Relating Phytoplankton Pnysiology to North Pacific Biogeochemistry

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Introduction

It is well known that phytoplankton systematically alter their physiology in response to changing environmental conditions, and that this entails changes in the ratios of nutrients and carbon contained in their biomass. In response to changes in the availability of nutrients, phytoplankton produce cellular components (e.g., chlorophyll and various enzymes) in different proportions, which requires that they take up and use nutrients in different ratios. We constructed a marine ecosystem model including a physiologically-based model for changes in nutrient uptake ratios (of N, Si and Fe) and applied it to examine the extensive data set from the SERIES (Subarctic Ecosystem Response to Iron Enrichment Study) iron-fertilization experiment in the subarctic North Pacific ocean. We applied data assimilation to mathematically compare the agreement of different models with the data set, which confirmed that changes in uptake ratios in response to nutrient limitation played an important role in determining the dynamics of phytoplankton and nutrients observed during SERIES. In cooperation with other researchers (Shigemitsu *et al.* 2011), we have incorporated the resulting improved model of nutrient uptake by phytoplankton into a global three-dimensional physical-biological coupled model, called the Marine Ecosystem Model (MEM).

Dynamics of nutrient ratios

Consistent with findings from previous laboratory experiments examining the effect of iron fertilization on phytoplankton (Hutchins and Bruland 1998; Franck *et al.* 2000), the ratio of Si to N drawdown increased at the return of iron limitation (after iron addition and its subsequent depletion) during the approximately two-week period of the SERIES field experiment (Boyd *et al.* 2004, 2005; Takeda *et al.* 2006). In the laboratory experiments, this increase in Si:N drawdown ratio resulted mostly from a decrease in the rate of N uptake. In contrast, during SERIES, the rate of N uptake actually increased (Boyd *et al.* 2005), and the rate of Si uptake increased by an even greater factor, so that the Si:N ratio increased. This suggested that a different mechanism could have caused the change in uptake ratio during

SERIES, and Boyd *et al*. (2005) suggested that further studies of nutrient uptake kinetics should be undertaken to clarify this matter.

The study of Smith *et al*. (2010) sought to examine the uptake kinetics of N, Si and Fe during SERIES, in terms of the recently developed SPONGE (Simple Phytoplankton Optimal Nutrient Gathering Equations) model (Smith and Yamanaka 2007), which is based on the concept that phytoplankton should re-arrange their physiology in order to maximize the uptake of whatever element is currently limiting their growth, in such a way that causes the uptake rates of all other nutrients to also depend on the ambient concentration of that growth-limiting nutrient.

Large-scale modeling

Our motivation for large-scale modeling is to find general process models of how phytoplankton, and ultimately planktonic ecosystems, respond to changes in physical conditions and nutrient supply. The goal is to use such process models within large-scale three-dimensional models to examine how marine ecosystems may respond to inter-annual variability of physical conditions (including, for example, short-term oscillations such as the El Nino/Southern Oscillation), longer-term climate change, and changes in nutrient supply (e.g., from human activities).

The process model for nutrient uptake kinetics (Smith and Yamanaka 2007) is one example of an "optimality-based" model for phytoplankton, as reviewed by Smith *et al*. (2011). Such optimality-based models are formulated based on the idea that natural selection should tend to produce organisms optimally suited to their environments. This idea applies particularly well to plankton, given their long evolutionary history. This implies that the species that have survived in natural selection, while competing with other species, should be those that make the most efficient use

of their resources, subject to inescapable trade-offs. This approach has recently yielded improved models for a variety of plankton processes (Pahlow 2005; Smith *et al*. 2009, 2011), and it is promising for developing large-scale models of greater generality for examining the response of marine ecosystems.

First, we present an overview of the equations used to describe nutrient uptake kinetics, which was the core element of the process studies described herein, contrasting the recently developed Optimal Uptake (OU) kinetics with the widely applied Michaelis-Menten (MM) kinetics. Then, we briefly summarize the methods for the studies presented, and present a summary of the results of Smith *et al*. (2010) with respect to modeling nutrient uptake during SERIES. Finally, we present the model of Shigemitsu *et al*. (2011), which incorporates the results of Smith *et al*. (2010) into a global three-dimensional coupled physical-biological model, developed with emphasis on the North Pacific Ocean.

