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A discrepancy between predictions of saturating nutrient uptake models and nitrogen-to-phosphorus stoichiometry in the surface ocean

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Abstract

We derive a simple prediction about euphotic zone N : P stoichiometry from a large class of models that use saturating nutrient uptake functions to characterize N and P acquisition by phytoplankton. The prediction is: At an ecological steady state, the ratio of phytoplankton N : P to inorganic N : P in the euphotic zone equals the ratio of phytoplankton maximum uptake rates of N and P. We estimate this predicted ratio using nutrient uptake parameters measured in laboratory growth experiments and compare the predicted ratio to empirical observations from long-term sampling in the Atlantic and Pacific oceans. The model predictions for the ratio of phytoplankton N : P to inorganic N : P are at odds with the majority of data from extensive long-term sampling in the Atlantic and the Pacific oceans. This discrepancy calls into question the scope of applicability of ecosystem models that explicitly describe phytoplankton growth as a function of N and P availability. We discuss efforts to resolve this discrepancy, including the need for performing more comprehensive N and P uptake experiments and by re-examining models of nutrient uptake.

Nitrogen-to-phosphorus (N : P) stoichiometry has been an organizing principle for studying aquatic ecosystems over the past 50 yr. Alfred Redfield first recognized the utility of characterizing an ecosystem by its stoichiometry when he noted the close correspondence between phytoplankton N : P and deep ocean inorganic N : P (Redfield 1958). The widely accepted heuristic explanation for the link between phytoplankton N : P and deep ocean inorganic N : P comes from our understanding of biogeochemistry and ocean circulation and provides support for Redfield's original hypothesis that deep ocean N : P is driven by phytoplankton N : P requirements (Klausmeier et al. 2008). Rapid production of organic matter with Redfieldian average N : P (16 : 1) in the euphotic zone is exported to the deep ocean where N and P are mineralized during decomposition and sequestered for orders of magnitude longer than their mean residence time in the euphotic zone (Falkowski and Davis 2004). Despite recent questioning about the universality of a particular N : P ratio in aquatic ecosystems (Quan and Falkowski 2009), the ''Redfield ratio'' of 16 : 1 for N : P stoichiometry is still used as a point of reference for inferring nutrient limitation and N fixation (Deutsch et al. 2007). Although the link between phytoplankton N : P and inorganic N : P of the deep ocean is widely accepted (Falkowski and Davis 2004), the influence of substantial N and P uptake by phytoplankton on inorganic N : P in the euphotic zone is not well understood.

Inorganic N : P stoichiometry in much of the euphotic zone, where phytoplankton actively take up nutrients, consistently differs from the canonical deep-water value of 15 : 1 (Cavender-Bares et al. 2001; Karl et al. 2001). This departure from the Redfield value has been used to make inferences about biogeochemical cycles. For example, chronically low inorganic N : P has been the basis for estimating the incidence and magnitude of N fixation throughout the world's oceans (Gruber and Sarmiento 1997), stemming from the assumption that inorganic N : P lower than phytoplankton N : P indicates N limitation and induces greater N acquisition. Additionally, taxon-specific differences in inorganic N and P uptake physiology have been used to infer shifts in phytoplankton community composition over geologic timescales (Tozzi et al. 2004; Falkowski and Oliver 2007) and to predict community responses to climate change (Litchman et al. 2006). Inorganic N : P stoichiometry differing from the perceived optimal Redfield value is thought to impose strong selection for particular life histories and to alter the structure of phytoplankton communities (Karl et al. 1997; Cavender-Bares et al. 2001). However, our understanding of how N and P uptake feeds back on inorganic N : P in the euphotic zone is incomplete. Because feedbacks between phytoplankton and inorganic N and P pools occur on the scale of days and nutrient cycling within the euphotic zone is responsible for the majority of new production in the oceans (Falkowski et al. 1998), accurately incorporating the influence of phytoplankton on N and P cycling is necessary to produce realistic ocean ecosystem models. Increasingly detailed descriptions of biological processes are being incorporated into large-scale climate models, making it important to understand the links between inorganic N : P, phytoplankton N and P requirements, N and P uptake kinetics, and primary production (Smith et al. 2009).

Extensive experimentation with phytoplankton cultures in the laboratory has led to the widespread adoption of

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particular functional descriptions of phytoplankton nutrient uptake and growth responses to varying nutrient availability. These functional descriptions are often incorporated into more complicated dynamic models. Uptake is most often characterized by a basic or modified Michaelis–Menten (saturating) function of available nutrient concentration (Smith et al. 2009). The ability of simple mathematical functions to capture the general and specific physiological responses of phytoplankton to nutrient availability in laboratory conditions has given rise to a suite of ecological models widely used to study competition and trophic interactions (Daufresne and Loreau 2001; Grover 2004), ecosystem processes (Moore et al. 2002*a*; Lima and Doney 2004; Salihoglu and Hofmann 2007), and the effects of climate change on phytoplankton community structure (Tozzi et al. 2004; Litchman et al. 2006; Falkowski and Oliver 2007). At the most general level, phytoplankton in such models have flexible stoichiometry, take up inorganic nutrients that are replenished by an external supply and recycling of organic matter, grow as a function of the nutrients they have taken up, and die or sink out of the euphotic zone. Michaelis–Menten nutrient uptake has been a fundamental pillar in the development of phytoplankton growth models (Legovic and Cruzado 1997).

Here, we derive a general prediction for the relationship between phytoplankton N : P and available N : P that emerges directly from including Michaelis–Menten uptake kinetics in a large class of ecosystem models. Specifically, we derive a simple expression that relates phytoplankton N : P to euphotic zone inorganic N : P, which is much simpler than the expressions for either N : P ratio individually. In the simplest case at steady state, the ratio of phytoplankton N : P to inorganic nutrient N : P is controlled solely by ratios of phytoplankton nutrient uptake parameters. We illustrate that this basic result is a general feature of dynamic ecosystem models that use independent Michaelis–Menten N and P uptake functions. Next, we use nutrient uptake parameters measured in laboratory experiments to compare the predicted relationship between phytoplankton N : P and inorganic N : P to empirically observed phytoplankton N : P and euphotic zone inorganic N : P in the Pacific and Atlantic oceans. The theoretical prediction that is based on Michaelis–Menten uptake kinetics is at odds with the majority of empirical observations. We demonstrate that more refined descriptions of N uptake that account for interactions between different forms of inorganic N and even internal N concentration are unable to resolve the discrepancy between model predictions and empirical observations. Finally, we discuss potential causes of the observed discrepancy and highlight potentially fruitful avenues for future research.

Methods

Empirical observations of phytoplankton and inorganic N : P—We compiled data from the literature and online databases to compare phytoplankton and inorganic N : P stoichiometry. Two recent studies provide relatively comprehensive descriptions of phytoplankton N : P. Geider and LaRoche (2002) and Klausmeier et al. (2004*a*) compiled phytoplankton N : P data for several marine species, summarized in Fig. 1. The arithmetic mean value of phytoplankton N : P for all but the one outlier species in Fig. 1 is approximately 14. Intensive sampling programs have collected data from the Atlantic and Pacific oceans, and provide a detailed picture of nutrient dynamics over a range of temporal and spatial scales. Figure 2 shows euphotic zone depth profiles of inorganic N : P for the 20-yr sampling period at station ALOHA (from the Hawaiian Ocean Time-series HOT). Mean values are relatively constant throughout the euphotic zone and the average inorganic N : P for the entire euphotic zone in the North Pacific Subtropical Gyre (0–80 m [Longhurst 1998]) is less than 0.14.

