Headwaters to estuaries: Complex responses to cultural eutrophication at the watershed scale

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Abstract

Aquatic scientists have long been concerned with understanding causes of eutrophication, and yet, even after decades of research, contradictory views remain concerning the need to control nitrogen inputs. At the heart of the current debate is the question of how well our understanding of ecosystem responses to nutrient loading can be applied at different scales and across systems. Here, we take a watershed-scale view of eutrophication. We review how aquatic ecosystems respond differently to nutrient inputs and discuss how processes such as nitrogen fixation, denitrification, and sorption/release of phosphorus can alter the relationship between nutrient loading in a watershed and downstream eutrophication. We recommend a context-specific approach to eutrophication management that considers ecosystem responses to nutrient loading throughout the watershed as well as controllability of various nutrient inputs. By beginning to develop a theory of eutrophication at the watershed scale, it is our hope that aquatic scientists can present a unified voice to managers.

Section 1. Introduction

Human activity in the past century has greatly increased fluxes of nutrients moving through the biosphere, as a result of the industrialization of agriculture and the rapid growth of urbanization (Vitousek et al. 1997; Carpenter et al. 1998). These fluxes of nitrogen and phosphorus now far exceed background rates and are considered by some researchers to have exceeded safe planetary thresholds (Rockstrom et al. 2009; Carpenter and Bennett 2011). Increased nutrient loading has resulted in elevated rates of primary production in many aquatic ecosystems, with undesirable effects including harmful algal blooms and the development of hypoxia (Smith 2003). In the United States alone, the economic losses attributed to eutrophication of lakes and rivers have been estimated at $2.2 billion annually (Dodds et al. 2008).

Understanding controls on eutrophication has been a central goal of aquatic scientists for decades. Early eutrophication research highlighted the impact of phosphorus (Edmonson et al. 1956; Schindler 1974), which led to regulations focusing on this nutrient. The question of whether it is also necessary to control nitrogen (N) has been a long-standing subject of debate in the literature (e.g., Ferguson 1968; Howarth and Marino 2006). This debate resurfaced in recent years after Schindler et al. (2008) used evidence from a long-term whole-lake experiment to argue that controlling N was ineffective or even counterproductive (Box 1). Other researchers disputed this interpretation (Scott and McCarthy 2010) and argued that N-loading drives eutrophication in many aquatic ecosystems due to physical and biological characteristics of these environments (Conley et al. 2009; Paerl and Scott 2010; Howarth et al. 2011).

Underlying the eutrophication debate are issues of scale and connectivity, yet these issues have received relatively little explicit consideration in the current debate. The effects of anthropogenic eutrophication are realized across a wide range of spatial scales, affecting local ponds, large river basins, and vast areas of the estuarine and coastal ocean. However, the

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Box 1. Nutrient limitation experiments at the Experimental Lakes Area.

David Schindler has argued that lakes have natural mechanisms to remedy N limitation (through N-fixation) and carbon limitation (through primary production and gas exchange; Schindler 1977). However, no such mechanism exists to increase P availability to the ecosystem. This N-sufficiency argument resulted from a series of experiments on three lakes at the Experimental Lakes Area in Northwestern Ontario. Initially, Lake 227 was fertilized at an N:P ratio of 14 (by weight), resulting in large increases in productivity, but no response of N fixing cyanobacteria (Schindler 1977). When another lake (Lake 226) was fertilized at an N:P ratio of 5 (by weight), blooms of N-fixing taxa occurred and fixed much of the N entering the lake. In Lake 227, 5 years after the initiation of the experiment, the fertilization treatment was switched to an N:P of 5. As in Lake 226, N fixers began to dominate, and eutrophic conditions remained. In the third lake (Lake 261), P additions were made in the absence of N, and also led to large increases in N fixing taxa and high productivity.

A 2008 paper revisited the Lake 227 research after 37 years of experimental manipulation, including a final phase of the experiment where P additions were continued, but N additions were ceased. Schindler and colleagues (2008) reported that N-fixation maintained the eutrophic state of the lake after external N-loading ceased, although their interpretation of data have been disputed with suggestions that denitrification may exceed N fixation, hence the system is growing more N limited and algal abundance is declining (Scott and McCarthy 2010). It is also noteworthy that chlorophyll *a* in Lake 227 was only related to P loading when N was also added (Scott and McCarthy 2011). The non–N-fixing cyanobacteria population also has essentially disappeared since N loading ceased in 1990. It has been replaced not by N fixing cyanobacteria, but by low cell-count, large cell-size mixotrophs such as cryptophytes and dinoflagellates (which may not be photosynthesizing) suggesting that the functional phytoplankton community has changed in response to increasing N limitation (Scott and McCarthy 2011). In terms of chlorophyll levels, recovery from eutrophication has not occurred (Paterson et al. 2011); however, a multi-decade extension of this work would be required to fully understand these changes in phytoplankton community structure and nutrient status. Also generating controversy was the suggestion by Schindler et al. (2008) that the results of the long-term Lake 227 experiment might inform eutrophication management in other aquatic ecosystems, including estuaries.

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challenges of mitigating eutrophication are amplified at large scales due to increased spatial and temporal heterogeneity in nutrient loading rates as the basin of influence increases in size. The eutrophication debate has largely focused on lakes and estuaries, as these bodies of water experience algal blooms that garner the attention of stakeholders and management agencies. However, these lakes and estuaries are embedded in a larger watershed. Nutrient loading, retention, and removal throughout the hydrologic continuum—the network of streams, lakes, and rivers within a watershed—determines the magnitude and timing of nutrient loading in sensitive downstream ecosystems. Moreover, the relationship between this nutrient loading and eutrophication within a downstream lake or estuary can depend on secondary responses such as N-fixation and sediment P-sorption and release within this ecosystem (Fig. 1).

