Constraining the pre-industrial and deglacial marine nitrogen cycle by combining models and observations

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Constraining the pre-industrial and deglacial marine nitrogen cycle by combining models and observations

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Abstract

This thesis deals with the marine nitrogen (N) cycle. Two questions are addressed: “Do pre-industrial estimates of rates of N-fixation and denitrification yield a balanced marine N-cycle?” and: “How did the marine N-cycle, and particularly the N inventory, evolve across the last glacial termination?” Observations and models are combined to address these questions. Tracers reflecting the N anomaly (\(N^*\)) and stable N isotopes (\(\delta^{15}N\)) are used to constrain a newly developed geochemical multi-basin box model and the Biogeochemical Elemental Cycling (BEC) model.

Two probabilistic box model approaches were developed to simultaneously estimate the pre-industrial rates of N-fixation and denitrification, as well as to compute the marine N budget. The approaches yield rates of N-fixation of 118 TgN yr\(^{-1}\) and 134 TgN yr\(^{-1}\) and rates of denitrification in the water column and sediment of 51 TgN yr\(^{-1}\) and 81 TgN yr\(^{-1}\), respectively. These rate estimates plus updated estimates of atmospheric deposition and riverine input of N yield a marine N-cycle that is balanced to within 15 TgN yr\(^{-1}\). A N residence time of 4,500 yr is computed. This residence time being shorter than the time-scale of the last glacial termination, the question is raised as to whether and how much the marine N-cycle has contributed to the variations of atmospheric level of carbon dioxide (\(CO_2\)) on this time-scale, through changes in the global inventory of N.

The change in the marine N inventory across the last glacial termination is evaluated using the box model developed for pre-industrial investigations. This is done by determining the temporal evolution of N-fixation and denitrification, which are affected by climate forcings. Deglaciation simulations are constrained by sediment \(\delta^{15}N\) records from several sites located in different ocean basins. A decrease of 26 to 48% in the global N inventory is simulated across the last deglaciation. This decrease is primarily a consequence of a 35% decrease in the global rate of N-fixation due to a strong iron forcing during the early deglaciation. A subsequent increase in N-fixation due to a strong internal N-feedback permits the global rate of N-fixation to remain nearly unchanged between the last glacial period and the Holocene. The decrease in the global inventory of N across the last deglaciation implies that global marine productivity possibly decreased, and hence the carbon sequestered in the deep ocean as well. This makes the marine N-cycle a potential candidate for explaining a part of the
increase in the atmospheric CO$_2$ level across the last glacial termination.

Simulations using the BEC model embedded in the Community Climate System Model (CCSM) help to gain insight not only into the processes and dynamics of the marine N-cycle, but also into the coupling between the marine N- and carbon (C) cycles and the Earth’s climate. Here, a complex N isotope model as well as a formulation of benthic denitrification are implemented in the BEC model. An initial model evaluation was carried out using the mean ocean and spatial distribution of $\delta^{15}$N of nitrate (NO$_3^-$), the global NO$_3^-$ budget and the global export flux of POC. Further investigations of the dynamics of the marine N-cycle under pre-industrial conditions and over abrupt climate events will be undertaken. These will help to better predict future variations in the N-cycle and the impacts of these variations on the C-cycle and the Earth’s climate in a changing world affected by the ongoing anthropogenic perturbation.

Deux approches probabilistiques ont été développées afin d’estimer simultanément les taux préindustriels de fixation d’azote et de dénitrification, ainsi que pour calculer le bilan du cycle océanique de l’azote. Ces approches révèlent des taux de fixation d’azote de 118 TgN yr$^{-1}$ et de 134 TgN yr$^{-1}$, et des taux de dénitrification dans la colonne d’eau et dans les sédiments de respectivement 51 TgN yr$^{-1}$ et 81 TgN yr$^{-1}$. La combinaison de ces estimations de taux avec les estimations plus récentes des apports d’azote par dépôt atmosphérique et par les rivières indique un cycle océanique de l’azote qui est à l’équilibre à plus ou moins 15 TgN yr$^{-1}$. Un temps de séjour de l’azote de 4500 ans est calculé. Ce temps de séjour étant plus court que l’échelle de temps de la dernière déglaciation, la question se pose si, et à quel point, le cycle océanique de l’azote a contribué, au travers de changements du stock d’azote, aux variations passées du taux de dioxyde de carbone ($CO_2$) dans l’atmosphère.

Le changement du stock océanique de l’azote durant la dernière déglaciation est évalué à l’aide du modèle en boîtes développé précédemment pour les études préindustrielles. L’évaluation de ce changement est obtenue une fois les évolutions temporelles des taux de fixation d’azote et de dénitrification déterminées, lesquelles sont influencées par des forçages climatiques. Les simulations glaciaires-interglaciaires sont contraintes par des reconstructions sédimentaires du $\delta^{15}N$ provenant de plusieurs sites localisés dans différents bassins océaniques. Une diminution de 26 à 48% du stock global de l’azote est calculée durant la dernière déglaciation. Cette diminution est principalement la conséquence d’une réduction de 35% du taux global de fixation d’azote en raison d’un important forçage du
au fer actif au début de la déglaciation. Suit une augmentation de la fixation d’azote en raison d’une importante réaction interne du cycle de l’azote, laquelle implique qu’au final le taux global de fixation d’azote n’a pratiquement pas changé durant la dernière transition glaciaire-interglaciaire. La diminution du stock d’azote implique que la productivité océanique a peut-être globalement diminué, d’où une possible diminution de la quantité de carbone isolée dans l’océan profond. Le cycle océanique de l’azote serait ainsi un candidat potentiel pour expliquer une partie de l’augmentation du taux de CO₂ dans l’atmosphère durant la dernière déglaciation.

Des simulations du modèle BEC qui est inclus dans le Community Climate System Model (CCSM) permettent d’acquérir des connaissances non seulement des processus et de la dynamique du cycle océanique de l’azote, mais aussi du couplage entre les cycles océaniques de l’azote et du carbone, et du climat. Ici, un modèle isotopique de l’azote ainsi qu’une paramétrisation pour la dénitrification dans les sédiments sont implémentés dans le modèle BEC. Une première évaluation du modèle, basée sur le δ¹⁵N du nitrate moyen de l’océan et sur sa distribution, ainsi que sur le bilan global de nitrate et sur le flux total de POC exporté, a été effectuée. De plus amples analyses de la dynamique du cycle océanique de l’azote soumis à des conditions préindustrielles et durant d’abruptes événements climatiques seront effectuées. Ces analyses aideront à mieux prédire les futures variations du cycle de l’azote et l’impact de ces variations sur le cycle du carbone et sur le climat dans un monde soumis à la perturbation anthropogénique.
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Chapter 1

Introduction

1.1 Setting the stage: C-N coupling and the Earth’s climate

Biologically available nitrogen (N) is an essential major element to life and its availability has the potential to limit biological production in the marine environment. Hence, N occupies a central role in ocean biogeochemistry. Biologically available N (called fixed N in the following) refers to all forms of N except the most abundant chemical form of N, dinitrogen, also called nitrogen gas ($N_2$). This is because $N_2$ is inert for marine organisms as a consequence of the strong triple bonds that link the two N atoms together. Fixed N compounds, either as oxidized (nitrite, $NO_2^-$ or nitrate, $NO_3^-$) or reduced (ammonium, $NH_4^+$ or organic N) forms, are limiting nutrients that regulate the growth of phytoplankton over half of the surface ocean. The availability of fixed N, but also of other nutrients, e.g. phosphorus (P) or iron (Fe), drives the production of organic matter.

Marine biological production removes $CO_2$ from the atmosphere. This tends to lower the atmospheric concentration of this dominant greenhouse gas through the so-called biological pump (see Fig. 1.1 and Sarmiento and Gruber [2006]). At low-latitudes, the biological pump is very efficient since biology is successful in taking up nutrients in the euphotic zone (in particular fixed N) and incorporating them into organic matter for export into the ocean interior. The fixed N concentration in surface waters is therefore very low. Consequently, fixed N availability can control the oceanic uptake of atmospheric $CO_2$ which strongly influences the Earth’s climate. An indirect link, therefore, exists between the marine inventory of fixed N (referred to as N inventory in the following) and the Earth’s climate through the C cycle.

Redfield et al. [1963] reported a relatively robust stoichiometric balance between dissolved and particulate C, N, and P in the marine environment. The stoichiometric ratios of C:N:P in proportions of 106:16:1 are classically referred to as the Redfield ratios. The Redfield ratios concept states that photosynthesis, respiration, and remineralization all happen with the same fixed stoichiometric ratio. This concept can be reformulated as a N anomaly ([Michaels et al., 1996; Gruber and Sarmiento, 1997]). This anomaly is associated with sources or sinks of fixed N which can alleviate/exacerbate the N limitation of phytoplankton.
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Figure 1.1 Cartoon of the biological pump based on Falkowski and Oliver [2007]. In the upper ocean, phytoplankton photosynthetically fix C into organic matter. At the same time, other nutrients like N, P and Fe are taken up and assimilated. Most of the organic matter is remineralized or respired locally by herbivores or bacteria, but a fraction of it is exported into the ocean interior where it is remineralized back and enriches the inorganic nutrient pool there. This export flux of organic matter implies that the deep concentration of inorganic C is higher than the atmospheric CO$_2$. This mechanism is called the Biological Pump. This pump transports organic matter to deep water against water circulation and mixing transport of deep water, which in turn transport nutrients-rich deep water back to the upper ocean. This transport of nutrient-rich water can fuel new phytoplankton growth, and closes the microbial loop. Only a small fraction of the organic matter that sinks gets buried into marine sediment. This burial represents a net sequestration of C.

1.2 Current understanding of the marine N-cycle

1.2.1 Overview of the cycle

A large fraction of primary production is supported by regenerated N or nutrients that have been recycled in the upper ocean. Since N is exported from the upper ocean to the interior, primary production requires extra N inputs. This new N enters the euphotic zone mainly via upwelling or mixing [Eppley and Peterson, 1979], and N enters the marine N-cycle through N-fixation carried out by prokaryotic microorganisms (bacteria or archaea) that are capable of converting N$_2$ into organic N [Capone et al., 2005] (see Fig. 1.2 and section 1.2.2), and
1.2. Current understanding of the marine N-cycle

atmospheric deposition and river discharge of N [Duce et al., 2008; Seitzinger and Mayorga, 2008].