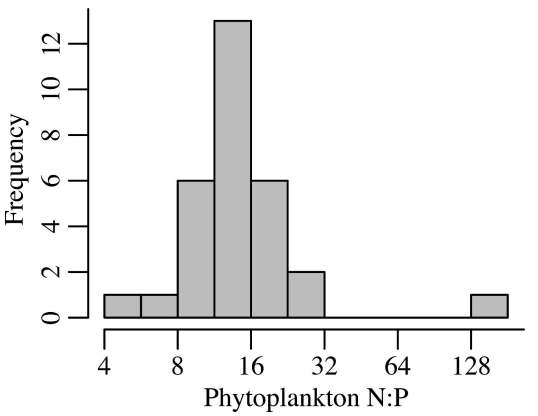

Fig. 1. Molar N : P ratios for marine phytoplankton species. Data taken from the compilations by Geider and LaRoche (2002) and Klausmeier et al. (2004*a*). Data from Geider and LaRoche (2002) taken from the original references used to produce their histogram of phytoplankton molar N : P (fig. 1B in their paper). Data from Klausmeier et al. (2004*a*) are available on-line in an electronic supplement to their article.

In contrast to the year-round stratification of surface waters in the North Pacific Subtropical Gyre, seasonal stratification occurs in the western North Atlantic, introducing significant variability into observed inorganic N and P concentrations and their resulting stoichiometry. Cavender-Bares et al. (2001) show that inorganic N : P varies with latitude and season in the Sargasso Sea. Euphotic zone depth profiles for the Atlantic (0–50 m [Longhurst 1998]) using winter BATS data and data collected by Cavender-Bares et al. (2001) are plotted in Fig. 2. Shallow euphotic zone (0–20 m) inorganic N : P during summer stratification in the western North Atlantic is less than 0.14 on average, consistent with station ALOHA during the summer, but increases with depth much more quickly than in the Pacific, reflecting the shallower stratified layer in the Atlantic. During the winter, significant mixing occurs between surface and deep waters in the Atlantic, increasing both inorganic N and P concentrations, but with greater relative effect on N. In contrast to the low values observed in the summer, inorganic N : P is 30 on average during the winter. The influence of mixing on euphotic zone inorganic N : P is also

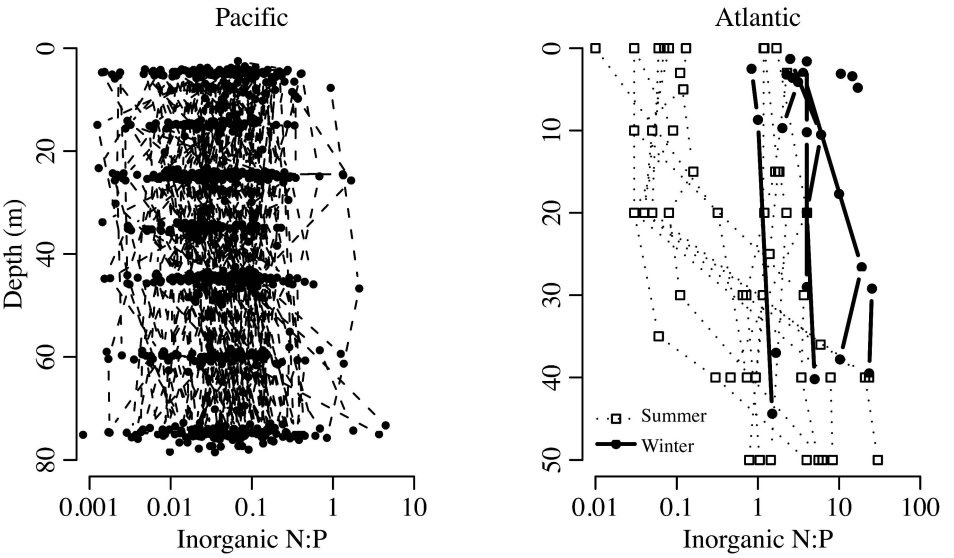

Fig. 2. Molar ratio of inorganic N (nitrite + nitrate) to inorganic P (soluble reactive phosphorus) in the euphotic zone as a function of depth at station ALOHA (Pacific), BATS (Atlantic winter), and for the cruises detailed in Cavender-Bares et al. (2001) (Atlantic summer). The euphotic depth is approximately 80 m in the Pacific and 50 m in the Atlantic (Longhurst 1998). All sampling dates for which measurements of both N and P are available are plotted. For the Atlantic, solid lines represent well-mixed winter conditions and dotted lines represent summer stratification.

observed across latitude. Inorganic N : P measured during the winter ranges from approximately 1 at 26°N (just south of the BATS station) to over 50 between 31°N and 36°N (Cavender-Bares et al. 2001) (just south of the Gulf Stream, where significant mixing occurs). In summary, phytoplankton N : P, with an average of approximately 14, is over two orders of magnitude greater than inorganic N : P for the Pacific and the Atlantic during the summer, and slightly greater than inorganic N : P during the winter in the Atlantic.

Deriving N : P stoichiometry from models of nutrient uptake—Inorganic N and P pools are highly exploited by phytoplankton and thus an important resource base for primary production. Inorganic N and P uptake by phytoplankton is almost universally described by a saturating response based on Michaelis–Menten kinetics (Smith et al. 2009). The Michaelis–Menten function characterizes a chemical reaction governed by a single enzyme, but its ability to describe nutrient uptake at the cellular level has been called into question (Smith et al. 2009). Still, nutrient uptake in ecosystem models is most commonly described by the Michaelis–Menten function in the following form (Smith et al. 2009),

$$f_i(R_i) = \frac{v_i R_i}{K_i + R_i} \tag{1}$$

in which R_i is the concentration of resource i in available form, v_i is the maximum uptake rate, and K_i is a half-saturation constant. The basic uptake function has been incorporated without modification in some models (Legovic and Cruzado 1997; Klausmeier et al. 2004*b*; Tozzi et al. 2004) and has been modified in others (Geider et al. 1998; Lima and Doney 2004; Litchman et al. 2006). Uptake functions are usually embedded in a dynamic ecosystem model describing changes in the concentrations of available nutrients (R_i), phytoplankton nutrient concentrations (O_i), and total phytoplankton biomass (B):

$$\frac{\mathrm{d}R_i}{\mathrm{d}t} = \text{external inputs} + \text{recycling} - \text{abiotic loss} - \text{uptake}, \tag{2}$$

$$\frac{\mathrm{d}O_i}{\mathrm{d}t} = \text{uptake} - \text{loss} \tag{3}$$

$$\frac{\mathrm{d}B}{\mathrm{d}t} = \text{growth} - \text{loss} \tag{4}$$

Descriptions of inputs and losses can be quite complicated as they are in large part the result of advection–diffusion terms, and although they are important for many applications, they do not modify the simple prediction for euphotic zone stoichiometry considered here. Similarly, the magnitude and controls of phytoplankton losses, which result from many influences (sinking loss, grazing, viral predation, etc.), do not influence the prediction on which we focus. Internal nutrient concentration can be expressed as either the total concentration in phytoplankton biomass as above or, as is often the case, the concentration per cell known as the cell quota (Legovic and Cruzado 1997; Klausmeier et al. 2004*b*; Smith and Yamanaka 2007). For ecosystem models with at least one stable equilibrium, we only need Eq. 3 to derive the steady-state relationship between phytoplankton N : P ($\hat{O}_N/\hat{O}_P$, where the $\hat{}$ symbol denotes steady state) and available N : P ($\hat{R}_N/\hat{R}_P$). Expressing O_i as total internal nutrient concentration (O_i for