Our objective in this chapter is to explore the complex relationship between nutrient loading in a watershed, and eutrophication in a downstream receiving body of water (e.g., lake or estuary). For the purposes of this chapter, we define eutrophication as a change in an aquatic ecosystem from a preindustrial state to a highly degraded state (characterized by high algal productivity, nuisance algal blooms, low oxygen, and altered biodiversity), which is induced by fertilization by nutrients (Box 2). We have organized this chapter by first presenting an overview of sources and controllability of nutrient loading in watersheds, followed by an examination of processes that alter the timing and magnitude of nutrient fluxes in a hydrologic network. We then explore the complex relationship between nutrient loading and eutrophication in a downstream receiving ecosystem, such as a lake or estuary. Finally, we present our vision for a watershed-scale theory of eutrophication, and review research efforts that have taken promising steps in that direction.

Section 2. Nutrient loading: Sources and controllability

Nitrogen (N) and phosphorus (P) enter aquatic ecosystems through a variety of natural and anthropogenic pathways including groundwater inputs, surface runoff, and atmospheric inputs (Allan and Castillo 2007). For management and regulatory purposes, nutrient inputs are typically characterized as point source (inputs at specific locations) or non-point source (diffuse inputs across the landscape). Point source pollution is relatively simple to monitor and regulate. The Clean Water Act in the United States, and Europe's EU Water Framework Directive, provide regulatory frameworks for controlling point source pollution (Christian-Smith et al. 2011). Technological advances have enabled the removal of most N and P from wastewater treatment systems, but achieving further reductions in loads can be prohibitively expensive (Daigger and Polson 1991; Baulch et al. 2013).
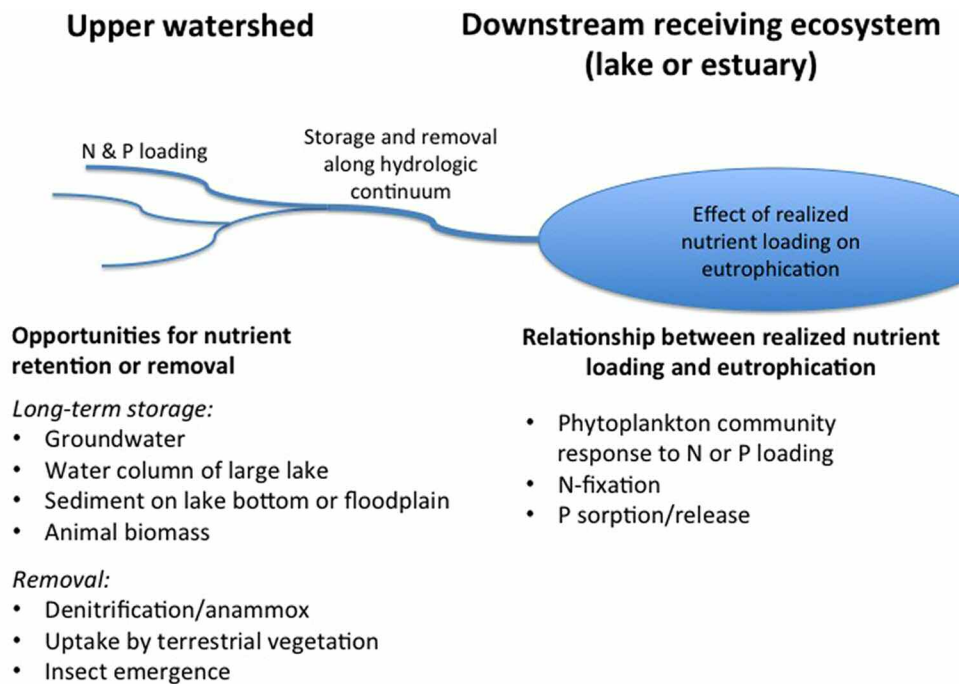
Fig. 1. Conceptual diagram of factors affecting the complex relationship between nutrient loading in a watershed and downstream eutrophication.

Box 2. Working definition of eutrophication.

We define eutrophication as a chance in an aquatic ecosystem from a pre-industrial state to a highly degraded state, characterized by high algal productivity, nuisance algal blooms, low oxygen, and altered biodiversity, as a result of nutrient fertilization. This differs from a typical regulatory definition where total phosphorus or chlorophyll concentrations are compared with defined thresholds for trophic status, and where eutrophication is then defined as a shift in these concentrations. We do so to focus on management objectives and the potential for state changes within ecosystems. We focus on these types of changes, rather than incremental changes within ecosystems that may not markedly impact ecosystem services, for example, heterotrophic responses to nutrient addition that do not induce low oxygen conditions. We note that the addition of allocthonous carbon via effluents (e.g., sewage, and pulp and paper) also contribute to oxygen depletion and major changes in ecosystem structure; however, this topic is not addressed within this chapter.

Nonpoint source pollution includes dissolved and particulate nutrients in agricultural and urban runoff, and inputs from atmospheric deposition. In an analysis of nutrient loading in the Mississippi River Basin, Alexander et al. (2008) identified corn/soybean agriculture as contributing 52% of the total N load, compared with 16% for atmospheric deposition and 9% for urban inputs. P loading, by contrast, was primarily attributed to losses of animal manure (37%), whereas production of corn and soybeans (25%), other crops (18%), and urban inputs (12%) were also substantial contributors. Compared with point source pollution, non-point source pollutants are more difficult to regulate, and achieving extensive reductions may require changes in farming practices, reductions in meat consumption, and decreased fossil fuel usage (Sutton et al. 2011).

