Technical description of prototype Tracers Of Phytoplankton with Allometric Zooplankton (TOPAZ) ocean biogeochemical model as used in the Princeton IFMIP* model†

John P. Dunne, Anand Gnanadesikan, Jorge L. Sarmiento and Richard D. Slater

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1 Introduction

The ecosystem model used in this paper is a prototype version of the GFDL ecosystem model now known as Tracers of Phytoplankton with Allometric Zooplankton (TOPAZ). This code was developed primarily by John Dunne of the Geophysical Fluid Dynamics Laboratory with assistance and feedback from a variety of colleagues including Jorge Sarmiento, Anand Gnanadesikan, Curtis Deutsch, Eric Galbraith, and Charles Stock among others. This prognostic ocean biogeochemistry/ecology model was built to represent the interaction of biologically active elements and ecological cycling with the carbon cycle by considering 25 tracers including three phytoplankton groups, two forms of dissolved organic matter, heterotrophic biomass, and dissolved inorganic species for coupled C, N, P, Si, Fe, $CaCO_3$, O_2 and lithogenic cycling with flexible N:P:Fe stoichiometry. The model includes such processes as gas exchange, atmospheric deposition, scavenging, N_2 fixation and denitrification, river inputs, and sediment processes.

The model was designed to represent the phytoplankton functional groups of a small (picoplankton/nanoplankton) group caught in a tight microbial loop loosely characterized as cyanobacteria, and a large (nanoplankton, microplankton) group of phytoplankton capable of being decoupled from grazing and to create sinking material. The latter are facultatively diatoms. This serves as an alternative to explicitly representing diatoms as the only exportable form of primary production after Dunne et al (2000). Loss of phytoplankton is parameterized through the size-based relationship of Dunne et al. (2005), which allows for the large plankton to dominate the ecosystem at high growth rates and biomass, while the small plankton dominate at low growth rates and biomass. The model includes the ballasting scheme of Klass and Archer (2002) for mineral protection. It represents iron cycling with both sediment and atmospheric sources of iron supply and scavenging.

The goal of this supplement is to be a repository of the equations solved by the model, making it possible to reconstruct the details of the calculations presented in the main paper. It is not intended to provide a rigorous justification of the formulations used here. It should also be noted that many of these formulations have been altered in the final version of the model that will be used for the IPCC Fifth Assessment. In what follows we introduce the state variables for the model (both prognostic and diagnostic tracers), describe how phytoplankton growth rates are calculated, relate these growth rates to nutrient uptake, calculate grazing sources of particulate and dissolved biogenic materials, describe the processing of this material through the water column and on the sea floor, summarize the resulting sources and sinks, and provide several tables listing important parameters.

1.1 Overall equation

For each state variable C (see list below), we solve the continuity equation

$$\frac{\partial C}{\partial t} = -\nabla \cdot \tilde{u} C + \nabla K \nabla C + S_C \qquad (1)$$

*Iron Fertilization Model Intercomparison Project

†Sarmiento et al (submitted)

where $\tilde{u}$ is the velocity vector from the Ocean General Circulation Model (OGCM), K is the diffusivity, and S_C is the sum of the sources and sinks for state variable C (detailed below).

1.2 State variables

1.2.1 Prognostic variables which are transported by the physical model

$$\text{Nitrate} = \left[NO_3^-\right] \tag{2}$$

$$\text{Ammonium} = \left[NH_4^+\right] \tag{3}$$

$$\text{Phosphate} = \left[PO_4^{-3}\right] \tag{4}$$

$$\text{Silicate} = \left[SiO_4^{-4}\right] \tag{5}$$

$$\text{Dissolved Oxygen} = [O_2] \tag{6}$$

$$\text{Dissolved Iron} = Fe_d \tag{7}$$

$$\text{Dissolved Inorganic Carbon} = DIC \tag{8}$$

$$\text{Alkalinity} = ALK \tag{9}$$

$$\text{Nitrogen in Small Phytoplankon} = N^{Sm} \tag{10}$$

$$\text{Nitrogen in Large Phytoplankon} = N^{Lg} \tag{11}$$

$$\text{Phosphorus in Large Phytoplankon} = P^{Lg} \tag{12}$$

$$\text{Nitrogen in Diazatrophs} = N^{Di} \tag{13}$$

$$\text{Iron in Small Phytoplankon} = Fe^{Sm} \tag{14}$$

$$\text{Iron in Large Phytoplankon} = Fe^{Lg} \tag{15}$$

$$\text{Iron in Diazatrophs} = Fe^{Di} \tag{16}$$

$$\text{Silica in Large Phytoplankon} = Si^{Lg} \tag{17}$$

$$\text{Labile Dissolved Organic Nitrogen} = LDON \tag{18}$$

$$\text{Semi-labile Dissolved Organic Nitrogen} = SDON \tag{19}$$

$$\text{Semi-labile Dissolved Organic Phosphorus} = SDOP \tag{20}$$

1.2.2 Diagnostic variables which are not transported by the physical model

$$\text{Particulate Iron} = \{Fe_p\} \tag{21}$$

$$\text{Chlorophyll} = \{Chl\} \tag{22}$$

$$\text{Large Phytoplankton Nitrogen Grazing Memory} = \{N^{Lg}_{graz}\} \tag{23}$$

1.2.3 Variables supplied by the General Circulation Model

$$\text{Shortwave Irradiance} = \{Irr\} \tag{24}$$

Note that the irradiance in the water column is a function of the surface irradiance from the GCM and the predicted chlorophyll from this ecosystem model.

1.2.4 Operators

$$\text{Summation operator over phytoplankton classes} = \sum \tag{25}$$

2 Phytoplankton growth, zooplankton grazing and nutrient uptake

2.1 Calculation of phytoplankton growth rates

In general terms, the model represents light, macronutrient and iron limitation of phytoplankton physiology and production based on the Geider et al. (1997) model of steady-state co-limitation of light and nutrients with several modifications described below. The details of these modifications in terms of the multiplicative versus Leibig-minimum-type combination of terms have important implications for the response to iron perturbations and regional behavior.

2.1.1 Calculate nutrient limitation terms

Nitrate limitation with ammonia inhibition is represented after Frost and Franzen (1992) with an additional term for saturation of inhibition at high ammonia of Sharada et al. (2005)

$$Lim^{Sm}_{NO_3^-} = \frac{[NO_3^-] \cdot \left(1 + \frac{[NH_4^+]}{\mathrm{K_{NO_3^-}}}\right)}{\left(\mathrm{K_{NO_3^-}} + [NO_3^-]\right) \cdot \left(1 + \frac{[NH_4^+]}{\mathrm{K^{Sm}_{NH_4^+}}}\right)} \tag{26}$$

$$Lim^{Lg}_{NO_3^-} = \frac{[NO_3^-] \cdot \left(1 + \frac{[NH_4^+]}{\mathrm{K_{NO_3^-}}}\right)}{\left(\mathrm{K_{NO_3^-}} + [NO_3^-]\right) \cdot \left(1 + \frac{[NH_4^+]}{\mathrm{K^{Lg}_{NH_4^+}}}\right)} \tag{27}$$

$$Lim^{Sm}_{NH_4^+} = \frac{[NH_4^+]}{\mathrm{K^{Sm}_{NH_4^+}} + [NH_4^+]} \tag{28}$$

$$Lim^{Lg}_{NH_4^+} = \frac{[NH_4^+]}{\mathrm{K^{Lg}_{NH_4^+}} + [NH_4^+]} \tag{29}$$

where $\mathrm{K_{NO_3^-}}$ is a half-sautration constant for nitrate, and $\mathrm{K^{Sm}_{NH_4^+}}$ and $\mathrm{K^{Lg}_{NH_4^+}}$ are half-saturation constants for ammonia for small and large phytoplankton (there is no nitrogen limitation for diazotrophs).

The remaining nutrient limitation terms are straight Michaelis-Menten.

$$Lim_{PO_4^{-3}} = \frac{[PO_4^{-3}]}{\mathrm{K}_{\mathrm{PO}_4^{-3}} + [PO_4^{-3}]} \tag{30}$$

$$Lim_{SiO_4^{-4}} = \frac{[SiO_4^{-4}]}{\mathrm{K}_{\mathrm{SiO}_4^{-4}} + [SiO_4^{-4}]} \tag{31}$$

$$Lim_{Fe}^{Sm} = \frac{Fe_d}{\mathrm{K}_{\mathrm{Fe}}^{\mathrm{Sm}} + Fe_d} \tag{32}$$

$$Lim_{Fe}^{Lg} = \frac{Fe_d}{\mathrm{K}_{\mathrm{Fe}}^{\mathrm{Lg}} + Fe_d} \tag{33}$$

$$Lim_{Fe}^{Di} = \frac{Fe_d}{\mathrm{K}_{\mathrm{Fe}}^{\mathrm{Di}} + Fe_d} \tag{34}$$

where the $\mathrm{K}_{\mathrm{Fe}}^{\mathrm{Sm,Lg,Di}}$ terms are half-saturation constants for iron for small, large and diazotrophic plankton.

