An intermediate-complexity model for simulating marine biogeochemistry in deep time: Validation against the modern global ocean

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Abstract

We present a new high-resolution 1-D intermediate-complexity box model (ICBM) of ocean biogeochemical processes for paleoceanographic applications. The model contains 79 reservoirs in three regions that should be generally applicable throughout much of Earth history: (1) a stratified gyre region, (2) a high-latitude convective region, and (3) an upwelling region analogous to those found associated with eastern boundary currents. Transport processes are modeled as exchange fluxes between boxes and by eddy diffusion terms. Significant improvement in the representation of middepth oxygen budgets was achieved by implementing nonlocal mixing between the high-latitude surface and gyre thermocline reservoirs. The biogeochemical submodel simulates coupled C, N, P, O, and S systematics with explicit
representation of microbial populations, using a process-based approach. Primary production follows Redfield stoichiometry, while water column remineralization is depth- and redox couple–dependent. Settling particulate organic matter is incorporated into a benthic submodel that accounts for burial and remineralization. The C/P ratio of burial depends on bottom water oxygen. Denitrification takes place both by classical and anammox pathways. The ICBM was tested against modern oceanographic observations from the Global Ocean Data Analysis Project, Joint Global Ocean Flux Study, and other databases. Comparisons of model output with circulation tracers including θ, salinity, CFC-12, and radiocarbon permit a test of the physical exchange scheme. Vertical profiles of biogeochemically reactive components in each of the three regions are in good agreement with observations. Under modern conditions the upwelling zone displays a pronounced oxygen minimum zone and water column denitrification, while these are not present in the high-latitude or gyre regions. Model-generated global fluxes also compare well to independent estimates of primary production, burial, and phosphorous and nitrogen cycling. The ICBM appears to adequately simulate the long-term (kyr) evolution of several biogeochemical cycles and improves on previous box models in several important ways. In a companion paper, the model's performance under euxinic conditions is tested against modern Black Sea data. The simple and adaptable structure of the model should make it applicable to a wide range of paleoceanographic problems. The model source code is available in MATLAB™ 7 m-files provided as auxiliary material.

1. Introduction

Understanding the biogeochemical evolution of Earth in response to tectonic, climatic and biological developments is a fundamental challenge for the Earth Sciences. Improved chronology of geological and paleontological events and rapidly growing data sets for biogeochemical proxies such as $\delta^{13}$C, $\delta^{34}$S, and biomarkers have led to new hypotheses for the evolution of biogeochemical cycles in deep time. Yet adequate simulation tools for exploring the consequences of these new ideas under conditions very different from present are not widely available. Here we present a new marine biogeochemical model designed to facilitate simulation of a wide range of past conditions so as to permit more explicit testing of hypotheses about the function of biogeochemical cycles through Earth history.

The new biogeochemical model represents the coupled major element cycles of carbon, nitrogen, phosphorus, oxygen, and sulfur (CNPOS), as the individual cycles of the major biogeochemical species cannot be treated separately over widely varying conditions. We have placed particular emphasis on the development of a realistic nitrogen cycle given its potential to respond dramatically to changes in the oxidation state of the ocean-atmosphere system. The biogeochemical model was coupled to a new intermediate-complexity box model developed to represent ocean mixing processes. The model explicitly represents a stratified ocean gyre, a high-latitude region of rapid vertical exchange, and an upwelling region such as those associated with eastern boundary currents. We expect that these three “geographical” regions were likely present at most times through Earth history and are characteristic of oceans on a rotating planet with significant meridional temperature gradients. We refer to the combined models of ocean exchange fluxes
and coupled biogeochemical cycles as an intermediate-complexity box model (ICBM).

Box models are advantageous for this application because of their simplicity, computational speed, and limited explicit dependence on detailed boundary conditions. Ocean biogeochemical models that target modern or Quaternary time intervals are often coupled to general circulation models (GCMs) that derive ocean circulation from boundary conditions including ocean basin geometry, wind stress, surface heat and freshwater fluxes. However, appropriate boundary conditions for deep time paleoceanography are often poorly known and so it is difficult to justify the extra computational cost and complexity of a GCM-type model. In the absence of well known boundary conditions, box models allow various hypothetical circulations to be rapidly constructed and the biogeochemical consequences of these circulations tested against the geologic record.

As part of the model development process, several well known shortcomings of ocean box models have been addressed. For example, the coarse discretization of many ocean box models can lead to unrealistic vertical gradients between surface and deep reservoirs. Excessive sensitivity to high-latitude nutrient utilization can arise from both low-resolution and “closed” nutrient dynamics that do not allow for nutrient inputs and removal [Hotinski et al., 2000; Sarmiento and Orr, 1991]. A third kind of difficulty is the ability of box models to represent thermocline ventilation processes effectively [Siegenthaler and Joos, 1992]. We propose a number of features designed to minimize the deficiencies commonly associated with box models while retaining the overall conceptual simplicity and computational speed.

In this paper we describe the basic implementation of the model, including the processes of exchange between reservoirs (“circulation”) and the biogeochemical equations. We present a detailed model-data comparison with modern oceanic data sets, and show that the model is capable of simulating modern tracer fields such as potential temperature, radiocarbon, and CFCs, as well as both vertical gradients and integrated global fluxes of the key CNPOS species for the modern ocean. In a companion paper [Romaniello and Derry, 2010], we demonstrate that, with appropriate modification of the circulation structure, the same biogeochemical model is capable of accurately simulating modern data from the anoxic Black Sea. This suggests that the ICBM can be used to investigate a wide range of paleoceanographic redox conditions. We present the ICBM as a useful tool for simulating marine biogeochemical processes in deep time across a wide range of redox conditions.

2. A Box Model for the Circulation of the Modern Global Ocean

Here we present a scheme for representing the physical circulation of the global ocean in a box model. We have two closely related goals. The first is to develop a general and robust circulation scheme that is capable of producing well-resolved modern profiles of circulation tracers using realistic ventilation rates, while avoiding many of the pathologies of early box models [e.g., Sarmiento and Orr, 1991; Siegenthaler and Joos, 1992]. Below, we outline the construction of such a model and then compare the model's output for tracer fields such as potential temperature, CFCs, and radiocarbon against modern observations. Once we demonstrate that the model does an adequate job of representing the dynamics of water mass exchange, we
can then focus on the second goal, assessing the performance of the biogeochemical submodel by comparing its output to ocean biogeochemical data. Does the model produce realistic vertical gradients and integrated fluxes of biogeochemically important species in the oceans? If the circulation model is reasonably accurate, then the skill of the model in simulating biogeochemical processes and fluxes primarily reflects the performance of the biogeochemical model. By testing the biogeochemical model using modern circulation parameters validated with observed circulation tracers, we can have greater confidence that comparison of model output with the distributions and fluxes of major biogeochemical components in the CNPOS system is an effective test of the model biogeochemistry, and not merely an artifact of an inappropriate circulation model. After examining the default behavior of the coupled transport-biogeochemistry model, we perform several numerical sensitivity experiments to assess the robustness of the combined model.

2.1. Geometry and Advective Fluxes

The box model used here consists of three spatial regions, the high-latitude ocean, the low-latitude ocean gyres, and a coastal upwelling zone (Figure 1). Each region is subdivided vertically, with high resolution in the upper 1000 m and coarser resolution at depth. The cross-section area, volume, and sediment surface area of each box was calculated from the benthic hypsometry derived for each region using the ETOPO2v2 database [U.S. Department of Commerce, 2006]. Hypsometric profiles calculated for each spatial region are shown in Figure 2.
Figure 1.

Open in figure viewer

Schematic of the 13-box circulation. All fluxes are in Sverdrups (1 Sv = 10$^6$ m$^3$ s$^{-1}$). Bidirectional arrows indicate eddy diffusive mixing, where the diffusion coefficient has been converted to an equivalent reciprocal flux. The 79-box ICBM model is derived by further vertical subdivision of the 13-box model.
The number of vertical levels in the model can be adjusted to change the effective vertical resolution. We outline the basic structure of the model with a low-vertical-resolution version with 13-box model of global ocean circulation, before introducing a 79-box version in section 2.5. The model's vertical levels were chosen to correspond to potential density surfaces, which can be traced across geographic regions to define realistic isopycnal circulation pathways. The advective circulation simulates the major features of the modern meridional circulation while combining the Northern and Southern Hemisphere regions of deepwater formation into a single "high-latitude" zone. Ventilation of the ocean gyres is considered to occur via four independent meridional circulation cells: bottom water (17 Sv), deep water (17 Sv), intermediate water (12 Sv), and ventilation of the gyre thermocline along shallow outcropping isopycnals [Schlitzer, 2007; Sloyan and Rintoul, 2001]. Ventilation of the gyre thermocline along outcropping isopycnals is set at 220 Sv based on CFC-derived estimates of transport as described in section 2.4. The global coastal upwelling flux is set at 18 Sv, based on the sum of estimates for the world's major coastal upwelling zones [Brink et al., 1995;
2.2. Vertical Mixing

Ocean circulation is dominated by turbulent processes driven by wind and tidal mixing. These processes occur as eddies which occur at large range of spatial scales, from centimeters to whole ocean basins. In numerical models of ocean circulation, this turbulent mixing is commonly represented as a diffusion-like process, characterized by an eddy diffusion coefficient. Considerable effort has been made to accurately determine the magnitude of these mixing terms. “Basin-averaged” geochemical inverse estimates of vertical eddy diffusion coefficients typically result in values of $O(10^{-4} \text{ m}^2 \text{ s}^{-1})$ [Ganachaud and Wunsch, 2000; Ganachaud, 2003; Munk and Wunsch, 1998]. On the other hand, in situ estimates from dye releases and microstructure measurements typically reveal values an order of magnitude lower than this, $O(10^{-5} \text{ m}^2 \text{ s}^{-1})$ [Gregg, 1987; Kunze et al., 2006; Ledwell et al., 1998; Polzin et al., 1997]. To reconcile these results, it is common for numerical models to assume a depth-dependent $\kappa$ which smoothly increases from $O(10^{-5} \text{ m}^2 \text{ s}^{-1})$ in the thermocline to $O(10^{-4} \text{ m}^2 \text{ s}^{-1})$ at depth as modeled by the inverse or hyperbolic tangent function [e.g., Bryan and Lewis, 1979]. This produces enough mixing in the deep ocean to allow for the use of realistic advective circulation, but prevents excessive mixing from fueling spurious primary production due to mixing of nutrients across the gyre thermocline. The thermocline and abyssal eddy diffusivities in the ICBM are set at $\kappa^s = 1.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and $\kappa^d = 1 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, where the superscripts $s$ and $d$ refer to shallow and deep, respectively. The depth dependence of $\kappa$ is then modeled as:

$$\kappa_z = \kappa_z^s + \frac{(\kappa_z^d - \kappa_z^s)}{2} \left( 1 + \tanh \left( \frac{z - z^t}{z^t} \right) \right)$$ (1)

where $z^t = z^t = 1000 \text{ m}$ are the transition depth and transition length scale, respectively. A number of investigations have pointed to very high vertical diffusivities around Greenland and in the Southern Ocean. Based on LADCP shear/CTD strain variance ratios, Naveira Garabato et al. [2004a] estimate diapycnal diffusivities approaching $10^{-2} \text{ m}^2 \text{ s}^{-1}$ below 2000 m in the Greenland Sea, relaxing to background values above 1500 m. High rates of deep mixing in the Greenland Sea are also supported by observations of CFC spreading [Visbeck and Rhein, 2000] and deliberate releases of SF$_6$ [Watson et al., 1999]. In the Southern Ocean, estimates of $\kappa_z$ vary from background values of $10^{-5} \text{ m}^2 \text{ s}^{-1}$ in the thermocline away from topography to values between $10^{-4} - 10^{-2} \text{ m}^2 \text{ s}^{-1}$ in regions where the Antarctic Circumpolar Current impinges on regions of complex topography [Naveira Garabato et al., 2004b; Sloyan, 2005; Thompson et al., 2007]. To account for these high rates of mixing, the deep high-latitude vertical eddy diffusion coefficient is set to $10^{-2} \text{ m}^2 \text{ s}^{-1}$, relaxing to $10^{-3} \text{ m}^2 \text{ s}^{-1}$ in the thermocline.

