Ammonium inhibition of nitrate uptake by phytoplankton: A new relation based on similarity and hyperbolicity

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A theoretical formulation based on the properties of similarity and hyperbolicity is given for ammonium inhibition of nitrate uptake by phytoplankton. It leads to a new kinetic relation for ammonium inhibition, which is found to represent the data of nitrogen kinetics experiments of McCarthy *et al.*[1] in the northwest Indian Ocean more accurately than the earlier relations of Wroblewski[2] and O'Neill *et al.*[3]. Analysis of the *f*-ratio (new production/the sum of new and regenerated production) implied by the three relations shows that there is a qualitative difference among the three. The relation of Wroblewski[2] tends to underestimate the new production, while that of O'Neill *et al.*[3] tends to overestimate it.

THE growth of phytoplankton in the open sea and over continental shelf often depends on the nitrogenous nutrient, which is available in several forms. Nitrate is brought into the mixed layer from deeper regions by the processes of upwelling, entrainment, mixing and advection. However, ammonium and nitrite are produced locally by biological processes involving zooplankton and bacteria. The uptake of the former inorganic form of nitrogen is associated with new production. It has been studied extensively following intense interest in elucidating the role of marine biological processes in the carbon cycle, and hence in global warming. While the uptake of each nitrogenous nutrient depends on its concentration according to the Michaelis–Menten relation[4], ammonium is well known to suppress[5] the uptake of nitrate. (Relations that represent the dependence of uptake of nutrients on their concentration and other variables are sometimes termed as laws and sometimes as models. We use the term 'relations' to avoid connotations associated with either word.) The mechanism[6–8] of this nutrient interaction is explained in terms of cell physiology. The nitrate pool within a phytoplankton cell induces synthesis of enzymes for reduction of nitrate through ammonium. However, when ammonium is assimilated into the cell, it gives rise to glutamine on reduction. The glutamine pool suppresses the synthesis of enzymes needed for the reduction of nitrate. What concerns us here is not the mechanism at the cellular level but rather the modelling of the suppressive effect of ammonium, as it affects the dynamics of the marine ecosystem.

The inhibitory effect on nitrate uptake of ammonium can be viewed as a particular case of the uptake of nutrients by phytoplankton in a multi-nutrient environment with possible nutrient interaction. There has been considerable interest in recent times in such cases, especially because limited availability of micronutrients such as iron is found to be limiting phytoplankton growth in some regions. We present here, a theoretical argument for obtaining the relations governing the uptake of nutrients for the two-nutrient case. Its generalization to the multi-nutrient case is given in the Appendix.

The argument rests on two properties, which are assumed. The first one, similarity, requires that the normalized uptake in nutrient-uptake experiments in which only one nutrient is varied depends only on the concentration of that nutrient. This property is ubiquitous in nonlinear phenomena. Since the dynamics of marine ecosystems is intrinsically nonlinear on account of the Michaelis–Menten relation, one might expect similarity to prevail. It is shown later that the observations of McCarthy *et al.*[1] show similarity[9].

The second property describes the geometry of the plot of the uptake of a nutrient by phytoplankton versus the concentration of a nutrient. If the curve is a rectangular hyperbola with asymptotes parallel to the nutrient uptake and the nutrient concentration axes, the relationship is called hyperbolic. The plot of uptake of a nutrient versus the concentration of the same nutrient is governed by the Michaelis–Menten relation and is known to be hyperbolic. We stipulate the same property for the plot of uptake of one nutrient with the concentration of another nutrient. The hyperbolic character can be traced to the steady-state kinetics of enzymes and is explained in many texts of enzyme kinetics[10] on the basis of Briggs–Haldane steady-state hypothesis. There is a class of inhibitory mechanisms in enzyme kinetics that have this character.

Marine ecosystems generally need several nutrients like N, P and Si, and micronutrients such as Fe, Zn, Cu, Mn, Co and Ni, many of which are available in adequate concentrations in the environment and are not considered

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limiting. There is a possibility that one of the micronutrients is not available in sufficient concentration and it is co-limiting along with nitrogen. If the plot of the uptake of a nutrient versus that micronutrient concentration shows a sigmoid character, a minor modification of the hypothesis of hyperbolicity can take care of this possibility (see Appendix).

The argument for the general two-nutrient case is given in the next section and it is applied to ammonium–nitrate interaction in the following section. This results in a new kinetic relation. The question of whether two widely used kinetic relations of Wroblewski[2] and O'Neill *et al.*[3] have the two properties, is discussed in the subsequent section. The three kinetic relations are then compared with several experimental investigations, including those of McCarthy *et al.*[1]. The consequence of inaccuracy in the representation of nutrient kinetics on the simulations of marine ecosystems is then discussed in general terms by examining the behaviour of the *f*-ratio, which is the ratio of the new production to the total primary production. This analysis indicates in qualitative terms, the effects that can be expected in 3D simulations with biological–physical models. A study of such effects has also been carried out recently at the CSIR Centre for Mathematical Modelling and Computer Simulation (C-MMACS), Bangalore for the Indian Ocean, with a physical oceanographic model (Modular Ocean Model; MOM) coupled with a biological model due to Fasham *et al.*[11,12], and its results are being published elsewhere[13].

Two-nutrient kinetic relations

We give here, arguments for the two-nutrient case for simplicity. The general treatment of the multi-nutrient case is given in the Appendix. Consider the nutrient kinetic relations in the following form:

$$\rho_i = PF_i(I, N_1, N_2), \tag{1}$$

where the i takes values 1 and 2. P and I stand for phytoplankton biomass and photosynthetically active irradiance. ρ_i and N_i denote the uptake and the concentration of the ith nutrient. F_i denotes the functional relation of per capita or specific uptake of the ith nutrient by a given phytoplankton population with the irradiance and the concentration of the two nutrients. The effect of temperature is not explicitly shown, but it is understood that since the rate constants of the underlying biochemical reactions depend on temperature, kinetic parameters such as half-saturation constants would, in general, depend on temperature.