Equations for Nutrient Uptake Kinetics

By far the most widely applied equation to describe rates of nutrient uptake by micro-organisms is the Michaelis-Menten (MM) equation:

$$V_{MM} = \frac{V_{max}S}{K_s + S}. \qquad (1)$$

Here, V is the nutrient uptake rate, V_{max} is the maximum possible value of V, K_s is the half-saturation constant, and S is the concentration of the nutrient. The widely applied Monod equation for growth of micro-organisms has precisely the same form, and, in fact, most large-scale (e.g., regional or global) models of lower-trophic marine ecosystems and biogeochemistry do not distinguish between growth and nutrient uptake (i.e., most such models assume a
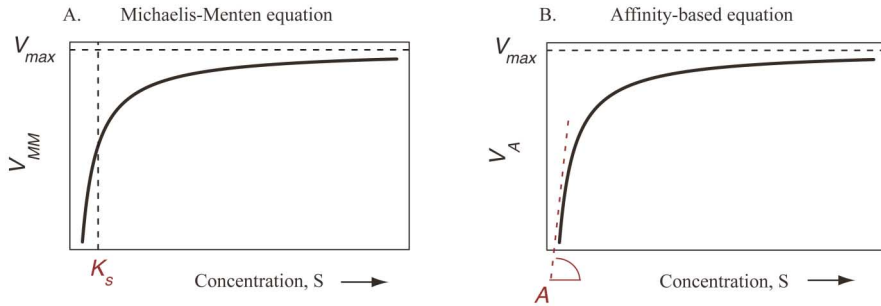
A.   Michaelis-Menten equation

B.   Affinity-based equation

Fig. 1. Equations (1) and (2) describe the same shape, only in terms of either the half-saturation constant, K_s, or the affinity, A, respectively. The affinity-based equation provides a more natural description, with a more intuitive interpretation, because at low nutrient concentrations the affinity is the primary determinant of the uptake (or growth) rate and the relevant indicator of competitive ability for nutrient (Button 1978; Healey 1980). With Eq. (1), changing either V_{max} or K_s changes the affinity, which is equal to V_{max}/K_s, whereas with Eq. (2) these two parameters are naturally separated.

constant composition of biomass, in which case growth and nutrient uptake differ only by a constant, e.g., the C:N ratio).

Although Eq. (1) is theoretically well founded for a chemical reaction governed by a single enzyme, for which it was originally derived, its application at the level of whole cells is not theoretically justified, but is only a matter of mathematical convenience; i.e., because the equation describes a saturating response curve as typically observed for both nutrient uptake and growth as a function of nutrient concentration (Dugdale 1967; Healey 1980). It was realized over 30 years ago (Button 1978; Healey 1980) that the half-saturation constant is not a fundamental property of micro-organisms at the cellular level, and that the initial slope of the rate vs. concentration curve, termed the *affinity*, is actually what determines the rate of uptake (or growth). Thus, in ecological terms, affinity is the indicator of a micro-organism's competitive ability at low nutrient concentrations (Button 1978; Healey 1980). In terms of Eq. (1), the affinity is $A = V_{max}/K_s$.

As a theoretically well founded alternative to Eq. (1), the following equation

can be derived for nutrient uptake (Aksnes and Egge 1991) or growth (Button and Robertson 1989) of micro-organisms explicitly in terms of the affinity, A:

$$V_A = \frac{V_{max}AS}{V_{max} + AS}. \quad (2)$$

Equation (2) is mathematically equivalent to Eq. (1) (Fig. 1), as can be seen by rearranging Eq. (2) to:

$$V_A = \frac{V_{max}S}{\dfrac{V_{max}}{A} + S}. \quad (3)$$

However, Eq. (2) provides a more natural description of nutrient uptake, and is part of a consistent theoretical framework, which allows variations in kinetic parameters (i.e., the uptake response) to be interpreted in terms of cellular physiology (Aksnes and Egge 1991; Button *et al*. 2004).

