Simulating the global distribution of nitrogen isotopes in the ocean

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We present a new nitrogen isotope model incorporated into the three-dimensional ocean component of a global Earth system climate model designed for millennial timescale simulations. The model includes prognostic tracers for the two stable nitrogen isotopes, $^{14}$N and $^{15}$N, in the nitrate ($\text{NO}_3^-$), phytoplankton, zooplankton, and detritus variables of the marine ecosystem model. The isotope effects of algal $\text{NO}_3^-$ uptake, nitrogen fixation, water column denitrification, and zooplankton excretion are considered as well as the removal of $\text{NO}_3^-$ by sedimentary denitrification. A global database of $\delta^{15}\text{NO}_3^-$ observations is compiled from previous studies and compared to the model results on a regional basis where sufficient observations exist. The model is able to qualitatively and quantitatively reproduce many of the observed patterns such as high subsurface values in water column denitrification zones and the meridional and vertical gradients in the Southern Ocean. The observed pronounced subsurface minimum in the Atlantic is underestimated by the model presumably owing to too little simulated nitrogen fixation there. Sensitivity experiments reveal that algal $\text{NO}_3^-$ uptake, nitrogen fixation, and water column denitrification have the strongest effects on the simulated distribution of nitrogen isotopes, whereas the effect from zooplankton excretion is weaker. Both water column and sedimentary denitrification also have important indirect effects on the nitrogen isotope distribution by reducing the fixed nitrogen inventory, which creates an ecological niche for nitrogen fixers and, thus, stimulates additional $\text{N}_2$ fixation quantitatively in a global budget. The size of the oceanic fixed $\text{N}$ inventory, which is an indicator of those processes [Brandes and Devol, 2002; Deutsch et al., 2004; Altabet, 2007]. Nitrogen isotopes (both in dissolved and organic $\text{N}$ species) in the water column and seafloor sediments are sensitive indicators of those processes [Brandes and Devol, 2002; Deutsch et al., 2004; Altabet, 2007].

1. Introduction

Bioavailable nitrogen (fixed $\text{N}$) is one of the major limiting nutrients for algal photosynthesis, which drives the sequestration of CO$_2$ from the surface ocean and atmosphere into the deep ocean via the sinking of organic matter. Changes in this so-called "biological pump" have been hypothesized to account for a significant amount of the glacial-interglacial fluctuations in atmospheric CO$_2$ [McElroy, 1983; Falkowski, 1997]. However, the relative contributions of the biological and physical carbon pumps to CO$_2$ variations remain controversial. The size of the oceanic fixed $\text{N}$ inventory, which regulates the strength of the biological pump, is controlled by different biogeochemical processes that are difficult to constrain quantitatively in a global budget [Codispoti, 2007]. Nitrogen isotopes (both in dissolved and organic $\text{N}$ species) in the water column and seafloor sediments are sensitive indicators of those processes [Brandes and Devol, 2002; Deutsch et al., 2004; Altabet, 2007].

Many $\text{N}$ transformational processes alter the ratio of the two stable forms of the nitrogen isotopes, $^{14}\text{N}$ and $^{15}\text{N}$, differently, a process referred to as fractionation. Resulting variations in $\text{N}$ isotopic composition can be described as deviations in $^{15}\text{N}/^{14}\text{N}$ ratio from an accepted standard

$$\delta^{15}\text{N} = \left(\frac{^{15}\text{N}/^{14}\text{N}}{^{15}\text{N}_\text{std}/^{14}\text{N}_\text{std}} - 1\right) \times 1000, \quad (1)$$

where $R_{\text{std}}$ is the $^{15}\text{N}/^{14}\text{N}$ ratio of atmospheric $\text{N}_2$ gas. Isotope fractionation can occur due to kinetic processes (i.e.,
different reaction rates for isotopes in a reactant product stream). It generally results in the enrichment of the heavier 15N isotope in the reaction substrate, and its depletion in the 14N product. For example, preferential discrimination against 15N relative to 14N during algal NO3 assimilation results in net enrichment of 15N in the residual NO3 and net depletion of 15N in organic matter (OM). The degree of isotopic discrimination, or fractionation, for each process can be quantified with an enrichment factor, ε = (14k/15k − 1) × 1000, where k is the specific reaction rate for each isotope [Mariotti et al., 1981].

{[The predominant source and sink terms of the oceanic fixed N inventory, N2 fixation and denitrification, respectively, have their own distinct effects on the signature of the N isotopes in the ocean. N2 fixing prokaryotes (diazotrophs) introduce bioavailable N into the ocean close to that of atmospheric N2 (δ15N N ≈ −2−0‰) [Delwiche and Steyn, 1970; Minagawa and Wada, 1986; Macko et al., 1987; Carpenter et al., 1997]. Trichodesmium, one of the most important and best studied diazotrophs, bloom more frequently and extensively in warm (>25°C) surface water where rates of aeolian Fe deposition are high such as the North Atlantic, Indian, and North Pacific compared to areas of low Fe deposition such as the South Pacific where the abundance of Trichodesmium is assumed to be much lower [Karl et al., 2002; Carpenter and Capone, 2008]. However, other unicellular diazotrophs have been observed to grow in cooler water near 20°C [Needoba et al., 2007], and it has been suggested that they also may significantly contribute to the global N2 fixation rate [Zehr et al., 2001; Montoya et al., 2004].