Consider now an experiment on a given phytoplankton population in which the concentration of nutrient 1 is varied keeping P, I and N_2 fixed. If the uptake of the ith nutrient normalized with its value for a selected reference value of N_1 depends only on N_1, then we say that the kinetic relation for the ith nutrient is similar with respect to N_1. That is, similarity with respect to the first nutrient requires, by definition, that

$$\frac{\rho_i}{\rho_i^{\mathrm{r}}} = \frac{F_i(I, N_1, N_2)}{F_i(I, N_1^{\mathrm{r}}, N_2)} = g_i(N_1), \tag{2}$$

where N_1^{r} is the reference value of N_1, ρ_i^{r} denotes the uptake at N_1^{r}, and g_i is some function of N_1. The above relation implies that if several such experiments are carried out for the given phytoplankton population under different conditions, i.e. for different I and N_2, and the observed values of normalized uptake are plotted against N_1, the datapoints would lie in a narrow band around a curve.

Similarity with respect to the nutrient N_2 requires that

$$\frac{F_i(I, N_1, N_2)}{F_i(I, N_1, N_2^{\mathrm{r}})} = h_i(N_2), \tag{3}$$

for some function h_i of N_2. If the kinetic relation is similar with respect to both the nutrients, then eqs (2) and (3) require that

$$\frac{g_i(N_1)}{F_i(I, N_1, N_2^{\mathrm{r}})} = \frac{h_i(N_2)}{F_i(I, N_1^{\mathrm{r}}, N_2)}. \tag{4}$$

Consequently, both the sides have to be independent of N_1 and N_2. Hence, the kinetic relation has to be of the following form:

$$\rho_i = PF_i(I)g_i(N_1)h_i(N_2), \tag{4}$$

for some functions f_i, g_i and h_i.

We could have started with this form as a definition of similarity. However, the argument given above breaks down one hypothesis in terms of the above form of product of functions of single variables into two hypotheses that are individually testable.

Are there any *a priori* reasons to expect similarity in nutrient kinetics? First, nutrient kinetics in the well-studied case when a single nutrient limits the growth of phytoplankton is based on the Michaelis–Menten relation which is nonlinear. Consequently, the dynamics of an ecosystem is fundamentally nonlinear. Nonlinear phenomena in a broad spectrum of disciplines, such as fluid dynamics and nonlinear dynamical systems, often show similarity in one form or another. Second, if similarity were not present, the half-saturation constants of various nutrients would depend on irradiance and the concentrations of other nutrients. In that case, there would be considerable variability in the experimentally determined values of half-saturation constants in the usual kinetics experiments for any given phytoplankton population. The

observed variability is limited and can be explained in terms of experimental techniques.

Consider the functions g_i and h_i in eq. (5). They determine the nature of the geometry of the plot of normalized uptake with either nutrient. It is instructive to recall that the Michaelis–Menten relation used in ecosystems when a single nutrient is limiting phytoplankton growth is based on its counterpart in enzyme kinetics. It is justified by the steady-state hypothesis of Briggs and Haldane[10], which assumes that free enzyme concentration remains approximately constant during the period of interest. The resulting curve of nutrient uptake with respect to nutrient concentration is a rectangular hyperbola, with asymptotes parallel to the two axes. The most general form of this type of curve is given by

$$f(N) = \frac{\mathrm{A} + \mathrm{B}N}{\mathrm{C} + N}, \tag{6}$$

where A, B and C are parameters. The straight lines $f = \mathrm{B}$ and $N = -\mathrm{C}$ are the asymptotes of the hyperbola.

Now consider the forms of g_1 and h_2 in eq. (5). These forms would determine the nutrient kinetics when either nutrient 1 or nutrient 2 is zero. Furthermore, the uptake of the ith nutrient is zero when its concentration is zero. So A has to be zero in these two cases. Thus the assumption of hyperbolicity in the case of g_1 and h_2 yields the well-known Michaelis–Menten relation. What can one say about the functions g_2 and h_1, which characterize the nutrient interaction? There is a class of inhibitory mechanisms that display hyperbolic form of kinetic relation. It is then reasonable to hypothesize that these two functions are also hyperbolic. We further note that since the uptake of nutrient 1 is not, in general, zero when the concentration of nutrient 2 is zero, and vice versa, A will not be in general zero in the case of g_2 and h_1.

Thus, if the kinetic relations in the two-nutrient case have the properties of similarity and hyperbolicity with respect to both the nutrients, their most general form is

$$\boldsymbol{r}_1 = PV_1 \frac{N_1}{\mathbf{k}_1 + N_1} \frac{1 + \mathbf{a}_{12} N_2}{1 + \mathbf{b}_{12} N_2}, \tag{7}$$

$$\boldsymbol{r}_2 = PV_2 \frac{1 + \mathbf{a}_{21} N_1}{1 + \mathbf{b}_{21} N_1} \frac{N_2}{\mathbf{k}_2 + N_2}, \tag{8}$$

where g_1 and h_2 have been normalized to have asymptotically maximum value of unity, g_2 and h_1 have been normalized so that their value is unity when N_1 and N_2 are respectively zero. V_i is proportional to $f_i(I)$ and is the asymptotic per capita uptake of the ith nutrient as its concentration approaches infinity in the absence of the other nutrient. $\mathbf{k}_1$ and $\mathbf{k}_2$ are half-saturation constants of the two nutrients and $\mathbf{a}_{12}$, $\mathbf{a}_{21}$, $\mathbf{b}_{12}$ and $\mathbf{b}_{21}$ are four kinetic coefficients characterizing the nutrient interaction.

When the concentration of the second nutrient is $1/\mathbf{b}_{12}$, the reduction in the uptake of the first nutrient is half of its asymptotic value for large N_2. So $1/\mathbf{b}_{12}$ can be termed as the half-inhibition constant. To highlight this aspect, one can rewrite the eq. (7) as

$$\boldsymbol{r}_1 = PV_1 \frac{N_1}{\mathbf{k}_1 + N_1} \left(1 - \frac{\mathbf{c}_{12} N_2}{\mathbf{k}_{12} + N_2} \right), \tag{9}$$

where $\mathbf{k}_{12} = 1/\mathbf{b}_{12}$ and $\mathbf{c}_{12} = 1 - \mathbf{a}_{12}/\mathbf{b}_{12}$, and a similar relation can be written for eq. (8). $\mathbf{c}_{12}$ can be termed as the asymptotic inhibition constant.