Optimal Uptake (OU) kinetics is an extension of affinity-based kinetics, based on a physiological trade-off between V_{max} and A, as postulated by Pahlow (2005). The

rationale for this trade-off is that both the "uptake sites" on the cell surface that transfer nutrients into the cell, and all of the other various enzymes within the cell that process nutrients and assimilate them into biomass, are largely composed of proteins, and therefore nitrogen rich. Thus, Pahlow (2005) formulated the problem of how best to allocated limited internal N resources for nutrient uptake in terms of the fractional allocation of whatever internal pool of N is allocated to nutrient uptake and assimilation. This N pool is assumed to be some portion of the subsistence quota (i.e., the minimum necessary N content to sustain a living cell). The formulation avoids the problem that the exact size of this pool is unknown by setting up the equations only in terms of the fraction of this internal N pool that is allocated to surface sites (contributing to affinity) vs. various internal enzymes for nutrient assimilation (which contribute to V_{max}). In nutrient-rich environments, it should be optimal (i.e., most efficient) to shift the balance towards higher V_{max}, and lower A, and conversely in nutrient-poor environments. The assumption is that phytoplankton *acclimate* by reversibly altering their physiology so as to maximize the uptake rate of whatever nutrient currently limits their growth, and that in so doing they can only increase V_{max} at the expense of decreasing A (or *vice-versa*). The details of the derivation are presented in Smith and Yamanaka (2007). Under the assumption that this physiological acclimation occurs instantaneously, the resulting equation (Pahlow 2005) for the uptake of the single nutrient that limits growth is:

$$V_{lim} = \frac{V_{0lim}S_{lim}}{\frac{V_{0lim}}{A_{0lim}} + 2\sqrt{\frac{V_{0lim}S_{lim}}{A_{0lim}}} + S_{lim}} \quad (4)$$

where V_{0lim} and A_{0lim} are the potential maximum values of V_{max} and A, respec-

tively the limiting nutrient (Smith and Yamanaka 2007).

Smith and Yamanaka (2007) extended OU kinetics to consider multiple nutrients, considering what happens to uptake rates of non-limiting nutrients when phytoplankton optimize their physiology to maximize uptake of the growth-limiting nutrient. Based on the results of continuous culture experiments which revealed that uptake of the same nutrient was faster when it was growth-limiting and slower when non-limiting, they obtained good model-data agreement under the assumption that the fractional allocation of internal N for uptake was the same for all nutrients, and was adjusted by acclimation to the ambient (external) concentration of only the growth-limiting nutrient, S_{lim}. This fractional allocation for affinity, f_A, is calculated as in Pahlow (2005):

$$f_A = \frac{1}{1 + \sqrt{\frac{A_{0lim}S_{lim}}{V_{0lim}}}}. \quad (5)$$

The remainder, $(1 - f_A)$, is assumed to be allocated to V_{max}. The uptake rate of any non-limiting nutrient, having concentration S_{non}, is then calculated as:

$$V_{non} = \frac{(1 - f_A)V_{0non}f_A A_{0non}S_{non}}{(1 - f_A)V_{0non} + f_A A_{0non}S_{non}}. \quad (6)$$

Equations (4), (5) and (6) together constitute the Simple Phytoplankton Optimal Nutrient Gathering Equations (SPONGE) model of multi-nutrient uptake kinetics of Smith and Yamanaka (2007), who showed that these equations agree with data from continuous culture experiments at both extreme nutrient ratios and more typical nutrient ratios, whereas the MM equation greatly overestimates uptake rates of non-limiting nutrients at extreme nutrient ratios.
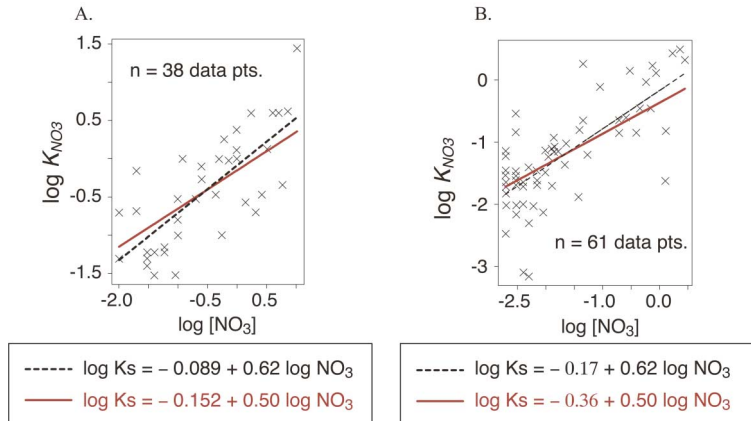
Fig. 2. Data (circles) from ship-board experiments using short-term incubations to determine values of MM half-saturation constants for nitrate uptake, plotted versus the ambient nitrate concentration in the ocean (for each sampling site), together with lines fitted by linear regressions. Black lines show the general linear (log-log) fit as by Collos *et al.* (2005), and red lines show the equation corresponding to the prediction of OU kinetics (Smith *et al.* 2009). (A) for data as compiled by Collos *et al.* (2005), and (B) for the independent data set compiled by Smith *et al.* (2009).