Temperature limitation on growth is handled using an expression equivalent to the Eppley (1972) formulation of growth rates. The nutrient and temperature-limited growth rates for the three phytoplankton types are

$$P_{C_m}^{Sm} = \mathrm{P}_{\mathrm{C_{max}}}^{\mathrm{Sm}} \cdot \min\left(Lim_{NO_3^-}^{Sm} + Lim_{NH_4^+}^{Sm},\ Lim_{PO_4^{-3}}\right) \cdot \mathrm{e}^{\kappa T} \tag{35}$$

$$P_{C_m}^{Lg} = \mathrm{P}_{\mathrm{C_{max}}}^{\mathrm{Lg}} \cdot \min\left(Lim_{NO_3^-}^{Lg} + Lim_{NH_4^+}^{Lg},\ Lim_{PO_4^{-3}},\ Lim_{SiO_4^{-4}}\right) \cdot \mathrm{e}^{\kappa T} \tag{36}$$

$$P_{C_m}^{Di} = \mathrm{P}_{\mathrm{C_{max}}}^{\mathrm{Di}} \cdot Lim_{PO_4^{-3}} \cdot \mathrm{e}^{\kappa T} \tag{37}$$

where κ is the constant governing temperature dependence of growth.

2.1.2 Light limitation

Phytoplankton are assumed to be photoadapted to the mean light level in the actively mixing layer as defined in the KPP routine plus 10 m to account for mixing directly below the boundary layer

$$\{\overline{Irr}\} = \{Irr\}\ \text{averaged over KPP Boundary Layer} \tag{38}$$

This model predicts the Chl:N ratio at each time-step as an equilibrated phytoplankton response to the combined pressures of light, major nutrient and iron limitation. Phytoplankton uptake is generally modeled after Geider et al. (1997) as a function of steady state nitrogen and CO_2 uptake, but also includes the following important modifications:

1. The temperature effect of Eppley (1972) is used instead of that in Geider et al (1997) for both simplicity and to incorporate combined effects on uptake, incorporation into organic matter and photorespiration. Values of $P_{C_{max}}$ are normalized to 0°C rather than 20°C as in Geider et al. (1997),

2. The Fe:N ratio is allowed to modulate the Chl:N ratio to be consistent with Sunda and Huntsman (1997) through the "chlorosis" factor - the phytoplankton Fe:N ratio normalized to a saturated value ($\mathrm{Fe:N_{irr}}$) necessary to synthesize chlorophyll,

3. Values of the maximum Chl:C ratio ($\theta_{\max}$) are increased and values of alpha decreased to account for the additional iron term in the theta equation,

4. A minimum $\theta_{\min}$ value is also incorporated to set a minimum level of chlorophyll per carbon.

While major nutrient limitation is handled through Michaelis Menten limitation of the phytoplankton specific growth prefactor (P_{C_m}), iron limitation is handled indirectly through modulation of the Chl:N ratio. This allows a compensatory relationship between irradiance and iron availability on phytoplankton specific growth, i.e. if plankton have a lot of light, they do not need a lot of iron and vice versa. Chlorosis is assumed to be a quadratic function of the Fe:N ratio nomalized to vary between 0 and 1. This relationship is a simple/crude representation of the complex physiological requirements and functionality of iron which separates phytoplankton iron into three components:

1. a "basal" requirement of iron for phytoplankton respiration and protein synthesis (e.g. the electron transport chain)
2. Chlorophyll synthesis for photosynthesis
3. Luxury uptake

While somewhat mathematically ad-hoc, this representation is grounded in the observed relationship between Chl:C, Fe:C, dissolved Fe and phytoplankton specific growth rates of Sunda and Huntsman (1997) as well our general understanding of the role of iron in phytoplankton physiology (e.g Geider and La Rocha, 1994).

The general form of the equations is thus that chlorosis, χ, is calculated as follows:

$$\chi = \frac{(\text{Fe:N})^2}{\left[(\text{Fe:N})^2_{\text{irr}} + (\text{Fe:N})^2\right]} = \frac{Fe^2}{(\text{Fe : N})^2_{\text{irr}} \cdot N^2 + Fe^2}$$

Chlorosis then affects the Chl:C calculation after Geider et al (1997) as follows:

$$Chl\text{:C} = \theta = \frac{\theta_{max}}{1 + \theta_{max} \cdot \frac{\alpha \cdot I}{2 \cdot P_{C_m}}} \cdot \chi$$

or, alternatively, as a Liebig-type formulation:

$$\theta = \min\left(\frac{\theta_{max}}{1 + \theta_{max} \cdot \frac{\alpha \cdot I}{2 \cdot P_{C_m}}}, \theta_{max} \cdot \chi\right)$$

The Liebig-type reformulation of θ eliminates one of the limitations of the baseline model's formulation of iron limitation of phytoplankton growth, which is the need to utilize elevated values of $\text{P}_{\text{C}_{\text{max}}}$ compared to observations of phytoplankton growth under ideal conditions (i.e. Eppley, 1972; Bissinger et al 2008). The sensitivity study described in the discussion utilizes an alternative formulation of iron limitation on phytoplankton growth by simply capping the θ_{max} value as a function of iron limitation rather than applying iron limitation as a multiplicative factor at all values of θ. Because of this reformulation, we are able to return $P_{C_{max}}$ values to the lower values (1.5x10^{-5} s^{-1}) corresponding to those observed in the SEEDS experiment for observed zero-temperature-normalized growth rates for *Chaetoceros debilis* of 0.98 d^{-1} (Tsuda et al., 2003).

The growth rate (after Geider et al., 1997) is then calculated as follows:

$$\mu = \frac{P_{C_m}}{(1+\zeta)} \cdot \left(1 - \text{e}^{(-\alpha \cdot I \cdot Chl\text{:C}/P_{C_m})}\right)$$

where ζ parameterizes the assimilatory efficiency. Thus for each functional group, the equation is

$$\chi^{Sm} = \frac{Fe^{Sm^2}}{\left(\text{Fe:N}_{\text{irr}} \cdot N^{Sm}\right)^2 + Fe^{Sm^2}} \tag{39}$$

$$\chi^{Lg} = \frac{Fe^{Lg^2}}{\left(\text{Fe:N}_{\text{irr}} \cdot N^{Lg}\right)^2 + Fe^{Lg^2}} \tag{40}$$

$$\chi^{Di} = \frac{Fe^{Di^2}}{\left(\text{Fe:N}^{\text{Di}}_{\text{irr}} \cdot N^{Di}\right)^2 + Fe^{Di^2}} \tag{41}$$

$$\theta^{Sm} = \frac{P^{Sm}_{C_m} \cdot \theta^{\text{Sm}}_{\text{max}}}{P^{Sm}_{C_m} + \frac{1}{2}\theta^{\text{Sm}}_{\text{max}} \cdot \alpha^{\text{Sm}} \cdot \left\{\overline{Irr}\right\}} \cdot \chi^{Sm} + \theta_{\text{min}} \tag{42}$$

$$\theta^{Lg} = \frac{P^{Lg}_{C_m} \cdot \theta^{\text{Lg}}_{\text{max}}}{P^{Lg}_{C_m} + \frac{1}{2}\theta^{\text{Lg}}_{\text{max}} \cdot \alpha^{\text{Lg}} \cdot \left\{\overline{Irr}\right\}} \cdot \chi^{Lg} + \theta_{\text{min}} \tag{43}$$

$$\theta^{Di} = \frac{P^{Di}_{C_m} \cdot \theta^{\text{Di}}_{\text{max}}}{P^{Di}_{C_m} + \frac{1}{2}\theta^{\text{Di}}_{\text{max}} \cdot \alpha^{\text{Di}} \cdot \left\{\overline{Irr}\right\}} \cdot \chi^{Di} + \theta_{\text{min}} \tag{44}$$

