**Technical description of Tracers of Ocean Phytoplankton with Allometric Zooplankton version 2 (TOPAZ2) used in GFDL’s ESM2M and ESM2G submitted as part of the Coupled Model Intercomparison Project phase 5.**

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**1. Introduction:**

The current GFDL ocean biogeochemical and ecological component is Tracers of Ocean Phytoplankton with Allometric Zooplankton code version 2 (TOPAZ2) as used in ESM2M and ESM2G (Dunne et al., 2012a, 2012b). A technical description of TOPAZ version 0 is available in Dunne et al. (2010) as used in Sarmiento et al. (2010). TOPAZ version 1 was discussed in Henson et al. (2009). The current TOPAZ2 includes 30 tracers to describe the cycles of carbon, nitrogen, phosphorus, silicon, iron, oxygen, alkalinity and lithogenic material as well as pelagic calcite and aragonite and surface sediment calcite dynamics (Dunne et al., 2012c). TOPAZ2 considers three explicit phytoplankton groups (‘small’, ‘large’, and diazotrophic) that utilize a modified growth physiology after Geider et al. (1997) with Eppley (1972) temperature functionality and iron co-limitation with luxury uptake after Sunda and Huntsman (1997). ‘Small’ represent mostly prokaryotic picoplankton and nanoplankton, while ‘large’ represents diatoms, greens and other large eukaryotes. Diazotrophs represent facultative nitrogen fixers with nitrogen fixation inhibited by nitrate (NO3), ammonia (NH4) and oxygen (O2). CO2:NO3:O2 stoichiometry is 106:16:150 after Anderson (1995). N:P is based on optimal allocation after Klausmeier et al. (2004).

Phytoplankton loss and production of sinking detritus utilize the size-based relationship of Dunne et al. (2005) with mineral-driven penetration of sinking detritus (Klaas and Archer, 2002; Dunne et al., 2007). TOPAZ2 diagnoses plankton mineral formation of opal, calcite, and aragonite. TOPAZ2 includes seasonal time scale dissolved organic material and heterotrophic biomass with fixed N:P and multiannual dissolved organic material with variable N:P. Gas exchange of O2 and CO2 follows Najjar and Orr (1998). Nitrification is inhibited by light after Ward et al. (1982). TOPAZ2 includes second-order iron scavenging with ligand kinetics, lithogenic particle scavenging, water column denitrification under suboxia, and sediment denitrification after Middelburg et al. (1996). In the absence of both NO3 and O2, a respiration deficit is accumulated as negative O2. TOPAZ2 includes external inputs of atmospheric nitrogen deposition (Horowitz et al., 2003), lithogenic dust and soluble iron (Fan et al., 2006), river nitrogen (Seitzinger et al., 2005), and river inputs of dissolved inorganic carbon, alkalinity and lithogenic material set to balance Holocene burial of calcite and lithogenic material (Dunne et al., 2007).

* 1. **Overall equation**

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

dC/dt = -∇.ῦC + ∇K∇C + SC

where ῦ is the velocity vector from the physical Ocean General Circulation Model (OGCM), K is the diffusivity, and SC is the sum of the sources and sinks for the state variable C which are detailed below.

**1.2 State variables**

**1.2.1 Prognostic state variables transported by the OGCM**

Aragonite in Detritus = [CaDet\_arag]

Calcite in Detritus = [CaDet\_calc]

Dissolved Alkalinity = [Alk]

Dissolved Ammonium = [NH4+]

Dissolved Inorganic Carbon = [DIC]

Dissolved Iron = [FeD]

Dissolved Nitrate = [NO3-]

Dissolved Oxygen = [O2]

Dissolved Phosphate = [PO4-3]

Dissolved Silicic Acid = [Si(OH)4]

Iron in Detritus = [FeDet]

Iron in Diazotrophic Phytoplankton = [FeDi]

Iron in Large Phytoplankton = [FeLg]

Iron in Small Phytoplankton = [FeSm]

Labile Dissolved Organic Nitrogen = [LDON]

Lithogenic Particles = [Lith]

Lithogenic Detritus = [LithDet]

Nitrogen in Detritus = [NDet]

Nitrogen in Diazotrophic Phytoplankton = [NDi]

Nitrogen in Heterotrophs = [NHet]

Nitrogen in Large Phytoplankton = [NLg]

Nitrogen in Small Phytoplankton = [NSm]

Phosphorus in Detritus = [PDet]

Phosphorus in Diazotrophic Phytoplankton = [PDi]

Phosphorus in Large Phytoplankton = [PLg]

Phosphorus in Small Phytoplankton = [PSm]

Semilabile Dissolved Organic Nitrogen = [SDON]

Semilabile Dissolved Organic Phosphorus = [SDOP]

Silicon in Large Phytoplankton = [SiLg]

Silicon in Detritus = [SiDet]

**1.2.2 Diagnostic variables which are not transported by the physical model**

Calcite in Sediments [CaSed]

Chlorophyll = [Chl]

Carbonate Ion = [CO3]

Detrital Aragonite Flux to Sediments = [BTF\_CaDet\_arag]

Detrital Calcite Flux to Sediments = [BTF\_CaDet\_calc]

Detrital Aragonite Flux to Sediments = [BTF\_LithDet\_arag]

Detrital Nitrogen Flux to Sediments = [BTF\_NDet]

Detrital Phosphorous Flux to Sediments = [BTF\_PDet]

Detrital Silicon Flux to Sediments = [BTF\_SiDet]

Hydrogen Ion = [H+]

Shortwave Irradiance memory = [Irrmem]

**1.2.3 Variables supplied by the General Circulation Model**

Shortwave Irradiance = [Irr]

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 via the two-band (red/blue) algorithm of Manizza et al (2004).

**1.2.4 Operators**

Summation operator over phytoplankton classes = ∑

**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 modications 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):

LimLgNO3 = [NO3]/((KLgNO3+[NO3]).(1+[NH4]/KLgNH4)

LimSmNO3 = [NO3]/((KSmNO3+[NO3]).(1+[NH4]/KSmNH4)

where KSmNO3 and KLgNO3 are a half-saturation constants for nitrate, and KSmNH4 and KLgNH4 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:

LimDiFe = [NH4]/((KDiFe+[NH4])

LimLgFe = [NH4]/((KLgFe+[NH4])

LimSmFe = [NH4]/((KSmFe+[NH4])

LimLgNH4 = [NH4]/((KLgNH4+[NH4])

LimSmNH4 = [NH4]/((KSmNH4+[NH4])

LimDiPO4 = [PO4]/((KDiPO4+[PO4])

LimLgPO4 = [PO4]/((KLgPO4+[PO4])

LimSmPO4 = [PO4]/((KSmPO4+[PO4])

LimLgSi(OH)4 = [Si(OH)4]/((KLgSi(OH)4+[Si(OH)4])

TOPAZ2 utilizes a quota representation of iron phosphorus deficiency in the Liebig limitation terms:

QDiFe:N = min(QDiFe:Nmax, [FeSm]/[NDi])

QLgFe:N = min(QLgFe:Nmax, [FeLg]/[NLg])

QSmFe:N = min(QSmFe:Nmax, [FeSm]/[NSm])

QDiP:N = min(QDiP:Nmax, [PDi]/[NDi])

QLgP:N = min(QLgP:Nmax, [PLg]/[NLg])

QSmP:N = min(QSmP:Nmax, [PSm]/[NSm])

DefDiFe = QDiP:N2/(KDiFe:N2 + QDiFe:N2)

DefLgFe = QLgP:N2/(KLgFe:N2 + QLgFe:N2)

DefSmFe = QSmP:N2/(KSmFe:N2 + QSmFe:N2)

DefDiP = QDiP:N/QDiP:Nmax

DefLgP = QLgP:N/QLgP:Nmax

DefSmP = QSmP:N/QSmP:Nmax

LiebigSm = min(DefDiP, DefDiFe)

LiebigLg = min(LimLgNO3 + LimLgNH4, DefLgP, DefLgFe)

LiebigSm = min(LimSmNO3 + LimSmNH4, DefSmP, DefSmFe)

where the KSm;Lg;Di Fe 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

PDiCm = PDiCmax.LiebigDi.eKEppley.T

PLgCm = PLgCmax.LiebigLg.eKEppley.T

PSmCm = PSmCmax.LiebigSm.eKEppley.T

where KEppley is the constant governing temperature dependence of growth.