Decreasing the nutrient load to a body of water requires identifying sources of pollution. Even among non-point source pollution, different sources can vary in their spatial and temporal characteristics, complicating control efforts. For example, atmospheric deposition of N originates through combustion of fossil fuels and by the volatilization of agricultural ammonia (NH_3), and creates a moderately high background loading of N across large regions. In some ecosystems, atmospheric deposition of P is another important input, resulting from wind erosion acting on susceptible urban and agricultural lands (Ramkellawan et al. 2009). By contrast, nutrient inputs due to runoff can be unevenly distributed across a watershed. For example, within six Oklahoma watersheds, an average of 5% of the area was responsible for 34% of P export (White et al. 2009).

Section 3. Nutrient transport, retention, and processing along the hydrologic continuum

Nutrients entering a stream or river may have multiple opportunities for retention and removal as they move downstream, before entering a lake or estuary that is sensitive to eutrophication. Here we review mechanisms that can decouple the timing and magnitude of the nutrient influx to a downstream receiving ecosystem, relative to nutrient loading higher in the watershed.

Time lags

Long-term storage of nutrients in slow-turnover pools can result in time lags, which may delay the downstream impact of nutrient pollution, but also hamper efforts to mitigate nutrient loading. Examples of slow-turnover pools include groundwater, the water column of large lakes, lake sediment, and biomass of animals or terrestrial plants. Sedimentation can be a major nutrient sink in lakes with long residence times (Saunders and Kalff 2001) and floodplains (Hamilton 2012). In the Laurentian Great Lakes, turnover times of N in sediments has been estimated to range from 28-117 years, and turnover times of water column nitrate ranges from 0.3-4.0 years (Small et al. in press). In streams, dissolved N and P that is taken up by algae or microbes and then enters consumer biomass can be sequestered for ~ 100 days (Small et al. 2009), and P attached to sediments deposited in a flood plain can be stored for centuries (Sharpley et al. 2013).

These slow-turnover pools can buffer the effects of upstream nutrient loading to downstream ecosystems, but they can also hamper efforts to restore downstream ecosystems. For example, many streams are fed by groundwater > 10 years old, and groundwater in many regions of the United States is contaminated by high levels of nitrate (Dubrovsky et al. 2010). "Legacy phosphorus"—P that has accumulated in soils and aquatic sediments from previous land uses—can offset management efforts aimed at reducing P inputs to aquatic systems (Sharpley et al. 2013).

Nutrient removal

Nutrient removal can be highly spatially variable in aquatic ecosystems. Biogeochemical hot spots such as the hyporheic zone, flood plains, and debris dams control nutrient dynamics in many streams and rivers (McClain et al. 2003).

Denitrification and anammox, both processes in which bacteria use nitrate as a terminal electron acceptor and generate N_2 as a waste product, can be significant sinks for nitrogen as water moves along the hydrologic continuum (Alexander et al. 2009). Because these processes require anaerobic conditions, rates are typically highest at the site of steep oxygen gradients, often the sediment-water interface (Small et al. 2013a).

Small streams contribute disproportionately to denitrification, as their high ratio of streambed area to water volume maximizes sediment-water interactions. This importance is amplified at the river network scale, as small streams comprise approximately 85% of the total stream length (Peterson et al. 2001). Headwater streams in the Mississippi River basin remove up to 45% of the N load each day through denitrification, compared with 0.5% removal per day in the Mississippi River (Alexander et al. 2000). Denitrification rates (on an areal basis) increase with nitrate loading rates, but the efficiency of nitrate removal in the stream network via denitrification decreases with higher loading rates (Mulholland et al. 2008).

Lakes and reservoirs can also be important sites of nitrogen removal, through denitrification and sedimentation (Saunders and Kalff 2001). Lakes have been conservatively estimated to remove nearly 20 Tg N year^{-1}, with small lakes (<50 km^2) accounting for nearly half of that total (Harrison et al. 2009). Lake denitrification efficiency is primarily influenced by water residence time (Jannson et al. 1994). Lake Superior, with a 190-year water residence time, is estimated to remove 86% of N inputs through denitrification (Small et al. in press). Lake trophic status can be an important control on denitrification efficiency in large lakes, as eutrophic conditions facilitate conditions in the sediment favorable for denitrification (Finlay et al. 2013).

Phosphorus can be retained in streams, lakes, and wetlands, through a number of mechanisms including biotic uptake (by vegetation, periphyton, phytoplankton, or microorganisms), sorption to soils and sediments, chemical precipitation in the water column, and sedimentation and entrainment (Reddy et al. 1999). Sedimentation in lakes and reservoirs can be an effective P sink (e.g., Vanni et al. 2011). In Lake Pepin, a large, natural riverine lake in the upper Mississippi River, traps approximately half of the suspended solids entering the lake, and generally acts as a net sink for *P* (Maurer et al. 1995). In Lake Winnipeg, which is experiencing nuisance algae blooms, eutrophication would likely be more severe were it not for the reduced P loading from the impoundments along two of its major tributaries (Wassenaar and Rao 2012).

Another avenue of nutrient removal in streams and lakes is through the biomass of emerging aquatic insects. Although rarely considered as a biogeochemical flux, the N flux out of small streams in the form of insect biomass can range from 5% to 20% of the magnitude of denitrification (Small et al. 2013b).

