediment metabolism. Even in estuarine sediments with low organic C, sulfate reduction makes up 25% or more of total sediment respiration. In the sediments of eutrophic estuaries, organic C concentrations are higher, and sulfate reduction contributes two-thirds or more of total sediment metabolism (Howarth 1984). As sulfate reduction rates increase and fewer of the resulting sulfides are re-oxidized back to sulfate – on account of decreased oxygen from bio-irrigation – more of the Fe in the sediments is transformed from adsorptive forms of Fe(III) oxides and hydroxides into non-sorptive Fe(II) sulfides, particularly pyrite (Krom and Berner 1980; Caraco *et al.* 1989; Blomqvist *et al.* 2004). Less remineralized P is adsorbed, resulting in more diffusing back to the overlying water. The loss of a surface trap of oxidized Fe can be particularly important in increasing the P flux to the water column as eutrophication increases (Sundby *et al.* 1992; Jensen and Thamdrup 1993). Other processes occur in sediments, including precipitation of P in fluorapatite (Ruttenberg and Berner 1993). As a result, variations across estuaries in fluxes of phosphate from sediments are large and not entirely understood. Some of this variation in P release may be due to differences in the mixing by the benthic fauna, particularly as mixing affects micro-scale variation in pH (Howarth *et al.* 1995).

Although our review focuses on temperate ecosystems, the feedbacks in biogeochemical cycles during eutrophication in tropical systems are worthy of comment. In many tropical lagoons, sediments are dominated by carbonate sands, which are extremely low in Fe. Consequently, sulfides build up more quickly as eutrophication progresses. Sulfide inhibition appears to make nitrification and denitrification less important than in temperate sediments experiencing a similar degree of N loading (Corredor *et al.* 1999). The carbonate sands are also fairly adsorptive of phosphate, which can lead to P limitation. Carbonate minerals have a lower affinity for phosphate than do the oxidized Fe minerals found in the surface of many temperate estuarine sediments (Krom and Berner 1980), but the huge mass of carbonates in many tropical sediments provides a major P sink nonetheless. However, as external P loads to a lagoon increase, the rate of adsorption of phosphate can decrease, in some cases shifting the ecosystem toward N limitation (McGlathery *et al.* 1994; Howarth *et al.* 1995).

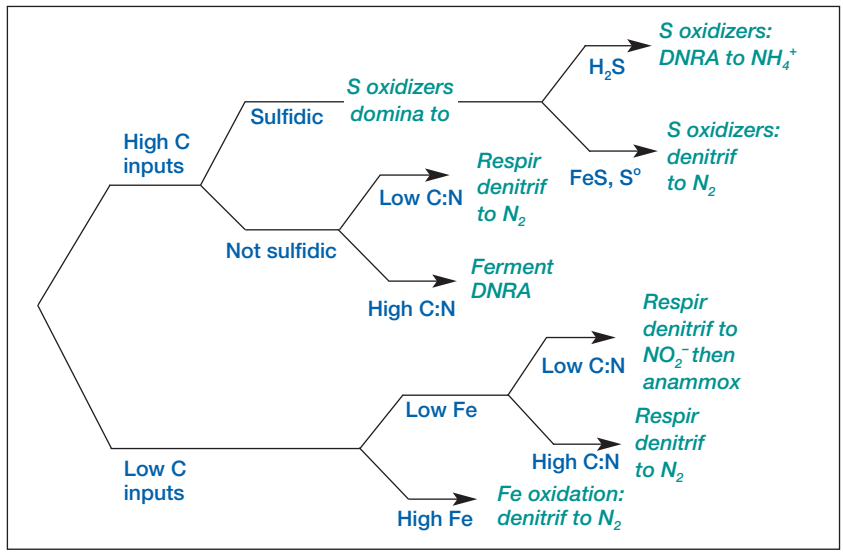

Figure 3. *Controls on denitrification, dissimilatory nitrate reduction to ammonium (DNRA), anaerobic ammonium oxidation (anammox) to N_2 gas, and similar processes in aquatic sediments based on the level of organic matter inputs to the sediments, the amount of sulfides and Fe present, and the C:N ratio in the organic matter in the sediments. Reprinted from Burgin and Hamilton (2007).*

■ Phosphorus limitation, N retention, and far-field transport

Primary production in a coastal marine ecosystem can switch from N limitation to P limitation if the N inputs from land become sufficiently large compared with P inputs (Billen *et al.* 2007; EPA SAB 2008; Conley *et al.* 2009). Partly for this reason, most coastal marine scientists believe that sensible coastal management calls for control of both N and P inputs (NRC 2000). In recent years, a switch from N to P limitation has probably occurred during summer months in the near-shore waters within the plume of the Mississippi River in the northern Gulf of Mexico (Sylvan *et al.* 2006). Whether a coastal ecosystem is driven to P limitation likely depends not only on the relative inputs of N and P from terrestrial sources, but also on the interaction with adjacent coastal ocean waters. The exchange of deep ocean waters with the waters on the continental shelf – and therefore the importation of nutrients with a low N:P ratio – is more limited in the Gulf of Mexico than on most other continental shelves (Boyer and Howarth 2008), which may make the Gulf hypoxic zone more prone to a switch to P limitation.