2.3. Horizontal Diffusion

At basin scales, the magnitude of horizontal (isopycnal) eddy diffusivity in the ocean is $10^7 - 10^8$ times larger than the vertical (diapycnal) eddy diffusivity due to the anisotropy of the density field. Dye release experiments have consistently returned estimates of horizontal eddy diffusion of $\kappa_h = O(1000 \text{ m}^2 \text{ s}^{-1})$ for length scales of 1000 km [Ledwell et al., 1998; Okubo, 1971], which is the value adopted here.
Several issues arise when attempting to implement this result in the ICBM. First, because the isopycnal diffusivity is much larger than the diapycnal diffusivity, significant spurious diapycnal diffusivity can arise from assuming that isopycnal surfaces are coplanar with Z coordinate levels. Isopycnals are often inclined to the horizontal, so horizontal “isopycnal” diffusion has a spurious component that acts like diapycnal diffusion [Veronis, 1977]. Moreover, the box model does not assume any specific horizontal geometry for each box, only a surface area, so it is impossible to implement conventional finite differences for the horizontal tracer gradients. To address these issues, two simplifications are made. The first is that horizontal mixing follows the pathways of advective fluxes between laterally adjacent regions. The second simplification is to specify reciprocal exchange fluxes instead of diffusivities, which can be shown to be equivalent for the discretized case:

\[
J = \kappa_h \cdot A_\perp \frac{\partial C}{\partial x} = \kappa_h \cdot \frac{A_\perp}{\ell} \Delta C
\]  

where \(J\) is the flux between the reservoirs (moles time\(^{-1}\)), \(\ell\) is a characteristic length separating the reservoirs, \(A_\perp\) is the cross-sectional area separating two “isopycnally” adjacent reservoirs, \(\Delta C\) is the difference in concentration between two model reservoirs, and the leading term on the far right hand side has units of volume time\(^{-1}\). If we allow that \(\ell\) is of the same order as the length of the interface separating the two regions, where \(\Delta z\) is the depth of the interface separating the two regions, we can approximate:

\[
A_\perp \approx \Delta z \cdot O(\ell)
\]  

\[
J \approx \kappa_h \cdot \Delta z \cdot \Delta C
\]

In this form, a basin-scale horizontal eddy diffusivity of 1000 m\(^2\) s\(^{-1}\) can be interpreted as approximately \(10^{-3}\) Sv of reciprocal mixing for each meter of depth.

### 2.4. Thermocline Ventilation

Observations of tritium and CFCs in the Atlantic and Pacific suggest that gyre thermocline waters are rapidly ventilated along shallow outcropping isopycnals by a combination of isopycnal mixing and geostrophic flow [Sarmiento, 1983a]. Tracer ventilation ages increase from 5 to 28 years between 100 to 800 m depth [Doney and Jenkins, 1988; Fine et al., 2001; Sarmiento, 1983a]. By computing the volume and mean tracer ages of water masses bounded by closely spaced isopycnals, it is possible to estimate the ventilation rate of these water masses. For the North Atlantic, Sarmiento [1983b] calculated tritium-based ventilation rate of 30–40 Sv for \(\sigma_\theta = 26.2–27.4\). Doney and Jenkins [1988] found tracer ages to be 50% lower above \(\sigma_\theta = 26.6\), implying a slightly greater total ventilation flux. If the flux for the South Atlantic is similar, this would bring the total Atlantic ventilation flux to 60–80 Sv. For the North and South Pacific, [Fine et al., 2001] estimates CFC ventilation rates of 111 Sv and 123 Sv, respectively, for \(\sigma_\theta = 24.5–27.3\). Even ignoring the contribution from the Indian Ocean, the global thermocline ventilation rate may be as large as 300 Sv. However, several steps in these calculations may lead to an upward bias. In the work by Sarmiento [1983b], the assumption that tracers are instantaneously mixed throughout the thermocline leads to a value 36% higher than the assumption that shoaling water masses contain no CFC-11. Likewise, the CFC-11/CFC-
12 ratio ages used by Fine et al. [2001] reflect only the age of the CFC-bearing component of the water mass and ignore the contribution of dilution by older CFC-free water. This causes the water mass ages to appear too young, thereby increasing the apparent ventilation rate. If the minimum rate of global gyre thermocline ventilation is taken as six times the lowest rate determined by Sarmiento for the North Atlantic (based on relative surface area), then the best estimate of the global gyre thermocline ventilation rate is between 150 and 300 Sv.

The problem is how to represent this large mixing term in a Z coordinate box model with low latitudinal resolution. Ventilation of an isopycnal layer occurs where it outcrops into the surface mixed layer. For deeper layers, these outcrops occur at high latitude (>50°) and are well described by the paradigm of high-latitude ventilation. However, water masses with $\sigma_\theta < 27.5$ generally outcrop equatorward of 50°, implying that vertical levels as deep as 1000 m can be ventilated directly from the “low-latitude” surface box. As represented by the thermocline ventilation model of Sarmiento [1983b], each successively deeper thermocline layer should outcrop further poleward. Explicit representation of this process would require that each vertical level in the model be accompanied by a corresponding spatial outcrop region, increasing the complexity and numerical cost of the model. As a compromise, the global ICBM model represents these outcrops as direct nonlocal mixing between each gyre thermocline reservoir and both the low-latitude and high-latitude surface reservoirs (Figure 3).
**Figure 3.**

Open in figure viewer

Schematic illustrating the thermocline ventilation schemes used in several box models. The ICBM model attempts to combine features of the thermocline ventilation model of Sarmiento [1983b] and the numerical version of the HILDA model [Siegenthaler and Joos, 1992]. Nonlocal mixing
between the high-/low-latitude surface reservoirs and the gyre thermocline layers is used to parameterize ventilation along outcropping isopycnals.

2.5. The 79-Box Model of the Modern Global Ocean

Sharp vertical redox gradients, such as those found in regions of intense coastal upwelling, are only coarsely resolved by the 13-box model. This might result in distortions of the steady state profiles and potentially large errors in the steady state fluxes. To examine the sensitivity of ICBM models to vertical resolution, a 79-box model was constructed by further vertically subdividing each reservoir in the 13-box model. The new model has an approximate vertical resolution of 50 m in the upper 1000 m, 100 m between 1000 and 2000 m, and 1000 m below 2000 m. Advection fluxes for the 79-box model were taken from the 13-box model, typically interpolated uniformly with depth. The upwelling entrainment was interpolated exponentially such that most of the entrainment is drawn from the upper 100–300 m of the gyre thermocline. Diffusive mixing fluxes were calculated as described in sections 2.2 and 2.3. Ventilation of the gyre thermocline (100–1000 m) was as described in section 2.4, with the total 220 Sv ventilation flux distributed proportional to the depth-dependent ventilation rates determined for the North Atlantic and Pacific Ocean [Fine et al., 2001; Sarmiento, 1983a] (Table 1). The fraction of high-latitude and gyre surface waters contributing to the ventilation of each thermocline layer was determined as a function of temperature. For each gyre thermocline layer, we assigned an approximate potential density range corresponding to the upper and lower boundaries of the layer. For each potential density range, we found the global mean wintertime outcrop temperature from the seasonal sea surface temperature fields of Locarnini et al. [2006]. This mean wintertime outcrop temperature was used to calculate the mixing ratio between the ICBM gyre surface water (20°C) and high-latitude water (−1°C) required to yield the observed outcrop temperature. Although the actual process of seasonal water mass formation is much more complicated than simple linear mixing between an equatorial and polar water mass [e.g., Large and Nurser, 2001], this approximation works for many different tracer variables (NO$_3^-$, PO$_4^{3-}$, O$_2$, DIC, CFC-12, etc.) because their meridional surface distribution is smooth and approximately linear with temperature.

Table 1. Gyre Thermocline Ventilation Parameters for the 79-Box Model

<table>
<thead>
<tr>
<th>Gyre Vertical Level</th>
<th>Depth (m)</th>
<th>Potential Density (kg m$^{-3}$)</th>
<th>Mean Winter Outcrop Temperature (°C)</th>
<th>Ventilation Flux (Sv)</th>
<th>High-Latitude Contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>100–150</td>
<td>25.74–26.17</td>
<td>14.84</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>200–250</td>
<td>26.42–26.60</td>
<td>10.72</td>
<td>40</td>
<td>44</td>
</tr>
<tr>
<td>5</td>
<td>250–300</td>
<td>26.60–26.73</td>
<td>10.37</td>
<td>20</td>
<td>46</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>300–350</td>
<td>26.73–26.83</td>
<td>9.54</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>400–450</td>
<td>26.91–26.99</td>
<td>7.31</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>9</td>
<td>450–500</td>
<td>26.99–27.07</td>
<td>6.10</td>
<td>10</td>
<td>66</td>
</tr>
<tr>
<td>10</td>
<td>500–550</td>
<td>27.07–27.13</td>
<td>5.29</td>
<td>6</td>
<td>70</td>
</tr>
<tr>
<td>11</td>
<td>550–600</td>
<td>27.13–27.19</td>
<td>4.47</td>
<td>4</td>
<td>74</td>
</tr>
<tr>
<td>12</td>
<td>600–650</td>
<td>27.19–27.25</td>
<td>3.53</td>
<td>4</td>
<td>78</td>
</tr>
<tr>
<td>13</td>
<td>650–700</td>
<td>27.25–27.30</td>
<td>2.43</td>
<td>4</td>
<td>84</td>
</tr>
<tr>
<td>14</td>
<td>700–750</td>
<td>27.30–27.34</td>
<td>1.78</td>
<td>4</td>
<td>87</td>
</tr>
<tr>
<td>15</td>
<td>750–800</td>
<td>27.34–27.39</td>
<td>0.99</td>
<td>4</td>
<td>91</td>
</tr>
<tr>
<td>16</td>
<td>800–850</td>
<td>27.39–27.43</td>
<td>0.94</td>
<td>1</td>
<td>91</td>
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<tr>
<td>17</td>
<td>850–900</td>
<td>27.43–27.47</td>
<td>0.51</td>
<td>1</td>
<td>93</td>
</tr>
<tr>
<td>18</td>
<td>900–950</td>
<td>27.47–27.50</td>
<td>0.17</td>
<td>1</td>
<td>94</td>
</tr>
<tr>
<td>19</td>
<td>950–1000</td>
<td>27.50–27.54</td>
<td>−0.09</td>
<td>1</td>
<td>96</td>
</tr>
</tbody>
</table>

a See section 2.5 for details.
2.6. Biogeochemistry Model

In each spatial region, a 1-D biogeochemical model simulates primary production, atmospheric gas exchange, dissolved and particulate organic matter export and remineralization, chemoautotrophic reactions, and benthic processes (Figure 4). At present, the model is capable of simulating two classes of phytoplankton (nitrogen-fixing and “conventional” phytoplankton), phosphorus, nitrate, nitrite, ammonium, particulate organic matter (POM), labile and semilabile dissolved organic matter (DOM), dissolved oxygen, dissolved nitrogen gas, total dissolved inorganic carbon (DIC), sulfate, sulfide, as well as the populations of five microbial functional groups: generalist heterotrophs, ammonium oxidizers, nitrite oxidizers, and anaerobic ammonium oxidizers. In addition, the model is capable of simulating potential temperature, CFC-11, and background and bomb radiocarbon, which are used to validate the transportation fields.

Figure 4.

Schematic of the biogeochemical submodel. Large outer boxes represent individual submodules which can be independently modified. Primary production and gas exchange occur only in the
surface layer, while other processes operate in both the surface and multiple subsurface layers (not individually shown). Arrows and circles represent important fluxes and regulation pathways. Smaller interior boxes represent explicitly simulated biomass pools. See sections 2.6–2.15 for details.

The basic features of the biogeochemistry submodel will be described briefly here, while the details will be provided in sections 2.7–2.15. The biogeochemical model is similar to many other models in the literature in that it describes the one-dimensional cycle of primary production in the photic zone, sinking and dissolved export, remineralization, secondary production (e.g., nitrification and anammox), and benthic processes. All of the particle, dissolved, and biomass organic matter pools in the model are assumed to have classical Redfield stoichiometry (C:N:P = 106:16:1 [Redfield, 1958]) and organic carbon is assumed to be in the zero oxidation state. The reason for this choice was to ensure that mass and redox balance of each process and the overall model were preserved exactly without invoking very complex stoichiometry in the initial version of the model.

