Review

Investigation of mechanistic formulations depicting phytoplankton dynamics for models of marine pelagic ecosystems and description of a new model

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Received 11 October 2005; received in revised form 19 May 2006; accepted 29 May 2006
Available online 24 August 2006

Abstract

Realistic modelling of marine ecosystems is necessary for improving our understanding of the ocean’s biogeochemical state and for predicting their response to anthropic perturbations. An essential step in achieving this task is the use of mechanistic formulations to describe the biogeochemical processes involved in the dynamics of marine pelagic ecosystems. This study provides a review on some modelling strategies for some of the key processes involved in the dynamics of phytoplankton. It encompasses the most advanced work in terms of mechanistic understanding and, therefore, mainly deals with photosynthesis (including photoacclimation and photoinhibition), respiration, and nutrient uptake (including multi-limitation of algal growth by nutrients). We highlight, that in many ecosystem models, phytoplankton processes are still described more or less empirically, mainly due to a lack of biochemical knowledge, or if a mechanistic formulation exists, the parameters are often difficult to assess experimentally. As a result of this investigation, a preliminary structure for a generic phytoplankton model is delivered in the last section of this paper. This model includes a mechanistic representation of photosynthesis/photoinhibition based on photosystem II status, as well as new formulations for photoacclimation and dissolved organic matter exudation processes. The model sensitivity analysis with regard to its parameters and a comparison with chemostat experimental data are presented in a companion paper [Baklouti, M., Faure, V., Pawlowski, L., Sciandra, A., 2006. Investigation and sensitivity analysis of a mechanistic phytoplankton model implemented in a new modular numerical tool (Eco3M) dedicated to biogeochemical modelling. Progress in Oceanography]. Finally, this new class of multi-element, multi-species phytoplankton models will provide the basis for future studies on ecosystem modelling.

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Keywords: Pelagic marine ecosystems; Ecological modelling; Phytoplankton; Mechanistic formulations
1. Introduction

The response of marine pelagic ecosystems to climatic forcings, hydrodynamic forcings or anthropic action (fishing, pollution, . . . ) is still difficult to understand, mainly due to numerous antagonistic feedbacks involved in this response (Falkowski et al., 2000). For example, the response of the marine biota to climate change may be theoretically divided into two components, i.e. changes in the magnitude of bulk rate processes, and shifts in the size-structure and composition of the plankton community (Falkowski et al., 1998). In practice however, recent studies using mechanistic or statistical models to predict the biological response to anthropic perturbations (Cox et al., 2000; Bopp et al., 2001; Boyd and Doney, 2002; Aumont et al., 2003; Moore et al., 2004; Sarmiento et al., 2004) produce a variety of results that are often difficult to interpret and even contradictory to previous studies.

Improving our understanding of how the marine pelagic ecosystem responds to direct or indirect anthropic effects remains a major challenge for oceanographers. The best tool to achieve this aim is undoubtedly modelling, especially models coupling the dynamics of water masses and pelagic ecosystems (e.g. Joos et al., 1999; Aumont et al., 2003). Over the last decade, much effort has been put into the development of deterministic models of marine biology (Sarmiento et al., 2004). However the current generation of ocean biogeochemical models is still in the early stages of development and exhibit a number of deficiencies already pointed out in several papers (Doney, 1999; Gnanadesikan et al., 2002).

One major deficiency is that the performance and behaviour of current ecosystem models strongly depends on the formulation of the key biogeochemical processes (Murray and Parslow, 1999; Gao et al., 2000; Lima et al., 2002). The existence of alternative formulations to describe a given process is actually due to the fact that the process under concern is mathematically described from an empirical point of view. Empirical relationships are generally derived from extensive field experiments and laboratory measurements that enable the
identification of the best set of parameters. The use of models driven by empirical formulations can be particularly appropriate for certain applications, such as the assessment of primary production from remote sensing or biogeochemical modelling on an ocean global scale. However, this approach also has several weaknesses. While appropriate in data-rich areas, this approach is less valid in under-sampled marine systems. Besides, the parameters determined in a given area, with specific ecosystem dynamics, are difficult to extrapolate to other ecosystems with different functioning. Moreover, empirical laws associate parameters that are often biologically and physically meaningless, making them difficult to estimate although many of them have turned out to be meaningful after that the underlying mechanisms have been understood. As a matter of fact, these parameters are hardly referred to as realistic or unrealistic, and they are liable to take on a wide range of values (Baird et al., 2004).

One approach to this issue consists in focusing on mechanistic descriptions in biogeochemical models (Baird and Emsley, 1999). This has the advantage of reducing the need for extrapolation of model parameters (Baird et al., 2003), and it also provides a greater flexibility to the model in the context of site-to-site modelling (Fulton et al., 2004). For example the latter authors showed that the less physiologically detailed an ecological model is, the more tuning of the parameters is required in order to model different ecosystems. The complexity arising from mechanistic models is often invoked as a potential drawback. However, if the description of a given process at the physiological level generally requires a fine scale of observation that subsequently generates intricate formulations, the resulting model can ultimately be simplified and adapted to a larger scale of observation depending on the available experimental measurements.

The actual limit of the mechanistic approach is that the physiological mechanisms driving the key biogeochemical processes (e.g. photosynthesis, uptake, ...) are far from being fully understood (Baird et al., 2003), and this is prejudicial to the development of ocean biogeochemical models that are entirely based on a mechanistic description of the ecological processes incorporated. Clearly advances in this domain depend directly on progress in the experimental knowledge of processes from a physiological i.e. mechanistic point of view, and, as recently stressed in the JGOFS Synthesis Modelling Project (Doney et al., 2002), some areas of field research are advancing more rapidly than others. Hence, although considerable attention has been devoted to some of the processes governing the phytoplankton dynamics and involving molecular biophysics, cellular physiology, seawater bio-optics and community dynamics, other processes such as phytoplankton respiration or loss terms (exudation, senescence, ...) have received less consideration.

The main objective of the present paper is to provide an overview of the mechanistic modelling strategies available in the literature for some of the key biogeochemical processes involved in the dynamics of phytoplankton in pelagic marine ecosystems. We focus on the most advanced work in terms of mechanistic understanding, including the following processes: photosynthesis (including photoacclimation and photoinhibition), autotrophic respiration, photorespiration and nutrient uptake by primary producers. The treatment of the latter process includes cases of algal growth limitation by several nutrients. For each of the aforementioned processes, a set of several potential formulations has been detailed, including empirical as well as mechanistic models when available.

The present work has the main characteristic of gathering together all the components to build a mechanistic model for the phytoplankton dynamics in the pelagic water column. As a result of our investigations, we propose in Section 5 a generic phytoplankton model that includes the available mechanistic formulations from literature only when they handle readily measurable variables and parameters. It also includes new formulations of the photoacclimation and exudation processes. This new class of phytoplankton models will provide the basis of the multi-element and multi-plankton-group models associated with different marine pelagic ecosystems that will be presented in future work.

2. Photosynthesis and photoacclimation

Until a few years ago, most photosynthesis models relied on empirical representations (e.g. Steele, 1962; Platt et al., 1980; Ebenhöh et al., 1997) based on experimental data sets that were interpolated, or even extrapolated. While the mechanistic bases of the $P$ vs. $E$ relationship have been recognized and discussed since the 1930s (Cullen, 1990), the recent effort made by researchers towards a mechanistic description of photosynthesis is now clearly apparent in the literature (Zonneveld, 1997; Zonneveld, 1998; Geider et al., 1998; Han, 2001,
These approaches use parameters that have physical or biological meaning even if they are not always easy to measure. Hence, this section reminds us, in the form of a short review, of the current formalisms describing photosynthesis (and therefore primary production), and it shows the step by step evolution from empirical to mechanistic models.

2.1. General

In this paper, there will be reference either to gross primary production or gross photosynthesis rates, respectively denoted $PP$ (units: mol C m$^{-3}$ s$^{-1}$) and $P$ (units: mol O$_2$ m$^{-3}$ s$^{-1}$), since each can be derived from the other through the photosynthetic quotient $\mathcal{PQ}$ which is the molar ratio of the rate of oxygen production to that of carbon assimilation. Mathematically, the transition from primary production rate to photosynthesis rate is

$$
P = \mathcal{PQ} \cdot PP \quad \text{and} \quad P^* = \mathcal{PQ} \cdot PP^*
$$

(1)

where symbol (*) indicates values normalized to Chl a concentration. $\mathcal{PQ}$ is generally greater than 1, suggesting that the absorbed energy in photosystems is not entirely dedicated to carbon fixation but also serves to reduce nitrate and even sulfur (Williams and Robertson, 1991; Sakshaug et al., 1997). $\mathcal{PQ}$ ranges between 1 and 1.4 (mol O$_2$ (mol C$^{-1}$)) (Babin et al., 1996), and although Williams and Robertson’s (1991) analysis of earlier observations provided a range of quotients from 0.5 to 3.5, these authors concluded that these discrepant $\mathcal{PQ}$ values could be attributed to analytical errors and that essentially all $\mathcal{PQ}$ are within the range 1–1.36.

Light is one of the main variables involved in photosynthesis, and we will be using irradiance, $E$ (e.g. Sakshaug et al., 1997) as the measure of light throughout. Rigorously, the irradiance for photosynthesis is a scalar irradiance $\mathcal{E}$ rather than a plane irradiance, as phytoplankton cells may collect radiant energy equally from all directions. Furthermore, from incident light, only the integrated value $\mathcal{E}_{\text{PAR}}$ over the spectral range [400; 700 nm] is available for photosynthesis, and hence we define:

$$
\mathcal{E}_{\text{PAR}} = \int_{400}^{700} E(\lambda) \, d\lambda
$$

(2)

However, the use of $\mathcal{E}_{\text{PAR}}$ as a measure of light is a simplification causing errors in depth-resolved numerical models (Lehman et al., 2004), and the use of the photosynthetically usable irradiance $\mathcal{E}_{\text{PUR}}$ is more relevant. Morel (1978) was the first to define $\mathcal{E}_{\text{PUR}}$ (see Eq. (3)). Unlike $\mathcal{E}_{\text{PAR}}$, $\mathcal{E}_{\text{PUR}}$ integrates the variations of the absorbed irradiance $a' E$ over the pertinent spectral range.

$$
\mathcal{E}_{\text{PUR}} = \frac{1}{a_m} \int_{400}^{700} a'(\lambda) \cdot \mathcal{E}(\lambda) \, d\lambda
$$

(3)

In Eq. (3) $a_m$ is the maximal value for the Chla-specific absorption coefficient over the spectral range [400; 700 nm].

In practice, the symbol $E$ will be used in this paper as a general term for irradiance, standing for plane or scalar irradiance, as well as for spectrally integrated irradiances. Last, some of the physiological variables handled in what follows make sense only when expressed on a per unit biomass basis, which could be the cell, the carbon amount, or the chlorophyll content. The last has been retained for normalization, as in oceans chlorophyll is exclusively encountered in phytoplankton, while carbon is present not only in phytoplankton but in non-photosynthetic organisms and organic matter (Falkowski and Kolber, 1995).

2.2. Empirical models

Photosynthesis involves a large number of enzymatic reactions for which kinetics can be deduced from the mass action law. Empirical models reduce the set of these sub-processes to a unique and global process supposed to represent the various steps of primary production. This global process is generally associated to an apparent primary production rate $PP$ (in mol C m$^{-3}$ s$^{-1}$) given in Eq. (4) in which $PP^C$ (s$^{-1}$) is the carbon-specific primary production rate.
\[
PP = PP^C \cdot C = PP^{\text{max}} \cdot f_L\left(\frac{E}{E_{\text{ref}}}\right)
\]

In Eq. (4), \(C\) (mol C m\(^{-3}\)) is the phytoplankton carbon concentration, \(PP^{\text{max}}\) is the maximal value of the primary production rate (generally a function of temperature \(T\)), \(E\) and \(E_{\text{ref}}\) the incident and the referent irradiances respectively, and \(f_L\), a dimensionless function representing control of photosynthesis by light. The canonical form of Eq. (4), as well as the introduction of the dimensionless irradiance \(x = E/E_{\text{ref}}\), facilitates the comparison between the different models available in the literature, as done by Platt and Sathyendranath (1993) and by Ebenhöh et al. (1997) to name just a few. The \(f_L(x)\) function is generally defined so as to reproduce the usual shape of the experimental \(P\) vs. \(E\) curve, which implies that it must fulfill the condition of null primary production at null irradiance \((f_L(0) = 0)\). Some additional constraints apply on the analytical function \(f_L(x)\), depending on whether photoinhibition (see Section 2.3.2 for further details) is taken into account. If photoinhibition is ignored, no optimum is observed on the \(P\) vs. \(E\) curve \((f_L(x)\) is strictly monotonic); whereas if photoinhibition is taken into account, the \(P\) vs. \(E\) curve exhibits a maximum at \(E^{\text{max}}\).

Table 1 presents a non-exhaustive list of some widely used expressions for the \(f_L\) function, and Fig. 1 reports their variations with the dimensionless irradiance \(x\). The choice of \(f_L\) is also essential for the initial slope \(\alpha\) (at \(x = 0\)) of the \(P\) vs. \(E\) curve, which is a key parameter as will be seen later.

Among this non-exhaustive panel of available expressions for \(f_L\), Sakshaug et al. (1997) concludes that no formulation is recommended above the others, but it is likely that the calculated primary production will depend significantly on the \(f_L\) analytical expression. That makes the choice of such a function somewhat delicate. Moreover, these models have been derived from measurements of \(P\) vs. \(E\) that are, especially when measured by \(^{14}\text{C}\) uptake, significantly dependent on the length of the incubation (MacIntyre et al., 2002). Hence, unless the incubation time is only a few minutes, some photoacclimation will take place during incubation, which renders the \(P\) vs. \(E\) measurements suitable only for representing the steady-state and fully adapted photosynthetic process (Cullen and Lewis, 1995; Sakshaug et al., 1997). Moreover, though empirical steady-state models involve parameters that have turned out to be physiologically meaningful after the underlying mechanisms have been investigated, they fail to represent the dynamics of photoacclimation, which can be essential in certain cases such as in natural mixed layers (Cullen, 1990; Baumert, 1996).