A switch from N to P limitation in a coastal marine

Figure 4. *Piles of scum from a bloom of* Phaeocystis*, a representative harmful algal bloom species, on the beaches of the North Sea in the Netherlands.*

ecosystem lessens N uptake by primary producers, and therefore probably lessens N retention and removal in the immediate estuarine and coastal marine ecosystems receiving the N inputs from land. As a result, the N is transported farther. In this way, the far-field effects of N enrichment are increased, even as N becomes less limiting in closer proximity to the source of nutrient inputs. Strong evidence for such a phenomenon comes from the Pamlico River Estuary–Cape Lookout Bight system (Paerl 2009) in North Carolina, and this may also be occurring in the northern Gulf of Mexico's hypoxic zone (EPA SAB 2008).

Silica, diatoms, and harmful algal blooms

Whereas changes in sediment biogeochemistry generally increase the availability of N and P in the water column along a eutrophication gradient, the availability of silica often decreases along this gradient. In part, this results from eutrophication and damming in upstream freshwater systems, which increase sedimentation and the trapping of silica (Humborg *et al.* 2000). Increased sedimentation of diatoms, the tests of which are composed of silica, in eutrophic estuaries and coastal marine ecosystems also contributes to lower dissolved silica concentrations (Billen *et al.* 1991; Conley *et al.* 1993). Once silica is in the sediments, decreased bio-irrigation in eutrophic systems (due to changes in the benthic faunal community) may further lower silica availability in the water column. Remineralization of silica is strongly regulated by the amount of dissolved silica in pore waters. Decreased porewater irrigation raises dissolved silica concentrations and thus results in lower rates of silica dissolution (Boudreau and Marinelli 1994).The availability of silica can have a pronounced influence on phytoplankton composition and subsequently on primary production. Most diatoms require silica in the amount of roughly 1 mol for every mole of N assimilated. As dissolved silica becomes relatively scarce, diatoms are replaced by other phytoplankton species that do not require silica and typically have higher growth rates (Figure 4). Species associated with HABs (and in some instances a less-silicified toxic diatom) become favored because there is less competition with non-harmful diatoms for N and P (Anderson *et al.* 2002). Silica limitation of diatoms has become a common feature of the biogeochemistry of eutrophic coastal waters throughout much of the world (Conley *et al.* 1993). Eutrophication and the large-scale perturbation of nutrient inputs are some of the reasons that HABs appear to be increasing in extent and duration in many locations (NRC 2000). Billen and Garnier (2007) developed an "indicator of coastal eutrophication potential" (ICEP) that is based on the input of dissolved silica to coastal waters from rivers relative to inputs of N and P. The ICEP value represents the potential rate of primary production supported by N and P inputs in excess of the quantity of silica required for diatom production. Negative values indicate an excess input of dissolved silica in rivers as compared with N and P inputs, suggesting a dominance by diatoms in the coastal marine receiving waters. Positive values suggest a relative shortage of dissolved silica in the river inputs and thus a greater probability that diatoms will be replaced by other species, including those responsible for HABs. Many of the river basins in Europe now have positive values, suggesting a high likelihood for HABs in the coastal marine receiving waters (Billen *et al.* 2011; Figure 5). At the global scale, values for ICEP are much higher in the North Atlantic Ocean as compared with values in the south Pacific and Indian Oceans (Garnier *et al.* 2010).

The role of physics in regulating hypoxia

Physics plays a major role in regulating the oxygen concentrations in estuaries and other coastal marine ecosystems, and therefore in further biogeochemical responses to eutrophication (Rabouille *et al.* 2008). Though very high nutrient inputs and intense eutrophication are required to drive a weakly stratified ecosystem to hypoxia or anoxia, even moderate increases in nutrient inputs and eutrophication can lead to these conditions in a strongly stratified water body (NRC 2000). Stratification in coastal waters is driven both by temperature and salinity gradients; both gradients are responsive to global change as freshwater inputs vary with rising temperatures and as surface wind and ocean circulation patterns are altered. These conditions are found in the northern Gulf of Mexico hypoxic-zone region: currently, bottom-water hypoxia is much more probable when the difference in surface- and bottom-water salinities is greater than 4.1 ppt. Between 1982 and 2002 this threshold changed, with hypoxia becoming more likely even when the salinity gradient is smaller, in all

probability a response to higher surface temperatures (Stow *et al.* 2005). Warm surface waters also hold less dissolved oxygen than colder waters can, which may further enhance hypoxia.

