Supplementary material

S1. Uptake of nitrate

This section gives some background to the approach taken to model the inhibition of nitrate assimilation by ammonium. This processes is modelled on the basis of the synthesizing unit (SU) (Kooijman, 1998, 2010). Here we analyze the case that substrate B inhibits the assimilation of substrate A. When a substrate molecule A or B arrives at the SU, it has a probability ρ to bind to the SU; this probability depends on the state of the SU. For each substrate there are two binding probabilities; (1) 0 if A, or B are bound, (2) for substrates A and B ρ_A or ρ_B, respectively, if neither A and B are bound. Therefore, the possible states of the SU are two. A free synthesizing unit ($SU..$) may bind substrate A or B, giving the states $SU_{A.}$ or $SU_{.B}$, respectively. $SU_{A.}$ can return to the state $SU..$ by delivering the assimilated substrate inside the cell. However, when substrate B is bound to the SU ($SU_{.B}$), it makes part of the SUs unavailable for assimilating the substrate A.

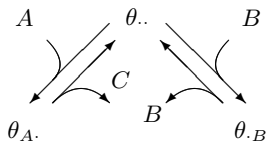

Figure S1. The inhibition scheme, where B inhibits the transformation A $\rightarrow$ C.

The dynamics of the fractions of SUs for this transformation mode are given by

$$\begin{aligned}
\frac{d}{dt}\theta.. &= -(\rho_A j_A + \rho_B j_B)\theta.. + k_A\theta_{A.} + k_B\theta_{.B} \\
\frac{d}{dt}\theta_{A.} &= \rho_A j_A \theta.. - k_A\theta_{A.} \\
\frac{d}{dt}\theta_{.B} &= \rho_B j_B \theta.. - k_A\theta_{.B} \\
\theta.. + \theta_{A.} + \theta_{.B} &= 1
\end{aligned} \tag{S1}$$

where j_A and j_B represent the arrival rates of the substrates A and B, respectively. $\theta..$, $\theta_{A.}$ and $\theta_{.B}$ denote the fraction of SUs present in a particular state. The quasi steady state solution of Eq. (S1) is given by

$$\begin{aligned}
\theta_{..}^{SS} &= (1 + (\rho_A j_A/k_A) + (\rho_B j_B/k_B))^{-1} \\
\theta_{A.}^{SS} &= (\rho_A j_A/k_A)(1 + (\rho_A j_A/k_A) + (\rho_B j_B/k_B))^{-1} \\
\theta_{.B}^{SS} &= (\rho_B j_B/k_B)(1 + (\rho_A j_A/k_A) + (\rho_B j_B/k_B))^{-1}
\end{aligned} \tag{S2}$$

Therefore, the assimilation rate of substrate A is given by $j_C = k_A\theta_{A.}^{SS}$

S2. Model assumptions for the excretion process of dissolved organic matter (DOM) and inorganic nutrients

Phytoplankton excretes DOM at all phases of growth (Myklestad, 2000). Depending on the growth phase, it has been found in phytoplankton cultures of various species excrete two distinct types of carbohydrates. In the exponential phase they excrete

simple carbohydrates that most likely pass the membrane by passive diffusion, whereas in the stationary phase they excrete complex heteropolysaccharides possibly through active exudation (Underwood et al., 2004; Urbani et al., 2005; Borchard and Engel, 2015; Mueller et al., 2016). In addition, in the exponential phase of growth phytoplankton cells have been found to excrete dissolved organic phosphorus (DOP) (Kuenzler, 1970) and dissolved organic nitrogen (DON) in the form of free dissolved amino acids (Admiraal et al., 1986; Chan and Campbell, 1978; Myklestad et al., 1989).

Apart from excretion of DOM, phytoplankton excretes inorganic nutrients. It has been found that phytoplankton release part of the assimilated nitrate in the form of nitrite (Parslow et al., 1984) which can be up to 50 % of the assimilated nitrate (Collos, 1998; Lomas et al., 2000). It seems that nitrite release is widespread in marine phytoplankton. It can be considered as an active exudation process that links to the nitrate uptake (Collos, 1998) and allows phytoplankton to avoid excessive nitrite intracellular concentration (Malerba et al., 2012). Excretion of nitrite has been observed when phytoplankton is replete with nitrate but experiences low-light availability conditions (Kiefer et al., 1976; Flynn and Flynn, 1998; Mordy et al., 2010; Shriwastav et al., 2014). This may result in decoupling of the assimilatory pathways as the relative activity of nitrite reductase to nitrate reductase is reduced (Sciandra and Amara, 1994; Lomas and Lipschultz, 2006; Mordy et al., 2010). This is due to the fact that nitrite reductase requires the light depended ferredoxin as the electron donor, which is synthesized only during photosynthesis (Collos, 1998). In addition, if there are enough carbon skeletons available the excess nitrogen may be exuded in an organic form therefore contributing to the DON pool (Lomas et al., 2000). Here, we hypothesize that once the nitrate reserve is mobilized, if is not further reduced to ammonium and channelled through the catabolic flux, due to stoichiometric constraints, it will be rejected by the SU_2 and excreted into the surrounding medium either as nitrite, which in the model is implicitly added to the NO or the DON pool, while part of it will be reincorporated in the $\mathrm{E_{NO}}$ reserve.