Denitrification occurs under suboxic conditions (O2 < 5 µmol/kg) in the water column and in the seafloor sediments. Here, microbes use NO3 instead of O2 as the electron acceptor during respiration and convert it into gaseous forms of N (N2O and N2), which can then escape to the atmosphere [Codispoti and Richards, 1976]. The volume and distribution of suboxic water is affected by the temperature-dependent solubility of O2 at the surface and the rate of subduction of oxygen-saturated water masses to greater depths, as well as the amount of organic matter that remineralizes in the ocean interior, both of which are sensitive to changes in climate. Anammox is another important process that occurs in anaerobic conditions and eliminates forms of fixed N (NO3, NH4) in the water column by converting them into N2 gas [Mulder et al., 1995; Thamdrup and Dalsgaard, 2002; Kuypers et al., 2003]. It has been suggested that anammox may even eliminate more fixed N than water column denitrification in some oxygen minimum zones [Kuypers et al., 2005; Lam et al., 2009], but just how important of a role anammox plays in the global fixed N inventory has yet to be determined.

Denitrifiers preferentially consume 14NO3 leaving the residual oceanic NO3 pool strongly enriched in the heavier 15N, with N isotope enrichment factors between 20–30‰ [Cline and Kaplan, 1975; Liu and Kaplan, 1989; Brandes et al., 1998; Altabet et al., 1999b; Voss et al., 2001]. Sedimentary denitrification is generally limited by the amount of NO3 that diffuses into the reactive zones within the sediments. Therefore, it consumes nearly all of the influxing NO3 available, leaving nearly unaltered δ15N values in the overlying waters [Brandes and Devol, 1997, 2002; Sigman et al., 2003; Lehmann et al., 2004, 2007]. The average oceanic δ15NO3 value near 5‰ [Sigman et al., 1997, 1999] can be interpreted as the balance between the isotope effects of water column denitrification, sedimentary denitrification, and N2 fixation [Brandes and Devol, 2002; Deutsch et al., 2004; Galbraith et al., 2004; Altabet et al., 2007].

The δ15N signal in the water column and seafloor sediments is also affected by fractionation processes within the food chain. Marine algae preferentially assimilate the lighter 14N into their biomass with a range of enrichment factors estimated in the field between 4–15‰ [Wada, 1980; Altabet et al., 1991, 1999b; Sigman et al., 1999; Altabet and Francois, 2001; Karsh et al., 2003; DiFiore et al., 2006]. Nitrogen is not lost or gained from the ocean during algal NO3 assimilation, but the spatial separation between net assimilation and remineralization can cause a trend of decreasing δ15NO3 with depth. Distinguishing between the different isotope effects remains a challenge, especially in regions where multiple N transformational processes are occurring within close proximity.

This study, for the first time to our knowledge, includes a dynamic nitrogen isotope module embedded within an existing global ocean-atmosphere–sea ice-biogeochemical model. This allows a direct comparison with nitrogen isotope observations, whereas previous box model studies could only be used more qualitatively [Giraud et al., 2003; Deutsch et al., 2004]. We provide a detailed description of the nitrogen isotope model and an assessment of its skill in reproducing present-day δ15NO3 observations. Comparison of model results with δ15N observations will also be used to help to quantify processes that affect the global oceanic distribution of δ15N. Sensitivity experiments illustrate the individual isotope effects of different processes on the spatial distribution of the N isotopes. In combination with measurements in ocean sediments and in the water column, the model can be a tool to better understand variations of δ15N and the nitrogen cycle in the past and present.

2. Model Description

2.1. Physical Model

The physical model is based on the University of Victoria Earth system climate model [Weaver et al., 2001], version 2.8. It includes a global, three-dimensional general circulation model of the ocean (Modular Ocean Model 2) with physical parameterizations such as diffusive mixing along and across isopycnals, eddy induced tracer advection [Gent and McWilliams, 1990] and a scheme for the computation of tidally induced diapycnal mixing over rough topography [Simmons et al., 2004]. Nineteen vertical levels are used with a horizontal resolution of 1.8° × 3.6°. To improve the simulation of equatorial currents, we have increased the meridional resolution in the tropics to 0.9° (between 10°S and 10°N and smoothly transitioning to 1.8° at 20°N/S) and added an anisotropic viscosity scheme [Large et al., 2001]. A more detailed description of this..
parameterization and its effect on the equatorial circulation is provided in Text S1 of the auxiliary material. To account for the overestimated ventilation in the North Pacific, an artificial stratifying force equal to 0.04 Sv of freshwater is applied over the surface north of 55° in the Pacific and compensated elsewhere. A two dimensional, single level energy-moisture balance model of the atmosphere and a state-of-the-art dynamic-thermodynamic sea ice model are used, forced with prescribed NCEP/NCAR monthly climatological winds.

2.2. Marine Ecosystem Model

[10] The marine ecosystem model is an improved version of the NPZD (Nutrient, Phytoplankton, Zooplankton, Detritus) ecosystem model of [Schmittner et al., 2008] (Figure 1). The organic variables include two classes of phytoplankton, N₂ fixing diazotrophs (P_D) and a “general” NO₃ assimilating phytoplankton class (P_G), as well as zooplankton (Z) and organic detritus (D). The inorganic variables include dissolved oxygen (O₂) and two nutrients, nitrate (NO₃⁻) and phosphate (PO₄³⁻), both of which are consumed by phytoplankton and remineralized in fixed elemental ratios (R_N:P = 16, R_O:P = 170). We note, though, that...

Figure 1. Schematic of the marine ecosystem model with the nitrogen isotope model parameters in color.
that most diazotrophs have been found to have a $R_{\text{N}:P}$ of 50:1 and sometimes higher [e.g., Letelier and Karl, 1996]. This simplification is one of the reasons why the nitrogen surplus $N' = N_{\text{NO3}} - 16 N_{\text{PO4}}$ is generally underestimated in surface waters in the model (Figure S3). In addition to water column denitrification and N$_2$ fixation, we now include a parameterization for sedimentary denitrification (see auxiliary material equation (S11) and Figure 2), based on the flux of organic carbon into the seafloor sediments [Middelburg et al., 1996]. Since the model underestimates coastal upwelling, which drives large fluxes of organic carbon to the seafloor sediments, this parameterization is tuned to fit the global mean $\delta^{15}$NO$_3^{-}$ of 5‰ by multiplying the sedimentary denitrification equation by a constant factor ($\alpha_{\text{SD}} = 6.5$). Global rates of model N$_2$ fixation, water column denitrification, and sedimentary denitrification are 102, 78.0, and 25.4 Tg N yr$^{-1}$, respectively.