The alternate formulations for θ for small and large phytoplankton are:

$$\theta^{Sm} = \min\left(\frac{P_{C_m}^{Sm} \cdot \theta_{\max}^{\mathrm{Sm}}}{P_{C_m}^{Sm} + \frac{1}{2}\theta_{\max}^{\mathrm{Sm}} \cdot \alpha^{\mathrm{Sm}} \cdot \{\overline{Irr}\}} + \theta_{\min},\ \theta_{\max}^{\mathrm{Sm}} \cdot \chi^{Sm}\right) \tag{45}$$

$$\theta^{Lg} = \min\left(\frac{P_{C_m}^{Lg} \cdot \theta_{\max}^{\mathrm{Lg}}}{P_{C_m}^{Lg} + \frac{1}{2}\theta_{\max}^{\mathrm{Lg}} \cdot \alpha^{\mathrm{Lg}} \cdot \{\overline{Irr}\}} + \theta_{\min},\ \theta_{\max}^{\mathrm{Lg}} \cdot \chi^{Lg}\right) \tag{46}$$

$$Lim_{Irr}^{Sm} = 1 - \mathrm{e}^{\left(-\alpha^{\mathrm{Sm}} \cdot \{Irr\} \cdot \theta^{Sm} / P_{C_m}^{Sm}\right)} \tag{47}$$

$$Lim_{Irr}^{Lg} = 1 - \mathrm{e}^{\left(-\alpha^{\mathrm{Lg}} \cdot \{Irr\} \cdot \theta^{Lg} / P_{C_m}^{Lg}\right)} \tag{48}$$

$$Lim_{Irr}^{Di} = 1 - \mathrm{e}^{\left(-\alpha^{\mathrm{Di}} \cdot \{Irr\} \cdot \theta^{Di} / P_{C_m}^{Di}\right)} \tag{49}$$

$$\mu^{Sm} = \frac{P_{C_m}^{Sm}}{1+\zeta} \cdot Lim_{Irr}^{Sm} \tag{50}$$

$$\mu^{Lg} = \frac{P_{C_m}^{Lg}}{1+\zeta} \cdot Lim_{Irr}^{Lg} \tag{51}$$

$$\mu^{Di} = \frac{P_{C_m}^{Di}}{1+\zeta} \cdot Lim_{Irr}^{Di} \tag{52}$$

Total chlorophyll is calculated for use in the short-wave absorption module of the OGCM.

$$\{Chl\} = \mathrm{C{:}N} \cdot 12000 \cdot \left(\theta^{Sm} \cdot N^{Sm} + \theta^{Lg} \cdot N^{Lg} + \theta^{Di} \cdot N^{Di}\right) \tag{53}$$

2.2 Nutrient uptake terms

The uptake of dissolved constituents by the different planktonic types are calculated as below.

- NO_3^- and NH_4^+ uptake are calculated as fractions of total nitrogen uptake.
- Diazotrophs produce organic nitrogen from N_2
- PO_4^{-3} uptake is assumed to be stoichiometric to nitrogen for Sm and NH_4^+ for Lg with the same stoichiometric ratio (N:P=16:1; Goldman, 1980). A higher stoichiometric ratio (N:P=50:1; Letelier and Karl, 1998) is used for diazotrophs Di.
- The ratio PO_4^{-3} to NO_3^- uptake in large phytoplankton $P{:}N_{NO_3}^{Lg}$ is variable based on the degree of iron limitation in order to represent the low N:P values observed in the Southern Ocean (Arrigo et al., 1999). The idea is that under iron limitation large phytoplankton are able to build an interior pool of NO_3^-, but are unable to reduce it and so end up with an apparent excess of PO_4^{-3}. The ratio of phosphate to nitrate uptake is then

$$P{:}N_{NO_3}^{Lg} = \left(1 - \chi^{Lg}\right) \cdot \mathrm{P{:}N}_{\chi} + \chi^{Lg} \cdot \mathrm{P{:}N}^{\mathrm{SmLg}} \tag{54}$$

- Large phytoplankton and diazotrophic iron uptake is limited not by the phytoplankton growth rate, but by the iron concentration in the cells, following Sunda and Huntman (1997). Iron uptake is thus limited by low environmental concentrations or high cell quotas. Small phytoplankton are forced to diminish their uptake at saturated levels of the Fe:C ratio in small phytoplankton (to mimic their general lack of luxury storage capacity).
- Silica uptake is made to be consistent with the Si:N ratio synthesis of Martin-Jezequel et al (2000) and the Droop quota argument of Mongin et al. (2003)
- $CaCO_3$ formation is set to go directly to detritus as a constant fraction of Sm production after Moore et al (2002)

The uptake terms are then

$$J^{Sm}_{prod_{NO_3^-}} = \mu^{Sm} \cdot N^{Sm} \cdot \frac{Lim^{Sm}_{NO_3^-}}{Lim^{Sm}_{NO_3^-} + Lim^{Sm}_{NH_4^+}} \tag{55}$$

$$J^{Lg}_{prod_{NO_3^-}} = \mu^{Lg} \cdot N^{Lg} \cdot \frac{Lim^{Lg}_{NO_3^-}}{Lim^{Lg}_{NO_3^-} + Lim^{Lg}_{NH_4^+}} \tag{56}$$

$$J^{Sm}_{prod_{NH_4^+}} = \mu^{Sm} \cdot N^{Sm} \cdot \frac{Lim^{Sm}_{NH_4^+}}{Lim^{Sm}_{NO_3^-} + Lim^{Sm}_{NH_4^+}} \tag{57}$$

$$J^{Lg}_{prod_{NH_4^+}} = \mu^{Lg} \cdot N^{Lg} \cdot \frac{Lim^{Lg}_{NH_4^+}}{Lim^{Lg}_{NO_3^-} + Lim^{Lg}_{NH_4^+}} \tag{58}$$

$$J^{Di}_{prod_N} = \mu^{Di} \cdot N^{Di} \tag{59}$$

$$J^{Sm}_{prod_{PO_4^{-3}}} = \mathrm{P{:}N^{SmLg}} \cdot \left(J^{Sm}_{prod_{NO_3^-}} + J^{Sm}_{prod_{NH_4^+}} \right) \tag{60}$$

$$J^{Lg}_{prod_{PO_4^{-3}}} = \mathrm{P{:}N^{SmLg}} \cdot J^{Lg}_{prod_{NH_4^+}} + P{:}N^{Lg}_{NO_3^-} \cdot J^{Lg}_{prod_{NO_3^-}} \tag{61}$$

$$J^{Di}_{prod_{PO_4^{-3}}} = \mathrm{P{:}N^{Di}} \cdot J^{Di}_{prod_N} \tag{62}$$

$$J^{Sm}_{prod_{Fe}} = \mathrm{V^{Sm}_{max_0}} \cdot Lim^{Sm}_{Fe} \cdot \mathrm{e}^{\kappa T} \cdot N^{Sm} \cdot \left(1 - \chi^{Sm} \cdot \mathrm{e}^{\left(-\mathrm{Fe{:}N_{sat}} \cdot Fe^{Sm}/N^{Sm}\right)}\right) \tag{63}$$

$$J^{Lg}_{prod_{Fe}} = \mathrm{V^{Lg}_{max_0}} \cdot Lim^{Lg}_{Fe} \cdot \mathrm{e}^{\kappa T} \cdot N^{Lg} \cdot \left(1 - \chi^{Lg}\right) \tag{64}$$

$$J^{Di}_{prod_{Fe}} = \mathrm{V^{Di}_{max_0}} \cdot Lim^{Di}_{Fe} \cdot \mathrm{e}^{\kappa T} \cdot N^{Di} \cdot \left(1 - \chi^{Di}\right) \tag{65}$$

$$Lim_{Si:N} = \left[\frac{Lim_{SiO_4^{-4}}}{\min\left(Lim^{Lg}_{N},\ Lim_{PO_4^{-3}},\ Lim^{Lg}_{Fe}\right)} \right]^2 \tag{66}$$

$$Si{:}N = \frac{\mathrm{Si{:}N_{max}} - \mathrm{Si{:}N_{min}}}{\mathrm{Si{:}N_{max}} + Lim_{Si:N}} \cdot Lim_{Si:N} + \mathrm{Si{:}N_{min}} \tag{67}$$

$$J_{prod_{SiO_4^{-4}}} = \mu^{Lg} \cdot Lim_{SiO_4^{-4}} \cdot Si{:}N \cdot N^{Lg} \tag{68}$$

$$J_{prod_{CaCO_3}} = \left(J^{Sm}_{prod_{NO_3^-}} + J^{Sm}_{prod_{NH_4^+}} \right) \cdot \mathrm{Ca{:}N} \tag{69}$$

2.3 Food Web Processing

2.3.1 Phytoplankton loss

A key feature of the model is the use of the relationship of Dunne et al. (2005) for grazing rates. Grazing of small and diazotrophic phytoplankton is proportional to their concentration to the 2nd power - consistent with a rapid approach to steady state with a grazer population whose growth rates are comparable to to those of the phytoplankton. Grazing of large phytoplankton is proportional to their concentration to the 4/3rd power - consistent with a moderate imbalance with an implicit grazer population after Dunne et al (2005) or potentially a greater top-down control on these grazers.

The grazing on the large phytoplankton is not actually calculated using the in-situ concentration but rather an implicit concentration- after incorporation of a term for a temperature-dependent time lag. The idea is to mimic the time-lag sometimes observed in zooplankton life cycles as they respond to the spring bloom.

$$\left\{N^{Lg}_{graz}\right\} = \left\{N^{Lg}_{graz}\right\}_{old} \cdot \mathrm{e}^{\left(\frac{N^{Lg}-\left\{N^{Lg}_{graz}\right\}_{old}}{N^{Lg}+\left\{N^{Lg}_{graz}\right\}_{old}}\right)\cdot 2\cdot \min\left(1,\, \mathrm{e}^{\kappa T}\cdot \frac{\Delta \mathrm{t}}{\tau_{\mathrm{graz}}}\right)} \tag{70}$$

Additionally two criteria for numerical stability are added:

1. The absolute first order rate constant is never allowed to be greater than $\mathrm{k_{graz_{max}}}$.
2. A Michaelis-Menton type of threshold using a half saturation value of $\mathrm{Phyto_{min}}$ is set to prevent phytoplankton from going extinct at low concentrations.