For short-term incubation experiments, as typically used to determine nutrient uptake rates in ship-board experiments, OU kinetics predicts that the values of kinetic parameters should depend on the ambient nutrient concentration in seawater. If phytoplankton do not have time to acclimate to the conditions in the bottles used for the ship-board incubations (to which graded nutrient additions are made in order to re-construct the uptake-vs.-concentration curve), Smith *et al.* (2009) showed that the value of K_s, as obtained by fitting the MM equation to data from such experiments, should increase as the square root of the ambient nutrient concentration. They found that this prediction agreed well with two compilations of field data for nitrate uptake in the ocean (Fig. 2).

Methods

Process modeling of nutrient dynamics during SERIES

We only briefly summarize the methods applied by Smith *et al.* (2010), as they have already been published. The model used is essentially the flexible composition model for phytoplankton, which allows their composition (C and multiple nutrients) to vary, as developed by Smith and Yamanaka (2007), embedded within the marine ecosystem model of Takeda *et al.* (2006), which itself is a variant of the NEMURO (North Pacific Ecosystem Model for Understanding Regional Oceanography) model (Kishi *et al.* 2007).

The key feature is the incorporation of the optimality-based SPONGE model for uptake of multiple nutrients. This model is compared to an otherwise identical model, which applies the widely used Michaelis-Menten kinetics for nutrient uptake, in which the uptake rates of various nutrients are entirely independent of one another (e.g., uptake of N depends only on the ambient concentration of N).

For a rigorous mathematical comparison of the two model versions against the observations, it was necessary to obtain the best possible fit of each version, respec-
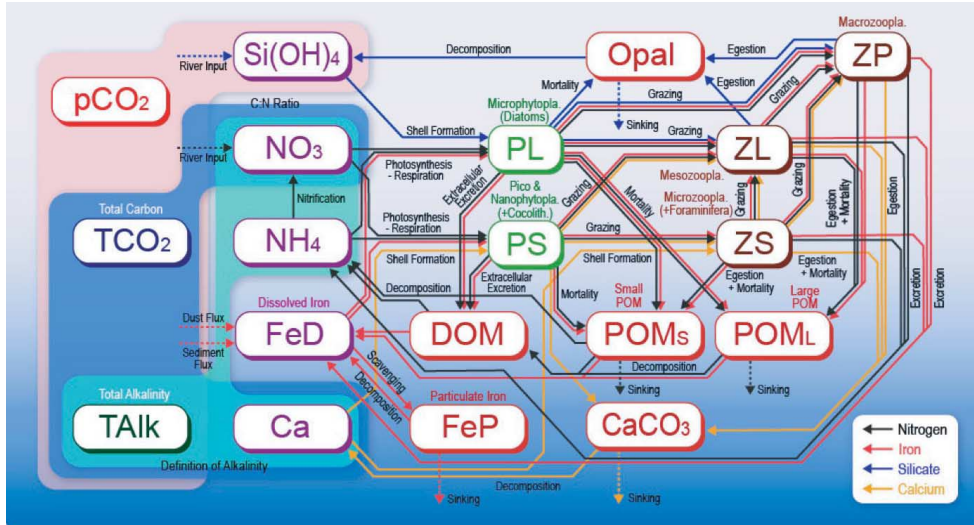
Fig. 3.   Schematic of the structure of the Marine Ecosystem Model (MEM) as described in detail by Shigemitsu *et al.* (2011).

tively, to the same observations. This was done using the Monte Carlo Markov Chain (MCMC), a statistical data assimilation method. Unlike other data assimilation methods, such as the adjoint method, because of its statistical nature MCMC is able to accurately fit strongly non-linear models to data, while avoiding the problem of being trapped in local minima. It also provides not only the best-fit value, but also a complete ensemble of model parameters and model output, which allows the statistics of the output (posterior) distributions to be quantified to assess the uncertainty in the fitted values of both model parameters and model output.