The relatively low model sedimentary to water column denitrification ratio of $\sim$1:3 compared to other estimates from one-box models ranging from $\sim$1:1 [Altabet, 2007] to 4:1 [Brandes and Devol, 2002] is mostly due to the “dilution effect” [Deutsch et al., 2004], which reduces the effective fractionation effect of water column denitrification as NO$_3$ is locally consumed, an effect not incorporated in one-box models. This results in a lower sedimentary to water column denitrification ratio needed to set the global mean $\delta^{15}$NO$_3^{-}$ to 5‰ (see section 4.2 for further discussion). The complete marine ecosystem model description is provided in Text S2 of the auxiliary material. A comparison of the global distribution of NO$_3$, O$_2$, and N’ with World Ocean Atlas 2005 (WOA05) observations is shown in Figure S3.

Suboxic water, where water column denitrification occurs, is present in three main locations of the present-day oceans: the Eastern Tropical North Pacific (ETNP), the Eastern Tropical South Pacific (ETSP) and the Arabian Sea (Figure S3). Deficiencies in the physical circulation model simulate suboxic water in only one of these locations, the ETNP. The physical circulation model integrates coastal upwelling over a horizontal extent that is too large (due to its coarse resolution), which results in the underestimation of upwelling, export production, and the remineralization of organic matter at depth. This bias leads to too high O$_2$ concentrations, larger than required for water column denitrification, in the ETSP and the Arabian Sea. Suboxia in the so-called “shadow zone” of the ETNP is simulated better and investigated more in section 4.2. In the model, some water column denitrification also occurs in the Bay of Bengal and off SW Africa (Figure 2c), which has not been observed in the real ocean. However, the anammox reaction,
Table 1. Nitrogen Isotope Model Enrichment Factors

<table>
<thead>
<tr>
<th>Process</th>
<th>Symbol</th>
<th>Model Enrichment Factor (%)</th>
<th>Field Estimates (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algal NO₃ assimilation</td>
<td>εₓₓₓₓₓ</td>
<td>5</td>
<td>4–15</td>
</tr>
<tr>
<td>N₂ fixation</td>
<td>εₓₓₓₓₓ</td>
<td>1.5</td>
<td>0–2</td>
</tr>
<tr>
<td>Excretion</td>
<td>εₓₓₓₓₓ</td>
<td>6</td>
<td>3–6</td>
</tr>
<tr>
<td>Water column denitrification</td>
<td>εₓₓₓₓₓ</td>
<td>25</td>
<td>22–30</td>
</tr>
<tr>
<td>Sedimentary denitrification</td>
<td>εₓₓₓₓₓ</td>
<td>0</td>
<td>0–4</td>
</tr>
</tbody>
</table>

*See Appendix A for references.

245 which also eliminates fixed N in the water column, has been found to occur off SW Africa [Kuypers et al., 2005]. Naqvi [2008] measured low decomposition rates in the Bay of Bengal. Effective ballasting and scavenging of organic matter by the massive riverine input of terrestrial matter, an effect not included in the model, may prevent water column denitrification in the Bay of Bengal, which is close to suboxic.

253 [12] Diazotrophs grow according to the same principles as algal phytoplankton in the model (see Text S2), but we also account for some of their different characteristics. N₂ fixation breaks down the three N bond of N₂, which is energetically more costly than assimilating fixed N [Holl 2585 and Montoya, 2005]. Therefore, in the model, the growth rate of diazotrophs is lower than that of general phytoplankton. It is zero in waters cooler than 15°C and increases 50% slower with temperature than the growth rate of general phytoplankton. Diazotrophs are not limited by NO₃ and will thrive in waters that are N deficient (i.e., low N' as a result of denitrification) in which sufficient P and Fe are available.

265 Denitrification and the propagation of N-deficient waters into the shallow thermocline by physical transport processes create an ecological niche for diazotrophs in the model, which stimulates N₂ fixation [Tyrrell, 1999].

269 [13] One of the most important and best-studied diazotrophs, Trichodesmium, also has large iron (Fe) requirements for growth [Sañudo-Wilhelmy et al., 2001].

272 Diazotrophs may depend on aeolian Fe in oligotrophic waters because deep pycnocline inhibits upward mixing of subsurface Fe-replete waters into the euphotic zone [Falkowski, 1997; Karl et al., 2002]. Therefore, their growth rate is further reduced according to the Fe Limitation parameter (Figure 2a), where an estimate of aeolian dust deposition [Mahowald et al., 2005] is scaled between 0–1 by multiplying it by a constant factor and setting the maximum value to 1. This is a simple parameterization of Fe limitation of diazotrophy and its full effects are described elsewhere [Somes, 2010]. The majority of N₂ fixation in the model occurs in oligotrophic waters “downstream” of denitrification zones where sufficient Fe exists (i.e., via aeolian Fe deposition) (Figure 2b). The pattern of N₂ fixation (such as high values in the tropical/subtropical North Pacific, the western tropical/subtropical South Pacific, the western tropical/subtropical South Atlantic, the tropical/subtropical North Atlantic and the Indian Ocean) is mostly consistent with direct observations [e.g., Karl et al., 2002; Carpenter and Capone, 2008], with estimates based on the 292 observed NO₃ deficit and simulated circulation [Deutsch et al., 2007], as well as with results from a more complex ecosystem model [Moore and Doney, 2007]. However, N₂ fixation in our model does not extend northward of 25–30°N in the North Pacific and North Atlantic, whereas some observations show N₂ fixation as far north as 35–40°N [Church et al., 2008; Kitajima et al., 2009].