2.3. Mechanistic approaches

2.3.1. General

Aware of the limits inherent to empirical models, scientists started to develop semi-empirical models and even mechanistic models. The former still use the light forcing function \(f_L\) although they include some underlying mechanisms, while the latter focus on the fundamental dynamic laws involved in the photosynthetic process and account for photoacclimation. Both these approaches are based on the widely admitted relationship (5) that can be found in several papers (e.g. Falkowski et al., 1985; Morel, 1991; Sakshaug et al., 1997) giving the photosynthesis rate \(P^*\) (in mol O\(_2\) (gChl\(^{-1}\) s\(^{-1}\)) vs. \(E\) (in mol quanta m\(^{-2}\)) relation as a function of the

<table>
<thead>
<tr>
<th>Index</th>
<th>(f_L(x))</th>
<th>(f_L(1))</th>
<th>Photoinhibition</th>
<th>(E_{\text{ref}})</th>
<th>(E_{\text{sat}})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\frac{1}{1 + e^{-x}})</td>
<td>1/2</td>
<td>No</td>
<td>(E_{1/2})</td>
<td>(\frac{1}{3})</td>
<td>Monod (1950)</td>
</tr>
<tr>
<td>2</td>
<td>(x \cdot e^{1-x})</td>
<td>1</td>
<td>Yes</td>
<td>(E_{\text{max}})</td>
<td>(\frac{1}{3})</td>
<td>Steele (1962)</td>
</tr>
<tr>
<td>3</td>
<td>(1 - e^{-x})</td>
<td>0.6321</td>
<td>No</td>
<td>(E_k)</td>
<td>(\frac{1}{3})</td>
<td>Webb et al. (1974)</td>
</tr>
<tr>
<td>4</td>
<td>(\text{tanh}(x))</td>
<td>0.7616</td>
<td>No</td>
<td>(E_k)</td>
<td>(\frac{1}{3})</td>
<td>Jassby and Platt (1976)</td>
</tr>
<tr>
<td>5</td>
<td>(e^{(1-x)}/e + e^{-x} + e^{-x} (0 \leq \xi \leq 1))</td>
<td>0.6989(^a)</td>
<td>No</td>
<td>(E_k)</td>
<td>(\frac{1}{3})</td>
<td>Chalker (1980)</td>
</tr>
<tr>
<td>6</td>
<td>((2+4\xi)/(1+\xi)) (A \geq 0)</td>
<td>1</td>
<td>Yes</td>
<td>(E_{\text{max}})</td>
<td>(\frac{2+4\xi}{\xi})</td>
<td>Klepper et al. (1988) in Ebenhöh et al. (1997)</td>
</tr>
</tbody>
</table>

\(E_{1/2}\) is the irradiance at half maximum productivity, and \(E_k\), the ‘light saturation index’ (see Section 2.3.2 for more details on \(E_k\)).

\(^a\) Calculated with \(\xi = 0.5\).
spectrally integrated chlorophyll a-specific absorption coefficient over the [400;700] nm range $\tilde{a}$ expressed in m$^2$ (gChl)$^{-1}$ and the quantum yield $\phi$ in (mol O$_2$) (mol quanta)$^{-1}$.

$$P^* = \phi \cdot \tilde{a} \cdot E \tag{5}$$

In Eq. (5), the quantum yield $\phi$ is rigorously spectrally dependent, but in practice, it is usually treated as a non-spectral parameter (Sakshaug et al., 1997) and $E$ stands for $E_{\text{PAR}}$.

From a physical point of view, Eq. (5) conveys that only a part ($\tilde{a}E$) of the incident irradiance is absorbed by the light harvesting pigments. The effective contribution of light to photosynthesis is ultimately reduced to $(\phi \tilde{a}E)$ while the remaining energy leads to photon emission (fluorescence) or thermal loss (Kolber and Falkowski, 1993).

### 2.3.2. Mechanistic considerations on photosynthesis

In the following, derivations will assume a spectrally invariant light source, and the wavelength dependence of the processes under consideration will be suppressed, in order to focus on key concepts regarding photosynthesis modelling. Semi-empirical models combine the empirical and mechanistic approaches. An illustration of this is given in the Morel (1991) model that relies on the mechanistic expression for photosynthetic rate given in Eq. (5) converted into a primary production rate (as shown in Eq. (6)) using the quantum yield of carbon fixation $\phi^C$ (expressed in mol C (mol quanta)$^{-1}$) instead of $\phi$. Moreover, the latter equation uses $E_{\text{PUR}}$ instead of $E_{\text{PAR}}$ and therefore $a^*_m$ is used instead of $\tilde{a}$ (see Eqs. (2) and (3)). This model also associates an empirical law given in Eq. (7) which is used to define $\phi^C$:

$$PP^* = a^*_m \cdot \phi^C \cdot E_{\text{PUR}} \tag{6}$$

$$\phi^C = \phi^C_m \cdot g_L(x) \tag{7}$$

In Eq. (7), $x = E/E_{\text{ref}}$, $\phi^C_m$ is the maximum quantum yield of carbon fixation and $x \cdot g_L(x)$ takes the form of a dimensionless $f_L$ function similar to those presented in Table 1.

Mechanistic approaches are attempts to formalize the main known biological relations among light absorption, light transformation into chemical energy and phytoplankton growth through analytical expressions involving biologically and/or chemically meaningful parameters. They also seek to provide a good compromise between simplicity and realism, including, as far as possible, the representation of the key photoacclimation processes. Before getting to the heart of the matter, we draw attention to the main theoretical features necessary for further developments in photosynthesis modelling.

In the presence of photoinhibition, all $P$ vs. $E$ curves exhibit three phases (see for example Steele function in Fig. 1) already identified by several authors (e.g. Falkowski et al., 1994; Sakshaug et al., 1997): at low irradiance, primary production linearly increases with irradiance and this characterizes a regime where primary
production control is exerted by photon absorption rate (at least in the absence of nutrient limitation). The second phase is no longer linear and corresponds to a progressive decrease in the photosynthetic yield (Falkowski et al., 1994). A transition occurs around the ‘light saturation index’, $E_k$, toward a regime controlled by the limiting step in electron transfer from the initial donor (H$_2$O) to the final acceptor (CO$_2$). In practice, $E_k$ is given by the intersection between the initial slope and the light-saturated rate of photosynthesis $P_{\text{max}}^*$ and is therefore equal to $P_{\text{max}}^*/\alpha^*$ where $P_{\text{max}}^*$ and $\alpha^*$ are the Chl-specific maximum photosynthetic rate and the initial slope of the $P$ vs. $E$ curve, respectively. Moreover, accounting for Eq. (5), and for the fact that the quantum yield has its maximum, $\varphi_m$, at vanishing irradiances, the initial slope $\alpha^*$ is defined by $\alpha^* = \bar{\alpha} \cdot \varphi_m$.

At light saturation, the rate of photosynthetic electron transport is independent of light absorption but controlled by the rate-limiting step (still subject to debate in literature) somewhere in the whole-chain of electron transport (Falkowski et al., 1994; Sakshaug et al., 1997). This down-stream limitation ultimately restricts electron turnover through photosystem II (PSII) (Behrenfeld et al., 1998). Hence, $P_{\text{max}}^*$ is proportional to the stationary rate of electron turnover through the functional PSII reaction centers (1/$\tau$). In addition, the maximum photosynthesis rate ($P_{\text{max}}^*$) is reached at a time when all potential light-harvesting sites per unit Chl a are activated, and $P_{\text{max}}^*$ is therefore proportional to the number of photosytetic units (PSU), and it is agreed that PSU contain both photosystem II (PSII) and photosystem I (PSI) per unit Chl a (Falkowski et al., 1994). This and additional features providing relationships between parameters $\varphi_m$ and $\bar{\alpha}$ and physiological parameters of photosystems ultimately provide the following expression for $E_k$ (Ley and Mauzerall, 1982; Falkowski et al., 1994; Sakshaug et al., 1997):

$$E_k = \frac{1}{\tau \cdot \sigma_{\text{PSII}}}$$

(8)

where $\sigma_{\text{PSII}}$ is the absorption cross-section of PSII. Finally, when $E$ is greater than $E_{\text{max}}$, the curve inflexion is the expression of the photoinhibition effect due to photosystem damage by excess light (cf. Section 2.3.3).

2.3.3. Photoacclimation and photoinhibition

Subject to variable external constraints, phytoplankton react in different ways in order to achieve optimal conditions for growth. In respect to light variations, these adjustments are known as photoacclimation and can take the form of short-term processes involving time scales from a few seconds to less than an hour. By contrast, long-term photoacclimation processes take 30–60 min and up to several days. The limit between short and long-term photoacclimation is imposed by a physiological constraint, i.e. the minimum time for synthesizing new proteins or pigments, which is greater than 30–60 min (Garčarek, 2000). In other words, short-term photoacclimation occurs without de novo synthesis of proteins/pigments, while long-term photoacclimation is a change in the stoichiometry of the phytoplankton that requires synthesis of protein, pigments or other cellular constituents.

2.3.3.1. Short-term photoacclimation (without de novo synthesis of proteins). In essence, phytoplankton maintains an equilibrium between photon absorption rate and electron transfer. This balance is effective for irradiances around $E_k$, as mentioned above. At lower irradiances, the quantum yield is higher, but the photosynthetic rate is lower. At higher irradiances, there is nothing to be gained (no major increase in photosynthetic rate), ‘but potentially much to be lost’ (Sakshaug et al., 1997). Hence, phytoplankton continuously adjusts its light saturation index by the interaction of the two factors $\tau$ and $\sigma_{\text{PSII}}$ that determine $E_k$ (see Eq. (8)).

Under high-light conditions, the energy absorbed by light-harvesting pigments of phytoplankton may exceed their photosynthetic capacity. First line of defense of algae is in a short-term photoprotection response through the deactivation of excitons formed by the absorption of photons. The excess excitons can be deactivated by thermal dissipation (e.g. Demmig-Adams and Adams, 1992). Non-photochemical quenching (NPQ) of chlorophyll fluorescence is indicative of the level of this non-radiative energy dissipation in the light-harvesting antenna of photosystem II. This NPQ shows that the level of excitation energy in the PSII antenna can be regulated. This is thought to prevent over-reduction in the electron transfer chain and, therefore, provides protection from photodamage. NPQ is ascribed to three major processes (Delphin et al., 1998): state transition which consists in the reversible redistribution of absorbed light energy between PSI and PSII,
although the associated mechanism is still subject to debate (Allen, 1992; Haldrup et al., 2001; Szabó et al., 2005), energy-dependent quenching and photoinhibition. Photoinhibition can not only result from damage to PSII (see next section) but also from an increase in thermal energy dissipation (Demmmig-Adams and Adams, 1992; Szabó et al., 2005).

It is thought that most of the energy-dependent quenching occurs directly within the light harvesting antenna complexes of PSI and PSII and is an exothermic reaction involving xanthophylls (Anderson et al., 1998; Demers et al., 1991). In eukaryotic algae, it consists in the conversion of xanthophyll violaxanthin, ultimately to zeaxanthin. This reaction is reversed under low light conditions and this reversible sequence of reactions is called the xanthophyll cycle (Demmig-Adams and Adams, 1996). Experimental evidence of the role of the xanthophyll cycle in NPQ, and therefore in excess energy dissipation, has been given for higher plants (Demmig-Adams and Adams, 1996) as well as for algae (Demers et al., 1991; Lavaud et al., 2002; Ruban et al., 2004).

Finally, at high light, any reaction that supports the photosynthetic electron flow contributes to photoprotection. This includes, in addition to the aforementioned energy dissipation processes, O₂ fixation by Rubisco (ribulose 1,5-bisphosphate carboxylase/oxygenase), which is the first step of photorespiration, and the direct reduction of O₂ by PSI in the Mehler reaction (Demmig-Adams and Adams, 1992). There are attempts in several models at quantifying the contributions of photorespiration and the Mehler reaction to electron flow, but it remains empirical so far. The former process is still debated in the literature and will be discussed in Section 4, while the Mehler reaction is less documented and generally represented as a percentage of gross primary production (GPP) varying around 10% (Laws et al., 2000), or considered to be negligible (Langdon, 1993).

### 2.3.3.2. Long term photoacclimation.

When exposed to frequently (and/or continuously) unfavourable light conditions, algae undertake structural and physiological changes to optimize light harvesting and minimize photoinhibitory damage. These transformations occur over longer time scales than those previously considered and two basic photoacclimation strategies have been identified in many algae: the first consists of an alteration of the amount of chlorophyll per PSU (i.e. the size of PSU), which changes their functional absorption cross-sections (e.g. σ₁₁), while the second affects the number of PSUs (Falkowski and LaRoche, 1991). These strategies are both associated with changes in the cellular chlorophyll content, and therefore in the Chl:C intracellular ratio. There is ample experimental evidence for this in the literature. For example, experiments using Dunalellia salina grown at high-light and low-light exhibited physiological differences, the former having lower pigment content, truncated chlorophyll antenna size and an accumulation of photodamaged PSII centers in the chloroplasts (Neidhart et al., 1998). In addition, Behrenfeld et al. (1998) demonstrated that the maximum photosynthetic rate $P_{\text{max}}$ remains insensitive to photoinhibition so long as the decrease in the number of functional PSII is compensated by a reciprocal increase in the rate of electron turnover through PSII (1/τ). This occurs until the maximum achievable rate (1/τ)th is reached. Any additional photodamage will then decrease $P_{\text{max}}$. Variations in τ are determined by the ratio between the quantity of Rubisco enzyme and the amount of electron transport system (ETS) components, hence, when the latter increases, τ decreases.