The estuary of the St Lawrence River provides another marked example of the interplay between ocean physics and hypoxia. Despite relatively modest fluxes of N and P down the St Lawrence River (Howarth *et al.* 1996), the estuary has become hypoxic in recent years (Figure 6). Bottom-water oxygen concentrations from 1984 to 2003 were approximately half of what they were in the 1930s, and in the summer of 2003 the estuary was hypoxic over a 1300-km^2 area (Gilbert *et al.* 2005). In this estuary, hypoxic conditions are attributable in part to eutrophication; however, another factor – the change in the water mass coming into the estuary from deep ocean waters – is probably responsible for one-half to two-thirds of the observed loss of dissolved oxygen in the bottom waters. This influx is a mixture of waters from the Labrador Current and the North Atlantic Central water mass. In the decades since the 1930s, the relative contributions of these currents to the incoming water mass have changed, with proportionately less water deriving from the Labrador Current and more from the North Atlantic Central water. The change in ocean physics over time means that the bottom water entering the estuary from the ocean has much lower oxygen concentrations, making hypoxia more likely (Gilbert *et al.* 2005).

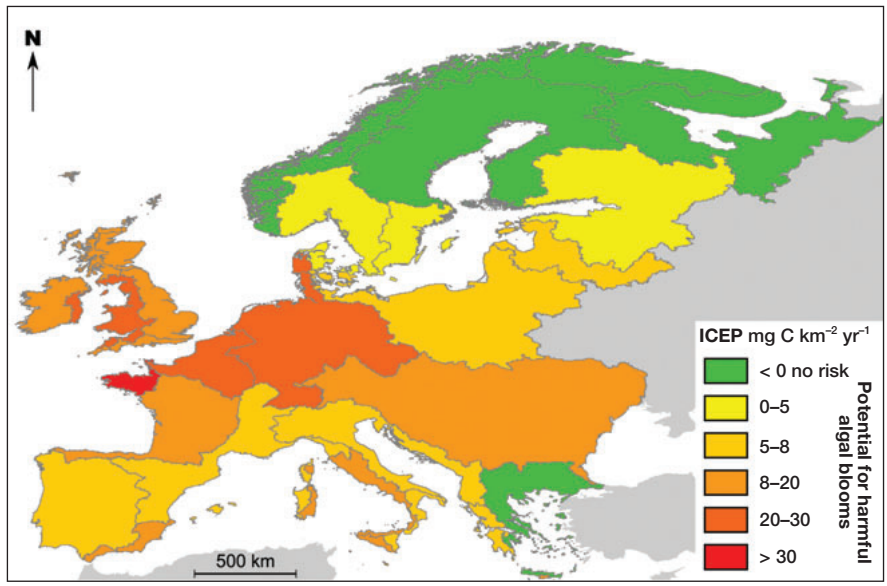

Figure 5. *Values of the "indicator of coastal eutrophication potential" (ICEP) calculated from the relative fluxes of N and silica in rivers flowing to the coast. Positive values (yellows, oranges, and reds) indicate the likely shortage of silica relative to N in estuaries and coastal marine receiving waters, making diatom production less likely and harmful algal blooms (HABs) more likely. See Billen* et al. *(2011) for details on the methodology.*

The strong influence of physical oceanography on the development of coastal hypoxia is most easily seen along eastern boundary currents, where winds moving toward the equator drive the upwelling of oxygen-poor but nutrient-rich water from the ocean interior into coastal waters. In the northern California Current System (CCS), upwelling currents can transport deep hypoxic water from the continental slope to the edge of the surf zone (Grantham *et al.* 2004). Upwelling currents also bring large amounts of nutrients to the surface, and the resultant phytoplankton blooms fuel bottom-water oxygen demands that can further accentuate the severity of hypoxia. Although coastal upwelling is a natural feature of eastern boundary currents, recent observations have revealed a multi-decadal shoaling of the upper boundary of the oxygen minimum zone in the southern CCS (Bograd *et al.* 2008) and the novel emergence of anoxia in the northern CCS (Chan *et al.* 2008). Because the biogeochemical cycles of upwelling shelves are so strongly tied to wind forcing and the flux of oxygen and nutrient content of the deeper ocean, projections of climate-driven increases in upwelling due to greater winds (Bakun *et al.* 2009) and reductions in oceanic oxygen inventory (Keeling *et al.* 2010) suggest the potential for further intensification of hypoxia.