290 2.3. Nitrogen Isotope Model

[14] The nitrogen isotope model simulates the distribution of the two stable nitrogen isotopes, ¹⁴N and ¹⁵N, in all N species throughout the global ocean that are included in the marine ecosystem model. Five prognostic variables of ¹⁵N are embedded within the marine ecosystem model for all species containing nitrogen: NO₃, diazotrophs, algal phytoplankton, zooplankton and organic detritus (Figure 1). The “isotope effect” is referred to in the following as the effect that each process has on the respective oceanic isotopic N pool, which depends on the δ¹⁵N value of the substrate, the process-specific enrichment factor (ε), and the degree of utilization (u) of the substrate during the reaction:

\[ \delta^{15}N_{\text{product}} = \delta^{15}N_{\text{substrate}} - \epsilon (1 - u) \]

where u is the fraction of the initial substrate used in the reaction. For example, if all of the available substrate is consumed in the reaction (i.e., u = 1), the product will incorporate the δ¹⁵N value of the substrate, nullifying any potential fractionation. However, if the rate of utilization is low (i.e., u ≈ 0), the product will incorporate a relatively light δ¹⁵N value compared to the substrate by the designated enrichment factor (Table 1).

[15] The processes in the model that fractionate nitrogen isotopes are nitrate assimilation (εₓₓₓₓₓ = 5%), zooplankton excretion (εₓₓₓₓₓ = 6%), and water column denitrification (εₓₓₓₓₓ = 25%) (Table 1). Fractionation results in the isotopic enrichment of the more reactive, thermodynamically preferred, light ¹⁴N into the product of each reaction by a process-specific fractionation factor. For a detailed discussion of nitrogen isotope fractionation dynamics see [Mariotti et al., 1981]. Although little fractionation occurs during N₂ fixation in the model, it has an important effect on δ¹⁵N by introducing relatively light atmospheric N₂ (δ¹⁵N = 0‰) into the oceanic fixed N inventory. Sedimentary denitrification also has been observed to have little effect on the oceanic isotopic N pool because denitrifiers consume nearly all NO₃ diffusing into the sediments [Brandes and Devel, 1997, 2002; Lehmann et al., 2004, 2007]. In the model, there is no fractionation during sedimentary denitrification (εₓₓₓₓₓ = 0%), although this is a simplification of observations [Lehmann et al., 2007]. Fractionation during the remineralization of organic matter is not included in the model. The complete nitrogen isotope model description is provided in Appendix A.

3. Nitrogen Isotope Model Results

[16] The model simulates complex spatial patterns of δ¹⁵NO₃ and δ¹⁵N organic matter (OM) throughout the global ocean (top panels of Figure 3). Patterns of surface δ¹⁵NO₃ and subsurface δ¹⁵N OM are very similar but values...
are offset by two processes. First, as much as 5% off set due 348 to fractionation during NO₃⁻ uptake by phytoplankton and 349 second, by fractionation during zooplankton excretion, 350 which increases the δ¹⁵N OM through zooplankton mor-

tality (Figure 1). High δ¹⁵NO₃⁻ values (>15‰) are simulated 351 in the eastern subtropical gyres, where surface NO₃⁻ is 352 depleted, and in regions in close proximity to simulated 353 suboxic zones in the Eastern Pacific, Bay of Bengal, and 354

Figure 3. (top) Surface δ¹⁵NO₃⁻ and δ¹⁵N of sinking detritus in the model. (bottom) Isotope effect sensitivity experiments where one isotope effect is neglected per simulation and its difference with CTL is shown to illustrate its individual effect on the CTL simulation.
Eastern Atlantic (again, note that water column denitrification has not been actually observed in the Bay of Bengal and Eastern Atlantic). A clear interhemispheric asymmetry appears between the subtropical gyres of the Pacific and Atlantic with higher values of 14–20% in the southern hemisphere and smaller values of 10–14% in the northern hemisphere. More intermediate δ^{15}N values of 4–8% are found at high latitudes and near the equator where nutrient utilization is incomplete. δ^{15}N minima (<4%) are located in the western tropical/subtropical ocean basins, where N₂ fixation occurs in the model (Figure 2b). The remainder of this section presents a more quantitative description of the contributions of individual processes to these relatively complex spatial patterns of δ^{15}NO₃ and δ^{15}N OM.

3.2. Denitrification

[20] Denitrification only occurs at depth but its isotope effect can reach the surface due to upwelling and vertical mixing. Water column denitrification has a large enrichment factor and displays a very strong N isotope effect in close proximity to the simulated suboxic zones in the Eastern Pacific, Bay of Bengal, and Eastern Atlantic (“Water Column Denitrification” experiment in Figure 3). The unresolved poleward undercurrents along the western continental margin of the Americas (which could, in the real world, propagate high δ^{15}NO₃ away from the sub-surface suboxic zones [Kienast et al., 2002]) may restrict the simulated water column denitrification isotope effect too much to regions proximal to the suboxic zones. Both water column and sedimentary denitrification also indirectly lead to lower δ^{15}NO₃ values “downstream” of denitrification zones because they create N-deficient water that stimulates additional N₂ fixation, which introduces low δ^{15}N into the ocean. This negative feedback also decreases the horizontal extension of high δ^{15}NO₃ signature originating from suboxic zones, because N₂ fixation introduces much lower δ^{15}N into the ocean.

3.3. N₂ Fixation

[21] The addition of newly fixed, isotopically light atmospheric N₂ (δ^{15}Nₐ = 0) by diazotrophs is the reason for the low δ^{15}N values in the western tropical/subtropical ocean basins. Since denitrification is the only process in the model that creates N-deficient water, and therefore an ecological niche for diazotrophs, the majority of N₂ fixation in the model occurs “downstream” of denitrification zones after phytoplankton have consumed all remaining surface NO₃ and where sufficient aeolian Fe deposition exists. This low δ^{15}NO₃ signature is evident in the subtropical North/ South Pacific, the subtropical North/South Atlantic, and the Bay of Bengal (“N₂ Fixation” experiment, Figure 3).