Table 1. Parameters for Michaelis–Menten nutrient uptake for phytoplankton. Units of v_N and v_P are pmol cell^{-1} h^{-1} and units of K_N and K_P are mol L^{-1}.

	v_N	v_P	K_N	K_P	v_N/K_N	v_P/K_P	$\Phi_{N:P}$	Notes	Source
Compilation data									
Diatoms	0.55	0.5	1.25	0.65	0.44	0.77	0.57	NO_3	Litchman et al. (2006)
Diatoms	0.81	0.5	1.1	0.65	0.74	0.77	0.96	NH_4	Litchman et al. (2006)
Coccolithophores	0.05	0.23	0.2	0.4	0.27	0.58	0.46	NO_3	Litchman et al. (2006)
Coccolithophores	0.31	0.23	0.2	0.4	1.55	0.58	2.70	NH_4	Litchman et al. (2006)
Green algae	0.16	0.56	3.41	0.71	0.05	0.79	0.06	NO_3	Litchman et al. (2006)
Green algae	0.13	0.56	0.08	0.71	1.63	0.79	2.06	NH_4	Litchman et al. (2006)
Dinoflagellates	0.004	0.17	5.0	1.39	0.0008	0.12	0.01	NO_3	Litchman et al. (2006)
Dinoflagellates	0.01	0.17	8.38	1.39	0.0012	0.12	0.01	NH_4	Litchman et al. (2006)
Additional data									
Chattonella antiqua	0.91	0.14	2.81	1.9	0.32	0.07	4.56	NO_3	Yamamoto et al. (2004)
Chattonella antiqua	0.85	0.14	2.98	1.9	0.29	0.07	4.01	NO_3	Nakamura and Watanabe (1983)
Chattonella antiqua	2.02	0.14	2.19	1.9	0.92	0.07	12.98	NH_4	Yamamoto et al. (2004)
Gymnodinium catenatum	6.48	1.42	7.59	3.4	0.85	0.42	2.04	NO_3	Yamamoto et al. (2004)
Gymnodinium catenatum	3.37	1.42	33.6	3.4	0.1	0.42	0.24	NH_4	Yamamoto et al. (2004)
Alexandrium tamarense		1.4	2.84	2.6		0.54		NO_3	MacIsaac et al. (1979)
Alexandrium tamarense		1.4	1.49	2.6		0.54		NH_4	MacIsaac et al. (1979)
Alexandrium catenella			7.7	0.72				NO_3	Matsuda et al. (1999)
Alexandrium catenella			3.3	0.72				NH_4	Matsuda et al. (1999)
Tricodesmium GBRTRLI101		7140		0.64		11160		P-limited	Fu et al. (2005)
Tricodesmium GBRTRLI101		1200		0.68		1760		P-replete	Fu et al. (2005)
Tricodesmium IMS101		3430		0.42		8167		P-limited	Fu et al. (2005)
Tricodesmium IMS101		590		0.34		1735		P-replete	Fu et al. (2005)

organically bound),

$$\frac{dO_i}{dt} = f_i(R_i)B - mO_i \tag{5}$$

in which m is the mortality rate. At steady state, the assumption of Michaelis–Menten uptake yields

$$f_i(\hat{R}_i)\hat{B} = \frac{v_i\hat{R}_i}{K_i + \hat{R}_i}\hat{B} = m\hat{O}_i \tag{6}$$

Steady-state phytoplankton N : P ($\hat{O}_N/\hat{O}_P$) is therefore

$$\frac{\hat{O}_N}{\hat{O}_P} = \frac{\dfrac{v_N\hat{R}_N}{K_N + \hat{R}_N}}{\dfrac{v_P\hat{R}_P}{K_P + \hat{R}_P}} \tag{7}$$

as in Eq. 5 of Klausmeier et al. (2004*b*) and is independent of how phytoplankton nutrient concentrations are expressed (i.e., using absolute concentration or cell quota yields the same result) and nutrient limitation. Although it is more standard to consider phytoplankton stoichiometry independently from inorganic stoichiometry, examining the ratio of the two will facilitate comparisons between models and data, as will become clear below. Therefore, we divide phytoplankton N : P (Eq. 7) by steady-state inorganic N : P ($\hat{R}_N/\hat{R}_P$) to obtain,

$$\hat{\Phi}_{N:P} = \frac{\dfrac{v_N}{(K_N + \hat{R}_N)}}{\dfrac{v_P}{(K_P + \hat{R}_P)}} \tag{8}$$

We will refer to this quantity, the ratio of phytoplankton N : P to inorganic N : P, as the "predicted N : P affinity index."

Empirical observations in both the Atlantic (Cavender-Bares et al. 2001) and the Pacific (Karl et al. 2001), combined with laboratory data on nutrient uptake parameters (Table 1), indicate that the value of $\hat{R}_i$ is often at least an order of magnitude smaller than K_i for both N and P, which is what we would expect if competitive interactions drive nutrient concentrations close to break-even levels ("supply limited" in Klausmeier et al. [2004*b*]). This observation ($K_i \gg \hat{R}_i$) allows both $\hat{R}_i$s to be removed from Eq. 8 to obtain

$$\hat{\Phi}_{N:P} \approx \frac{\dfrac{v_N}{K_N}}{\dfrac{v_P}{K_P}} \tag{9}$$

Equation 9 indicates that the steady-state ratio of phytoplankton N : P to inorganic N : P in the euphotic zone predicted by models using basic Michaelis–Menten uptake kinetics is a ratio of nutrient uptake parameters, and is independent of nutrient limitation, nutrient inputs and losses, biomass, cell quotas, and mortality. Specifically, $\hat{\Phi}_{N:P}$ is the ratio of the maximum slope of the N uptake function or N affinity (Healey 1980) to the maximum slope of the P uptake function or P affinity (Healey 1980), which is realized at low nutrient concentrations (from Eq. 1). Equation 9 implies that for phytoplankton N : P to be significantly greater than available N : P when assuming Michaelis–Menten uptake kinetics, N affinity must be considerably greater than P affinity.