The mobilization of the $\mathrm{E_{NH}}$ reserve can also result in a rejection flux due to the stoichiometric constraints. Although DON exudation by phytoplankton is well documented, there aren't much data on ammonium exudation as a dissipatory mechanism. However it has been found that the diazotrophic cynobacteria *Trichodesmium erythreum* and *Nodularia spumigenaevidence* release a significant amount of the N_2 that is fixed both as ammonium and DON, while this release was not necessarily linked to the recently assimilated nitrogen but rather on the nitrogen reserves (Wannicke et al., 2009). This finding suggests that the exudation of nitrogenous compounds may be, in analogy with DOC exudation, a dissipating mechanism of the intracellular nitrogen that is in excess. This mechanism links to the rejection flux from the SU suggested by DEB theory. Thus, as for the $\mathrm{E_{NO}}$ reserve, a part of the rejection flux due to the mobilization of the $\mathrm{E_{NH}}$ will be exuded in the surrounding medium in the form of NH and DON and the rest will be reincorporated back to the $\mathrm{E_{NH}}$–reserve.

In analogy, SU kinetics imply a rejection flux for the mobilization of the $\mathrm{E_P}$–reserve. Although there is no much information about exudation of phosphate, Jansson (1993) reports that phosphate was excreted by phytoplankton cells growing in cultures with high phosphate concentration, while Wen et al. (1997) showed that in 11 species of freshwater algae, about half of the phosphate taken up was excreted. On the other hand, phosphate replete cells of *Thalassiosira pseudonana* have been found to produce DOP in the form of P–esters (Saad et al., 2016). Thus we assume that a part of the rejection flux due to the mobilization of the $\mathrm{E_P}$ will be exuded in the surrounding medium in the form of P and DOP and the rest will be reincorporated back to the $\mathrm{E_P}$–reserve.

S3. Sensitivity analysis

The method of local sensitivity analysis was used in order investigate the sensitivity of the model to parameter values. Thus, only small deviations from the reference set of parameter values (Table S1) are considered. ΔW is the change of the quantity of interest as a result of the perturbation of the parameter value p from the reference parameter and Δp is the change of the parameter. Then the ratio between the relative change in W to the relative change in p is defined as the sensitivity index SI given by

$$SI = \frac{\Delta W/W}{\Delta p/p} \tag{S3}$$

A negative value of SI would indicate that an increase of the (positive) parameter causes a decrease in the output. The absolute value of the sensitivity index expresses the magnitude of the output change that is caused by a parameter change.