3.4. Excretion

[22] According to our model results, the N isotope effect of excretion has a smaller influence on the simulated distribution of δ^{15}N in the global ocean (“Excretion” experiment, Figure 3) compared to the other processes discussed...
4. Model Evaluation

The relatively small number of δ15N observations and the sparse spatial and temporal coverage make a full global model assessment difficult. However, certain regions have been sampled sufficiently to provide a meaningful comparison with the model results. All observations presented here are interpolated horizontally onto a 0.9° × 1.8° grid using a Gaussian weighted algorithm. The 33 depth levels are consistent with WOA05 and a linear interpolation is used for depths of missing data if nearby data exist. A global database of δ15NO3 measurements has thus been constructed and is available for download (http://mgg.coas.oregonstate.edu/~andreas/Nitrogen/data.html). Figure 4 shows the annually averaged global distribution of measured δ15NO3, averaged over 200–300 m depth to illustrate the spatial coverage. Seasonal sampling biases exist depending on the region. More details on the data sets can be found in the respective ocean region subsections that follow. Comparisons are presented for the Southern Ocean (Indian-Pacific sector), the Eastern Tropical North Pacific, the Central Equatorial Pacific and the Subtropical North Atlantic. Other regions with available δ15NO3 observations included in the data set but not discussed in the text are the Bering Sea [Lehmann et al., 2005], the Northeast Pacific [Galbraith, 2006], the Arabian Sea [Altabet et al., 1999a] and the eastern Pacific sector of the Southern Ocean [Sigman et al., 1999].

4.1. Southern Indian-Pacific Ocean

The Southern Ocean represents a critical region of biogeochemical cycling in the ocean because it is the largest open ocean region with incomplete drawdown of the major nutrients. This results in an excess amount of CO2 at the surface that may have profound implications for future climate change. The relatively small number of δ15N observations and the sparse spatial and temporal coverage make a full global model assessment difficult. However, certain regions have been sampled sufficiently to provide a meaningful comparison with the model results. All observations presented here are interpolated horizontally onto a 0.9° × 1.8° grid using a Gaussian weighted algorithm. The 33 depth levels are consistent with WOA05 and a linear interpolation is used for depths of missing data if nearby data exist. A global database of δ15NO3 measurements has thus been constructed and is available for download (http://mgg.coas.oregonstate.edu/~andreas/Nitrogen/data.html). Figure 4 shows the annually averaged global distribution of measured δ15NO3, averaged over 200–300 m depth to illustrate the spatial coverage. Seasonal sampling biases exist depending on the region. More details on the data sets can be found in the respective ocean region subsections that follow. Comparisons are presented for the Southern Ocean (Indian-Pacific sector), the Eastern Tropical North Pacific, the Central Equatorial Pacific and the Subtropical North Atlantic. Other regions with available δ15NO3 observations included in the data set but not discussed in the text are the Bering Sea [Lehmann et al., 2005], the Northeast Pacific [Galbraith, 2006], the Arabian Sea [Altabet et al., 1999a] and the eastern Pacific sector of the Southern Ocean [Sigman et al., 1999].

Table 2. Global Measures of δ15NO3 Model Performance

<table>
<thead>
<tr>
<th>Model</th>
<th>r</th>
<th>P</th>
<th>RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.68</td>
<td>&lt;0.0001</td>
<td>0.73</td>
</tr>
<tr>
<td>Algal NO3 assimilation</td>
<td>0.60</td>
<td>0.00046</td>
<td>0.85</td>
</tr>
<tr>
<td>N2 fixation</td>
<td>0.52</td>
<td>0.0026</td>
<td>2.1</td>
</tr>
<tr>
<td>Excretion</td>
<td>0.65</td>
<td>0.00010</td>
<td>0.80</td>
</tr>
<tr>
<td>Water column denitrification</td>
<td>0.29</td>
<td>0.12</td>
<td>1.1</td>
</tr>
<tr>
<td>Sedimentary denitrification</td>
<td>0.64</td>
<td>0.00010</td>
<td>0.82</td>
</tr>
</tbody>
</table>

*Correlation coefficient (r), correlation significance (P), and root mean squared (RMS) error normalized by the standard deviation of the observations.
surface, which is released to the atmosphere (under preindustrial conditions). The degree to which surface nutrients are utilized here may have profound impacts on ocean-atmosphere exchanges of CO2. Figure 5 shows a comparison with observations recorded in the region [Sigman et al., 1999; Altabet and Francois, 2001; DiFiore et al., 2006]. This data subset compiles observations from 8 cruises covering various seasons. Since all cruises do not cover the same location, some seasonal biases can be expected, yet, we still decided to use annual averages for maximum spatial coverage. The model does not simulate interannual variability due to the prescribed monthly climatological winds and temporally constant biogeochemical parameters.

[26] Qualitatively, the inverse trend of increasing $\delta^{15}$NO$_3^-$ with decreasing NO$_3^-$ (Figure 5a) is reproduced by the model. However, the slope is underestimated suggesting that the enrichment factor for algal NO$_3^-$ assimilation used in the model ($\varepsilon_{\text{ASSIM}} = 5\%$) is too low, in agreement with [DiFiore et al., 2006] that suggests at least 7\%. The simulated vertical gradient is in good agreement with the observations. Deep water $\delta^{15}$NO$_3^-$ at 2000 m depth is around 5\% and slowly increasing throughout the lower pycnocline to around 6\% at 500 m depth. The model slightly overestimates $\delta^{15}$NO$_3^-$ between 200 m and 400 m depth, whereas near surface values are slightly underestimated.