Development of the Marine Ecosystem Model (MEM) for large-scale modeling

The Marine Ecosystem Model (MEM) of Shigemitsu *et al.* (2011) is based on a previously developed ecosystem model (Yamanaka *et al.* 2004; Fujii *et al.* 2007), which is essentially the same as the NEMURO model (Kishi *et al.* 2007). The MEM model includes as compartments: two phytoplankton functional groups (non-

diatom small phytoplankton (PS) and diatoms (PL)), three zooplankton functional groups (micro-(ZS), meso-(ZL) and predatory zooplankton (ZP)), nitrate (NO_3^-), silicate ($Si(OH)_4$), ammonium (NH_4^+), dissolved organic nitrogen (DON), detrital nitrogen (PON), and biogenic silica (Opal). The biomass of each biological component is calculated in terms of nitrogen, and growth rates of phytoplankton may be limited by the ambient concentration of nitrogen, iron, or silicic acid (the last for diatoms only). MEM also includes the carbon cycle, based on the assumption of constant (Redfield) ratios of C:N in all biological components, and accounting for the production of calcium carbonate, assuming that it is produced by a fixed fraction of the small phytoplankton (PS), with a fixed ratio of $C:CaCO_3$ production in their biomass. Figure 3 shows a diagram of the model structure.

The following significant extensions were made, beyond the previous NEMURO model:

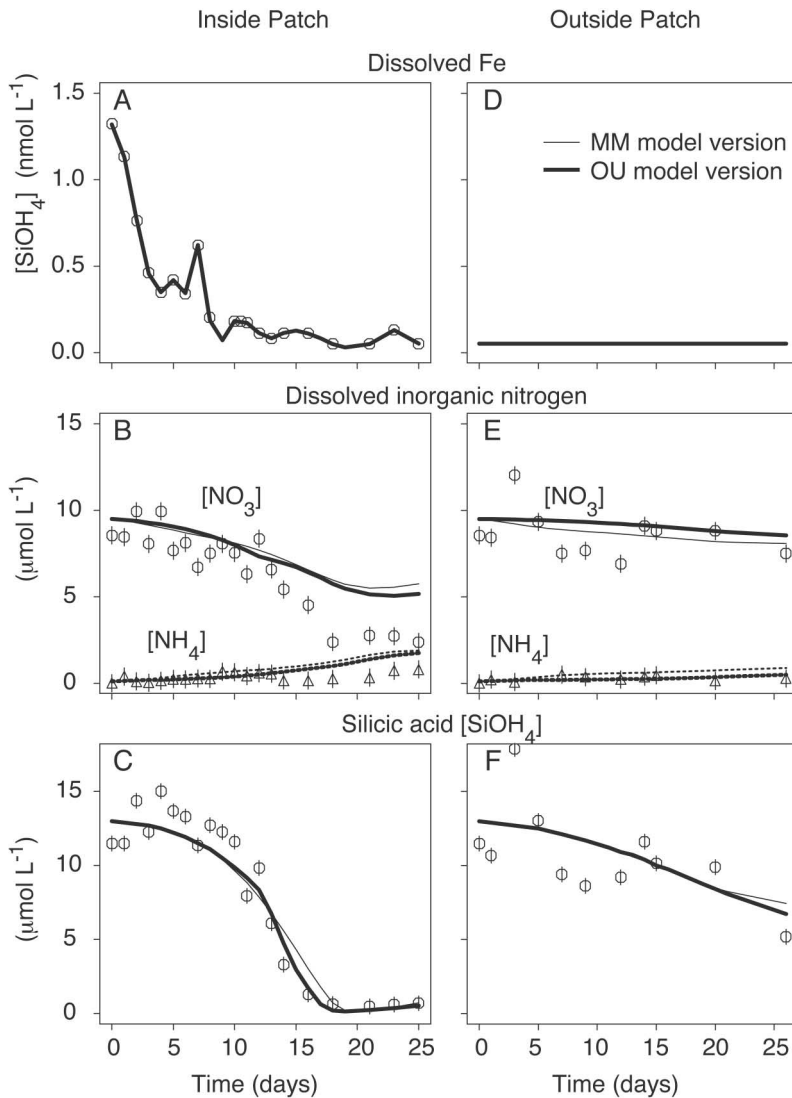(1) The iron cycle was included, mainly based on the parameterization used by

Inside Patch   Outside Patch

Fig. 4.   Observed (circles) and modelled (lines) mean concentrations within the mixed layer during SERIES, both inside and outside the iron-fertilized patch. For dissolved iron, the lines are interpolations (spline fits) between the observations. The addition of iron stimulated growth of phytoplankton within the fertilized patch, which caused the drawdown of dissolved inorganic nitrogen and dissolved silicon.

