From limitation to excess: the consequences of substrate excess and stoichiometry for phytoplankton physiology, trophodynamics and biogeochemistry, and the implications for modeling

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**Abstract**

Current parameterization of several important physiological rates using rectangular hyperbolic saturation formulations is inadequate to capture our expanding understanding of the dynamic regulation of nutrients and energy at the primary producer level across all substrate levels, from limiting to super-saturating. Nutrient regulation by primary producers can affect chemical composition, in turn affecting predator–prey interactions and biogeochemical feedbacks in complex foodwebs. Anthropogenically altered nutrient loads are accentuating these challenges by altering nutrient stoichiometry. Using examples derived from the development of phytoplankton physiological dynamic regulation, the case is made that dynamic regulatory concepts are relevant at all levels of ecosystem regulation, that elemental stoichiometry must be considered in physiological, trophodynamic and biogeochemical constructs, and that the classical notion that nutrients and nutrient stoichiometry are only regulatory for physiology when at the limiting end of the spectrum must be laid to rest. Advancing models will require new emphasis on physiology including both dissipatory regulation and assimilatory regulation and the feed-back mechanisms between them.

**Keywords:**
Dynamic balance models
Kinetics
Nutrient supersaturation
Dissipatory strategies
Ecological stoichiometry

1. Introduction

Ecosystem modeling has advanced tremendously in the past decade- with increasing sophistication in our ability to visualize large data sets, conceptualize complex interactions and formulate predictive scenarios based on model ensembles. Operational forecasting models for many aspects of global change now range from the regional to the global ocean. The need for predictive models is large and increasing, particularly with climate change and the increasing observations of acidification and harmful algal blooms (HAB).

Models depend on parameters that are not always easily measured or available and as a result, mass fluxes, dynamics, and physiological variables are often not adequately captured. Traditional mass-based models (often either single nutrient, N or C) are generally relatively simple and operate using classic uptake kinetic relationships. Yet, even these classic relationships are poorly characterized for many species or are highly variable under different growth conditions (Gilbert and Burkholder, 2006). Several authors (e.g., Allen and Polimene, 2011; Flynn, 2010) have recently argued the need for a new generation of plankton models based on emerging knowledge of dynamic cellular and ecophysiological behavior.

Here we add our voice to this chorus. Much has been learned about organismal adaptation and physiological responses to variable environments — from phytoplankton growth to competition, mixotrophy, allelopathy, prey switching and/or prey rejection, and the relationships between these processes and various abiotic factors such as temperature, pH, and light. Physiological traits of marine organisms are now being applied in models of emergent marine biodiversity (Follows et al., 2007) and some new-generation, mechanistic population dynamic models and three-dimensional ocean biogeochemical models incorporate phytoplankton functional groups, multiple limiting nutrients, flexible elemental composition, and iron limitation (e.g., Baird and Emsley, 1990; Klausmeier et al., 2004; Le Quéré et al., 2005; McGillicuddy et al., 2010; Moore et al., 2004; Ramin et al., 2012). These latter approaches have made significant advances but they still often depend on poorly characterized physiological relationships.

Flynn (2010) highlighted the inability of classic kinetic relationships and fixed elemental stoichiometric concepts to capture phytoplankton interactions when cells are nutrient stressed. In fact, it has been argued that these models are unsuitable, or even dysfunctional for descriptions of algal nutrient uptake or growth under more natural, variable nutrient conditions (Flynn, 2005, 2009; Goldman and Glibert, 1983). This is, in part, due to the fact that nutrient stress develops before the nutrient becomes completely exhausted (Flynn et al., 1999, p. 356). Adding to these difficulties is the recognition...
that both nutrient limitation and nutrient saturation result in dynamic
ic phytoplankton physiological changes which have consequences for
chemical composition which, in turn, affect trophodynamics.

This later observation, that nutrient saturation may be a cellular
stress, is pertinent to those systems that have chronically high nutrient
concentrations resulting from eutrophication. However, conven-
tional kinetic models that incorporate a saturation response
would dictate that nutrients cannot be regulatory at saturating
concentrations with respect to rate processes, such as growth rate
(e.g., Reynolds, 1999). Here, this premise is challenged.

The central premise of this paper is that the use of classic, satura-
tion formulations used to parameterize physiological rates are inade-
quate for modeling the dynamic regulation of nutrients and energy at
the primary producer level across all substrate concentrations and
that complex dynamics at the physiological scale has important
implications in understanding predator–prey interactions and bioge-
chemical feedbacks. That is, the reductionist approach of quantifying
the parameters defining limitation and saturation as fixed entities con-
strains both our understanding of the dynamic regulation of physiologi-
cal and metabolic processes across all substrate or resource levels and
hampers our ability to capture this dynamic regulation in complex
food web models. Current parameterization of kinetics and rate pro-
cesses is challenging for both physiologists and modellers because of
1) experimental and methodological difficulties in “getting the curve
right”, especially in light of our advancing tools; 2) failure to consider
changes in rates or organismal physiology beyond the concentration
range that typically bounds the limit of saturation of the rate process;
3) lack of consideration of more than one element or substrate; and
4) difficulties in relating dynamically changing physiology and stoici-
ometry to food webs and to biogeochemical feedbacks. The goal of
this paper is to underscore that advances in physiology are funda-
mental to achieve advances in models at various scales, that consid-
eration of dynamic regulation and stoichiometry are keys to these
advances, and to emphasize how anthropogenic nutrient loads are
accentuating these challenges by altering nutrient stoichiometry.

2. Rate processes as a function of substrate availability

2.1. A “curve for all reasons”

Phytoplankton physiologists often measure, and modelers often
parameterize, processes as a function of substrate availability by a cur-
vilinear function, a rectangular hyperbola (Fig. 1). Growth as a function
of nutrient concentration (Monod, 1942), nutrient uptake as a function
of external nutrient availability (Mention and Michaelis, 1913), nutrient
uptake as a function of cellular internal nutrient concentration (Droop,
1973, 1979), and photosynthesis as a function of irradiance are all
examples of such formulations. For grazers, similar relationships define
grazing or ingestion as a function of food availability. Indeed, the rectan-
gular hyperbola has been termed “a curve for all reasons” (Rao, 2000;
Table 1). In each of these formulations, a maximum (saturating) rate
is identified, as is a half-saturation constant or an index of the concen-
tration at which the rate plateaus (e.g., Kₚ for photosynthesis), and the rate
of change (initial slope) are characterized (Fig. 1). In some cases, for
example, photosynthesis models, an inhibiting term may be incor-
porated. These basic functions are central to many plankton models,
such as nutrient–phytoplankton–zooplankton models (e.g., Franks,
2002).

The concept of a saturating relationship in relation to “resources”
is also applied at the population level. Applying the Verhulst model
of population dynamics,

\[
dN/dt = rN(1 - (N/K))
\]

“r” selected species are those with rapid growth rates, whereas “K”
selected species are slower-growing, but are adapted to living at densi-
ties close to carrying capacity, K, of the environment (Verhulst, 1938). In
nutrient-rich aquatic environments, r-strategist phytoplankton are
typified by bloom-forming diatoms, whereas K-strategists dominate in
more nutrient-poor, “mature” systems, typified by dinoflagellates
(many of which are mixotrophic) (Flynn et al., in press).