Inside the marine N-cycle, essential and unique transformations are performed by various microbes (see Fig. 1.2). Phytoplankton take up either $\text{NO}_3^-$, the dominant biologically available form of N, or $\text{NH}_4^+$ and fix them into organic N. $\text{NH}_4^+$ assimilation is favored over $\text{NO}_3^-$ assimilation because this conversion into organic material uses less energy. Organic N is then remineralized through ammonification, which produces $\text{NH}_4^+$. In this transformation, heterotrophic bacteria use the oxidation of organic C to $\text{CO}_2$ as a source of energy. $\text{NH}_4^+$ is in turn aerobically transformed in two steps into $\text{NO}_3^-$. The two processes in combination are referred to as nitrification and are mediated by a specialized group of bacteria. In the first step, $\text{NH}_4^+$ is oxidized to $\text{NO}_2^-$ and some intermediates are produced, e.g. the greenhouse gas nitrous oxide ($\text{N}_2\text{O}$) [Suntharalingam et al., 2000]. On the other hand, $\text{NH}_4^+$ is also consumed back into organic N through ammonium assimilation. In addition to phytoplankton uptake, $\text{NO}_3^-$ is consumed by denitrification, which converts $\text{NO}_3^-$ back into $\text{N}_2$. Denitrification is performed by anaerobic heterotrophic bacteria (see section 1.2.3). It is the dominant sink for fixed N in the marine environment.

The marine inventory of N is altered by several external inputs and outputs and internal sources and sinks of N. External inputs of fixed N are atmospheric deposition [Duce et al.,
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2008] and river discharge of N [Seitzinger and Mayorga, 2008], while external outputs of fixed N are sediment N burial and ocean to atmosphere outgassing of \( N_2O \), which is produced by denitrification and nitrification (see Fig. 1.2). Pre-industrial riverine input and atmospheric deposition of N together are of smaller magnitude than N-fixation (Tab. 1.3). The biggest sink in the marine N-cycle, after denitrification, is sediment burial while \( N_2O \) outgassing represents only a very small output of fixed N (Tab. 1.3). It is interesting to point out that there are other minor, not well known and quantified, sources of N to the marine environment, for example hydrothermal vents. Hydrothermal vents (fissures in the sea-floor from which geothermally heated water issues) are a source of N to the deep ocean. It is commonly acknowledged that they have low concentrations of dissolved nitrogen compounds and that their N emissions are very small relative to N-fixation, atmospheric and river input of N. This source is likely to account for less than 1% of cumulated sources, and is generally neglected in studies about the marine N-cycle.

1.2.2 N-fixation

N-fixers are capable of converting the most abundant oceanic form of N, \( N_2 \), into organic N (Fig. 1.2) (see review on N-fixation by Karl et al. [2002]). Because \( NO_3^- \) is usually depleted before \( PO_4^{3-} \) in surface waters, N-fixers are crucial since they release newly fixed N, which in turn can drive new production. In the oligotrophic ocean, the rate and location of N-fixation by diazotrophs determine the rate of primary production and the export of C. For instance, Gruber and Sarmiento [1997] reported that N-fixation may fuel as much as 50% of the export production in the oligotrophic North Atlantic. Since N and C are consumed and exported below the thermocline in Redfield ratio [Redfield, 1934; Redfield et al., 1963], it is N-fixation and oceanic input of fixed N from the atmosphere and from rivers that can generate a net deep ocean sequestration of C (see Fig. 1.1).

N-fixation in the marine environment has long been controversial. This source of fixed N was detected by Dugdale et al. [1961] in the Sargasso Sea and then in the Arabian Sea in association with the cyanobacteria Trichodesmium [Dugdale et al., 1964]. Research throughout the 1970s indicated that N-fixation can be of regional significance. The contribution of N-fixation to the N-cycle was however considered minimal. Recent research cruises in the tropical North Atlantic, the Arabian Sea and the Eastern Indian Ocean confirmed that N-fixation by Trichodesmium can be significant and, at times, match or exceed the \( NO_3^- \) flux coming from the ocean interior into the upper water column. Another relatively recent finding suggested that other organisms fix N. Zehr et al. [2000] “discovered” some previously unknown biodiversity of N-fixers. Several recent works have highlighted the importance of unicellular N-fixers, despite the fact that they are more difficult to detect than Trichodesmium [Zehr et al., 2000, 2001; Montoya et al., 2004; Moisander et al., 2010; Hamersley et al., 2011]. The diversity of
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microorganisms capable of N-fixation is therefore greater than previously thought, and it is likely that there are still some N-fixing microorganisms which have evaded detection to date.

Large spatial and temporal variability, and large uncertainties in the estimated rates of N-fixation

N-fixers can be identified and their rate of N-fixation quantified through direct measurements or geochemically-based approaches. Over the past decades numerous field studies have been conducted, some including direct estimation of N-fixation rates [Capone et al., 1997]. In the early 1970s field studies of N-fixation made progress with the introduction of a convenient enzymological assay, the C$_2$H$_2$ reduction method (the Acetylene Reduction Assay, ARA) [Capone, 1993]. More recently, new molecular methods designed to target the nifH gene, which is part of the enzyme system nitrogenase (e.g. the polymerase chain reaction, PCR), or the $^{15}$N$_2$-tracer addition method [Montoya et al., 1996] have been used to identify N-fixers and quantify rates of N-fixation. Additionally, geochemical approaches using stochiometric anomalies of the N:P ratio have also been used to estimate rates of N-fixation [Michaels et al., 1996; Gruber and Sarmiento, 1997] (see below in this section). Each method has its own limitations. For example, in the ARA, the factor used to convert moles of acetylene to moles of N$_2$ has been a matter of debate [Mulholland et al., 2006; LaRoche and Breitbarth, 2005].

There are discrepancies between rates of N-fixation derived from field and laboratory studies, between studies from various laboratories, and among independent geochemical estimates. Extrapolations to the global-scale of rates of N-fixation measured in laboratories or field populations of _Trichodesmium_ yield ranges that vary by up to 6 orders of magnitude. This is due to the fact that (i) rates vary by orders of magnitude within _Trichodesmium_ populations [Mulholland et al., 2006], (ii) rates vary depending on the method used to estimate N-fixation, (iii) N-fixation has a high spatio-temporal variability, and (iv) there is an under sampling of direct rate measurements. The comparison of rates of N-fixation measured simultaneously using the $^{15}$N$_2$-tracer addition and the ARA methods shows that the $^{15}$N$_2$-tracer addition method generally yields lower rates of N-fixation, because the $^{15}$N tracer introduced as a gas bubble into a seawater sample does not attain equilibrium with the surrounding water quickly enough [Mohr et al., 2010]. The discrepancies between N-fixation derived from field and laboratory studies could, in part, be explained by the underestimation of the true rate of N-fixation due to methodological uncertainty (see e.g. Mohr et al. [2010]). These examples highlight the difficulties in extrapolating global rates from direct measurements.

The high spatio-temporal variability of N-fixation makes under-sampling of direct rate measurements a chronic problem which can be alleviated by applying indirect geochemical ap-
proaches. Geochemical approaches based on the distribution of nutrients [Michaels et al., 1996; Gruber and Sarmiento, 1997] and stable N isotopes [Montoya et al., 2002] help to overcome the sampling bias thanks to the tracer’s property of integrating the signal in space and time, but leave room for interpretation due to their indirect nature (e.g., Hansell et al. [2004]). The existence of a relatively constant N:P ratio of 16:1 in phytoplankton and particulate matter, that became know as the Redfield ratio [Redfield et al., 1963], can be reformulated as a \( \text{NO}_3^- \) anomaly, often referred to as \( N^* \). The quasi-conservative tracer \( N^* (N^* = \text{NO}_3^- - 16 \text{PO}_4^{3-} + 2.9 \text{mmol m}^{-3}) \) was derived and applied by Michaels et al. [1996] and by Gruber and Sarmiento [1997]. During N-fixation, P is not gained, and thus the \( \text{NO}_3^-/\text{PO}_4^{3-} \) ratio ratio is altered, with a long-term signature of high (> 16 : 1) N:P ratios, i.e., a high \( N^* \) anomaly, in the underlying thermocline (Fig. 1.4). A drawback of the \( N^* \) tracer is that it is necessary to choose the N:P ratio of diazotroph biomass in order to convert a formation rate of \( N^* \) into an estimate of N-fixation rate, and the rate of N-fixation derived from \( N^* \) is highly sensitive to this ratio. Some authors assumed a ratio of 125 (e.g. Gruber and Sarmiento [1997]), whereas field studies have also reported N:P ratios of 40 for \textit{Trichodesmium} [Letelier and Karl, 1998]. Unfortunately, we do not know well the N:P ratio of \textit{Trichodesmium} sinking out of the euphotic zone. Additionally, high \( N^* \) could also result from remineralization of organic matter with high N:P ratio or from exported dissolved and particulate organic matter with preferentially remineralized nitrogen. Nevertheless, \( N^* \)-type tracers have been extensively used to investigate N-fixation in the Atlantic Ocean [Michaels et al., 1996; Gruber and Sarmiento, 1997; Hansell et al., 2004; Bates and Hansell, 2004; Hansell et al., 2007], and to a lesser extent in the Pacific Ocean [Deutsch et al., 2001]. In a recent modeling approach, Deutsch et al. [2007] estimated N-fixation rates based on nutrient restoring. Finally, several biogeochemical models have also simulated N-fixation, e.g. the Biogeochemical Elemental Cycling model [Moore et al., 2004], or Goebel et al. [2007] who reported on modeling the abundances and growth rates of different cyanobacterial diazotrophs.

To date, it has been difficult to quantify the importance of N-fixation because of the stochastic occurrence of diazotroph blooms, although it seems safe to assume that N-fixation has been the dominant input term of the N budget in the present and past ocean [Capone et al., 1997; Gruber, 2008]. Most current N-fixation rate estimates range from 100 to 200 TgN yr\(^{-1}\) (T means tera, prefix in the metric system for \(10^{12}\)) (Tab. 1.3). Model simulations based on \( N^* \) in surface waters have revealed rates that do not exceed 150 TgN yr\(^{-1}\) [Deutsch et al., 2007], and shipboard rate measurements have shown substantial N inputs into the surface ocean via N-fixation [Capone et al., 2005; Montoya et al., 2004, 2007].

Irrespective of these large uncertainties, recent estimates of N-fixation are nearly an order of magnitude greater than those from pre-1980. Now, it appears that N-fixation by \textit{Trichodesmium}, the best studied N-fixer, is much more important that previously suspected [Capone et al., 2005]. In addition, the contribution of unicellular N-fixers to the global N in-
1.2. Current understanding of the marine N-cycle

Ventory is unknown, but it has been suggested that these unicellular N-fixers could fix at least as much N as *Trichodesmium* [Zehr et al., 2001; Montoya et al., 2004]. There is accumulating evidence indicating that the global rate is likely to be higher than estimates based on *Trichodesmium* abundance and direct rate measurements.