Several types of interactions can be distinguished by examining the value of $\mathbf{a}_{12}/\mathbf{b}_{12}$.

Case I: $\mathbf{a}_{12}/\mathbf{b}_{12} = 0$. Here, as the second nutrient increases, the uptake of the first nutrient asymptotically approaches zero. This type of interaction can be termed as total or unlimited inhibition.

Case II: $0 < \mathbf{a}_{12}/\mathbf{b}_{12} < 1$. There is a positive threshold below which the uptake of the first nutrient cannot be reduced, no matter how large the concentration of the second nutrient.

Case III: $\mathbf{a}_{12}/\mathbf{b}_{12} = 1$. Here, the uptake of the first nutrient is not affected by the concentration of the second nutrient.

Case IV: $\mathbf{a}_{12}/\mathbf{b}_{12} > 1$. The uptake of the first nutrient increases as the concentration of the second nutrient increases. The second nutrient enhances the uptake of the first nutrient.

Case V: $\mathbf{a}_{12}/\mathbf{b}_{12} < 0$. Since negative values of uptake do not make any sense, negative values of $\mathbf{a}_{12}/\mathbf{b}_{12}$ are inadmissible.

Similar comments apply to $\mathbf{a}_{21}/\mathbf{b}_{21}$. Consider the case when $\mathbf{a}_{21}/\mathbf{b}_{21}$ is one. Then, eq. (8) simplifies to

$$\boldsymbol{r}_2 = PV_2 \frac{N_2}{\mathbf{k}_2 + N_2}. \tag{10}$$

Further, if $\mathbf{a}_{12}/\mathbf{b}_{12}$ is not one, the number of kinetic coefficients characterizing the interaction reduces to two. If $\mathbf{k}_{12}$ $(= 1/\mathbf{b}_{12})$ happens to be equal to $\mathbf{k}_2$, the number of additional coefficients needed to characterize the interaction of the second with the first reduces to one.

Ammonium–nitrate interaction

Now we assume that the kinetic relations of the nitrate–ammonium system have the properties of similarity and hyperbolicity with respect to both nutrients. We further assume, on the basis of extensive experiments[5], that the

nitrate concentration does not affect the uptake of ammonium. It then follows from the previous arguments that eqs (7) and (10) govern the kinetics of these nutrients. Finally, we assume that V_2/V_1 is unity. This assumption means that for any irradiance and temperature, the asymptotically maximum uptake of nitrate when ammonium is absent is equal to the asymptotically maximum uptake of ammonium when nitrate is absent. Then the kinetics of the ammonium–nitrate system is characterized by three or four parameters depending on whether $1/\mathbf{b}_{12}$ is equal to $\mathbf{k}_2$ or not. While $\mathbf{k}_1$ and $\mathbf{k}_2$ can be determined from the usual experiments, the remaining coefficients have to be determined from interaction experiments. Since these kinetic coefficients are dependent ultimately on the metabolic reactions, they would, in general, depend on the species structure of the phytoplankton population and temperature.

Comparison with other kinetic relations

We now compare eqs (7) and (10) with two sets of kinetic relations that are currently in use in simulations of marine ecosystems. Wroblewski[2] proposed the following relation for the uptake of nitrate in the presence of ammonium on the basis of experiments of Walsh and Dugdale[14].

$$\rho_1 = PV_1 \frac{N_1}{k_1 + N_1} e^{-\psi N_2}, \tag{11}$$

where Ψ is the inhibition parameter. He also assumes that the uptake of ammonium is not influenced by the nitrate concentration, and uses eq. (10), and $V_2/V_1 = 1$. The above relations have been extensively used in marine ecosystem simulations[15–19]. Clearly, the above relations have the property of similarity with respect to both the nutrients. However, eq. (11) is hyperbolic with respect to nitrate only.

The following relations, which have found some acceptance recently[20,21] in the marine ecosystem simulations, are due to O'Neill *et al.*[3]:

$$\rho_1 = PV_1 \frac{\mathbf{k}_2 N_1}{\mathbf{k}_1\mathbf{k}_2 + \mathbf{k}_2 N_1 + \mathbf{k}_1 N_2}, \tag{12}$$

$$\rho_2 = PV_1 \frac{\mathbf{k}_1 N_2}{\mathbf{k}_1\mathbf{k}_2 + \mathbf{k}_2 N_1 + \mathbf{k}_1 N_2}. \tag{13}$$

The above relations are hyperbolic with respect to both the nutrients, but neither of them is similar with respect to either nutrient. Also, the inhibition of nitrate uptake is near total at large ammonium concentrations. It should be noted that there is no additional parameter arising from the interaction between nitrate and ammonium.

Although a few other relations have been proposed[22–24], we will however confine our discussion to the above two here, as they have found significant acceptance in marine ecosystem simulations. A critical evaluation of six sets of kinetic relations, including these two and the present relations, is given elsewhere[13].

Comparison with experimental observations

Dortch[5], in her extensive study of the effect of ammonium on nitrate uptake in 1990, concluded that 'Even though it is not possible at present to model nitrate uptake accurately because of uncertainty about the interaction between ammonium and nitrate uptake, it is quite evident that the simplistic view that nitrate uptake is reduced to zero if ammonium exceeds 1 μM, would often result in large underestimates of nitrate uptake and new production.' Since the relations of Wroblewski as well as O'Neill *et al.* require that the nitrate uptake goes to zero when ammonium is sufficiently large, these relations have been known to be inaccurate, especially at large values of ammonium concentrations. The present kinetic relation given by eqs (7) and (10) does not suffer from this deficiency, as limited inhibition occurs if $0 < \mathbf{a}_{12}/\mathbf{b}_{12} < 1$.