Then the formulation for the grazing terms is

$$J^{Sm}_{graz_N} = \min\left(\mathrm{k_{graz_{max}}},\ \lambda_0 \cdot \mathrm{e}^{\kappa T} \cdot \frac{N^{Sm}}{\mathrm{P*}}\right) \cdot \frac{N^{Sm^2}}{(N^{Sm} + \mathrm{Phyto_{min}})} \tag{71}$$

$$J^{Lg}_{graz_N} = \min\left(\mathrm{k_{graz_{max}}},\ \lambda_0 \cdot \mathrm{e}^{\kappa T} \cdot \left[\frac{\left\{N^{Lg}_{graz}\right\}}{\mathrm{P*}}\right]^{\frac{1}{3}} \cdot \frac{\left\{N^{Lg}_{graz}\right\}}{N^{Lg} + \mathrm{Phyto_{min}}}\right) \cdot N^{Lg} \tag{72}$$

$$J^{Di}_{graz_N} = \min\left(\mathrm{k_{graz_{max}}},\ \lambda_0^{\mathrm{Di}} \cdot \mathrm{e}^{\kappa T} \cdot \left[\frac{N^{Di}}{\mathrm{P*}}\right]^{\frac{1}{3}} \cdot \frac{N^{Di}}{N^{Di} + \mathrm{Phyto_{min}}}\right) \cdot N^{Di} \tag{73}$$

2.3.2 Detritus and DON production

Grazing results in the production of detritus and dissolved organic material. Constant fractions of the grazed materials are converted to semilabile dissolved organic nitrogen $SDON$ and labile dissolved organic nitrogen $LDON$.

The remaining grazing production is converted to sinking detritus and excreted as ammonia. Sinking detritus production is a temperature dependent fraction of small (plus diazotrophic) and large phytoplankton grazing, with a single temperature dependence, but different maximal detritus-production-efficiencies after Dunne et al (2005).

$$J^{Sm}_{SDON} = \phi_{\mathrm{SDON}} \cdot J^{\ Sm}_{graz_N} \tag{74}$$

$$J^{Sm}_{LDON} = \phi_{\mathrm{LDON}} \cdot J^{Sm}_{graz_N} \tag{75}$$

$$J^{Sm}_{prod_{PON}} = \mathrm{f^{Sm}_{det_0}} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}}\cdot T} \cdot J^{Sm}_{graz_N} \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) \tag{76}$$

$$J^{Sm}_{graz_{NH_4^+}} = \left(1 - \mathrm{f^{Sm}_{det_0}} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}}\cdot T}\right) \cdot J^{Sm}_{graz_N} \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) \tag{77}$$

$$J^{Lg}_{SDON} = \phi_{\mathrm{SDON}} \cdot J^{\ Lg}_{graz_N} \tag{78}$$

$$J^{Lg}_{LDON} = \phi_{\mathrm{LDON}} \cdot J^{Lg}_{graz_N} \tag{79}$$

$$J^{Lg}_{prod_{PON}} = \mathrm{f^{Lg}_{det_0}} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}}\cdot T} \cdot J^{Lg}_{graz_N} \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) \tag{80}$$

$$J^{Lg}_{graz_{NH_4^+}} = \left(1 - \mathrm{f^{Lg}_{det_0}} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}}\cdot T}\right) \cdot J^{Lg}_{graz_N} \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) \tag{81}$$

$$J^{Di}_{SDON} = \phi_{\mathrm{SDON}} \cdot J^{\ Di}_{graz_N} \tag{82}$$

$$J^{Di}_{LDON} = \phi_{\mathrm{LDON}} \cdot J^{Di}_{graz_N} \tag{83}$$

$$J^{Di}_{prod_{PON}} = \mathrm{f^{Sm}_{det_0}} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}}\cdot T} \cdot J^{Di}_{graz_N} \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) \tag{84}$$

$$J^{Di}_{graz_{NH_4^+}} = \left(1 - \mathrm{f}^{\mathrm{Sm}}_{\mathrm{det}_0} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}} \cdot T}\right) \cdot J^{Di}_{graz_N} \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) \tag{85}$$

$$J^{Sm}_{graz_P} = \mathrm{P{:}N}^{\mathrm{SmLg}} \cdot J^{Sm}_{graz_N} \tag{86}$$

$$J^{Lg}_{graz_P} = \frac{P^{Lg}}{N^{Lg}} \cdot J^{Lg}_{graz_N} \tag{87}$$

$$J^{Di}_{graz_P} = \mathrm{P{:}N}^{\mathrm{Di}} \cdot J^{Di}_{graz_N} \tag{88}$$

$$P{:}N_{graz} = \frac{\sum J_{graz_P}}{\sum J_{graz_N}} \tag{89}$$

$$J^{Sm}_{SDOP} = \phi_{\mathrm{SDOP}} \cdot J^{Sm}_{graz_P} \tag{90}$$

$$J^{Sm}_{LDOP} = \phi_{\mathrm{LDON}} \cdot J^{Sm}_{graz_P} \tag{91}$$

$$J^{Sm}_{prod_{POP}} = \frac{P{:}N_{graz}}{\mathrm{P{:}N}^{\mathrm{SmLg}}} \cdot \mathrm{f}^{\mathrm{Sm}}_{\mathrm{det}_0} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}} \cdot T} \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) \cdot J^{Sm}_{graz_P} \tag{92}$$

$$J^{Sm}_{graz_{PO_4^{-3}}} = \left[\left(1 - \frac{P{:}N_{graz}}{\mathrm{P{:}N}^{\mathrm{SmLg}}} \cdot \mathrm{f}^{\mathrm{Sm}}_{\mathrm{det}_0} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}} \cdot T}\right) \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) + (\phi_{\mathrm{SDOP}} - \phi_{\mathrm{SDON}})\right] \cdot J^{Sm}_{graz_P} \tag{93}$$

$$J^{Lg}_{SDOP} = \phi_{\mathrm{SDOP}} \cdot J^{Lg}_{graz_P} \tag{94}$$

$$J^{Lg}_{LDOP} = \phi_{\mathrm{LDON}} \cdot J^{Lg}_{graz_P} \tag{95}$$

$$J^{Lg}_{prod_{POP}} = \frac{P{:}N_{graz}}{P^{Lg}/N^{Lg}} \cdot \mathrm{f}^{\mathrm{Lg}}_{\mathrm{det}_0} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}} \cdot T} \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) \cdot J^{Lg}_{graz_P} \tag{96}$$

$$\begin{aligned} J^{Lg}_{graz_{PO_4^{-3}}} = J^{Lg}_{graz_P} \cdot \\ \left[\left(1 - \frac{P{:}N_{graz}}{P^{Lg}/N^{Lg}} \cdot \mathrm{f}^{\mathrm{Lg}}_{\mathrm{det}_0} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}} \cdot T}\right) \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) + (\phi_{\mathrm{SDOP}} - \phi_{\mathrm{SDON}}) + \left(1 - \frac{\mathrm{P{:}N}^{\mathrm{SmLg}}}{P^{Lg}/N^{Lg}}\right) \cdot \phi_{\mathrm{LDON}}\right] \end{aligned} \tag{97}$$

$$J^{Di}_{SDOP} = \phi_{\mathrm{SDOP}} \cdot J^{Di}_{graz_P} \tag{98}$$

$$J^{Di}_{LDOP} = \frac{\mathrm{P{:}N}^{\mathrm{SmLg}}}{\mathrm{P{:}N}^{\mathrm{Di}}} \cdot \phi_{\mathrm{LDON}} \cdot J^{Di}_{graz_P} \tag{99}$$

$$J^{Di}_{prod_{POP}} = \frac{P{:}N_{graz}}{\mathrm{P{:}N}^{\mathrm{Di}}} \cdot \mathrm{f}^{\mathrm{Sm}}_{\mathrm{det}_0} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}} \cdot T} \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) \cdot J^{Di}_{graz_P} \tag{100}$$

$$\begin{aligned} J^{Di}_{graz_{PO_4^{-3}}} = J^{Di}_{graz_P} \cdot \\ \left[\left(1 - \frac{P{:}N_{graz}}{\mathrm{P{:}N}^{\mathrm{Di}}} \cdot \mathrm{f}^{\mathrm{Sm}}_{\mathrm{det}_0} \cdot \mathrm{e}^{\kappa_{\mathrm{remin}} \cdot T}\right) \cdot (1 - \phi_{\mathrm{SDON}} - \phi_{\mathrm{LDON}}) + (\phi_{\mathrm{SDOP}} - \phi_{\mathrm{SDON}}) + \left(1 - \frac{\mathrm{P{:}N}^{\mathrm{SmLg}}}{\mathrm{P{:}N}^{\mathrm{Di}}}\right) \cdot \phi_{\mathrm{LDON}}\right] \end{aligned} \tag{101}$$