**Key role of iron**

Since diazotrophs are successful in oligotrophic regions due to their ability to utilize the largest reservoir of oceanic N, i.e., the gaseous \( \text{N}_2 \), their growth must be constrained by other limiting factors. The availability of Fe, P, and dissolved oxygen, as well as high temperature, have been reported as limiting factors (see review by Karl et al. [2002]). Diazotroph organisms do not continue to fix N if they can obtain their required N by taking up \( \text{NO}_3^- \) or \( \text{NH}_4^+ \) due to the high energy requirement of N-fixation.

Fe is thought to be the most important overall control on N-fixation. Fe has been shown to limit *Trichodesmium* N-fixation under field conditions [Paerl et al., 1994]. This limitation is due to the large Fe requirement of the nitrogenase enzyme, which fixes \( \text{N}_2 \) in diazotrophs [Sanudo-Wilhelmy et al., 2001]. In the open ocean, Fe is supplied both through upwelling and mixing from the deep ocean and by atmospheric dust deposition. For instance, the atmospheric transport of Saharan dust has been shown to be a major source of dissolved Fe to the tropical North Atlantic [Gao et al., 2001], promoting N-fixation [Mills et al., 2004]. Model studies have also shown that atmospheric Fe deposition is important for N-fixation in the Pacific Ocean [Somes et al., 2010a].

The fundamental sensitivity of N-fixers to the availability of Fe confers a great significance of N-fixation over geological time-scales (Falkowski [1997]; Broecker and Henderson [1998]). Marine sediment and ice core data both suggest that atmospheric deposition of iron-rich dust was 2 to 20 times higher during the last glacial maximum (LGM) than it is currently (compilation in Mahowald et al. [1999]). These changes in dust deposition appear to be caused by changes in the total global desert source area and atmospheric transport patterns. Changes in the deposition of iron-rich dust would have played a key role in the oceanic storage of C, since Fe could have selected for N-fixing microorganisms and ultimately served to decouple the otherwise linked C-N-P cycles, and hence might ultimately have altered the sequestration of atmospheric \( \text{CO}_2 \) (section 1.3.3).

After Fe, P is probably the most important control on N-fixation. Mills et al. [2004] reported experiments that indicate that N-fixation is co-limited by Fe and P in the North Atlantic. Hynes et al. [2009] reported that *Trichodesmium* are more P-limited in this basin, but Fe-limited in the North Pacific. Nevertheless, the potential control of P availability on N-fixation has not been extensively investigated. The distribution of *Trichodesmium* appears well constrained
by water temperature [Capone et al., 1997]. However, since temperature and \( \text{NO}_3^- \) are negatively correlated in the marine environment, it is not certain whether the distribution of \textit{Trichodesmium} is a consequence of an inhibition of nitrogenase by low temperature or whether it is due to selection against N-fixers under conditions of high \( \text{NO}_3^- \) concentrations.

To summarize, several environmental factors may influence N-fixers: Fe bioavailability, changes in the N:P ratio, atmospheric \( \text{CO}_2 \) concentration, and water temperature. The primary limiting factor for \textit{Trichodesmium} can differ from region to region. \textit{Trichodesmium} are more P limited in the North Atlantic compared to the North Pacific or waters along North Australia, while Fe could potentially control N-fixation in the Pacific Ocean [Sohm et al., 2008, 2011].

### Largest rate of N-fixation in the Atlantic or Pacific Ocean?

The North Atlantic has long been recognized as a major region of N-fixation. This was an implication of the limiting factors of diazotrophs, especially of \textit{Trichodesmium}. Extensive and frequent observations of the diazotroph \textit{Trichodesmium} (e.g. Carpenter and Price [1977];

<table>
<thead>
<tr>
<th>Author</th>
<th>Atlantic</th>
<th>Indian</th>
<th>Pacific</th>
<th>Others</th>
<th>Method</th>
</tr>
</thead>
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<td>Capone et al. [2005]</td>
<td>22 to 34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>direct measurements of N-fixation by \textit{Tricho}. scaled over ocean basin</td>
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<tr>
<td>Gruber and Sarmiento [1997]</td>
<td>28 (42)</td>
<td>~30</td>
<td>~50</td>
<td>-</td>
<td>integrated N*, N:P method</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N:P of 125:1 (of 40:1)</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>59 (\pm) 15</td>
<td>-</td>
<td>(N^*), mass balance</td>
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<tr>
<td>Deutsch et al. [2007]</td>
<td>20</td>
<td>22</td>
<td>95</td>
<td>-</td>
<td>(P^*)</td>
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<tr>
<td>Moore and Doney [2007]</td>
<td>14</td>
<td>27</td>
<td>19</td>
<td>-</td>
<td>CCSM-BEC model w/o benthic denitrification analyses of N isotopes</td>
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<td></td>
<td>-</td>
<td>-</td>
<td>box model; restoring approach (Pl)</td>
</tr>
<tr>
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<td>52 to 117</td>
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<tr>
<td>Eugster</td>
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<td>-</td>
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**Table 1.1** Basin-scale estimates of pre-industrial and modern rates of N-fixation based on various direct, geochemical, and modeling approaches \((P^* = P_{\text{O}_4}^{3-} - \text{NO}_3^-/16, \text{Pl: pre-industrial, Tricho: Trichodesmium})\). Fluxes in TgNyr\(^{-1}\).
1.2. Current understanding of the marine N-cycle

Carpenter [1983]), as well as high in situ rates of N-fixation [Capone and Carpenter, 1982; Carpenter and Romans, 1991; Capone et al., 2005] solidified this view. Using the $N^*$ tracer and assuming a Redfield N:P ratio of 125:1 for diazotrophs, Gruber and Sarmiento [1997] estimated N-fixation to be 28 TgN yr$^{-1}$ in the North Atlantic (Tab. 1.1 and Fig. 1.4). A ratio of 40:1 would increase the rate to 40 TgN yr$^{-1}$. Low $\delta^{15}N$ values in the North Atlantic thermocline also suggest high rates of N-fixation since $\delta^{15}N$ of $NO_3^-$ provide a measure of the addition of $NO_3^-$ to the thermocline from the remineralization of newly fixed N (see chapter A in Appendix and Figs. A.1 and A.2 in Appendix). However, recent data analyses and modeling results argued for substantial N-fixation in the Pacific Ocean (about 100 TgN yr$^{-1}$) with areal rates approaching or exceeding those observed in the North Atlantic [Deutsch et al., 2001, 2007] (see Tab. 1.1). These high rates may be supported by the recent discovery of the large diversity of N-fixers, with unicellular diazotrophs that could be responsible for substantial N-fixation thriving under different environmental conditions [Zehr et al., 2001; Montoya et al., 2004; Moisander et al., 2010; Hamersley et al., 2011].

1.2.3 Denitrification

Denitrification is a microbially facilitated process in which $NO_3^-$ is used as the terminal electron acceptor and $N_2$ is ultimately produced through a series of intermediate N products (Fig. 1.2). During cellular respiration, a terminal electron acceptor is required to receive an electron. $O_2$ is the preferred electron acceptor. In oxygen-deficient environments, however, $NO_3^-$ is used as electron acceptor for the remineralization of organic matter. This microbially generated process of dissimilatory nitrate reduction is called denitrification (see Fig. 1.2, and review by Devol [2008]). Denitrification is carried out by heterotrophic bacteria and involves the sequential reduction of $NO_3^-$ to $NO_2^-$ and then nitric oxide ($NO$), $N_2O$ and finally to $N_2$. The potent greenhouse gas $N_2O$ is produced as an intermediate and as a terminal product and accumulates in the environment during denitrification. $N_2O$ production is one of the two ways in which denitrification influences atmospheric greenhouse gas concentrations and thus the Earth’s climate. The second way is through the consumption of $NO_3^-$, which modifies the fixed N inventory and hence affects the biological pump (see Fig. 1.1).

$O_2$ as the most important control on water column denitrification

One necessary requirement for denitrification appears to be low dissolved oxygen concentrations. The effect of oxygen on denitrification is usually described in terms of a threshold concentration below which denitrification is initiated. There has been considerable debate in the literature about the value of this threshold (e.g. Naqvi et al. [2008]). Most water column denitrification appears to occur in water with $O_2$ less than 2 $\mu$M, although it also takes place
Chapter 1. Introduction

Figure 1.3 Annual mean climatological $O_2$ [$\mu$M] from the World Ocean Atlas 2001 [Conkright et al., 2002].

Figure 1.4 $N^*$ computed on the basis of annual mean climatological $NO_3^-$ and $PO_4^{3-}$ from the World Ocean Atlas 2001 [Conkright et al., 2002] (metric defined as $N^* = NO_3^- - 16 PO_4^{3-} + 2.9$ mmol m$^{-3}$). Low/high $N^*$ is indicative of denitrification, N-fixation respectively.

In 5 $\mu$M $O_2$ waters, another threshold concentration which is also sometimes applied [Codispoti et al., 2001; Devol, 2008; Bulow et al., 2010]. Oxygen-deficient environments are found in the oxygen minimum zones (OMZs) of the water column and in marine sediments (see review on OMZ by Paulmier and Ruiz-Pino [2009]).
1.2. Current understanding of the marine N-cycle

Distinct spatial distribution of water column and benthic denitrification

Denitrification occurs in both marine sediments and the water column, in the OMZs. There are three major OMZs in the global ocean, located in upwelling areas of the Arabian Sea (e.g. [Naqvi, 1987]), and of the Eastern Tropical North and the South Pacific (e.g. [Brandhorst, 1959]) (see Fig. 1.3). Additionally, since denitrification consumes N but no P, low $N^*$ anomalies are indicative of denitrification (see $N^*$ distribution in Fig. 1.4). When water column denitrification occurs, the residual $\text{NO}_3^-$ in the subsurface waters becomes progressively enriched in $\delta^{15}\text{NO}_3$ (see section A.3 in Appendix). Stable N isotopes are therefore indicative of regions of water column denitrification (see $\delta^{15}\text{NO}_3$ in the Arabian Sea and Eastern Tropical North and South Pacific in Fig. A.1 in Appendix). OMZs are located in the intermediate waters between $\sim$150 and 1000 m depth (see vertical $\delta^{15}\text{NO}_3$ profiles in Fig. A.2 in Appendix). The low $O_2$ levels are due to a combination of (i) high primary productivity resulting in elevated organic matter export, which drives waters to low $O_2$ concentration, and (ii) regional circulation patterns (sluggish ventilation) [Devol, 2008]. As a result of large-scale gyre circulation defining the locations of OMZs, it is assumed that the zones have not changed over the Quaternary.