The model is open to riverine and atmospheric inputs of nitrate and phosphate. This open cycle is crucial for realistic long-term simulations of ocean biogeochemistry [Hotinski et al., 2000]. In the surface layer of each one-dimensional region, nutrients are taken up by “conventional” phytoplankton and nitrogen-fixing diazotrophs [Tyrrell, 1999]. Both phytoplankton and diazotrophs compete for phosphorus, but phytoplankton are additionally restricted by the availability of fixed nitrogen species while diazotrophs are limited to regions with surface temperatures above 17°C [Breitbarth et al., 2007]. Phytoplankton limitation by light, silica, and iron are neglected in the current version of the model. The mortality rate of phytoplankton is specified by a single first-order rate constant. Upon mortality, a fraction of newly formed detritus is allocated to particulate organic matter (POM) and sinks out of the surface layer [Eppley and Peterson, 1979], while the remainder is converted to DOM. The particle flux is attenuated with depth [Martin et al., 1987] as the sinking POM is converted into labile and semilabile dissolved organic matter (DOM). A small fraction of the sinking POM, determined by the model hypsometry and depth attenuation of the particle flux, is intercepted by the sediment surface in each vertical level and enters the benthic submodel.

Remineralization of organic matter takes place via labile and semilabile dissolved organic carbon, and utilizes a variety of potential oxidants in order of free energy yield. The nutrients released by remineralization are available for uptake during secondary chemoautotrophic production. Repeated cycles of production and remineralization are made possible by advective and diffusive mixing, while burial of phosphorus in sediments provides the long-term (geological) constraint on primary production under modern mostly oxic conditions. A complete list of default parameter values can be found in Appendix A.

### 2.7. Surface Gas Exchange

Atmospheric exchange of O$_2$, N$_2$, CO$_2$, and CFC-11 are modeled using the Wanninkhof [1992] U$^2$ gas transfer velocity formulation using a globally averaged mean oceanic squared wind speed $(U^2/10)$ of 75 m$^2$ s$^{-2}$ as calculated from the Quickscat climatology [Risien and Chelton, 2008]. During the model spin-up integration, the partial pressures of atmospheric gases are set at 0.21 atm, 0.78 atm, and 280 µ atm for O$_2$, N$_2$, and CO$_2$ respectively, and sea surface salinity is assumed to be 35.
Because only about 0.5% of DIC is in the form of dissolved CO\(_2\) (H\(_2\)CO\(_3^*\))\), the following expression is used to convert from DIC to dissolved CO\(_2\):

\[K_1 \text{ and } K_2 \text{ are the first and second carbonic acid dissociation constants, calculated for the specified surface temperature and salinity [Millero, 1995], and [ALK] is the alkalinity (} \mu \text{ eq kg}^{-1}\). The current version of the model does not include an alkalinity submodel. Instead, the air-sea exchange of CO\(_2\) is forced with the Global Ocean Data Analysis Project (GLODAP)-derived annual average sea surface alkalinity for the high-latitude, gyre, and upwelling regions (2300, 2325, and 2280 \mu\text{ eq kg}^{-1}, respectively). Because the modern validation runs are forced with observed sea surface alkalinity, the ICBM is not currently suited for studying oceanic CO\(_2\) uptake or changes in the global weathering rate for which a more detailed model of the carbon chemistry including a dynamic alkalinity state variable would be required. Currently, the simulation of [DIC] is meant only to support simulation of the radiocarbon age for validation of the model circulation.

### 2.8. Primary Production and Diazotrophy

Primary production and diazotrophy are simulated using populations of conventional phytoplankton (PP) and diazotrophs (NF) which compete for phosphorus and nitrogen [Tyrrell, 1999]:

\[
\frac{\partial PP}{\partial t} = \mu_{PP} \cdot \min \left( \frac{PO_4^-}{PO_4^3^- + K_P}, f \left( NO_3^-, NO_2^-, NH_4^+ \right) \right) - m \cdot PP
\]

\[\frac{\partial NF}{\partial t} = \mu_{NF} \cdot \left( sst \right) \cdot \frac{PO_4^-}{PO_4^3^- + K_P} \cdot NF - m \cdot NF
\]

where \(\mu_{PP}\) and \(\mu_{NF}\) are the maximum growth rates of conventional phytoplankton and nitrogen fixers, respectively; \(K_P\) is the Monod half-saturation parameter for phosphate-limited growth; and \(m\) is the mortality rate encompassing maintenance energy, grazing, and sinking. The maximum growth rate of the diazotrophs is reduced to zero when the specified surface temperature is less than 17°C, following experimental work with *Trichodesmium* IMS-101 [Breitbarth et al., 2007]. In addition to phosphate, conventional phytoplankton can be limited by the availability of various fixed nitrogen species. The nitrogen limitation term of Tyrrell [1999] was extended include NO\(_2^-\) and NH\(_4^+\) following [Gruber et al., 2006; Parker, 1993]:

\[
f \left( NO_3^-, NO_2^-, NH_4^+ \right) = \frac{NO_3^- + NO_2^-}{NO_3^- + NO_2^- + K_{N_{ox}}} \cdot \frac{K_{N_{red}}}{NH_4^+ + K_{N_{red}}} + \frac{NH_4^+}{NH_4^+ + K_{N_{red}}}
\]
where NO$_3^-$ and NO$_2^-$ have been summed in place of NO$_3^-$ alone. This formulation assumes a preference for NH$_4^+$ because phytoplankton must first reduce NO$_3^-$ prior to incorporation into biomass.

The model does not currently include a parameterization of the iron cycle, even though it has become widely accepted that broad regions of the ocean are limited by iron availability and that this may have important implications for nutrient cycling [e.g., *Jickells et al.*, 2005; *Moore and Doney*, 2007]. In place of true Fe limitation, the model offers an option to set a minimum level of PO$_4^{3-}$ drawdown in the mixed layer to simulate the effects of Fe limitation:

\[
P - \text{limitation} = \min \left( \frac{P O_4^{3-} - P O_4^{3-}_{\text{min}}}{(P O_4^{3-} - P O_4^{3-}_{\text{min}}) + K_P}, 0 \right)
\]

where \(P O_4^{3-}_{\text{min}}\) is the minimum allowed drawdown. By default, high-latitude \(P O_4^{3-}_{\text{min}} = 1.5 \ \mu \text{mol kg}^{-1}\) for modern global ocean simulation in agreement with observations. The effect of removing this limitation will be examined below.

The model also offers an option to limit nitrogen fixation in the upwelling zone surface. As reviewed by *Canfield* [2006], direct measurements in the Arabian Sea and nitrogen isotope studies of sinking POM in the eastern tropical Pacific suggest that there is only very limited nitrogen fixation occurring in intense regions of coastal upwelling. However, a global geochemical estimate of nitrogen fixation suggests that there may instead be an unusually high rate of nitrogen fixation in the eastern tropical Pacific [ *Deutsch et al.*, 2007]. To handle either of these two cases, a user flag is supplied which can be specified to reduce the maximum growth rate of diazotrophs in particular spatial regions. By default, nitrogen fixation is disabled in the model upwelling region \((\mu_{NF} = 0)\) because preliminary experiments showed this to yield results more similar to the modern observations.

### 2.9. Particle Export and Hydrolysis

Upon mortality, photosynthetic biomass is transferred to one of two pools. It is either removed from the mixed layer as sinking particulate organic matter (POM) or converted to dissolved organic matter (DOM) in situ. The fraction of particle export is related to total primary production (NPP) by an empirical saturation relation fit to the data of *Eppley and Peterson* [1979]:

\[
\hat{f}_{E_xport} = 0.5 \cdot \frac{NPP^2}{NPP^2 + 92.8^2}
\]

where NPP is the net primary production in units of g C m$^{-2}$ yr$^{-1}$. To represent high productivity coastal areas, total export production is allocated such that the surface export flux is 2.5× higher over water depths <1000 m than over open water areas. We have found that this parameterization is essential for maintaining sufficient P burial in box models which do not explicitly represent highly productive ocean margins.

Exported organic matter is either intercepted by the sediment surface or converted to DOM at depth. A modified formulation from *Martin et al.* [1987] is used to describe the depth-dependent attenuation of the
sinking particle flux due to hydrolysis:

$$F_{POM} = F_{POM}^{Z_{mix}} \cdot \left( \frac{Z + (100 - Z_{mix})}{100} \right)^{-0.86}$$  \hspace{1cm} (11)$$

where $F_{POM}$ is the flux of POM in at depth $Z$; $F_{POM}^{Z_{mix}}$ is the flux of POM at the base of the mixed layer; $Z$ is the depth in meters (positive down); and $Z_{mix}$ is the depth of the base of the mixed layer.

The fraction of export production intercepted by the sediment surface is a function of both depth attenuation of the particle flux and the basin hypsometry:

$$F_{POM}^{Sed} = \int_{Z_1}^{Z_2} F_{POM}(z) \cdot \frac{dSA}{dz} dz$$  \hspace{1cm} (12)$$

where $F_{POM}^{Sed}$ is the flux of POM to the sediment surface, $dSA/dz$ is the derivative of the basin cross-sectional area with respective to depth, and $Z_1$ and $Z_2$ are the depths at the top and bottom of a given reservoir, respectively.

Particles which sink into a given reservoir, but do not sink out or sediment onto the seafloor are converted to DOM. The total DOM flux is allocated with 30% of the flux going to LDOM and 70% to SDOM.

**2.10. Organic Matter Remineralization**

Heterotrophic microbial reaction rates are simulated based on mult-substrate Monod kinetics where the volume-specific reaction rates depend on both the substrate concentrations and the organism population. Simulated heterotrophs consume oxidants in order of free energy yield: $O_2$, $NO_3^-$, $NO_2^-$, and $SO_4^{2-}$, in an extended and simplified version of the multiple-substrate inhibition model used by Kornaros and Lyberatos [1998] to model laboratory growth of *Pseudomonas denitrificans* under oxic and anoxic conditions. Oxidation of organic matter by iron and manganese oxides is not currently simulated, since these elements are present at relatively low concentrations and their biogeochemistry is less well understood than that of oxygen, nitrogen, and sulfur.

Conceptually, the remineralization model has two parts, balanced stoichiometric redox equations and kinetic rate laws for each reaction. In general, the stoichiometric redox equations have the form:

$$\frac{1}{1 - Y} LDOC + n \cdot Ox \xrightarrow{Heterotrophs} \frac{Y}{1 - Y} \cdot Hetr + n \cdot Ox_{reduced} + CO_2 + \frac{16}{106} NH_4^+ + \frac{1}{106} PO_4^{3-}$$  \hspace{1cm} (13)$$

where $Y$ is the bacterial growth efficiency (moles biomass/moles of carbon consumed), $n$ is the number of moles of oxidant (Ox) required to oxidize one mole of LDOC (1 mol of C(0)/mole LDOC) to CO$_2$. $Hetr$ represents the moles of organic carbon in the new heterotrophic biomass, which can be converted to cells L$^{-1}$ assuming 15 fg C cell$^{-1}$ [Nagata et al., 2000]. In the current version of the model, the growth yield is
held constant at 0.24 for all oxidants [Bendtsen et al., 2002].

The rate of remineralization via each oxidant is determined by the instantaneous growth rate of heterotrophs on that oxidant:

\[
\left( \frac{\partial \text{Hetr}}{\partial t} \right)_{O_2} = \mu_{O_2} \cdot [\text{Hetr}]
\]

(14)

where \( \mu_{O_2} \) is determined by a rate expression for the substrate limitation and inhibition of that particular oxidization pathway:

\[
\mu_{O_2} = \mu_{\text{max},O_2} \cdot \left( \frac{L\text{DOM}}{L\text{DOM} + K_{S,O_2}} \right) \cdot \left( \frac{O_2}{O_2 + K_{O_2}} \right)
\]

\[
\mu_{NO_3^-} = \mu_{\text{max},NO_3^-} \cdot \left( \frac{L\text{DOM}}{L\text{DOM} + K_{S,NO_3^-}} \right) \cdot \left( \frac{NO_3^-}{NO_3^- + K_{NO_3^-}} \right) \cdot \left( \frac{K_{I1,O_2}}{O_2 + K_{I1,O_2}} \right)
\]

\[
\mu_{NO_2^-} = \mu_{\text{max},NO_2^-} \cdot \left( \frac{L\text{DOM}}{L\text{DOM} + K_{S,NO_2^-}} \right) \cdot \left( \frac{NO_2^-}{NO_2^- + K_{NO_2^-}} \right) \cdot \left( \frac{K_{I2,NO_3^-}}{NO_3^- + K_{I2,NO_3^-}} \right) \cdot \left( \frac{K_{I2,O_2}}{O_2 + K_{I2,O_2}} \right)
\]

\[
\mu_{SO_4^{2-}} = \mu_{\text{max},SO_4^{2-}} \cdot \left( \frac{L\text{DOM}}{L\text{DOM} + K_{S,SO_4^{2-}}} \right) \cdot \left( \frac{SO_4^{2-}}{SO_4^{2-} + K_{SO_4^{2-}}} \right) \cdot \left( \frac{K_{I3,NO_3^-}}{NO_3^- + K_{I3,NO_3^-}} \right) \cdot \left( \frac{K_{I3,O_2}}{O_2 + K_{I3,O_2}} \right)
\]

(15)

Finally, the overall growth rate of heterotrophs is given by:

\[
\frac{\partial \text{Hetr}}{\partial t} = (\mu_{O_2} + \mu_{NO_3^-} + \mu_{NO_2^-} + \mu_{SO_4^{2-}}) \cdot [\text{Hetr}] - \text{mortality}
\]

(16)

where the mortality term is discussed specifically in section 2.13.