Moore *et al*. (2004) and Moore and Braucher (2008), considering two components, dissolved iron (Fed) and particulate iron (Fep).

(2) The Michaelis-Menten (MM) equation used to describe nutrient uptake in the NEMURO model (and nearly all planktonic ecosystem models), have been replaced with Optimal Uptake (OU) kinetics (Smith and Yamanaka 2007; Smith *et al.* 2009, 2010), in order to provide a more accurate description of the large-scale pat-
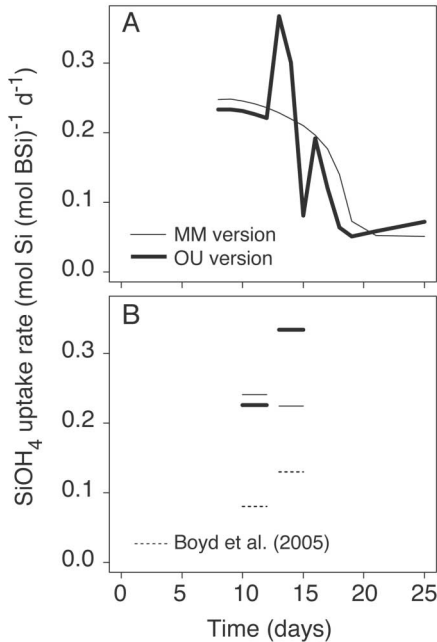
Fig. 5. Changes in uptake rates inside the fertilized patch during SERIES. (A) Instantaneous rates from the model, and (B) time averaged to match the intervals for which Boyd *et al.* (2005) reported observation-based estimates.
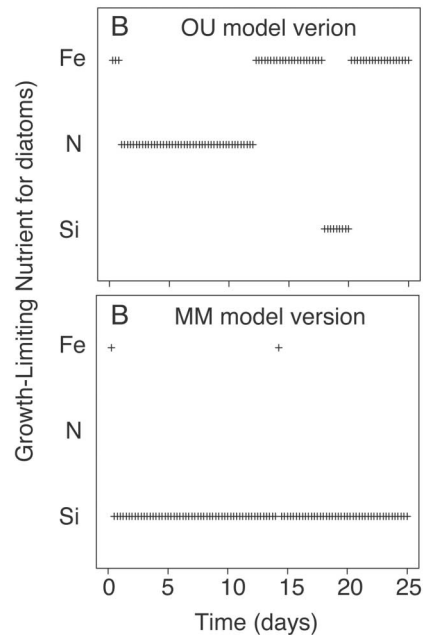

Fig. 6. Patterns of nutrient limitation for diatoms in the OU and MM versions of the ecosystem model, from the best-fit simulation with each model version, respectively.

tern of nutrient uptake response.

(3) PON was divided into two classes, small (PONS) and large (PONL), with distinct settling velocities, and aggregation processes among PONS, PONL and DON are considered as in Aumont and Bopp (2006).

(4) The Wroblewski-type inhibition of nitrate uptake by phytoplankton in the presence of ammonium was replaced with that of Vallina and Le Quéré (2008).

(5) The Steele-type light dependency of phytoplankton photosynthesis (Steele, 1962) was changed into the parameterization proposed by Platt *et al.* (1980).

(6) As in Sumata *et al.* (2010), MEM does not include vertical migration of ZL (as applied in NEMURO), in order to allow the model to be implemented consist-

ently in a three-dimensional Ocean General Circulation Model (OGCM).