Nutrient inputs due to N-fixation in upper watershed

While streams are capable of removing a large fraction of N inputs through denitrification, streams and rivers can also gain N through N-fixation. N fixation rates can be high in streams with low dissolved N availability. Physical factors such as cold temperatures and low light availability can constrain rates of N-fixation in streams and rivers. In N-limited desert streams, N fixation is a major N input (up to 85% of total inputs; Minshall 1978; Grimm and Petrone 1997). However, rates of N fixation are much lower in many streams, contributing less than 5% to annual N loads in the few (mostly

Table 1. Complex ecosystem responses to adding or removing nutrients.

Process	Effect	Controls
Nitrogen fixation (cyanobacterial)	N-fixing cyanobacteria reduce atmospheric N_2 to NH_4^+ under conditions of N-starvation. Can represent an important influx of N into N-limited aquatic ecosystems.	Requires anaerobic conditions, including anoxic sediments, biofilms, or particle aggregates with anoxic regions, and within heterocytes attached to filamentous cyanobacteria. Energy intensive process requires severe N deficiency, which may be influenced by light, turbulence, mixing depth. May be limited by micronutrients (especially Fe and Mo).
Denitrification/ anammox	Some bacteria can use NO_3^- as an electron acceptor in anaerobic conditions, producing N_2 as respiratory end product. Represents significant sink for fixed N in aquatic ecosystems. Declining water column oxygen can result in increased greenhouse gas production (N_2O).	Requires low oxygen conditions, and organic C or NH_4^+ as electron donors.
Algal uptake	Uptake of dissolved N and P by algae can decreases availability of these dissolved nutrients.	Light availability, availability of limiting nutrients (including micronutrients).
Mineralization	Processes such as excretion by grazers or viral lysis return nutrients to the water column, which can fuel additional primary production.	Grazer biomass, temperature.
Algal sedimentation	In lakes, reservoirs, and estuaries, a fraction of nutrients bound in phytoplankton biomass and other particulate matter is lost from the water column by sedimentation.	Influenced by physical conditions (mixing in the water column), the size of particulates, and the size and identity of dominant grazers.
Sedimentation of entrained particles	Rivers can carry high sediment loads during floods, and this sediment, with associated nutrients, is deposited as water velocity slows at the margins of floodplains, or in riparian zones.	Water velocity (including factors affecting velocity, such as the presence of macrophytes).
Abiotic retention/ release of phosphorus	Sediments can bind P through adsorption or precipitation, effectively acting as a buffer against P loading. Conversely, when external P loading is diminished, P release from sediments ("internal loading") can delay recovery from eutrophication.	Controlled by a variety of physical and chemical factors, including particle size, sediment geochemistry, redox conditions, and pH.

North American) streams for which these rates have been quantified (Marcarelli et al. 2008).

Temporal disconnect between nutrient transport and processing

Nutrient transport and processing in aquatic ecosystems is highly variable in time. As a result, the timing of nutrient inputs in the watershed can greatly affect the fraction of these nutrients that ultimately end up in the downstream receiving ecosystem, where they might contribute to eutrophication. Discharge and nutrient loading may increase rapidly in small streams following a precipitation event, during which the throughput increases and the amount of processing diminishes (Meyer and Likens 1979). Nutrient export is often dominated by high flow periods where biotic processing is limited (Royer et al. 2006) or when external inputs of nutrients exceed biotic uptake capacity (O'Brien and Dodds 2010). One analysis found that a major challenge of using wetlands as a means

of reducing N transport in southern Sweden is that most N transport occurs during high flow periods in the winter, when retention time in wetlands is too short for extensive removal through denitrification (Jannson et al. 1994). Indeed, in cold climates, a large proportion of nutrient export may occur during snowmelt, when frozen ground and limited biotic activity may minimize the effectiveness of natural retention processes (Corriveau et al. 2011).

Section 4. Effects of nutrient loading in downstream receiving ecosystem

In the previous section, we reviewed factors affecting the timing and magnitude of nutrient inputs to downstream lakes or estuaries. Once these nutrients enter these downstream receiving ecosystems, whether or not they exacerbate eutrophication depends on a complex set of factors including nutrient limitation by phytoplankton, and potential feedbacks such as N-fixation, and P sorption or release (Table 1). Similarly, these

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Box 3. Assessing nutrient limitation: effects of scale.

The seemingly straightforward task of assessing nutrient limitation in an aquatic ecosystem is beset with the problem of complex ecological and biogeochemical responses at multiple spatial and temporal scales. The most common evidence for assessing nutrient limitation comes from bioassays, in which combinations of nutrients are added (typically NO_3^- and PO_4^{3-}, but can also include organic carbon and micronutrients), and a response is measured (typically chlorophyll concentration) after a given time. Bioassays range in spatial and temporal scale from bottle incubations ($\sim 10^{-3}$ m^3, $\sim 10^1$ day) to mesocosms ($\sim 10^1$ m^3, $\sim 10^2$ days) to whole-lake manipulations ($\sim 10^5$ m^3, $\sim 10^3$ days) (Fig. 3). Whereas bottle bioassays are easy to replicate and apply across a variety of aquatic ecosystems, they only assess nutrient limitation by a static algal assemblage and do not account for changes in algal composition and complex biogeochemical responses that could alter the trajectory of eutrophication (Sterner 2008). Whole-lake manipulations are valuable for observing how these complex responses unfold over ecologically relevant time scales, but the logistical constraints of these experiments typically preclude replication, and these experiments have been limited in their geographic extent. Ecosystem-level, long-term manipulations in saline estuaries are lacking (Schindler and Hecky 2009), although extensive evidence from physiological indices, bioassays, and mesocosms supports N-limitation in these systems (Howarth and Marino 2006 and references therein). Although small-scale work has been criticized for its relevance to management at broader spatial and temporal scales, evidence from comparative studies has found that results from small-scale experiments are relevant to large-scale processes (Elser et al. 1990; Spivak et al. 2011).