**2.1.2 Light limitation**

Phytoplankton are assumed to be photo-adapted 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:

Irrmix = [Irr] averaged over KPP Boundary Layer

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 CO2 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 PCmax are normalized to 0C rather than 20C 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 a "chlorosis" factor - the phytoplankton Fe:N ratio normalized to a saturated value (Fe : NIrr) necessary to synthesize chlorophyll,

3. Values of the maximum Chl:C ratio (θDimax) are increased and values of alpha decreased to account for the additional iron term in the θ equation,

4. A minimum min value is also incorporated to set a minimum level of chlorophyll per carbon.

While nitrogen limitation is handled through Michaelis-Menten limitation of the phytoplankton specific growth prefactor (PCm), iron and phosphorus limitation is handled indirectly through Monod quotas. This allows a compensatory relationship between irradiance, iron and phosphorus availability on phytoplankton specific growth. Chlorosis is assumed to be a quadratic function of the Fe:N ratio normalized to vary between 0 and 1, and a linear function of the P:N ratio. This relationship is a simple/crude representation of the complex physiological requirements and functionality of phosphorus as a function of ribosome/assembly capacity, and iron as it separates phytoplankton iron into three components of the rate and minimum chlorophyll:C ratio (θmin):

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

The Liebig-type reformulation 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 PCmax compared to observations of phytoplankton growth under ideal conditions (i.e. Eppley, 1972; Bissinger et al 2008). Because of this reformulation, we are able to return PCmax values to the lower values (1.5x105 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:

θDimin = max(0.0, θnolimmin - θlimmin).LiebigDi + θlimmin

θLgmin = max(0.0, θnolimmin - θlimmin).LiebigLg + θlimmin

θSmmin = max(0.0, θnolimmin - θlimmin).LiebigSm + θlimmin

θDi = (θDimax - θDimin)/(1.0 + (θDimax - θDimin).αDi.[irrmem].0.5/PDiCm) + θDimin

θLg = (θLgmax - θLgmin)/(1.0 + (θLgmax - θLgmin).αLg.[irrmem].0.5/PLgCm) + θLgmin

θSm = (θSmmax - θSmmin)/(1.0 + (θSmmax - θSmmin).αSm.[irrmem].0.5/PSmCm) + θSmmin

[Chl] = QC:N.12.0x106.(θDi.[NDi] + θLg.[NLg] + θSm.[NSm])

LimDiIrr = (1.0 - exp(-αDi.[Irr].θDi/PDiCm))

LimLgIrr = (1.0 - exp(-αLg.[Irr].θLg/PLgCm))

LimSmIrr = (1.0 - exp(-αSm.[Irr].θSm/PSmCm))

µDi = PDiCm/(1.0 + ζ).LimDiIrr

µLg = PLgCm/(1.0 + ζ).LimLgIrr

µSm = PSmCm/(1.0 + ζ).LimSmIrr

**2.2 Nutrient uptake terms**

The uptake of dissolved constituents by the different planktonic types are calculated as below. NO3 and NH4 uptake are calculated as fractions of total nitrogen uptake. Diazotrophs produce organic nitrogen from N2. Nitrogen fixation is assumed to be inhibited by high oxygen after Stewart and Pearson (1970; Effects of aerobic and anaerobic conditions on growth and metabolism of blue-green algae. Proc. Soc. Lond. B., 175, 293-311). Nitrogen fixation is also assumed to be limited by nitrate after Holl and Montoya (2005; Interactions between fixed nitrogen uptake and nitrogen fixation in continuous cultures of the marine diazotroph trichodesmium cyanobacteria); J. Phycol, 41, 1178-1183).

jprodDinterm = mu.[NDi].(1.0 – [O2]o2inpow/([O2inDisat]o2inpow + [O2]o2inpow))/([NO3] + [NH4] + kDiNin)

jprodDiN2 = jprodDinterm.kNinDi

jprodDiNH4 = jprodDinterm.[NH4]

jprodDiNO3 = jprodDinterm.[NO3]

jprodDiN = jprodDiN2+ jprodDiNH4+ jprodDiNO3

jprodLgNO3 = muLg.[NLg].LimLgNO3/(LimLgNO3 + LimLgNH4)

jprodLgNH4 = muLg.[NLg].LimLgNH4/(LimLgNO3 + LimLgNH4)

jprodLgN = jprodLgNH4+ jprodLgNO3

jprodSmNO3 = muSm.[NSm].LimSmNO3/(LimSmNO3 + LimSmNH4)

jprodSmNH4 = muSm.[NSm].LimSmNH4/(LimSmNO3 + LimSmNH4)

jprodSmN = jprodSmNH4+ jprodSmNO3

Phosphate uptake patterned after the optimal allocation theory of Klausmeier et al. 2004 in which N:P is determined by the allocation towards photosynthetic machinery, nutrient uptake, assembly, and other. Allocation for "other" is held fixed at 0.2 after Klausmeier et al. (2004). Allocation towards photosynthetic machinery is taken from the instantaneous C:Chl ratio which is renormalized to the ratio of chlorophyll to chloroplasts in the cell, allocation towards uptake is taken from the degree of nutrient limitation normalized to the remaining space, and assembly is then taken from the difference. For efficiency, this is all condensed into a single calculation. Phytoplankton are then allowed to accelerate their approach towards this optimum by taking up more or less phosphate than the optimum N:P linearly with respect to their relative N:P offset. In order to simulate the role of storage/vacuoles, Eukaryotes (Lg) are allowed to maximize rassem while Prokaryotes (Sm, Di) are forced to maximize rother. Here, the maximum assembly rate is assumed to be equal to the maximum photosynthetic rate multiplied by 1/(1 - rothermin). However, there is some indication that the maximum assembly rate should be double the maximum photosynthetic rate based on comparisons of the envelope for maximum growth rates of bacteria of ~0.72e-5.exp(0.063.T) [s-1] for whole organism phytoplankton after Eppley (1972, Fish. Bull., 70, 1063-1084) and ~1.6e-5 .exp(0.063.T) [s-1] for whole organism heterotrophic bacteria after Ducklow and Hill (1985). Assuming that the rassem of heterotrophic bacteria is 0.8 at the maximum growth rate (e.g. rother=0.2 after Klausmeier et al., 2004) and rassem of phytoplankton is 0.64 at the maximum growth rate (Klausmeier et al., 2004) gives PCmaxassem = 1.6e-5 / 0.72e-5 . 0.64 / 0.8 . PCmax. The conversion is highly uncertain however, and leave room for future tuning.

rDiphoto = plast:chlDi.θDi

rDiuptake = (1.0 - min(LimDiPO4, LimDiFe)).rDiuptakemax

Diazotrophic phytoplankton are assumed to take up only as much PO4 for assembly as they need based on their overall nutrient limited growth rate, thereby assuming that they cannot store extra PO4.