In preparation for the implementation of MEM in a three-dimensional OGCM, Shigemitsu *et al.* (2011) implemented it in a one-dimensional (vertical) model of the water column, in order to optimize its parameters and understand its behavior. This model, like most large-scale ecosystem models, assumes a constant composition (e.g., C:N:Si:Fe ratios) for biological components. Under this assumption, uptake rates are directly proportional to the growth rate. The SPONGE model, which was originally formulated for variable composition of phytoplankton, was adapted to this assumption of fixed composition by assuming that growth rate is limited by a single nutrient at any given time, and that uptake of all other nutrients
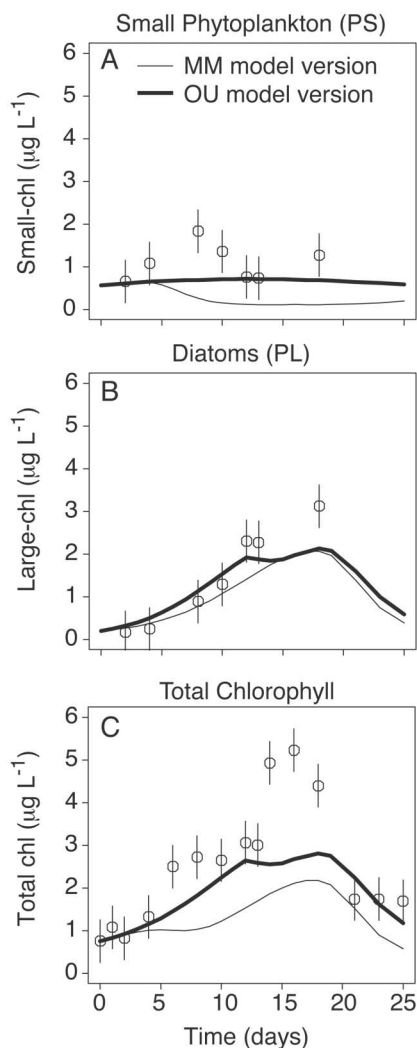
Fig. 7.   Size fractionated chl observations (circles with +/– one standard deviation error bars) for (A) small-size fraction corresponding to non-diatoms (PS in the model), (B) large-size fraction corresponding to diatoms (PL in the model), and (C) total Chl. Lines are the best-fits for each version of the model, respectively. The model version with MM kinetics under-estimates the contribution of PS to total chlorophyll, even in the best-fits obtained using the data assimilation method to adjust model parameters. The OU model version better reproduces the contributions of non-diatoms vs. diatoms, which is important for determining the Si:N drawdown ratio, because only diatoms take up silicon.

is in proportion to the fixed nutrient ratios for each phytoplankton component (PS or PL).

This one-dimensional model was fitted to observations from field studies, consisting of nutrients (nitrate and iron) and chlorophyll, using a micro-genetic data assimilation algorithm as the optimization routine (Krishnakumar 1989). An important goal was to quantify the parameters of the iron cycle, the values of several of which are not well known.

Results and Discussion

Process modeling for nutrient uptake during SERIES

Both versions of the model, using MM and OU kinetics, respectively, could reproduce the drawdown of nutrients inside the iron-fertilized patch (Fig. 4). The model using OU kinetics reproduced the sudden increase in the uptake rate of Si, and the concomitant increase in the Si:N drawdown ratio, as iron again became limiting midway through the experiment, whereas the model using MM kinetics could not reproduce this steep change (Fig. 5). Diatoms (PL in the model) are can be limited by Si, but other small phytoplankton (PS in the model) are not subject to Si limitation.

The patterns of nutrient limitation for non-diatoms (PS) and diatoms (PL) differed greatly in the best-fitted simulations with the MM vs. OU model versions (Fig. 6). This is an important reason for the differences in the reproduction of the dynamics of both the Si:N drawdown ratio (Fig. 5) and the floristic shift between diatoms and non-diatoms (Fig. 7).