### 2.3.3.3. Photoinhibition.

Short and long-term photoprotective strategies act together to help algae to balance energy supply with energy consumption under all light levels. However, under long exposure to a high-light irradiance, these are not sufficient to protect algae from loss of photosynthetic electron transport and photosynthetic capacity due to photodamage in the PSII reaction centers (Anderson et al., 1998). Photoinhibition is “a light-dependent irreversible inactivation of the PSII reaction center activity, which can be restored only via the degradation (subsequent to photoinhibition) and synthesis of the D1 protein” (Tyystjarvi and Aro, 1996).

In the literature, there is indeed a general consensus that the primary target of photoinhibition is the PSII photosystem where the D1-polypeptide in the reaction center is damaged and degraded. This affects the number of functional PSII. Furthermore, PSII damage occurs even at low light irradiances, but in that case the repair mechanism is rapid enough to prevent the symptoms of photoinhibition. This has been reported for higher plants (Tyystjarvi and Aro, 1996) as well as for green algae (Baroli and Melis, 1996) and diatoms (Garczarek, 2000).
2.3.3.4. Modelling photoacclimation. At present, short-term photoacclimation is not accounted for in models due to the complex underlying mechanisms. A model reflecting the complexity of these photoprotective responses should involve additional state variables such as specific compound contents per unit Chl (e.g. xanthophylls) in a model that would be strongly process-based and supported with substantial fundamental understanding of mechanisms based on molecular-scale observations. From this complex model, reduction methods (variables aggregation, singular perturbation, ... ) could help to derive simplified models that would be representative of the original model in a time and space relevant to the large-scale global studies performed with coupled circulation/biogeochemical ocean models. Obviously, this is a challenge for future research in the field. By contrast, long-term photoacclimation is often taken into account through a variable Chl:ratio and a specific conservation equation dedicated to Chl cellular concentration (see Section 2.4). Moreover, while photoinhibition is included in some empirical models (see Table 1), the present study aims at a mechanistic description of this process. Han’s (2002) model achieves this purpose (see next section). Finally, phytoplanktonic populations have to cope with other environmental stresses besides high or low irradiance: low temperature and nutrient availability. These would result in photosynthetic alterations similar to those considered here for growth at high irradiance (Maxwell et al., 1995). The combined effects of nutrient and light stresses are accounted for in the present class of models and will be discussed later (see Sections 2.4 and 3).

In conclusion, the class of models depicted in Section 5 includes the photoacclimation process through a light- and nutrient-variable Chl:C ratio and a specific conservation equation dedicated to Chl cellular concentration (see Section 2.4). Moreover, while photoinhibition is included in some empirical models (see Table 1), the present study aims at a mechanistic description of this process. Han’s (2002) model achieves this purpose (see next section). Finally, phytoplanktonic populations have to cope with other environmental stresses besides high or low irradiance: low temperature and nutrient availability. These would result in photosynthetic alterations similar to those considered here for growth at high irradiance (Maxwell et al., 1995). The combined effects of nutrient and light stresses are accounted for in the present class of models and will be discussed later (see Sections 2.4 and 3).

2.3.4. Mechanistic modelling of photosynthesis

Several mechanistic models of photosynthesis rely on the assumption that photosystems can be found in three different states, namely open (or reactive), closed (or already activated), or photoinhibited (Eilers and Peeters, 1988; Zonneveld, 1997; Han, 2002). Zonneveld (1997) did not consider the photoinhibited state of photosystems, arguing that algae tend to adapt to light excess over a sufficient time and that this phenomenon only occurs in the superficial layers of oceans. Hence, his model includes the effect of photoacclimation on four parameters, namely the size of a PSU, the number of PSUs per cell, the average turnover time of PSUs and the Chl a-specific absorption cross-section. In this model, parameters are expressed on a per cell basis, which makes it difficult to use in large scale eulerian modelling, unless assumptions are made on the relationship between cell number and biomass concentration. However, Zonneveld (1997) came to the important conclusion that, even though the four aforementioned parameters are likely to be affected by photoacclimation, the cellular chlorophyll content (and therefore the Chl:C ratio) would be sufficient to characterize the state of photoacclimation. This is confirmed in Geider et al. (1997).

Han (2002) proposes another mechanistic model that represents a good compromise between simplicity and realism using measurable parameters. This model is based on the earlier one of Eilers and Peeters (1988). It assumes that each PSU contains an unique PSII and its open, closed or photoinhibited states are associated with their probabilities of occurrence: \( n_o \), \( n_c \) and \( n_in \), respectively. A schematic presentation of the possible transfers among the three states is presented in Eq. (9). It involves \( k_o \) (= \( k^H \cdot \sigma_{PSII} \cdot E \)) and \( k_r \), the rate constants (in \( s^{-1} \)) relative to PSII damage and repair, respectively.

\[
\text{open}(o) \xrightarrow{\sigma_{PSII} \cdot E} \text{closed}(c) \xrightarrow{k_o} \text{inhibited}(i) \rightarrow \xrightarrow{k_r} \text{open}(o)
\]

(9)

Applied to the schematic reactions (9), the law of mass action combined with first order kinetics and the obvious relationship between probabilities \( (n_o + n_c + n_in = 1) \) gives the subsequent mass balances for \( n_o \), \( n_c \), and \( n_in \):

\[
\frac{dn_o}{dt} = -\sigma_{PSII} \cdot E \cdot n_o + \frac{n_c}{\tau}
\]

(10a)

\[
\frac{dn_c}{dt} = \sigma_{PSII} \cdot E \cdot n_o - \frac{n_c}{\tau} + k_r \cdot n_in - k^H \cdot \sigma_{PSII} \cdot E \cdot n_c
\]

(10b)

\[
n_in = 1 - n_o - n_c
\]

(10c)
Han considers that the quantum yield of carbon fixation is proportional to the probability of PSII being open, i.e. \( \phi^C = n_o \cdot \phi^C_m \). This is the actual link between photosynthesis and photoinhibition in the present model, and according to Eq. (5) the carbon-specific primary rate can be written as

\[
P^C = \bar{\alpha} \cdot n_o \cdot \phi^C_m \cdot E \cdot \theta
\]

where \( \theta \) is the Chl:C ratio (see hereafter in Section 2.4). The steady-state solution \((n_o^*, n_c^*, n_m^*)\) of system (10) can be derived easily and provides the following expression for the steady-state carbon-specific primary-production rate (Eq. (12)):

\[
PP^C = \frac{\theta \cdot \phi^C_m}{1 + \sigma_{PSII} \tau E + (k^H_d / k_s)(\sigma_{PSII} E)^{\tau}} \cdot \bar{\alpha}^* E
\]

Finally, both the dynamic and the static solution of this model can be used to simulate photosynthesis, but the dynamic solution will be preferred in the case of rapid light changes as observed in mixed layers (see Baklouti et al., 2006).

### 2.3.5. Discussion on the parameters handled by Han (2002) model

Han’s (2002) model of photosynthesis (Eq. (10)) involves six parameters that are all measurable. The spectrally integrated Chl-specific absorption coefficient \( \bar{\alpha} \) is determined through spectrophotometry (Dubinsky et al., 1986). The most common method used to determine the maximum quantum yield of carbon fixation \( \phi^C \) is the \(^{14}\)C-fixation technic, with \( \phi^C_m \) calculated from the chlorophyll-specific initial slope of the \( PP^* \) vs. \( E \) curve determined from incubation experiments. The PSII absorption cross-section \( \sigma_{PSII} \) can be calculated through the oxygen-flash method, while the turnover time \( \tau \) can be derived independently through the same method combined with continuous-light measurements of the primary production rate (Dubinsky et al., 1986). Recent experimental techniques based on active fluorescence can also be used to determine \( \sigma_{PSII} \) (Kolber and Falkowski, 1993) and \( \phi^C \) (Babin et al., 1996). These techniques (among which the fast repetition rate fluorimetry (FRRF) (Kolber and Falkowski, 1993; Falkowski and Kolber, 1995; Kolber et al., 1998)) have good prospects as they are non-intrusive and non-destructive, offering rapid, sensitive, real-time continuous in situ measurements. The latter are likely to be used in dynamic models for photosynthesis, though slight quantitative differences are observed between \( PP \) estimates based on FRRF and traditional measurements (Suggett et al., 2001; Moore et al., 2003; Suggett et al., 2004).

Finally, damage \( (k_d) \) and repair \( (k_s) \) rates can be estimated through variable chlorophyll a fluorescence techniques. Repair rate can be measured under low-irradiance conditions in the absence of damage. Unlike repair, the measurement of damage in absence of repair is not easily achieved without using chemical inhibitors of the repair process (Heraud and Beardall, 2000). An alternative has been proposed by Oliver et al. (2003) through a mathematical approach that produces simultaneous estimation of both rates with a single set of data measurements. Following Melis (1999), photoinhibitory damage depends on light intensity and on the PSII chlorophyll antenna size. A linear relationship between irradiance \( E \) and the rate constant \( k_d \) for D1 photodamage was also found by Baroli and Melis (1996) through measurements on Dunaliella salina. This linear relationship is explicitly included in Han’s (2002) model through a damage rate constant having the form:

\[
k_d = k^H_d \cdot \sigma_{PSII} \cdot E
\]

where \( k^H_d \) is dimensionless. Other surveys give alternative formulas. For example, Rubio et al. (2003) suggest that the rate of photodamage is proportional to \( \sqrt{E} \) rather than \( E \) arguing that photoinhibition breaks biomolecules into two radicals, the concentration of which is proportional to \( \sqrt{E} \).

Further research could relate the repair rate constant to physiological characteristics of the phytoplankton cells, as done for the photodamage constant \( k_d \) in Han’s (2002) model. Moreover, this model has the advantage that the photoinhibition contribution can be easily removed if the kinetics for repair and damage are unavailable or unreliable. These additional advantages have motivated our choice of Han’s (2002) formalism to represent photosynthesis in our generic model (see Section 5).

### 2.4. Chlorophyll:carbon ratio

Another key point in phytoplankton models is the intracellular chlorophyll:carbon ratio, denoted \( \theta \), which is not only a conversion factor between two essential biomass units, but an indicator of the algal photoaccli-
mative state (Zonneveld, 1997). For a given species, θ is maximal at high temperature (25–30 °C) and low irradiances (<20 μmol quanta m⁻² s⁻¹) for nutrient replete conditions (Geider et al., 1997). At low irradiances, photoacclimation produces an increase in the Chl content of algae and subsequently in θ contributing more efficient harvesting of light. For high values of θ, this positive effect is partially counterbalanced by the so-called “package effect” or “self-shading” induced by the elevated chlorophyll concentrations in chloroplasts. The arguments outlined above suggest that the Chl:C ratio is not merely inversely proportional to light irradiance.

Mathematical models of phytoplankton often consider a constant Chl:C ratio, even if this is far from the observed reality: values from 0.003 to more than 0.1 mg Chl (mg C)⁻¹ have been reported (Geider et al., 1997). Moreover, chlorophyll is the most widely used index of phytoplankton abundance and productivity in oceans, but the constant fluctuations in cellular chlorophyll quotas impede a simple conversion from chlorophyll to biomass (Cullen, 1990; Fennel and Boss, 2003). Accounting adequately for changes in Chl:C in models is, therefore, necessary; otherwise important features of ocean biogeochemistry would be ignored by the model.

The way of considering the Chl:C ratio in biogeochemical models is manifold, and varies from basic empirical correlations to analytical formulations based on underlying mechanisms. In the former category, Cloern et al. (1995) propose an empirical formulation for θ that has been elaborated on the basis of 219 published measurements. A simple interpolation by a least-square method provides the following expression for the Chl:C ratio (in mg Chl (mg C)⁻¹):

\[
\theta = 0.003 + 0.0154 \cdot e^{0.050T} \cdot e^{-0.059E} \cdot \mu'
\]  

(13)

where \(T\) is expressed in °C, \(E\) in (mol quanta) m⁻² d⁻¹ and \(\mu'\) is the nutrient-limited growth rate. Although empirical, Eq. (13) includes some apparent effects of temperature and light intensity in its exponential terms. Following Flynn (2003a), multi-nutrient models based on an empirically derived Chl:C, using Eq. (13) for example, should be adequate in models for most oceanographic modelling scenarios. In Zonneveld (1998), a mechanistic model for representing the dynamics of the Chl:C ratio is proposed. The model characterizes a phytoplankton cell in terms of three variables: a permanent volume and two transient pools, one for carbon and one for nutrient. Under nutrient-limited conditions, the absolute rate at which cellular chlorophyll is produced is proportional to the amount of nitrogen in the transient pool, while the proportionality constant should depend on irradiance as stated by Zonneveld. Comparisons of outputs from the model with experiments on Dunaliella tertiolecta show a good agreement. Finally Zonneveld’s (1998) model is relative to the cell unit and best suited for algal growth in controlled environments, while it is less relevant to description of ocean-scale biogeochemical dynamics.