2.2. Challenges of getting the curve right

Models must balance simplicity with realism and complexity. Saturating response curves have a great appeal because they contain
not only an efficiency parameter, but a constraint on the maximum
rate, which is necessary to satisfy inherent biological metabolism
(i.e., growth rate cannot be unconstrained) (Rao, 2000). For reasons
of computational efficiency and/or availability of calibration data,
many models operate with a single set of kinetic parameters or with
the simplifying assumption that a single efficiency parameter (i.e., Kₚ
or Kₛ) or rate (i.e., Vₘₐₓ or Pₘₐₓ) is applicable to all species or all condi-
tions. There are several major challenges to “getting the curve right”.
The first is adequately characterizing it and understanding its variability
(Burmaster and Chisholm, 1979; Goldman and Gilbert, 1982, 1983;
Gotham and Rhee, 1981; Morel, 1987; Rhee, 1973). Kinetic relation-
ships ranging from enzymatic control to in vivo rates exhibit variation
and this variation increases in complexity at higher levels of organiza-
tion as processes of cellular control over enzyme synthesis and control
of auxillary factors become part of cellular function. The fact is, there
is no higher level process that can be fully constrained by a single sub-
strate kinetic curve, even at the simplest level of enzyme reactions.
The challenge is to identify a relationship that is representative of the
process under relevant conditions and to identify the family of curves
that envelop the response of individual species or communities,
depending on model purpose. Toward this end, it is necessary to define
the pertinent scale (typically temporal) and relationships between
kinetics measured at one scale and the extent to which they may be
applied to a different scale (e.g., uptake kinetics applied to growth
kinetics; Goldman and Gilbert, 1983). Ecosystem modeling, by its
nature, deals with longer temporal scales compared to the scales on
which biochemistry and physiology operate. Nutrient kinetic relation-
ships or photosynthesis rates are typically determined on the physio-
logical scale, but the relationship of those kinetics is ‘filtered’ by cell
metabolism and cellular functions (e.g. nutrient storage or release)
that ultimately influence the transfer of material at the ecosystem level.

The second challenge is that many kinetic or process relationships
are difficult to measure well, especially under in situ conditions,
and that measurements made with one technique are not necessarily
equivalent to those made with another technique, leading to wide un-
certainty in what kinetic parameters to apply in models. For example,
the measurement of productivity may be made by use of ¹⁴C, ¹⁸O, or
variable fluorescence, but data are not interchangeable. Whereas $^{14}$C measurements determine the rate of incorporation of C, $^{18}$O experiments measure the water splitting reaction and non-cyclic electron transport, and variable fluorescence instruments (e.g. FRRF, PAM) measure photochemical efficiency of the photosystem II pathway; these rates are not equivalent nor are the kinetic parameters derived from them (Suggett et al., 2009). This presents a challenge for correctly incorporating kinetic constants in model formations. As another example, some nutrient kinetic measurements are made following depletion of substrate over time, while others are made using stable isotopic techniques and the comparative kinetic parameters derived differ (Harrison et al., 1989). Furthermore, measurements made over different periods of incubation or with different competing substrates have long been known to complicate interpretation of in situ rates or uptake kinetics (Dugdale and Wilkerson, 1986; Gandhi et al., 2011). Whereas short term experiments measure uptake, longer scale experiments are skewed towards measurement of assimilation or growth (Wheeler et al., 1982; Goldman and Gilbert, 1983, Fig. 2). Different species have vastly different capabilities for taking up nutrients and storing them in excess of their growth capabilities (e.g., Flynn et al., 1999; Goldman and Gilbert, 1982). Most parameterizations of rate processes as a function of substrate assume a steady-state condition for the cell. When cells are not in steady-state the relationship between uptake and growth becomes uncoupled (Goldman and Gilbert, 1983).

While uptake or transport rates are generally assumed to be constant for a given process because they are enzymatic reactions, there is, in fact, a wide range of variability in uptake kinetics even for a given substrate and species or functional group (reviewed by Litchman et al., 2006). This, too, presents challenges for model applications. For example, the rate of nutrient uptake as a function of external nutrient availability (Michaelis–Menten model) can be highly variable depending on the physiological state of the cells, the time of exposure to the limiting nutrient, and other environmental factors (Lan Smith et al., 2009; Wheeler et al., 1982 and references therein). Uptake rates of a given element are also a function of physiological state, the time of exposure to the limiting nutrient; and $K_{m}$ is the half-saturation for growth (Monod, 1942).

Regulation across the entire curve

Only under conditions of steady-state — a condition rarely achieved in natural environments — is the uptake rate of nutrients equivalent to growth or the rate of photosynthesis equal to growth (Goldman and Gilbert, 1983; Kana and Gilbert, 1987a, b). Generally, homeostatic mechanisms keep the acquisition of materials and energy in balance with the cellular growth demands and the observation of relatively constrained rates varying little with increasing temperature (Fan et al., 2003). This is a function of different temperature optima of the respective enzymes associated with transport and assimilation of these substrates. Time of day is also another important factor; as such processes of uptake and assimilation are highly coupled to the light-day cycle. In this regard, rates of NO$_3^-$ uptake by phytoplankton are particularly sensitive to time of day; the enzyme nitrate reductase (NR) is generally at its daily maximum at first light, and thus rates of NO$_3^-$ uptake are generally significantly higher at this time of day (Cochlan and Harrison, 1991; Gilbert et al., 1991). While it is “neither practical, not justifiable, to include all these facets of control within a model” (Flynn et al., 1999, p. 361), the challenge for physiologists is to not only describe the variability but to understand the control of this variability with the expectation that an understanding of controls will lead to more robust general models.

![Fig. 2](image.png)

Fig. 2. The specific uptake rate of nitrogen for natural samples from the Chesapeake Bay in which duration of incubation varied (curve a — 1 min; curve b — 15 min; curve c — 60 min). Replotted from Wheeler et al. (1982) with permission of the publisher.
elemental ratios for phytoplankton (e.g., Redfield elemental ratios) is corroborative. However, under non-steady-state conditions relating to variable nutrient or energy availability, cellular adjustments in acquisition efficiency and capacity decouple these ‘simple’ relationships and the underlying kinetic relationships are always ‘chasing’ the environmental change. This is part of the general notion that ‘physiological state’ (the physiological condition as determined by the immediate past history of the cell) can have an important impact on kinetic or energy relationships. A significant challenge is to find tractable ways to tune the parameters of basic kinetic relationships based on physiological states and environmental variability. The evolution of one fruitful approach that was developed in parallel with advances in our understanding of mechanisms of photosynthetic regulation is described below.