In contrast to the localized water column denitrification zones, benthic denitrification is more uniformly distributed with highest rates in the organic matter rich sediments near continental margins [Christensen et al., 1987; Devol, 1991]. Middelburg et al. [1996] derived a meta-model, i.e., a regression-based model, that can reproduce benthic denitrification of a full diagenetic model originally developed by Soetaert et al. [1996]. They reported that sedimentation of labile organic C and bottom water concentrations of $O_2$ and $\text{NO}_3^-$ are the most important factors controlling benthic denitrification. Consequently, roughly one third of the estimated denitrification is located in continental shelf sediments.

Discrepancies between methods to estimate rates of water column denitrification

Water column denitrification rates are determined via various methods: measurements of the enzymatic activity of the electron transport system (e.g. Codispoti and Packard [1980]), measurements of the excess $N_2$ production from $N_2$-to-argon ratio (e.g. Emerson et al. [1991], Codispoti et al. [2001], Devol et al. [2006]), methods based on stoichiometric relationships (based on the Redfield ratio, e.g. $N^*$ tracer, [Gruber and Sarmiento, 1997; Deutsch et al., 2001]), or on the basis of the N isotopes ratios of $\text{NO}_3^-$ in incubation experiments (e.g. [Devol et al., 2006]).

The $N_2$-argon method is based on the fact that there is no significant sink of $N_2$ in the ocean interior, that the only $N_2$ source is denitrification and consequently that the $N_2$ excess of the
background is assumed to represent the amount of denitrification. The method was first described by Emerson et al. [1991] and has become a common method to estimate water column denitrification (e.g. Codispoti et al. [2001], Devol et al. [2006], Chang et al. [2010]). Gruber recently questioned the applicability of this method for estimating denitrification in light of the high denitrification estimates by Codispoti et al. [2001] derived from \(N_2\)-argon ratios. It is known indeed that the \(N_2\)-argon method gives higher denitrification rates than rates estimated based on canonical stoichiometry [Codispoti et al., 2001; Devol et al., 2006].

Water column denitrification rates have traditionally been estimated by calculating the \(NO_3^-\) deficit \((N^*)\) in a parcel of OMZ. This approach has the advantage of integrating denitrification rates over time and space, but depends on the N:P ratio of remineralized organic matter. In contrast to the \(N_2\)-argon method, the \(N^*\)-based estimates may yield artificially low estimates of water column denitrification due to several factors: oxidation of the \(NH_4^+\) regenerated during water column denitrification, denitrification fueled by non-Redfieldian organic matter, and contributions from benthic processes [Devol et al., 2006; Mooy et al., 2002].

Different methods have been developed for determining rates of benthic denitrification, for instance: the acetylene inhibition technique [Sorensen, 1978], measurement of \(NO_3^-\) disappearance [Yu et al., 2008], direct measurement of \(N_2\) production [Seitzinger et al., 1980], and \(^{15}N\)-pairing technique (e.g. Nielsen [1992] and review by Steingruber et al. [2001]). The global rate of benthic denitrification can also be constrained by the mean ocean \(\delta^{15}N\) of \(NO_3^-\), and the fact that water column denitrification strongly fractionates while benthic denitrification hardly fractionates (see use of this method in chapter 2 and section A.3 in Appendix). Each method has its own advantages and disadvantages. For instance, the \(NO_3^-\) disappearance method can overestimate the rate of benthic denitrification because \(NO_3^-\) may not only be denitrified but also reduced to ammonia or assimilated (e.g. [Steingruber et al., 2001]). Direct measurement of \(N_2\) production has the advantage to include coupled nitrification-denitrification but requires a very sensitive analysis because of the small \(N_2\) production compared to the background concentration of \(N_2\).

**Global rate of denitrification of 150 or 450 TgN yr\(^{-1}\)?**

Globally, OMZs are estimated to be responsible for 30 to 50% of N loss from the world’s oceans [Gruber and Sarmiento, 1997; Codispoti et al., 2001]. Published estimates of rates of water column denitrification in the Arabian Sea range from 0.1 to 44 TgN yr\(^{-1}\) making this the largest permanent OMZ [Naqvi, 1987; Howell et al., 1997; Codispoti et al., 2001]. A more recent study by Devol et al. [2006] based on \(^{15}N\) incubation techniques found rates of denitrification of 41 ± 18 TgN yr\(^{-1}\). The Eastern Tropical North and South Pacific are the two other major OMZs where denitrification is important. Using the \(N^*\) tracer, Deutsch et al.
1.2. Current understanding of the marine N-cycle

Table 1.2 Basin-scale estimates of pre-industrial and modern rates of benthic denitrification based on various geochemical and direct approaches (PI: pre-industrial). Fluxes in TgN yr$^{-1}$.

[2001] estimated a rate of water column denitrification of $48 \pm 5$ TgN yr$^{-1}$ in these two OMZs. Most literature estimates of the global rate of water column denitrification are between 60 and 80 TgN yr$^{-1}$, with the exception of the rate of Codispoti et al. [2001] (see rates and references in Tab. 1.3 and discussion in chapter 2).

Few studies have attempted to estimate the basin-scale and global rates of benthic denitrification, either on the basis of in situ measurements extrapolated to the global domain, or using modeling approaches (Tabs. 1.2 and 1.3). In the early 1990s, the rate of benthic denitrification was assumed to be on the order of 100 TgN yr$^{-1}$ [Gruber and Sarmiento, 1997]. Then, Middelburg et al. [1996] estimated a rate of 220 to 280 TgN yr$^{-1}$ for the global ocean using a metamodel. This higher global rate than previous literature estimates was due to an upward revision of benthic denitrification rates in deep sea sediments. A couple of years later, Codispoti et al. [2001] found a slightly higher rate of about 300 TgN yr$^{-1}$ on the basis of the benthic-to-water column denitrification ratio (see use of this method in chapter 2). It has been suggested that Codispoti et al. [2001] estimates might be overestimated through the use of a too large benthic-to-water column denitrification ratio, and that some high rates may be partly due to anthropogenic influences. The rate of benthic denitrification would be smaller than Codispoti et al. [2001] estimates if a weaker benthic-to-water column denitrification ratio was adopted. There is good evidence that the adopted ratio was too high since it did not take into consideration the strong dilution effect of water column denitrification introduced by Deutsch et al. [2004]. Considering the dilution effect decreases this ratio and thus reduces the estimate of the rate of benthic denitrification. Another argument that would support the hypothesis that Codispoti et al. [2001] benthic denitrification rates are overestimated is based on anthropogenic influences. Their rates could partly reflect the ongoing anthropogenic perturbation, since this perturbation has only appeared in the last few decades, the
isotopic signal has not yet had time to propagate throughout the ocean. These arguments, therefore, suggest that the global rate of benthic denitrification is less than 300 TgN yr\(^{-1}\), although the global rate of this sink of N remains one of the most poorly quantified terms in the present-day marine N budget.

**Another sink as dominant N loss?**

Our knowledge about denitrification has been expanded significantly with the discovery of new processes such as anammox (Anaerobic Ammonium Oxidation) (see Fig. 1.2, Mulder et al. [1995], Strous et al. [1999] and review by Lam and Kuypers [2011]). Water column and benthic denitrification have traditionally been considered as the two processes removing most fixed N from the marine environment. Recent findings have challenged this view as anammox appears to be widespread in many oxygen deficient zones, in marine sediments [Thamdrup and Dalsgaard, 2002], and within the water column [Kuypers et al., 2003; Dalsgaard et al., 2003; Lam et al., 2009]. Anammox requires \(\text{NH}_4^+\), \(\text{NO}_2^-\), and oxygen depleted water. This sink has been found to be closely coupled to the reduction of \(\text{NO}_3^-\) to \(\text{NO}_2^-\) and a new process termed Dissimilatory Nitrate Reduction to Ammonium (DNRA) has been suggested to provide the necessary \(\text{NH}_4^+\) for anammox [Lam et al., 2009] (Fig. 1.2). Anammox has been discovered using stable-isotope pairing techniques [Thamdrup and Dalsgaard, 2002] that can distinguish between this process and denitrification and give independent estimates of both. This technique has revealed that anammox is the dominant pathway removing fixed N in the Eastern Tropical South Pacific [Thamdrup et al., 2006], while denitrification plays a major role in the Arabian Sea [Ward et al., 2009]. It seems safe to assume that Anammox occurs and is a non-negligible sink of fixed N, although its amplitude has not yet been determined.

**1.2.4 Source-sink coupling**

Historically, it was believed that N-fixation and denitrification were spatially separated from each other and that the rates of these processes were coupled only over decadal to centennial time-scales, typical for the large-scale ocean circulation [Gruber and Sarmiento, 1997]. This view was based largely on the observation that surface waters in the tropical and subtropical North Atlantic appear to support high rates of N-fixation [Michaels et al., 1996; Gruber and Sarmiento, 1997; Capone et al., 2005], while most of the denitrification occurs in the OMZs of the Indian and Pacific Oceans [Deutsch et al., 2001] (see sections 1.2.2 and 1.2.3). This makes the Atlantic Ocean a net source of fixed N, while the Indian and Pacific Oceans act as net sinks, requiring ocean circulation to balance the basin-scale budgets. This old picture that primary sites of N-fixation and denitrification are spatially decoupled would
allow transient imbalances in N input and output terms. However, modeling efforts have revealed that N-fixation is intimately associated, both geographically and temporally, with the N-deficient waters emanating from denitrification zones in the Indian and Pacific Oceans [Deutsch et al., 2007]. This closer source-sink coupling results from the new picture of larger N-fixation rates in the Pacific Ocean and would promote a rather stable N-cycle as a result of negative feedback mechanisms.

1.2.5 Negative feedbacks stabilizing the N-cycle

N-fixation and denitrification react to each other through two negative feedbacks involving changes in the N inventory (these feedbacks are discussed in detail in chapter 3). The first feedback involves diazotrophic organisms. Diazotrophs out-compete other phytoplankton when the N:P ratio is low (see section 1.2.2) [Niemi, 1979; Karl et al., 2002]. When the N:P ratio decreases, N-fixation increases and thus the amount of newly fixed N released by N-fixers increases. Hence, the N:P ratio raises and the competitive advantage of N-fixers is slowly removed. N-fixation is discouraged since non-fixing phytoplankton are again dominant. Haug et al. [1998] first reported evidence of such a feedback. The second feedback is based on denitrification [Codispoti, 1989]. An increase in the rate of denitrification implies a decrease in the N:P ratio transported to surface waters. This lowering of the N:P ratio in surface water implies smaller export production and thus lower oxygen demand in the ocean. In the end, the change in the oxygen demand impacts the rate of denitrification. As a result, denitrification is indirectly controlled by changes in the N inventory. The fact that the N-cycle could be in an approximate balance, while N-fixation and denitrification rates are controlled by different processes (see sections 1.2.2 and 1.2.3), is a consequence of these negative feedbacks that couple these sources and sinks of N.