Finally, a nitrification term, which is inhibited by light as in Ward et al. (1982), is calculated.

$$J_{nitrif} = \frac{1}{\tau_{\mathrm{nitrif}}} \cdot \left[\mathrm{NH}_4^+\right] \cdot \mathrm{e}^{(-\mathrm{nitrif}_{\mathrm{inhibit}} \cdot \{Irr\})} \tag{102}$$

2.3.3 Iron and Silicon Processing

Iron proceeds through the grazing cycle with the same efficiency as nitrogen so that

$$J^{Sm}_{graz_{Fe}} = J^{Sm}_{graz_N} \cdot \frac{Fe^{Sm}}{N^{Sm}} \tag{103}$$

$$J^{Lg}_{graz_{Fe}} = J^{Lg}_{graz_N} \cdot \frac{Fe^{Lg}}{N^{Lg}} \tag{104}$$

$$J^{Di}_{graz_{Fe}} = J^{Di}_{graz_N} \cdot \frac{Fe^{Di}}{N^{Di}} \tag{105}$$

$$J_{prod_{POFe}} = \frac{\sum J_{graz_{Fe}}}{\sum J_{graz_N}} \cdot \sum J_{prod_{PON}} \tag{106}$$

Silica grazing occurs in proportion to its concentration in large phytoplankton (there is no preference for or against diatoms) but it dissolves differently from nitrogen. Nelson et al. (1995), find that the fraction of biogenic opal SiO_2 that dissolves within the mixed layer as a result of grazing is 50%, but they and others (Blain et al., 1999, Brzezenski, 1985) find that there is also a temperature dependence to this dissolution. The temperature functionality is set to a combination Michaelis Menton and Eppley (1972) to roughly match the range of observations in Nelson et al. (1995), Blain et al. (1999) and Brzezenski (1985). This is ad hoc, but without the temperature dependence it was not possible to reproduce the high tropical surface SiO_4 concentrations.

$$J_{graz_{SiO_2}} = J^{Lg}_{graz_N} \cdot \frac{Si^{Lg}}{N^{Lg}} \tag{107}$$

$$J_{diss_{SiO_2}} = J_{graz_{SiO_2}} \cdot \frac{\mathrm{e}^{\kappa T}}{\mathrm{K}_{\mathrm{diss}_{\mathrm{SiO_2}}} + \mathrm{e}^{\kappa \mathrm{T}}} \tag{108}$$

2.4 Ballast Protection Interior Remineralization Scheme

Following Armstrong et al., (2002) and Klass and Archer (2002) we divide the organic material produced by grazing into two components, an unprotected component that has a short remineralization scale of $\mathrm{w_{sink}}/\gamma_{\mathrm{det}} = 187\,\mathrm{m}$ and a protected component, which is associated with ballast materials. In this version of the model the ballast materials are calcium carbonate (with a remineralization depth scale $\mathrm{Ca_{remin\text{-}depth}} = 3500\,\mathrm{m}$) and biogenic silica (with a remineralization depth scale $\mathrm{Si_{remin\text{-}depth}} = 2000\,\mathrm{m}$). Particulate iron is formed through a simple quadratic removal term and associated with both organic detritus and ballast materials and is returned to the water column when these materials remineralize.

The remainder of this section describes the sequence of calculations, as performed in the code.

2.4.1 Surface Layer

The flux, $F(k)$, of ballast materials and organic detritral material through the bottom of the surface box ($k = 1$) is calculated.

$$F_{SiO_2}(1) = \left(J_{graz_{SiO_2}}(1) - J_{diss_{SiO_2}}(1)\right) \cdot \Delta z_1 \tag{109}$$

$$F_{CaCO_3}(1) = J_{prod_{CaCO_3}}(1) \cdot \Delta z_1 \tag{110}$$

$$F_{PON}(1) = \left(J^{Sm}_{prod_{PON}}(1) + J^{Lg}_{prod_{PON}}(1) + J^{Di}_{prod_{PON}}(1)\right) \cdot \Delta z_1 \tag{111}$$

$$F_{POP}(1) = \left(J^{Sm}_{prod_{POP}}(1) + J^{Lg}_{prod_{POP}}(1) + J^{Di}_{prod_{POP}}(1)\right) \cdot \Delta z_1 \tag{112}$$

where Δz_1 is the thickness of the surface box.

The code allows for adsorption and desorption of iron onto this material, as listed below, but this functionality was turned off in these runs. Iron adsorption is made a simple quadratic function of dissolved iron concentration.

$$J_{Fe_{ads}}(1) = Fe_d(1) \cdot \min\left(\mathrm{k'_{Fe_{max}}},\ \mathrm{k''_{Fe}} \cdot Fe_d(1)\right) \tag{113}$$

$$J_{Fe_{des}}(1) = \mathrm{k_{Fe_{des}}} \cdot \{Fe_p(1)\} = 0 \tag{114}$$

Since it is the fluxes of PON and POP through the bottom of the grid cell are already calculated, there no sink is necessary in the top layer. There is also no denitrification from either sedimentary or water column processes in this layer.

$$J_{PON}(1) = 0 \tag{115}$$

$$J_{denit_{wc}}(1) = 0 \tag{116}$$

$$J_{denit_{sed}}(1) = 0 \tag{117}$$

$$J_{POP}(1) = 0 \tag{118}$$

$$J_{POFe}(1) = 0 \tag{119}$$

$$J_{SiO_4^{-4}}(1) = 0 \tag{120}$$

$$J_{CaCO_3}(1) = 0 \tag{121}$$

$$J_{Fe_{sink}}(1) = \frac{-\{Fe_p(1)\}}{\Delta z_1} \cdot \mathrm{w_{sink}} \tag{122}$$

2.4.2 Sub-surface layers

At each level, k, below the surface, the remineralization term of the sinking ballast materials entering the box from above is calculated implicitly.

$$F_{SiO_2}(k) = \frac{F_{SiO_2}(k-1)}{1 + \frac{\Delta z_k}{\mathrm{Si_{remin\text{-}depth}}}} \tag{123}$$

$$F_{CaCO_3}(k) = \frac{F_{CaCO_3}(k-1)}{1 + \frac{\Delta z_k}{\mathrm{Ca_{remin\text{-}depth}}}} \tag{124}$$

where Δz_k is the thickness of box k.

Next, remineralization of unprotected organic material and previously protected particulate organic material entering the box from above is calculated.

$$F_{PON_{prot}}(k) = \min\left(F_{PON}(k-1),\ \mathrm{rp_{SiO_2}} \cdot F_{SiO_2}(k) + \mathrm{rp_{CaCO_3}} \cdot F_{CaCO_3}(k)\right) \tag{125}$$

If $[\mathrm{O_2}] > \mathrm{O_{2_{min}}}$ then [under oxic conditions]

$$F_{PON}(k) = \min\left(F_{PON}(k-1),\ \left[F_{PON}(k-1) + \frac{F_{PON_{prot}}(k) \cdot \gamma_{\mathrm{det}} \cdot \Delta \mathrm{z_k}}{\mathrm{w_{sink}}}\right] \cdot \frac{\mathrm{w_{sink}}}{\mathrm{w_{sink}} + \gamma_{\mathrm{det}} \cdot \Delta \mathrm{z_k}}\right) \tag{126}$$

$$J_{denit_{wc}}(k) = 0 \tag{127}$$

$$J_{denit_{sed}}(k) = 0 \tag{128}$$

else [under suboxic conditions]

$$F_{PON}(k) = \min\left(F_{PON}(k-1),\ \left[F_{PON}(k-1) + \frac{F_{PON_{prot}}(k) \cdot \gamma_{\mathrm{denit}} \cdot \Delta \mathrm{z_k}}{\mathrm{w_{sink}}}\right] \cdot \frac{\mathrm{w_{sink}}}{\mathrm{w_{sink}} + \gamma_{\mathrm{denit}} \cdot \Delta \mathrm{z_k}}\right) \tag{129}$$

$$J_{denit_{wc}} = \left(F_{PON}(k-1) - F_{PON}(k)\right) \cdot \frac{\mathrm{N{:}N_{denit}}}{\Delta \mathrm{z_k}} \tag{130}$$

The nitrogen change is applied to phosphorus assuming equal partitioning between protected, previously protected and unprotected particulate organic material

$$F_{POP}(k) = F_{PON}(k) \cdot \frac{F_{POP}(k-1)}{F_{PON}(k-1)} \tag{131}$$

The adsorption and desorption of iron is calculated.

$$J_{Fe_{ads}}(k) = Fe_d\,(k) \cdot \min\left(\mathrm{k}'_{\mathrm{Fe_{max}}}, \mathrm{k}''_{\mathrm{Fe}} \cdot Fe_d(k)\right) \tag{132}$$

$$J_{Fe_{des}}\,(k) = \mathrm{k}_{\mathrm{Fe_{des}}} \cdot \{Fe_p\,(k)\} = 0 \tag{133}$$