There are several advantages of using the affinity index to describe N : P stoichiometry in the euphotic zone. First, the unwieldy mathematical expressions for steady-state phytoplankton or inorganic N and P (Klausmeier et al. 2004*b*; Ballantyne et al. 2008) can be avoided, so the only data needed to parameterize the model prediction are uptake rates. Second, the ratio of phytoplankton N : P to inorganic N : P provides a more comprehensive description of whole ecosystem N : P stoichiometry than considering phytoplankton N : P alone. A third advantage is that nutrient affinities (v_i/K_i) often exhibit less intraspecific variability than either v_i or K_i (Duata 1982; Collos et al. 2005), both of which can be highly influenced by local environment and growth history (Morel 1987; Harrison et al. 1989). Significant interspecific variation in affinities exists (Duata 1982; Collos et al. 2005), but a recent analysis suggests that even this variability is predictable across species (Litchman et al. 2007). The absence of growth and mortality rates as well as N and P input rates from the simplified expression for $\hat{\Phi}_{N:P}$ (Eq. 9) is noteworthy, as it indicates that the particular formulations of growth limitation and other ecosystem processes are irrelevant for determining the steady-state link between phytoplankton N : P and inorganic N : P. If steady-state nutrient concentrations are small relative to half-saturation constants, neither input rates nor concentrations influence the affinity index, which is not the case for the ratio of cell quotas (Klausmeier et al. 2004*b*).

In real-world conditions, growth is frequently supply limited, and thus approximating the exact expression for the N : P affinity index (Eq. 8) with Eq. 9 is often reasonable. However, approximating the N : P affinity index with Eq. 9 is potentially problematic if growth is known to be kinetically limited or if steady-state N and P concentrations are of the same order as half-saturation constants. If steady-state N and P concentrations are of the same order as half-saturation constants, the approximation may be off by up to a factor of two. To illustrate the sensitivity of our approximation, we used data for steady-state N and P limitation, supply-limited growth, and kinetically limited growth presented in Klausmeier et al. (2004*b*) to compute the exact (Eq. 8) and approximate (Eq. 9) values of the N : P affinity index. Under steady-state N limitation (input N : P = 10), $\hat{\Phi}_{N:P} = 1.43$; under P limitation (input N : P = 60), $\hat{\Phi}_{N:P} = 1.23$; and under kinetically limited conditions $\hat{\Phi}_{N:P}$ varies from 0.36 to 4.5, with a value of 1 corresponding to an input N : P ratio of just under 30, which is slightly greater than the optimal N : P of 27.7 for *Scenedesmus* sp. (Klausmeier et al. 2004*b*). The approximation of the affinity index (Eq. 9), which is independent of nutrient limitation and assumes that steady-state inorganic N and P concentrations are low relative to half-saturation constants, equals 1 in all cases because it only depends on N and P affinities, which are the same in Klausmeier et al. (2004*b*). Only under kinetically limited growth with extreme N : P input values does the approximation deviate substantially from the exact expression.

This same result holds for many variations of the model incorporating basic Michaelis–Menten uptake kinetics (Eqs. 1–3), and similar results can be derived for models with modified descriptions of N uptake. Adding differential N and P recycling to the basic model has no effect on $\hat{\Phi}_{N:P}$ because recycling terms only enter into the equations for resource dynamics (Ballantyne et al. 2008) and steady-state N ($\hat{R}_N$) and P ($\hat{R}_P$) concentrations are removed in the derivation of $\hat{\Phi}_{N:P}$. With linear uptake ($f_i[R]_i) = v_iR_i/K_i$) in place of Michaelis–Menten, $\hat{\Phi}_{N:P}$ is exactly $(v_N/K_N)/(v_P/K_P)$, which is to be expected because assuming $K_i \gg \hat{R}_i$ linearizes the Michaelis–Menten function. Adding density-dependent mortality from virus infection and lysis (Suttle 2007; Menge and Weitz 2009) or from grazing by mesozooplankton (Morales et al. 1993), which can account for a large fraction of phytoplankton mortality, also yields the same result for $\hat{\Phi}_{N:P}$. Adding a general consumer trophic level C (grazers, viruses, etc.) yields the augmented model

$$\frac{dR_i}{dt} = \text{external inputs} + \text{recycling} - \text{abiotic loss} - \text{uptake} \tag{10}$$

$$\frac{dO_i}{dt} = f_i(R_i)B - (m + g[C])O_i \tag{11}$$

$$\frac{dB}{dt} = \text{growth} - \text{background mortality} - \text{grazing mortality} \tag{12}$$

$$\frac{dC}{dt} = \text{consumer growth} - \text{mortality} \tag{13}$$

in which the new term $g(C) \times O_i$, where $g(C)$ is some function of C, denotes grazing or lysis-derived mortality. Steady-state loss from the phytoplankton nutrient pools thus occurs at a rate $m + g(C)$, which simply replaces m in steady-state expressions for phytoplankton nutrient concentrations

$$f_i(\hat{R}_i)\hat{B} = \frac{v_i\hat{R}_i}{K_i + \hat{R}_i}\hat{B} = (m + g[\hat{C}])\hat{O}_i \tag{14}$$

and ultimately cancels out of the expression for $\hat{\Phi}_{N:P}$, as does m in our original derivation.

More detailed models of N uptake exist, incorporating the ammonium inhibition of nitrate uptake (Lima and Doney 2004; Litchman et al. 2006) and feedback inhibition from N quotas (Geider et al. 1998; Litchman et al. 2006; Salihoglu and Hofmann 2007). These alter the steady-state expression for N concentrations, but do not alter $\hat{\Phi}_{N:P}$ significantly. For quota-limited uptake of N, as formulated by Geider et al. (1998) and Lima and Doney (2004), phytoplankton N concentration is represented as the "quota" or amount per cell (Q_N) and the governing equation is

$$\frac{dQ_N}{dt} = \frac{v_N R_N}{K_N + R_N}\left[\frac{Q_{N,max} - Q_N}{Q_{N,max} - Q_{N,min}}\right] - \mu Q_N \tag{15}$$

in which μ is a growth function that typically depends on the quota of the limiting nutrient. As N quota increases, uptake rate decreases and at steady state, growth rate equals mortality rate ($\mu = m$), leading to

$$\frac{1}{m}\frac{v_N\hat{R}_N}{\left(K_N+\hat{R}_N\right)}\left[\frac{Q_{N,max}}{Q_{N,max}+\frac{1}{m}\frac{v_N\hat{R}_N}{K_N+\hat{R}_N}-Q_{N,min}}\right]=\hat{Q}_N \quad (16)$$

By realizing that $1/m\times\left[\left(v_N\hat{R}_N\right)/\left(K_N+\hat{R}_N\right)\right]$ is the steady-state quota for phytoplankton N for basic Michaelis–Menten uptake (Klausmeier et al. 2004*b*) and is always greater than the minimum quota $Q_{N,min}$, we see that $\hat{Q}_N$ for quota-limited uptake will always be smaller than $\hat{Q}_N$ for basic Michaelis–Menten uptake. Although P dynamics are not included in Geider et al. (1998) or in Lima and Doney (2004), standard practice for modeling P uptake does not depart from basic Michaelis–Menten uptake. Therefore, $\hat{\Phi}_{N:P}\times\left[\left(\hat{Q}_N/\hat{Q}_P\right)/\left(\hat{R}_N/\hat{R}_P\right)\right]$ from models incorporating quota-limited N uptake will be smaller in magnitude than $\hat{\Phi}_{N:P}$ from models with basic Michaelis–Menten N uptake.