This floristic shift changed the ratio of Si to N uptake rates, because only diatoms take up silicon. However, in the OU model version, the increase in Si uptake rate that occurs as iron again becomes limiting (midway through SERIES) also contributes substantially to the overall increase
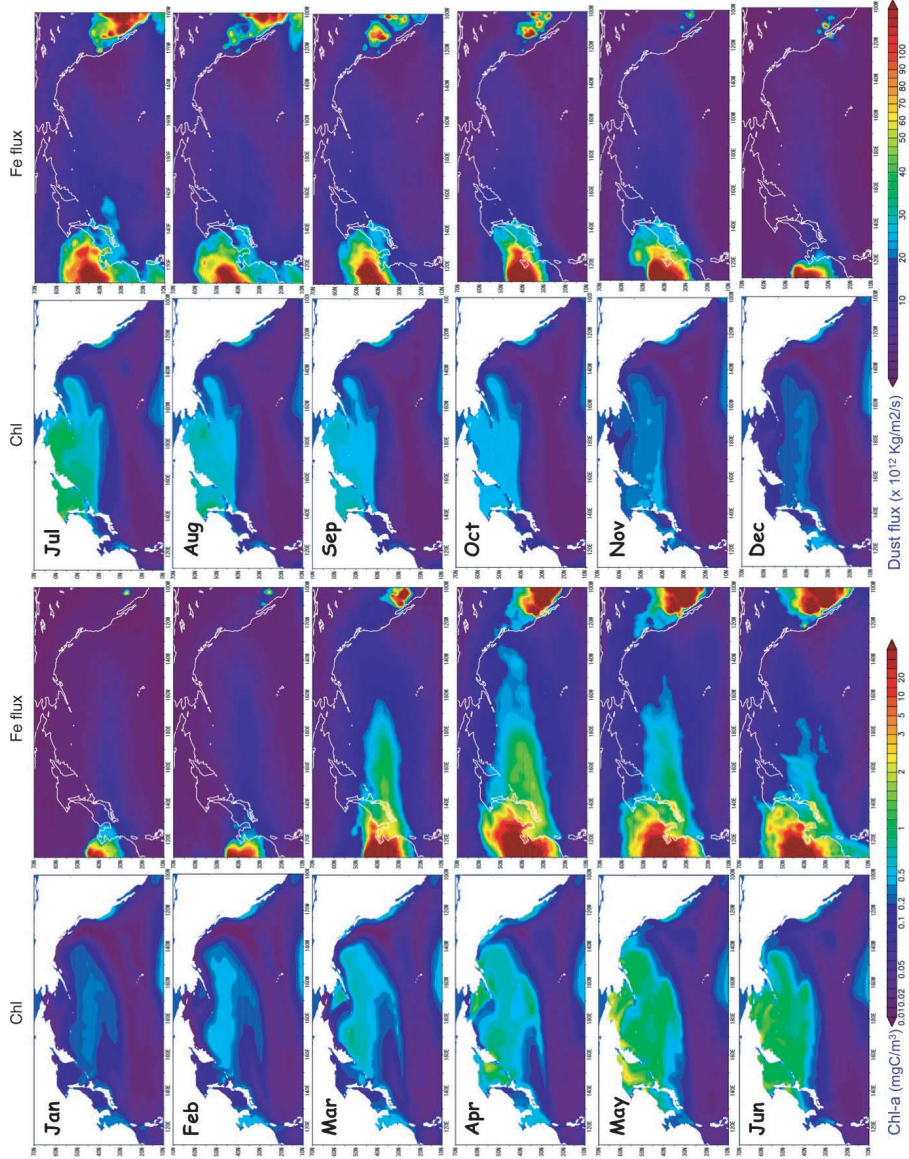
Fig. 8. Preliminary results of a simulation using climatological values of iron flux (prescribed for each month) used as input to the MEM model and the resulting patterns of near-surface chlorophyll concentrations.

in the Si:N uptake ratio. In contrast, with MM kinetics, the uptake rate for each nutrient changes only as a function of its own concentration, and, thus, there is no interdependence of uptake rates. Hence, the smoother changes in the ratio of Si:N uptake rates with the MM model in Fig. 5. With the OU model version, the step changes in uptake rates correspond to changes in the identity of the growth-limiting nutrient, and uptake rates of all nutrients are affected (some positively, others negatively) by changes in the concentration of the growth-limiting nutrient (through Eqs. (5) and (6)).

Development of the Marine Ecosystem Model (MEM) for large-scale modeling

The newly developed MEM will allow large-scale studies of the effects of atmospheric deposition of iron (or other nutrients, such as nitrogen) on the patterns of production by marine ecosystems. Figure 8 illustrates preliminary simulations of patterns of chlorophyll and the corresponding patterns of iron flux (from atmosphere to ocean) used as input to the model. The dust flux data were from SPRINTARS (Takemura *et al*. 2005). Because it incorporates the physiologically-based OU kinetics, it should provide a more realistic representation of how phytoplankton respond to changes in nutrient supply, compared to most existing models which do not account for the adaptive capacity (either physiological acclimation or evolutionary adaptation) of phytoplankton.

Conclusions

The process modelling of SERIES produced a clearly-improved planktonic ecosystem model including multi-nutrient uptake kinetics, as demonstrated by the rigorous comparison (using data assimilation) to the extensive set of data from SERIES (Smith *et al*. 2010). The most important component of this model, the SPONGE model for multi-nutrient uptake (Smith and Yamanaka 2007) was incorporated into the newly developed MEM model for large-scale applications. MEM provides an advanced tool for examining the large-scale response of marine ecosystems and biogeochemistry to changes in nutrient supply and physical forcing, including climate change.

Acknowledgements

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