The dissolution and remineralization terms are calculated as the difference between the incoming flux at the top and fraction of this flux that makes it to the bottom of the grid box.

$$J_{SiO_4^{-4}}\,(k) = \frac{F_{SiO_2}\,(k-1) - F_{SiO_2}\,(k)}{\Delta z_k} \tag{134}$$

$$J_{CaCO_3}\,(k) = \frac{F_{CaCO_3}\,(k-1) - F_{CaCO_3}\,(k)}{\Delta z_k} \tag{135}$$

$$J_{PON}\,(k) = \frac{F_{PON}\,(k-1) - F_{PON}\,(k)}{\Delta z_k} \tag{136}$$

$$J_{POP}\,(k) = \frac{F_{POP}\,(k-1) - F_{POP}\,(k)}{\Delta z_k} \tag{137}$$

The particulate iron associated with the sinking biogenic material is then returned to dissolved form according to the mass fraction of the particulate material that is dissolved.

$$J_{POFe}\,(k) = \frac{J_{PON}\,(k) \cdot \mathrm{Mass{:}N} + 60 \cdot J_{SiO_4^{-4}}\,(k) + 100 \cdot J_{CaCO_3}\,(k)}{F_{PON}\,(k-1) \cdot \mathrm{Mass{:}N} + 60 \cdot F_{SiO_2}\,(k-1) + 100 \cdot F_{CaCO_3}\,(k-1)} \cdot \{Fe_p\} \cdot \mathrm{w_{sink}} \tag{138}$$

The production of silicate, calcium carbonate and organic material within a box is added to the flux at at bottom of box.

$$F_{SiO_2}\,(k) = F_{SiO_2}\,(k) + \left(J_{graz_{SiO_2}}\,(k) - J_{diss_{SiO_2}}\,(k)\right) \cdot \Delta z_k \tag{139}$$

$$F_{CaCO_3}\,(k) = F_{CaCO_3}\,(k) + J_{prod_{CaCO_3}}\,(k) \cdot \Delta z_k \tag{140}$$

$$F_{PON}\,(k) = F_{PON}\,(k) + \left(J^{Sm}_{prod_{PON}}\,(k) + J^{Lg}_{prod_{PON}}\,(k) + J^{Di}_{prod_{PON}}\,(k)\right) \cdot \Delta z_k \tag{141}$$

$$F_{POP}\,(k) = F_{POP}\,(k) + \left(J^{Sm}_{prod_{POP}}\,(k) + J^{Lg}_{prod_{POP}}\,(k) + J^{Di}_{prod_{POP}}\,(k)\right) \cdot \Delta z_k \tag{142}$$

A sinking flux is computed for particulate iron

$$J_{Fe_{sink}}\,(k) = \frac{\{Fe_p\,(k-1)\} - \{Fe_p\,(k)\}}{\Delta z_k} \cdot \mathrm{w_{sink}} \tag{143}$$

This is then repeated through the water column down to the ocean bottom.

2.5 Apply sediment flux to all ocean cells adjacent, or with a corner in contact, to land

Near the coast, a sedimentary source of iron is associated with flux to the bottom.

$$J_{Fe_{sed\text{-}coast}} = \frac{\mathrm{Fe_{coast_{max}}}}{\Delta z} \cdot \frac{F_{PON}}{\mathrm{Fe_{sed_{sat}}} + F_{PON}} \tag{144}$$

2.6 Account for remineralization/dissolution of sinking flux, and sediment processed in bottom box

In the bottom box, the following steps are applied.

A sedimentary denitrification sink is calculated after Middelburg et al. (1996)

$$log_{bottom\text{-}flux} = \log_{10}(F_{PON} \cdot \text{C:N} \cdot 86400) \tag{145}$$

$$J_{denit_{sed}} = \frac{1}{\Delta z} \cdot \min\left(F_{PON}, \frac{10^{-0.9543+0.7662 \cdot log_{bottom\text{-}flux} - 0.235 \cdot log^2_{bottom\text{-}flux}}}{\text{C:N} \cdot 86400}\right) \tag{146}$$

Iron addition from sediments is calculated as a function of organic matter supply

$$J_{Fe_{sed\text{-}coast}} = \frac{\text{Fe}_{\text{sed}_{\text{max}}}}{\Delta z} \cdot \frac{F_{PON}{}^2}{\text{Fe}_{\text{sed}_{\text{sat}}} + F_{PON}} \tag{147}$$

Sinking fluxes of silicate, calcium carbonate and organic material are dissolved/remineralized in the bottom box.

$$J_{SiO_4^{-4}} = J_{SiO_4^{-4}} + \frac{F_{SiO_2}}{\Delta z} \tag{148}$$

$$J_{CaCO_3} = J_{CaCO_3} + \frac{F_{CaCO_3}}{\Delta z} \tag{149}$$

$$J_{PON} = J_{PON} + \frac{F_{PON}}{\Delta z} \tag{150}$$

$$J_{POP} = J_{POP} + \frac{F_{POP}}{\Delta z} \tag{151}$$

2.7 Calculate total source and sink terms

The individual source and sink terms calculated above are then summed to produce total source and sink terms for each prognostic tracer.

2.7.1 Phytoplankton Nitrogen and Phosphorus

Small Phytoplankton Nitrogen

$$S_N^{Sm} = J^{Sm}_{prod_{NO_3^-}} + J^{Sm}_{prod_{NH_4^+}} - J^{Sm}_{graz_N} \tag{152}$$

Large Phytoplankton Nitrogen

$$S_N^{Lg} = J^{Lg}_{prod_{NO_3^-}} + J^{Lg}_{prod_{NH_4^+}} - J^{Lg}_{graz_N} \tag{153}$$

Diazotrophic Phytoplankton Nitrogen

$$S_N^{Di} = J^{Di}_{prod_N} - J^{Di}_{graz_N} \tag{154}$$

Large Phytoplankton Phosphorus

$$S_P^{Lg} = J^{Lg}_{prod_{PO_4^{-3}}} - J^{Lg}_{graz_N} \cdot \frac{P^{Lg}}{N^{Lg}} \tag{155}$$

2.7.2 Phytoplankton Silicon and Iron

Large Phytoplankton Silicon

$$S_{Si}^{Lg} = J_{prod_{SiO_4^{-4}}} - J_{graz_{SiO_2}} \tag{156}$$

Small Phytoplankton Iron

$$S_{Fe}^{Sm} = J^{Sm}_{prod_{Fe}} - J^{Sm}_{graz_{Fe}} \tag{157}$$

Large Phytoplankton Iron

$$S_{Fe}^{Lg} = J^{Lg}_{prod_{Fe}} - J^{Lg}_{graz_{Fe}} \tag{158}$$

Diazotrophic Phytoplankton Iron

$$S_{Fe}^{Di} = J^{Di}_{prod_{Fe}} - J^{Di}_{graz_{Fe}} \tag{159}$$

2.7.3 Other nutrients

NO_3^-

$$S_{NO_3^-} = J_{nitrif} - \left(J^{Sm}_{prod_{NO_3^-}} + J^{Lg}_{prod_{NO_3^-}} + J_{denit_{wc}} + J_{denit_{sed}} \right) \tag{160}$$

NH_4^+

$$S_{NH_4^+} = -\left(J^{Sm}_{prod_{NH_4^+}} + J^{Lg}_{prod_{NH_4^+}} + J_{nitrif} \right) + \sum J_{graz_{NH_4^+}} + \frac{1}{\tau_{\text{SDON}}} \cdot SDON + \frac{1}{\tau_{\text{LDON}}} \cdot LDON + J_{PON} \tag{161}$$

PO_4^{-3}

$$S_{PO_4^{-3}} = -\sum J_{prod_{PO_4^{-3}}} + \sum J_{graz_{PO_4^{-3}}} + \frac{1}{\tau_{\text{SDOP}}} \cdot SDOP + \frac{1}{\tau_{\text{LDON}}} \cdot LDON \cdot \text{P:N}^{\text{SmLg}} + J_{POP} \tag{162}$$

SiO_4^{-4}

$$S_{SiO_4^{-4}} = J_{SiO_4^{-4}} - J_{prod_{SiO_4^{-4}}} + J_{diss_{SiO_2}} \tag{163}$$

2.7.4 Dissolved and Particulate Iron

$$S_{Fe_d} = \sum J_{graz_{Fe}} + J_{Fe_{des}} + J_{POFe} + J_{Fe_{sed\text{-}coast}} - \left(J_{prod_{POFe}} + J^{Sm}_{prod_{Fe}} + J^{Lg}_{prod_{Fe}} + J^{Di}_{prod_{Fe}} + J_{Fe_{ads}} \right) \tag{164}$$

$$\{Fe_p(t)\} = \{Fe_p(t-1)\} + [J_{prod_{POFe}} + J_{Fe_{ads}} + J_{Fe_{sink}} - (J_{Fe_{des}} + J_{POFe})] \cdot \Delta t \tag{165}$$