We now consider the results of the recent nitrogen kinetics experiments of McCarthy *et al.*[1]. These investigations were conducted during two US JGOFS Arabian Sea Process Study cruises aboard R/V *T. G. Thompson*. The first one (January–February 1995) is estimated to have occurred during the late NE monsoon and the second (October–November 1995) during the early part of the subsequent NE monsoon. Further details can be found elsewhere[1,9]. Figure 1 shows the results of six experiments reported by McCarthy *et al.*[1], in which the nitrate

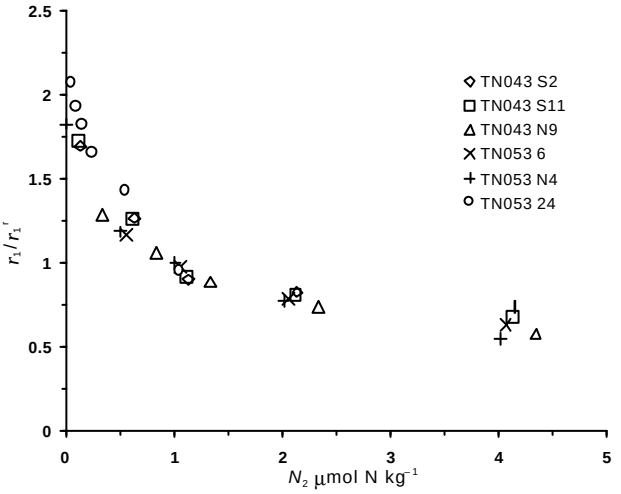

Figure 1. Normalized nitrate uptake vs ammonium concentration in the experiments of McCarthy *et al.*[1]. $N_1^r = 1$ μM. The experiments were performed on the cruises TN043 and TN053 during the NE monsoon in 1995. Notation for JGOFS stations is as in McCarthy *et al.*[1].

uptake is measured by varying ammonium concentration, keeping nitrate and irradiance fixed. The reference value of ammonium used for normalizing nitrate uptake has been taken at 1 μM. The values of nitrate uptake at the reference value are determined by linear interpolation from the experimental data in numerical form supplied by the authors. One could have taken another reference value such as zero ammonium. In that case, extrapolation would have resulted in greater errors in the reference value and hence in larger scatter. Figure 1 shows that if one allows for a certain amount of scatter, the normalized nitrate uptake depends only on ammonium concentration. If one supposes that the phytoplankton populations at the six stations during the two cruises have essentially the same species structure, the experimental observations are consistent with the hypothesis of similarity. Considering that the two cruises were in the northwestern Indian Ocean and during two successive NE monsoon seasons, the assumption of homogeneity of the species structure of phytoplankton population is not unreasonable.

A time-tested method for verifying the correctness of a nonlinear representation of experimental data is to transform, if possible, the variables in such a way that the representation appears as a linear relationship amongst the transformed variables. We apply this method to test the two earlier relations.

We first examine the validity of Wroblewski's relations. It follows from eq. (11) that

$$\ln(r_1 / r_1^{\mathrm{r}}) = \Psi(N_2^{\mathrm{r}} - N_2). \tag{14}$$

The plot of logarithm of normalized uptake versus ammonium is a straight line, according to Wroblewski's relation. The observations of McCarthy *et al.*[1] are shown in Figure 2, along with the straight line given by the above relation with $\Psi = 1.5\ \mu M^{-1}$. Clearly, the experimental data do not show an exponential trend. Since the experimental curve is not linear, one can fit straight lines with different slopes. For example, one could choose different values of Ψ so that the line is tangential at different points. Indeed, if the reference value of ammonium for normalization had been chosen as zero, the line given by eq. (14) would be approximately tangential. Although eq. (11) is not an accurate representation over the range of ammonium concentrations of the experiment, it is a useful approximation for small values of ammonium. A more serious difficulty from a fundamental point of view is that there are no known mechanisms of inhibition in enzyme kinetics that have an exponential trend. So, there are no biochemical grounds for believing that an exponential representation is qualitatively correct.

Now, let us turn to the relations of O'Neill *et al.* The reciprocal nitrate uptake varies linearly with ammonium concentration, according to eq. (12). Figure 3 is a plot of $1/r_1$ vs N_2 for the observations. If eq. (12) were an accurate representation of experimental data, the experimental curves would be straight lines. There is, however, a detectable curvature for low values of ammonium. A more serious problem is that eq. (12) does not have the property of similarity with respect to ammonium, which experimental data of McCarthy *et al.*[1] show. Clearly, eq. (12) cannot be viewed as a qualitatively correct representation.

Finally, we evaluate the present relation in a direct way. Open symbols in Figure 4 give the experimental values of nitrate uptake and those given by curves have been calculated using eq. (8) with the kinetic parameters $\mathbf{a}_{12} = 1\ \mu M^{-1}$, $\mathbf{b}_{12} = 3\ \mu M^{-1}$. The nitrate uptake in the absence of ammonium for each experiment (Table 1) is first obtained by using a least square fit for each experiment. This value is used in calculating the values of nitrate uptake based on eq. (8) in Figure 4. The present relation not only captures the qualitative trend, but also is rather accurate.

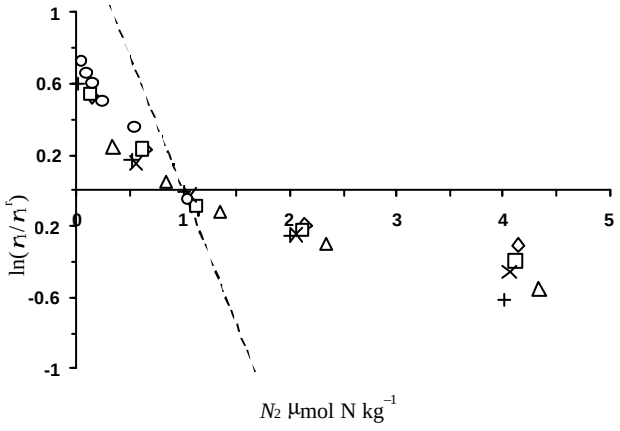

Figure 2. Natural logarithm of normalized nitrate uptake vs ammonium. The data of Figure 1 are replotted in log-linear scale. The dotted line is for eq. (14) with $\Psi = 1.5\ \mu M^{-1}$. This is the commonly used value of the inhibition parameter and is close to that used by Wroblewski. The remaining notations are as in Figure 1.