During denitrification, the oxidation of organic matter is coupled to the reduction of \( NO_3^- \) to \( N_2 \) in a five step
process ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$) [Zumft, 1997]. The trace gas products accumulate to only very low levels, and thus can be ignored for the present (e.g., $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2$). At present, it is unclear what fraction of reduced $\text{NO}_3^-$ actually accumulates as free, extracellular $\text{NO}_2^-$ during marine denitrification, as opposed to complete intracellular reduction to $\text{N}_2$ intracellular via tight coupling of the two enzymatic steps. To allow for a range of possibilities, the model provides a flag, $f_{\text{N}_2}$ ($0 \leq f_{\text{N}_2} \leq 1$), which controls the fraction of $\text{NO}_3^-$ reduced directly to $\text{N}_2$ with appropriate consideration of the change in redox stoichiometry. By default, this flag is set at 0.5, which was found to produce good agreement with existing data in preliminary simulations.

2.11. Nitrification

Oxidation of organic matter releases ammonium. Under aerobic conditions, nitrifying bacteria oxidize $\text{NH}_4^+$ to $\text{NO}_3^-$ in a two-step chemolithoautotrophic process, with $\text{NO}_2^-$ as a free intermediate. No single nitrifying organism is known to oxidize $\text{NH}_4^+$ directly to $\text{NO}_3^-$ [Konneke et al., 2005]. The first step is carried out by ammonia-oxidizing bacteria (AOB), which oxidize $\text{NH}_4^+$ to $\text{NO}_2^-$. The second step in nitrification is carried out by nitrite-oxidizing bacteria (NOB), which oxidize $\text{NO}_2^-$ to $\text{NO}_3^-$ [Ward, 2000]. The overall stoichiometry of these reactions, including electrons required to reduce carbon dioxide and nutrient uptake in Redfield proportions, can be written:

$$11.15\text{NH}_4^+ + 15.5\text{O}_2 + \text{CO}_2 + 0.01\text{PO}_4^{3-} \xrightarrow{\text{AOB}} \text{AOB} + 11\text{NO}_2^- + 22\text{H}^+ + 21\text{H}_2\text{O}$$

$$50\text{NO}_2^- + 24\text{O}_2 + \text{CO}_2 + 0.15\text{NH}_4^+ + 0.01\text{PO}_4^{3-} + \text{H}_2\text{O} \xrightarrow{\text{NOB}} \text{NOB} + 50\text{NO}_3^-$$

(17)

where $\text{AOB}$ and $\text{NOB}$ represent 1 mol C of nitrifier biomass. Estimates of N oxidized/C fixed by moles range from 7 to 16.6 for AOB and 40–80 for NOB [Brion and Billen, 1998, and references therein; Glover, 1985]. The equation above assumes values of 11 and 50.

The kinetics of these reactions are controlled by the growth rates (i.e., carbon assimilation rates) of nitrifying organisms. The double-Monod growth model of Koch et al. [2000], used to simulate growth of aerobic and anaerobic nitrogen oxidizing bacteria in a rotating biological contactor, is adopted here:

$$\frac{\partial \text{AOB}}{\partial t} = \mu_{\text{AOB}} \cdot \frac{\text{O}_2}{K_{\text{O}_2}^{\text{AOB}} + \text{O}_2} \cdot \frac{\text{NH}_4^+}{K_{\text{NH}_4^+}^{\text{AOB}} + \text{NH}_4^+} \cdot \text{AOB} - \text{mortality}$$

$$\frac{\partial \text{NOB}}{\partial t} = \mu_{\text{NOB}} \cdot \frac{\text{O}_2}{K_{\text{O}_2}^{\text{NOB}} + \text{O}_2} \cdot \frac{\text{NO}_2^-}{K_{\text{NO}_2^-}^{\text{NOB}} + \text{NO}_2^-} \cdot \text{NOB} - \text{mortality}$$

(18)

where $\mu$ is the maximum growth rate, and the $K$ terms are half-saturation constants. The endogenous respiration terms in the Koch et al. [2000] model have been replaced with an additional bacterial mortality term described below. Reactions rates are coupled to the whole organism stoichiometry equations via
specification of the cellular organic carbon content for average marine bacteria (15 fg C/cell [Nagata et al., 2000]). Photoinhibition of nitrification is thought to be a major control on pelagic marine nitrification rates [Guerrero and Jones, 1996a, 1996b; Hooper and Terry, 1974; Horrigan et al., 1981; Olson, 1981a, 1981b; Ward et al., 1982; Ward, 1987], although it has been demonstrated that the nitrification does occur at very low but measurable rates in the photic zone [Lipschultz, 2001; Raimbault et al., 1999; Ward, 1987]. For lack of more detailed understanding, photoinhibition of nitrification is currently specified in the ICBM as a user-defined flag in the range 0–1, which directly scales the maximum rates of nitrification in the surface layer. By default, this flag is set to zero, consistent with early arguments for complete photoinhibition of nitrification in the photic zone.

2.12. Anaerobic Ammonium Oxidation

The anaerobic ammonium oxidation (anammox) is now understood to be a major pathway of fixed N loss in marine sediments and pelagic anoxic zones, possibly accounting for as much as 50% of total fixed N loss [Dalsgaard et al., 2005]. The ICBM model represents the anammox reaction, including carbon fixation and nutrient uptake, according to the following reaction:

\[
16\text{NO}_2^- + 14.15\text{NH}_4^+ + \text{CO}_2 + 0.01\text{PO}_4^{3-} \rightarrow 14\text{N}_2 + 2\text{NO}_3^- + \text{AMX} + 27\text{H}_2\text{O}
\]

(19)

assuming that the oxidation of ammonium is coupled to nitrite and that the reduction of carbon dioxide is coupled to nitrite oxidation to nitrate [Mulder et al., 1995; van de Graaf et al., 1995].

The kinetics of this reaction are simulated using a double Monod expression with an additional inhibition term for \(O_2\) [Koch et al., 2000]:

\[
\frac{\partial \text{AMX}}{\partial t} = \mu_{\text{AMX}} \cdot \frac{\text{NH}_4^+}{K^\text{AMX}_{\text{NH}_4^+} + \text{NH}_4^+} \cdot \frac{\text{NO}_2^-}{K^\text{AMX}_{\text{NO}_2^-} + \text{NO}_2^-} \\
\cdot \frac{K^\text{AMX}_{\text{O}_2}}{K^\text{AMX}_{\text{O}_2} + \text{O}_2} \cdot \text{AMX} - \text{mortality}
\]

(20)

where \(\text{AMX}\) is the population density of anammox bacteria, \(\mu\) is the maximum growth rate, \(K_{\text{NO}_2}\) and \(K_{\text{NH}_4}\) are half-saturation constants, and \(K_{\text{O}_2}\) is the inhibition constant. Parameters for this expression have been drawn from the available literature [Jetten et al., 2001]. While this manuscript was in preparation, new environmental kinetic data became available from the Black Sea [Jensen et al., 2008], but have not yet been incorporated into an updated version of the model.

2.13. Microbial Mortality and Endogenesis Metabolism

The ICBM simulates microbial mortality following the empirical approach of Bendtsen et al. [2002], who assume a general form:
$mortality = a \cdot B^b$ \hspace{1cm} (21)

where $a$ and $b$ are empirical constants and $B$ is the microbial biomass. To determine appropriate values for the constants, Bendtsen et al. [2002] applied a simple steady state model of carbon mass balance to measurements of particle flux and bacterial biomass in the central Pacific. Alternatively, it is also possible to estimate the mortality function directly given independent estimates of microbial production and biomass:

$$\frac{dB}{dt} = Production - a \cdot B^b = 0$$ \hspace{1cm} (22)

$$\log(Production) = b \cdot \log(B) + \log(a)$$

Independent estimates of microbial heterotrophic production can be obtained by monitoring the incorporation of $[^3]H$-leucine. By this method, it is only necessary to estimate a conversion factor between radiolabel uptake and bacterial production, which is thought to be between 1.5 and 3 kg C (mol Leu)$^{-1}$ [Simon and Azam, 1989].

This method was applied to eight sites in the Atlantic, Pacific, Indian and Mediterranean oceans where both bacterial abundance and production data were available (Figure 5 and Table 2). The results indicate that the exponent is close to quadratic ($b = 1.4$–$2.1$), though the leading term is only poorly constrained. Default values for the ICBM model are taken from the weighted mean estimate of the log-transformed variables for all points shown in Figure 5, yielding $a = 13.45 \times 10^9$ cells L$^{-1}$ yr$^{-1}$ and $b = 1.71$. Currently, the mortality model is applied to each population individually, since applying it in aggregate quickly causes slower growing functional groups to go “extinct.” However, the model was derived from bulk cell counts and production numbers, and thus it probably best represents microbial heterotrophs which numerically dominate the pelagic water column.
Figure 5.
Open in figure viewer

Log-log plot of bacterial production versus bacterial cell count for several different data sets used to estimate the microbial mortality term using equation (22). Results for each data set are provided in Table 2. See section 2.13 for details.

Table 2. Sources of Data and Analysis of Microbial Mortality Parameters Using Equation (22)\(^a\)

<table>
<thead>
<tr>
<th>Author/Principle Investigator</th>
<th>Location</th>
<th>(a \ (10^9 \text{ cells L}^{-1})^{1+b} \text{ yr}^{-1})</th>
<th>(B \ (\text{Unitless}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nagata et al. [2000]</td>
<td>N. Pacific</td>
<td>0.7 +1.8/−0.5</td>
<td>1.6 ± 0.6</td>
<td>0.95</td>
</tr>
<tr>
<td>Nagata et al. [2000]</td>
<td>N. Pacific</td>
<td>1.4 +25/−1.3</td>
<td>1.6 ± 1.2</td>
<td>0.86</td>
</tr>
<tr>
<td>Tanaka and Rassoulzadegan [2004]</td>
<td>NW Med</td>
<td>11 +29/−7.9</td>
<td>1.4 ± 0.6</td>
<td>0.70</td>
</tr>
<tr>
<td>Azam and Smith [2001] (accessed 4 April 2008)</td>
<td>Arabian</td>
<td>32 +64/−21</td>
<td>1.7 ± 0.4</td>
<td>0.91</td>
</tr>
<tr>
<td>Azam and Smith [2001] (accessed 4 April 2008)</td>
<td>Arabian</td>
<td>18 +20/−10</td>
<td>1.4 ± 0.4</td>
<td>0.91</td>
</tr>
</tbody>
</table>

The current version of the ICBM sulfur cycle is limited to two species, $\text{SO}_4^{2-}$ and $\text{H}_2\text{S}$, in a closed cycle. Neither inputs from rivers, hydrothermal vents, and submarine volcanism, nor outputs due to evaporite formation and sediment burial are simulated. It is implicitly assumed that these processes are at steady state and the mass of global marine sulfur reservoir can be specified as a constant variable, an assumption consistent with the observation that the residence time of sulfur [Holland, 1978; Turchyn and Schrag, 2004] is long relative to the typical duration of our simulations ($10^5$ years).