rDiassem = min(1.0 - rDinfix - rDiothermin - rDiphoto - rDiuptake, (1.0 - rDiothermin - rDinfix).LiebigDi)

QDiP:NOpt = P:Nassem.rDiassem + P:Nuptake .rDiuptake + P:Nphoto.rDiphoto + P:NRKR.(1.0 - rDinfix - rDiphoto - rDiuptake - rDiassem)

jprodDiPO4 = min(LimDiPO4.PDiCmax.eKEppley.T .[NDi], jprodDiN2 + jprodDiNO3 + jprodDiNH4).QDiP:NOpt

rLgphoto = plast:chlLg.θLg

rLguptake = (1.0 – min(LimLgNO3 + LimLgNH4, LimLgPO4, LimLgFe)) .rLguptakemax

Large phytoplankton are assumed to take up only as much PO4 for assembly as they need based on their overall PO4 nutrient limited growth rate, thereby assuming that they can store extra PO4.

rLgassem = min(1.0 - rLgothermin - rphoto - ruptake, (1.0 - rLgothermin) . LimLgPO4)

QLgP:NOpt = P:NLgassem.rLgassem + P:Nuptake .rLguptake + P:Nphoto.rLgphoto + P:NRKR.(1.0 - rLgphoto - rLguptake - rLgassem)

jprodLgPO4 = min(LimLgPO4.PLgCmax.eKEppley.T .[NLg], jprodLgNO3 + jprodLgNH4).QLgP:NOpt

rSmphoto = plast:chlSm.θ Sm

rSmuptake = (1.0 – min(LimSmNO3 + LimSmNH4, LimSmPO4, LimSmFe)) .rSmuptakemax

Small phytoplankton are assumed to take up only as much PO4 for assembly as they need based on their overall nutrient limited growth rate, thereby assuming that they cannot store extra PO4.

rSmassem = min(1.0 - rSmothermin - rSmphoto - rSmuptake, (1.0 - rSmothermin).LiebigSm)

QSmP:NOpt = P:NSmassem.rSmassem + P:Nuptake .rSmuptake + P:Nphoto.rSmphoto + P:NRKR.(1.0 - rSmphoto - rSmuptake - rSmassem)

jprodSmPO4 = min(LimSmPO4.PSmCmax.eKEppley.T .[NSm], jprodSmNO3 + jprodSmNH4).QSmP:NOpt

Large and Small phytoplankton are allowed to always take up as much Iron as they can after Sunda and Huntman (1997). 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).

JprodDiFe = PDiCmax.eKEppley.T .[NDi] .LimDiFe.(Fe:NDimax - QDiFe:N)/Fe:NDimax.Fe:NDinorm

JprodLgFe = PLgCmax.eKEppley.T .[NLg] .LimLgFe.(Fe:NLgmax - QLgFe:N)/Fe:NLgmax.Fe:NLgnorm

jprodSmFe = PSmCmax.eKEppley.T .[NSm] .LimSmFe.(Fe:NSmmax - QSmFe:N)/Fe:NSmmax.Fe:NSmnorm

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):

[NLgdiatoms] = [NLg].LimSi(OH)4

QLgSi:Ndiatoms = min(Si:NLgmax, [SiLg]/[NLgdiatoms]

jprodLgSi(OH)4 = PLgCmax.eKEppley.T .[NLgdiatoms] .LimSi(OH)4.max(0.0, Si:NLgmax - QLgSi:Ndiatoms)

**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 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.

Additionally two criteria for numerical stability are added:

1. The absolute first order rate constant is never allowed to be greater than kgrazmax.

2. A Michaelis-Menten type of threshold using a half saturation value of Phytomin is set to prevent phytoplankton from going extinct at low concentrations.

Then the formulation for the grazing terms is:

grazLgterms = λ0.eKEppley.T . (([NDi] + [NLg])/P\*)(1/3) .([NDi] + [NLg])/ ([NDi] + [NLg] + Pmin) / ([NDi] . [NDi] + [NLg] . [NLg])(1/2)

jgrazDiN = min(1/Δt, grazLgterms ] . [NDi]) . [NDi]

jgrazLgN = min(1/Δt, grazLgterms ] . [NLg]) . [NLg]

jgrazSmN = min(1/Δt, λ0.eKEppley.T . (([NSm] . [NSm] / (P\*.([NSm] + Pmin))) .[NSm]

jgrazN = jgrazDiN + jgrazLgN + jgrazSmN

jgrazP = jgrazDiN.QDiP:N + jgrazLgN.QLgP:N + jgrazSmN.QSmP:N

**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).

jprodNDet = (fSmDet0.(jgrazSmN + jgrazDiN) + fLgDet0.(jgrazLgN. (1.0 - φSDON - φLDON) .eKremin.T

fDetprod = jprodNdet/jgrazN

LimNhetP = min(1.0, jgrazP/jgrazN/P:NRKR)

jprodPdet = fDetprod.jgrazP.LimNhetP

jSDON = φSDON.jgrazN

jSDOP = φSDOP.jgrazP

jLDON = φLDON.jgrazN.LimNhetP

jprodNhet = (jgrazN - jprodNdet – jSDON - jLDON).φLDON.LimNhetP

jNH4graz = jgrazN - jprodNdet – jSDON - jLDON - jprodNhet

jPO4graz = jgrazP - jprodPdet - jSDOP - (jLDON + jprodNhet) .P:NRKR

jNhet = γNhet .eKEppley.T  .[Nhet]

jnitrif = γnitrif  . eKEppley.T  .[NH4]  .LimSmNH4  . (1.0 – [Irrmem]/(Irrin + [Irrmem])

**2.3.3 Calcite, Aragonite and Lithogenic Production**

CaCO3 solubility taken from the UNESCO 87 recommendation (Mucci for 1-atm solubility with a tuning prefactor times Millero's pressure dependence) gives a result that splits the difference between the low-end solublities (Mucci/Morse) and the high-end solubilities (Ingle/Plath). Following UNESCO, this calculation has a fudge factor built in that will give 4.5e-7 at 2c, 35 psu, 1-atm. This is because the UNESCO group couldn't decide between the low solubility of Mucci (4.3 e-7) and the higher solubility of Plath (4.7e-7) and so they split the difference. It should be noted that the salinity normalization for Ca++ breaks down below S = 5.

TK = T + 273.15

Pinsitu = 0.1016. z + 1.013

PKSPA = 171.945 + 0.077993. TK - 2903.293 / TK - 71.595. log10(TK) - (-0.068393 + 1.7276e-3 . TK + 88.135 / TK) .Salt(1/2) + 0.10018.Salt - 5.9415e-3 .Salt(3/2) - 0.02 - (48.76 - 2.8 - 0.5304.T) . (Pinsitu - 1.013) / (191.46.TK) + (1e-3. (11.76 - 0.3692.T)) . (Pinsitu - 1.013) . (Pinsitu - 1.013) / (382.92 .TK)

CO3aragsol = 10-PKSPA / (2.937e-4 . max(5.0, Salt))

Ωarag = [CO3]/CO3aragsol

PKSPC = 171.9065 + 0.077993.TK - 2839.319/TK - 71.595.log10(TK) - (-0.77712 + 2.8426e-3.TK + 178.34 / TK) .Salt(1/2) + 0.07711.Salt - 4.1249e-3.Salt(3/2) - 0.02 - (48.76 - 0.5304.T) . (Pinsitu - 1.013) / (191.46.TK) + (1e-3. (11.76 - 0.3692.T)) . (Pinsitu - 1.013) . (Pinsitu - 1.013) / (382.92.TK)

CO3calcsol = 10-PKSPC / (2.937e-4 . max(5.0, Salt))