The existence of a transient, imbalanced, N-cycle depends on the sensitivities of the stabilizing feedbacks. Assuming the old picture of decoupled N-fixation/denitrification regions (see section 1.2.4), changes in the rates of N-fixation (denitrification) due to external perturbations, i.e., climate forcings, will not start to be compensated by changes in rates of denitrification (N-fixation) before the signal of the perturbation (in the form of an altered N:P ratio) is transported by the intermediate water circulation to denitrification (N-fixation) regions. Once the signal of changes in N-fixation (denitrification) has reached denitrification (N-fixation) regions, this sink (source) of N will react depending on its sensitivity to the change in N:P ratio. The sensitivities of the feedbacks associated with N-fixation and denitrification in the water column and sediment are not well known. Deutsch et al. [2004] examined the degree of coupling between N-fixation and denitrification across the last deglaciation and concluded that the sensitivities of the feedbacks might be strong. Strong sensitivities of the feedbacks imply that it is very unlikely that the N-cycle may reach a state far from a steady-state since
a strong imbalance between sources and sinks of N cannot exist.

1.2.6 Was the pre-industrial marine N inventory balanced?

The large spread of estimates of the source and sink terms of fixed N led to distinctly diverging views on whether the marine N budget is balanced. In the evaluation of the budget, the major sources of uncertainty are the rates of N-fixation and denitrification in the water column and sediment, while small uncertainties are associated with river input and atmospheric deposition of N, since these external inputs of N are relatively well constrained. Gruber [2004] estimated that the N budget is in approximate balance, whereas Codispoti [2007] concluded that the N-cycle is in severe deficit due to much larger sinks than sources (Tab. 1.3). In the latter study, measurements of N removal processes averaged over the entire ocean appear to exceed measurements of N-fixation rates and other inputs by $\sim 200 \text{TgN yr}^{-1}$. It has been suggested that this strong imbalance may result from the fact that we are not going to the right places to measure rates of N-fixation. This means that the apparent imbalance would be a consequence of sparse sampling and the low number of measurements, rather than an indication that the ocean is losing N. Conversely, Gruber [2004] estimate of a cycle in approximate balance is a consequence of lower denitrification rates, especially in the water column.

While there is a priori no reason to expect the N-cycle to be in equilibrium, sediment $\delta^{15}\text{N}$ records and past atmospheric CO$_2$ favor a near-balanced N budget over the pre-industrial time-period. Sensitivity investigations show that the $\delta^{15}\text{N}$ of deep ocean NO$_3^-$ has remained constant over the last 10 kyr (Fig. 1.5G) [Kienast, 2000]. In addition, the atmospheric CO$_2$ level did not vary over the last thousand years before the Anthropocene (absence of atmospheric CO$_2$ variations above $\sim 10$ ppm over the last 10 kyr [Indermühle et al., 1999], see Fig. 1.5D). If the pre-industrial cycle was in a strong imbalance, this would have left an imprint in the $\delta^{15}\text{N}$ signal of organic matter stored in marine sediments (see section A.5 in Appendix), the same way glacial-interglacial variations in sources and sinks are recorded. Additionally, since changes in denitrification/N-fixation may be counteracted by changes in N-fixation/denitrification according to stabilizing feedbacks (see section 1.2.5), there is little evidence that would support that the pre-industrial N budget was out of balance.

The key question at this point is whether the apparent imbalance in sources and sinks suggested by some authors is real or whether it is due to under/over-estimation of sources/sinks (Tab. 1.3). Since sediment $\delta^{15}\text{N}$ and the atmospheric CO$_2$ level are indeed reporting a nearly balanced pre-industrial N budget, it is possible that these studies either underestimated the sources of N or overestimated the sinks. Given the previously discussed argumentations on the limitation of extrapolating direct measurements of N-fixation and denitrification in time
### Table 1.3

Non-exhaustive compilation of global pre-industrial and modern estimates of sources and sinks of N in the marine environment (not impl. = not implemented, $P^*$ is defined as $P^* = PO_3^-_{3} - NO_3^- / 16$, PI: pre-industrial). Galloway et al. [2004]: river input of N to coastal areas.

<table>
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<td>-</td>
<td>65</td>
<td>not impl.</td>
</tr>
<tr>
<td>Somes et al. [2010b]</td>
<td>-4</td>
<td>67</td>
<td>38</td>
<td>not impl.</td>
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<td></td>
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<tr>
<td>Gruber [2004]</td>
<td>-10</td>
<td>65 ± 20</td>
<td>180 ± 50</td>
<td>25 ± 10</td>
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<tr>
<td>Middelburg et al. [1996]</td>
<td></td>
<td>-</td>
<td>230 to 285</td>
<td>-</td>
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<tr>
<td>Codispoti et al. [2001]</td>
<td>-187</td>
<td>150</td>
<td>300</td>
<td>25</td>
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<tr>
<td>Christensen et al. [1987]</td>
<td></td>
<td>-</td>
<td>75</td>
<td>200 to 280</td>
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<td>50 to 75</td>
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<tr>
<td>Eugster and Gruber [in prep]</td>
<td>-24 to 52</td>
<td>39 to 66</td>
<td>56 to 108</td>
<td>14 (fixed)</td>
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<td>(see chapter 2)</td>
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<tr>
<td>Eugster (see chapter 4)</td>
<td>-20</td>
<td>30</td>
<td>85</td>
<td>not impl.</td>
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</table>

Table 1.3: Non-exhaustive compilation of global pre-industrial and modern estimates of sources and sinks of N in the marine environment (not impl. = not implemented, $P^*$ is defined as $P^* = PO_3^-_{3} - NO_3^- / 16$, PI: pre-industrial). Galloway et al. [2004]: river input of N to coastal areas.
and space, geochemical methods based on $N^*$ and stable N isotope of $\text{NO}_3^-$ (see sections 1.2.2 and 1.2.3) would allow for a finer calculation of these integrated terms. In addition, since geochemical investigations are only as reliable as the dataset used, a better characterization of the uncertainties associated with estimating the rates of the sources and sinks of N would help address the question as to the state of the pre-industrial N budget with more confidence.

1.3 Current understanding of the marine N-cycle across the last glacial termination

1.3.1 Past climate, atmosphere, and oceanic environments

Ice core: natural recorder of climate and climate change

Ice cores from Antarctica and Greenland are extensively used to reconstruct the climate of the Earth in the past. The air bubbles of ancient atmospheric gas trapped in ice contain an abundance of information on past climate. Past atmospheric $\text{CO}_2$, $\text{N}_2\text{O}$, and methane ($\text{CH}_4$) (the three dominant greenhouse gases), variations in local temperature, and variations in atmospheric dust deposition are commonly reconstructed [Petit et al., 1999; Spahni et al., 2005; Schilt et al., 2010a]. In the 1990s, the Vostok ice core record in Antarctica with a length of 3,310 m extended to as far as 400 kyr before present (BP) [Petit et al., 1999]. A couple of years later, the EPICA Dome C ice core pushed the limit up to 800 kyrBP [Luethi et al., 2008].

Cyclic oscillation in climate over the last 800 kyr

Over the last 800 kyr, ice cores recorded eight glacial-interglacial cycles [Petit et al., 1999; Luethi et al., 2008]. They show remarkable degrees of correspondence between temperature and atmospheric $\text{CO}_2$ and $\text{N}_2\text{O}$ [Flückiger et al., 1999], with lower values of all gases during glacial compared to interglacial periods. The last glacial period began 110 kyrBP and culminated with the LGM, i.e., the time of the maximum ice sheet extent during the last glaciation, approximately 20 kyrBP. The LGM was followed by the transition to the Holocene, that is the current interglacial period, which covered the last 10 kyr (see timeseries of climatic properties across the last glacial termination in Fig. 1.5).

Nowadays, it is well established that cyclic variations of the Earth’s orbit, known as $M$-
Figure 1.5  See next page for caption
Figure 1.5  Time-series of several properties across the last glacial termination (figure adapted from Gruber [2004], see therein for references, δ^{15}N Arabian Sea from Altabet et al. [2002] and δ^{15}N from the South China Sea from Kienast [2000]). (A) δ^{18}O of ice (temperature proxy) from GRIP Greenland, and (B) from Dome C Antarctica. (C) Antarctic dust flux reconstructed from the sea-salt corrected Ca^{2+} and the accumulation rate. (D) Atmospheric CO_{2} and (E) N_{2}O recorded in air bubbles from various ice cores from Antarctica and Greenland. (F) Sediment δ^{15}N records from the Arabian Sea and (G) the South China Sea. The grey zone depicts the last glacial period, the vertical band the last glacial maximum (LGM), and the white zone the current interglacial period (Holocene).

lankovitch cycles, are the primary trigger of glacial-interglacial oscillations [Hays et al., 1976]. These variations are linked through strong feedbacks to the observed temperature and greenhouse gas variations in the Earth’s atmosphere. However, understanding how the climate system responds to initial orbital forcing is still an important issue. In particular, we remain quite ignorant of the mechanisms responsible for the glacial-interglacial CO_{2} fluctuations. One central challenge is to develop a mechanistic understanding of these feedbacks so as to resolve the intricate earth-climate-oceanic system in that time-scale.

1.3.2 The 100 ppm challenge

The atmospheric CO_{2} level increased from roughly 180 to 280 ppm across the last glacial termination (see variation across the last deglaciation in Fig. 1.5D). In spite of the clear importance of CO_{2} as a greenhouse gas, changes of this magnitude might have amplified and thus played a significant role in the energetics of glacial-interglacial cycles. However, the causes responsible for the 100 ppm atmospheric CO_{2} increase are unknown. A good starting point is to put an emphasis on the last glacial termination because most of the paleo records/data are available, with high resolution, for this deglaciation period.

Plenty of candidates have been suggested

It has been argued that a substantial fraction of the 100 ppm decrease in the atmospheric CO_{2} level between the Holocene and last glacial period was sequestered in the ocean. This reservoir is the best candidate, even though the mechanisms that would have been involved remain elusive. Physical mechanisms as well as changes in marine biology are often invoked as potential mechanisms to lower glacial atmospheric CO_{2} [Archer et al., 2000]. Physical mechanisms include, among others:

- lower wind-driven upwelling in the Antarctic and stronger salinity-driven stratification in this region which could have lowered the rate of nutrient and CO_{2} transport to the surface [Francois et al., 1997; Sigman and Boyle, 2000],
1.3. Current understanding of the N-cycle across the last deglaciation

- reduced ventilation of C-rich deep water because of sea-ice cover [Stephens and Keeling, 2000],
- and changes in the location of deep water formation [Toggweiler et al., 2003].