[27] A large discrepancy between simulated and observational $\delta^{15}$NO$_3^-$ is apparent in surface waters north of 40°S off the southern coast of Australia (Figure 5c). This bias is due to the fact that the model overestimates the utilization of surface NO$_3^-$ relative to observations there (Figure 5c). Where the simulated NO$_3^-$ is almost completely consumed (i.e., NO$_3^-$ < 1 \mu M) (see Figure 5c contour line), the remaining $\delta^{15}$NO$_3^-$ values become as high as 18\%. Since none of the existing $\delta^{15}$NO$_3^-$ observations was collected in such low NO$_3^-$ concentrations (Figure 5a), it is impossible, at this time, to falsify this aspect of the N isotope model response. We note this heavy $\delta^{15}$NO$_3^-$ signature in these low NO$_3^-$ waters has little effect on $\delta^{15}$NO$_3^-$ across the nitracline in the model because the $\delta^{15}$N signature of very low NO$_3^-$ water becomes diluted out as it mixes with much higher NO$_3^-$ water (see section 3.1).

4.2. Eastern Tropical North Pacific
[28] The ETNP contains the largest suboxic zone in the ocean, where water column denitrification occurs. The relatively small spatial scale of suboxic zones makes them difficult for the model to simulate accurately and deficiencies in the coarse resolution physical model prevent it from fully resolving some important physical processes, especially in coastal regions. Underestimating coastal upwelling (due to coarse resolution) results in corresponding underestimation of primary production, organic matter remineralization, and O$_2$ consumption at depth. This is a major reason for overestimated dissolved O$_2$ at depth in areas with

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**Figure 5.** Comparison of the Indian-Pacific sector of the Southern Ocean with the $\delta^{15}$NO$_3^-$ database and CTL: (a) $\delta^{15}$NO$_3^-$ versus NO$_3^-$, (b) horizontally averaged (over available data) depth $\delta^{15}$NO$_3^-$ profiles, and (c) surface $\delta^{15}$NO$_3^-$ and with a 1 \mu M NO$_3^-$ contour line.
significant coastal upwelling (e.g., off Peru and NW Mexico) (Figure S3), too large for water column denitrification to occur. Preliminary experiments suggest that increased vertical resolution can improve the simulation of productivity and suboxia in the Eastern Tropical South Pacific (not shown).

[29] The ability to reproduce the equatorial undercurrents that transport relatively oxygen-rich water from the western basin is also important for the simulation of the Eastern Pacific suboxic zones. The anisotropic viscosity scheme [Large et al., 2001] improves equatorial dynamics considerably (Text S2 and Figure S1). The Pacific Equatorial Undercurrent increases from 0.15 m/s to nearly 0.8 m/s, just slightly weaker than observations, which show velocities near 1 m/s (Figure S2). The North Equatorial Countercurrent in the model also displays lower current velocities than observed, and does not deliver enough oxygen-rich water directly to the ETNP suboxic zone. This is likely the main reason why the simulated suboxic zone is too large and located too far south (by ~5°) relative to observations (Figure S3). This results in higher rates of water column denitrification and higher $\delta^{15}$NO$_3$ values, as well as more N-deficient water in the suboxic zone compared to observations (Figure 6).

[30] Since the locally high $\delta^{15}$NO$_3$ values exist in too small NO$_3$ concentrations, when they transport out of the denitrification zone and mix with water with much higher NO$_3$, the high $\delta^{15}$NO$_3$ value is largely diluted away because the resulting $\delta^{15}$NO$_3$ value is weighted toward the water parcel with more NO$_3$. This “dilution effect” [Deutsch et al., 2004] reduces the impact that water column denitrification has on $\delta^{15}$NO$_3$ outside of denitrification zones, and thus decreases its actual isotope effect on setting the global mean $\delta^{15}$NO$_3$. This is the main reason why the model requires a relatively low sedimentary to water column denitrification ratio of 1:3 to set the global mean $\delta^{15}$NO$_3$ to 5‰ compared to estimates from one-box models [Brandes and Devol, 2002; Altabet, 2007], which cannot account for any important effects that occur locally within the denitrification zone. However, note that our model significantly overestimates NO$_3$ consumption via water column denitrification in the ETNP compared to observations (Figure 6a). Therefore, it is likely that our sedimentary to water column denitrification ratio of 1:3 is too low, but it does highlight the importance that the NO$_3$ consumption/dilution effect can have on determining the global mean $\delta^{15}$NO$_3$.

[31] Figure 6 shows model $\delta^{15}$NO$_3$ compared to observational $\delta^{15}$NO$_3$ data collected during November 1999 [Sigman et al., 2005] and October 2000 (M. Altabet, unpublished data, 2010). The model captures the general observed trend of increasing $\delta^{15}$NO$_3$ as NO$_3$ is consumed during water column denitrification (Figure 6a). The model’s too low N:P ratio for diazotrophs may partly explain its incapacity to simulate some of the relatively high N' values.
production must be supported by $\text{N}_2$ fixation in order to account for the low surface $\delta^{15}\text{NO}_3$. Other observations also suggest that the decrease in $\delta^{15}\text{NO}_3$ toward the surface is likely due to the fixation of atmospheric $\text{N}_2$ and the subsequent, closely coupled remineralization-nitrification cycle [Sigman et al., 2005]. We test this hypothesis by comparing the observations with the model experiment in which the isotope effect of $\text{N}_2$ fixation is neglected ("No NFIX"). In this case, the model overestimates surface $\delta^{15}\text{NO}_3$ by $\sim12\%$ (Figure 6b) and the surface minimum is not simulated. This experiment demonstrates that the input of isotopically light fixed N from $\text{N}_2$ fixation is not well constrained. Although atmospheric N deposition may be significant in this region [Michaels et al., 1996; Lipschultz et al., 2002; Knapp et al., 2005, 2008], its isotopic composition is not well known and therefore is not included in the model at this time. Figure 7 shows the comparison of annual model $\delta^{15}\text{NO}_3$ with available observations from cruises in May 2001 and 2004 (M. Altabet and J. P. Montoya, unpublished data, 2010), October 2002 [Knapp et al., 2008], and May 2005 [Bourbonnais et al., 2009].