Hypoxia and ocean acidification

Increased anthropogenic CO_2 emissions have caused measureable declines in pH throughout the world's oceans, as the average concentration of CO_2 has increased (Feely *et al.* 2009; Doney 2009). Continued ocean acidification will change the solubility relationship for important carbonate minerals such as calcite and aragonite, making these minerals less likely to precipitate and more likely to dissolve. For estuaries and coastal marine ecosystems, eutrophication can greatly exacerbate this acidification. Hypoxic and anoxic waters are far more acidic than average ocean waters, because the respiratory consumption of oxygen that drives hypoxia and anoxia is coupled to the production of very high levels of dissolved inorganic carbon (DIC), including CO_2 gas, which is an acid (Borges and Gypens 2010; Figure 7). For a model saline estuary, the release of CO_2 associated with the development of hypoxia is sufficient to reduce pH levels by more than 0.5 units and to decrease aragonite solubility to levels where dissolution would be favored. Although perturbations to the carbonate system of estuaries remain an under-examined consequence of eutrophication, the risk of pH declines accompanying hypoxia is probably already occurring and is likely pervasive. Emerging studies indicate that respiration-driven DIC excess can result in what has been termed "death by dissolution" for juvenile bivalves in estuarine sediments (Green *et al.* 2009).

The full impacts of the perturbations to estuarine inor-

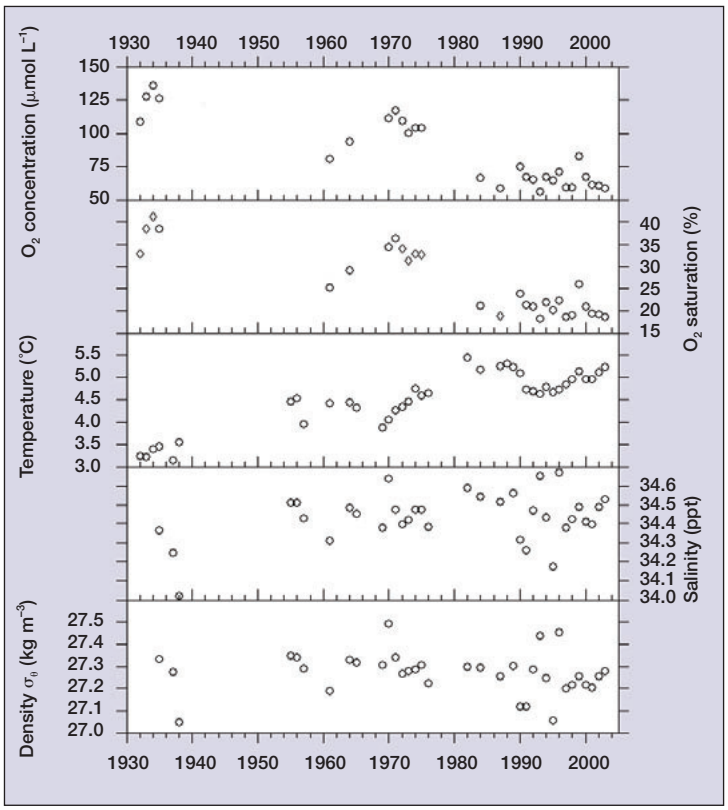

Figure 6. *Changes in oxygen concentration, oxygen saturation, and temperature in the bottom waters of the lower St Lawrence Estuary between 1930 and 2003. Changes in circulation patterns in the North Atlantic Ocean have made the estuary more sensitive to hypoxia. Reprinted from Gilbert* et al. *(2005).*

ganic C chemistry will reflect both biogeochemical and hydrological changes at the watershed scale and the rate of anthropogenic CO_2 emissions in the future. Whether carbonate minerals – including those that form shells – dissolve or precipitate depends on a number of chemical conditions, including the concentrations of DIC and CO_2 as well as the alkalinity of the water and the calcium ion concentration (Salisbury *et al.* 2008). These factors can vary widely along estuarine salinity gradients, but the strong tendency for alkalinity and calcium ion availability to decline toward freshwater end-members makes dissolution of carbonate minerals more likely. This tendency is furthered by the very high levels of CO_2 in rivers entering estuaries. The process of eutrophication-driven DIC enrichment highlighted here is of course occurring against a backdrop of increasing oceanic uptake of anthropogenic CO_2 emissions. As a whole, the great potential for additive DIC enrichment from internal and external processes suggests that nutrient-enriched estuaries will be among the ecosystems most vulnerable to ecological and biogeochemical perturbations from ocean acidification.