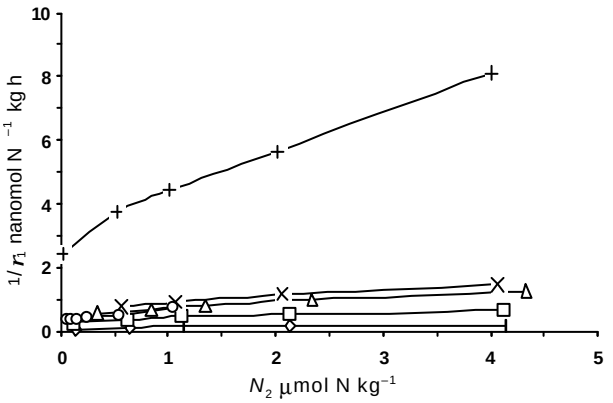

Figure 3. Reciprocal nitrate uptake vs ammonium concentration for the observations of McCarthy *et al.*[1]. Notation is as in Figure 1.

Table 1. Normalizing scales for normalization of nitrate uptake for six datasets in the experiments of McCarthy *et al.*[1]

Cruise	TN043	TN043	TN043	TN053	TN053	TN053
Station	S2	S11	N9	6	N4	24
Nitrate uptake in the absence of ammonium $PV_1N_1/(\mathbf{k}_1 + N_1)$ (n mol kg^{-1} h^{-1})	13.58	4.63	2.58	2.09	0.42	3.20

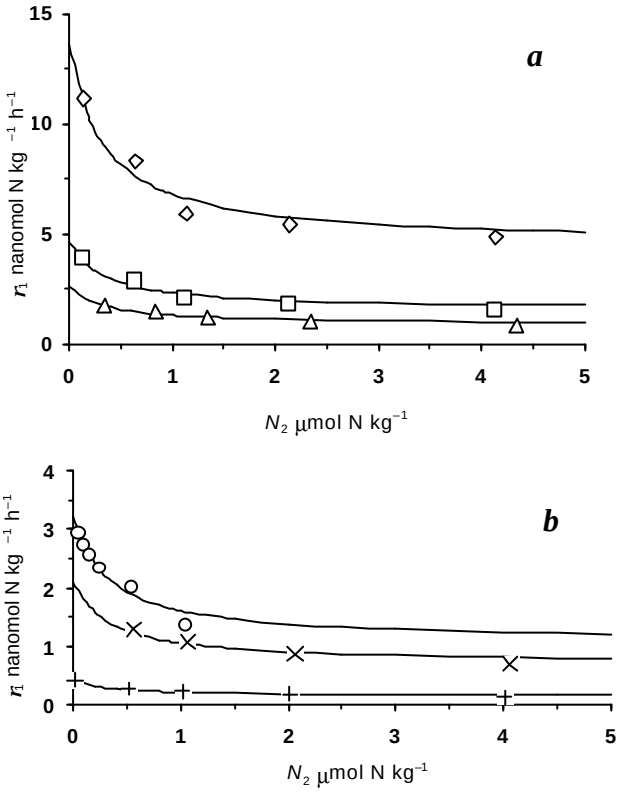

Figure 4 *a* and *b*. Nitrate uptake vs ammonium concentration: Comparison of values calculated using the eq. (8) (——) with experimental data. $\mathbf{a}_{12} = 1$, $\mathbf{b}_{12} = 3$. Values of nitrate uptake in the absence of ammonium are given in Table 1. Notation is as in Figure 1.

The above experiments were examined in some detail, as they are considered definitive. The ranges of nitrate uptake as well as ammonium concentration are rather large (the ratio of maximum to minimum values being above 20). Finally, when the ambient concentration of nitrate or ammonium was very low, McCarthy *et al.*[1] used high precision methods of Garside[25] and Brzezinski[26].

Harrison *et al.*[27] have reported results of ammonium inhibition of nitrate uptake on several cruises in the North Atlantic. As the relations used earlier did not adequately represent their data on nutrient kinetics, Harrison *et al.*[27] correlated their data by expressing normalized nitrate uptake as a function of ammonium addition rather than ammonium concentration. They explained their decision by stating that they found that their measurements of ambient ammonium concentration were not reliable. In retrospect, one realizes that they were at a disadvantage, as they did not use a sensitive method such as that of Brzenzski[26], which is capable of detecting nanomolar concentrations of ammonium. In order to interpret the findings of Harrison *et al.*[27] in the context of the present work, let N_2^{a}, r_1^{a}, and $\Delta N_2 (= N_2 - N_2^{\mathrm{a}})$ denote the ambient ammonium of the sea water sample, the nitrate uptake under the ambient conditions and the ammonium addition to a particular subsample. Then eq. (7) can be written as follows:

$$\frac{\boldsymbol{r}_1}{\boldsymbol{r}_1^{\mathrm{a}}} = 1 - \frac{c'_{12}\Delta N_2}{k'_{12} + \Delta N_2}, \tag{15}$$

where c'_{12} and k'_{12} are given by

$$c'_{12} = 1 - \frac{\mathbf{a}_{12}(1 + \mathbf{b}_{12} N_2^{\mathrm{a}})}{\mathbf{b}_{12}(1 + \mathbf{a}_{12} N_2^{\mathrm{a}})}, \tag{16}$$

$$k'_{12} = \frac{1 + \mathbf{b}_{12} N_2^{\mathrm{a}}}{\mathbf{b}_{12}}. \tag{17}$$

Harrison *et al.*[27] determine the quantities c'_{12} and k'_{12} by fitting an equation essentially equivalent to eq. (15), without reporting the ambient ammonium concentration. They interpret these quantities as kinetic parameters. Clearly, their determination of these quantities is consistent with eq. (8). But the reported quantities are not true kinetic parameters; Harrison *et al.*[27] find considerable variability in the values of c'_{12} and k'_{12}, some of which is evidently due to the variability in the ambient ammonium concentration. This dependence of their reported quantities on the ambient concentration makes it difficult to correlate their values with other results.

Lomas and Glibert[28] have conducted laboratory experiments on the interaction between ammonium and nitrate uptake in two species of diatoms (*Chactoceros* sp. and *Thalassiosira weissflagii*) and two species of dinoflagellates (*Prorocentrum minimum* and *Gyrodinium uncatentum*) at three temperatures (4, 10 and 20°C). Addition of ammonium was varied from 0 to 200 μM. They applied an equation equivalent to eq. (10). In their case, the initial ammonium concentration of the culture, i.e. N_2^{a} was zero. Hence, the quantities c'_{12} and k'_{12} reduce to true kinetic parameters, $\mathbf{c}_{12}$ $(= 1 - \mathbf{a}_{12}/\mathbf{b}_{12})$ and $\mathbf{k}_{12}$ $(= 1/\mathbf{b}_{12})$. They determined that the half inhibition constant $\mathbf{k}_{12}$ varied from 0.24 to 4.64 μmol N l^{-1} depending on species and temperature. Similarly, the asymptotic inhibition constant $\mathbf{c}_{12}$ varied from 0.60 to 0.99.