Among the various biologically-based explanations that have been put forward, several generate changes in oceanic C sequestration because of:

- changes in the nutrient content or variations in the N:P ratio [Broecker, 1982a], or shift in C:N ratios of primary producers [Archer et al., 2000],
- Fe fertilization of new productivity from atmospheric dust deposition [Martin, 1990] (see proxy for past dust deposition in Fig. 1.5C),
- shifts in the plankton types [Archer and Maierreimer, 1994],
- higher efficiency of the biological pump south of the modern Polar Front, i.e., increase in the \( \text{NO}_3^- \) utilization [Francois et al., 1997] (see section 1.1 and Fig. 1.1).

Sarmiento and Gruber [2006] and Sigman et al. [2010] reviewed many of these hypotheses and concluded that physical and biogeochemical mechanisms related to Southern Ocean changes are at the forefront of the candidates for regulating the atmospheric CO\(_2\) on glacial-interglacial time-scales.

The emergence of the marine N-cycle as a candidate

A “tempting” mechanism to explain the glacial drawdown in the level of atmospheric CO\(_2\) is the strengthening of the biological pump as a consequence of a larger reservoir of nutrients. A larger glacial inventory of N would have changed the magnitude and spatial pattern of oceanic production, with a strengthening of the biological pump, especially at low latitudes where fixed N is currently depleted. This would have led to an increase in the pool of inorganic C stored in the deep ocean, and would therefore have permitted lower atmospheric CO\(_2\) [Broecker, 1982b; McElroy, 1983; Falkowski, 1997; Broecker and Henderson, 1998]. A strong argument for significant past changes in the N inventory comes from its short residence time of 2 to 4 kyr [Gruber and Sarmiento, 1997; Eugster and Gruber, in prep] relative to the timescale of deglaciation (~10 kyr).

A larger glacial N inventory is suggested by many authors [McElroy, 1983; Altabet et al., 1995; Falkowski, 1997; Ganeshram et al., 2002]. McElroy [1983] first made the proposition that climate may influence the marine N-cycle. Thunell et al. [2004] argued that the N pool was 30 to 50% larger than today. A 50% larger glacial N inventory would cause a 80 ppm
decrease in the level of atmospheric CO$_2$ [Archer et al., 2000; Sigman and Boyle, 2000]. This in turn implies that a glacial-Holocene change in the marine N inventory could be one of the best candidates to resolve the 100 ppm challenge. Although the change in the inventory is not well quantified, all studies suggest a larger glacial inventory albeit with different mechanistic explanations invoked.

Glacial-Holocene changes in the N inventory depend on the magnitude and timing of changes in sources and sinks of fixed N. Throughout this time period, the dominant sources and sinks of fixed N have been N-fixation and denitrification, and hence it is assumed that it is mainly changes in the magnitude of rates of these sources and sinks that have determined the change in size of the N inventory. The magnitude of change in the N inventory is controlled by the magnitude and duration of imbalance between sources and sinks of fixed N during the deglaciation. Both magnitude and duration of the imbalance between sources and sinks of N depend on the strengths of the climate forcings and on the sensitivities of the stabilizing feedbacks (see sections 1.2.4 and 1.2.5).

### 1.3.3 An intricate N-Cycle across the last deglaciation

In this section, I define and discuss four scenarios with an increase or a decrease of either N-fixation or denitrification, due to a climate forcing, across the last glacial termination (scenarios are depicted in sketches of Fig. 1.6). For each scenario, I try to assign one of the following three climate forcings as having affected N-fixation or denitrification (these forcings are explained in detail in the next sections):

- variation in deposition of iron-rich dust, which affects the rate of N-fixation because of the sensitivity of N-fixers to the availability of Fe (see section 1.2.2),
- changes in suboxia, which affects water column denitrification since denitrification is controlled by the O$_2$ concentration (see section 1.2.3), or
- change in sea-level, which affects benthic denitrification due to the fact that the sea-level controls the flooding of sediments in shallow continental shelves where intense denitrification occurs.

It is assumed that the climate forcing disrupts a balanced glacial marine N-cycle and forces the N-cycle into an imbalance. The source or sink of N, which is perturbed by the climate forcing, starts first to decrease or increase and is considered as the “leader” across the deglaciation. The N-cycle will end up in a new equilibrium given the negative feedbacks that tend to stabilize the N-cycle (see section 1.2.5). The sign of the glacial-Holocene change in the global inventory of N depends on whether N sources exceed or are exceeded by N
1.3. Current understanding of the N-cycle across the last deglaciation

sinks during the transition. I discuss the current hypotheses found in the literature and the supporting paleoceanographic evidence that would support each scenario.

Lower glacial rates of water column and benthic denitrification

The first scenario invokes an increase in water column denitrification across the last deglaciation due to a climate forcing (scenario D- in Fig. 1.6). Lower glacial rates of water column denitrification were demonstrated for the three major OMZs: the Arabian Sea [Altabet et al., 1995, 1999a], the Eastern Tropical North Pacific [Ganeshram et al., 2002] and the Eastern Tropical South Pacific [Pol-Holz et al., 2006]. A compilation of sediment $\delta^{15}$N records show coherent characteristics over the past, with low $\delta^{15}$N during interglacial periods (see sections A.3 and A.5 in Appendix, and sediment $\delta^{15}$N records from the Arabian Sea in Fig. 1.5F). Low $\delta^{15}$N is interpreted as evidence of reduced water column denitrification. Besides $\delta^{15}$N evidence, other paleoceanographic evidence confirms that thermocline suboxia was expanded during high $\delta^{15}$N periods in the Santa Barbara basin in the North Pacific [Kennett and Ingram, 1995]. In addition, reconstruction of past atmospheric $N_2O$ shows an abrupt increase by $\sim 16$ kyrBP (Fig. 1.5E). This increase is interpreted as a consequence of changes in the marine $N_2O$ production which likely involves mechanisms occurring at low $O_2$ concentration, i.e., nitrification and water column denitrification [Gruber, 2004]. Various candidates can explain a change in the rate of water column denitrification across the last deglaciation. They all invoke expansion or strengthening of the OMZs. The extent of the OMZs can be altered by changing the export rate of organic matter to the subsurface [Altabet et al., 1995; Ganeshram et al., 2000], or by changing the ocean circulation and ocean temperature resulting in changes in the physical supply of $O_2$ [Galbraith et al., 2004; Meissner et al., 2005]. Altabet et al. [1995] and Ganeshram et al. [2000] proposed that variations in the extent and intensity of the Arabian Sea OMZ may be controlled by changes in upwelling that stimulate the production and export flux of organic matter which leads to a change in the remineralization rates and to the drawdown of $O_2$. Instead of changes in the $O_2$ consumption, changes in the $O_2$ supply would also affect the extent of OMZs and thus control water column denitrification. In the past, $O_2$ flux input varied due to higher solubility as a result of lower glacial sea surface temperature and enhanced rate of ventilation in the 200 - 1000 m depth range. This was due to stronger winds in high latitudes [Broecker and Peng, 1982; Galbraith et al., 2004; Meissner et al., 2005]. In this scenario, changes in suboxia increase the global rate of water column denitrification, which implies a decrease in the global inventory of N across the last deglaciation.

Instead of an increase in water column denitrification, benthic denitrification may have increased across the last deglaciation due to a climate forcing (scenario D- in Fig. 1.6). A lower global rate of benthic denitrification during glacial periods was suggested by Chris-
Chapter 1. Introduction

**SCENARIO**

**D**
- denitrification leads
- smaller global rate of denitrification during the last glacial period

**D+**
- denitrification leads
- larger global rate of denitrification during the last glacial period

**F**
- N-fixation leads
- smaller global rate of N-fixation during the last glacial period

**F+**
- N-fixation leads
- larger global rate of N-fixation during the last glacial period

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**Figure 1.6** Four scenarios of the evolution of the global rates of N-fixation and denitrification across the last glacial termination. *(D−)* lower glacial rate of denitrification (lower water column denitrification: e.g. Ganeshram et al. [2000], Altabet et al. [2002]; lower N-fixation as a consequence of lower water column denitrification: e.g. Haug et al. [1998], Ren et al. [2009]; lower benthic denitrification: e.g. Christensen et al. [1987]), *(D+)* larger glacial rate of denitrification, *(F−)* lower glacial rate of N-fixation, and *(F+)* larger glacial rate of N-fixation (e.g. Falkowski [1997]; Broecker and Henderson [1998]). Glacial-Holocene change in the N inventory is a consequence of the transient imbalance between N-fixation and denitrification.
1.3. Current understanding of the N-cycle across the last deglaciation

tensen et al. [1987] and Christensen [1994]. At that time, sea-level was lower by up to 120 m, exposing much of the global shelf area where a large fraction of the benthic denitrification occurs. As a consequence, organic matter from highly productive coastal ecosystems would have settled through a greater height of water column, which implies that more organic matter would have been oxidized there instead of in marine sediments. One would expect, therefore, that the lower glacial sea-level would have significantly reduced benthic denitrification. This potential forcing on benthic denitrification results in a decrease in the global inventory of N across the last deglaciation.

The second scenario invokes a decrease in either water column or benthic denitrification across the last deglaciation due to a climate forcing (scenario D+ in Fig. 1.6). This scenario is not supported by any lines of evidence. For example, sediment $\delta^{15}N$ records from OMZ do not promote higher glacial rates of water column denitrification (see $\delta^{15}N$ records from the Arabian Sea in Fig. 1.5F). In conclusion, established climate forcing affecting denitrification in the water column and sediment as well as paleoceanographic evidence promote lower rates of denitrification in the water column and sediment during the last glacial period.

Larger or reduced glacial rate of N-fixation?