Conclusions

The scientific community has made great progress over the past several decades in understanding eutrophication and hypoxia in estuaries and coastal marine ecosystems. The changes in biogeochemical cycles and the coupling among different element cycles – the topic of this review – are now well recognized in broad context for relatively large estuarine systems in temperate zones. However, important questions remain, particularly regarding feedbacks between ecological structure and biogeochemical cycles and the nature of non-linearities in the coupling of element cycles as eutrophication progresses. How do these processes interact with physical factors in controlling the variable sensitivity of coastal systems to nutrient pollution? Do important thresholds or tipping points exist, with accelerated eutrophication and hypoxia resulting from only modest increases in nutrient load as these points are passed? Such responses seem likely, due, for instance, to decreases in denitrification, increases in DNRA, and increases in P fluxes from sediments. Without further study of the interactions of nutrient cycles and feedbacks in the context of whole ecosystems and over a gradient of nutrient loading, our understanding of potential threshold responses remains poor.

The responses of shallow-water ecosystems to eutrophication and hypoxia are less well understood than those of larger, deeper estuaries and coastal marine ecosystems. In shallow systems, light can penetrate to the bottom, allowing high rates of primary productivity by benthic species, including seagrasses, macro-algae, and benthic micro-algae. These primary producers add complexity to the coupling of biogeochemical cycles observed in deeper ecosystems by acting, for example, as a filter on nutrient fluxes through their assimilation (McGlathery *et al.* 2007). These benthic primary producers are frequently lost from the ecosystem as eutrophication progresses, leading potentially to complex and non-linear responses in the biogeochemistry of the system.

Eutrophication and hypoxia are less well studied in tropical systems than in temperate ecosystems. Some of the largest increases in the rate of nutrient inputs to coastal waters are expected in tropical regions over the next few decades (Galloway *et al.* 2004), and, as noted above, tropical ecosystems may be more sensitive to these nutrient inputs than are temperate systems (Corredor *et al.* 1999). The biogeochemical response to eutrophication in tropical estuaries and coastal marine ecosystems deserves far more study.

Finally, researchers know remarkably little about the recovery of estuaries and coastal marine ecosystems from eutrophication and hypoxia, even as societies successfully reduce nutrient pollution. Major changes occur in ecological structure and in the coupling of biogeochemical cycles during eutrophication. Are these changes reversed as external nutrient inputs are reduced? Or will the ecosystem retain some "memory" of the eutrophic state, resulting from long-lasting changes in sediment chemistry or

the stability of some new ecological structure? Such state shifts in the biogeochemistry or ecology of an estuarine system may require a far greater magnitude of nutrient reduction to reach a desired state of recovery than the magnitude of increased nutrient input that drove eutrophication. If such scenarios prove true, preventing eutrophication in the first place becomes even more critical.

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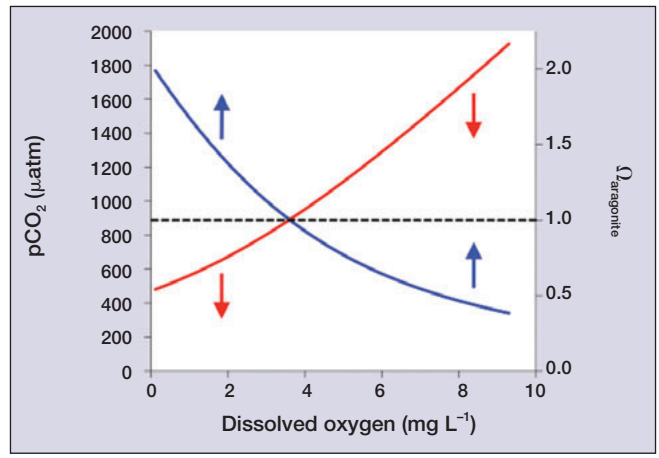

Figure 7. *Illustration of the increases in partial pressure of CO_2 (pCO_2; blue line) and declines in the saturation state of aragonite ($\Omega_{aragonite}$; red line) that stoichiometrically accompanies the onset of hypoxia. Above the horizontal dashed line, aragonite shell formation is favored, whereas dissolution is favored at levels below the line. Continued increases in CO_2 emissions from human activities will cause the system to reach dissolution conditions at increasingly higher threshold oxygen levels (arrows).*

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