Ωcalc = [CO3]/CO3calcsol

Aragonite formation is set to go directly to detritus as a function of temperature, degree of aragonite supersaturation, and the large phytoplankton production after:

jprodCadet\_arag = jgrazLgN.Ca:Narag.min(Ωsatmax, max(0.0, Ωarag - 1.0))

Calcite formation is set to go directly to detritus as a function of temperature, degree of calcite supersaturation, and the small phytoplankton production after Dunne et al (2012):

jprodCadet\_calc = jgrazSmN . Ca:Ncalc .e(-0.0539.T) .min((Ωsatmax, max(0.0, Ωcalc - 1.0))

Lithogenic material is assumed to get converted into the sinking particulate phase through incorporation into mesozooplankton fecal pellets with an efficiency of φlith.

jprodlithdet = (jgraz\_n / [NLg] . φlith + klith) . [lith]

**2.3.4 Iron and Silicon Processing**

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

jgrazDiFe = jgrazDiN.QDiFe:N

jgrazLgFe = jgrazLgN.QLgFe:N

jgrazSmFe = jgrazSmN.QSmFe:N

jgrazFe = jgrazDiFe + jgrazLgFe + jgrazSmFe

jprodFedet = fDetprod.jgrazFe

jFegraz = jgrazFe - jprodFedet

jgrazLgSiO2 = jgrazLgN.[SiLg]/[NLg]

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), and that the fraction of biogenic opal SiO2 that dissolves within the mixed layer as a result of grazing is 50%, but they and others (Blain et al., 1999, Brzezenski, 1985) and that there is also a temperature dependence to this dissolution. The temperature functionality is set to a combination Michaelis-Menten 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 Si(OH)4 concentrations.

jdissSiO2 = jgrazLgSiO2. exp(-QSi:NLgdiatoms / (QSi:Ndiss .eKEppley.T))

**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 wsink=det = 187m 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 Caremin-depth = 3500m) and biogenic silica (with a remineralization depth scale Siremin-depth = 2000m). 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. 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.

jCaDet\_arag = γCaDet\_arag.max(0.0, 1.0 - Ωarag) . [CaDet\_arag]

jCaDet\_calc = γCaDet\_calc.max(0.0, 1.0 - Ωcalc) . [CaDet\_calc]

jSidet = γSidet.[SiDet]

**2.4.2 Interior Layer remineralization**

Remineralization of unprotected organic material and previously protected particulate organic material:

Under oxic conditions

jNDet = γNdet.[O2] / (kO2 + [O2]) .max(0.0, [NDet] - (rpCaCO3. ([CaDet\_arag]+[CaDet\_calc) + rplith.[lithDet] + rpSiO2.[SiDet]))

Under suboxic conditions, including NO3 limitation

jNDet = γNdet. O2min / (kO2 + O2min). [NO3] / (kSmNO3 + [NO3]) .max(0.0, [NDet] - (rpCaCO3 . ([CaDet\_arag]+[CaDet\_calc) + rplith.[lithDet] + rpSiO2.[SiDet]))

jNO3denit\_wc = jNDet. N:Ndenit

Apply N change to P assuming equal partitioning between protected, previously protected and unprotected particulate organic material

jPDet = jNDet/[NDet].[PDet]

**2.4.3 Fe remineralization, adsorption, and desorption**

Calculate free and inorganically associated iron concentration for scavenging based on chemical equilibrium with ligand bound iron using the following three equations:

kFeeqlig = [FePrime] . [L] / [FeL]

[FeD] = [FePrime] + [FeL]

[LTotal] = [L] + [FeL] = [Feligbkg] + Felig:DON. ([LDON] + [SDON])

These equations are solved for FePrime using the quadratic formula: (-b +/- sqrt(b2 - 4.a.c))/(2.a) where: a = kFeeqlig; b = 1.0 + kFeeqlig . ([Feligbkg] + Felig:DON . ([LDON] + [SDON]) – [FeD]); c = -1

[FePrime] = 1.0 + kFeeqlig . ([Feligbkg] + Felig:DON. ([LDON] + [SDON]) – [FeD])

[FePrime] = (-FePrime + sqrt([FePrime]2 + 4.0.kFeeqlig. [FeD])) / (2.0. kFeeqlig)

The absolute first order rate constant is never allowed to be greater than 1/dt for numerical stability.

jFeads = min(1/Δt, kFe2ndorder.[FePrime]) .[FePrime]

jFedes=kFedes.[FeDet]

jFeDet = (jNDet.mass:N + jSiDet.60.0 + (jCaDet\_arag + jCaDet\_calc) .100.0) / ([NDet].mass:N + [SiDet].60.0 + ([CaDet\_arag] + [CaDet\_calc]) .100.0 + [lithDet]) .[FeDet]

**2.4.4** **Iron source from coasts and sediments**

Apply sediment flux to all ocean cells adjacent or corner to land normalizing to the grid scaling:

jFecoast = Fecoast . maskcoast / griddat0.5

Calculate iron addition from sediments as a function of organic matter supply

fFesed = Fe:Nsed.BTF\_NDet

**2.4.5 Denitrification loss to sediments**

Account for remineralization/dissolution of sinking flux, and sediment processed in bottom box. Subtract sedimentary denitrification after Middelburg et al. (1996) with additional limitation terms to disallow the consumption of both more ndet than the incoming flux (wsink.[NDet]) and more NO3 that is available in the lowest 1 m (NO3.ρ0.1m/dt). The original algorithm was edited to add a maximum flux input in order to avoid extrapolating the polynomial into unobserved space which would otherwise give low denitrification rates at very high bottom fluxes. Convert previous sediment N inventory into a total flux equivalent assuming a 10 cm thick sediment layer and convert flux to µmol C cm-2 d-1 and add max value.

logbtmflx = log10(min(43.0, BTF\_NDet .C:N . 86400 . 100.0))

fNO3denit\_sed = min([NO3] . ρ0/Δt, min(BTF\_NDet .N:Ndenit, 10^(-0.9543 + 0.7662 .logbtmflx - 0.235 .logbtmflx .logbtmflx) / (C:N .86400 .100.0) .N:Ndenit . [NO3]/ (kSmNO3 + [NO3])))

Only under oxic conditions:

fNoxic\_sed = max(0.0, min([O2]. ρ0/Δt, BTF\_NDet - fNO3denit\_sed / N:Ndenit))

fNO3denit\_sed = fNO3denit\_sed + min([NO3]. ρ0.Δt, (BTF\_NDet - fNoxic\_sed - fNO3denit\_sed/N:Ndenit) .N:Ndenit)

fNFeSO4red\_sed = max(0.0, BTF\_NDet - fNoxic\_sed - fNO3denit\_sed/N:Ndenit)

**2.4.6 Sediment calcite cycling**

Determine the flux of CaCO3 retained in sediment using prototype values from the Dunne et al (2012) metamodel calibrated to the Hales (2003) steady state model of CaCO3 burial using bottom water Ω and organic-based dissolution and ultimate burial of sediment CaCO3 assuming a 10 cm mixed layer advecting downward at lithogenic- and CaCO3- based sediment accumulation rate assuming a density of 2.7 g cm-3, a porosity of 0.7 and molecular weight of 100 to give: 2.7e6.(1-0.7)/100 = 8.1e3 mol m-3. At steady state, burial efficiency (f = fCaSedburial/ BTF\_CaDet\_calc) reduces to:

spy=86400 . 365

f = min(BTF\_CaDet\_calc,0.165 . BTF\_NDet . C:N) / (0.1244 / spy.max(0.0, 1.0 - Ωcalc + 4.38. BTF\_NDet. C:N . spy)2.91 . (BTF\_lithDet . spy + BTF\_CaDet\_calc. 100.0 . spy)-2.55 + BTF\_CaDet\_calc)

which can be used to generate a useful initial condition. For numerical stability, the redissolution rate is limited to only consume less than half of the sediment calcite in a time step. For bulk consistency with the mechanisms of Hales (2003), the ability of organic flux to instantaneously consume calcite is limited to half the calcite flux.