The photosynthetic vs. irradiance (PE) relationship is one of the fundamental transfer functions for converting irradiance to photosynthesis. A suite of photosynthesis-irradiance measurements conducted on the marine cyanobacterium Synechococcus (strain WH7803) grown across a gradient of irradiances illustrates the large plasticity of the PE relationship depending on growth irradiance (Kana and Gilbert, 1987a,b). A classical saturation curve was observed for growth rate with maximal rates occurring above 200 μM photons m⁻² s⁻¹ and up to 2000 μM photons m⁻² s⁻¹, the highest irradiance tested (Kana and Gilbert, 1987a). However, at each steady-state growth irradiance, a unique PE curve was identified (Kana and Gilbert, 1987b; Fig. 3). While the rate of photosynthesis measured at the growth irradiance balanced the demand for growth, the overall shapes of the PE curves for cells growing at the different irradiances were significantly different. The different PE curves were a consequence of photoacclimation of photosynthetic pigmentation. At irradiances that saturated growth rate, the cells produced only enough pigmentation to satisfy the energy demands for growth (i.e., the initial slope, α, in per cell or per C units was adjusted to yield a photosynthetic rate that matched the growth demand). Over irradiances that limited growth rate, α increased with diminishing irradiance, but not sufficiently to maintain photosynthesis at a rate that could support maximum growth rate. In those experiments, the maximum photosynthesis rate, P_max, identified from the PE curve, exceeded the operational photosynthetic rate in the range of growth limiting irradiances, implying that regulation of photosynthetic capacity (analogous to V_max) was not matched to the ‘needs’ of the cell.

These data exemplify the fact that a generalized saturation curve is characteristic of phytoplankton photosynthesis in that there must be a proportional region (initial slope) and a saturation region (both a consequence of fundamental constraints of the biophysics and biochemistry of photosynthesis), but that the curves are continuously variable within the bounds of the extremes of growth irradiance. In other words, a single PE curve cannot be used to describe a species’ photosynthetic activity. More useful, however, is the observation that since the derived parameters (α and P_max) can be described by simpler relationships to irradiance and that these parameter ranges exhibit relationships to irradiance and that these parameter ranges exhibit.

From a modeling perspective, Geider et al. (1996, 1997, 1998) and Kana et al. (1997) were first to apply these principals of photoacclimation and introduced a method for combining the effects of irradiance, temperature and nutrient supply on the photoacclimative state of microalgae based on the dynamic balance of energy flow through the entire photosynthetic apparatus and cell, rather than considering photoacclimation as simply a response to absolute irradiance. The critical point is that photosynthetic stress and/or energy poise is as much related to the ability of the cell to utilize the energy as it is the availability of energy at photosystem II (PSII). The modeling applications are that cellular pigmentation (photoacclimation state) can be driven by the ratio of light absorption (a function of pigmentation concentration) to assimilation (constrained by P_max; Kana et al., 1997). Whereas prior growth and photosynthesis models of microalgae provided good mass balance, they generally required prior knowledge of the response of photoacclimation (i.e., a catalog of PE curves or pigment concentrations) in order to define the system. The use of this regulatory term (ratio) eliminated that empirical requirement and provided a ‘self-regulating’ feed-back formulation for determining photoacclimation state.
of the regulatory term, and assumptions of nutrient utilization and temperature effects and the species specific parameterization of the models, it was demonstrated that all phytoplankton species are similar in that they regulate their pigmentation around the hinge point of the growth-saturating irradiance that matches assimilation capacity (Geider et al., 1997; Kana et al., 1997).

A similar conceptual approach, undertaken by Ågren (1988), explored the relationships between elemental composition and growth rate of *Micromonas lutheri* and a highly contrasting autotroph, the tree, *Betula pendula*. When scaled to their respective optimal nutrient content (limiting nutrient) and growth rate, the relationships between nutrient content and growth were remarkably similar. Both species regulated their elemental composition similarly with regard to their relative growth rates. In both cases, when rapidly growing they were nutrient rich (low C: nutrient), and when growing more slowly, they were comparatively nutrient poor (elevated C: nutrient).

A number of lessons come out of these examples. One is that if there is a focus on characterizing species diversity and identifying differences among species there is a risk of not identifying fundamental regulatory structures that universally embrace all species. Data on diversity, however, is critical and a precursor as it feeds the analysis of regulatory structures. Another lesson well recognized by modelers is that metabolic details are not always necessary in formulations and that adequate, but robust results pertaining to complex multifactor systems can be obtained by ‘stepping back’. Whereas the devil is in the details and that is often where vigorous debates originate, and where interest in species, or functional group differences may lie, vis à vis regulatory control, those details may not be where the important advances are made in modeling complex ecosystems. Lastly, the photoacclimation model originated from a physiological perspective with a basis in photosynthetic regulation. There is a long tradition of phytoplankton models being based on ‘physiology’ though the temptation is often to take a deterministic approach that combines suites of response curves. Kinetic relationships are dynamic in biological systems and formulations that describe the biology of those dynamics rather than relying on ‘calibration curves’ should lead to greater insight into the behavior of phytoplankton and greater efficiency in computation. This is a challenge for both modelers and physiologists. Following from this insight into photosynthetic dynamic regulation, a number of dynamic model approaches for physiology are being developed and applied (e.g., Jacob et al., 2007; Lan Smith et al., 2009; Pahlow, 2005; Ross and Geider, 2009).

As with irradiance, regulation of nutrient uptake also does not cease in cells exposed to growth-saturating nutrient concentrations. Because of the perpetual focus on the role of “limiting substrates”, the potential for regulation of processes at high concentrations has been significantly understudied. Inhibition of nutrient uptake at high concentrations has been recognized for decades (e.g., Gotham and Rhee, 1981) but has been virtually ignored in nutrient kinetics, unlike its counterpart in photosynthesis physiology, photoinhibition. Alternatively, non-saturable kinetics are observed. This is illustrated by NO$_3^-$ uptake, which at saturating to supersaturating concentrations, does not follow a classic saturating hyperbolic relationship in many algal species (Collos et al., 1992, 1997; Lomas and Gilbert, 1999b; Watt et al., 1992). In this region of the kinetic curve, uptake may be linear or biphasic (up to concentrations of ~300 μM-N), with the first transition point occurring at ~60 μM-N (Fig. 4). Nonsaturable kinetics likely involve a diffusion-controlled transfer into the cell (Neame and Richards, 1972). Falkowski (1975) has shown for several diatoms that the cell membrane-associated active carrier transporter for NO$_3^-$ is very efficient (Km, ~1 μM-N) but does saturate, and therefore diffusion may well be an important process contributing to nonsaturating NO$_3^-$ uptake kinetics at high substrate concentrations. Biphasic kinetic uptake of NO$_3^-$ appears to be more prevalent in cool waters and it has been hypothesized that cells (especially diatoms) may take up and store NO$_3^-$ at high intracellular concentrations and use this NO$_3^-$ as an oxidant to dissipate the periodic overflow of electron energy through the activity of NR. At low temperatures, while carbon uptake and metabolism may be limited by temperature and unable to buffer sudden changes in the flow of electrons from the light reactions (particularly on sudden changes in light and/or temperature), NO$_3^-$ uptake and reduction should remain high, allowing for dissipation of these electrons. Therefore, NO$_3^-$ reduction may be characterized as a “futile cycle” for at least those species known to display such non-saturable kinetics (Lomas and Gilbert, 1999b). The overall point to be emphasized is that physiological regulation can and does occur across the entire spectrum of substrate conditions and classic kinetic curves do not capture the extent of physiological regulation at substrate super-saturation.