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same factors can complicate recovery from eutrophication upon reduction of upstream nutrient loading. We review each of these factors below.

Nutrient limitation

For living cells to synthesize biomolecules, chemical elements are required in relatively fixed proportions (Sterner and Elser 2002), such that algal production has been thought to be commonly constrained by the ability of a single limiting nutrient. The central approach to managing eutrophication therefore has focused on identifying which nutrient limits algal production (reviewed in Lewis and Wurtsbaugh 2008). Nutrient limitation is more complex at the community level, as species may differ in optimal N:P ratios (Smith 1982) and their ability to store nutrients or take up nutrients at low concentrations (Sterner and Hessen 1994; Burger et al. 2007). Furthermore, many aquatic ecosystems are characterized by seasonal or spatial heterogeneity that can alter the availability of potentially limiting nutrients (Stoddard 1994).

Despite this complexity (Box 3), a paradigm of P-limitation in lakes gradually emerged, highlighted by a series of whole-lake nutrient addition experiments at the Experimental Lakes Area (Schindler 1974, 1977; Box 1). The P-limitation paradigm has been scrutinized in recent years, as recent analyses indicate that N and P are commonly co-limiting for in situ algal assemblages in freshwater ecosystems over short time scales (Elser et al. 2007; Lewis and Wurtsbaugh 2008; Johnson et al. 2009), and that the P limitation paradigm may be specific to certain oligotrophic lakes (Sterner 2008). In marine waters, the general consensus is that N is most limiting to phytoplankton growth (Conley 1999). In contrast, estuaries can switch from P limitation in spring to N limitation in summer (D'Elia et al. 1986).

Complex responses to nutrient loading: N fixation and P sorption/release

Complex interactions among aquatic nutrient cycles were first described by Redfield (1958), who theorized that N cycling in the ocean is brought into balance with P availability, through altering rates of denitrification and N-fixation. A distinction in the marine literature between proximate limitation (the nutrient-limiting production by the current algal assemblage) and ultimate limitation (the nutrient-limiting production by an "adapted" algal assemblage) accounts for these dynamic ecosystem responses (Tyrrell 1999). In this model, whereas marine phytoplankton are typically N-limited, P availability (controlled by weathering rates) ultimately controls productivity on geologic time scales. However, the extent to which N-fixation can respond to N deficiency at the ecosystem level varies across different aquatic ecosystems.

Arguments to focus on P control in inland waters are often predicated on the notion that ecosystems have the capacity to meet their nitrogen demand via nitrogen fixation (N sufficiency, Box 1), an assumption that has never been fully assessed. There are a complex suite of controls on N fixation at the scale of cells and whole ecosystems. Lake morphometry is one factor determining the response of a lake ecosystem to nutrient loading. Small lakes tend to have shallower mixing depths and more stable stratification (Gorham and Boyce 1989). Under low-N conditions, small lakes can support high rates of N-fixation by heterocystous N-fixers (Paerl 2009). In contrast, wind mixing in large lakes can lead to light limitation for cyanobacteria, limiting potential rates of N-fixation due to its high-energy intensity (Paerl 2009). Studies of N-fixation rates for cyanobacteria indicate that they may often be unable to fully compensate for N-limitation in lakes (Howarth et al. 1988; Scott and McCarthy 2010), due constraints on N-

fixation such as light limitation or trace metal deficiency (Paerl 1990). Even in lakes with high N-fixation rates, high denitrification rates and nutrient loading at low N:P ratios can lead to N limitation (Paerl and Scott 2010). For example, despite having some of the highest measured planktonic N-fixation rates, reservoirs studied by Scott and Grantz (2013) remain seasonally N-limited.

In estuaries, N limitation is likely due to a combination of increased P supply and a decreased capacity for algal N-fixation (Howarth et al. 2011). As suspended clay and silt particles enter higher salinity water, P is released through desorption (Froelich 1988; Howarth et al. 1995; Némery and Garnier 2007). Meanwhile, cyanobacteria capable of N-fixation are largely absent in saline estuaries (Howarth and Marino 2006; Marino et al. 2006; Howarth and Paerl 2008) due to limited availability of molybdenum (due to high sulfate levels) as well as from grazing pressure (Marino et al. 2006; Chan et al. 2006). These factors may limit the capacity of estuaries to internally obtain N.

In the Baltic Sea (the largest coastal area in the world suffering eutrophication-induced hypoxia) large internal P loading occurs with hypoxia, with the amount of P released from sediments being an order of magnitude larger than external inputs from rivers (Conley et al. 2002). This injection of P to surface waters alleviates P limitation, stimulating phytoplankton production and acting as a positive feedback to increase eutrophication and hypoxia (Conley 1999; Conley et al. 2009). Additionally, ocean water can supply a significant source of P in some estuaries (Boynton and Kemp 1985; Nixon et al. 1996).