In view of the results of these experimental investigations, one concludes that the hypotheses of similarity and hyperbolicity find sufficient support from experiments.

Implications on *f*-ratio

The question of the nature of effects of inaccuracies in the representation of interaction of ammonium and nitrate uptake on the dynamics of the marine ecosystem can be broadly addressed by considering the effect of the interaction on the *f*-ratio. It is defined as the ratio of the new primary production to the total primary production and given in present notation by

$$f = \frac{\rho_1}{\rho_1 + \rho_2}. \tag{18}$$

If the *f*-ratio is larger than 0.5, the nutrients brought into the euphotic layer by physical processes are the major contributors to the primary production. If it is smaller than 0.5, the recycled nutrients contribute more to the primary production. The expressions of *f*-ratio for the three formulations are given in Table 2.

Figure 5 compares the variation of the *f*-ratio with nitrate concentration for three values of ammonium concentration. The values of half-saturation parameters $\mathbf{k}_1$ and $\mathbf{k}_2$ have been taken as 1.7 and 0.47 μmol N kg^{-1} on the basis of measurements by McCarthy *et al.*[1]. $\mathbf{a}_{12}$ and $\mathbf{b}_{12}$ have been taken as 1 and 3 μmol N^{-1} kg, as explained earlier. V_2/V_1 has been set as unity for all the relations. The inhibition parameter Ψ in Wroblewski's relation has been taken as 1.5 μmol N^{-1} kg, which is the customary value. These values of parameters can be viewed as applicable to natural populations of phytoplankton in the northwest Indian Ocean. All the three relations give an increasing trend of *f*-ratio with increasing nitrate, for a fixed concentration of ammonium. Also, the *f*-ratio variation with increasing nitrate for Wroblewski's relation is indistinguishable from that for the present relation at ammonium concentration of 0.1 μmol N kg^{-1}. Indeed, it can be shown that if the following condition is satisfied, the difference between *f*-ratio values given by Wroblewski's relation differs form that given by the present relation by less than 10%:

$$\left|1 - \frac{V_2(1+\mathbf{b}_{12}N_2)\mathrm{e}^{-\Psi N_2}}{V_1(1+\mathbf{a}_{12}N_2)}\right| < 0.1. \tag{19}$$

Table 2. Expressions for *f*-ratio in three formulations

Relation	Expression for *f*-ratio
Wroblewski	$\dfrac{N_1(\mathbf{k}_2 + N_2)\mathrm{e}^{-\Psi N_2}}{\mathbf{k}_2 N_1 \mathrm{e}^{-\Psi N_2} + \mathbf{k}_1 N_2 + N_1 N_2 (1+\mathrm{e}^{-\Psi N_2})}$
O'Neill *et al.*	$\dfrac{\mathbf{k}_1 N_2}{\mathbf{k}_1 N_2 + \mathbf{k}_2 N_1}$
Present	$\dfrac{V_1 N_1 (\mathbf{k}_2 + N_2)(1+\mathbf{a}_{12}N_2)}{V_1 N_1 (\mathbf{k}_2 + N_2)(1+\mathbf{a}_{12}N_2) + V_2 N_2 (\mathbf{k}_1 + N_1)(1+\mathbf{b}_{12}N_2)}$

Thus if ammonium concentration is less than 0.347 μmol N kg^{-1} for the values of parameters mentioned earlier, the *f*-ratio given by Wroblewski's relation agrees with that for the present relation to within 10%. However, for larger values of ammonium concentration, the value of *f*-ratio for Wroblewski's relation differs from that for the present relation by more than 10%.

One qualitative difference amongst the three relations is that unlike the one by O'Neill *et al.*[3], ammonium concentration sets a limit to how large the *f*-ratio can be for the other two relations (Table 3 and Figure 6).

As shown in Figure 6, the maximum value is one for all ammonium concentrations in the case of the relation by O'Neill *et al.*[3], and it goes exponentially to zero in the case of Wroblewski's relation. In the present case, the maximum value of the *f*-ratio varies between 1 and $V_1\mathbf{a}_{12}/(V_1\mathbf{a}_{12} + V_2\mathbf{b}_{12})$. So, the present formulation sets a limit