2.7.5 Dissolved Organic Matter

Semilabile Dissolved Organic Nitrogen

$$S_{SDON} = J_{SDON} - \frac{1}{\tau_{\text{SDON}}} \cdot SDON \tag{166}$$

Semilabile Dissolved Organic Phosphorus

$$S_{SDOP} = J_{SDOP} - \frac{1}{\tau_{\text{SDOP}}} \cdot SDOP \tag{167}$$

Labile Dissolved Organic Nitrogen

$$S_{LDON} = J_{LDON} - \frac{1}{\tau_{\text{LDON}}} \cdot LDON \tag{168}$$

O_2 production from nitrate, ammonia and nitrogen fixation and O_2 consumption from production of NH_4^+ from non-sinking particles, sinking particles and DOM and O_2 consumption from nitrification

if $[O_2] > \text{O}_{2_{\text{min}}}$ then

$$\begin{aligned} S_{O_2} = {} & \text{O}_2\text{:NO}_3^- \cdot \left(J^{Sm}_{prod_{NO_3^-}} + J^{Lg}_{prod_{NO_3^-}} \right) + \text{O}_2\text{:NH}_4^+ \cdot \left(J^{Sm}_{prod_{NH_4^+}} + J^{Lg}_{prod_{NH_4^+}} + J^{Di}_{prod_N} \right) - \\ & \left(\text{O}_2\text{:NH}_4^+ \cdot \left[\sum J_{graz_{NH_4^+}} + J_{PON} + \frac{1}{\tau_{\text{SDON}}} \cdot SDON + \frac{1}{\tau_{\text{LDON}}} \cdot LDON \right] + \text{O}_2\text{:Nitrif} \cdot J_{nitrif} \right) \end{aligned} \tag{169}$$

else

$$S_{O_2} = \text{O}_2\text{:NO}_3^- \cdot \left(J^{Sm}_{prod_{NO_3^-}} + J^{Lg}_{prod_{NO_3^-}} \right) + \text{O}_2\text{:NH}_4^+ \cdot \left(J^{Sm}_{prod_{NH_4^+}} + J^{Lg}_{prod_{NH_4^+}} + J^{Di}_{prod_N} \right) \tag{170}$$

end

2.7.6 The Carbon system

Alkalinity

$$S_{ALK} = 2 \cdot J_{CaCO_3} + S_{NH_4^+} + J_{denit_{wc}} + J_{denit_{sed}} - \left(2 \cdot J_{prod_{CaCO_3}} + S_{NO_3^-} + J_{prod_N}^{Di}\right) \tag{171}$$

Dissolved Inorganic Carbon

$$S_{DIC} = \text{C:N} \cdot \left(S_{NO_3^-} + S_{NH_4^+} + J_{denit_{wc}} + J_{denit_{sed}}\right) + J_{CaCO_3} - \left(J_{prod_{CaCO_3}} + \text{C:N} \cdot J_{prod_N}^{Di}\right) \tag{172}$$

3 Parameters

3.1 Stoichiometric ratios

Parameter	Description	Value	Description	Reference
C:N	Carbon to Nitrogen ratio	$\frac{117}{16}$	mol-C mol-N^{-1}	Values taken from OCMIP-II biotic protocols after Najjar and Orr (1998) and Anderson and Sarmiento (1994)
Ca:N	Calcium to Nitrogen ratio	$\frac{0.007 \cdot 117}{16}$	mol-Ca mol-N^{-1}	"
Mass:N	Mass to Nitrogen ratio (used for iron remineralization calculation)	$\frac{117 \cdot 12 \cdot 1.87}{16}$	g mol-N^{-1}	"
N:N$_{\text{denit}}$	Nitogen consumption ratio for denitrification	6.5	dimensionless	"
O_2:C	Oxygen to Carbon ratio	$\frac{170}{16}$	mol-O_2 mol-C^{-1}	"
O_2:NO_3^-	Oxygen to Nitrate ratio	$\frac{170}{16}$	mol-O_2 mol-N^{-1}	"
O_2:NH_4^+	Oxygen to Ammonium ratio	$\frac{138}{16}$	mol-O_2 mol-N^{-1}	"
O_2:Nitrif	Oxygen:N consumption ratio during nitrification	2	mol-O_2 mol-N^{-1}	Assuming ammonia oxidation and nitrate reduction
P:N$^{\text{SmLg}}$	Phosphorus to Nitrogen ratio for small and large phytoplankton	$\frac{1}{15}$	mol-P mol-N^{-1}	Goldman (1980) as reprinted in Broeker and Peng (1982)
P:N$^{\text{Di}}$	Phosphorus to Nitrogen ratio for diazatrophs	$\frac{1}{50}$	mol-P mol-N^{-1}	Letelier and Karl (1998)
P:N$_\chi$	Minimum P:N for large phytoplankton undergoing severe iron limitation - realized values are within the P:N$^{\text{SmLg}}$ and P:N$_\chi$ range	$\frac{1}{10}$	mol-P mol-N^{-1}	hypothesized explanation of mechanism behind result of Arrigo et al (1998)
Si:N$_{\text{max}}$	Maximum diatom silicon to nitrogen uptake ratio realized as a function of nutrient limitation	5	mol-Si mol-N^{-1}	Brzezinski (1985)
Si:N$_{\text{min}}$	Minimum diatom silicon to nitrogen uptake ratio realized as a function of nutrient limitation	0.2	mol-Si mol-N^{-1}	Brzezinski (1985)

3.2 Half-saturation constants

Parameter	Description	Value	Units	Reference
$K^{Lg}_{NH_4^+}$	Half-saturation coefficient for ammonium uptake by large phytoplankton	1.0×10^{-4}	mol-NH_4^+ m^{-3}	Moore et al. (2002) and Moore et al. (2004) for initial values, but some were varied from those original values in the optimization for surface chlorophyll, nitrate, phosphate and iron concentrations
$K^{Sm}_{NH_4^+}$	Half-saturation coefficient for ammonium uptake by small phytoplankton	5.0×10^{-6}	mol-NH_4^+ m^{-3}	"
$K_{NO_3^-}$	Half-saturation coefficient for nitrate uptake by phytoplankton	5.0×10^{-4}	mol-NO_3^- m^{-3}	"
$K_{PO_4^{-3}}$	Half-saturation coefficient for phosphate uptake by phytoplankton	3.0×10^{-5}	mol-PO_4^{-3} m^{-3}	"
$K_{SiO_4^{-2}}$	Half-saturation coefficient for nitrate silicate by phytoplankton	5.0×10^{-3}	mol-SiO_4^{-4} m^{-3}	"
K^{Di}_{Fe}	Half-saturation coefficient for iron uptake by diazatrophs	1.0×10^{-7}	mol-Fe m^{-3}	"
K^{Lg}_{Fe}	Half-saturation coefficient for iron uptake by large phytoplankton	3.0×10^{-7}	mol-Fe m^{-3}	"
K^{Sm}_{Fe}	Half-saturation coefficient for iron uptake by large phytoplankton	1.0×10^{-7}	mol-Fe m^{-3}	"

3.3 Iron

Parameter	Description	Value	Units	Reference
$Fe_{ballast-assoc}$	Whether or not to allow mineral ballast dissolution to return iron to the dissolved phase - a "false" value assumes that all iron is associated with organic material. A true value assumes that iron is distributed between mineral and organic matter by mass (leading to a deeper regeneration length scale)	true	none	Non-specificity of Iron adsorption shown in Balistrieri and Murray (1981)
$Fe_{coast_{max}}$	Maximum rate kinetics of iron influx from coastal boundaries	2.0×10^{-14}	mol-Fe m^{-3} s^{-1}	Represents unresolved coantinental shelves. Tuned to reproduce 500 km dropoff of surplus Iron away from coast as seeen by Johnson et al. (1999)
$Fe{:}N_{irr}$	Iron limitation of the Chl:C, through the chlorosis factor, to allow iron to modulate small and large phytoplankton light utilization efficiency.	$\frac{3 \cdot 1.0 \times 10^{-6} \cdot 117}{16}$	mol-Fe mol-N^{-1}	Calibrated to data of Sunda and Huntsman (1997)