Sulfide is formed in the water column and sediments by heterotrophic sulfate reduction. Reoxidation of sulfide is simulated via two inorganic pathways. The first pathway is oxidation by molecular oxygen:

$$\text{H}_2\text{S} + 2\text{O}_2 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$$

The rate constant, $k_{\text{H}_2\text{S}}$, for this process has been shown to vary significantly as a function of several redox-sensitive trace metals which act as catalysts [Millero, 1991]. Here $k_{\text{H}_2\text{S}} = 54 \ \mu \text{M}^{-1} \ \text{yr}^{-1}$ is equivalent to the 30 min $\text{H}_2\text{S}$ half-life observed for deep Black Sea samples exposed to air [Millero, 1991]. The second oxidation pathway is thiodenitrification as simulated by [Konovalov et al., 2006]:

$$5\text{H}_2\text{S} + 8\text{NO}_3^- \rightarrow 4\text{N}_2 + 5\text{SO}_4^{2-} + 4\text{H}_2\text{O} + 2\text{H}^+$$

Thiodenitrification has been found to be biologically catalyzed in laboratory experiments [Krishnakumar and Manilal, 1999], as well as wastewater systems [Yang et al., 2005]. It is now also recognized to be carried out by Beggioata sp., Thioploca sp., and Thiomargarita sp. in marine and freshwater sediments [Kamp et al., 2006; Otte et al., 1999; Schulz et al., 1999; Sweerts et al., 1990], and has been reported in the anoxic water column of the Black Sea [Tuttle and Jannasch, 1973], Baltic [Brettar and Rheinheimer, 1991], and Namibian coast [Lavik et al., 2006]. However, there appears to be little published information about the kinetics of this reaction in natural waters. Therefore, the same rate constant for aerobic oxidation of
sulfide is assumed, although this is clearly subject to revision. Note that both of the reactions are modeled inorganically. Chemoautotrophic sulfur oxidation is an important omission, which should be explicitly included in a more detailed model of the sulfur cycle in the future.

### 2.15. Sediment Model

In each vertical level, the shoaling sediment surface intercepts a fraction of sinking particle export as given by the model hypsometry. This intercepted POM is instantaneously processed by the sediment submodel. Carbon burial efficiency (\( CBE \)), the percent of total organic carbon flux which is ultimately buried, is calculated from the organic carbon rain rate following \textit{Dunne et al. [2007]}. Of the remineralized carbon (i.e., 1-CBE), a fraction is remineralized via denitrification following the full metamodel of \textit{Middelburg et al. [1996]}. Because this metamodel was only calibrated from bottom water oxygen and nitrate concentrations of 10–350 \( \mu \text{mol O}_2 \text{kg}^{-1} \) and 1–60 \( \mu \text{mol NO}_3^- \text{kg}^{-1} \), respectively, the predicted contribution of denitrification to total remineralization can sometimes exceed 100\% for BW O\_2 < 10 \( \mu \text{mol kg}^{-1} \) in combination with high BW NO\_3\(^-\) and low organic carbon flux. To prevent unphysical values, the denitrification was limited when the denitrified fraction of organic carbon exceeded 90\%.

To estimate the fraction of denitrification coming from nitrification-denitrification, the remineralized fraction of benthic PON flux, \( f_{\text{Re min}}^N \), is estimated as:

\[
 f_{\text{Re min}}^N = 1 - CBE \cdot \frac{106}{16 \cdot C/N_{\text{Burial}}} \quad (25)
\]

where \( C/N_{\text{Burial}} = 10 \), a typical value for marine sediments [\textit{Hedges et al., 1999}]. Of the remineralized nitrogen, the fraction oxidized to nitrate (\( f_{\text{OX}}^N \)) in the sediments is simulated as:

\[
 f_{\text{OX}}^N = \frac{O_2}{O_2 + KO_2 + kO_2 \cdot (1 - CBE) \cdot F_{\text{Corg}}} \quad (26)
\]

where \((1 - CBE) \cdot F_{\text{Corg}}\) is the total remineralization rate. When the predicted nitrification is less than the total predicted denitrification, a fraction of the denitrified nitrate (\( f_{\text{Diff}}^N \)) must be diffusing from the overlying water column. This fraction is limited according to:

\[
 f_{\text{Diff}}^N = \frac{NO_3^-}{NO_3^- + \min (K_{NO_3} + k_{NO_3} \cdot (1 - CBE) \cdot F_{\text{Corg}}, 0)} \quad (27)
\]

Values for the empirical constants, \( K_{O_2} = 25 \mu \text{mol O}_2 \text{kg}^{-1} \), \( k_{O_2} = 400 \mu \text{mol kg}^{-1} \), \( K_{NO_3} = 25 \mu \text{mol kg}^{-1} \), and \( k_{NO_3} = 10 \mu \text{mol NO}_3^- \text{kg}^{-1} \), were determined by fitting the simulated fluxes to those presented by \textit{Middelburg et al. [1996]}. The remaining remineralization is modeled via aerobic respiration when the overlying water column is oxic (>1 \( \mu \text{mol kg}^{-1} \text{O}_2 \)), or sulfate reduction otherwise, with all sulfide being returned to the water column.

Following the suggestions of \textit{Ingall and Jahnke [1997]} and \textit{Ingall and Van Cappellen [1990]}, we...
parameterize the $C:P_{\text{Reac}}$ ratio of the organic matter burial flux as a function of bottom water dissolved oxygen (BW $O_2$) using:

$$\left(\frac{C_{\text{Org}}}{P_{\text{Reac}}}\right)_{\text{Burial}}^{\text{oxic}} = \frac{(C_{\text{Org}}/P_{\text{Reac}})_{\text{Burial}}^{\text{oxic}} + \frac{K_{P_{\text{BB}}}}{K_{P_{\text{BB}}} + \text{BW } O_2}}{\left[\left(\frac{C_{\text{Org}}}{P_{\text{Reac}}}\right)_{\text{Burial}}^{\text{Anox}} - \left(\frac{C_{\text{Org}}}{P_{\text{Reac}}}\right)_{\text{Burial}}^{\text{oxic}}\right]}$$

where $(C_{\text{Org}}/P_{\text{Reac}})_{\text{Burial}}^{\text{oxic}} = 48.5$, $(C_{\text{Org}}/P_{\text{Reac}})_{\text{Burial}}^{\text{Anox}} = 472$, and $K_{P_{\text{BB}}} = 10 \mu$ mol kg$^{-1}$. From the carbon burial flux, it is then possible to calculate the phosphorus burial flux. Unburied phosphorus is returned to the overlying water column. Note that the $C_{\text{Org}}:P_{\text{Reac}}$ ratios used here are somewhat more extreme than the values proposed by Handoh and Lenton [2003] but bracket the range of $C_{\text{Org}}:P_{\text{Reac}}$ ratios observed by Anderson et al. [2001] for a variety of depositional environments.

### 3. Global Model Boundary Conditions and Spin-Up

The temperatures of the surface boxes in the high-latitude, gyre, and upwelling regions were fixed at $-1\degree C$, $20\degree C$, and $25\degree C$, respectively. Validation model runs were carried out in two steps. First, a 100 kyr spin-up was conducted to bring all components to steady state. During this step, preanthropogenic $P_{\text{CO}_2}$ (280 ppmv) and atmospheric $\Delta^{14}\text{C}$ (0‰) were used to calculate the simulated background $\Delta^{14}\text{C}$. During the second step, the spin-up integration was extended by 300 years (corresponding to the period 1700–2000) to validate the model's transport of bomb radiocarbon and CFC-11. During this integration, the model was forced with the observed atmospheric $p\text{CO}_2$, $p\text{CFC-11}$, and $\Delta^{14}\text{C}$ values shown in Figure 6. For both integrations, external inputs of reactive phosphate and nitrogen (as nitrate) were taken as $15 \times 10^{10}$ [Benitez-Nelson, 2000] and $4.87 \times 10^{12}$ moles yr$^{-1}$ [Tyrrell, 1999], respectively.
Figure 6.

Atmospheric forcing functions for CFC-11 and bomb radiocarbon simulations. (top) Atmospheric $P_{CO_2}$ forcing function derived from the Law Dome ice core and Mauna Loa atmospheric $P_{CO_2}$ data [Etheridge et al., 1996; Keeling and Whorf, 2005]. (middle) Atmospheric bomb $\Delta^{14}C$ forcing function derived from measurements in Wellington, New Zealand, Vermunt, Austria, and Georgian wines [Burchuladze et al., 1989; Levin et al., 1985; Manning et al., 1990]. (bottom) CFC-11 forcing derived from reconstructed Northern and Southern Hemisphere atmospheric CFC-11 concentrations [Walker et al., 2000].

4. Reference Data

Reference data for model validation were taken from the discrete bottle observations compiled for the GLODAP Data Atlas [Sabine et al., 2005]. WOCE radiocarbon and CFC-11 observations were made between 1983 and 1997, but most observations date from 1992 to 1996. Because of this, radiocarbon and
CFC-11 data were compared with the simulated CFC-11 and radiocarbon distributions for 1994. Additional data on total organic carbon (TOC) [Peltzer and Hansell, 2001; Peltzer, 2002] (accessed 4 April 2008), dissolved organic carbon (DOC) [Hansell and Carlson, 1998] (accessed 4 April 2008), ammonium [Codispoti, 2000a, 2000b] (accessed 4 April 2008), and heterotrophic bacterial cell counts [Ducklow, 2002a, 2002b; Azam and Smith, 2001] were drawn from the Joint Global Ocean Flux Study (JGOFS) AESOPS and Arabian Sea process studies as well as the HOT and BATS sites [Karl, 2008; Knap et al., 2008] (accessed 4 April 2008). AESOPS, Arabian, and HOT/BATS data are compared to the model high-latitude, upwelling, and gyre regions, respectively. All data corresponding to each model region were binned by depth and presented as the frequency of observations within a given depth bin. This approach avoids explicitly averaging geographically disparate observations (e.g., North Atlantic and North Pacific radiocarbon) as has been done in previous similar box model studies [e.g., Siegenthaler and Joos, 1992].

5. Simulation Results

5.1. Circulation Tracers

For both the 13- and 79-box models, simulated potential temperature and background radiocarbon agree well with observations (Figure 7). Simulated high-latitude background radiocarbon better approximates observations from the Southern Ocean than the North Atlantic, consistent with the construction of the model's high-latitude circulation. The simulated background radiocarbon for the ocean gyre regions (~156‰) is intermediate between observations in the deep Atlantic (~75‰ to ~150‰) and Pacific (~150‰ to ~250‰). In the upwelling region, the departure of the model from the observed Δ^{14}C data reflects the predominance of Pacific upwelling. The very small Δ^{14}C offset between the simulated model gyre and upwelling zone is in good agreement with the similarity of Pacific Δ^{14}C in upwelling and gyre regions.
Simulated tracer profiles for the high-resolution (black) and low-resolution (red) global ocean ICBM model. Different rows correspond to the different geographic regions represented by the models. Data for validation were taken from the GLODAP database. Bimodal observations represent data from spatially distinct regions, such as the North Atlantic and Southern Ocean or Atlantic and Pacific.

The model simulation of CFC-11 and bomb $^{14}$C transient tracers is also quite good (Figure 7). The penetration of bomb radiocarbon into the high-latitude region may be overestimated by 10–20‰; however, the sparse geographic distribution of observations and an inherent 10‰ uncertainty in separating the background and bomb radiocarbon signals may also partially explain the discrepancy [Rubin and Key, 2002]. Simulated CFC-11 distributions are consistent with observations.

5.2. Nutrients, Oxygen, and Dissolved Inorganic Carbon

Model nutrient profiles are typically well within the range of observations (Figures 8–10); however, the lower-
resolution model is clearly subject to overshooting in regions with sharp vertical gradients, while the 79-box model displays smooth extrema. In detail, dissolved nitrate and phosphate are more similar to observations from the Pacific and Southern oceans. This is a consequence of limiting high-latitude mixed layer phosphorus drawdown below 1.5 $\mu$M, which results in higher levels of preformed nitrate and phosphate throughout the model. In the gyre region of the high-resolution model, simulated surface nitrate and phosphorus concentrations are 0.89 $\mu$M and 0.15 $\mu$M, giving a surface NO$_3^-$:PO$_4^-$ ratio of 5.9 (Figure 11). In upwelling regions, simulated surface nutrient concentrations are approximately twice as high, 1.8 $\mu$M and 0.38 $\mu$M, with a slightly lower NO$_3^-$:PO$_4^-$ ratio, while surface concentrations in high-latitude region remain elevated, 23.46 $\mu$M and 1.62 $\mu$M, with a NO$_3^-$:PO$_4^-$ ratio of 14.5. There are no significant differences between the surface nutrient concentrations predicted by the high- and low-resolution models.