fCaSedredis = max(0.0, min(0.5.[CaSed] /Δt, min(0.5.BTF\_CaDet\_calc, 0.165.BTF\_NDet . C:N) + 0.1244 / spy . max(0.0, 1.0 - Ωcalc + 4.38 . BTF\_NDet.C:N.spy)2.91 . max(1.0, BTF\_lithDet . spy + BTF\_CaDet\_calc.100.0 .spy)-2.55 . [CaSed]))

fCaSedburial = max(0.0, BTF\_CaDet\_calc. [CaSed]/8.1e3)

[CaSed] = [CaSed] + (BTF\_CaDet\_calc - fCaSedredis - fCaSedburial) / zSed . dt

**2.4.7 External bottom fluxes**

Calculate external bottom fluxes for tracer\_vertdiff tridiagonal solver that performs vertical diffusion on all tracers and advects sinking tracers with the sinking velocity wsink. Note that all terms require a reversal in sign relative to how they would be applied to the tracer concentrations.

bAlk = - 2.0. (fCaSedredis + BTF\_CaDet\_calc) - BTF\_NDet - Alk:Ndenit.fNO3denit\_sed

bDIC = - fCaSedredis - BTF\_CaDet\_arag - BTF\_NDet .C:N

bFeD = - ffe\_sed

bNH4 = - BTF\_NDet

bNO3 = fNO3denit\_sed

bO2 = O2:NH4. (fNoxic\_sed + fNFeSO4red\_sed)

bPO4 = - BTF\_PDet

bSi(OH)4= - BTF\_SiDet

**2.7 Application of total source and sink terms**

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

**2.7.1 Phytoplankton Nitrogen and Phosphorus**

Diazotrophic Phytoplankton Nitrogen:

[NDi] = [NDi] + (JprodDiN2 + JprodDiNO3 + JprodDiNH4 – JgrazDiN) .Δt

Large Phytoplankton Nitrogen:

[NLg] = [NLg] + (JprodLgNO3 + JprodLgNH4 – JgrazLgN) .Δt

Small Phytoplankton Nitrogen:

[NSm] = [NSm] + (JprodSmNO3 + JprodSmNH4 – JgrazSmN) .Δt

Diazotrophic Phytoplankton Phosphorus:

[PDi] = [PDi] + (JprodDiPO4 – JgrazDiN.QDiP:N) .Δt

Large Phytoplankton Phosphorus:

[PLg] = [PLg] + (JprodLgPO4 – JgrazLgN.QLgP:N) .Δt

Small Phytoplankton Phosphorus:

[PSm] = [PSm] + (JprodSmPO4 – JgrazSmN.QSmP:N) .Δt

**2.7.2 Phytoplankton Silicon and Iron**

Large Phytoplankton Silicon:

[SiLg] = [SiLg] + (JprodLgSi(OH)4 – JgrazSiO2) .Δt

Diazotrophic Phytoplankton Iron:

[FeDi] = [FeDi] + (JprodDiFe – JgrazDiFe) .Δt

Large Phytoplankton Iron:

[FeLg] = [FeLg] + (JprodLgFe – JgrazLgFe) .Δt

Small Phytoplankton Iron:

[FeSm] = [FeSm] + (JprodSmFe – JgrazSmFe) .Δt

**2.7.3 Nutrients**

NO3:

jNO3 = jnitrif - jprodDiNO3 - jprodLgNO3 - jprodSmNO3 - jNO3denit\_wc

[NO3] = [NO3] + jNO3 .Δt

NH4:

jNH4 = jNH4graz + jNHet + γLDON.[LDON] + γSDON.[SDON] + jNDet - jprodDiNH4 - jprodLgNH4 - jprodSmNH4 - jnitrif

[NH4] = [NH4] + jNH4 .Δt

PO4:

jPO4 = jPO4graz + (jNHet + γLDON.[LDON]) .P:NRKR + γSDOP.[SDOP] + jPDet - jprodDiPO4 - jprodLgPO4 - jprodSmPO4

[PO4] = [PO4] + jPO4 .Δt

Si(OH)4:

jSi(OH)4 = jSiDet - jprodLgSi(OH)4 + jdissSiO2

[Si(OH)4] = [Si(OH)4] + jSi(OH)4 .Δt

FeD:

jFeD = jFegraz - jprodDiFe - jprodLgFe - jprodSmFe - jFeads + &

jFedes + jFeDet + jFecoast

[FeD] = [FeD] + jFeD .Δt

**2.7.4 Detrital Components**

Heterotrophic N:

[NHet] = [NHet]+ (jprodNHet - jNHet) .Δt

Lithogenic aluminosilicate particulates:

[lith] = [lith] + jprodlithDet .Δt

CaDet\_Arag:

[CaDet\_arag] = [CaDet\_arag] + (jprodCaDet\_arag - jCaDet\_arag) .Δt

CaDet\_Calc:

[CaDet\_calc] = [CaDet\_calc] + (jprodCaDet\_calc - jCaDet\_calc) .Δt

FeDet:

[FeDet] = [FeDet] + (jprodFeDet + jFeads – jFedes – jFeDet) .Δt

LithDet:

[LithDet] = [LithDet] + jprodlithDet .Δt

Ndet:

[NDet] = [NDet] + (jprodNDet – jNDet) .Δt

Pdet:

[NDet] = [NDet] + (jprodNDet – jNDet) .Δt

Sidet:

[SiDet] = [SiDet] + (jgrazSiO2 – jdissSiO2 - jSiDet) .Δt

**2.7.5 Dissolved Organic Matter**

Semilabile Dissolved Organic Nitrogen:

jSDON = jSDON - γSDON. [SDON]

[SDON] = [SDON] + jSDON .Δt

Semilabile Dissolved Organic Phosphorus:

jSDOP = jSDOP - γSDOP. [SDOP]

[SDOP] = [SDOP] + jSDOP .Δt

Labile Dissolved Organic Nitrogen:

JLDON = jLDON - γLDON. [LDON]

[LDON] = [LDON] + jLDON .Δt

O2:

O2 production from nitrate, ammonia and nitrogen fixation and O2 consumption from production of NH4 from non-sinking particles, sinking particles and DOM and O2 consumption from nitrification:

jo2 = (O2:NO3. (jprodDiNO3 + jprodLgNO3 + jprodSmNO3) + O2:NH4. (jprodDiNH4 + jprodLgNH4 + jprodSmNH4 + jprodDiN2))

If O2 is present:

jO2 = jO2 - O2:NH4. (jNH4graz + jNHet + jNDet + γSDON.[SDON] + γLDON.[LDON]) - O2:nitrif .jnitrif

[O2] = [O2] + jO2 .Δt

**2.7.6 The Carbon system**

Alkalinity:

CaCO3 cycling affects Alkalinity by a factor of 2. Nitrate-based Production increases alkalinity by NO3 equivalents. Ammonia-based Production decreases alkalinity (and reverse for remineralization) by NH4 equivalents. N2 Production has no effect on alkalinity. Nitrification decreases alkalinity by 2 NH4 equivalents. Denitrification decreases alkalinity by 552/472 = 1.169 NO3 equivalents.