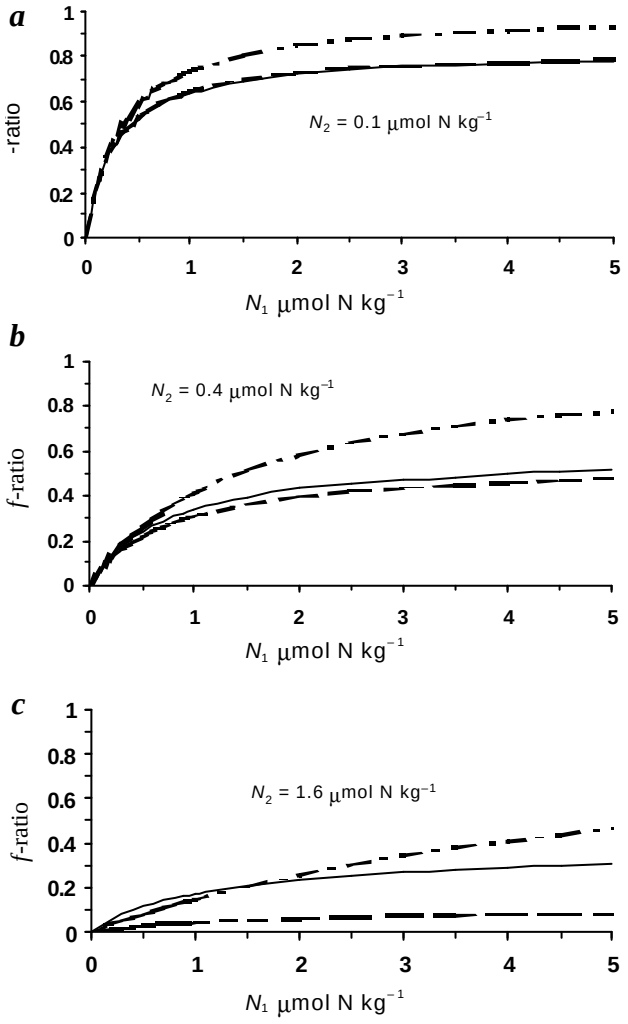

Figure 5 *a–c*. Variation of *f*-ratio with nitrate concentration for a given ammonium concentration for Wroblewski's relation (- - - -), O'Neill *et al.*'s relation (— - —), and the present relation (——). $\mathbf{k}_1$ = 1.7 μmol N kg^{-1}, $\mathbf{k}_2$ = 0.47 μmol N kg^{-1}, Ψ = 1.5 μmol N^{-1} kg, $\mathbf{a}_{12}$ = 1 μmol N^{-1} kg, $\mathbf{b}_{12}$ = 3 μmol N^{-1} kg, V_2/V_1 = 1.

Table 3. Maximum values of *f*-ratio for a given ammonium concentration

Relation	Maximum *f*-ratio
Wroblewski	$1-\frac{N_2}{(\mathbf{k}_2+N_2)e^{-\mathbf{Ø}N_2}+N_2}$
O'Neill *et al*.	1
Present	$1-\frac{V_2N_2(1+\mathbf{b}_{12}N_2)}{V_1(\mathbf{k}_2+N_2)(1+\mathbf{a}_{12}N_2)+V_2N_2(1+\mathbf{b}_{12}N_2)}$

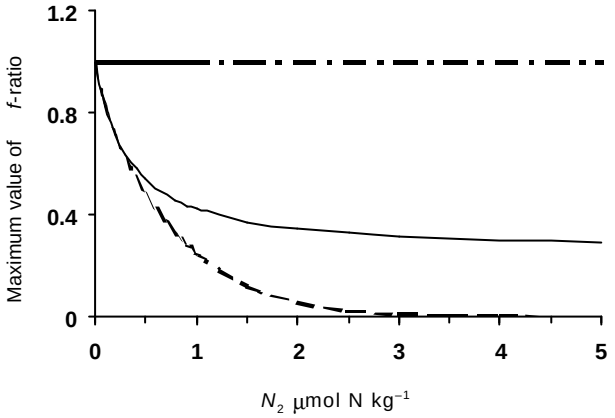

Figure 6. Maximum value of *f*-ratio for a given ammonium concentration vs ammonium concentration. Notations and values of parameters are the same as in Figure 5.

on the maximum relative share of recycled nutrients in the primary production to a value that is intermediate between the two extremes given by the other two formulations.

Concluding remarks

A new formulation for the interaction of ammonium and nitrate uptake is given. It is shown that there is a fair amount of experimental evidence to support the hypotheses of similarity and hyperbolicity on which the formulation rests. The present kinetic relation of ammonium inhibition of nitrate uptake is shown to provide a more accurate representation of experimental data than those of Wroblewski[2] and O'Neill *et al.*[3]. The value of the *f*-ratio for Wroblewski's relation agrees with that for the proposed relation within 10%, if the ammonium concentration is less than 0.347 μmol N kg^{-1} for the selected values of kinetic parameters on the basis of JGOFS experiments in the Indian Ocean. For larger ammonium concentration, the former is smaller than the latter by more than 10%. The variation of the *f*-ratio with nitrate for the relation by O'Neill *et al.*[3] for a given ammonium concentration, on the other hand, differs qualitatively from that for the other two relations, as ammonium concentration does not limit the maximum value of the *f*-ratio for this relation. The implications on the *f*-ratio highlight the effects of inaccuracies in the modelling of interaction of ammonium and nitrate uptake on the possibility of significant errors in the simulations for marine ecosystems. A related investigation has been carried out at C-MMACS on the effects of various representations of nutrient interaction on the simulations of the marine ecosystem in the Indian Ocean, with a three-dimensional physical oceanographic model coupled with a biological model; the results are published elsewhere[13].

Appendix

Nutrient kinetics in an interactive multi-nutrient environment

We give here a generalization of the preceeding arguments to a general multi-nutrient case. Let the environment of phytoplankton have M nutrients and let the concentration of the ith nutrient be denoted by N_i, with the index i running from 1 to M. Let ρ_i denote the uptake (in moles per unit volume or mass per unit time) of the ith nutrient by a marine ecosystem of given species structure in the environment. It will, in general, depend on the phytoplankton biomass P, photosynthetically active irradiance I, and the concentration of the nutrients. We stipulate that, for any i and j (for $i, j = 1, 2, \ldots, M$), the relation governing the specific uptake of the ith nutrient under the given environmental conditions is a product of two functions, one depending solely on the concentration of the jth nutrient and the other depending on all other variables. That is,

$$\rho_i(P, I, N_1, \ldots, N_j, \ldots, N_M) = Pf_i(N_j)g_i(I, N_1, \ldots, N_{j-1}, N_{j+1} \ldots, N_M), \quad \text{(A1)}$$

where f_i and g_i are some functions of the arguments given above. The above condition implies that if an experiment is conducted by varying N_j and keeping all other nutrient concentrations and variables fixed, the uptake of the ith nutrient normalized with its value for some reference value N_j^{r} of concentration of the jth nutrient depends only on the concentration of the jth nutrient.

$$\frac{\rho_i}{\rho_i^{\mathrm{r}}} = \frac{f_i(N_j)}{f_i(N_j^{\mathrm{r}})}, \quad \text{(A2)}$$

where ρ_i^{r} $(= \rho_i(P, I, N_1, \ldots, N_j^{\mathrm{r}}, \ldots, N_M))$ is the nitrate uptake at a reference value N_j^{r} of ammonium. Consequently, the datapoints in the plot of the normalized uptake with concentration of the jth nutrient from several such experiments on the same phytoplankton population but under different conditions, would lie in a band around a single curve.