One approach that is showing promise in capturing dynamic regulation of nutrient kinetics is that of optimal kinetics (Aksnes and Egge, 1991; Lan Smith et al., 2009). This approach recognizes that the ability of the cell to up- or down regulate nutrient uptake is a function of the potential maximum uptake sites, internal enzymes and rates of assimilation. Instead of a half-saturation constant, this approach calculates an affinity uptake rate:

$$V_{aff} = \frac{(V_{max} \cdot S)}{(V_{max} / A + S)}$$

wherein the relationship substitutes the more classic half-saturation constant (Ks) with an affinity constant, V$_{max}$/A. In such a formulation, both the affinity and V$_{max}$ may vary with cellular physiology. Thus, as with the photosynthetic “regulatory term”, here, too, a ratio provides a more robust measure of the relative abilities of all species to compete for nutrients (Lan Smith et al., 2009). In essence, optimal kinetics assumes that the cells dynamically balance the efficiency of nutrient acquisition at the cell surface and the maximal rate at which these nutrients can be assimilated within the cell, a balance between surface uptake sites and internal enzymes (Lan Smith et al., 2009).

Although nontraditional kinetic relationship modeling has lagged, there have been numerous advances in multi-nutrient kinetic modeling. As an example, Klausmeier et al. (2007) developed a multi-nutrient Droop model to illustrate the dynamics of adaptation of uptake rates over time.

2.4. Emergent properties in response to dynamic balance

Conceptualizing the relationships between physiological processes and growth as a dynamic balance between uptake, assimilative, and dissipative processes has further implications for cell properties. Emergent properties of cells in response to this dynamic balance include the relative proportions of ribosomes, enzyme activities, gene regulation, cellular pigmentation complement, and ultimately the cell elemental composition. Thus, properties such as chlorophyll:carbon (Chl:C), C:N, N:P or other elemental properties are highly dynamic with growth rate and substrate. The *Synechococcus* example above (Kana and Gilbert, 1987a,b) further illustrates the dynamic regulation of cell composition. Across the irradiance range for growth, Chl:C and C:N ratios were highly variable (Fig. 5). Most of the variability was in the light-saturated range for growth, reflecting down-regulation of the pigment complement at high irradiance. In another example of dynamic cell regulation, the diatom *Thalassiosira pseudonana*, when grown under growth-saturating conditions for light and nutrients, was found to display >2-fold difference in C, leading to variable C:N and Chl:C ratios as a function of saturating, but variable, NO$_3^-$ (Fig. 6). Most of the variation in cellular composition was in the nutrient-saturated region of the curve (>50 μM-N) again reflecting the role of down-regulation at saturation. While flexibility in N:P or C:P in phytoplankton have long been shown in culture experiments (e.g., Finkel et al., 2010; Goldman et al., 1979; Leonardos and Geider, 2004a,b; Quigg et al., 2003; Rhee, 1978), the emphasis in previous experiments has largely been on the effect of nutrient limitation. Variability
in elemental stoichiometry is thus not strictly a response to substrate limitation.

The Geider et al. (1998) model explicitly includes down-regulation of pigment content at high irradiance and (or) when growth rate is limited by nutrient availability or temperature (Falkowski and LaRoche, 1991; Geider et al., 1996); the accumulation of energy-storage polymers when growth rate is light saturated and (or) nutrient limited, as well as the subsequent mobilization of these polymers when light is limiting or nutrients are resupplied (Foy and Smith, 1980); and it includes feedback between N and C metabolism. Dynamic balance models such as those of Kana et al. (1997) or Geider et al. (1998) and many derivatives have advanced the application of multiple currency considerations for phytoplankton growth and take into account the interdependencies of the energy, C, and N metabolism of phytoplankton. These types of models also predict the time course of changes in chemical composition and growth rate that occur when environmental conditions change. In an effort to relate cellular physiological regulation to functional traits across species, a three-way model of the trade-off between cell size and competitive abilities for N and P in marine and freshwater phytoplankton was recently developed (Edwards et al., 2011).

3. Dynamic regulation and ecological stoichiometry

Kinetic models (including photosynthesis models) are fundamentally rate-based models and such structure is essential for describing dynamic processes. Nevertheless, food webs are not merely summations of a series of rate processes (and kinetic curves), but are an outcome of both the quantity and quality of the substrate (or food) provided, not just the rate at which it is produced. The ecophysiology (nutritional quality) of the component organisms present in the ecosystem affects not only their own growth potential but also the activities of others: the cellular composition of algae, for instance, has consequences for grazers. Thus, for grazers, the nutritional value of the prey, not the rate at which it is produced is a key aspect of their population success. From the population standpoint, however, rate of growth of the prey population is important. Therefore robust foodweb/ecosystem models should incorporate not only kinetic parameterization, but also sufficient description of material composition that relates to nutrition. Toward this end, there have been significant advances in our understanding of how essential elements and chemicals structure foodwebs.

3.1. Dynamic nutrient regulation at the producer vs. consumer level

The relative balance of nutrients affects all aspects of behavior of their consumers, such as growth rate, fecundity, and ultimately the success of different populations (Jeyasingh and Weider, 2005, 2007). Compensatory feeding can also occur when grazers are provided food of poor nutritional composition (e.g., Augustin and Boersma, 2006). Classic ingestion relationships emphasizing food quantity (Table 1), not quality,

![Fig. 4. Examples of biphasic relationships between ambient concentrations of nitrate and specific uptake rate. Panels A and B are for cultures of Skeletonema costatum; C and D are for cultures of Prorocentrum minimum. Panels A and C illustrate the relationship for concentrations <60 μM; panels B and C illustrate the relationship when the concentration gradient is increased. Replotted from Lomas and Gilbert (2000) with permission of the publisher.](image)

![Fig. 5. Comparison of the growth–irradiance relationship (solid line, left axis) and the cellular composition (dashed line, right axis) of Synechococcus WH7803 when pre-adapted to the irradiance indicated on the X-axis. Panel A, Chl:C ratio and growth; panel B, C:N ratios and growth. Data derived from Kana and Gilbert (1987b).](image)
do not take this into account. Ecological stoichiometry (sensu Sterner and Elser, 2002) provides “an integrated framework for merging perspectives across individual, population, community, and ecosystem levels” (McIntyre and Flecker, 2010, p. 539). In essence, a stoichiometry approach applies the “curve for all reasons” by “imagining" both consumer and prey not as organisms but as amalgams of numerous chemical elements. Prey serve as the reactants...and the consumer’s tissues are a product…” (McIntyre and Flecker, 2010, p. 540).

Using the same Synechococcus example described above (Fig. 5), all other conditions being equal, it can be inferred that grazers consuming cells growing at 300 μM m⁻² s⁻¹ will gain more C relative to N than those grazing Synechococcus growing at 2000 μE m⁻² s⁻¹, even though the cyanobacteria are growing at the same, maximal rate under nutrient replete conditions. Similarly, grazers consuming T. pseudonana growing at a NO₃⁻ concentration of 50 μM-N will acquire about twice the cellular N compared to grazers consuming those diatoms growing at a NO₃⁻ concentration of 150 μM-N (not unheard of for eutrophic conditions), even though in both cases, the NO₃⁻ was in excess of classic kinetic considerations (Fig. 6).