**Figure 8.**

Simulated high-latitude biogeochemical profiles for the high-resolution (black) and low-resolution (red) global ocean ICBM model. Colored fields represent frequency of observations in the combined GLODAP and JGOFS AESOPS data sets. Where the observed tracer fields are bimodal, text labels denote the Southern Ocean (SO) and North Atlantic (NA) data fields.
Figure 9.
Open in figure viewer

Simulated gyre biogeochemical profiles for the high-resolution (black) and low-resolution (red) global ocean ICBM models. Colored fields represent frequency of observations in the combined GLODAP, HOT, and BATS data sets. Where the observed tracer fields are bimodal, text labels denote the Atlantic (Atl) and Indo-Pacific (IP) data fields.
**Figure 10.**

Open in figure viewer

Simulated upwelling biogeochemical profiles for the high-resolution (black) and low-resolution (red) global ocean ICBM models. Colored fields represent frequency of observations in the combined GLODAP and JGOFS Arabian Sea data sets.
In the upwelling region, simulated phosphate is elevated 0.5 \( \mu \text{M} \) above observed values at depths greater than 500 m. In this region, DIC is correspondingly elevated and \( \text{O}_2 \) is slightly depleted. These trends reverse in the deepest portion of the upwelling model, with elevated \( \text{O}_2 \) and depleted \( \text{PO}_4^- \) and DIC. At the depth of the oxygen minimum zone (OMZ), the model predicts an intense region of nitrate depletion which is not clearly recorded in the global-scale GLODAP data (Figures 10 and 11). However, specific sites close to the core of the upwelling oxygen minimum in the Arabian Sea and eastern tropical Pacific do record such depletion. An example from the Arabian Sea is presented in Figure 11f.

Both simulated nitrite and ammonium the follow observed trends reasonably well. Ammonium is \(<0.01 \ \mu \text{M}\) throughout the deep water column, with a surface maximum of 0.4–0.6 \( \mu \text{M} \), consistent with observations. In the upwelling region, both models predict a subsurface ammonium peak of 0.15–0.2 \( \mu \text{M} \) at the core of the oxygen minimum zone that is not apparent in any observed data set of which we are aware, although
scattered values as high as 0.2 \( \mu M \) can be found at the depth of the OMZ in the Arabian Sea JGOFS data [Codispoti, 2000b] (accessed 4 April 2008). In the high-latitude and gyre regions, simulated nitrite is consistently below 0.01 \( \mu M \). The current biogeochemical model has no mechanism for generating the primary nitrite maximum (typically \( \sim 0.5 \mu M \)) at the bottom of the euphotic zone, which is thought to be the results of incomplete nitrate reduction by phytoplankton or differential light limitation of ammonium- and nitrite-oxidizing nitrifiers [Lomas and Lipschultz, 2006; Olson, 1981b]. In the upwelling region, the magnitude of secondary nitrite maximum associated with the oxygen minimum zone is simulated well with a peak concentration of 3.75 \( \mu M \). However, the 600 m depth of the simulated nitrite maximum is deeper than the 50–500 m typically observed for this feature.

As with nutrients, simulated gyre and high-latitude dissolved oxygen and DIC are typically immediate between Atlantic and Pacific and North Atlantic and Southern Ocean values, respectively. In general, simulated profiles show good agreement with observations. The only substantial deviation is in the lower 3000 m of upwelling region, where the small box volumes and poorly detailed circulation make it difficult to simulate this region accurately. Higher in the upwelling water column, the depth of the oxygen minimum zone where simulated \( O_2 < 10 \mu M \) extends from 300 to 1000 m. The depth of onset of suboxia is deeper than is typically observed, but the lower bound is within the observed range. The production of sulfide was not observed in these simulations, even in the anoxic upwelling region.

5.3. Dissolved Organic Matter

Simulated semilabile dissolved organic matter (SDOM) concentrations are generally within the range of observations. Surface concentrations of SDOM in the high-latitude and gyre regions are 12 \( \mu M \) C and 38 \( \mu M \) C, respectively. Surface concentrations of SDOM in the upwelling region, 77 \( \mu M \), are somewhat higher than the values of 21–59 \( \mu M \) observed in the Arabian Sea. All simulated SDOM profiles decay toward zero by 1000 m, similar to observations. The remaining \( \sim 42 \mu M \) of DOC in the deep ocean is thought to be highly recalcitrant and is not simulated in the current version of this model. The LDOM pool is thought to have a turnover time of hours to weeks and represents only a few percent of total DOM, 0–2 \( \mu M \), as simulated here [Carlson and Ducklow, 1995].

5.4. Simulated Microbial Populations

In each region, the simulated heterotroph profile captures the observed exponential decline in heterotrophic cell count with depth and correctly predicts the magnitude of surface and deep water populations. However, in detail the model overpredicts the surface populations of microbial heterotrophs in the gyre region by a factor of 2. Moreover, observations from HOT and BATS also show a decline in microbial heterotrophs above 100 m, while the model predicts a continuous exponential decrease with increasing depth.

Compared to bulk “heterotrophic” bacterial cell counts, much less is known about the abundance of nitrifiers and anammox bacteria in pelagic marine environments. Simulated populations of ammonium oxidizers increase from 2% to 3% of heterotrophic microbial cells in the mixed layer to >20% below 1000 m. Absolute simulated abundances of ammonium oxidizers display a strong subsurface maximum immediately below the mixed layer, with peak abundances ranging from \( 0.6 \times 10^8 \) cells L\(^{-1} \) in to the high-latitude region to \( 1.6 \times 10^8 \)
cells L\(^{-1}\) in the upwelling region. Abundances declined to 0.05–0.1 \(\times 10^6\) cells L\(^{-1}\) at >4000 m. Simulated nitrite oxidizer abundance displayed similar trends, but absolute abundances were only 43%–75% of ammonium oxidizers. Early work enumerating specific species of marine ammonium oxidizing bacteria using immunofluorescent methods reported nitrifier abundances of 2–8 \(\times 10^4\) cells L\(^{-1}\) between 0 and 100 m [Ward et al., 1982]. This is between 3 and 4 orders of magnitude lower than predicted here. However, an important contribution to marine ammonium oxidation from marine crenarchaeotes has been recently reported [Wuchter et al., 2006]. Previous immunofluorescent techniques were not sensitive to ammonium oxidizing crenarchaeotes, and so these counts may have underestimated the nitrifier community. Working at the HOT site, Ingalls et al. [2006] used a compound-specific radiocarbon method to determine that 80% of archaeal biomass from 670 m was supported by direct autotrophic production incorporating ambient aged DIC. At this same site, Karner et al. [2001] determined that the relative abundance of crenarchaeotes rose sharply from 2% to 3% of the total DAPI count in the photic zone to 20%–40% of total counts at depth. This profile bears a strong resemblance to the simulated abundance of ammonium oxidizers. If 80% of the crenarchaeotes at the HOT site were indeed autotrophic nitrifiers, the resulting cell count profiles would closely match the simulated gyre nitrifier populations.

Below the uppermost reservoir, where nitrification rates are set to zero by default to simulate photoinhibition, simulated rates of ammonium and nitrite oxidation are tightly coupled and decrease exponentially with depth. These patterns are similar to field observations, which indicate that maximum rates of ammonium oxidation occur at the base of the euphotic zone [Ward et al., 1989; Ward, 2000]. Maximum simulated rates in each region are 6.2, 8.4, and 21.4 nM N d\(^{-1}\) in the high-latitude, gyre, and upwelling regions respectively. These estimates are in good agreement with the most recent measurements of ammonium oxidation rates at the base of the euphotic zone, between 1 and 10 nM d\(^{-1}\) in the open ocean [Clark et al., 2008; Raimbault et al., 1999; Sutka et al., 2004] rising to 12–80 nM d\(^{-1}\) in the upwelling regions [McCarthy et al., 1999; Sutka et al., 2004]. In the upwelling region, simulated rates of nitrite oxidation display a small local maximum of 1 nM N d\(^{-1}\) in excess of ammonium oxidation rates at the upper and lower boundaries of the oxygen minimum zone.

Cell counts of Planctomycete-like anammox bacteria in have been determined for the Benguela and Peru upwelling systems [Hamersley et al., 2007; Kuypers et al., 2005]. Counts range from 0.4–3 \(\times 10^7\) cells L\(^{-1}\) for the Benguela system and 4–15 \(\times 10^7\) cells L\(^{-1}\) off of Peru. These values bracket the anammox population of 1.8 \(\times 10^7\) cells L\(^{-1}\) simulated for the core of the upwelling zone OMZ. However, the observed cell counts come from shallow water, shelf environments (0–300 m), while the model's OMZ core is located at 625 m. At an open water site off Chile, the maximum rate of anammox was found just below the mixed layer between 50 and 100 m [Thamdrup et al., 2006]. Thus, it is apparent that while the simulated anammox cell abundance is comparable in magnitude to observed values, improved hydrodynamic models of specific upwelling regions may be required to simulate the detailed spatial pattern of observations.

5.5. Integrated Fluxes

A limitation of ocean biogeochemical box models has been their inability to produce realistic globally integrated fluxes of primary production and nutrient cycling. Below, we present results for globally integrated...
values of primary production and nutrient cycling predicted by the model and compare these values with observational constraints. We consider this an important test of the overall behavior and utility of the ICBM.

5.6. Primary Production and Export

Table 3 compares simulated regional and global carbon fluxes to estimates from the literature. Global marine net primary production is simulated at 43.4 Gt C yr\(^{-1}\) and 40.2 Gt C yr\(^{-1}\) for the 13- and 79-box models, respectively. This is slightly lower than the range of estimates in a recent review of global primary production estimates from satellite observations and GCM models, which ranged from 44 to 57 Gt C yr\(^{-1}\) \cite{Carr2006}. Predicted high-latitude primary production is much higher in the low-resolution than in the high-resolution models, 5.7 and 2.4 Gt C yr\(^{-1}\), respectively, but both estimates are within the current range of satellite-based estimates, 1.1–6.1 Gt C yr\(^{-1}\) \cite{Carr2006}. Globally, the estimated export flux of particulate organic carbon is 12.1 and 10.8 Gt C yr\(^{-1}\) for the two models, which is similar to a number of other recent estimates (Table 3). This is a marked improvement over earlier box models which have historically underestimated marine new production by a factor of 2 or more \cite{Archer2000} but is in agreement with more recent box models \cite{Lane2006,Popova2000}. Broken down by region, the model-estimated particle export ratios are 30%, 27%, and 44%, for the high-latitude, gyre, and upwelling regions, respectively, for the low-resolution model, and 10%, 27%, and 42% for the high-resolution model. Low-latitude POC fluxes across 1000 and 2000 m are slightly greater than previous estimates, but the benthic carbon flux and carbon burial flux are well within the range of published estimates (Table 3).

Table 3. Comparison of Simulated and Published Estimates of Global Marine Carbon Fluxes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>13 Box ICBM</th>
<th>79 Box ICBM</th>
<th>Literature Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global net primary production</td>
<td>43.4</td>
<td>40.2</td>
<td>44–57</td>
<td>Carr et al. \cite{2006}, and references therein</td>
</tr>
<tr>
<td>High-latitude net primary production</td>
<td>5.7</td>
<td>2.4</td>
<td>1.1–6.1</td>
<td>Carr et al. \cite{2006}, and references therein</td>
</tr>
<tr>
<td>Global export production</td>
<td>12.1</td>
<td>10.8</td>
<td>9.6 ± 3.6</td>
<td>Dunne et al. \cite{2007}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.1–12.9</td>
<td>Laws et al. \cite{2000}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.2</td>
<td>Aumont et al. \cite{2003}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.6</td>
<td>Heinze et al. \cite{2003}</td>
</tr>
<tr>
<td>Export flux south of 50°S (versus entire ICBM high latitude)</td>
<td>1.7</td>
<td>0.24</td>
<td>0.69 ± 0.26</td>
<td>Dunne et al. [2007]</td>
</tr>
<tr>
<td>-------------------------------------------------------------</td>
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<td>-------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Flux across 1000 m (60°N–60°S versus ICBM gyre)</td>
<td>1.11</td>
<td>1.14</td>
<td>0.63 ± 0.22</td>
<td>Dunne et al. [2007]</td>
</tr>
<tr>
<td>Flux across 2000 m (30°S–47°N versus ICBM gyre)</td>
<td>0.61</td>
<td>0.63</td>
<td>0.20 ± 0.08</td>
<td>Dunne et al. [2007]</td>
</tr>
<tr>
<td>Global flux to bottom</td>
<td>1.82</td>
<td>1.67</td>
<td>2.3 ± 0.9</td>
<td>Dunne et al. [2007]</td>
</tr>
<tr>
<td>Burial in margins (50–2000 m)</td>
<td>0.12</td>
<td>0.12</td>
<td>0.29 ± 0.15</td>
<td>Dunne et al. [2007]</td>
</tr>
</tbody>
</table>

8.7–10.0 Gnanadesikan et al. [2004]
9.6 Schlitzer [2004]
5.8–6.6 Moore et al. [2004]
1.1 ± 0.2 Pollard et al. [2006]
0.86 Jahnke [1996]
0.71–0.86 Gnanadesikan et al. [2004]
0.16 ± 0.11 Ganachaud and Wunsch [2002]
0.22–0.32 Gnanadesikan et al. [2004]
0.93 Muller-Karger et al. [2005]
0.06 ± 0.06 Muller-Karger et al. [2005]
5.7. Nitrogen Fixation, Denitrification, and Anammox

Table 4 compares simulated and published estimates of marine nitrogen fluxes. Nitrogen cycling in the low-resolution model is much more vigorous than in the high-resolution model, though the rate of nitrogen fixation predicted by the two models brackets published estimates. Since both models have been run to steady state, new inputs of nitrogen (nitrogen fixation and allochthonous inputs) exactly balance fixed N losses (benthic denitrification, pelagic denitrification and anammox, and N burial).