The third scenario invokes a decrease in N-fixation across the last deglaciation due to a climate forcing (scenario F+ in Fig. 1.6). This scenario corresponds to the hypothesis of Falkowski [1997] of larger global rate of N-fixation during the last glacial period due to larger atmospheric deposition of iron-rich dust. A larger global deposition of iron-rich dust would have increased the rate of N-fixation due to the high Fe requirement of diazotroph organisms (see section 1.2.2). Glacial atmospheric dust deposition has been demonstrated to be larger than at present not only according to ice cores [Petit et al., 1999] (Fig. 1.5C) but also to several marine sediment cores (see Kohfeld et al. [2005] SOM and references therein). Three factors have been invoked to explain the higher atmospheric dust loadings and dust deposition rates during glacials: increased wind speeds, a reduced intensity of the hydrological cycle, and the expansion of dust source areas [Harrison et al., 2001]. This hypothesis was promoted by comparing reconstruction of the past level of atmospheric $CO_2$ with records of past rates of dust deposition [Broecker and Henderson, 1998]. In this scenario, the decrease in atmospheric deposition of iron-rich dust implies a decrease in the global rate of N-fixation, and hence a decrease in the N inventory across the last glacial termination.

The fourth scenario invokes an increase in N-fixation across the last deglaciation due to a climate forcing (scenario F- in Fig. 1.6). Since no established climate forcing could explain an increase in the global rate of N-fixation across the last deglaciation, this scenario has to be rejected. However, this does not mean that the global rate of N-fixation does not increase
across the transition.

The first scenario implies an increase in N-fixation across the last deglaciation as a consequence of an increase in the global rate of denitrification and an increase in N-fixation given negative N-feedback (scenario D- in Fig. 1.6). There is evidence for reduced glacial N-fixation from the Caribbean Sea and the Gulf of Mexico. Haug et al. [1998] reported high $\delta^{15}$N measurements at LGM that are best explained by lower rates of N-fixation in the Cariaco Basin. Other evidence comes from foraminifera test-bound $\delta^{15}$N measurements (see section A.5 in Appendix) from the Caribbean Sea [Ren et al., 2009] and from the Gulf of Mexico [Meckler et al., 2011], that are best interpreted by invoking reduced N-fixation rates in the glacial Atlantic Ocean. In this respect, lower glacial rates of N-fixation disprove the iron-rich dust hypothesis (scenario F+ in Fig. 1.6, and see above). In the first scenario (scenario D- in Fig. 1.6), it has been suggested that local or regional rates of N-fixation responded to changes in the oceanic N:P ratio driven by changes in the global rate of denitrification due to direct climate forcing (see discussion above) [Haug et al., 1998]. N-fixation rates would have reacted to readjust the N-cycle with a time lag and thus a transient imbalance with larger sinks of N than sources would have decreased the N inventory across the deglaciation. To summarize, the change in the global rate of N-fixation between the last glacial period and the Holocene remains elusive. The iron-rich dust hypothesis promotes higher rates of N-fixation, while sediment $\delta^{15}$N records from the Atlantic Ocean are interpreted as evidence of lower rates of N-fixation under glacial conditions.

Various climate forcing with specific strength and timing

The situation was likely more complicated than the scenarios described here, since this discussion oversimplifies the N-cycle across the last deglaciation. N-fixation and denitrification in the water column and sediment were affected by several climate forcings, i.e., variation in deposition in iron-rich dust, changes in suboxia and change in sea-level, with specific strength and timing.

Ultimately, the change in N inventory between the last glacial period and the Holocene depends on the temporal variability of N-fixation and denitrification in the water column and sediment over this time period. The variability of these sources and sinks of N depends not only on the strengths of climate forcings they are affected by, but also on the negative feedbacks (see section 1.2.5) that tend to stabilize the cycle and the N inventory. The stabilizing feedbacks tend to limit excursions in the N-cycle generated by the external climate forcings (see section 1.2.5). One of the few quantitative estimates of the change in the N inventory between the last glacial period and the Holocene demonstrated that the glacial inventory of N was no more than 30% larger than the Holocene [Deutsch et al., 2004]. However, this study
1.4 Objectives and structure of the thesis

The aims of this thesis are:

- to estimate the pre-industrial magnitude of rates of N-fixation and denitrification in the water column and sediment, to determine whether the global N budget is balanced or out of balance, and to quantify the magnitude of the associated uncertainties (see section 1.4.1),

- to investigate the dynamics of the marine N-cycle, i.e., the variations in N-fixation, denitrification, and inventories of N, with a particular emphasis on the changes in the global inventory of N across the last glacial termination (see section 1.4.2).

1.4.1 Do pre-industrial estimates of rates of N-fixation and denitrification yield a balanced marine N-cycle?

In the first part of this thesis, I determine and combine the pre-industrial rates and associated uncertainties of N-fixation and denitrification in the water column and sediment to assess whether the pre-industrial marine N-cycle was balanced (see chapter 2). A probabilistic geochemical box model approach is adopted which permits to infer, in an inverse manner, the global and basin-scale best estimate of the rates of sources and sinks of N and their uncertainties, mainly those coming from the poorly known ocean circulation and mixing fields.

This novel approach distinguishes itself by (i) fully characterizing the uncertainties associated with estimates of rates of N-fixation and denitrification in the water column and sediment, (ii)
evaluating the rates of N-fixation and denitrification in the water column and sediment simultaneously. The multi-basin box model is constrained by a large number of geochemical data (e.g. anomalies in the stoichiometric relationship of nutrients, i.e., $N^*$, and stable nitrogen isotopes). These tracers offer the advantage that they naturally integrate in space and time rates of N-fixation and denitrification, and hence offer the ability to overcome the under-sampling problem of approaches based on extrapolation of *in situ* measurements to infer integrated rates (see section 1.2.2).

1.4.2 How did the marine N-cycle, and particularly the N inventory, evolve across the last glacial termination?

In the second part of this thesis, I investigate the marine N-cycle across the last glacial termination (see chapter 3). Much emphasis is put on evaluating the change in the global inventory of N, so as to address the question of the potential implications of changes in the N inventory for the evolution of the atmospheric $CO_2$ level over this time-scale. Changes in the N inventory are attained by computing rates of N-fixation and denitrification in the water column and sediment across the transition using a geochemical box model constrained by sediment $\delta^{15}N$ records. The dynamics of the cycle is also examined, with special emphasis on variability of each source and sink term over this time-scale. Examining the glacial-Holocene changes in N-fixation settle the arguments between the iron hypothesis, i.e., higher rates of N-fixation under glacial conditions, and lower rates as suggested by downcore sediment $\delta^{15}N$ records and foraminifera test-bound $\delta^{15}N$ data.

For the first time a geochemical model, which incorporates climate forcings on N-fixation and denitrification, simulates $\delta^{15}N$ in different ocean basins. Four climate forcings are taken into consideration. Two different forcings on N-fixation are incorporated which involve changes in the deposition of iron-rich dust and atmospheric $CO_2$. A climate forcing on water column denitrification through changes in suboxia is implemented, as well as a climate forcing on benthic denitrification through variations in the sea-level. The model attempts to reconstruct at the same time sediment $\delta^{15}N$ records from several sites located in different ocean basins, i.e., in OMZs (Arabian Sea, and Eastern Tropical Pacific), in the South China Sea, and in the low-latitude Atlantic (Caribbean Sea and Gulf of Mexico). A Genetic Algorithm is adopted to solve the optimization of $\delta^{15}N$ records with regard to the strength of each climate forcing, and the sensitivities of the internal feedbacks that tend to stabilize the cycle.
1.4. Objectives and structure of the thesis

1.4.3 Exploring the marine N-cycle with the CCSM-BEC model

In the last part of this thesis, I describe the incorporation of a complex N isotope model as well as the formulation of benthic denitrification in the Biogeochemical Elemental Cycling (BEC) model embedded in the ocean component of the Community Climate System Model (CCSM), a three dimensional coupled climate model (see chapter 4). The long-term goal is to investigate the dynamics of the marine N-cycle on a finer scale than previously addressed with the geochemical box model. Stable N isotopes are for the first time implemented in such a complex multiple limiting nutrients ecosystem model which simulates various N pools. The strength of the CCSM compared to the geochemical box model is its spatial resolution, fine enough to take full advantage of available sediment $\delta^{15}$N records.

1.4.4 Structure of the manuscript

The present thesis is structured as follows. Global and basin-scale rates of N-fixation and denitrification in the water column and sediment are estimated with their associated uncertainties in a probabilistic way using a geochemical box model that has been developed for this purpose (chapter 2). A deglacial model is then included in the geochemical box model in order to simulate the dynamics of the N-cycle across the last deglaciation, with special emphasis on past changes in N inventories, N-fixation, water column and benthic denitrification, and on the sensitivities of the internal feedbacks (chapter 3). A more technical chapter presents the implementation of the N isotopes and the incorporation of a benthic denitrification metamodel in the BEC model embedded in the CCSM as well as first long equilibrium runs (chapter 4). In the end, I summarize the most important findings and provide an outlook (chapter 5).
Chapter 2

A Probabilistic Estimate of Global Marine N-fixation and Denitrification


Abstract

Current estimates of the global rates of marine N-fixation and denitrification diverge strongly, reflecting major limitations in our ability to constrain the oceanic fixed N budget. Here, we determine these rates and their associated uncertainties by combining marine geochemical and physical data with a new two-dimensional box model that captures the inter-basin distribution of N-fixation and denitrification. We estimate the uncertainties using a probabilistic approach on the basis of a suite of 2500 circulation configurations of this box model. N-fixation and denitrification are diagnosed in an inverse manner for each of these configurations using \( N^* \), \( P^* \), and the stable nitrogen isotope composition of nitrate as data constraints. Our approach yields a median water column denitrification rate of 51 TgN yr\(^{-1}\) (39 to 66 TgN yr\(^{-1}\), 5th to 95th percentile) and a median benthic denitrification rate of 81 TgN yr\(^{-1}\) (56 to 108 TgN yr\(^{-1}\)). The resulting benthic-to-water column denitrification ratio of 1.6 confirms the importance of the dilution effect proposed by Deutsch et al. [2004]. On the basis of two different approaches, we diagnose a global N-fixation rate of between 82 TgN yr\(^{-1}\) and 160 TgN yr\(^{-1}\), with a best estimate of 118 TgN yr\(^{-1}\) and 134 TgN yr\(^{-1}\) depending on the approach. Most of the N-fixation occurs in the Indian and Pacific suggesting a relative close spatial coupling between sources and sinks in the ocean. Our N-fixation and denitrification estimates plus updated estimates of atmospheric deposition and riverine input yield a pre-industrial marine N-cycle that is balanced to within 16 TgN yr\(^{-1}\) (-24 to 52 TgN yr\(^{-1}\)). Our budget implies a median residence time for fixed N of 4,500 yr (3,700 to 5,600 yr).
2.1 Introduction

Dinitrogen (N)-fixation and water column and benthic denitrification are the main source and sinks of biologically available nitrogen (fixed N) in the marine environment, yet estimates of the global rates of these processes differ widely (Tab. 2.1) (e.g., Gruber [2008]). These processes occur in distinct marine environments. Water column denitrification is confined to suboxic waters, located primarily in the Arabian Sea (e.g., Naqvi [1987]) and the Eastern Tropical Pacific (e.g., Brandhorst [1959]). Benthic denitrification occurs in most sediments of the world’s oceans, with highest rates found in regions of high organic matter sedimentation and low oxygen concentrations in the overlying waters, i.e., particularly in the sediments of the continental margins [Middelburg et al., 1996; Devol, 2008]. In contrast, N-fixation tends to be restricted to oligotrophic conditions as found in the warm surface waters of the low latitudes [Karl et al., 2002; Carpenter and Capone, 2008]. The spatio-temporal variability of these processes, the relative paucity of direct rate measurements, as well as the many methodological difficulties in measuring such biological rates have resulted in widely different direct assessments of denitrification and N-fixation (Tab. 2.1) (see also Mahaffey et al. [2005]). Geochemical approaches on the basis of the distribution of nutrients and nitrogen isotopes (e.g., Gruber and Sarmiento [1997]; Michaels et al. [1996], etc) have helped to overcome the sampling bias thanks to the tracer’s property of integrating the signal in time and space, but leave room for interpretation due to their indirect nature (e.g., Hansell et al. [2004]).