An alternative model given by Geider et al. (1997) achieves an independent mass balance for the intracellular chlorophyll content, which is coupled to that of the carbon content. In this model, the chlorophyll synthesis rate varies as follows:

\[
\frac{d\text{Chl}}{dt} = \rho_{\text{chl}} \cdot PP_{\text{nr}}^C \cdot C
\]  

(14)

In Eq. (14), \(PP_{\text{nr}}^C\) is the carbon-specific primary production rate under nutrient-replete conditions, \(C\) is the phytoplankton carbon and \(\rho_{\text{chl}}\) stands for the ratio of chlorophyll-a synthesis to carbon fixation. It is given by the maximum Chl:C ratio \(\theta_m\) observed in algae acclimated to extremely low light (Eq. 15), and this value is regulated by a dimensionless factor aimed at reducing the internal Chl concentration at high light exposure. This is represented by the Chl-specific primary production rate achieved in nutrient replete conditions over the maximum potential rate:

\[
\rho_{\text{chl}} = \theta_m \frac{PP_{\text{nr}}^C \cdot C/\text{Chl}}{\alpha' E} = \theta_m \frac{PP_{\text{nr}}^C}{\alpha' E \theta}
\]  

(15)

In the case of nutrient limitation, Chl synthesis is also affected by nutrient availability, as they are required for elaboration of the pigment-protein complexes located in chloroplasts. For this purpose, Geider et al. (1998) have developed a second model on the same basis, but in which chlorophyll synthesis is coupled to nitrogen uptake, resulting in a new expression for \(\rho_{\text{chl}}\):
In Eq. (16), \( PP^C \) stands for the Chl-specific primary production rate when limited by nutrients and \( \theta_m^N \) is the maximum reported (Chl:N) ratio achieved under extremely low light. In addition, the right term in Eq. (14) is replaced in the second model by \( \rho_{\text{chl}} \cdot V_N^C \cdot C \), where \( V_N^C \) is the phytoplankton carbon-specific nitrate assimilation rate. That means that in this case chlorophyll synthesis rate is no longer proportional to the photosynthesis rate, but rather to the nitrogen assimilation rate (the processes of N transport and incorporation are combined as assimilation in Geider et al. (1998) model).

Flynn et al. (2001) compare several expressions for the chlorophyll mass conservation equation originating from different models (Geider et al., 1996, 1997, 1998; Flynn et al., 1997; Flynn and Fasham, 1997; Flynn and Flynn, 1998). The main conclusion is that both Geider et al. (GM) and Flynn et al. (FM) models have failings. GM fails in its assimilation component, since chlorophyll synthesis is a function of concurrent N assimilation (synthesis cannot occur even in N-replete cells without N assimilation), and FM fails in its photoacclimation component. Hybrid models (FMGM) using the successful features of FM and GM models have, therefore, been investigated and this allowed improvement of model fits to Chl:C data.

In the same spirit, we propose to use an hybrid between FM and GM models that is not only simpler than the FMGM ones investigated in Flynn et al. (2001) but more suitable to be included in our phytoplankton model. It describes the chlorophyll synthesis rate as follows:

\[
\frac{d\text{Chl}}{dt} = V_m^\text{chl} \cdot \frac{PP^C}{x^C \cdot E \cdot \theta} \cdot \frac{N^e}{N^e + K_N} \cdot \left( \frac{1 - \theta_N^N / \theta_m^N}{(1 - \theta_N^N / \theta_m^N) + 0.05} \right) \quad \text{where} \quad V_m^\text{chl} = V_m^N \cdot \theta_m^N
\]

Eq. (17) conveys the fact that the maximum chlorophyll synthesis rate \( V_m^\text{chl} \) is proportional to the maximum N uptake rate \( V_m^N \) that would be achieved at steady state if nitrogen was sufficient and to the maximum cellular Chl:N ratio (i.e. \( \theta_m^N \)). In this equation, the influence of nutrient availability (\( N^e \) is the external nitrogen source concentration) and effect of light in the regulation of chlorophyll synthesis rate are also accounted for. Light regulation is actually considered in the same way as in the Geider et al. (1998) model through the \( \rho_{\text{chl}} \) coefficient defined in Eq. (16). Finally, synthesis of chlorophyll is made a function of the Chl:N ratio (\( \theta_N^N \)) (term within brackets), which has the same shape as in FM models (though the Chl:C ratio is used in the FM). This enables us to include the feedback of assimilated N on chlorophyll synthesis, since the latter process is necessarily coupled to protein synthesis and thus to nitrogen assimilation (Geider et al., 1998). Hence, chlorophyll synthesis is allowed until the maximum achievable Chl:N ratio (i.e. \( \theta_m^N \)) is reached. This formulation has therefore been included in the model that we propose in Section 5, to represent the chlorophyll synthesis rate and has been compared to data in our companion paper (Baklouti et al., 2006).

3. Control by nutrient availability of growth, uptake and exudation

To complement light supply, phytoplankton need nutrients for growth, in the form of macronutrients (nitrate, phosphate, silicic acid) and micronutrients (iron, zinc, ...). So far, it has been implicitly considered that growth was by nutrient replete cells (see Section 2), but this is seldom the case in natural conditions. The literature reveals a number of methodological and conceptual breakthroughs regarding nutrient-growth relationships, and what follows is an overview of the main model families identified. Along with growing knowledge, and starting from the well-known Monod–Michaelis–Menten formulation, uptake models have been improved with the introduction of phytoplanktonic cells' internal status through intracellular quotas. Furthermore, it is now commonly admitted that elemental stoichiometry in the ocean does not conform to the Redfield ratio (Geider and LaRoche, 2002; Sanudo-Wilhemy et al., 2004) and therefore that rigorously the knowledge of one element does not enable us to calculate the concentrations of the other elements. By inference multi-element models have become necessary, and associated with this, multi-nutrient limitation and co-limitation concepts have become widespread.
3.1. Control of nutrient availability on growth and DOC exudation

In a recent article, Flynn (2003b) identifies three main modelling strategies for phytoplankton growth and nutrient uptake, namely (in order of increasing complexity), Monod, quota and mechanistic (including feedback processes and multiple internal pools). In Cullen et al. (1993), a nutrient-limited growth rate at steady-state is described in a generic context. In the same spirit, the carbon-specific production rate is described in the present model by the general formulation given in Eq. (18). This relation expresses the fact that, under nutrient replete conditions, growth at a temperature $T_{\text{ref}}$ and an irradiance $E$ is described by the specific primary production rate $PP^C_{\text{ref}}(E, T_{\text{ref}})$, which has already been studied in detail in Section 2.3.4 and will not be considered here. Furthermore, at a temperature $T$ different from $T_{\text{ref}}$, production rate is changed and this is taken into account through the $f_T$ function (generally of Arrhenius type). The low-availability of one or several nutrients also introduces some additional constraints on growth rate. The subsequent rate-limitation is accounted for through a dimensionless function, $f_Q$, the expression of which has been subject to substantial evolution through the years.

$$PP^C(T) = \theta \cdot PP^* = PP^C_{\text{ref}}(E, T_{\text{ref}}) \cdot f_T(T) \cdot f_Q$$  \hspace{1cm} (18)

### 3.1.1. Single-nutrient control

Historically, $f_Q$ was first considered to be dependant on the external concentration $X^e$ of the limiting nutrient as expressed by the widespread Monod empirical law (Monod, 1950) that can be rewritten:

$$f_Q = f_{X^e} = \frac{X^e}{K_x + X^e}$$  \hspace{1cm} (19)

The empirical basis, its inability to simulate growth when the external nutrient is exhausted ($X^e = 0$) while growth can actually proceed thanks to internal nutrient reserves, as well as its unsatisfactory transposition to multiple nutrients (Flynn, 2003b) makes the Monod model unsatisfactory.

Quota models, the first proposed by Droop (1968), have arisen as an alternative to the Monod description. This class of models integrates the ability of algae to accumulate nutrients in dedicated intracellular storage pools. They postulate that the primary production rate is governed by the size of the internal pool of limiting nutrient (represented by the nutrient quota: $Q = X/C$), and only indirectly by the medium concentration (Droop, 1968). These internal pools can therefore buffer the intrinsic environmental variability in carbon and nutrient supplies (Riebesell, 2002). The nutrient quota $Q$ is generally relative to cellular carbon ($C$) but can also be expressed per cell. In practice, primary production rate is limited by the intracellular nutrient concentration through the dimensionless function $f_Q$ (see Eq. (18)) related to the cellular nutrient quota. Usual expressions for the $f_Q$ function are given in Table 2. The quota function $f_Q$ infers that, as growth is the result of cell division, the latter becomes possible only for cell quotas higher than $Q_{\text{min}}$ while out of this range, algal cells will be subject to deficiency.

In other words, feedback regulation by algal nutritional state affects the primary production rate $PP$ through the quota function $f_Q$. However, this regulation does not directly affect light utilization by light-harvesting pigments, and the pool of dissolved intracellular carbon (DOC) can be saturated with newly synthesized organic compounds when photosynthesis takes place more rapidly than is required to supply the needs of growth. When this situation occurs (for example when nutrients are depleted), DOC excess may be released in the medium as

<table>
<thead>
<tr>
<th>$f_Q$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $\frac{Q - Q_{\text{min}}}{Q}$</td>
<td>Droop (1968)</td>
</tr>
<tr>
<td>(2) $\frac{Q - Q_{\text{min}}}{Q_{\text{max}} - Q_{\text{min}} + K_Q}$</td>
<td>Caperon and Meyer (1972)</td>
</tr>
<tr>
<td>(3) $\frac{Q - Q_{\text{min}}}{Q_{\text{max}} - Q_{\text{min}}}$</td>
<td>Geider et al. (1998)</td>
</tr>
<tr>
<td>(4) $\frac{Q - Q_{\text{min}}}{Q_{\text{max}} - Q_{\text{min}} + K_Q} \cdot \frac{Q_{\text{max}} - Q_{\text{min}} + K_Q}{Q_{\text{max}} - Q_{\text{min}}}$</td>
<td>Flynn (2001)</td>
</tr>
</tbody>
</table>

In expressions (2) and (3), $K_Q$ is a quota curvature constant.
suggested by several experimental works (see Mague et al., 1980; Fogg, 1983; Obernosterer and Herndl, 1995). Usually, the percent extracellular release (PER) of dissolved organic carbon relative to gross primary production is used for assessing the quantitative role of DOC released by phytoplankton. However, PER varies greatly depending on local environmental conditions and species compositions (Kirchman, 2000), and it seems that these variations are mainly due to changes in photosynthetic rate (Mague et al., 1980). Moreover, in natural environments, the extracellular release of DOC typically accounts for about 13% of primary production, but empirical evidence indicates that this value is not sufficient to sustain bacterial production (Kirchman, 2000). In this context, we suggest to relate, as in the ERSEM III model (Vichi et al., 2004), the DOC extracellular release to the internal nutrient status, rather than using PER or a constant extracellular rate of DOC release:

$$\frac{d[DOC]}{dt} = \frac{1}{C_0 \cdot f_Q} \cdot C_1 \cdot PP \cdot \frac{C_{nr}}{C_1} \cdot C_1$$

where \(C\) is the phytoplankton carbon concentration. Eq. (20) conveys the fact that from the fixed inorganic carbon pool, only the necessary part of newly synthetized organic compounds is incorporated into protein and carbohydrate, while the excess of this newly synthetized carbon is released from the cell.

### 3.1.2. Multi-nutrient control

The complexity of the primary production rate expression is increased when several \((n)\) nutrients simultaneously control phytoplankton growth. This case involves an additional function \(g^{ml}\), which is in relation to the different limiting ratios \(f_Q\) \((1 \leq i \leq n)\), as shown in Eq. (21).

$$PP^C(T) = PP^C_{max}(T^{ref}) \cdot f_T(T) \cdot g^{ml}(f_Q_{(i \geq 0)})$$

Expression (21) has the advantage of representing a large panel of models from the simplest Monod expression up to complex mechanistic formulations. It can also be used when no nutrient is limiting \((g^{ml} = 1)\), or when there is a single limitation \((g^{ml}(f_Q) = f_Q)\). Different strategies are achieved by authors for representing multi-nutrient limited growth, inducing different expressions for \(g^{ml}\). A classical method consists of having growth controlled by the most restricting of the potential limitations (Liebig’s law). Examples are shown in system (22) in which \(Q_i\) is the \(X_i \cdot C\) intracellular quota, and \(X^e_i\) the external concentration of nutrient \(X_i\):

\[

g^{ml} = \min_i \left( \frac{X^e_i}{K_{X_i} + X^e_i} \right)
\]

\[

g^{ml} = \min(f_Q_i)
\]

\[

g^{ml} = (f_{ch}), \quad \text{where} \quad \frac{Q_i}{Q_{i,max}} = \min_i \left( \frac{Q_i}{Q_{i,max}} \right) \text{ and expressions for } f_{ch}\text{ are given in Table 2.}
\]

Another usual approach suggests that the overall limitation is the product of each limiting contribution (Eq. (23)), which amounts to considering a cumulative effect of individual limitations on growth.

$$g^{ml} = \prod_i f_Q_i$$

The validity of the classical multi-limitation laws given by Eqs. (22b) and (23) have been tested by Davidson and Gurney (1999) in culture experiments on the diatom *Thalassiosira pseudonana*. They revealed that none of the models could reproduce the actual effect of N and Si exhaustion on growth, although the former gave

<table>
<thead>
<tr>
<th>Example of functions $f_Q^{opt}$ for quota models where $K_Q$ and $n$ are curve fitting constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_Q^{opt}$</td>
</tr>
<tr>
<td>Reference</td>
</tr>
<tr>
<td>(1) $Q_{max} - Q$</td>
</tr>
<tr>
<td>Lehman et al. (1975)</td>
</tr>
<tr>
<td>(2) $\left( \frac{Q_{max} - Q}{Q_{max} - Q_{min}} \right)^n$</td>
</tr>
<tr>
<td>Geider et al. (1998)</td>
</tr>
<tr>
<td>(3) $\frac{1 - Q/Q_{max}}{1 - Q/Q_{max} + K_Q}$</td>
</tr>
<tr>
<td>Flynn (2003b)</td>
</tr>
</tbody>
</table>
better results. Therefore, a new model was proposed by them, based on the perceived functional and structural roles of N and Si, respectively. Hence, even in the case where N is not the most limiting, its functional nature means that the rate of cell metabolic processes may still be influenced by N stress. In the opposite situation ($Q_{N}/Q_{N}^{\text{max}} > Q_{Si}/Q_{Si}^{\text{max}}$), intracellular levels of Si will not affect the rate of N metabolism. The corresponding formalism is given in Eq. (24) where $\beta$ is a shape parameter for function $\gamma$, $k$ is analogous to a half-saturation constant, and $f_Q$ is given by the Caperon and Meyer (1972) expression given in Table 2.

$$g_{\text{ml}} = f_Q \cdot \gamma$$ where $\gamma = \begin{cases} Q_{N}/(Q_{N}^{\beta} + k^{\beta}) & \text{if Si is limiting (} L \equiv \text{Si)} \\ 1 & \text{otherwise (} L \equiv \text{N)} \end{cases}$

Equation (24)

Comparisons with Thalassiosira pseudonana culture experiments were improved with the formalism given in Eq. (24), albeit this was partly due to the additional degrees of freedom provided through parameters $k$ and $\beta$. This alternative to classical laws remains empirical, and no generalization can be expected from it. Baird et al. (2001) proposes another expression for multi-limitation, given by Eq. (25). For this, the intracellular nutrient quota has been divided into a variable reserve pool ($Q^{R}$) and a constant structural pool ($Q^{S}$).

$$g_{\text{ml}} = \prod_{i} (f_{Q_{i}})^{p_{i}}$$ where $f_{Q_{i}} = Q_{i}^{R}/Q_{i}^{\text{max}}$

Equation (25)

However, this model again fails in being generalized since the exponents $p_{i}$ result from fitting with laboratory experiments, rather than from any mechanistic consideration. A few other models are also available in the literature for multi-nutrient-limited growth (e.g. Si–N control on diatom growth in Flynn and Martin-Jézéquel (2000)), but none of them currently prevails and further research in the field, including experimental aspects, will be likely necessary. Moreover, it can be asked if a single mathematical expression that would be applicable for all nutrients can even be expected, because of different interdependencies of various nutrients in phytoplankton (Riebesell, 2002). Pragmatically, we therefore envisage using different available formulations of $g_{\text{ml}}$ depending on the growth-limiting nutrient(s) considered.