If ammonium inhibition of nitrate uptake is incorporated, as in Fasham et al. (1990), Moore et al. (2002*a*), and Salihoglu and Hofmann (2007), phytoplankton N quota dynamics can be described by

$$\frac{dQ_N}{dt}=\left[\frac{v_{NO_3}R_{NO_3}}{K_{NO_3}+R_{NO_3}}e^{-\Psi R_{NH_4}}+\frac{v_{NH_4}R_{NH_4}}{K_{NH_4}+R_{NH_4}}\right]-\mu Q_N \quad (17)$$

with NO_3 denoting nitrate and NH_4 denoting ammonium, and the exponential term reflecting the ammonium inhibition. At steady state,

$$\frac{1}{m}\left[\frac{v_{NO_3}\hat{R}_{NO_3}}{K_{NO_3}+\hat{R}_{NO_3}}e^{-\Psi\hat{R}_{NH_4}}+\frac{v_{NH_4}\hat{R}_{NH_4}}{K_{NH_4}+\hat{R}_{NH_4}}\right]=\hat{Q}_N \quad (18)$$

Assuming that there are at least trace quantities of ammonium, the exponential term is between 0 and 1, so

$$\frac{1}{m}\left[\frac{v_{NO_3}\hat{R}_{NO_3}}{K_{NO_3}+\hat{R}_{NO_3}}+\frac{v_{NH_4}\hat{R}_{NH_4}}{K_{NH_4}+\hat{R}_{NH_4}}\right] > \frac{1}{m}\left[\frac{v_{NO_3}\hat{R}_{NO_3}}{K_{NO_3}+\hat{R}_{NO_3}}e^{-\Psi\hat{R}_{NH_4}}+\frac{v_{NH_4}\hat{R}_{NH_4}}{K_{NH_4}+\hat{R}_{NH_4}}\right] \quad (19)$$

The expression on the left-hand side of Eq. (19) is the expression for steady-state $\hat{Q}_N$ without ammonium inhibition,

$$\hat{Q}_N=\hat{Q}_{NO_3}+\hat{Q}_{NH_4}=\frac{1}{m}\left[\frac{v_{NO_3}\hat{R}_{NO_3}}{K_{NO_3}+\hat{R}_{NO_3}}+\frac{v_{NH_4}\hat{R}_{NH_4}}{K_{NH_4}+\hat{R}_{NH_4}}\right] \quad (20)$$

so adding ammonium inhibition of nitrate uptake can only decrease $\hat{Q}_N$ relative to the case without ammonium inhibition. This decrease is only likely to be considerable if nitrate affinity is significantly greater than ammonium affinity and if the ambient ammonium concentration is high. Decreasing the quota only exacerbates the discrepancy between the model prediction and empirical data (*see* below).

If ammonium inhibition of nitrate uptake is combined with quota-limited nitrate uptake, as in Litchman et al. (2006), phytoplankton N quota dynamics are written as

$$\frac{dQ_N}{dt}=\left[\frac{Q_{N,max}-Q_N}{Q_{N,max}-Q_{N,min}}\right]\frac{v_{NO_3}R_{NO_3}}{K_{NO_3}+R_{NO_3}}e^{-\Psi R_{NH_4}}+\frac{v_{NH_4}R_{NH_4}}{K_{NH_4}+R_{NH_4}}-\mu Q_N \quad (21)$$

with subscripts as above. At steady state,

$$\frac{1}{m}\left[\left[\frac{Q_{N,max}-\hat{Q}_N}{Q_{N,max}-Q_{N,min}}\right]\frac{v_{NO_3}\hat{R}_{NO_3}}{K_{NO_3}+\hat{R}_{NO_3}}e^{-\Psi\hat{R}_{NH_4}}+\frac{v_{NH_4}\hat{R}_{NH_4}}{K_{NH_4}+\hat{R}_{NH_4}}\right]=\hat{Q}_N \quad (22)$$

Combining the two above arguments allows us to conclude that adding quota limitation to ammonium-inhibited nitrate will only decrease steady-state N quotas. Thus, quota limitation and uptake inhibition of N may decrease the value of $\hat{Q}_N$ significantly.

Finally, we consider the optimization model of Smith and Yamanaka (2007), which is an extension of the Aksnes and Egge (1991) affinity model. Smith and Yamanaka (2007) formulate nutrient uptake as

$$f_i(R_i)=\frac{v_{i,max}R_i}{\frac{v_{i,max}}{A_{i,max}}+R_i} \quad (23)$$

in which $A_{i,max}$, referred to as the affinity, depends on the surface area of uptake sites and equals $v_{i,max}/K_i$ so $K_i = v_{i,max}/A_{i,max}$ in Eq. (23). Phytoplankton allocate the same fraction (F_A) of all internal resource pools toward affinity-related enzymes on the surface of cells and the remaining fraction ($1 - F_A$) to internal uptake-related enzymes. As a consequence the following substitutions are made

$$A_{i,max}=F_A A_i \quad (24)$$

$$v_{i,max}=(1-F_A)v_i \quad (25)$$

in which $A_{i,max}$ and $v_{i,max}$ are the realized maximum affinity and maximum uptake rate respectively. Substituting Eqs. 24 and 25 into Eq. 23 and subsequently into Eq. 5 allows us to derive

$$\hat{\Phi}_{N:P}=\frac{\frac{v_N}{\left(\frac{v_N}{A_N}\frac{1-F_A}{F_A}+\hat{R}_N\right)}}{\frac{v_P}{\left(\frac{v_P}{A_P}\frac{1-F_A}{F_A}+\hat{R}_P\right)}} \quad (26)$$

The effects of supply vs. kinetic limitation of nutrient uptake can be deduced from Eq. 26. Under kinetically limited conditions, phytoplankton should decrease F_A to increase their ''handling'' capability, which all but eliminates the influence of $\hat{R}_i$ on the N : P affinity ratio. Under supply-limited conditions, $\hat{R}_i$ for the limiting

nutrient will be small relative to K_i and phytoplankton should increase F_A to increase the encounter rate with the limiting nutrient. If steady-state nutrient concentrations are low relative to half-saturation constants and if allocation is not heavily biased toward affinity or uptake, the approximation

$$\hat{\Phi}_{N:P} \cong \frac{A_N}{A_P} = \frac{\frac{v_N}{K_N}}{\frac{v_P}{K_P}} \quad (27)$$

for the ratio of phytoplankton N : P to available N : P at steady state introduces minimal error.

Relating models and laboratory data to empirical observations—To compare model-predicted to empirically observed N : P affinity indices, which we denote $\tilde{\Phi}_{N:P}$, we first searched the literature for studies that measured N and P uptake parameters for marine phytoplankton in the laboratory to parameterize $\hat{\Phi}_{N:P}$ using Eq. 9. Many studies measure a subset of the parameters required to compute $\hat{\Phi}_{N:P}$ (v_N, v_P, K_N, and K_P), but only a small number measure all simultaneously in the same environment, forcing modeling efforts to rely on summary statistics for parameterization (Litchman et al. 2006). Table 1 shows our uptake parameter data set, which adds several studies on dinoflagellate species to the compilation from Litchman et al. (2006), who report median uptake parameter values for four broad taxonomic groups of phytoplankton. In reality, as discussed in Litchman et al. (2006) and Collos et al. (2005), maximum uptake rates (v_N and v_P) and half-saturation constants (K_N, and K_P) are plastic, varying in response to temperature, growth history, and light intensity in the case of N (Morel 1987; Harrison et al. 1989; Collos et al. 2005). However, maximum uptake rates and half-saturation constants tend to covary considerably (Collos et al. 2005), rendering affinity a more robust metric for describing N and P uptake than either maximum uptake rate or half-saturation concentration alone. Thus, predictions from the affinity index will minimize the influence of parameter variation compared with using maximum uptake rates or half-saturation constants alone. Despite the inherent variability in uptake parameters and the relative paucity of data, parameter value summaries are the only realistic options for establishing general patterns (Litchman et al. 2006). Using the maximum uptake rates and half-saturation constants for either nitrate or ammonium and inorganic phosphorus (from Table 1), we calculated $\hat{\Phi}_{N:P}$ using Eq. 9 for each taxonomic group in Table 1 to obtain a total of 13 predicted values. The distribution of the predicted N : P affinity index is plotted as a histogram with dark gray bars in Fig. 3.