$Fe{:}N_{irr}^{Di}$	Iron limitation of the Chl:C, through the chlorosis factor, to allow iron to modulate small and diazotrophic phytoplankton light utilization efficiency	$\frac{10 \cdot 1.0 \times 10^{-6} \cdot 117}{16}$	mol-Fe mol-N^{-1}	Interpretation of enhanced iron limiation of N_2 fixation as described by Raven (1988)
$Fe{:}N_{sat}$	Fe:N level where saturation begins for Small Phytoplankton (*i.e.*, where the phytoplankton begin to get "full" of iron)	$\frac{3 \cdot 1.0 \times 10^{-6} \cdot 117}{16}$	mol-Fe mol-N^{-1}	Added to prevent runaway uptake.
$Fe_{sed_{max}}$	Rate kinetics of iron influx from bottom sediment boundaries	1.0×10^{-4}	mol-Fe m^{-2} s^{-1}	Tuned to reproduce 500 km dropoff of surplus Iron away from coast as seeen by Johnson et al. (1999)
$Fe_{sed_{sat}}$	Rate kinetics of iron influx from bottom sediment boundaries	1.0×10^{-9}	mol-Fe m^{-2} s^{-1}	Tuned to reproduce 500 km dropoff of surplus Iron away from coast as seeen by Johnson et al. (1999)
k''_{Fe}	Second-order iron scavenging in order to prevent high iron accumulations in high deposition regions (like the tropical Atlantic)	50	mol-Fe m^{-3} d^{-1}	Tuned to reproduce observed Iron concentration of 0.6 nM in deep ocean
$k_{Fe_{bal}}$	adsorption rate coefficient for ballast. This was set to zero to prevent iron from accumulating in the deep ocean.	0	g-ballast m^{-3} d^{-1}	
$k_{Fe_{des}}$	desorption rate coefficient. After initial trials assuming 0.0068 d^{-1} after Bacon and Anderson (1982), this term was deemed unncessary after the inclusion of remineralization as a loss of particulate iron.	0	d^{-1}	
k'_{Fe}	Maximum adsorption rate coeficient	1	d^{-1}	for numerical stability
$k_{Fe_{org}}$	Adsorption rate coefficient for detrital organic material. This was set to obtain a deep ocean	0	d^{-1}	
$V_{max_0}^{Di}$	Velocity of iron uptake at 0°C temperature. Diazatrophs are assumed to have the same value as diatoms.	2.0×10^{-4}	mol-Fe mol-N^{-1} d^{-1}	Tuned to achieve observed growth rates of 0.7 in central equatorial Pacific upwelling of Landry et al (1997)
$V_{max_0}^{Lg}$	Velocity of iron uptake at 0°C temperature.	2.0×10^{-4}	mol-Fe mol-N^{-1} d^{-1}	Accounts for Sunda and Huntsman (1997) observation of surface area to volume effect
$V_{max_0}^{Sm}$	Velocity of iron uptake at 0°C temperature.	2.0×10^{-3}	mol-Fe mol-N^{-1} d^{-1}	"

3.4 Phytoplankton growth

Parameter	Description	Value	Units	Reference
κ	Eppley's temperature coefficient	0.063	deg-C^{-1}	Eppley (1972)
α^{Sm}	α values are set 2x high relative to observations to compensate for artificially low light levels in the current version of MOM4. This necessity is a consequence of the multiplicative nature of iron and light limitation in this model.	3.0×10^{-5}	g-C g-Chl^{-1} m^2 W^{-1} s^{-1}	Altered from Geider et al (1997) and Moore et al (2002)
α^{Lg}	"	3.0×10^{-5}	g-C g-Chl^{-1} m^2 W^{-1} s^{-1}	"
α^{Di}	"	3.0×10^{-6}	g-C g-Chl^{-1} m^2 W^{-1} s^{-1}	"
$\mathrm{P}^{\mathrm{Sm}}_{\mathrm{C_{max}}}$	specific growth prefactor	3.0×10^{-5}	s^{-1}	"
$\mathrm{P}^{\mathrm{Lg}}_{\mathrm{C_{max}}}$	"	3.0×10^{-5}	s^{-1}	"
$\mathrm{P}^{\mathrm{Di}}_{\mathrm{C_{max}}}$	"	2.0×10^{-6}	s^{-1}	"
$\mathrm{P}^{\mathrm{Sm}}_{\mathrm{C_{max}}}$	specific growth prefactor for alternate formulation for θ	2.0×10^{-5}	s^{-1}	Tsuda et al., 2003
$\mathrm{P}^{\mathrm{Lg}}_{\mathrm{C_{max}}}$	"	1.5×10^{-5}	s^{-1}	"
$\theta^{\mathrm{Sm}}_{\mathrm{max}}$	Maximum chlorophyll to carbon ratio. Values are at the high end in order to account for the additional iron limitation term.	0.018	g-Chl g-C^{-1}	Altered from Geider et al (1997) and Moore et al (2002)
$\theta^{\mathrm{Lg}}_{\mathrm{max}}$	"	0.038	g-Chl g-C^{-1}	"
$\theta^{\mathrm{Di}}_{\mathrm{max}}$	"	0.018	g-Chl g-C^{-1}	"
θ_{min}	minimum chlorophyll to carbon ratio	0.002	g-Chl g-C^{-1}	"
ζ	assimilatory efficiency	0.1	dimensionless	"

3.5 Grazing and remineralization

Parameter	Description	Value	Units	Reference
$\mathrm{f}^{\mathrm{Sm}}_{\mathrm{det_0}}$	Values of fractional detritus production from the global synthesis	0.18	dimensionless	Dunne et al. (2007)
$\mathrm{f}^{\mathrm{Lg}}_{\mathrm{det_0}}$	"	0.93	dimensionless	"
γ_{denit}	The denitrification length scale is set to half this value	0.002	s^{-1}	after Devol and Hartnett (2001)
γ_{det}	Value of gamma_det to approximate upper e-folding of the "Martin curve" used in the OCMIP-II biotic configuration of 228 m from 75 m.	0.016	s^{-1}	Najjar and Orr (1998); Martin et al. (1987)
$\mathrm{k_{diss_{SiO_2}}}$	Dissolution of SiO_2 was set as a temperature-dependent fraction of grazed material to be roughly in line with Kamatani (1982)	3	s^{-1}	Kamatani (1982)
$\mathrm{k_{graz_{max}}}$	For numerical stability, not to allow extremely high grazing rates	6	d^{-1}	numerical stability
κ_{remin}	Temperature-dependence of fractional detritus production from the global synthesis	-0.032	deg-C $^{-1}$	Dunne et al. (2007)
λ_0	T=0 phytoplankton specific grazing rate from the global synthesis	0.19	d^{-1}	Dunne et al. (2007)

Parameter	Description	Value	Units	Reference
${\lambda_0}^{Di}$	T=0 phytoplankton specific grazing rate for Diazotrophs	$\frac{0.19}{4}$	d^{-1}	Crudely approximates role of prey switching/grazing refuge with low population density after Fasham et al (1990)
τ_{graz}	Temperature-dependent response timescale for grazers... in this case set to a very small number to simulate instantaneous response.	0.001	d^{-1}	stability value
$O_{2_{min}}$	Minimum oxygen concentration for oxic remineralization. This is necessary for both numerical stability and to queue the switch to denitrification	5×10^{-3}	mol-O_2 m^{-3}	Suntharalingam et al (2000)
$NO^-_{3_{min}}$	Minimum NO_3^{-1} concentration for remineralization through denitrification. This is necessary for numerical stability.	1×10^{-4}	mol-NO_3^- m^{-3}	stability value
$P^\star$	Pivot phytoplankton concentration for grazing-based variation in ecosystem structure from the global synthesis	$\frac{1.9\times10^{-3}\cdot16}{117}$	mol-N m^{-3}	Dunne et al. (2005)
$Phyto_{min}$	Minimum phytoplankton concentration for grazing.	1×10^{-6}	mol-N m^{-3}	numerical stability
rp_{CaCO_3}	Organic matter protection by mineral	$\frac{0.070\cdot16\cdot100}{12\cdot117}$	mol-N mol-Ca^{-1}	Klaas and Archer (2002)
rp_{SiO_2}	Organic matter protection by mineral	$\frac{0.026\cdot16\cdot60}{12\cdot117}$	mol-N mol-Si^{-1}	Klaas and Archer (2002)
$Si_{remin\text{-}depth}$	Remineralization length scales to match global profiles	2000	m	Gnanadesikan (1999)
$Ca_{remin\text{-}depth}$	Remineralization length scales to match global profiles	3500	m	Najjar and Orr (1998)
w_{sink}	Sinking velocity of detritus to allow build-up of particulate iron. Value is used in γ/w_{sink} as the depth scale of remineralization.	3	m d^{-1}	Dunne et al (1997)
τ_{nitrif}	Nitrification timescale assumed to be light-limited...	60	d	Tuned to match Ward (1982)
$nitrif_{inhibit}$	...with an inhibition factor	1	m^2 W^{-1}	Tuned to match Ward (1982)
τ	Dissolved Organic Material remineralization timescales and fractional production ratios	30	d	consistent with the work of Abell et al. (2000)
τ_{SDON}	"	18	a	"
τ_{SDOP}	"	4	a	"
ϕ_{SDON}	" Warning: $\phi_{SDON} + \phi_{LDON}$ must be less than 1. Ideally, it will be *much* less than 1 as this component will directly reduce the pe_ratio.	0.02	dimensionless	"

Parameter	Description	Value	Units	Reference
ϕ_{SDOP}	"	0.04	dimensionless	"
τ_{LDON}	The remineralization timescale for labile DOP (τ_{LDON}) was set to 3 months	90	d	after Archer et al (1997)
ϕ_{LDON}	The fraction going to labile DOC was inspired by data-model comparisons	0.20	dimensionless	Libby and Wheeler (1997)

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