### 3.2. Control of nutrient availability on uptake, assimilation and exudation processes

Uptake of an external nutrient by phytoplankton is implicitly governed by a series of biochemical reactions and transport processes, each exerting a potential control over the whole process: (i) nutrient diffusion outside the cell (including molecular and turbulent diffusions) (ii) enzyme-mediated transport across the cell membrane facilitated by way of specific protein porters (Dyhrman and Palenik, 2001; Riebesell, 2002). Uptake is followed by intracellular processes including (iii) intracellular transport and (iv) intracellular enzyme reactions for growth or storage into internal pools.

Basically, variations of internal concentration of a nutrient element are driven by the most limiting of these processes, which depend on the external conditions (mixing, cell size, nutrient availability, . . . ), as well as on the intracellular characteristics of the phytoplankton cells (internal quota, . . . ). In practice, as nutrient uptake rate is usually measured by the disappearance of substrate from the medium or the accumulation of total labeled material within the cell, it is not easy to distinguish between transport and metabolic processes involved in the process of nutrient uptake (McCarty, 1981). If we assume that external transport is the rate-limiting step, then the phytoplankton cell can consume the nutrient more rapidly than it can reach the cell wall (Pasciak and Gavis, 1974). As a consequence, a nutrient concentration gradient will establish from the external medium $X^{e}$ down to the cell wall $X^{w}$ ($X^{w} < X^{e}$). The relationship between nutrient concentrations $X^{e}$ and $X^{w}$ depends on the magnitude of the extracellular transport characteristics (i.e. nutrient diffusivity in the medium $D$, cell radius $R$, velocity field) as well as on the kinetic parameters relative to intracellular enzymatic processes i.e. the half-saturation constant $K$ and the maximum uptake rate $V_{m}$. In Pasciak and Gavis (1974, 1975), the authors define a criterion $\mathcal{P} = 14.4\pi R D K / V_{m}$ involving the aforementioned extracellular and intracellular parameters by which the importance of transport limitation can be ascertained. Although the authors assume that diffusion can play a significant role in limiting the uptake rate when $\mathcal{P} < 2$, the application of this criterion to a group of organisms revealed that transport limitation occurred for only 2 out of 13 organisms. Moreover, the experiments of Pasciak and Gavis (1975) on
Ditylum brightwellii showed that diffusion is the limiting step for smaller $P$ around 0.3–0.6. Finally, even if uptake limitation by external diffusion can occur, it seems that this is far from being the most common situation in natural conditions.

On the other hand, the use of the standard Michaelis–Menten model to drive the dynamics of the intracellular nutrient concentrations suggests that an enzymatic process controls the whole uptake/assimilation process, which can be the enzyme-mediated uptake through the cell membrane or the intracellular enzyme reactions. This assumption seems reasonably well founded since “much of the experimental work carried out on nutrient uptake in phytoplankton is amazingly well described by the Michaelis–Menten model” as stated by Aksnes and Egge (1991). The latter argument as well as the mechanistic basis of the Michaelis–Menten model (see later) led us to include this formulation to represent nutrient uptake in the model hereafter presented (see Eq. (27)).

It is however worthwhile mentioning that other mechanistic approaches are available in the literature to represent nutrient uptake in models. Baird and Emsley (1999) for example present a steady-state model in which the extracellular diffusion rate and the intracellular enzyme reaction rate are equal, thus considering that none of these steps is limiting a priori. Aksnes and Egge (1991) investigate a theoretical model for nutrient uptake involving parameters such as the time required for handling one nutrient ion or the cellular number of uptake sites.

### 3.2.1. Modelling uptake, assimilation and exudation of a single nutrient

The simplest description of nutrient uptake is provided in the Michaelis–Menten (MM) function (Eq. (26)) relating the uptake rate $V$ (in mol $X$ (mol C)$^{-1}$ s$^{-1}$) of nutrient $X$ to $X_e$, the medium (external) concentration of nutrient $X$:

$$V = \frac{V_m \cdot X_e}{K_X + X_e}$$

(26)

In Eq. (26), the half-saturation constant $K_X$ is equivalent to the concentration necessary to achieve half the maximal rate of uptake and is often considered independent from the external characteristics of the medium, as well as from cell’s nutrient status (McCarthy, 1981). The Michaelis–Menten model has a mechanistic basis, as it is derived from the law of mass action applied to a basic enzymatic reaction (see Murray (1993) or McCarthy (1981) for the full development and corresponding hypothesis).

As far as we know, the idea of uptake being a function of the intracellular nutrient status was first introduced by Lehman et al. (1975) and this is represented by the quota function $f_Q^{upt}$ (which differs from the growth-controlling $f_Q$ function in Eq. (21)) as shown below in Eq. (27). Different expressions for $f_Q^{upt}$ are now available in the literature, according to the model or the nutrient in consideration. Some of the usual expressions are exhibited in Table 3.

$$V = \frac{V_m \cdot X_e}{K_X + X_e} \cdot f_Q^{upt}$$

(27)

The $f_Q^{upt}$ function includes a feedback factor to account for end-product inhibition of uptake by nutrients that accumulate in the algae. Eq. (27) actually conveys the fact that the intracellular quota affects external processes such as the uptake of external nutrient at the cell membrane. However, internal cell quota should rigorously only affect the intracellular processes (Baird and Emsley, 1999). In these conditions, $V$ as defined in the latter equation should not serve to calculate the uptake rate but rather the internal nutrient accumulation rate. Moreover, Eq. (27) does not account for the fact that phytoplankton can take up nutrients in excess of nutritional requirements, as observed by Lomas and Glibert (1999b) for diatoms. These authors suggest that the reduction of this surplus nitrate would serve as a sink for electrons during periods of imbalance between light energy harvesting and utilization.

For these reasons, we suggest that nutrient uptake proceeds at a rate which only depends on external concentrations and enzymatic activity at the cell membrane as expressed in the original Michaelis–Menten function (Eq. (26)). We will refer to this rate as the *gross* uptake rate $V^g$ hereafter. We also suggest that the feedback of nutrients that accumulate in the cell will control the exudation of dissolved organic matter by phytoplankton. Mathematically, this can be written:
\[ V^g = \frac{dX^e}{dt} = -V_m \cdot \frac{X^e}{K_X + X^e} \]  
(28)

\[ V^n = \frac{dX}{dt} = V_m \cdot f_{\text{upt}} \cdot \frac{X^e}{K_X + X^e} \]  
(29)

\[ \frac{d\text{DOX}}{dt} = \left(1 - f_{\text{upt}}^{\text{opt}}\right) \cdot V_m \cdot \frac{X^e}{K_X + X^e} \]  
(30)

The rate of internal nutrient accumulation is given in Eq. (29) and will be referred to as the net uptake rate \( V^n \), in which \( X \) stands for the intracellular nutrient concentration and \( Q \) for the \( X:C \) quota. In Eq. (30), \( \text{DOX} \) refers to the dissolved organic matter content of element \( X \) (where \( X \) is N or P). Eq. (30) predicts an increase in DOM release with increasing cellular carbon concentrations, and therefore conveys the fact that DOM release will be indicative of the excess of photosynthetically derived energy (ATP and NADPH) relative to biochemical energy demand (Fogg, 1983; Lomas and Glibert, 1999b). The latter equation also represents the idea that when the concentrations of dissolved organic matter in living cells are high (i.e. in nutrient-replete algae), the steep gradient over the cell membrane is a cause of DOM release as suggested in Admiraal et al. (1991). Moreover, in Eqs. (28)–(30), an explicit dependence of \( V_m \) on temperature can be added through a temperature dependence function \( f_T \) of Arrhenius-type as done for growth rate in Eq. (18).

Hence, though the physiological mechanisms for exudation are still poorly understood (Kirchman, 2000 and references therein), this formulation of coupled uptake-exudation processes that is proposed here relies on much experimental evidence: First, this model reproduces the significant amount of experimental work carried out on nutrient uptake (sensu \( V^g \)) in phytoplankton that is well described by the Michaelis–Menten model (Aksnes and Egge, 1991). Second, Eq. (30) infers that nutrient exudation will be weak or non-existent in nutrient-deprived cells (for which \( f_{\text{upt}}^{\text{opt}} \) tends toward 1) and elevated in nutrient-replete cells. This is in agreement with Bronk et al. (1994), who found higher exudation rates in coastal and estuarine environments than in oligotrophic waters of the Caribbean Sea. Bronk (1999) also observed the highest rates of DON release during N-sufficient growth and pointed out that release rates decreased when ammonium was depleted in the culture medium. This is also consistent with the experimental work of Admiraal et al. (1991) who found that (i) the lowest concentrations of amino acids were observed in nitrogen-limited cultures and (ii) \( C. \) granii was able to suppress its amino acid release when deprived of nitrate. Third, Eq. (30) also infers that DON release is higher in darkness than in light, since the intracellular quota increases when photosynthesis stops. This is in agreement with the results of Clark and Flynn (2002) showing that when the uptake of N sources (disappearance from the medium) was compared with assimilation into cellular-N, much of the nitrate-N taken up in darkness was not incorporated.

Though DOP exudation has already been shown (e.g. Bjorkman et al., 2000; Fernández et al., 1997), the understanding of light and phosphorus quota influences on DOP extracellular release is less advanced. However, the assumption has been made of analogous mechanisms for DOP and DON release in the present model.

The exudation process is generally poorly addressed in ecosystem pelagic models. It has often been ignored even in the latest modelling studies (see Fasham et al., 2006), or at best the rates of DOM release are a constant fraction of phytoplankton biomass as in Eq. (31) (see Table 4). However, a low and constant exudation rate \( k_{\text{ex}}^X \) is likely not suitable for all conditions (Laroche et al., 1999), and the way the exudation process is represented in the present model offers another alternative.

\[ R_{\text{ex}}^X = -k_{\text{ex}}^X \cdot X \]  
(31)

### 3.2.1.1. The maximum uptake rate

The variable nature of the maximum rate of nutrient uptake permits phytoplankton populations to grow at near maximal rates even in oligotrophic conditions (McCarthy, 1981), and it has been shown that the maximum uptake rate \( V_m \) usually exhibits a much stronger light dependence than the half-saturation constant \( K_X \) (Litchman et al., 2004 and references herein). On the other hand, much evidence suggests that uptake of the main nutrients by various phytoplankton species continues at night (Serra et al., 1978; Nakamura and Watanabe, 1983; Vergara et al., 1998; Martin-Jézéquel et al., 2000; Flynn et al.,...
Table 4
Phytoplankton dynamics as represented in some of the widely used ecosystem models (only the processes relative to phytoplankton are presented here for the purpose of comparison with our phytoplankton model)

<table>
<thead>
<tr>
<th>Model reference</th>
<th>Structure</th>
<th>Photosynthesis</th>
<th>Photoacclimation</th>
<th>Respiration</th>
<th>Uptake/assimilation</th>
<th>Exudation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moore et al. (2002)</td>
<td>MN (N, P, Si, Fe)</td>
<td>PE curve (Poisson) $g^\text{ml}$ as in Eq. (22a)</td>
<td>Eq. (16)</td>
<td>Constant fraction of biomass</td>
<td>Quota (Eq. (27)); $f^\text{opt}$ (1, in Table 3)</td>
<td>Not included except for N$_2$ fixers at a constant rate (Eq. (31))</td>
</tr>
<tr>
<td>Mongin et al. (2003)</td>
<td>MN (C, N, Si)</td>
<td>PE curve (same shape as 3)</td>
<td>Not included</td>
<td>Not included</td>
<td>MM (Eq. (26))</td>
<td>Constant rate as in Eq. (31)</td>
</tr>
<tr>
<td>PISCES model</td>
<td>MN (P, Si, Fe)</td>
<td>PE curve 4; $g^\text{ml}$ as in Eq. (22b)</td>
<td>Chl is not a state variable</td>
<td>not explicit</td>
<td>MM (Eq. (26))</td>
<td>Constant rate as in Eq. (31)</td>
</tr>
<tr>
<td>ERSEM III</td>
<td>MN (C, N, P, Si)</td>
<td>PE curve 2 or 6; $g^\text{ml}$ as in Eq. (22a) for diatoms and $g^\text{ml} = 1$ otherwise</td>
<td>Not included</td>
<td>As Eq. (34)</td>
<td>$V = \min(V^\text{ext}, V^\text{int}) \cdot C$ where $V^\text{ext} = \delta_X \cdot X^e$ and $V^\text{int} = \mu C Q_{\text{max}} + \gamma (Q_{\text{max}} - Q)^a$</td>
<td>DOC exudation only, as in Eq. (20)</td>
</tr>
</tbody>
</table>

The numbers associated with the $P$ vs. $E$ (PE) curves refer to the index in Table 1. MN refers to a multi-nutrient model and MM to Michaelis–Menten kinetics.

