Journal of Marine Systems 125 (2013) 14–28

Contents lists available at ScienceDirect

Journal of Marine Systems

journal homepage: www.elsevier.com/locate/jmarsys

# 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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ARTICLE INFO

*Article history:*
Received 20 January 2012
Received in revised form 26 September 2012
Accepted 9 October 2012
Available online 26 October 2012

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

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.

## 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 (Glibert 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, 1999; Klausmeier et al., 2004; Le Quéré et al., 2005; McGillicudy 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

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http://dx.doi.org/10.1016/j.jmarsys.2012.10.004

that both nutrient limitation and nutrient saturation result in dynamic 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, conventional nutrient 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, saturation formulations used to parameterize physiological rates are inadequate 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 biogeochemical feedbacks. That is, the reductionist approach of quantifying the parameters defining limitation and saturation as fixed entities constrains both our understanding of the dynamic regulation of physiological 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 processes 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 stoichiometry to food webs and to biogeochemical feedbacks. The goal of this paper is to underscore that advances in physiology are fundamental to achieve advances in models at various scales, that consideration 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 curvilinear function, a rectangular hyperbola (Fig. 1). Growth as a function of nutrient concentration (Monod, 1942), nutrient uptake as a function of external nutrient availability (Menten 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 rectangular 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 concentration at which the rate plateaus (e.g., $I_k$ 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 incorporated. These basic functions are central to many plankton models, such as nutrient–phytoplankton–zooplankton models (e.g., Franks, 2002).

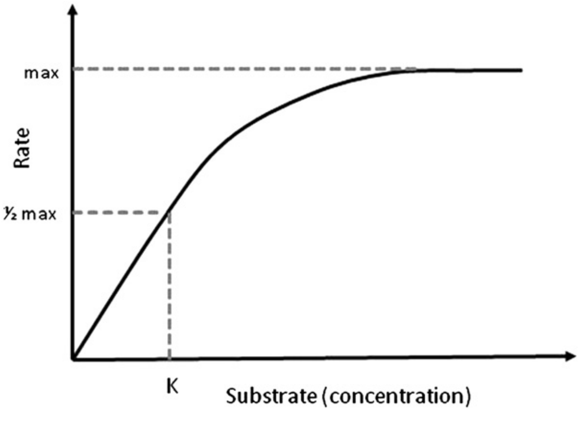

**Fig. 1.** The classic kinetic rectangular hyperbola indicating the change in a rate or process as a function of substrate availability.

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

$$dN/dt = rN(1-(N/K)) \tag{1}$$

"r" selected species are those with rapid growth rates, whereas "K" selected species are slower-growing, but are adapted to living at densities 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., $K_s$ or $I_k$) or rate (i.e., $V_{max}$ or $P_{max}$) is applicable to all species or all conditions. 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 Glibert, 1982, 1983; Gotham and Rhee, 1981; Morel, 1987; Rhee, 1973). Kinetic relationships ranging from enzymatic control to *in vivo* rates exhibit variation and this variation increases in complexity at higher levels of organization as processes of cellular control over enzyme synthesis and control of auxiliary factors become part of cellular function. The fact is, there is no higher level process that can be fully constrained by a single substrate 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 Glibert, 1983). Ecosystem modeling, by its nature, deals with longer temporal scales compared to the scales on which biochemistry and physiology operate. Nutrient kinetic relationships or photosynthesis rates are typically determined on the physiological 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 uncertainly in what kinetic parameters to apply in models. For example, the measurement of productivity may be made by use of $^{14}C$, $^{18}O$, or