Table 4. Comparison of Simulated and Published Estimates of Global Marine Nitrogen Fluxes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>13 Box ICBM</th>
<th>79 Box ICBM</th>
<th>Literature Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pelagic N fixation</td>
<td>146</td>
<td>80</td>
<td>117</td>
<td><em>Codispoti et al</em>. [2001]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>120 ± 50</td>
<td><em>Gruber</em>. [2004]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>138</td>
<td><em>Deutsch et al</em>. [2007]</td>
</tr>
<tr>
<td>Total allochthonous inputs</td>
<td>68</td>
<td>68</td>
<td>41.2</td>
<td><em>Galloway et al</em>. [2004]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(preanthropogenic)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td><em>Brandes and Devol</em>. [2002]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>130 ± 25</td>
<td><em>Gruber</em>. [2004] (modern)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>160</td>
<td><em>Codispoti et al</em>. [2001]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>150</td>
<td>(modern)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>65 ± 20</td>
<td><em>Gruber</em>. [2004]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>70</td>
<td><em>Deutsch et al</em>. [2004]</td>
</tr>
</tbody>
</table>

*Compilation after *Dunne et al*. [2007]. Units are Gt C yr⁻¹ (1 Gt = 10¹⁵ g).
In the low-resolution model, both benthic denitrification and pelagic denitrification/anammox are significantly higher than in the high-resolution model, while N burial remains constant. The increase in pelagic denitrification appears to be entirely due to model resolution. At low resolution, the sharp redox gradients associated with the upwelling oxygen minimum zone are poorly resolved, artificially broadening the suboxic region (Figure 10). The large difference in the rates of benthic denitrification in the high- versus low-resolution model is a consequence of a small 4 Tg yr\(^{-1}\) (5\%) increase of benthic denitrification in the gyre region, apparently due to decreased vertical resolution, and a large increase in high-latitude benthic denitrification, from near 0 Tg yr\(^{-1}\) to 22 Tg yr\(^{-1}\), due to increased high-latitude export production.

In general, the simulated marine nitrogen fluxes are lower than literature estimates, especially for the 79-box model. There are several possible explanations for this. The first possibility is that the steady state simulations described here are discordant with modern estimates because the modern marine nitrogen budget is in severe deficit [Codispoti et al., 2001; Codispoti, 2007]. A second possibility is that there is still sufficient uncertainty in the global flux estimates to allow agreement between the model and observational estimates. Altabet [2007] has recently argued that estimates of benthic denitrification determined from \(\delta^{15}\)N budgeting approaches may be overestimated by a factor of 2 due to uncertainty in the apparent fractionation factor resulting from reaction transport in denitrifying oxygen minimum zones. On the

<table>
<thead>
<tr>
<th>% anammox of total pelagic fixed N loss</th>
<th>13%</th>
<th>21%</th>
<th>29%</th>
<th>Dalsgaard et al. [2003]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>19%–35%</td>
<td>Dalsgaard et al. [2003] (Gulfo Dulce)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100%</td>
<td>Hamersley et al. [2007] (Peru Margin)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100%</td>
<td>Kuypers et al. [2005] (Benguela Margin)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Benthic denitrification</th>
<th>115</th>
<th>88</th>
<th>300</th>
<th>Codispoti et al. [2001]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>180 ± 50</td>
<td>Gruber [2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>Deutsch et al. [2004]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Burial</th>
<th>24</th>
<th>24</th>
<th>15</th>
<th>Codispoti et al. [2001]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 ± 10</td>
<td>Gruber [2004]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Units are Tg N yr\(^{-1}\) (1 Tg = 10\(^{12}\) g).
other hand, recent observations of excess N\(_2\) in the Arabian Sea suggest high rates of pelagic denitrification/anammox totaling 41 ± 18 Tg N yr\(^{-1}\) for this region alone [Devol et al., 2006], providing a counterexample in support of higher N fluxes. Finally, the model itself may simply underestimate modern fluxes. However, the uncertainty for observational estimates will need to improve significantly before it is clear which of these hypotheses is correct and how to adjust the model, if necessary.

5.8. Phosphorus Cycling

Table 5 compares the ICBM marine phosphorus cycle with data from several recent reviews of global phosphorus cycling. Unfortunately, literature estimates of preanthropogenic inputs and burial vary widely from 3 to 21 × 10\(^{10}\) mol P yr\(^{-1}\). Thus, at present it seems impossible to constrain the marine phosphorus cycle precisely. Nevertheless, the ICBM models are able to reproduce the observed deep water phosphate concentration and global primary production while employing realistic particle export, remineralization, sedimentation, and burial parameterizations, using a riverine reactive phosphorus input of 15 × 10\(^{10}\) mol P yr\(^{-1}\). This value is well within the range of global reactive phosphorus input and burial estimates.

Table 5. Comparison of Simulated and Published Estimates of Global Marine Phosphorus Fluxes\(^a\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>13 Box ICBM</th>
<th>79 Box ICBM</th>
<th>Literature Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total preanthropogenic</td>
<td>15</td>
<td>15</td>
<td>3.8–7.2</td>
<td>Paytan and McLaughlin [2007] (^b)</td>
</tr>
<tr>
<td>Reactive P inputs</td>
<td></td>
<td></td>
<td>10–15.5</td>
<td>Compton et al. [2000]</td>
</tr>
<tr>
<td>(Riverine + Aeolian)</td>
<td></td>
<td></td>
<td>18.4</td>
<td>Follmi [1996]</td>
</tr>
<tr>
<td>Total anthropogenic</td>
<td>0</td>
<td>0</td>
<td>0.8–3.8</td>
<td>Paytan and McLaughlin [2007] (^b)</td>
</tr>
<tr>
<td>Reactive P inputs</td>
<td></td>
<td></td>
<td>1–17</td>
<td>Compton et al. [2000]</td>
</tr>
<tr>
<td>Total reactive P burial</td>
<td>15</td>
<td>15</td>
<td>3.2–8.1</td>
<td>Compton et al. [2000]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>21</td>
<td>Filippelli and Delaney [1996]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.4</td>
<td>Berner and Berner [1996]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15.2</td>
<td>Follmi [1996]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8–18.5</td>
<td>Ruttenberg [1993]</td>
</tr>
</tbody>
</table>
P removal at mid-ocean ridges  0  0  1.2–1.6  Froelich et al. [1982]

| 5 |  
|---|---|

a Units are $10^{10}$ mol P yr$^{-1}$.

b Assumes 10%–30% of total riverine P is reactive and 25% of reactive P is exported from estuaries.

5.9. Sensitivity Testing

The global ICBM model displays several advantages over previous generations of ocean box models. The model is able to simultaneously reproduce observed high-latitude and gyre temperature, background $\Delta^{14}$C, bomb $\Delta^{14}$C, and CFC-11 profiles, which was not previously possible using the HILDA model [Siegenthaler and Joos, 1992]. The combination of both explicit high-latitude ventilation of the deep ocean and parameterized isopycnal ventilation of the gyre thermocline (Figure 3) is essential for simultaneously simulating the distribution of these tracers.

An early generation of three- or four-box ocean models [Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984] was excessively sensitive to high-latitude nutrient drawdown and resulted in predictions of extensive anoxia of the deep ocean at odds with observations [Sarmiento et al., 1988; Sarmiento and Orr, 1991]. We duplicated those experiments using the ICBM model to show that high-latitude nutrient drawdown in the ICBM more closely resembles the results of GCM experiments than three-box models. Specifically, sudden release of the phosphate drawn-down limitation in the global ICBM high-latitude surface reservoir results in a small region of anoxia in the high-latitude water column at approximately 500 m depth but has only a small impact on gyre oxygen profiles (Figure 12). At the deepest gyre depths, where the oxygen perturbation is largest, the ICBM simulates a 130 $\mu$M decrease in dissolved oxygen which compares to a decrease of 100–125 $\mu$M found by Sarmiento and Orr [1991] using a 3-D GCM model. Simulations with the simplified 13-box global ICBM model display similar results.
Figure 12.

Open in figure viewer

Perturbations to ICBM-simulated dissolved oxygen profiles as a result of high-latitude nutrient drawdown for the 13-box model (red lines) and 79-box model (black lines). Profiles at t = 0 are the steady state results of previous standard simulations. At t = 0, the restriction on high-latitude nutrient drawdown is removed (previously set at 1.5 \( \mu \text{M PO}_4^{3-} \)). (a–d) The release of nutrient limitation allows for a rapid increase in high-latitude export production and onset of high-latitude suboxia occurs within 100 years. (e–h) However, gyre profiles are only modestly perturbed. These results are similar to those found by previous workers using an early 3-D OGCM model \[\text{Sarmiento and Orr, 1991}\] and differ from early three-box models of ocean biogeochemistry which predicted complete anoxia of the deep ocean.
6. Discussion and Conclusions

We have presented an integrated intermediate-complexity box model (ICBM) designed to simulate the coupled CNPOS cycles in the oceans. The model includes a number of novel features that address known deficiencies in box models yet remains computationally efficient. In particular, the ICBM shows improved performance in simulating modern circulation tracer fields through a combination of improved representation of high-latitude ventilation and midlatitude thermocline ventilation. Both vertical profiles of biogeochemically relevant species and integrated biogeochemical fluxes are in satisfactory agreement with data and estimates from the modern ocean. We consider the ability to produce realistic integrated fluxes an important test of the model dynamics. It is possible to produce reasonable depth profiles of the major species while failing to produce accurate fluxes if the representation of water mass exchange is inadequate.

The ICBM biogeochemical model incorporates several important features for the simulation of deep time marine biogeochemistry. In particular, the addition of explicit, oxygen-dependent nitrogen cycling (including, nitrogen fixation, ammonium oxidation, nitrite oxidation, pelagic denitrification and anammox, and sedimentary denitrification) was designed to allow simulation of changes in the marine nitrogen cycle in response to variations in ocean redox. This work complements previous models of nitrogen and phosphorus cycling [Bjerrum et al., 2006; Deutsch et al., 2004; Handoh and Lenton, 2003; Lenton and Watson, 2000; Lenton and Klausmeier, 2007; Shaffer, 1989; Slomp and Van Cappellen, 2007; Tyrrell, 1999; Van Cappellen and Ingall, 1994; Wallmann, 2003] by simulating the role of oxygen, deepwater ventilation, and upwelling processes in controlling feedbacks on marine nitrogen cycling. The ICBM model also provides a framework suitable for the future incorporation of carbonate cycling, as well as carbon and sulfur isotopes as implemented in previous studies [e.g., Canfield et al., 2000; Donnadieu et al., 2006; Godderis and Joachimski, 2004].

The ICBM was developed with the goal of simulating scenarios relevant to deep time paleoceanography and biogeochemistry. Consequently, we chose to develop a model with simple boundary conditions that do not depend heavily on the details of past configurations of the ocean basins or continents. This is not to say that the model will be readily applicable to all possible past configurations, but we believe the basic architecture can be modified to suit a variety of plausible cases. Here we have presented results that show the model performs well when simulating modern marine biogeochemical processes. However, we have had data from multiple tracers (θ, 14C, CFCs, σθ) with which to validate the “circulation” submodel. While these data do not drive the model, they provided a target to which we could adjust water mass exchange parameters until the modeled tracer distributions agreed reasonably well with the tracer field data. In this way we could then test the biogeochemical submodel while having confidence that the water mass exchange fluxes were indeed appropriate, and so focus on the performance of the biogeochemical submodel. For application to some deep time questions, the dynamic fields from GCM models could be used when available to guide parameterization of the ICBM circulation fluxes. However, paleogeography is not well constrained over much of the early Proterozoic, restricting the use of GCM models. In this case, it may be necessary to test directly the impact of different hypothetical circulation models for a given scenario in deep time.