An important question for ecosystem dynamics, and ultimately for modelers, is the extent to which elemental stoichiometry alters food webs. Grazers and producers operate in a dynamic balance with respect to nutrient composition and availability (Gilbert, 1998). Grazers release nutrients directly, but they also consume producers which are the primary consumers of nutrients, and other grazers, which are also nutrient regenerators. Preferential grazing on different predators will affect the flow of regenerated nutrients. Grazers are thus affected by food quality and they, in turn, affect food quality by altering the composition of nutrients available to them.

While individual nutrients, light availability, and cellular nutrient ratios regulate the growth of phytoplankton, the wide plasticity of cell composition in algae under both nutrient limited and nutrient-saturated conditions alters the elemental quality of the algal food available to grazers. In other words, while primary production can constrain secondary production, N and P availability to the phytoplankton can regulate the types of organisms found in the upper trophic levels via effects of elemental composition at the primary producer level (Gilbert et al., 2011). As noted by Sterner and George (2000, p. 127), “Nutrient flux from resources to consumers and then to waste products can be thought of as a chemical reaction wherein mass must balance” (emphasis added). Moreover, as noted by Malzahn et al. (2007, p. 2063) based on Brett (1993), “stoichiometric needs of secondary consumers and the stoichiometry of prey are normally finely tuned.” Thus, grazers, like algae, are continually challenged with maintaining their nutrient and energy balance.

However, unlike algae, which generally have wide plasticity in their C:N:P stoichiometry (but see Hall et al., 2005), grazers are generally more constrained in stoichiometry; there is typically a mismatch between the stoichiometry of grazers and their food (Sterner and Elser, 2002). Grazers are able to stabilize their biomass stoichiometry more than phototrophs because they have more dissipatory pathways (release and excretion) to eliminate nutrients acquired in excess (Sterner and Elser, 2002). The relationship between stoichiometry of resource or prey and that of the consumer can be related conceptually. Grazers may 1) reflect the stoichiometry of their prey (within reasonable limits), 2) be more restrictive in their stoichiometry than their prey, or 3) be highly constrained in their stoichiometry (Fig. 7; Sterner and Elser, 2002).

Whether grazers are highly constrained or more flexible in their stoichiometry has large consequences for nutrient regeneration, as those grazers that are highly constrained will, by necessity, regenerate the nutrients that are consumed but not needed to maintain their biomass. By regenerating the nutrients not needed, but sequestering those that are needed, positive feedbacks are developed, further accentuating the limiting nutrient and skewing the system toward that in excess (Elser et al., 2000; Sterner and Elser, 2002). For example, in principle, grazers with strict stoichiometry feeding on phytoplankton that are N-rich will excrete proportionately more N than those grazing on phytoplankton that are more balanced in their N:P or N:C ratio. By excreting more N, the condition of excess N is maintained for the phytoplankton (Sterner and Elser, 2002). Such a condition creates wide variations in the stoichiometry of producers and consumers, and presents further cellular challenges for producers to regulate both the limiting and saturating nutrient cellular levels. There are, as yet, no dynamic models that fully capture the positive and negative feedbacks of variable producer and consumer stoichiometry. However, Grover (2002, 2003, 2004), in models of predator–prey interaction involving several prey and one predator with three essential elements, has taken a dynamic balance approach and has illustrated that the long-term outcomes of competition, predation and nutrient cycling are complex but are fundamentally governed by the balance between assimilation and recycling of nutrients, i.e., the extent to which predators sequester or recycle their nutrients. Ramin et al. (2012) also recently developed a complex biogeochemical model of multiple chemical elements (C,N,P, Si and O), and multiple primary and secondary producer functional groups to address the interaction of nutrient regeneration on plankton food webs. They highlighted the interaction between nutrients, the recycling of nutrients, trophic state and the physical structure of lake ecosystems.

An ecological stoichiometric approach is based on the transfer of elements, N and P, as well as C and other elements through the food web, rather than on the rate of production of organic C. Improving the empirical basis for modeling variable stoichiometry and its effects through the food web requires recognition that phytoplankton stoichiometry is not a fixed proportion and that it varies as a function of both nutrient limitation and nutrient saturation. In ecological stoichiometric terms, r-strategists generally have a low N:P ratio and have a higher proportion of growth machinery (ribosomal RNA; high P), whereas K strategists have a higher N:P ratio and have more resource acquisition machinery (enzymes and proteins; high

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**Fig. 6.** Comparison of the cellular composition of *Thalassiosira pseudonanna* as a function of nitrate concentrations in the media when grown in turbidostat culture at growth saturating light intensity, and at nutrient concentrations normally taken to be saturating for growth. Panel A illustrates the ratio of C:N, and panel B the ratio of chlorophyll:C.
For grazers, the challenge of acquiring the requisite nutrients and balancing biomass stoichiometry is compounded by several factors and the scale on which the relationship is examined. Stoichiometry affects various life stages of the predator differently (Moe et al., 2005). As a specific example, there is a greater need for C, N, and P for developing copepod juveniles, but at a later stage, while C is still needed for metabolism, more P must be allocated to eggs; thus, P-poor food can disproportionately affect egg production while not affecting survival (Færøvig and Hessen, 2003; Laspoumaderes et al., 2010).

Thus, just as nutrient uptake and growth (or photosynthesis and growth) can be uncoupled, so too is the case for food ingestion and assimilation by zooplankton. And, as the case for phytoplankton, most models assume a fixed relationship across the prey concentration spectrum when the relationship is highly variable (Flynn, 2010). The complex relationships between food quality, feeding rates, and grazer growth rates on trophic interactions are only beginning to be modeled with any degree of skill (Mitra and Flynn, 2007).

3.2. Food quality beyond stoichiometry

While the relative balance of elemental availability affects all aspects of the grazer’s ability to meet its nutritional and reproductive demands, it ultimately may be a necessary but insufficient characterization of food quality. Trophic fitness parameters, such as rate of growth or fecundity, are related to the nutritional composition of the food on which they graze, and thus ultimately food quality affects the transfer of energy and nutrients through the food web (e.g., De Troch et al., 2012). Nutritional quality of the algae may be interpreted in terms of elemental composition in the context of the requirements by grazers for acquisition of particular fatty acids, as a measure of the food quality of algae (e.g., Ågren et al., 1990; Brett and Müller-Navarra, 1997; Coutteau and Sorgeloos, 1997; Weers and Gulati, 1997). Some diatom species, for instance, produce certain highly unsaturated fatty acids that are essential for zooplankton reproduction (reviewed by Kilham et al., 1997) while flagellates generally produce different fatty acids than diatoms (Olsen, 1999). Different types of copepods preferentially graze on algae at different growth stages in order to obtain food of a higher C:N content or different fatty acid composition (De Troch et al., 2012). Moreover, while some heterotrophic protists may alter biochemical components that can improve poor algal quality for subsequent higher trophic levels, trophic “upgrading” by such a phenomenon is also highly species specific at the level of both prey and predator (Klein Bretelet et al., 2004; Tang and Taal, 2005; Tang et al., 2001).