jAlk = (2.0. (jCaDet\_arag + jCaDet\_calc - jprodCaDet\_arag - jprodCaDet\_calc) + jprodDiNO3 + jprodLgNO3 + jprodSmNO3 + jNH4graz + jNHet + γSDON.[SDON] + γLDON.[LDON] + jNDet - jprodDiNH4 - jprodLgNH4 - jprodSmNH4 - 2.0 . jnitrif + Alk:Ndenit.jNO3denit\_wc)

[Alk] = [Alk] + jAlk .Δt

Dissolved Inorganic Carbon:

jDIC =(C:N.(jNO3 + jNH4 + jNO3denit\_wc - jprodDiN2) + jCaDet\_arag + jCaDet\_calc - jprodCaDet\_arag - jprodCaDet\_calc)

[DIC] = [DIC] + jDIC .Δt

**3 Parameters**

**3.1 Gas Exchange parameters**

Values taken from OCMIP-II Biotic protocols, except for revised numbers from R. Wanninkof (pers. comm.) to extend Schmidt numbers beyond 30C up to 42C.

tt = 298.15 - T

tk = 273.15 + T

ts = log(tt / tk)

ts2 = ts.ts

ts3 = ts2.ts

ts4 = ts3.ts

ts5 = ts4.ts

O2saturation = (1000.0/22391.6) .exp(a0 + a1.ts + a2.ts2 + a3.ts3 + a4.ts4 + a5.ts5 + (b0 + b1.ts + b2.ts2 + b3.ts3 + c0.salt) .salt)

Compute the Schmidt number of O2 in seawater using the formulation proposed by Keeling et al. (1998).

O2sc\_no = a1O2 + ST. (a2O2 + ST. (a3O2 + ST.a4O2 ))

CO2sc\_no = a1CO2 + ST. (a2CO2 + ST. (a3CO2 + ST.a4CO2))

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameter | Description | Value | Units | Reference |
| ρ0 | Reference seawater density | 1035 | g kg-1 |  |
| a0 | O2 sat. coeff. | 2.00907 | dimensionless | Wanninkhof (1992) |
| a1 | O2 sat. coeff. | 3.22014 | dimensionless | Wanninkhof (1992) |
| a2 | O2 sat. coeff. | 4.05010 | dimensionless | Wanninkhof (1992) |
| a3 | O2 sat. coeff. | 4.94457 | dimensionless | Wanninkhof (1992) |
| a4 | O2 sat. coeff. | -2.56847e-01 | dimensionless | Wanninkhof (1992) |
| a5 | O2 sat. coeff. | 3.88767 | dimensionless | Wanninkhof (1992) |
| b0 | O2 sat. coeff. | -6.24523e-03 | dimensionless | Wanninkhof (1992) |
| b1 | O2 sat. coeff. | -7.37614e-03 | dimensionless | Wanninkhof (1992) |
| b2 | O2 sat. coeff. | -1.03410e-02 | dimensionless | Wanninkhof (1992) |
| b3 | O2 sat. coeff. | -8.17083e-03 | dimensionless | Wanninkhof (1992) |
| c0 | O2 sat. coeff. | -4.88682e-07 | dimensionless | Wanninkhof (1992) |
| a1CO2 | CO2 Schmidt Number coeff. | 2068.9 | dimensionless | Wanninkhof (pers. comm.) |
| a2CO2 | CO2 Schmidt Number coeff. | -118.63 | dimensionless | Wanninkhof (pers. comm.) |
| a3CO2 | CO2 Schmidt Number coeff. | 2.9311 | dimensionless | Wanninkhof (pers. comm.) |
| a4CO2 | CO2 Schmidt Number coeff. | -0.027 | dimensionless | Wanninkhof (pers. comm.) |
| a1O2 | O2 Schmidt Number coeff. | 1929.7 | dimensionless | Wanninkhof (pers. comm.) |
| a2O2 | O2 Schmidt Number coeff. | -117.46 | dimensionless | Wanninkhof (pers. comm.) |
| a3O2 | O2 Schmidt Number coeff. | 3.116 | dimensionless | Wanninkhof (pers. comm.) |
| a4O2 | O2 Schmidt Number coeff. | -0.0306 | dimensionless | Wanninkhof (pers. comm.) |

**3.2 Stoichiometric ratios**

Values taken from OCMIP-II Biotic protocols after Anderson (1995) for an organic material of C106H172O38N16(H3PO4) which gives an average oxidation state for carbon of (3.16+2.38-172)/106 = -0.4528. These calculations ignore organic matter normalization to P and changes in alkalinity associated with H3PO4.

Nitrate Production:

16.H+ + 16.NO3- + 106.CO2 + 78.H2O <-> C106H172O38N16 + 150.O2

Effect is to increase alkalinity by 16 NO3 equivalents.

Ammonia Production (and reverse for remineralization):

16.NH4+ + 106.CO2 + 62.H2O <-> C106H172O38N16 + 118.O2 + 16.H+

Effect is to decrease (increase for remineralization) alkalinity by 16 NH4 equivalents.

N2 Production:

8.N2 + 106.CO2 + 86.H2O <-> C106H172O38N16 + 130.O2

N2 production is assumed to have no effect on alkalinity.

Nitrification:

NH4+ + 2.O2 <-> NO3- + H2O + 2.H+

Effect on alkalinity is to decrease alkalinity by 2 NH4 equivalents.

Denitrification:

C106H172O38N16 + 472/5.NO3- + 552/5.H+ <-> 106.CO2 + 16.NH4+ + 236/5.N2 + 546/5.H2O

Effect on alkalinity is to increase alkalinity by 552/472 = 1.169 NO3 equivalents.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameter | Description | Value | Units | Reference |
| Alk:Ndenit | Alkalinity gain during denitrification | 552/472 | Eq.Alk molN-1 | Anderson et |
| C:N | Organic Carbon to Nitrogen ratio | 106/16 | molC molN-1 |  |
| Mass:N | Organic matter mass to Nitrogen ratio | 106 /16 .12 .1.87 | g molNorg-1 |  |
| N:Ndenit | NO3 consumed during denitrification | 472 /5 /16 | molNO3 molNorg-1 |  |
| O2:C | Organic O2 to Nitrogen ratio | 150 /106 | molO2 molN-1 |  |
| O2:Nfix | O2 to N2-based production | (118+3/(5+3).(150-118))/16) | molO2 molN-1 |  |
| O2:NH4 | O2 to NH4-based production | 118/16 | molO2 molN-1 |  |
| O2:nitrif | O2 consumed during nitrification | 2 | molO2 molN-1 |  |
| O2:NO3 | O2 to NO3-based production | 150/16 | molO2 molN-1 |  |
| Ca:Narag | Aragonite CaCO3 to nitrogen uptake ratio | 0.01.106/16 | molCa molN-1 | tuned to preserve the upper ocean Alkalinity gradient |
| Ca:Ncalc | Calcite CaCO3 to nitrogen uptake ratio | 0.005.106/16 | molCa molN-1 | Tuned to obtain a global calcite export flux of ~0.5 Pg C after Dunne et al (2007) |
| Ωsatmax | Maximum saturation state | 10 | dimensionless | To limit possible extreme values |
|  |  |  |  |  |
|  |  |  |  |  |

**3.2 Nutrient uptake**

P:N limitation of phytoplankton growth, is taken from the fraction of the cell dedicated to assembly after Klausmeier et al. (2004), but also consistent with other work on the limitation of growth and optimal stoichiometry by Geider et al. (1998), Christian (2005) and Hall et al. (2005). P:Nassem is based on the N:P of ribosomes of 7.2 for eukaryotes (large) and 6.0 for prokaryotes (small, diaz) from Elser et al. (1996). Allocation of phytoplankton cell structures to "other" is set to a minimum for large phytoplankton and small phytoplankton to be consistent with their different sizes, organelle structures and corresponding θmax values. Allocation to photosynthesis is taken from the realized Chlorophyll to Carbon ratio (θ) using the plastids to chlorophyll ratio. For diazotrophs, an additional allocation is specified for nitrogenase and other structures necessary for nitrogen fixation, and rothermin is correspondingly lowered in order to match the observed range in N:P ratios of 14-182 in White et al. (2006). To avoid negative allocations, θmax.plastid:chl+rothermin+rnfix must be < 1. The relationship between chlorophyll and carbon is taken from Kirk and Tilney-Bassett (1978) for eukaryotes (large) that have chloroplasts and 6.0 for prokaryotes (small, diaz) which only have the thylakoid.