In a companion paper [Romaniello and Derry, 2010], we have used the ICBM to simulate biogeochemical
fluxes in the modern Black Sea. This necessitated reconfiguring the water exchange fluxes substantially to reasonably represent the circulation of the Black Sea, which differs considerably from the open ocean. However, once coupled to an applicable circulation model, the same biogeochemical model described here was used to obtain realistic results for both the profiles and integrated fluxes of important biogeochemical components. The model's current structure is able to represent both oxic and anoxic processes and compute reasonable fluxes across the oxic-anoxic interface in the modern Black Sea. We believe that this inherent flexibility will be of great value in investigating a range of deep time scenarios, such as those associate with ocean anoxic events or lower levels of atmospheric oxygen.

To facilitate further use and development of the model, we have made the model source code available as MATLAB™ 7 m-files provided as auxiliary material. The model architecture permits modification of a number of important processes that may be relevant to certain deep time problems. For example, it is possible to modify or generalize the Redfield ratio as long as redox balance is maintained in the relevant biogeochemical processes, thus the model could be used to explore the impact of biological stoichiometry significantly different from the classical Redfield ratios. Similarly, the functional dependence of export production on primary production or the depth-dependent attenuation of the particle export flux could be modified to test the impact of possible functional differences in ocean ecosystems and POC export fluxes. Many other changes are possible. The MATLAB code is written in a modular way to permit modification or addition of new biogeochemical pathways without requiring modification of the remaining code. The biogeochemical code is separate from the transport fluxes, so that they can be modified independently. Workers in the field may find the model useful in essentially its present form, or wish to modify, improve or extend the representation of key biogeochemical processes in order to test novel ideas about the function of the ancient oceans. We welcome exploration with and extension of the ICBM from the community of deep time researchers.

Appendix A

Table A1 provides default values, units, and the source (where applicable) for each of the parameters in the ICBM biogeochemistry model.

Table A1. ICBM Biogeochemistry Default Parameter Values

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{PP}$</td>
<td>conventional phytoplankton growth rate</td>
<td>yr$^{-1}$</td>
<td>91.25</td>
<td>Tyrrell [1999]</td>
</tr>
<tr>
<td>$\mu_{NF}$</td>
<td>diazotroph growth rate</td>
<td>yr$^{-1}$</td>
<td>87.6</td>
<td>Tyrrell [1999]</td>
</tr>
<tr>
<td>$M$</td>
<td>phytoplankton and diazotroph mortality rate</td>
<td>yr$^{-1}$</td>
<td>73</td>
<td>Tyrrell [1999]</td>
</tr>
<tr>
<td>( K_p )</td>
<td>phosphate half-saturation constant</td>
<td>( \mu M )</td>
<td>0.03</td>
<td>Tyrrell [1999]</td>
</tr>
<tr>
<td>( K_{\text{NOx}} )</td>
<td>nitrate+nitrite half-saturation constant</td>
<td>( \mu M )</td>
<td>0.75</td>
<td>Gruber et al. [2006]</td>
</tr>
<tr>
<td>( K_{\text{Nired}} )</td>
<td>ammonium half-saturation constant</td>
<td>( \mu M )</td>
<td>0.50</td>
<td>Gruber et al. [2006]</td>
</tr>
<tr>
<td>( PO_4^{3-}_{\text{min}} )</td>
<td>high-latitude limit on phosphate drawdown</td>
<td>( \mu M )</td>
<td>1.5</td>
<td>this work</td>
</tr>
</tbody>
</table>

### Heterotrophic Remineralization

\[
\mu_{\text{max}, O_2} \quad \text{heterotroph max. growth rate using oxygen} \quad \text{yr}^{-1} \quad 1840 \quad \text{fit to data of Bendtsen et al. [2002, Table 1]}
\]

\[
\mu_{\text{max}, NO_3^-} \quad \text{heterotroph max. growth rate using nitrate} \quad \text{yr}^{-1} \quad 450 \quad \text{scaled from } O_2 \text{ growth rate following Kornaros and Lyberatos [1998]}
\]

\[
\mu_{\text{max}, NO_2^-} \quad \text{heterotroph max. growth rate using nitrite} \quad \text{yr}^{-1} \quad 450 \quad \text{scaled from } O_2 \text{ growth rate following Kornaros and Lyberatos [1998]}
\]

\[
\mu_{\text{max}, SO_4^{2-}} \quad \text{heterotroph max. growth rate using sulfate} \quad \text{yr}^{-1} \quad 450 \quad \text{same as nitrite reduction}
\]

\[
K_{S,O_2} \quad \text{heterotroph LDOC half-saturation using oxygen} \quad \mu M \quad 45 \quad \text{fit to data of Bendtsen et al. [2002, Table 1]}
\]

\[
K_{S,NO_3^-} \quad \text{heterotroph LDOC half-saturation using nitrate} \quad \mu M \quad 250 \quad \text{scaled from } O_2 \text{ rate following Kornaros and Lyberatos [1998]}
\]

\[
K_{S,NO_2^-} \quad \text{heterotroph LDOC half-saturation using nitrite} \quad \mu M \quad 185 \quad \text{scaled from } O_2 \text{ substrate saturation constant following Kornaros and Lyberatos [1998]}
\]

\[
K_{S,SO_4^{2-}} \quad \text{heterotroph LDOC half-saturation using sulfate} \quad \mu M \quad \text{same as nitrite reduction}
\]

\[
K_{O_2} \quad \text{heterotroph oxygen half-saturation constant} \quad \mu M \quad 2.0 \quad –
\]

\[
K_{NO_3^-} \quad \text{heterotroph nitrate half-saturation constant} \quad \mu M \quad 10.0 \quad –
\]
<table>
<thead>
<tr>
<th></th>
<th>Unit</th>
<th>Value</th>
<th>Notes</th>
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</thead>
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<tr>
<td>$K_{NO_2^-}$</td>
<td>µM</td>
<td>2.75</td>
<td>heterotroph nitrite half-saturation constant</td>
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<tr>
<td>$K_{I_2,O_2}$</td>
<td>µM</td>
<td>20</td>
<td>heterotroph oxygen inhibition constant using nitrite</td>
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<td>$K_{I_2,NO_2^-}$</td>
<td>µM</td>
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<td>heterotroph nitrate inhibition constant using nitrite</td>
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<td>$K_{SO_4^{2-}}$</td>
<td>µM</td>
<td>625</td>
<td>heterotroph nitrate inhibition constant using sulfate</td>
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<td>$K_{I_3,O_2}$</td>
<td>µM</td>
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<tr>
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<td>µM</td>
<td>10</td>
<td>heterotroph nitrate inhibition constant using sulfate</td>
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<tr>
<td>$K_{I_3,NO_2^-}$</td>
<td>µM</td>
<td>20</td>
<td>heterotroph nitrite inhibition constant using sulfate</td>
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**Nitrification**

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<tr>
<td>$\mu_{AOB}$</td>
<td>yr^-1</td>
<td>350</td>
<td>Ammonium oxidizer maximum growth rate</td>
</tr>
<tr>
<td>$\mu_{NOB}$</td>
<td>yr^-1</td>
<td>350</td>
<td>Nitrite oxidizer maximum growth rate</td>
</tr>
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<td>$K_{AOB}^{O_2}$</td>
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<td>23</td>
<td>Ammonium oxidizer oxygen half-saturation constant</td>
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<tr>
<td>$K_{NOB}^{O_2}$</td>
<td>µM</td>
<td>55</td>
<td>Nitrite oxidizer oxygen half-saturation constant</td>
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<tr>
<td>$K_{AOB}^{NH_4}$</td>
<td>µM</td>
<td>0.15</td>
<td>Ammonium oxidizer ammonium half-saturation constant</td>
</tr>
</tbody>
</table>

*Ingvorsen and Jorgensen [1984]*

*Hashimoto et al. [1983]* and *Jetten et al. [2001]*

*same as ammonium oxidation [Prosser, 1989]*

*Guisasola et al. [2005]*

*Hashimoto et al. [1983]*
### An intermediate-complexity model for simulating marine biogeochemistry

<table>
<thead>
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<th>Unit</th>
<th>Value</th>
<th>Reference</th>
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</thead>
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<tr>
<td>$K_{NO_2}$</td>
<td>nitrite oxidizer nitrite half saturation constant</td>
<td>$\mu$M</td>
<td>0.07</td>
<td>Olson [1981a]</td>
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### Anammox

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<td>$\mu_{AMX}$</td>
<td>anammox maximum growth rate</td>
<td>yr$^{-1}$</td>
<td>26</td>
<td>Jetten et al. [2001]</td>
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<tr>
<td>$K_{NH_4}$</td>
<td>anammox ammonium half saturation constant</td>
<td>$\mu$M</td>
<td>5</td>
<td>Jetten et al. [2001]</td>
</tr>
<tr>
<td>$K_{NO_2}$</td>
<td>anammox nitrite half saturation constant</td>
<td>$\mu$M</td>
<td>3</td>
<td>Dalsgaard et al. [2005]</td>
</tr>
<tr>
<td>$K_{O_2}$</td>
<td>anammox oxygen inhibition constant</td>
<td>$\mu$M</td>
<td>0.05</td>
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</table>

### Microbial Mortality

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<th>Unit</th>
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<th>Reference</th>
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<tr>
<td>A</td>
<td>mortality scaling coefficient</td>
<td>$(10^9 \text{ cells L}^{-1})^{1-b} \text{ yr}^{-1}$</td>
<td>13.45</td>
<td>this work</td>
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<tr>
<td>B</td>
<td>mortality power coefficient</td>
<td>unitless</td>
<td>1.71</td>
<td>this work</td>
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### Sulfide Oxidation

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<th>Reference</th>
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<tr>
<td>$K_{NO_3}$</td>
<td>inorganic sulfide oxidation rate</td>
<td>$\mu$M$^{-1}$yr$^{-1}$</td>
<td>54</td>
<td>Millero [1991]</td>
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### Sediment Model

<table>
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<th>Unit</th>
<th>Value</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>$C/N_{Burial}$</td>
<td>C:N burial ratio of organic matter</td>
<td>Ratio</td>
<td>10</td>
<td>Hedges et al. [1999]</td>
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<tr>
<td>$K_{O_2}$</td>
<td>sediment nitrification switchpoint</td>
<td>$\mu$M</td>
<td>25</td>
<td>fit to results of Middelburg et al. [1996]</td>
</tr>
<tr>
<td>$k_{O_2}$</td>
<td>sediment nitrification</td>
<td>$\mu$ M O$_2$ ( $\mu$ mol</td>
<td>400</td>
<td>fit to results of Middelburg et al.</td>
</tr>
</tbody>
</table>
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[Table]

<table>
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<th>Unit</th>
<th>Value</th>
<th>Source</th>
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<tbody>
<tr>
<td>$K_{NO_3}$</td>
<td>Nitrate diffusion switchpoint</td>
<td>µ M</td>
<td>25</td>
<td>fit to results of Middelburg et al. [1996]</td>
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<tr>
<td>$k_{NO_3}$</td>
<td>Nitrate diffusion coefficient</td>
<td>µ M NO$_3$</td>
<td>10</td>
<td>fit to results of Middelburg et al. [1996]</td>
</tr>
<tr>
<td>$(C_{Org}/P_{Reac})_{Burial}^{Oxic}$</td>
<td>C:P burial ratio of organic matter under oxic conditions</td>
<td>ratio</td>
<td>48.5</td>
<td>Anderson et al. [2001]</td>
</tr>
<tr>
<td>$(C_{Org}/P_{Reac})_{Burial}^{Anox}$</td>
<td>C:P burial ratio of organic matter under anoxic conditions</td>
<td>ratio</td>
<td>472</td>
<td>Anderson et al. [2001]</td>
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<tr>
<td>$K_{PBE}$</td>
<td>C:P oxic/anoxic switchpoint</td>
<td>µ M</td>
<td>10</td>
<td>–</td>
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**Supporting Information**

**References**

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