The model overestimates the $\delta^{15}\text{NO}_3$ values everywhere, by 0.9‰ on average and by 2‰ at 200 m depth, presumably due mostly to the underestimation of $\text{N}_2$ fixation, but possibly also because atmospheric N deposition and/or fractionation during the remineralization of organic matter are not included. Both of these processes would act to decrease subsurface values of $\delta^{15}\text{NO}_3$. Underestimated N$^\prime$ in the North Atlantic (Figure S3) also indicates too little $\text{N}_2$ fixation, but we again note the too low N:P ratio for diazotrophs also contributes to this N$^\prime$ underestimation to some degree.

$\text{N}_2$ fixation is most likely underestimated in the model because it does not consider dynamic elemental cycling of the microbial loop. It has been suggested that DOP is more labile relative to DON and recycles through the microbial loop more efficiently, which can help relieve diazotrophs of P limitation in this region [Wu et al., 2000] and enhance $\text{N}_2$ fixation. The model is able to reproduce the pattern of low $\delta^{15}\text{NO}_3$ in the thermocline qualitatively, just not quantitatively to the extent present in the observations. Sedimentary denitrification in the North Atlantic stimulates enough N$^\prime$ fixation in the model to generate a subsurface $\delta^{15}\text{NO}_3$ minimum. When sedimentary denitrification is
switched off (“No SD”), the thermocline minimum is not simulated. This suggests that sedimentary denitrification is an important factor influencing N₂ fixation in the Subtropical North Atlantic, but not the only factor.

5. Discussion and Conclusions

A new model of nitrogen isotopes has been implemented into the three-dimensional ocean component of a global Earth system climate model capable of millennial timescale simulations. Despite some model deficiencies, we have shown that this model can successfully reproduce the general spatial patterns of δ¹⁵NO₃ measured in the ocean. Sensitivity experiments allowed us to isolate the individual N isotope effects of various N transformational processes on the global distribution of δ¹⁵N. Algal NO₃ assimilation, water column denitrification, and N₂ fixation all have strong influences in setting the global patterns of δ¹⁵NO₃ in the ocean, whereas the effect of zooplankton excretion is weaker.

These simulations show that the isotope effect of algal NO₃ assimilation can drive very large spatial gradients in both δ¹⁵NO₃ and δ¹⁵N OM depending on the ocean environment (Figure 3). In HNLC areas where surface NO₃ is utilized and algae are able to fractionate NO₃ at their designated enrichment factor, the δ¹⁵N OM signature decreases. However, when NO₃ utilization is high, the δ¹⁵N OM signature is more similar to the δ¹⁵NO₃ value it contributes because the effective degree of fractionation becomes much lower (see section 3.1). Surface NO₃ utilization gradients can transition rapidly, for example due to changes in ocean circulation, and can possibly drive large and rapid changes in δ¹⁵NO₃ and δ¹⁵N OM. The important influence of surface NO₃ utilization on the global distribution of N isotopes in the model suggests that changes in surface NO₃ utilization patterns throughout Earth’s history could contribute to large fluctuations in δ¹⁵N observed in sediment records, especially near fronts where large surface NO₃ gradients exist (see also Altabet and Francois, 1994; Farrell et al., 1995; Sigman et al., 1999; Brunelle et al., 2007; Galbraith et al., 2008; Robinson and Sigman, 2008).

The model simulates a strong direct and indirect isotope effect of denitrification. High δ¹⁵NO₃ produced by water column denitrification has clear regional impacts and is also responsible for overall elevated δ¹⁵NO₃ of the ocean relative to the N₂ fixation source (see below). The indirect effect of both water column and sediment denitrification is mediated by the production of N-deficient water, which creates an ecological niche for diazotrophs. This stimulates additional N₂ fixation when other suitable conditions for N₂ fixation also exist (e.g., warm (>20°C), N-depleted water with sufficient P and Fe). This indirect effect also attenuates the horizontal circulation of high δ¹⁵NO₃ waters, originating from regions of water column denitrification, which causes its direct isotope effect to be regionalized to suboxic zones.

Key features of the model have been identified that are in need of further development. The coarse resolution physical circulation model does not fully resolve the dynamics of coastal upwelling regimes, which in part drive the flux of organic matter toward the seafloor sediments and its remineralization in the water column, as well as indirectly influences ventilation of suboxic zones. This is critical in the simulation of water column denitrification and sediment denitrification, which are important processes with respect to the global N isotope balance. Future model versions will include additional vertical levels to better resolve continental shelves as well as higher horizontal resolution.

The model neglects dynamic elemental stoichiometry such as high N:P ratios of diazotrophs and the more efficient recycling of DOP relative to DON in microbial loops, which can help relieve diazotrophs of their P limitation and allow them to fix additional N₂ into the oceanic fixed N pool in oligotrophic waters. The ecosystem model also suffers from the exclusion of Fe as a prognostic tracer preventing it from being able to simulate differences in ecosystems limited by micronutrients (NO₃, PO₄³⁻) versus micronutrients (Fe).

Future applications of this model will include simulations of past climates, and direct comparison with δ¹⁵N sediment records will be used to test the model results. This approach may be a useful to quantify past interactions between the marine N cycle and its isotopes, as well as their impact on climate and may provide new insights into important physical and biogeochemical changes throughout Earth’s history.