$^a\delta_X$ is a permeability coefficient of the membrane for nutrient $X$ and $\gamma$ is the maximum specific replenishment rate.
2002; Moutin et al., 2002; Sciandra and Amara, 1994), though it seems that the ability to assimilate nutrients in darkness is extremely variable, especially for the nutrients that require more energy to be assimilated (e.g. nitrate vs. ammonium) (Clark and Flynn, 2002; Litchman et al., 2004).

In terms of modelling, an explicit dependence of the uptake rate on light is generally not included in models, since this relation is still not fully understood and is liable to be highly dependent on phytoplankton species as well as on the specific nutrient. An implicit dependence of the uptake on light is, however, considered by Flynn et al. (2002) through relative rates of dark-to-light assimilation of the N-source. They concluded that model output (especially growth rate) is relatively insensitive to these factors. In this context, we have considered in the present model (see Section 5) that uptake can proceed at night at a maximal rate $V_m$ which is similar to that of the day (see Eq. (32)). However, though $V_m$ is constant, the net uptake rate (Eq. (29)) de facto decreases in darkness since the $X:C$ ratio will rapidly increase as photosynthesis stops, not only due to nutrient assimilation but to the associated energetic costs (transport, assimilation, ...).

$$V_m(T_{	ext{req}}) = (P P_{nr}^C)^{\text{max}} \cdot Q_{\text{max}} = a^* \cdot \phi_m^C \cdot E_k \cdot \theta \cdot Q_{\text{max}}$$

(32)

In the latter equation, $V_m$ is proportional to the maximum primary production rate at steady-state under nutrient replete conditions and to the maximum $X:C$ quota $Q_{\text{max}}$. Eq. (32) is similar to that used in other models (e.g. Geider et al., 1998; Flynn, 2003b), though in the latter, the maximum primary production rate is not related to physiological parameters as this is done here (see Section 2.3.4).

3.2.1.2. Towards a purely mechanistic model for nutrient uptake. Besides the Baird and Emsley (1999) approach, which has already been mentioned, other models for uptake based on mechanistic considerations are promising. Accounting for the important conclusion that cell quota variability is largely due to stored nutrients, while the structural composition is relatively constant (Klausmeier et al., 2004), modelling the ability to distinguish between these two intracellular pools is a key step towards purely mechanistic models for nutrient uptake. This idea is not new and already exploited by Shuter (1979) and later by Geider et al. (1996) to derive a model of physiological adaptation to environmental changes based on a division of cellular carbon into distinct compartments. In like manner, the Kooijman (2000) dynamic energetic budget (DEB) theory considers that organisms have clear constraints on how they can partition resources and uses internal reserves and structural body mass as state variables. This class of models has already been applied successfully in population ecology, but requires careful parametrization for individual species, which is still a strong constraint for the extension of such models in natural conditions. The model of Klausmeier et al. (2004) characterizes each phytoplankton species by its allocations to two broad classes of cellular machinery: assembly machinery corresponding to ribosomes and resource-acquisition machinery including both nutrient-uptake proteins and chloroplasts. In addition, each type of machinery has its own chemical composition. These approaches constitute significant improvements resulting in suitable tools for enhancing our understanding of nutrient quota regulation in oceans. The extension of such approaches to ocean modelling, associated with model reduction techniques in order to derive simpler models to account for the key processes at the space and time scales considered, are probably the two key ingredients for future improvement in biogeochemical modelling. Finally, representing the uptake-exudation process by Eqs. (28)–(30) also offers some perspectives about the efflux of inorganic nutrients as a function of cellular quota. As a matter of fact, it has been shown that DON is not the only compound that phytoplankton may release in the aquatic environment (Lomas and Glibert, 2000). Nitrate efflux has been measured in several experimental studies (Serra et al., 1978; Shearer et al., 1991; Needoba and Harrison, 2004) and could be due to an accumulation of nitrate in an internal pool when uptake is faster than assimilation (Needoba and Harrison, 2004). Likewise, ammonium and nitrite efflux have been measured in N-replete phytoplankton (e.g. Collos et al., 1998; Lomas and Glibert, 1999b, 2000) and orthosilicic efflux has been evidenced in diatoms (Milliman et al., 2004). However, the underlying processes are still poorly understood and it seems premature to include these features in the model.

3.2.2. Modelling co-limited uptake and assimilation

Elemental needs can be met with nutrient material in a variety of different forms. In the case of silicon nutrition in diatoms, the source is believed to be exclusively orthosilicic acid (McCarthy, 1981; Milliman et al., 2004), while phosphorus nutrition of phytoplankton is mainly met by orthophosphate. For nitrogen nutrition,
needs can be met by at least two forms of dissolved inorganic nutrients (nitrate and ammonium), in addition to some ability to use DON (urea and some amino acids). This greatly increases the possibility of competitive interaction among the processes responsible for transport and assimilation of different forms of this element (McCarthy, 1981).

In the present paper, the concept of co-limitation is clearly restricted to the effect of a given nutrient on one or more parameters driving the uptake of another nutrient. It is equivalent to the so-called biochemical co-limitation in the recent paper of Arrigo (2005). We will focus here on the best documented example, that of the ammonium effect on nitrate utilization (e.g. Dortch, 1990; Flynn et al., 1997; Lomas and Glibert, 1999b), though a few other examples of co-limitation have also been studied (e.g. iron control on nitrogen uptake in Ragueneau et al. (2000)). Though the mechanism of ammonium inhibition of nitrate utilization is still debated in the literature (Lomas and Glibert, 1999a), the NH\(_4^+\)/NO\(_3^-\) interaction was immediately taken into account in ecosystem models for two main reasons. First, abundant experimental background based on \(^{15}\)N-tracer technique (e.g. Maclsaac and Dugdale, 1972; Glibert, 1982) has been produced over four decades, making possible the parameterization of formulations by data fitting. Second, one of the most important attempts with pelagic ecosystem models based on N-currency (e.g. Fasham et al., 1990; Pondaven et al., 1999) has been to provide computations as accurate as possible of new and regenerated productions in the context of C-export flux assessment. Modelling approaches to simulate the interaction between nitrate uptake and ambient ammonium availability can be divided between two categories: (i) Regulation by external content: This is generally achieved by the use of an inhibition term that acts more or less implicitly on the nitrate uptake rate formulation (Wroblewski, 1977; O’Neill et al., 1989). However these formulations while used widely (e.g. Sarmiento et al., 1993; Kühn and Radach, 1997) have been shown to be inadequate owing to their tendency to either under- or overestimate the new production term in case of high ammonium availability. A slightly different approach developed in Hurtt and Armstrong’s (1999) model considers a top-up by nitrate uptake only when the entire nitrogen requirement is not covered by ammonium utilization. More recently, the relationships proposed by Harrison et al. (1996) and by Yajnik and Sharada (2003) have been shown to be better representations of nitrate uptake control by ammonium and to provide significant improvements in the results of pelagic ecosystem models (Sharada et al., 2005). (ii) Regulation by feedback biochemical mechanisms, an approach developed by Flynn et al. (1997), Flynn and Hipkin (1999) and Flynn (2001) considers that repression of nitrate transport is regulated by the size of the internal glutamine pool. While likely the most mechanistic, this model involves numerous variables and parameters (like the glutamine internal pool, constants for transport rates, ...) that are far from easily measurable. This led us to include in our model the Harrison et al. (1996) formulation for nitrate gross uptake rate (see Eq. (33)), which is an acceptable compromise between simplicity and ability to meet a wide range of trophic conditions. Moreover, this formulation also supports the theory that a direct or indirect (i.e. via the glutamine pool) ammonium effect is principally exerted on uptake of nitrate (e.g. Collos, 1989; Flynn et al., 1997).

\[
V_{\text{NO}_3}^g = V_m \cdot \frac{\text{NO}_3}{K_N + \text{NO}_3} \cdot \left(1 - I_m \cdot \frac{\text{NH}_4}{K_I + \text{NH}_4}\right)
\]  

(33)

In Eq. (33), \(K_I\) is the NH\(_4^+\) concentration at which NO\(_3^-\) uptake is reduced to half its original level and \(I_m\) (values from 0 to 1) is the maximum realized inhibition.

4. Phytoplankton respiration and photorespiration

Through the oxidation of C-substrate to CO\(_2\), phytoplankton respiration (also called “dark” respiration) generates energy in the form of ATP (adenosine triphosphate), a high-energy molecule and reducing power (NADPH) from ADP\(^1\) and NADP\(^2\), which are then used to drive active intracellular processes, among which growth takes a significant part. The consensus in the literature seems to be that phytoplankton respiration is directly influenced by primary production and light availability (Langdon, 1993; Martinez, 1992; Laws et al.,

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\(^1\) ADP: adenosine diphosphate.

\(^2\) NADP: nicotinamid adenosine dinucleotide phosphate.
Martinez (1992), however, showed that “increases in respiratory activity during cell growth are directly promoted by growth rate increases of the algal cells and only indirectly by higher irradiance”. This analysis is the result of surveys performed on the mitochondrial electron transport system (ETS), activity of which seems to be a reliable index of respiratory metabolism. Experimentally, respiration contributes to the difference observed between gross and net primary production (GPP and NPP, respectively), and the ratio of respiration to net photosynthetic rate seems to lie between a minimum value observed for cyanobacteria and a maximum for flagellates, while dark respiration rates are about twice as high for flagellates as for diatoms (Langdon, 1993; Laws et al., 2000).

The theory that mitochondrial respiration rate is higher in the light than in the dark, which is defended by Weger et al. (1989) and Grande et al. (1989), is more controversial. Some scientists (see Laws et al., 2000) observe the opposite (i.e. a decrease in mitochondrial respiration in the light) or that the mitochondrial respiration rate remains unchanged between the dark and the light. If we consider the former theory, the main cause of the respiration enhancement in the light remains subject to debate. Some authors believe that the higher O$_2$ uptake rates observed in the light can be attributed to photorespiration (Laws et al., 2000) or to the Mehler reaction (Beardall and Raven, 1990), while others (Weger et al., 1989) suggest it is due to an increase in substrate supply from photosynthesis and therefore to cell anabolism. The latter would substantiate the aforementioned indirect influence of light (Martinez, 1992). Such considerations will bring us to focus later in this paper on the other O$_2$-consuming processes apart from autotrophic respiration.

4.1. Modelling autotrophic “dark” respiration

The respiration rate is still widely represented in the literature by an empiric division into two components (Langdon, 1993; Beardall and Raven, 1990): (i) the basal or maintenance respiration rate $R^m$ and (ii) a growth-rate dependent component $R^g$ as shown in Eq. (34).

$$R = R^m + R^g \text{ (GPP)}$$

In many models, $R^m$ is constant (and depends only on the species considered), while the function $R^g$ varies linearly with GPP. Experimental values of $R^g$ measured by several authors under inorganic carbon-saturated conditions are regrouped in Beardall and Raven (1990) and vary from 1.5% for the dinoflagellate *Amphidinium carterae* to 48.2% of GPP for the marine diatom *Ditylum brightwellii*. Langdon (1993) suggests that $R^g$ is rather a function of the integrated value of GPP over 24 h (as GPP is zero at night), and a ratio $R_L$ of light respiration to dark respiration ($R_L > 1$) is introduced for the computation of the respiration rate over a 24 h period. Maintenance respiration mainly consists of protein turnover and active processes to maintain specific ion gradients within cells, including processes of physiological adaptation to variable external constraints (Penning de Vries, 1975). Quantitative estimations of each of these contributions, seems too ambitious, but considering a constant maintenance rate constitutes an additional approximation (Cannell and Thornley, 2000). Despite its extensive use (e.g. Shut, 1979; Cullen et al., 1993), the paradigm of subdividing respiration into two categories of ‘growth’ and ‘maintenance’ respiration seems to be irrelevant, because some of the energy-requiring processes cannot be unambiguously allocated to one of these categories (Cannell and Thornley, 2000), and because maintenance respiration is subtracted as a fixed cost unrelated to the C substrate supply (Thornley and Cannell, 2000). Finally, rough estimates of respiration rates are available in the literature, and Laws et al. (2000) affirm that most respiration rates are less than 0.03 h$^{-1}$.