Both N-fixation and internal loading of P can hamper the recovery of an aquatic ecosystem from eutrophication, so that reductions in external nutrient loading do not achieve immediate reductions in primary production. Whereas these two processes can have similar effects on eutrophication, they are fundamentally different in the potential for substrate limitation. N-fixation taps into an essentially inexhaustible pool of atmospheric N. When other environmental conditions are favorable for N-fixation, this process turns on in response to intra-cellular N-starvation, partially compensating for "lost production" due to N-limitation. This newly formed N can eventually be recycled and excreted by grazers, potentially increasing N-availability to other producers. Internal P loading, on the other hand, is an equilibrium reaction dependent upon P concentrations in parental material, sediment, and water column (as well as concentrations of other chemical species). This abiotic process acts to buffer changes in external P loading, but eventually the stores of P retained in sediment will become depleted following reductions in external loading. However, this process could take decades, depending on the flushing time of the water body and amount of P in the sediments.

Other barriers to ecosystem recovery

In addition to factors such as legacy P loading, complex environmental responses such as regime shifts and shifting baselines (Duarte et al. 2009) may prevent a return to pre-eutrophic conditions following reduced nutrient loading.

Regime shifts cause a hysteresis pattern in response to nutrient loading, where reductions in loading may have minimal effect on phytoplankton biomass. In transparent, shallow lakes and estuaries dominated by macrophytes, excessive nutrient inputs can create algal blooms that shade out macrophytes. Subsequent reductions in nutrient inputs do not necessarily result in the re-establishment of macrophytes and return to clear water conditions (Zhang et al. 2003; Smith and Schindler 2009). For example, in Lake Veluwe in The Netherlands, macrophytes disappeared in the 1960s at total P levels rose above 0.20 mg L^{-1}. Despite reduced P loading over ensuing decades, the lake's turbid state was maintained through non-algal light attenuation associated with wind mixing and benthivorous fish feeding. The eventual re-establishment of macrophytes in the lake required reducing nutrient loading (lake TP of 0.10 mg L^{-1}) in concert with shifts in the biotic community (a decrease in the density of bottom-feeding fish, and a return of zebra mussels to the lake) (Ibelings et al. 2007).

Shifting baselines result from other forcing factors (such as climate or biological invasions) that interact with nutrient availability to affect the state of the ecosystem. For example, changes in currents and consequent increased upwelling intensity in San Francisco Bay were reported to lead to food web changes resulting in increased phytoplankton biomass despite a parallel decline in nutrient inputs (Cloern et al. 2007). Recent record harmful algal blooms in Lake Erie occurred in part because of warm summer conditions and weak circulation in the lake's Western Basin, characteristics that are predicted to increase in future years (Michalak et al. 2013). Species invasions can also alter the eutrophication response to a given level of nutrient loading. In Lake Erie, the invasion of zebra mussels (*Dreissena polymorpha*) in the late 1980s coincided with a dramatic decline in phytoplankton densities (Nicholls and Hopkins 1993). Selective filtering by zebra mussel has also been shown to promote toxic *Microcystis* blooms in Saginaw Bay (Lake Huron) and western Lake Erie (Vanderploeg et al. 2001).