It can be shown using a variation of the argument given earlier that the eq. (A1) can only be met for any i, j

($i, j = 1, 2, \ldots, M$), only if the uptake of the ith nutrient ($i = 1, 2, \ldots, M$) can be expressed in the following form.

$$r_i(P, I, N_1, \ldots, N_j, \ldots, N_M) = PV_i(I)\prod_{j=1}^{j=M} f_{ij}(N_j). \qquad \text{(A3)}$$

The functions V_i give the effect of the irradiance on the uptake of the ith nutrient. As before, the effect of temperature is not explicitly shown. The functions f_{ij} can be normalized suitably.

We next stipulate that the functions f_{ij} are hyperbolic in the sense discussed earlier. The justification for this stipulation comes from steady-state enzyme kinetics, as mentioned earlier. The general form of such functions is

$$f(N) = \frac{\mathbf{A} + \mathbf{B}N}{\mathbf{C} + N}, \qquad \text{(A4)}$$

where **A**, **B** and **C** are parameters and we have not shown the indices for simplicity. The straight lines $f = \mathbf{B}$ and $N = -\mathbf{C}$ are the asymptotes of the hyperbola.

There are two cases to be considered. The case of $\mathbf{A} =$ zero is relevant when $i = j$. In this case the effect of the ith nutrient on the uptake of the ith nutrient can be written in the familiar form of the Michaelis–Menten relation,

$$f_{ii} = \frac{N_i}{\mathbf{k}_i + N_i}, \qquad \text{(A5)}$$

where $\mathbf{k}_i$ are the half-saturation or Michaelis–Menten constants, and the functions f_{ii} are normalized so that their maximum value is one.

The case of non-zero **A** is appropriate for the nutrient inhibition case, i.e. when i and j are different. The functions can then be written in one of two convenient forms, namely either

$$f_{ij} = \frac{1 + \mathbf{a}_{ij}N_j}{1 + \mathbf{b}_{ij}N_j}, \quad i \neq j, \qquad \text{(A6)}$$

or

$$f_{ij} = \left[1 - \frac{\mathbf{c}_{ij}N_j}{\mathbf{k}_{ij} + N_j}\right], \; i \neq j, \qquad \text{(A7)}$$

where $\mathbf{a}_{ij}$, $\mathbf{b}_{ij}$, $\mathbf{c}_{ij}$ ($= 1 - \mathbf{a}_{ij}/\mathbf{b}_{ij}$) and $\mathbf{k}_{ij}$ ($= 1/\mathbf{b}_{ij}$) are the parameters of nutrient interaction, and the functions are normalized so that their value is one when N_j is zero. $\mathbf{c}_{ij}$ is a measure of the maximum inhibition or enhancement possible. If it is positive, there is inhibition and if it is negative, there is enhancement. If $\mathbf{c}_{ij}$ is zero, the jth nutrient does not affect the uptake of the ith nutrient. $\mathbf{k}_{ij}$ is the half-saturation constant of inhibition or enhancement.

Earlier the possibility of sigmoid kinetics of interaction, especially with micronutrient was mentioned. Such a possibility can be easily handled in the above framework by generalizing eq. (A4),

$$f = \frac{\mathbf{A} + \mathbf{B}N^n}{\mathbf{C}^n + N^n}. \qquad \text{(A8)}$$

Here, the index n is taken to be 1 for hyperbolic kinetics and 2 for sigmoid kinetics. Equations (A6) and (A7) can be accordingly modified.

Equation (A3) constitutes M relations governing the kinetics of nutrient interaction, where the functions f_{ij} are of the form eqs (A5) and (A6) or eqs (A5) and (A7), as a consequence of the assumptions of similarity and hyperbolicity. Modifications needed for sigmoid kinetics are clear on the basis of eq. (A8).

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Empirical modelling and forecasting of Indian monsoon rainfall

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Indian monsoon rainfall data is modelled as a nonlinear time series. It is demonstrated that the proposed model accounts for about 50% of the inter-annual variability of the rainfall, as observed in eight sets of data representing All India and regional rainfall values. The model is capable of statistically forecasting seasonal rainfall value one year in advance. The model predicts the drought of 2002, with the help of only antecedent data. For the year 2003, the predicted All India rainfall value is 82.65 ± 4.88 cm.

THE importance of the summer monsoon rainfall, also popularly called south-west monsoon (SWM) rainfall, to Indian society and economy is well known. Efforts to forecast the rainfall at different spatial and temporal scales have been in vogue for nearly a century. These are generally based on developing suitable mathematical models which in turn may be broadly classified as empirical or dynamical. The present work is concerned with empirical models only. Any modelling effort will have to be based on an understanding of the variability of past data. Thus, considerable literature is available on analysis of variability of SWM rainfall data. The works of Mooley and Parthasarathy[1], Gregory[2], Hastenrath and Greischar[3], Rupa Kumar *et al.*[4], Thapliyal[5], Iyengar and Basak[6] may be mentioned in this connection. A general discussion on forecasting of monsoon rainfall is available in the paper by Gadgil *et al.*[7]. A review of the literature on empirical modelling and forecasting has been recently presented by Sahai *et al.*[8,9] and hence will not be repeated here. A basic feature of rainfall data is its non-gaussianness on several temporal and spatial scales. Weekly, monthly and seasonal data at station levels or at regional scales still exhibit strong non-gaussianness even though they can be treated as sums of large number of random variables. Thus, linear time series models based on past rainfall which capture the behaviour near the mean value fairly well, fail to forecast extreme values, such as floods and droughts which are the ones of main concern to the community at large. This property of rainfall data has been recognized by Kedem and Chiu[10] who argue that at a small time scale rain rate has to be a lognormal random variable. These authors highlight that the lognormal distribution is a natural outcome of the law of proportionate effect,

$$R_{j+1} - R_j = \varepsilon_j R_j, \tag{1}$$

where ε_j's are independent identically distributed random variables and are also independent of R_j's. They demonstrate further that this model fits well the hourly rainfall data obtained from the Global Atlantic Tropical Experiment (GATE). Now, since rainfall at other time scales such as weekly and monthly also exhibit strong non-gaussianness, it is natural to ask how eq. (1) can be generalized to model such data. The present paper addresses this question with respect to Indian monsoon seasonal (June–September) data. It is shown that eq. (1) can be systematically extended to account for year-to-year and long term relationships known to exist in monsoon rainfall data. The new model is shown to account for nearly

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