Appendix A: Nitrogen Isotope Model

The open system fractionation equation is used for fractionation during algal NO₃ assimilation [Altabet and Francois, 2001]:

\[ \delta^{15}P_0 = \delta^{15}NO_3 - \varepsilon_{ASSIM}(1 - u_{NO3}). \]  

where \( \delta^{15}P_0 \) is the δ¹⁵N of phytoplankton biomass assimilated during one time step, \( \Delta t \), and \( u_{NO3} \) is the fraction of NO₃ available that is converted into biomass (\( u_{ASSIM} = J_PD_0 \times \Delta t/NO_3 \)). When algae assimilate all available NO₃ into their biomass (i.e., \( u_{ASSIM} = 1 \)) they will incorporate the same δ¹⁵N value as that of the source material. Many studies have estimated the fractionation factor in both laboratory and ocean environments. A wide variety of values have been reported in culture settings ranging from 0.7‰ to 23‰ [Wada and Hattori, 1978; Montoya and McCarthy, 1995; Waser et al., 1998; Needoba et al., 2003; Granger et al., 2004]. A more confined range has been observed in field estimates from 4‰ to 15‰ [Wada, 1980; Altabet et al., 1991, 1999b; Sigman et al., 1999; Altabet and Francois, 2004; Karsh et al., 2003; DiFiore et al., 2006]. In our model we choose a constant value of 5‰ because the effective degree of fractionation becomes weaker.

Nitrate in suboxic waters have been observed to have much higher δ¹⁵N values due to fractionation during denitrification. Observations from present-day suboxic zones in the Eastern Tropical North Pacific (ETNP) and the Arabian Sea (AS) have reported fractionation factors ranging from 22 to 30‰ [Cline and Kaplan, 1975; Liu and Kaplan, 1989; Brandes et al., 1998; Altabet et al., 1999b; Voss et al., 2001].
where $\delta^{15}\text{NO}_3$ is the oxygen-equivalent reduction of nitrate converted into N$_2$ gas during denitrification. The term $u_{\text{DENI}}$ is the fraction of available NO$_3$ which is reduced into N$_2$ gas ($u_{\text{NO3}} = \mu_D D \times 0.8 \times R_{\text{O:N}} \times r_{\text{NO3 sos}} \times L_{\text{NO3}} \times \Delta t/\text{NO3}$).

[42] Excretion is the process responsible for the stepwise enrichment of $\delta^{15}$N along the trophic chain in our model and is simulated using the instantaneous fractionation equation:

$$\delta^{15}\text{N}_3 = \delta^{15}Z - \varepsilon_{\text{EXCR}}.$$  

(A3)

The instantaneous fractionation equation is used because excretion will always be a small fraction of the total zooplankton biomass and has been measured to be depleted by $\sim 6\%$ relative to its body. Excretion is the source of the excreted nitrogen. This leads to the average enrichment of $\sim 3.4$ per trophic level.[Minagawa and Wada, 1984.]

[43] Implementing these fractionation equations into the marine ecosystem model requires us to consider the changes of $^{14}$N and $^{15}$N between the various N pools separately. Total nitrogen abundance now has the form

$$N = ^{14}\text{N} + ^{15}\text{N}$$  

(A4)

for each variable in the isotope model. A fractionation coefficient is calculated for each process so the sum of all equations for total N can be applied to $^{15}$N.[Giraud et al., 2000]. For example, consider fractionation during algal uptake and denitrification. The isotopic ratio of new nitrogen biomass ($P_O$) is found using equations (1) and (2):

$$^{15}P_O = \beta_{\text{ASSIM}}^{14}P_O$$  

(A5)

where

$$\beta_{\text{ASSIM}} = \frac{^{15}\text{NO}_3}{^{14}\text{NO}_3} - \varepsilon_{\text{ASSIM}}(1 - u_{\text{NO3}})R_{\text{nd}}.$$

(A6)

[44] Applying equations (S4) and (S5) in Text S2 gives the amount of new $^{15}P_O$ relative to the amount of total new nitrogen biomass, which is given by the primary production ($J_D P_O$), calculated by the marine ecosystem model:

$$^{15}P_O = \frac{\beta_{\text{ASSIM}}}{1 + \beta_{\text{ASSIM}}}J_D P_O.$$  

(A7)

where

$$R_S - P_O, PD, Z, D = ^{15}\text{N}/(^{14}\text{N} + ^{15}\text{N})$$

is the ratio of heavy over total nitrogen. The complete parameter description is provided in Text S2. Here it suffices to note that the equations for total nitrogen ($^{14}$N + $^{15}$N) are identical to the ones of $^{15}$N except that $R_X = \beta_Z/(1 + \beta_Z) = 1$ in the total nitrogen equations.

[45] The model was carefully tested with zero fractionation in order to quantify and minimize numerical errors, which can occur for example due to slightly negative values of biological tracers caused by inaccuracies of the advection scheme. The biological code was adjusted to avoid negative concentrations as much as possible. Initially numerical errors in $^{15}$N ranged from $\pm 1\%$ in grid points at the seafloor to $\pm 0.1\%$ in the upper ocean. Setting $R_{\text{nd}} = 1$ instead of $R_{\text{nd}} = 0.0036765$, the actual atmospheric N$_2$ isotope ratio, reduces the numerical errors by over an order of magnitude. $R_{\text{nd}}$ is set to the value 1 so both isotope variables will be on the same order of magnitude. This prevents $^{15}$N from becoming very close to zero as often, where inaccuracies of the advection scheme can cause it to be negative. This modification amounts to a scaling of $^{15}$N and $^{14}$N by a constant factor which does not affect the $\delta^{15}$N dynamics. The remaining numerical errors of $\pm 0.1\%$ in the deep ocean and $\pm 0.01\%$ in the upper ocean are 2

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orders of magnitude smaller than the observed variability. The model is integrated for over 5,000 years as it approaches equilibrium.

References


nitrate uptake by phytoplankton grown in continuous culture, p. 1277.