Stoichiometry of the prey can also affect other aspects of food quality, including toxin production, cell membrane thickness, and other chemical constituents that have been considered to turn good food “bad” (Mitra and Flynn, 2005). For example, toxin production by numerous harmful algae has been shown to increase when the cells are not grown under nutrient-balanced conditions and when they sustain a change in N or P availability or depletion (Flynn et al., 1994; Johansson and Granéli, 1999a, 1999b; Granéli and Flynn, 2006). Production of toxins rich in N might be regarded as a dissipatory mechanism of algae, whereby cells acquire the nutrient(s) they need but release nutrients that are not needed (reviewed by Gilbert et al., 2011; Gilbert and Burkholder, 2011). In some algal flagellates, toxin production increases under P stress (Granéli et al., 1998; John and Flynn, 2002). Toxin production for stoichiometric balance under N limitation appears to be less common than under P limitation, perhaps in part because many toxins are N-rich (Granéli and Flynn, 2006). The dominance of toxin-producing species can result in a failure of normal predator–prey interactions, which, in turn, enhances the transfer of nutrients that sustain HABs at the expense of competing algal species (Irigoien et al., 2005; Mitra and Flynn, 2006; Sunda et al., 2006).

Superimposed on these factors is also the consideration of whether substrate quality or food quality is altered on an episodic basis, or whether changes are long-term and sustained. As conceptualized by Hood and Sterner (2010), a change in predator growth rate to altered diet depends on the extent to which the diet is sustained or switches, with variable frequency, between low-quality food and high-quality food— in this case, defined by the relative P content (Fig. 8). In natural environments, poor quality food such as detritus, may be an important food for many grazers. From a stoichiometric perspective, detritus, high in C, may result in metabolic costs to consumers, including altered metabolic rate and growth rate (Hessen and Anderson,
3.3. Organismal demands and community assembly

In spite of all of the complexities noted above as well as others not covered herein, there is a growing recognition that ecological stoichiometry has proven to be a valuable construct at all levels of the food web, but it may be that its value increases with trophic level and long time scales, as higher trophic levels are more stoichiometrically constrained, and reproduction and skeletal investment is a function of nutrient availability rather than energy availability (McIntyre and Flecker, 2010; Sterner and Elser, 2002). However, developing bottom–up, or reductionist, models of large-scale trophodynamic relationships that provide the same outcomes as the conceptual stoichiometric ecological theory is daunting. The observation that annually averaged data (nutrient and biotic) provide good correlated relationships in the context of the ecological stoichiometry theory (Glibert et al., 2011; Smith, 2006) argues that control of such broad patterns involves a significant ‘filtering’ of seasonal, event scale, diet and physiological scale processes. Conceptually, the ‘filtering’ may be analogous to phytoplankton assimilative metabolism described above in the example of photoacclimation. In both contexts, the underlying mechanisms adhere to certain higher level constraints (e.g., regulation of material and energy balance) that are quantifiable and understandable. Logically, for ecosystem processes that exhibit relationships to nutrient (element) stoichiometries, mass balancing element flows should be tractable, but it requires identifying the principal agents and getting the kinetics ‘right’ for those agents. Such an approach is important in that it can be used to identify the ‘ecological engineers’ from the ‘ecological passengers’. (The rigorous ongoing debate about whether chemical changes from physiological assimilation and dissimilation constitutes ‘ecological engineering’ bears relevance but will not be elaborated here (Wright and Jones, 2006; Byers, 2007; Berke, 2010). Importantly, as trophic complexity changes, so too does regulation by stoichiometric control (Leiss et al., 2006; McIntyre and Flecker, 2010).

Several recent reviews have addressed the stoichiometry of higher aquatic food webs, namely fish (Hendrixson et al., 2007; McIntyre and Flecker, 2010; Sterner and George, 2000). Not only is there a strong shift in body N:P with growth stage (Pilati and Vanni, 2007), but there are also strong phylogenetic contrasts. In fact, Hendrixson et al. (2007) demonstrated, for 20 families of fish, that a phylogenetic tree could be developed based on the body P, C:P, and N:P, but not in C or N. For fish, the most important determinant of stoichiometry is structural demand; growth demands appear to be secondary (McIntyre and Flecker, 2010). The variability in diet presents enormous challenges for dynamic regulation of biomass stoichiometry in fish. Diets may vary in C:N from 5 to 75 times that required for growth, and C:P may be up to several orders of magnitude higher, depending on species and environmental conditions (McIntyre and Flecker, 2010). Bioenergetic models coupled with stoichiometric models (e.g., Frost et al., 2006; Hood et al., 2005; Schindler and Eby, 1997) will be required to fully understand the physiological and nutritional regulation at all dietary levels. At all levels of the food web, energy regulation (C flow) and nutrient regulation are fundamentally regulated differently. Where energy flow and elemental cycling have been explicitly examined in a two-trophic level chain population model, for example, dynamical behavior emerges that illustrates that energy enrichment of the system results in very different trophic stability and altered predator–prey interactions than does nutrient enrichment (Loladze et al., 2000). Population models with stoichiometric constraints between predators and prey behave quite differently from those without stoichiometric regulation (Anderson et al., 2004). In a recent analysis of internal regulation of species in relation to external forcings, Klausermeier (2010) developed a predator–prey model illustrating multiple stable annual trajectories and year-to-year irregularity in successional trajectories. Clearly, there are opportunities for advancing these approaches with realistic understanding of dynamic elemental regulation at all levels.

The long-term changes in the food web of the San Francisco Estuary Bay Delta provide an interesting example of how populations at all levels of the food web may self-assemble in relation to long-term nutrient changes via feedbacks with trophic and biogeochemical stoichiometric changes (Gilbert et al., 2011). At the phytoplankton level, there has been a loss of diatoms over the past several decades, related to several factors, among them an increase in N:P in the land-based nutrient load and an increase in the relative availability of NH4+ in the N pool (Dugdale et al., 2007; Gilbert, 2010; Gilbert et al., 2010). Diatoms, being generally considered an “r” selected group, would be expected to have a low N:P ratio and thus would be expected to be outcompeted if N:P in the environment increases. In this system, dinoflagellate abundance was positively correlated with N:P ratio over the decadal scale. Dinoflagellates are generally considered a “K” selected algal group. At the zooplankton level, among other changes, there has been a long-term change in the relative abundance of the calanoid Eurytemora and the cyclopoid Limnoithona. The former has not only declined with time, but the most precipitous change was in the mid 1980s. The latter is considered an invasive species (Kimmerer, 2004), with its population increasing several orders of magnitude since its introduction also in the mid 1980s. Calanoid copepods generally have a high N:P ratio of their biomass, ~20–35 by atoms, whereas cyclopoid copepods have N:P ratios much closer to Redfield atomic ratios (Sterner and Elser, 2002; Walve and Larsson, 1999). The oscillation of the calanoid copepod Eurytemora with the cyclopoid copepod Limnoithona over time is a near mirror image of the oscillation in the N:P ratio, a pattern consistent with these grazers being responsive to changes in elemental stoichiometry and maintenance of altered dynamic equilibria on a long-term scale.