To establish the maximum possible variation in the observed affinity index, $\tilde{\Phi}_{N:P}$, we divided all phytoplankton N : P values from literature compilations (Geider and LaRoche 2002; Klausmeier et al. 2004*a*) (shown in Fig. 1) by all possible euphotic zone inorganic N : P values using electronically available data from HOT and BATS and data from Cavender-Bares et al. (2001) (shown in Fig. 2).

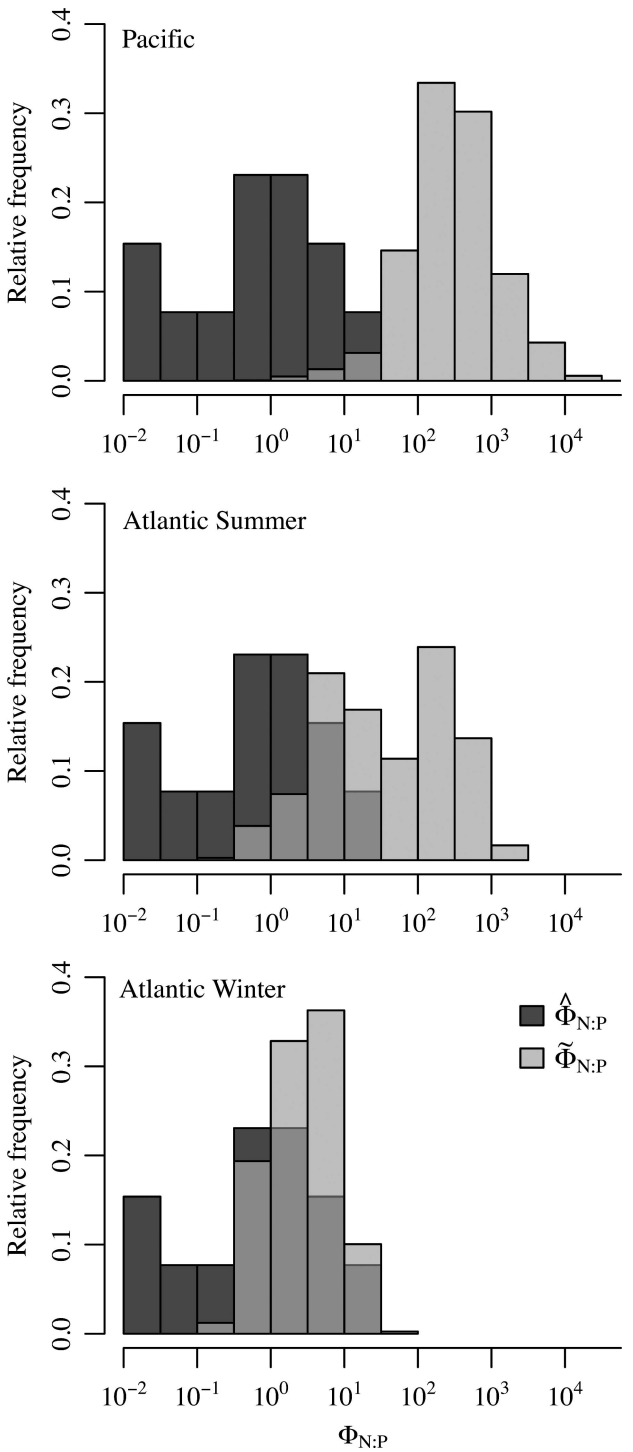

Fig. 3. Comparison of the N : P affinity index ($\Phi_{N:P}$, the steady-state ratio of phytoplankton N : P to inorganic N : P in the euphotic zone) computed from the model and nutrient uptake parameters (predicted, $\hat{\Phi}_{N:P}$) and computed from empirical observations of phytoplankton N : P and euphotic zone inorganic N : P ($\tilde{\Phi}_{N:P}$). The predicted values (dark gray bars) are derived using N and P uptake parameters from Table 1 and the N : P affinity index (Eq. 9). The empirical histograms (light gray bars) are generated by dividing each phytoplankton N : P value in Fig. 1 by each of the observed inorganic N : P values from the HOT data, the Cavender-Bares et al. (2001) data (Atlantic summer), and the BATS data (Atlantic winter) in Fig. 2.

Values of $\widetilde{\Phi}_{N:P}$ are plotted as histograms with light gray bars. Such estimates of the variability of $\widetilde{\Phi}_{N:P}$ come with a caveat, since many of the species for which N : P data have been measured are not major components of the phytoplankton communities in the North Pacific Subtropical Gyre or the Sargasso Sea. Furthermore, phytoplankton N : P values for all species in the compilations were determined in laboratory settings. We obtained separate distributions of observed $\widetilde{\Phi}_{N:P}$ for the euphotic zone in the Pacific, the Sargasso Sea in the summer, and the Sargasso Sea during winter for comparison with $\hat{\Phi}_{N:P}$, the model prediction parameterized with N and P uptake data from laboratory experiments. Distributions of $\hat{\Phi}_{N:P}$, the model-predicted N : P affinity index (dark gray bars), and $\widetilde{\Phi}_{N:P}$, the observed N : P affinity index (light gray bars), are plotted together in histograms for the Pacific, the Atlantic summer, and the Atlantic winter in Fig. 3. The predicted N : P affinity index is derived from Michaelis–Menten uptake kinetics and parameterized with data from pure culture experiments in the laboratory, whereas the observed N : P affinity index is the ratio of actual phytoplankton N : P stoichiometry to in situ inorganic N : P stoichiometry in the Atlantic and Pacific oceans. We compared the distributions of $\hat{\Phi}_{N:P}$ and $\widetilde{\Phi}_{N:P}$ using Kolmogorov–Smirnov tests.