Iron limitation of the Chl:C, through the defFe factor, to allow iron to modulate small phytoplankton light utilization efficiency. This value is set to a very low value after Sunda and Huntsman (1995) for Small phytoplankton and is assumed to have an allometric relationship.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameter | Description | Value | Units | Reference |
| P:NDiassem | Stoichiometry of Di assembly material | 1/6 | molP molN-1 | Elser et al. (1996) |
| P:NLgassem | Stoichiometry of Lg assembly material | 1/7.2 | molP molN-1 | Elser et al. (1996) |
| P:NSmassem | Stoichiometry of Sm assembly material | 1/6 | molP molN-1 | Elser et al. (1996) |
| P:Nphoto | Stoichiometry of photosynthetic material | 0.0128 | molP molN-1 |  |
| P:NRKR | Stoichiometry of heterotrophs | 1/16 | molP molN-1 | Redfield et al (1963) |
| P:Nuptake | Stoichiometry of uptake material | 0.0128 | molP molN-1 |  |
| rDinfix | Fraction of cell dedicated for N2 fixation | 0.5 | dimensionless |  |
| rDiothermin | Minimum fraction of Di cell for maintenance | 0.1 | dimensionless |  |
| RLgothermin | Minimum fraction of Lg cell for maintenance | 0.2 | dimensionless |  |
| RSmothermin | Minimum fraction of Sm cell for maintenance | 0.2 | dimensionless |  |
| rDiuptakemax | Maximum fraction of Di cell for uptake | 0.2 | dimensionless |  |
| RLguptakemax | Maximum fraction of Lg cell for uptake | 0.2 | dimensionless |  |
| RSmuptakemax | Maximum fraction of Sm cell for uptake | 0.4 | dimensionless |  |
| Plast:chlDi | C to Chl ratio within photosynthetic material | 1.0 / 1.87 / 0.08 | gC gChl-1 | Kirk and Tilney-Bassett (1978) |
| Plast:chlLg | C to Chl ratio within photosynthetic material | 1.0 / 1.87 / 0.043 | gC gChl-1 | Kirk and Tilney-Bassett (1978) |
| Plast:chlSm | C to Chl ratio within photosynthetic material | 1.0 / 1.87 / 0.08 | gC gChl-1 | Kirk and Tilney-Bassett (1978) |
| Si:NLgmax | Maximum diatom silicon to nitrogen uptake ratio | 5 | molSi molN-1 | Mongin et al (2003) |
| kDiFe | Fe uptake half sat. | 9e-9 | molFe kg-1 | Allometric assumption |
| KLgFe | Fe uptake half sat. | 9e-9 | molFe kg-1 | Allometric assumption |
| KSmFe | Fe uptake half sat. | 3e-9 | molFe kg-1 | T. weissflogii 3 nM in Hudson and Morel (1990) |
| KLgNH4 | NH4 uptake half sat. | 2e-7 | molN kg-1 | Allometric assumption |
| KSmNH4 | NH4 uptake half sat. | 6e-7 | molN kg-1 | From PO4 |
| KLgNO3 | NO3 uptake half sat. | 6e-6 | molN kg-1 | Allometric assumption |
| KSmNO3 | NO3 uptake half sat. | 2e-6 | molN kg-1 | Ratio to NH4 |
| KDiPO4 | PO4 uptake half sat. | 6e-7 | molN kg-1 | Allometric assumption |
| KLgPO4 | PO4 uptake half sat. | 6e-7 | molN kg-1 | Allometric assumption |
| KSmPO4 | PO4 uptake half sat. | 2e-7 | molN kg-1 | Tuned to get minimum of 5 nM ambient PO4 in Cotner et al (1997) . |
| kDiFe:N | Half sat of iron deficiency | 36e-6 . 106 / 16 | molFe molN-1 | Handicapped |
| KLgFe:N | Half sat of iron deficiency | 18e-6 . 106 / 16 | molFe molN-1 | Initially allometric assumption, but tuned down |
| KSmFe:N | Half sat of iron deficiency | 12e-6 . 106 / 16 | molFe molN-1 | Sunda and Huntsman (1995) |
| Fe:NDimax | Maximum Fe:N limit | 666e-6 . 106 / 16 | molFe molN-1 | 333 umolFe / molC observed for T weissflogii (Sunda and Huntsman, 1995) |
| Fe:NLgmax | Maximum Fe:N limit | 666e-6 . 106 / 16 | molFe molN-1 | 333 umolFe / molC observed for T weissflogii (Sunda and Huntsman, 1995) |
| Fe:NSmmax | Maximum Fe:N limit | 46e-6 . 106 / 16 | molFe molN-1 | 23 umolFe / molC observed for Synechococcus (Porta et al., 2003) |
| Fe:NDinorm | Normalization factor for Fe uptake rate | 100e-6 . 106 / 16 | molFe molN-1 | Same as Lg |
| Fe:NLgnorm | Normalization factor for Fe uptake rate | 50e-6 . 106 / 16 | molFe molN-1 | Tuned for surface Chl and NO3 |
| Fe:NSmmax | Normalization factor for Fe uptake rate | 50e-6 . 106 / 16 | molFe molN-1 | Handicapped |

3.3 Iron Chemistry

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Feligbkg | Background ligand concentration | 2e-9 | molFe eq. kg-1 | Rue and Bruland (1995) |
| Felig:don | Ligand to DON ratio | 2e-3/40.106/16 | molFe eq. molN-1 | ratio of ligand to dissolved organic carbon in deep water. |
| Fecoast | Rate kinetics of iron influx from side boundaries | 1e-11 | molFe m-1 s-1 | Tuned to reproduce 5deg dropp-off in Johnson (1997) |
| kFe2ndorder | 2nd order adsorption rate constant | 1e10/86400 | molFe-1 m3 s-1 | Tuned to reproduce 5deg dropp-off in Johnson (1997) |
| kFedes | Desorption rate constant | 0.0068/86400 | s-1 | Bacon and Anderson (1982) |
| KFeeqlig | Ligand equilibrium constant | 1e11 | molFe-1 m3 | Parekh et al (2005) |

**3.4 Photosynthesis**

Phytoplankton growth is altered from Geider et al (1997) and Moore et al (2002). θmax values are at the high end in order to account for the additional iron limitation term. The factor of 6.022e17 is to convert from umol to quanta and 2.77e18 to convert from quanta/sec to Watts given the average energy spectrum for underwater PAR from the Seabird sensor. Values of PCmax are decreased relative to Geider et al. (1997) by a factor of 4 to account the difference in reference temperatures and, for Small and Large increased by a factor of 5 to account for the addition of po4 limitation.

Values of thetamax are increased relative to Geider et al. (1997) by a factor of 2 to account for the defFe factor.

α is assumed to not have a size relationship.

θmax is assumed to have an implicit allometric relationship of

eff\_size(2/3) from the surface area to volume relationship. Values all reset 20% higher to reflect lower light regime in generic TOPAZ.