Section 5. Toward a watershed-scale theory of eutrophication

Due to the spatial and temporal heterogeneity in nutrient loading and biogeochemical processing, nutrient availability and nutrient limitation are likely to vary along a hydrologic continuum. Phosphorus inputs may control eutrophication in some lakes due to the potential for N-fixation; however, inputs of N also contribute to eutrophication and productivity may be N and P co-limited. In estuaries, additional sources of P (from oceanic inflows, P-desorption from particles, and lower rates of P sequestration in sediments), as well as constraints on N fixation (salinity, trace metal concentrations, and grazers) may make N-limitation and N-driven eutrophication more likely (Howarth et al. 2011).
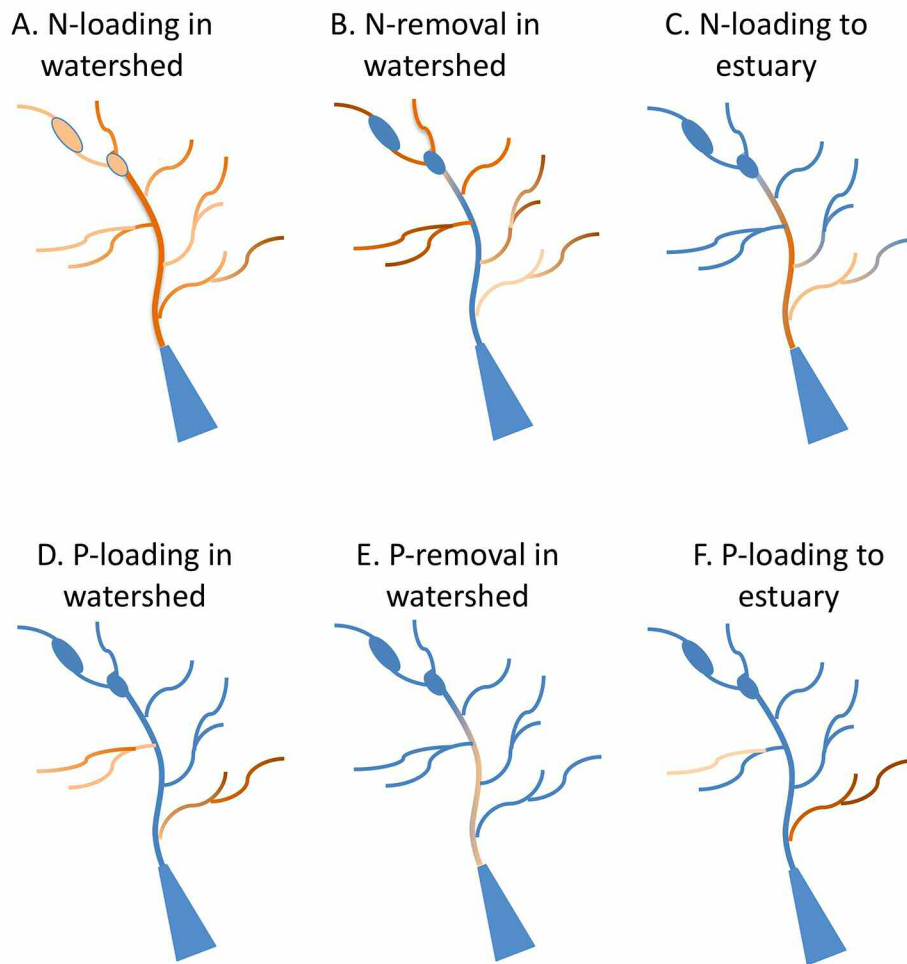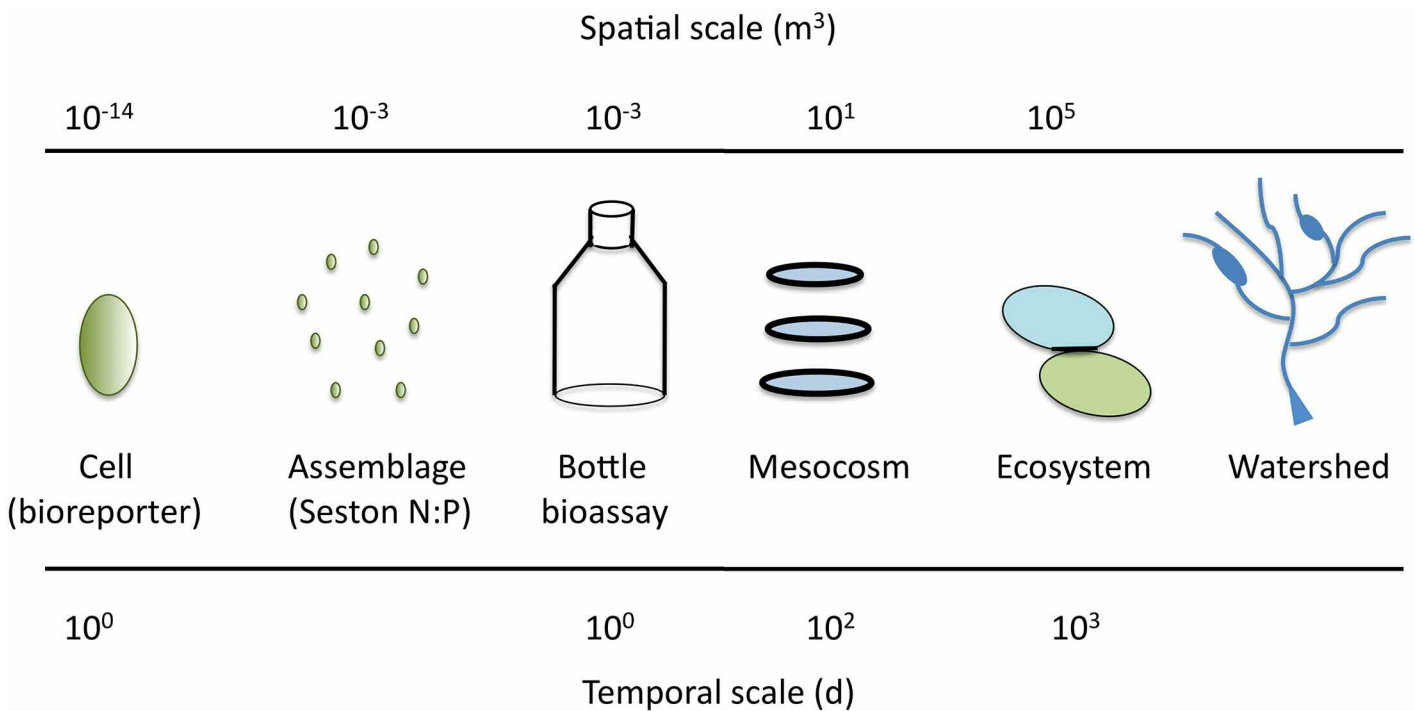
Fig. 2. Because of spatial heterogeneity in nutrient loading and removal along a hydrologic continuum, there may be critical control regions where reducing nutrient loading may have the largest effects on nutrient inputs to the downstream receiving ecosystem. Here, we illustrate spatial heterogeneity in nutrient loading (A, D) and removal (B, E) in a hypothetical watershed to identify critical control regions for nutrient management for an estuary (C, F). Warmer colors denote higher rates of loading or removal.

Even if anthropogenic inputs of N and P were spatially and temporally uniform across a watershed, spatial differences in denitrification, N-fixation, and P sorption and release would still lead to spatial heterogeneity in nutrient concentrations and N:P ratios. Loading is typically spatially heterogeneous, however, adding another piece to the mosaic. Atmospheric deposition of N and P can contribute to background loading, whereas non-point source inputs (such as urban and agricultural runoff) can lead to swaths of nutrient inputs in parts of the hydrologic network. Point source inputs (such as wastewater effluent and storm water runoff) contribute to nutrient heterogeneity at an even finer scale. Urban development near coastal areas may cause higher rates of nutrient loading in these most downstream regions of the watershed.