At the opposite extreme, mechanistic models describing the details of the metabolic steps of respiration are proposed. The Hahn (1991) model has the advantage of being restricted to three state variables, namely the cellular concentrations of RuBP (ribulose biphosphate enzyme), PGA (3-phosphoglycerate) and TP (triose phosphate). Unfortunately, there is a weakness in this approach, since none of the initial values of these metabolites, nor the rate constants involved in the model are known. It appears that this level of complexity is unsuitable for the present model that is dedicated to ocean biogeochemical modelling. However, it is necessary that the model render these metabolic processes. In this respect, an acceptable compromise between complexity and realism is given by the energetic costs approach, despite the fact that all available theories elaborated so far are dedicated to higher plants (Penning de Vries et al., 1974; Cannell and Thornley, 2000; Thornley and Cannell, 2000). The purpose of these studies is to estimate respiratory fluxes associated with the
energy-consuming processes by considering the relevant biochemistry of energy conversion reactions. For this, the respiration costs generated by growth, by nitrate, ammonium or other ion uptake, by nitrate reduction, and by N₂ fixation are estimated. For example, nitrate uptake consumes 0.35 g glucose C respired per g of nitrate nitrogen, while the respiratory cost of the uptake of ions other than N is less (i.e. 0.06 g glucose C respired per g mineral taken up) (Cannell and Thornley, 2000). All forms of respiration, among which are those associated with protein turnover and the maintenance of cell ion concentrations and gradients, should be accounted for in the same way, but there is too little information on these processes (Cannell and Thornley, 2000). Hence, a global respiration rate can be derived by considering for each active process its respiratory cost per process unit (or specific unit cost) and the rate at which this process takes place:

\[
\text{respiration rate} = \sum (\text{specific unit cost})_i \times (\text{rate of the process})_i
\]

We will assume in our model (see Section 5) that the specific unit cost of a given process is the same for marine algae as for higher plants, since to our knowledge no data are available for the former group. Such an approximation seems acceptable, however, and it has already been used by Geider et al. (1998).

In conclusion, this approach appears to be the best compromise between realism and simplicity and would deserve to be used in marine ecosystem models. Comparisons with the classical maintenance/growth subdivisions of respiration rate would be an interesting feature for future work. In addition, the separation of intracellular carbon into substrate and structural pools, as suggested by Cannell and Thornley (2000), can be envisaged, so that the dependence of respiratory components on C substrate supply can be represented apart from structural carbon quantities.

4.2. Other oxygen-consuming processes

Apart from autotrophic “dark” respiration, oxygen uptake in the light by photosynthetic organisms depends on at least two processes: photorespiration and the Mehler reaction (Kana, 1992). Photorespiration occurs in the light when the Rubisco enzyme binds with O₂ rather than CO₂ and therefore directly competes with photosynthesis in chloroplasts. This leads to formation of glycolate that is partially released, while the main part is metabolised in further respiration and to a lesser extent in biosynthesis. In marine algae however, photorespiration is usually low, presumably due to the presence of a CO₂ concentrating mechanism (CCM) observed in many phytoplankton groups (Beardall and Raven, 1990; Laws et al., 2000; Kana, 1992). To overcome the low substrate affinity of Rubisco, most phytoplankton species have indeed developed CO₂ concentrating mechanisms to enhance their intracellular CO₂ concentration. Bender et al. (1999) deduced from measurements of O₂ fluxes and ¹⁴C fixation rates during incubations of equatorial Pacific samples that respiration and photorespiration, respectively account for 35% and 15% of GPP. In Dunaliella tertiolecta culture experiments, cells grown in low light were found to allocate up to 20% of the total reduced CO₂ into extracellular glycolate (considered as an indicator of photorespiration activity) against 7% for the cells grown in high light (Leboulanger et al., 1998). Other experiments showed no evidence of significant photorespiration during in situ incubations in the North Pacific subtropical gyre (see Laws et al., 2000), and Weger et al. (1989) and Beardall and Raven (1990) suggest that among the oxygen-consuming processes, photorespiration can be comparatively negligible. The Mehler reaction is another O₂ consuming process that occurs in algae when oxygen (instead of CO₂) acts as a terminal electron acceptor for photosynthetic electron transport. Raven and Beardall (1981) estimate that the Mehler reaction accounts for 10% of gross O₂ evolution when the photosynthetic carbon reduction cycle is not CO₂ limited, while it was not a significant process in the experiments of Weger et al. (1989).

The discrepancies in the literature can presumably be ascribed to the fact that photorespiration and the Mehler reaction, act as photoprotective processes, which would explain their highly variable influence depending on the species type and also on the algal cells' history (e.g. high-light or low-light grown cells). As a matter of fact, the onset of the Mehler activity at the light saturation index \( E_k \) supports the idea that oxygen becomes an alternative sink for electrons from PSI when photon availability exceeds the light harvesting capacity of photosystems (Kana, 1992). In addition, experiments on Synechococcus (Kana, 1992) showed that the contribution of the Mehler reaction was higher for low-light than high-light grown cells. Likewise, because of the
high energy requirement of photorespiratory metabolism, it has been suggested that photorespiration is important for maintaining electron flow to prevent photoinhibition under stress conditions. Again, photorespiration activity was found to depend on the algal cells history (Leboulanger et al., 1998) although it has not been established that photorespiration itself has a protective function (Wingler et al., 2000).

In conclusion, with the exception of the Hahn (1991) model, investigation of the literature for mechanistic modelling of photorespiration and the Mehler reaction processes was not successful, especially in the case of algae. Using assumptions (steady-state, known stationary values, . . .), simulations with Hahn’s model showed that photosynthesis is inhibited by photorespiration and that the apparently wasteful process of photorespiration actually stabilizes the Calvin cycle. However, as already mentioned, this model is not deemed suitable for the present study. Considering present understanding, and as several aforementioned authors consider these processes to be negligible, we omitted photorespiration and the Mehler reaction in the present version of our model. The alternative solution would have been to dedicate fixed proportions of the total oxygen-consumption to each process, but this is far from the observed reality (Grande et al., 1989) and seems to us at least as potentially erroneous as our choice of omitting these processes.

5. The generic mechanistic model

As a result of our investigations, we propose a general formulation for a new group of plankton models through Eqs. (36)–(44). The model includes $n_{\text{phy}}$ phytoplankton functional groups, $n_X$ nutrient elements, as well as DOM and detrital pools. These equations apply for $1 \leq i \leq n_{\text{phy}}$ and $1 \leq j \leq n_X$, and involve state variables, parameters and symbols that are defined in Tables 5–10. Eq. (38) is the conservation equation for phytoplankton carbon. Eqs. (36) and (37) describe the dynamic evolution of the proportion of PSII respectively in the open and inhibited states with (26) serving to calculate the carbon-specific primary production rate $PP_{C_{nr}}$ under nutrient-replete conditions (see Section 2.3.4). Here we remind that the stationary expression for $PP_{C_{nr}}$ given in Eq. (12) can be used as well depending on the rapidity of light variations (see Baklouti et al., 2006, for more details). In this case, Eqs. (36) and (37) can be removed from the model and Eq. (47) must be replaced by Eq. (12).

The carbon-specific primary production rate $PP_C$ (Eq. (46)) is assumed to be a function of nutrient-to-carbon ratio ($Q$) and includes possible multi-nutrient limitation (see Section 3.1.2 for more details). The expression

Table 5
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_{oi}$</td>
<td>Probability of PSII being open in phytoplankton $i$</td>
<td>–</td>
</tr>
<tr>
<td>$n_{mi}$</td>
<td>Probability of PSII being inhibited in phytoplankton $i$</td>
<td>–</td>
</tr>
<tr>
<td>$pC_{i}$</td>
<td>Carbon internal concentration in phytoplankton $i$</td>
<td>(mol C) m$^{-3}$</td>
</tr>
<tr>
<td>$p_{\text{Chl}i}$</td>
<td>Chlorophyll internal concentration in phytoplankton $i$</td>
<td>(g Chl a) m$^{-3}$</td>
</tr>
<tr>
<td>$pX_{ji}$</td>
<td>$X^j$ internal concentration in phytoplankton $i$</td>
<td>(mol $X^j$) m$^{-3}$</td>
</tr>
<tr>
<td>$X_{ji}$</td>
<td>Nutrient external concentration in element $X^j$</td>
<td>(mol $X^j$) m$^{-3}$</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
<td>(mol C) m$^{-3}$</td>
</tr>
<tr>
<td>DOX$^j$</td>
<td>Element $X^j$ in dissolved organic matter</td>
<td>(mol $X^j$) m$^{-3}$</td>
</tr>
<tr>
<td>P0X$^j$</td>
<td>Element $X^j$ in particulate organic matter</td>
<td>(mol $X^j$) m$^{-3}$</td>
</tr>
</tbody>
</table>

$X^j$ refers to the biogenic elements involved in the model ($X^j = \text{N, Si, P, . . .}$).

Table 6
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>Incident irradiance</td>
<td>(mol quanta) m$^{-2}$</td>
</tr>
<tr>
<td>$Q^{X}$</td>
<td>Internal $X^j$:C ratio (quota) in phytoplankton $i = p_{X^j}/p_C$</td>
<td>mol $X^j$ (mol C)$^{-1}$</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Chl:C ratio in phytoplankton $i = p_{\text{Chl}i}/p_C$</td>
<td>g Chl a (mol C)$^{-1}$</td>
</tr>
</tbody>
</table>
for a growth limitation function, $f_Q$, (as well as the one for uptake limitation, $f^{upt}_Q$) are deliberately omitted, as it is advisable to assign a specific function to each nutrient (see Section 3.2). Some of the available formulations for $f_Q$ and $f^{upt}_Q$ are therefore given in Tables 2 and 3, respectively. In Eq. (46), the dependence of the primary production rate on temperature is also considered. We assume that temperature-response function $f_T$ takes the form of an Arrhenius law as given by Eq. (48), but further investigation should be carried out to provide a better representation of the temperature effect on each of the temperature-dependent parameters of the model. Autotrophic respiration (Eqs. (49)–(53)) is represented through the Thornley and Cannell (2000) model, which accounts for the energetic costs $r_g$, $r_{uX}$ and $r_{rN}$ in terms of carbon respectively associated with the three main activities of phytoplanktonic cells, namely growth, nutrient uptake and nitrate reduction (if nutrient $X$ is nitrate). Phytoplankton mortality is classically represented as a function of the standing phytoplankton biomass through a mortality rate constant $m_{p}$. The model includes a variable Chl:C ratio through a specific equation (Eq. (39)) devoted to chlorophyll conservation which has been derived in Section 2.4.

Eq. (40) describes nutrient element $X^l$ accumulation in phytoplankton cells (i.e. gross uptake minus losses due to exudation and mortality). Feedback of intracellular nutrients (through the quota function $f^{upt}_Q$) affects DOM exudation (see Eq. (43)) (see Section 3.2.1). Nutrient gross uptake uses the classical Monod formalism involving the external nutrient concentration $X_e$ (Eq. (41)). In addition to inorganic nutrient uptake, DON and DOP uptake are accounted for (see Eqs. (57) and (58)), as well as nitrate uptake inhibition by ammonium (Eq. (55)).

Table 7
Subscripts and superscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$</td>
<td>Index relative to a phytoplankton group ($1 \leq i \leq n_{phy}$)</td>
</tr>
<tr>
<td>$j$</td>
<td>Index relative to a biogenic element ($1 \leq j \leq n_X$)</td>
</tr>
<tr>
<td>$j_{N_{0}}$</td>
<td>Index relative to nitrate-N: $X^{N_{0}} = (NO_{3})$</td>
</tr>
<tr>
<td>$j_{N_{u}}$</td>
<td>Index relative to ammonium-N: $X^{N_{u}} = (NH_{4})$</td>
</tr>
<tr>
<td>$j_{DON}$</td>
<td>Index relative to DON: $X^{DON} = (DON)$</td>
</tr>
<tr>
<td>$n_{phy}$</td>
<td>Number of phytoplankton groups</td>
</tr>
<tr>
<td>$n_{X}$</td>
<td>Number of nutrient elements</td>
</tr>
</tbody>
</table>

Table 8
Dimensionless functions used in the model

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_T$</td>
<td>Temperature-response function</td>
</tr>
<tr>
<td>$f_Q$</td>
<td>Quota function for growth</td>
</tr>
<tr>
<td>$f_{Q}^{upt}$</td>
<td>Quota function for uptake</td>
</tr>
<tr>
<td>$g^{ml}$</td>
<td>Growth multi-nutrient limitation function (see Eqs. (22) and (23))</td>
</tr>
</tbody>
</table>

Table 9
Symbols and definitions of the rates of processes

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PP_{C_{i}}$</td>
<td>Phytoplankton $i$ carbon specific primary production rate</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$PP_{C_{i}}^{p}$</td>
<td>Phytoplankton $i$ specific PP rate under nutrient replete conditions</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$m_{p}^{i}$</td>
<td>Specific rate of senescence for phytoplankton $i$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$V_{g_{i}}^{l_{i}}$</td>
<td>Carbon specific gross uptake rate of nutrient $X^l$ by phytoplankton $i$</td>
<td>mol $X^l$ (mol C)$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$V_{n_{i}}^{l_{i}}$</td>
<td>Carbon specific net uptake rate of nutrient $X^l$ by phytoplankton $i$</td>
<td>mol $X^l$ (mol C)$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$V_{m_{i}}^{l_{i}}$</td>
<td>Maximum value for $V_{g_{i}}^{l_{i}}$</td>
<td>(mol X$^l$) (mol C)$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$R_{w}^{i}$</td>
<td>Respiration rate relative to process $w$ in phytoplankton $i$</td>
<td>(mol C) m$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>$R_{rem}$</td>
<td>Specific remineralization rate of nutrient $X^l$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$R_{bd}$</td>
<td>Specific breakdown rate of detritus $POX^l$</td>
<td>s$^{-1}$</td>
</tr>
</tbody>
</table>
In the present version, neither zooplankton, nor bacteria have been included, but grazing could be implicitly considered through an enhanced mortality term. Moreover, the bacterial activity is implicitly considered through a remineralization rate $R_{\text{rem}}$ of the dissolved organic compartment (Eqs. (43) and (41)), and a detritus breakdown rate of the particulate organic matter compartment (POM, Eq. (44)). Finally, the source of detritus is phytoplankton mortality, while detrital losses occur through detritus breakdown (see Eq. (44)).