The sensitivity analysis was performed by running the model under the N–limited scenario and by increasing the reference parameter by 10 $\%$. Then the three phases of nutrient availability (nutrient–replete, intermediate, nutrient–limited) were identified in each simulation using the criteria described in Sect. 3.2.1. The sensitivity index for each parameter was calculated based on the mean biomass and the mean specific DOC release rate for the three phases. Table S1 includes the parameters that result in sensitivity index with absolute value >0.05 at least at one phase of nutrient availability. The parameters a_L and I as well as ρ_N, $v_{P_{max}}$ and $y_{NA,E_{CH}}$ are redundant and, thus, only one is shown in Table S1, namely a_L and $y_{NA,E_{CH}}$. The results of the sensitivity analysis (Table S1) indicate that the model (in terms of both DOC release rate and biomass) was most sensitive to parameters related to photosynthesis light and dark reactions (a_L, $\rho_{L_{max}}$, $j_{IC_{max}}$, ρ_{IC}) and the stoichiometric coefficients $y^{NO}_{CH,E}$ $y_{E,V}$ $y_{IC,E_{CH}}$ $y_{NA,L}$ $y_{NA,E_{CH}}$ at all three nutrient availability phases. In addition, the parameters ρ_{NO}, b_N, $k_{E_{NO}}$ although they where rather insensitive ($|SI| < 0.05$) during the nutrient replete phase, they became rather important ($|SI| > 0.2$) during the intermediate and nutrient–limited phase. Also, biomass wasn't very sensitive to changes in the parameters ρ_{CH} and $k_{E_{CH}}$ during the first two phases, but it had $|SI| > 0.2$ in the N–limited phase, while DOC release rate was sensitive to those two parameters during both the intermediate and N–limited phase. Furthermore, the model was very sensitive to the parameter $\kappa_{E_{CH}}$. The model outputs where sensitive to handling of nitrate k_1 (assimilation SU) but at different phases for mean biomass and DOC release rate. Finally, κ_{ENO} although was relatively important ($|SI| > 0.05$) for biomass it was not important for the specific DOC release rate while the opposite was observed for the specific death rate, h. The sensitivity analysis performed for the P–limited scenario, generally, indicated the same parameters related to photosynthesis and the stoichiometric coefficients appeared to have the major effect on Biomass and DOC release rate. In addition in the P–limited scenario, the model was also sensitive ($|SI| > 0.05$) to the parameters b_P, $j_{P_{max}}$, k_{E_P}, κ_{E_P},$n_{P,E}$,$n_{P,V}$,ρ_P and $v_{P_{min}}$, all related to phosphorus, during the intermediate and nutrient–limited phase (results not shown).

Table S1. Sensitivity of the predicted mean biomass and DOC release rate in the three nutrient availability phases. The values represent the sensitivity index for a 10% increase in each of the model parameters.

	Biomass			DOC release		
Parameter	N–replete	intermediate	N–limited	N–replete	intermediate	N–limited
a_L	0.44	0.61	0.52	0.30	0.56	0.98
$j_{IC_{max}}$	0.46	0.32	0.10	0.31	0.30	0.14
k_L	0.20	0.21	0.06	0.13	0.15	0.07
k_{CH}	0.11	0.11	0.03	0.08	0.08	0.03
k_1	-0.40	-0.02	0.17	-0.03	0.25	0.42
K_{IC}	-0.12	-0.01	-0.04	-0.08	-0.09	-0.11
$\rho_{L_{max}}$	0.44	0.59	0.42	0.30	0.54	0.77
$\rho_{L_{min}}$	0.00	0.13	0.08	0.00	0.01	0.10
ρ_{NO}	-0.03	-0.23	-0.39	-0.04	-0.42	-1.03
ρ_{CH}	-0.05	0.01	-0.21	-0.10	-0.35	-0.57
ρ_{NH}	0.01	-0.04	-0.18	0.00	-0.12	-0.50
ρ_{IC}	0.46	0.32	0.10	0.31	0.30	0.14
k_E	0.13	0.10	-0.08	0.17	-0.08	-0.23
$k_{E_{CH}}$	0.00	-0.07	-0.26	0.13	0.47	0.25
$k_{E_{NO}}$	0.00	-0.31	-0.55	-0.06	-0.59	-1.38
$k_{E_{NH}}$	0.02	0.00	-0.07	-0.01	-0.06	-0.21
j_{E_M}	-0.13	-0.03	-0.08	-0.10	-0.08	-0.15
h	-0.02	-0.04	-0.04	0.03	0.06	0.07
$y_{NA,L}$	0.65	0.82	0.59	0.44	0.73	1.07
$y_{NA,E_{CH}}$	-0.27	-0.54	-0.56	-0.44	-0.66	-1.04
$y_{IC,E_{CH}}$	-0.47	-0.26	-0.12	-0.32	-0.33	-0.23
$y^{NO}_{CH,E}$	-0.62	-0.36	-0.14	-0.72	-0.37	-0.14
$y^{NH}_{CH,E}$	-0.08	-0.14	-0.17	-0.06	-0.14	-0.34
$y_{E,V}$	-0.55	-0.75	-0.62	-0.69	-0.17	0.47
$n_{N,E}$	0.01	0.20	0.19	0.01	0.02	-0.10
$n_{N,V}$	-0.06	-0.50	-0.66	-0.04	-0.52	-1.31
$\kappa_{E_{CH}}$	0.05	1.63	1.48	-0.48	-6.19	-8.62
$\kappa_{E_{NO}}$	0.00	0.16	0.08	0.00	0.05	0.02
b_N	0.02	0.30	0.33	0.01	0.26	0.63

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