As both the loading of nutrients and the response of the ecosystem to these nutrients are spatially variable along a hydrologic network, in order to achieve nutrient reductions at a given point in the watershed, it is important to identify where in the watershed these nutrients originated. The basin of influence for a given point in the hydrologic network increases with distance downstream, of course, but spatially variable rates of loading and removal can lead to critical control points for eutrophication within the watershed that might be targeted for management. For example, curtailing nutrient loading in an upper watershed may have a limited impact on eutrophication management for a downstream estuary, due to the time lags in hydrologic transport, as well as by removal of N through denitrification and retention of P through sorption along the hydrologic flowpath (Fig. 2). By contrast, nutrient loading lower in the watershed may have fewer biogeochemical opportunities for removal and retention, functioning as a more direct conduit to the area vulnerable to eutrophication. Due to heterogeneity in ecosystem processes at the watershed scale, the effects of nutrient loading cannot be assessed only by load-

Spatial scale (m³)

| 10⁻¹⁴ | 10⁻³ | 10⁻³ | 10¹ | 10⁵ |

| Cell (bioreporter) | Assemblage (Seston N:P) | Bottle bioassay | Mesocosm | Ecosystem | Watershed |

| 10⁰ | | 10⁰ | 10² | 10³ |

Temporal scale (d)

Fig. 3. Nutrient limitation has been measured at spatial and temporal scales ranging from the individual cell to entire ecosystems. Smaller-scale studies have the advantage of replication within and across sites, whereas larger-scale experiments encompass environmental heterogeneity and can allow for compensatory ecosystem responses. We argue that explicit consideration of nutrient limitation at the watershed scale is especially relevant in eutrophication management, because of differing ecosystem responses to nutrient loading along the hydrologic continuum.

ing rates per unit area. Rather, the location of these nutrient inputs, relative to the spatial configuration of the hydrologic network, as well as the state of the aquatic ecosystems along the network (e.g., degree of P saturation in sediments) all influence the downstream effects of nutrient loading. In coming years, the development of spatially explicit models of nutrient loading and processing at the watershed scale (Helton et al. 2011) will allow for more effective nutrient management by identifying areas of greatest sensitivity to loading and enabling improved cost-benefit analyses.

Because of the spatial and temporal dynamics controlling downstream eutrophication responses to nutrient loading in a watershed (Fig. 3), we argue that any "one-size-fits-all" approach to eutrophication management is likely to be met with frustration by managers and will lead to continued disagreement within the aquatic science community. Instead, an analysis specific to spatial patterns of nutrient inputs and retention for a given watershed is likely to lead to better information for managers. Site-specific analyses pose challenges: model-based approaches that can account for spatial complexity require parameterization based on local conditions, which may be costly. Even so, this approach of watershed-based eutrophication management has shown promise. A detailed spatial analysis has recently been published for nitrogen loading from the Scheld River into the North Sea (Vermaat et al. 2012). In this study, N loading was modeled at a 1 km²

resolution across the 20,200 km² watershed, and N export was simulated based on hydrologic, biogeochemical, social, and climatic variables. This approach allowed for 30-y forecasts of N loading under different land use scenarios. This analysis indicated that increasing the degree of sewage treatment in this watershed would lead to greater reductions in the N load compared with policy measures directed at non-point agricultural sources. Another model, the Soil and Water Assessment Tool (SWAT), has been used for the last 20 years to predict effects of agricultural management decisions on water, sediment, and chemical yields in watersheds (Gassman et al. 2007). For example, this model was applied to the Nagwan watershed in India to identify and prioritize critical sub-watersheds for soil conservation management (Tripathi et al. 2003). Ideally, a similar modeling framework, parameterized for a specific watershed, could be used to inform understanding how N and P loading throughout a watershed result in eutrophication of sensitive ecosystems, incorporating input from researchers and managers with expertise in lakes, streams, rivers, estuaries, and the coastal ocean. However, the high degree of uncertainty in nutrient modeling must be considered when making management decisions, and conservative management to maximize reductions in nutrient loads may be prudent. This is particularly true in light of climate change, climate variability, and the long-term legacy of land use change in the environment.

Ultimately, understanding eutrophication at a watershed scale is not enough. Reversing the effects of eutrophication also requires regulatory authority at the watershed scale. Of course, many watersheds extend across state and national boundaries, complicating management efforts. An example of successful management of a shared watershed is the Great Lakes Water Quality Agreement, developed by the International Joint Commission, an independent organization established by the United States and Canada.

Section 6. Conclusion

The debate among aquatic scientists on nutrient limitation has focused on specific ecosystems of interest, with little explicit consideration for how these ecosystems are embedded within hydrologic networks. This reductionist approach has led to disagreements among scientists in applying results of eutrophication studies across systems and across scales. These disagreements among researchers regarding the importance of controlling N have also generated mixed messages for managers and policy makers.

However, it is clear that nutrient-loading rates across landscapes vary spatially, and that responses to nutrient loading vary longitudinally along the hydrologic continuum, creating a complex biogeochemical mosaic that affects eutrophication. While this complexity poses challenges, explicit consideration of eutrophication at the watershed scale can present opportunities for improved management, if critical control points can be identified and targeted. Eutrophication management in the Twenty-First Century requires a holistic view of humans' role in nutrient cycling, not only as sources of nutrient pollution, but also modifying the capacity of aquatic ecosystems to respond to nutrient loading. Important questions remain, however, especially with regard to the generality of spatial patterns within watersheds. To what extent is each watershed unique in its spatial configuration of nutrient loading and removal? To what extent can management recommendations be generalized? By beginning to develop a theory of eutrophication at the watershed scale, it is our hope that aquatic scientists can present a more unified voice to managers, and encourage an approach to eutrophication management that extends beyond individual ecosystems, accounting for the connectivity inherent to watersheds.

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