![Fig. 8. Conceptual relationships between long-term growth rate of consumers in relation to normalized food quality (expressed as the phosphorus:carbon (P:C) ratio). The dashed line indicates food that is comparatively rich in P; the dotted line indicates food that is comparatively poor in P; the solid line indicates a diet that switches between low and high quality food with variable frequency. With constant, but mixed diet food supply, a saturating response develops between growth of the consumer and food quality. The shape of the curve varies when food is of high or low food quality. Repotted from Hood and Sterner (2010) with permission of the publisher.](image-url)
(Fig. 9). Other changes in community composition also have been shown to have paralleled changes in N:P ratio over the decadal scale in this system. Numerous changes in invertebrates and in fish community composition changed in relation to diatoms, and to N:P (Fig. 10; Glibert, 2010; Glibert et al., 2011). Proportionately greater sequestration of P in the biomass of the omnivorous fish would lead to them being proportionately more abundant when P is less available (in the water column). Using the kinetic analogy, proportionately greater sequestration of nutrient is equivalent to a highly efficient uptake strategy. Clearly, changes in nutrient stoichiometry in this system, achieved through both external forces (altered land-based nutrient loads) and internal, organism-driven, assimilative and dissimilative processes, related to community compositional changes (Glibert et al., 2011).

4. Dynamic regulation and biogeochemical cycles

4.1. Oceanic biogeochemistry

Well recognized is the fact that interest in stoichiometric regulation of biogeochemistry has its origin in the seminal Redfield descriptions of elemental nutrient ratios (Redfield, 1934, 1958). Stoichiometric regulation of biogeochemistry recognizes the biotic feedbacks that regulate not only the flow of nutrients and their proportions, but also their effects on ecosystem structure. In simple terms, competition between N-fixing and non-N-fixing phytoplankton regulate this balance along with losses of N due to denitrifiers, and such dynamics have been captured in varying stoichiometric ocean models (e.g., Lenton and Klausmeier, 2007; Tyrell, 1999). It is generally accepted that the biota controls oceanic N:P (Falkowski, 2000; Redfield, 1958). Yet, coupled biogeochemical models typically link biological C production to nutrient fluxes assuming fixed elemental proportions. In the context of climate change the focus of marine ecosystem modeling activity has largely been on C cycling at a global scale (Le Quéré et al., 2005; Moore et al., 2002).

Some advances are being made in considering different elemental pools (including, to greater or lesser extent, C, N, P, Si and Fe) in biogeochemical ocean or global flux models. These models depend on capturing multi-nutrient regulation of different phytoplankton functional groups, including accurate relationships between cell size, sinking rate (export ratios), and other aspects of cell physiology (layered onto the need for accurate three-dimensional physics). The construct of such models is fundamental and the recognition of the role of variable stoichiometry is rapidly advancing. Only a few recent examples are highlighted. Litchman et al. (2006) have developed a multi-nutrient, multi-group model of phytoplankton and applied the model to test various scenarios of future change. They found that the model was not only very sensitive to the kinetic parameters used for the different elements and different functional groups, but that the effect of changing N:P stoichiometry differed for different oceanic regions. Community assembly was sensitive to both levels and ratios of resources. Lan Smith et al. (2009) compared the University of Victory Earth System Climate Model of global climate and biogeochemical cycles when run with standard Michaelis–Menten kinetics and those of the optimal kinetic relationship. Large regional differences in biogeochemistry emerged with the revised kinetic application, including large spatial and temporal differences in primary production. Tagliabue et al. (2011) compared fixed stoichiometric models with ocean biogeochemical models that allowed C, N and P to vary independently and found large variations in net primary production and carbon export in the different models in response to ocean acidification, leading to the conclusion that non-Redfieldian models need to be further developed in ocean-climate applications. Rastetter (2011) recently described the effects of formulating growth of component organisms in a forest ecosystem as a function of classic nutrient limitation or more dynamic regulatory balance and the result was very different predictions of ecosystem function to increased CO2 and global warming. Using an ocean circulation model, Weber and Deutsch (2010) showed that latitudinal gradients in nutrient

![Fig. 9](image-url). Conceptual diagram of the ecological stoichiometric relationship between different phytoplankton and zooplankton genera. Panel A represents the relationships between diatoms and the copepod *Eurytemora affinis*; panel B, the relationship between small flagellates and the cyclopoid copepod *Limnoithona tetraspina*. The X axis represents the biomass N:P of the organisms. The wide arrow represents ingestion of the phototrophs by the grazer; the lighter arrow represents nutrient regeneration in the grazer’s excretions. Note that the stoichiometry of the regenerated nutrients differs with zooplankton taxon and the N:P ratio of the food on which they graze. Panel C represents the comparison of the ratio of *Eurytemora/Limnoithona* and the ratio of dissolved inorganic nitrogen:phosphorus (DIN:DIP) for the period from 1980–2000 for Suisun Bay, San Francisco Bay Delta. Panel D is the correlation of the data from (C); the coefficient of determination was significant (p<0.05). Panels A and B reproduced from Glibert et al. (2011) with permission of the publisher.
complex challenges because of the diversity and complexity of sediment exchange processes. Processes such as denitrification, anaerobic ammonium oxidation (anammox), dissimilatory nitrate reduction to ammonia (DNRA) all alter the proportion of fixed N in the system. In the sediment (or in anoxic or hypoxic water columns), remineralization pathways also alter stoichiometry. There are a series of trophic and biotic, as well as abiotic conditions, that may promote fluxes of nutrients in and out of the benthic zone, and transformations of nutrients, altering the stoichiometry for producers. Bioturbators and excretion processes of benthic macrofauna may alter nutrient cycling processes (e.g., Solan et al., 2008). Moreover, colonization of sediments by benthic macrophytes may have both direct and indirect effects on nutrient remineralization and its stoichiometry. Bioturbators may change sediment-nutrient dynamics through sediment mixing and tube or burrow-building; they also alter redox conditions at the sediment–water boundary (Aller, 1994; Kristensen, 2000). Macrophytes take up nutrients from the water column and the sediment, but may also increase the surrounding pH from their high productivity under some conditions. The latter fit the classic definition of ‘ecosystem engineers’ in that they alter both the biotic and abiotic habitat (Berke, 2010; Jones et al., 1994).

Highly productive nearshore areas affected by high macrophyte productivity alter the pathways by which N and P are cycled in many ways. By their production, pH can be locally elevated, affecting the biogeochemical cycling of N, including the chemistry of NH$_4^-$–NH$_3$ and processes such as nitrification, denitrification, and DNRA (e.g., Huesemann et al., 2002; Kemp et al., 2005; Gilbert et al., 2011). Both bacterial production and respiration can be negatively affected by alkaline pH resulting from high rates of macrophyte photosynthesis which, in turn, affects C cycling and energy flow and reduces rates of remineralization (Tank et al., 2009). Classic work by Barko and Smart (1980) showed that PO$_4^{3-}$ turnover in the interstitial water increased 1000-fold in sediments supporting Eurasian milfoil or Egeria dense growth. As pH increases, the fundamental physical-chemical relationships related to P adsorption–desorption change. Enhancement of sediment P release under elevated water-column pH conditions has been observed in eutrophic lakes (i.e., Drake and Heaney, 1987; Jensen and Andersen, 1992; Xie et al., 2003) and tidal freshwater/oligohaline estuaries (Seitzinger, 1991).

Positive feedback mechanisms thus exist between microbial processes, macrobenthos, macrophytes, pH, nutrient efflux, and other biogeochemical processes affecting stoichiometry, and in turn, food webs. Incorporating the full complexity of these interactions is an enormous challenge for modelers, but there are important steps being made in recognizing these complex interactions. Understanding and parameterizing these important feedbacks not only has implications for modeling current and projected changes in climate, nutrient loads, and land use, but it also has direct application in understanding thresholds of system response or altered stable states (sensu Scheffer et al., 1993).