Results

There is a wide discrepancy between empirically observed ($\widetilde{\Phi}_{N:P}$) and model-predicted ratios ($\hat{\Phi}_{N:P}$) of phytoplankton N : P to inorganic N : P in surface waters of the ocean. Because phytoplankton N : P (14 on average) is much greater than inorganic N : P (less than 0.14 on average) in the North Pacific Subtropical Gyre, $\widetilde{\Phi}_{N:P}$ is greater than 100 on average. In comparison, because N affinity and P affinity tend to be similar, the ratio predicted by the model, $\hat{\Phi}_{N:P}$, is typically 1 or less. In fact, the distributions of the two (Fig. 3) exhibit virtually no overlap ($p < 0.0001$). There is also little overlap when using summer euphotic zone inorganic N : P from the Sargasso Sea to compute $\widetilde{\Phi}_{N:P}$ and the empirical and predicted distributions are again statistically different ($p < 0.0001$). However, using winter euphotic zone inorganic N : P from well-mixed, unstratified surface waters near the Gulf Stream to compute observed $\widetilde{\Phi}_{N:P}$, the distributions of $\widetilde{\Phi}_{N:P}$ and $\hat{\Phi}_{N:P}$ are statistically indistinguishable ($p = 0.60$). Although the predicted relationship is observed for well-mixed surface waters, the fact that it does not hold for stratified, more oligotrophic regions is problematic, especially since they comprise the vast majority of the surface ocean and are where we expect nutrient uptake to exert the greatest influence on inorganic N : P stoichiometry. The quantity of data used to compute euphotic zone inorganic N : P provides a comprehensive picture of inherent variability, but the relative paucity of data for in situ phytoplankton N : P and nutrient uptake parameters may misrepresent their true variability. The number of studies that comprehensively measure all relevant uptake parameters is small, and thus the data we have compiled should accurately reflect laboratory-derived estimate of phytoplankton N and P uptake kinetics. Despite these differences in sample sizes, we claim that a real discrepancy exists, given the resolution afforded by available data.

Discussion

We have shown that a simple prediction of a large class of phytoplankton models does not agree with the inferred distribution of N : P stoichiometry in the majority of the surface oceans. The discrepancy between models and in situ observations may exist because either the models themselves, or the particular type of analysis we used to derive the result, do not accurately reflect pelagic marine ecosystems. Despite the fact that such models have been developed in synergy with laboratory experimentation (Dugdale 1967; Legovic and Cruzado 1997; Klausmeier et al. 2004*b*), their direct application to the euphotic zone apparently fails to capture a well-established stoichiometric relationship. Below, we list and discuss potential causes for the discrepancy between model predictions and empirical observations.

Assuming a steady state—A central assumption of our analysis was that the pools we are considering (phytoplankton populations and surface inorganic nutrients) are at or close to equilibrium. Although inorganic nutrient pools and phytoplankton populations typically equilibrate rapidly (Falkowski et al. 1998), it is possible that further model analysis could reveal long-term transient, periodic, and chaotic dynamics that yield different results for the relationship between phytoplankton N : P and euphotic zone inorganic N : P. Burmaster (1979) has shown that the results from multinutrient phytoplankton growth models can differ between dynamic situations and steady states. The relatively constant N : P stoichiometry in the oceans has historically been observed over spatiotemporal scales distinctly separated from the scales over which phytoplankton community dynamics occur, potentially disconnecting steady states for phytoplankton communities and ocean basins. Using a more dynamic approach to study the link between nutrient uptake and community structure may have the potential to reconcile the discrepancy discussed here, while remaining consistent with the N : P stoichiometry of the deep ocean. For example, it would be useful to know the extent to which large deviations or quasistationary transients in N : P can persist in phytoplankton-nutrient models with seasonal or intermittent forcing (as might be caused by upwelling).

Functional forms in the model—The specific functional forms in the model could also be the source of the divergence between empirical data and model-derived results. Myriad laboratory experiments have shown saturating nutrient uptake for a limiting nutrient (Yamamoto et al. 2004). However, the generality of independent dual nutrient uptake, specifying that each nutrient is taken up independently of demand for the other, has not been widely confirmed to our knowledge. As shown above, ecosystem models incorporating ammonium inhibition of nitrate uptake (Moore et al. 2002*a*; Litchman et al. 2006; Salihoglu

and Hofmann 2007) and quota-limited N uptake (Geider et al. 1998; Lima and Doney 2004; Litchman et al. 2006) cannot eliminate the discrepancy between models parameterized with laboratory culture data and in situ observations of N : P stoichiometry, and we are not aware of any models that allow the uptake of one nutrient to be directly regulated by the internal and external concentrations of other nutrients, although the chain model of Pahlow and Oschlies (2009) makes a significant step toward linking N and P quotas to uptake kinetics. Adding quota-limited N uptake, ammonium inhibition of nitrate, or the two together decreases overall N uptake, shifting the distribution of predicted values toward smaller $\hat{\Phi}_{N:P}$, to the left in Fig. 3, and increases the discrepancy. By allowing nutrient uptake to depend on the internal and external concentrations of multiple nutrients and by incorporating dynamic allocation of resources, steady-state model predictions may become more realistic.

Omissions of the model—Alternatively, the discrepancy between the empirically estimated ($\widetilde{\Phi}_{N:P}$) and model-predicted ($\hat{\Phi}_{N:P}$) N : P affinity index may arise from omitting biologically relevant features in relatively simple models. Matter transformations associated with both higher and lower trophic levels are known to affect nutrient dynamics, and at first glance may be seen as potential modifiers of the nutrient index ratio. Consumer-driven nutrient recycling (Elser and Urabe 1999), microbially driven recycling (Priddle et al. 1995; Ballantyne et al. 2008), and higher trophic effects (Gilbert 1998) may all influence phytoplankton N : P and inorganic N : P. However, as we have shown here, neither nutrient recycling nor density-dependent mortality exert any influence on $\hat{\Phi}_{N:P}$. Although the link between phytoplankton N : P and steady-state inorganic nutrient N : P has typically not been the focus of models with more trophic complexity (Elser and Urabe 1999), and could be explored in more detail, we do not expect such analysis to yield different results. The expression for $\hat{\Phi}_{N:P}$ presented here is so robust because in models of this type, phytoplankton draw nutrient concentrations down to levels prescribed by obligate uptake functions irrespective of internal demand, predation pressure, or other higher-level trophic dynamics.

Potentially more problematic is that such models do not allow phytoplankton to use other forms of N and P for growth. In addition to differentiating between different inorganic forms of N (Moore et al. 2002*b*), phytoplankton species are known to take up organically bound nutrients. For example, *Prochlorococcus*, the dominant cyanobacterium at station ALOHA in the North Pacific Gyre, is able to take up organically bound N (Moore et al. 2002*b*) and P (Bjorkman and Karl 2005), meaning that a more complicated and interwoven set of nutrient cycles may be responsible for observed values of $\widetilde{\Phi}_{N:P}$. If a significant fraction of the phytoplankton community is relying on organically bound N and P, we would expect a less constrained relationship between phytoplankton N : P and inorganic N : P. In fact, if models match data when only one source pool exists, deviations in empirically estimated $\widetilde{\Phi}_{N:P}$ from model-predicted $\hat{\Phi}_{N:P}$ may provide a basis for estimating the relative importance of different nutrient pools to the phytoplankton community as a whole. Incorporating additional nutrient pools known to be used by phytoplankton into models is a necessary step to advance our understanding of whole-ocean N : P stoichiometry.