Model equations

Phytoplankton:

\[
\frac{d n_i^o}{dt} = -\alpha^i E n_i^o + \left(1 - n_i^o - n_i^m\right) \tau^i \\
\frac{d n_i^m}{dt} = -k^i_r n_i^m + k^i_H \alpha E \left(1 - n_i^o - n_i^m\right) \\
\frac{d p_i^c}{dt} = PP^{c,i}(T) \cdot p_i^c - \sum_r R_r^c - m_r^p \cdot p_i^c \\
\frac{d p_i^{\text{chl}}}{dt} = \rho_{\text{chl}} \cdot V_i^{\text{chl}} - m_r^p p_i^{\text{chl}} \\
\frac{d p_i^{x,j}}{dt} = V_i^{x,j}(T) \cdot p_i^{x,j} - m_r^p \cdot p_i^{x,j} \\
\frac{d X_j^e}{dt} = -\sum_{i=1}^{n_{\text{phy}}} V_{i,j}^e(T) \cdot p_i^c + R_{\text{rem}}^j DOX^j
\] (36, 37, 38, 39, 40, 41)

Table 10
Model parameters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha^*$</td>
<td>[400; 700 nm] mean Chl a-specific absorption coefficient</td>
<td>$m^2 \ (g \text{Chl a})^{-1}$</td>
</tr>
<tr>
<td>$A_E$</td>
<td>Slope of the linear region of the Arrhenius function</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$E_k$</td>
<td>Light saturation index on the $P$ vs. $E$ curve</td>
<td>mol quanta $m^{-2} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$k_d^H$</td>
<td>Dimensionless PSII damage rate</td>
<td>–</td>
</tr>
<tr>
<td>$k_r$</td>
<td>Rate of repair of damaged PSII</td>
<td>$s^{-1}$</td>
</tr>
<tr>
<td>$K_X$</td>
<td>Half-saturation constant for $X$ uptake</td>
<td>(mol X) $m^{-3}$</td>
</tr>
<tr>
<td>$Q_{\text{max}}^{i}$</td>
<td>Maximum internal quota of $X^i:C$ in phytoplankton $i$</td>
<td>(mol X) (mol C)$^{-1}$</td>
</tr>
<tr>
<td>$Q_{\text{min}}^{i}$</td>
<td>Minimum internal quota of $X^i:C$ in phytoplankton $i$</td>
<td>(mol C) (mol X)$^{-1}$</td>
</tr>
<tr>
<td>$r_{uX}$</td>
<td>Respiration cost for nutrient $X$ uptake</td>
<td>(mol C) (mol X)$^{-1}$</td>
</tr>
<tr>
<td>$r_g$</td>
<td>Respiration cost for growth</td>
<td>(mol C in glucose substrate)$^{-1}$</td>
</tr>
<tr>
<td>$r_{\text{rN}}$</td>
<td>Respiration cost for nitrate reduction</td>
<td>(mol NO$_3$–N reduced to NH$_4$)$^{-1}$</td>
</tr>
<tr>
<td>$T_{\text{ref}}$</td>
<td>Reference temperature</td>
<td>K</td>
</tr>
<tr>
<td>$\alpha^*$</td>
<td>Initial slope of $P^*$ vs. $E$ curve = ‘photosynthesis efficiency’</td>
<td>(mol O$_2$) (g Chl a)$^{-1}$ quanta$^{-1}$ $m^2$</td>
</tr>
<tr>
<td>$\phi_m^{C}$</td>
<td>Maximum quantum yield of carbon fixation</td>
<td>(mol C) quanta$^{-1}$</td>
</tr>
<tr>
<td>$\phi_{\text{chl}}$</td>
<td>Chl a synthesis regulation term (Geider et al., 1998)</td>
<td>(g Chl a) (mol N)$^{-1}$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Absorption cross-section of photosystem II (PSII)</td>
<td>$m^2$ quanta$^{-1}$</td>
</tr>
<tr>
<td>$\theta_m$</td>
<td>Phytoplankton $i$ maximum Chl:C ratio</td>
<td>(g Chl a) (mol C)$^{-1}$</td>
</tr>
<tr>
<td>$\theta_m^{x}$</td>
<td>Phytoplankton $i$ maximum Chl:X ratio</td>
<td>(g Chl a) (mol N)$^{-1}$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Minimum (or stationary) turnover time of electrons</td>
<td>s</td>
</tr>
</tbody>
</table>
Dissolved organic matter:

\[
\frac{d\text{DOC}}{dt} = \sum_{i=1}^{n_{\text{phy}}} (1 - g^m(f_{Qi})) \cdot PP_{nr}^C \cdot f_T \cdot P_C^i \tag{42}
\]

\[
\frac{d\text{DOX}^j}{dt} = \sum_{i=1}^{n_{\text{phy}}} \left[ (1 - f_{Qi}^{\text{ref}}) \cdot V_{i,j}^g(T) \cdot P_C^i - V_{i,j,\text{DOX}}^g \cdot P_C^i \right] - \mathcal{R}_{\text{rem}}^j \text{DOX}^j + \mathcal{R}_{\text{bd}}^j \cdot \text{POX}^j \text{ for } X^j = \text{N or P} \tag{43}
\]

Detritus:

\[
\frac{d\text{POX}^j}{dt} = \sum_{i=1}^{n_{\text{phy}}} m_p^i \cdot P_C^i - \mathcal{R}_{\text{bd}}^j \text{POX}^j \tag{44}
\]

Biogeochemical processes

Primary production:

\[
n^i_e = 1 - n^i_o - n^i_{in} \tag{45}
\]

\[
PP_{C}^j(T) = PP_{nr}^C(T^{\text{ref}}) \cdot g^m(f_{Qi}) \cdot f_T \tag{46}
\]

\[
PP_{nr}^C(T^{\text{ref}}) = a^{ij} \cdot n^i_o \cdot \phi_m^{C} \cdot E \cdot \theta^j \tag{47}
\]

\[
f_T = \exp \left[ A_E \cdot \left( \frac{1}{T} - \frac{1}{T^{\text{ref}}} \right) \right] \tag{48}
\]

Autotrophic respiration:

\[
\sum_{r} R^i_r = R^i_{\text{N}} + R^i_{\text{NH}_4/(j=j_N)} + R^i_{\text{NO}_3} \tag{49}
\]

\[
R^i_{\text{N}} = (r^i_{\text{N}_{\text{NO}_3}} \cdot V_{i,j,\text{NO}_3}^g + r^i_{\text{N}_{\text{NH}_4}} \cdot V_{i,j,\text{NH}_4}^g + r^i_{\text{N}_{\text{DON}}} \cdot V_{i,j,\text{DON}}^g) \cdot P_C^i \tag{50}
\]

\[
R^i_{\text{NH}_4/(j \neq j_N)} = r^i_{\text{NH}_4} \cdot V_{i,j}^g \cdot P_C^i \tag{51}
\]

\[
R^i_{\text{NO}_3} = r^i_{\text{NO}_3} \cdot V_{i,j}^g \cdot P_C^i \tag{52}
\]

Net and gross uptake:

\[
V_{i,j}^g(T) = V_{i,j}^m(T^{\text{ref}}) \cdot f_T(T) \cdot \frac{X^i_e}{K_{X^i} + X^i_e} \text{ if } X^i \neq \text{N and } X^j \neq \text{P} \tag{54}
\]

\[
V_{i,j,\text{NO}_3}^g = V_{i,j}^m(T^{\text{ref}}) \cdot f_T(T) \cdot \frac{\text{NO}_3}{K_{\text{NO}_3} + \text{NO}_3} \cdot \left( 1 - \frac{I_m \cdot \text{NH}_4}{K_I + \text{NH}_4} \right) \tag{55}
\]

\[
V_{i,j,\text{NH}_4}^g = V_{i,j}^m(T^{\text{ref}}) \cdot f_T(T) \cdot \frac{\text{NH}_4}{K_{\text{NH}_4} + \text{NH}_4} \tag{56}
\]
\begin{align*}
V^{\text{\text{N}}}_{ij,\text{DOX}} &= V^{\text{m}}_{ij}(T_{\text{ref}}) \cdot f_T(T) \cdot \frac{\text{DOX}^i}{K_{\text{DOX}}^i + \text{DOX}^j} \quad \text{for } X^j = N \text{ or } P \\
V^{\text{\text{N}}}_{ij,N} &= V^{\text{\text{N}}}_{ij,\text{NO}_3} + V^{\text{\text{N}}}_{ij,\text{NH}_4} + V^{\text{\text{N}}}_{ij,\text{DOX}} \\
V^{\text{\text{N}}}_{ij,P} &= V^{\text{\text{N}}}_{ij}(T_{\text{ref}}) \cdot f_T(T) \cdot \left( \frac{\text{PO}_4}{K_{\text{PO}_4}} + \frac{\text{DOP}}{K_{\text{DOP}} + \text{DOP}} \right) \\
V^{\text{\text{N}}}_{ij}(T) &= V^{\text{\text{N}}}_{ij,N} \cdot \frac{X^i_{\text{Chl}}}{X^i_{\text{Chl}} + X^i_{\text{c}}} \cdot x^{\text{up}}_{ij} \\
V^{\text{\text{N}}}_{ij}(T_{\text{ref}}) &= \alpha^{i} \cdot \phi^{c,i}_{\text{Chl}} \cdot E^{i} \cdot \theta^{i} \cdot Q_{\text{max}}^{ij} \quad \text{where } E^{i} = \frac{1}{\sigma^{i} \cdot \tau^{i}}
\end{align*}

Chlorophyll synthesis:

\begin{align*}
\rho^{N}_{\text{Chl}} &= \frac{\text{PP}^C_{ij}(T)}{\alpha^{i} \cdot \phi^{c,i}_{\text{Chl}} \cdot \theta^{i} \cdot E} = \theta^{N}_{\text{m}} \cdot n^{i}_{o} \cdot g^{\text{ml}}(f^{ij}_{ij}) \cdot f_T \\
V^{\text{\text{N}}}_{\text{Chl}} &= V^{\text{\text{N}}}_{ij,N} \cdot \rho^{C}_{\text{Chl}} \cdot \frac{1 - \theta^{N}_{\text{m}}}{(1 - \theta^{N}_{\text{m}}/\theta^{N}_{\text{m}}) + 0.05}
\end{align*}

### 6. Conclusion

We have investigated the mechanistic formulations available in the literature for the key biogeochemical processes driving the dynamics of phytoplankton in pelagic marine ecosystems, namely photosynthesis (including photoacclimation and photoinhibition), respiration and photorespiration, and control of algal growth by a single or several limiting nutrients.

Our review highlighted that some of the aforementioned processes are now well understood from a physiological point of view. This accurate knowledge recently acquired for marine phytoplankton photosynthesis provides the modelling community with mechanistic formulations, and some of them are discussed in the present study. One of the major strengths of these formulations is that they rely on physical and biochemical bases, which theoretically makes them independent of external parameters. In other words, when a process is mechanistically described by one or a set of mathematical functions, only the physiological parameters that compose these functions are open to (quantitative) change with regard to the ecosystem, but the nature of the mathematical laws should remain unchanged. The use of such mechanistic functions is all the more straightforward since the capability for experimentally measuring the associated physiological parameters now exists. Since the work of Geider et al. (1997, 1998), the photoacclimation process has been included in some biogeochemical models through a specific equation describing phytoplankton chlorophyll. The photoacclimation component of these models (i.e. the $\rho_{\text{Chl}}^{C}$ and $\rho_{\text{Chl}}^{N}$ terms defined in Eqs. (15) and (16), respectively) proved to be successful, but these models fail in representing chlorophyll synthesis in N-replete cells (see Section 2.4). We have therefore proposed a new formulation for the chlorophyll conservation equation which uses the Geider et al. (1998) photoacclimation component, but regulates chlorophyll synthesis by the Chl:N intracellular quota.

The underlying mechanisms of the other processes studied are not wholly described. This typically concerns the control by nutrient availability of algal growth, nutrient uptake and assimilation, and DOM exudation. Purely mechanistic models of these controls have not yet been available because the intimate biochemical knowledge required is still incomplete. The best compromise at present seems to lie with quota models that incorporate some mechanistic elements, but it is likely that a model’s ability to distinguish between structural and storage intracellular pools is a key step towards a realistic representation of the nutrient assimilation process. Moreover, since the exudation process is poorly represented in models, a new formulation in which DON exudation is regulated by the intracellular quota has also been proposed.
Finally, investigation of algal respiration models showed a lack of experimental investigation of marine phytoplankton. While experimental and theoretical studies have already been undertaken for qualifying and quantifying the rates of the main processes involved in the respiration of higher plants and subsequently for obtaining a mechanistic model, similar work has not yet been performed for marine algae, though techniques for measuring such enzymatic-based kinetic rates have been developed for a long time. The alternatives offered to the modellers of marine pelagic ecosystems are thus either to transpose the higher plants model to phytoplankton or to classically subdivide respiration in the two categories of ‘growth’ and ‘maintenance’ respiration.

The preliminary generic phytoplankton model described in Section 5 is the result of the present investigations and intended to be useful to the modelling community. A global sensitivity analysis of this model has been undertaken in order to identify the most influential parameters and to quantify model output uncertainties. This work is presented in a companion paper (Baklouti et al., 2006) in which the outputs of the present model have been successfully compared with experimental measurements. However, it is clear that our model encompasses only a part of the interactions observed at the microbial scale in the Ocean. In the next versions, an explicit bacterial compartment will be integrated due to the crucial roles of microorganisms in the recycling of the organic matter and as potential prey for protozooplankton. Higher trophic levels (from mesozooplankton to fishes) would need to be accounted for also in future work because of their multiple ecological and biogeochemical roles and their implication in the regulation of trophic structure.

Acknowledgments

The authors are deeply grateful to Prof. J.J. Cullen as well as to anonymous reviewers for their insightful remarks.

References