4.3. Eutrophication and future nutrient change

Eutrophication and nutrient pollution is occurring due to the increase in human population, the increasing demands on energy, increases in nitrogen (N) and phosphorus (P) fertilizer use for agriculture, changes in diet, leading to more meat production and animal waste, and expanding aquaculture industries (e.g., Galloway and Cowling, 2002; Galloway et al., 2002; Gilbert et al., 2006, 2010; Howarth, 2008; Howarth et al., 2002; Smil, 2001; Wassmann, 2005). While the effects of eutrophication are well known, such as changes in species diversity, excessive algal growth, reductions in dissolved oxygen, fish kills, and the increased prevalence or frequency of toxic algal blooms, two specific issues with regard to nutrient pollution are relevant here. First, in eutrophied systems, primary producers are often exposed to saturating- or super-saturating nutrient concentrations. Thus, these algae are subject to the kinds of cellular regulatory stoichiometry were governed by species compositional differences and that (p. 553), “a 25% increase in high-latitude C/P ratios, reflecting an increase in N/P from 16:1 to 20:1, would reduce the concentration of atmospheric CO$_2$ by ~15% ppm. from interglacial levels.” Parameterization of models for the study of global change, and end-to-end trophic dynamics are thus being rapidly developed and implemented, but capturing dynamic behavior, including adaptation to nutrient change will continue to be a challenge.

4.2. Nearshore biogeochemistry

Nearshore biogeochemical processes are well recognized to balance assimilative and dissimilative process and may present even more
processes described above and that have consequences at all levels of the food web. A few such responses were described above, but there are many adaptations at growth-saturating or super-saturating substrate levels that have important bearing on production and nutrient transport and ultimately on ecosystem function — photoadaptation, photoinhibition, antioxidant production, toxin production, DMS production, photospiration, among others. These dissipatory processes are not now captured in assimilatory model constructs of phytoplankton metabolism and present additional opportunities for advancement.

Second, anthropogenic nutrient loads are not in classic stoichiometric proportion — or are rapidly changing — and thus external drivers may have effects and feedbacks on nutrient availability that are complex at all levels. Of potentially large importance for ecosystem structure is the enhanced enrichment of the globe with N relative to P (e.g., Galloway and Cowling, 2002; Galloway et al., 2002; Glibert et al., 2006, 2010; Howarth, 2008; Howarth et al., 2002; Smil, 2001; Wassmann, 2005). It has been estimated that the atmospheric deposition of nutrients in the ocean is now ~20 times the Redfield ratio for N:P (Jickells, 2006; Peñuelas et al., 2012) and is having large consequences for N:P stoichiometry in lakes (Elser et al., 2009). Global use of N has increased relative to that of P, especially since the mid-1990s (Fig. 11). Aggressive removal of P loads relative to N — for example, from sewage effluent and laundry detergents — is also accelerating this change (e.g., Litke, 1999). These changes are thought to be affecting biodiversity from land to the sea, beginning at the level of the N content at the genome and proteome level (Acquisti et al., 2009; Peñuelas et al., 2012).

In typical eutrophic conditions the minimum configuration of multiple models should consider C:N:P. Many systems will also require inclusion of Si, and some may require inclusion of Fe. Variable elemental stoichiometric models should become the norm. Multi-element descriptions, as opposed to fixed Redfield constructs, provide a basis for the development of mechanistic models that contain functional response descriptors with recognized physiological bases (Flynn, 2010; Glibert et al., 2010). Multi-element descriptions also support bioenergetic descriptions, which may be important for predicting the survival of organisms under unfavorable conditions. Variable stoichiometric parameterizations in models must also begin to recognize that physiological processes and organismal stoichiometry can and does vary even at growth-saturating substrate concentrations.

5. Implications, challenges and future opportunities

Varying biomass stoichiometry has enormous ramifications for affecting organismal traits and ultimately trophic transfer. They, in turn, affect biogeochemistry — and are affected by — those changes. The efforts to incorporate dynamic balance models for physiology and for trophodynamics need to be advanced. The plasticity of nutritional pathways, as well as the plasticity of food web interactions, including grazing, allelopathy, symbioses and other interactions, creates immense challenges for model constructs. Monod and Michaelis–Menten kinetics which assume a fixed half-saturation constant and maximal rate are inadequate, and in many (most?) cases incorrect, to capture variable physiological processes. Even cellular Droop kinetic relationships do not classically capture regulation beyond saturation. A new generation of models is needed to capture stress at the supersaturating end of the spectrum as well as at the limiting end; the dynamic equilibria (Allen and Polimene, 2011; Flynn, 2010). As noted by Allen and Polimene (2011), it is time to conduct the experimental work required at all scales that will “fully capture ecosystem dynamics...the physiology of the component organism, their behavioral traits and the interactions between them.” As described above from the lessons of photosynthetic regulation, it is both the fundamental regulatory structures that universally embrace all species that need further elucidation, but also critical are data on diversity as they feed the analysis of regulatory structures.

Models are dependent on data, and at the physiological scale there is a much to be done. More work is needed at the “stress scale”, including substrate saturation as a “stress”. With the expansion of eutrophication, many coastal, estuarine and freshwater systems now have nutrient loads and concentrations that well exceed those of “saturation” and can be thought of as “super-saturating”. Similarly, efforts to control or regulate nutrients are leading to nutrient loads with highly altered stoichiometry. Yet, with the exception of the types of examples provided above, there is little data on substrate uptake at the supersaturating level or its consequence on cellular metabolism and stoichiometry. There is much work to be done to understand physiological trade-offs at varying substrate (both nutrients and light) across functional groups, parameterizing rates, characterizing traits, and how they are both externally driven and internally dynamically regulated. Without question, “model solutions are dependent on choices made for implementation approaches and parameterizations that arise because of the scales that are addressed by the model...and improvements in simulation of phytoplankton distribution and production will require inclusion of more than one functional group” (Hofmann et al., 2011, p. 114, 115).
It is time to lay to rest the notion that nutrients and nutrient stoichiometry are only regulatory for physiology at the limiting end of the spectrum. It is time to dispel the notion that high energy input (C flow) is all that is required for a highly productive ecosystem. The increasing nutrient loads to coastal systems, combined with their disproportionate composition in both space and time make the issue of stoichiometry ever more important (Gilbert et al., 2006; Howarth et al., 2005; Seitzinger et al., 2002, 2005). Disproportionate N and P loads globally are now recognized to have effects at all scales, from genomic to ecosystem that need further empirical resolution (Peñuelas et al., 2012). Even relatively small changes in nutrient supply are being shown to have large consequences on many important properties of the ecosystems (Nielsen, 2003). Understanding the full suite of processes and factors that underlie variable stoichiometry at all scales — and for elements beyond N and P emphasized here — and the feedbacks between them is a grand challenge (Frigstad et al., 2011). Imbalances in stoichiometry not only have consequences for trophic transfer and biogeochemistry as described here, but can and will change patterns of succession of C and many other processes of the structure and function of ecosystems. Climate change, altered CO2 levels, and their implications for altered productivity of a global ocean should motivate both new dynamic balance model architectures and new experimental investigations that support them.

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