High values of 2.4 equal to the maximum values seen in Geider et al. (1997) for skeletonema and Microcystis.

Value for Di set to half the total to reflect the relative assembly limit of rDiassemmax/rLgassem = P:NDimax/P:NLgmax = (1-0.1-0.5)/(1-0.2).

Diazotrophs are assumed to be inhibited by nitrate after Holl and Montoya (2005).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameter | Description | Value | Units | Reference |
| αDi | Light harvest coef. | 1.2e-5 .2.77e18 / 6.022e17 | g C g Chl-1 m2 W-1 s-1 | Geider et al (1997) |
| αLg | Light harvest coef. | 2.4e-5 .2.77e18 / 6.022e17 | g C g Chl-1 m2 W-1 s-1 | Geider et al (1997) |
| αSm | Light harvest coef. | 2.4e-5 .2.77e18 / 6.022e17 | g C g Chl-1 m2 W-1 s-1 | Geider et al (1997) |
| PDiCmax | Max. growth rate at 0C | 0.75e-5 | s-1 | Geider et al (1997) |
| PLgCmax | Max. growth rate at 0C | 1.5e-5 | s-1 | Geider et al (1997) |
| PSmCmax | Max. growth rate at 0C | 1.5e-5 | s-1 | Geider et al (1997) |
| KEppley | Temperature coeff for growth | 0.063 | C-1 | Eppley (1972) |
| θDimax | Max. Chl:C | 0.04 | gChl gC-1 | Geider et al (1997) |
| θLgmax | Max. Chl:C | 0.06 | gChl gC-1 | Geider et al (1997) |
| θSmmax | Max. Chl:C | 0.04 | gChl gC-1 | Geider et al (1997) |
| θnolimmin | Min. Chl:C without nutrient limitation | 0.01 | gChl gC-1 | Geider et al (1997) |
| θlimmin | Min. Chl:C with complete nutrient limitation | 0.001 | gChl gC-1 | Geider et al (1997) |
| ζ | Photorespiration loss | 0.1 |  |  |
| kDiin | Nitrogen inhibition of N2 fixation | 7e-6 | molN kg-1 | Holl and Montoya (2005) |
| O2inpow | Power to take [O2] for inhibition of N2 fixation | 4 | dimensionless | Stewart and Pearson (1970); Berman-Frank et al (2005) |
| [O2inDisat] | Half sat. for [O2] inhibition of N2 fixation | 3e-4 | molO2 kg-1 | Stewart and Pearson (1970); Berman-Frank et al (2005) |
| γIrrmem | Chl:C response rate | 1/86400 | s-1 | Owens et al (1980) |

**3.5 Grazing and Remineralization**

Grazing is mostly after Dunne et al. (2005; 2007). SiO2 dissolution is set to globally dissolve 50% after Nelson et al. (1995) through grazing. The temperature functionality is set to a combination of stoichiometry and Eppley temperature formulation to give roughly the range of observations in Kamatani (1982) with respect to frustrule thickness and temperature by utilizing the inverse of the Eppley temperature functionality and a normalization to stoichiometry (QSi:Ndiss). The value of QSi:Ndiss was set so as to simultaneously reproduce the low silicon export efficiencies (~0.1) observed in the equatorial Pacific by Blain et al. (1997, DSR I; Dunne et al., 1999, GBC) and high export efficiencies of ~0.64 observed in the Southern Ocean by Bzrezinski et al., 2001, retaining a ~0.5 global average after Nelson et al. (1995).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameter | Description | Value | Units | Reference |
| fLgDet0 | Fraction of Lg grazing to detritus at 0C | 0.93 | dimensionless | Dunne et al (2005; 2007) |
| fSmDet0 | Fraction of Sm grazing to detritus at 0C | 0.18 | dimensionless | Dunne et al (2005; 2007) |
| γNHet | Rate constant for remin. of NHet at 0C | 1/30/86400 | s-1 | Tuned to give ~ ½ heterotrophic biomass |
| kO2 | O2 half sat. for oxic remin. rate | 20e-6 | molO2 kg-1 | Dunne (in prep) |
| kremin | Temp dependence of detritus fraction | -0.032 | C-1 | Dunne et al (2005; 2007) |
| λ0 | Grazing rate constant at 0C | 0.19/86400 | s-1 | Dunne et al (2005; 2007) |
| O2min | Min. O2 for oxic remineralization | 1e-6 | molO2 kg-1 | Dunne (in prep) |
| P\* | Pivot phyto. conc. for grazing allometry | 1.9e-6. 16 / 106 | molN kg-1 | Dunne et al (2005; 2007) |
| Pmin | Min. Phyto. Conc. threshold for grazing | 1e-10 | molN kg-1 | Added for stability |
| φNHet | Fraction of non-detritus grazing going to NHet | 0.5 | dimensionless | Max bacterial growth efficiencies. Tuned to give ~ ½ heterotrophic biomass |
| QSi:Ndiss | Pivot Si to N ratio for frustrule dissolution | 3 | molSi molN-1 | See above |
| rpCaCO3 | CaCO3 protection from remin. | 0.070/12.16/106.100 | molN molCa-1 | Klaas and Archer (2002) |
| rpSiO2 | SiO2 protection from remin. | 0.026/12.16/106.100 | molN molSi-1 | Klaas and Archer (2002) |
| rplith | lith protection from remin. | 0.065/12.16/106.100 | molN glith-1 | Klaas and Archer (2002) |
| γNDet | Rate constant for remin. of NDet | wSink/188 | s-1 | Reproduce the first e-folding length in Martin et al (1989) |
| γCaDet\_arag | Rate constant for dissolution of CaDet\_arag | wSink/760 | s-1 | Betzer et al (1984) 20N–46N, 170E, 900-2200m aragonite attenuation of 47.5% |
| γCaDet\_calc | Rate constant for dissolution of CaDet\_calc | wSink/1343 | s-1 | Wong et al (1999) 67% transfer efficiency at Station PAPA between 1000-3800 m with an ΩCalc of 0.81 |
| γSiDet | Rate constant for dissolution of CaSiDet | wSink/2000 | s-1 | Gnanadesikan (2000) |
| γSDON | Rate constant for remineralization of SDON | 1/(18.365.86400) | s-1 | Abell et al (2000) |
| γSDOP | Rate constant for remineralization of SDOP | 1/(4.365.86400) | s-1 | Abell et al (2000) |
| γLDON | Rate constant for remineralization of LDON | 1/(90.86400) | s-1 | Tuned to Hansell database for surface DON |
| φSDON | Fraction of non-detritus grazing going to SDON | 0.025 | dimensionless | Abell et al (2000) |
| φSDON | Fraction of non-detritus grazing going to SDOP | 0.05 | dimensionless | Abell et al (2000) |
| φLDON | Fraction of non-detritus grazing going to LDON | 0.06 | dimensionless | Tuned to Hansell database for surface DON |
| γnitrif | Rate constant for nitrification | 1/(90.86400) | s-1 | Ward et al (1982) |
| IRRin | Irradiance inhibition constant for nitrification | 0.1 | W m-2 | Olson (1981) |
| φLith | Scavenging rate coefficient for Lith for NLg grazing. | 0.002 | dimensionless | Tuned to sediment lith distribution of Dunne et al. (2007) |
| kLith | Adsorption rate coefficient for Lith to LithDet | 1e-6/86400 | s-1 | Set to a small but non-zero to prevent accumulation in the deep ocean. |
| zSed | Depth of active sediment layer | 0.1 | m | Dunne et al (2012) |
|  |  |  |  |  |

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