Inappropriate use of data—A different explanation for the discrepancy between observations and model predictions could be the inappropriate use of data for our comparisons. This possibility brings up several questions to which we do not claim to have the answers: How accurately can experimental data from the lab be applied to real-world oceanography? How big a problem is it to use N : P data from a small subset of species or ecotypes found in the ocean? Would a different result be obtained if uptake for entire communities or ecosystems was measured? And finally, how much will variability in nutrient inputs and spatial heterogeneity in environmental conditions affect empirical $\widetilde{\Phi}_{N:P}$? Obviously, laboratory conditions do not capture all the complexities of life in the euphotic zone, but patterns of uptake in laboratory conditions have been integrated into the phytoplankton component of global-scale climate models, and thus it is important to determine how accurately they represent real oceans. It would take considerable effort to estimate parameters of multiple intake functions in situ and we are aware of only one study that focuses solely on N (Harrison et al. 1996). In the study of Harrison et al. (1996), estimates of v_N and K_N are considerably lower than those from laboratory experiments but N affinities computed from in situ parameter estimates range from 0.02 to 0.14, well within the range in Table 1. The consistency of N affinity from the laboratory to the North Atlantic underscores the utility of using it for cross-species and cross-ecosystem comparisons. Using uptake parameters for a relatively small number of species or ecotypes may underestimate the plasticity of phytoplankton community-level nutrient uptake rates, but the relatively exhaustive compilation of Litchman et al. (2006) suggests that variability in uptake physiology measured in the lab is low among broad taxonomic units. And although up-regulation of N and P uptake can occur in response to nutrient limitation, increasing v_N and v_P 5-fold and 40-fold respectively (Morel 1987), the correlation between maximum uptake rates and half-saturation constants (Collos et al. 2005) limits the extent to which such variability influences the N : P affinity index for a given species (Harrison et al. 1996). However, as stated earlier, the disparity in sample sizes between N and P uptake data used to parameterize $\hat{\Phi}_{N:P}$ and data to compute observed $\widetilde{\Phi}_{N:P}$ may introduce bias into our comparison if the available data are a nonrandom subset of all N and P uptake kinetics. One must also keep in mind that phytoplankton N : P values were determined in laboratory experiments and that phytoplankton growing in the oceans may have different N : P stoichiometry from laboratory cultures.

If, as discussed above, organically bound N and P are a significant component of the total N and P taken up by phytoplankton, the comparison of $\widetilde{\Phi}_{N:P}$ and $\hat{\Phi}_{N:P}$ could be

invalid. Most models only consider single N and P pools, when in actuality, some constituents of the phytoplankton community may be utilizing different pools of each nutrient. Differentiating among different pools of inorganic N (nitrate, nitrite, and ammonium) is less of a cause for concern because even if ammonium was the dominant source of N, the discrepancy between $\widetilde{\Phi}_{N:P}$ and $\hat{\Phi}_{N:P}$ would only be exacerbated and the available pool in the model (all inorganic N) corresponds well to the observed pool used to compute $\widetilde{\Phi}_{N:P}$ (dissolved nitrate + nitrite, abbreviated DNO_x). But if uptake kinetics differ substantially for ammonium and nitrate, omitting the concentration of ammonium from the inorganic N pool will substantially bias $\widetilde{\Phi}_{N:P}$ if ammonium is heavily utilized by the phytoplankton community. Furthermore, as we have little to no information about uptake kinetics of organically bound N and P, and even less about the size of "available" dissolved organic N and P pools, our comparison of $\widetilde{\Phi}_{N:P}$ and $\hat{\Phi}_{N:P}$ may be problematic. Simply adding the entire dissolved organic pools of N and P to DNO_x and soluble reactive P (SRP), used for the comparisons here, will not alleviate all potential problems because it is unclear what components of the dissolved organic N and P pools are biologically available. Determining exactly what the biologically available N and P pools consist of and how they are used by the entire phytoplankton community remains a significant challenge that must be addressed to fully understand the link between phytoplankton N : P and inorganic N : P in the euphotic zone.

Community dynamics—Perhaps the most significant hurdles appear when considering the relationship between available N : P stoichiometry and whole community phytoplankton N : P stoichiometry. For example, *Prochlorococcus* does not have the ability to take up nitrate and relies on organically bound N and highly ephemeral ammonium (Moore et al. 2002*b*; Salihoglu and Hofmann 2007). Thus, directly comparing $\widetilde{\Phi}_{N:P}$ computed using *Prochlorococcus* N : P and DNO_x : SRP to $\hat{\Phi}_{N:P}$ predicted from inorganic nutrient uptake parameters is inconsistent with phytoplankton biogeography. In this case, other members of the phytoplankton community, not the dominant group, are responsible for drawing down nitrate and nitrite concentrations. *Prochlorococcus* N : P may still be tied to inorganic N : P stoichiometry, but without explicitly incorporating other bioavailable pools into models, the discrepancy will persist. Further complicating the problem is that to our knowledge, N and uptake physiology for *Prochlorococcus* has not been characterized. Again, a more dynamic view of the relationship between N : P stoichiometry of the entire resource spectrum in the euphotic zone and guild-level variability in nutrient uptake physiology may be required to reconcile the inconsistencies presented here. Extending single-species models to communities remains a largely unexplored avenue for research and such a trait-based approach has recently been suggested (Litchman and Klausmeier 2008).

Understanding what controls N : P stoichiometry in both phytoplankton and inorganic pools is critical for understanding global nutrient cycles and predicting primary production and carbon export from the euphotic zone, especially in the face of global climate change. Nutrient availability drives carbon uptake, storage, and export in much of the ocean, which is by far the largest biologically influenced carbon reservoir on Earth. Ocean ecosystem models, which are used for global carbon accounting and predicting net carbon fluxes between the oceans and the atmosphere, are parameterized using the nutrient uptake data presented here (Moore et al. 2002*a*), and often use stoichiometric ratios to infer nutrient limitation and rates of nutrient cycling (Gruber and Sarmiento 1997). Consequently, it is imperative that phytoplankton growth models better reflect the realities and complexities of nutrient uptake. Here, we have shown that widely used formulations of nutrient uptake predict stoichiometries that are at odds with the majority of empirical observations of the ratio of phytoplankton N : P to inorganic N : P in the surface ocean. This discrepancy calls into question the ability of such models to accurately describe and predict coupled nutrient dynamics in the oceans, which is important given that N and P often colimit the production of autotrophs and heterotrophs (Mills et al. 2008). The fact that models of this sort reproduce various empirically observed features of marine ecosystems is evidence that they capture some realistic dynamics, but the results presented here argue for re-examining some of our often used underlying assumptions.

We see three avenues for research that will allow us to check our assumptions about nutrient uptake and reconcile the apparent disconnect between models and empirical observations. First, there is a need to develop more sophisticated mathematical descriptions of nutrient uptake that explicitly include regulation on the basis of internal stores and dynamic substitutability of resources. An approach that explicitly includes reaction pathways and constrains N and P allocation to molecular structures using cell quotas has the potential to inform models using data for enzyme production and function. Second, laboratory experiments using ecologically relevant suites of species that measure whole community rates of nutrient uptake and N : P stoichiometry, relative uptake rates of functional phytoplankton types and their respective N : P stoichiometry, and the N : P stoichiometry of all exploited nutrient pools are necessary to fully understand how phytoplankton N : P is linked to N : P of available nutrients. Third, simultaneous in situ measurements of the N : P of multiple nutrient pools in the euphotic zone (phytoplankton, dissolved organic and inorganic, and particulate) across time and space combined with stable isotope tracer experiments to estimate N and P uptake rates would provide a more complete picture of the feedbacks that conspire to generate the N : P stoichiometry of the surface ocean. Integrated mathematical model development and laboratory experimentation, a hallmark of the study of phytoplankton, has advanced our knowledge of nutrient dynamics considerably faster than either approach would have alone, and will continue to be key for developing a synthetic description of N : P stoichiometry in the oceans.

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