The large spread of estimates led to distinctly diverging views on whether the marine N budget is balanced. On the one hand, Codispoti et al. [2001] and Codispoti [2007] argued that the sinks of fixed N strongly exceed the sources (Tab. 2.1) causing the fixed N budget to be out of balance by several hundred TgNyr$^{-1}$ (1 Tg = $10^{12}$ g). On the other hand, Gruber and Sarmiento [1997] and later Gruber [2004] proposed a fixed marine N budget in approximate balance, albeit with considerable uncertainties. One hypothesis to explain this large discrepancy is that the different estimates reflect different time-periods. Codispoti et al. [2001] extrapolated a limited set of in-situ measurements of water column denitrification, and hence his budget may apply primarily to the present-day marine N-cycle. In contrast, the rate estimates used by Gruber and Sarmiento [1997] and Gruber [2004] were based on the large-scale interior ocean distribution of nutrients that may not have been subject to substantial modifications by humans, thus reflecting more the pre-industrial state [Codispoti, 2007]. Given the growing anthropogenic perturbation of the ocean N-cycle [Galloway et al., 2002, 2004; Gruber and Galloway, 2008], such as increasing denitrification due to the expansion of hypoxic zones from coastal eutrophication [Naqvi et al., 2000], enhanced fixed N supply through rivers [Seitzinger and Mayorga, 2008] and atmospheric deposition [Duce et al., 2008], the modern N-cycle may operate in a transient state characterized by a temporary
Table 2.1 Non-exhaustive literature compilation of pre-industrial or modern estimated sources and sinks in the global marine nitrogen budget. We give the median, and the 5th and 95th percentile range, computed across 2500 circulation configurations, for N-fixation and water column and benthic denitrification. Residence time computed on the basis of all N sinks. We show the conservative estimates of N-fixation and denitrification proposed by Galloway et al. [2004]. Our N-fixation rate from the restoring approach does not include N-fixation diagnosed in the Southern Ocean.
imbalance between sources and sinks.

In these discussions, relative little consideration has been given to the large uncertainties associated with the rate estimates. In most studies, no quantitative error assessment was conducted at all and thus no uncertainty estimate are usually provided. Gruber and Sarmiento [1997] and Gruber [2004] reported uncertainties with their global fixed N budgets, but these error estimates were largely based on subjective assessments rather than a thorough analysis of the sources of uncertainty and the propagation of these uncertainties to the global value. Therefore, the question of whether the fixed N budget of the ocean is balanced or not cannot be answered unless the errors associated with the individual source and sink terms are truly quantified.

Our study aims to address these open issues, i.e., i) magnitude of rates and ii) magnitude of the associated uncertainties, using a novel approach. To this end, we use a multi-basin geochemical model that we constrain with a large number of data, including anomalies in the nutrient distributions and information contained in the stable isotopic ratio of nitrate ($^{15}$NO$_3$). This permits us to infer, in an inverse manner, the global and regional rates of N-fixation and denitrification in the water column and sediments. We adopt a probabilistic approach to determine the uncertainties, primarily those coming from the ill known ocean circulation and mixing fields.

In the next section, we provide some additional background on the specific geochemical constraints that we will make use of in our study. After the method section, we first discuss our global-scale estimates of denitrification (section 2.4.1) and N-fixation (section 2.4.2), and then combine them to assess the question of how far from balance the pre-industrial marine N-cycle might have been (section 2.4.3). We then investigate the robustness of these results to additional sources of uncertainty that were not considered in the probabilistic estimates (section 2.4.4). Finally, we discuss the N-fixation rates (section 2.4.5) and budgets at the basin-scale and the implied lateral transports (section 2.4.6). We finish with a conclusion section (section 5).

### 2.2 Geochemical constraints on the marine N-cycle

While much progress has been made in the understanding of the fundamental processes that govern the marine N-cycle, the ability to accurately measure it and to determine integrated rates across time and space has not grown commensurably. In essence, integrated rates of N-fixation and denitrification are determined on the basis of either direct in situ measurements or making use of geochemical tracers. In situ measurements offer the most direct access to the process under consideration and permit detailed assessments of their sensi-
2.2. Geochemical constraints on the marine N-cycle

tivity to environmental conditions, but the poor coverage of measurements, especially when considering the high spatial and temporal variability, seriously limits the ability to infer integrated rates. A second approach is based on geochemical tracers such as anomalies in the stoichiometric relationship of nutrients (e.g., \(N^*\) introduced by Michaels et al. [1996] and Gruber and Sarmiento [1997]), the isotopic composition of the different nitrogen compounds, or anomalies in the dissolved concentrations of \(N_2\) to argon [Codispoti et al., 2001; Devol et al., 2006; Chang et al., 2010]. These approaches offer the advantage that they naturally integrate in space and time, and hence offer the ability to overcome the under-sampling problem. However, they tend to be indirect and often multiple assumptions have to be made in order to convert the tracer signals into nitrogen specific rates.

The most frequently employed geochemical approach involves the quasi-conservative tracer \(N^*\) (cf. Gruber and Sarmiento [1997]) defined as:

\[
N^* = \text{NO}_3^- - 16 \text{PO}_4^{3-} + 2.9 \text{ mmol m}^{-3} \tag{2.1}
\]

This tracer is built on the premise that regular phytoplankton consume nitrate (\(\text{NO}_3^-\)) and phosphate (\(\text{PO}_4^{3-}\)) in the classical Redfield ratio of 16 to 1, and that these two nutrients are also released with this ratio when the resulting organic matter is further processed within the food chain and during bacterial degradation (see e.g., Weber and Deutsch [2010] for limitations). If this assumption is met, any non-conservative behavior of \(N^*\) is a quantitative indication of a net addition or removal of fixed N. An alternative means to express the same concept is the quasi-conservative tracer \(P^*\) [Deutsch et al., 2007]:

\[
P^* = \text{PO}_4^{3-} - \frac{\text{NO}_3^-}{16} \tag{2.2}
\]

which is related to \(N^*\) through \(P^* = (-N^* + 2.9 \text{ mmol m}^{-3})/16\), i.e., it reflects the same processes as \(N^*\), but from the perspective of phosphorus rather than nitrogen.

The stable isotope ratio of \(^{15}\text{N}\) over \(^{14}\text{N}\) provides a second important avenue into the study of the sources and sinks of marine fixed N [Montoya, 2008]. This is because most relevant processes of the marine N-cycle fractionate, i.e., one isotope (usually the lighter) reacts faster than the other one, leading to changes in the stable isotope ratio of the substrate and product pools. The nitrogen isotopic composition of a given pool is expressed as:

\[
\delta^{15}\text{N} = \left( \frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{pool}} \left/ \left( \frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{air}} - 1 \right) \cdot 1000 \text{‰}, \tag{2.3}
\]

where \((^{15}\text{N}/^{14}\text{N})_{\text{pool}}\) is the isotopic ratio of the pool under consideration, and \((^{15}\text{N}/^{14}\text{N})_{\text{air}}\) is the isotopic ratio of atmospheric N, which is commonly used as the reference. The isotopic
preference of a process for the light isotope is often expressed by the isotopic enrichment $\varepsilon$, which in very good approximation is equal to the difference in the $\delta^{15}$N value of the product and the substrate:

$$
\varepsilon = \delta^{15}\text{N}_{\text{product}} - \delta^{15}\text{N}_{\text{substrate}} \tag{2.4}
$$

Marine N-cycle processes have varying degrees of isotopic fractionation. $\text{NO}_3^-$ assimilation by phytoplankton occurs with a light isotopic enrichment of $-5\%_o$ [Sigman et al., 1999; Di-Fiore et al., 2006]. N-fixation exhibits very little to no fractionation [Carpenter et al., 1997]. Similarly, benthic denitrification has almost no effective isotopic fractionation as local $\text{NO}_3^-$ is usually completely consumed [Brandes and Devol, 2002]. In contrast, water column denitrification is a key fractionating process that preferentially consumes $^{14}$N with a high isotopic enrichment of $\varepsilon_{\text{wcd}} = -25\%_o$ [Brandes et al., 1998; Sigman et al., 2003]. Since this estimate of the isotopic enrichment comes from field data, we interpret it to reflect also the possible contribution of fixed N removal by the anammox process. Sediment N burial occurs with a small enrichment of $\varepsilon = 6\%_o$ [Brandes and Devol, 2002].

In addition, the isotopic composition of a pool can also be altered by the addition of/mixing with another nitrogen pool that has another $\delta^{15}$N. For example, fixed N deposited onto the surface ocean from the atmosphere has been reported to have a $\delta^{15}$N of $-4 \pm 5\%_o$ [Brandes and Devol, 2002], i.e., substantially lower than the mean $\delta^{15}$N of the ocean, which is about $4.8 \pm 0.2\%_o$ [Liu and Kaplan, 1989; Sigman et al., 2000]. Also the addition of newly fixed atmospheric nitrogen into the oceanic fixed N pool leads to a lowering of the oceanic $\delta^{15}$N, because the nearly absent fractionation of N-fixation essentially leads to the addition of the atmospheric $\delta^{15}$N signature of 0\%o to the ocean. Nitrogen brought into the ocean by rivers has a $\delta^{15}$N value rather close to that of the mean ocean, i.e., about $4 \pm 4\%_o$ [Brandes and Devol, 2002].

Given the strong fractionation associated with water column denitrification, the absence of fractionation during benthic denitrification, and the small difference between N-fixation derived fixed N and the $\delta^{15}$N of the mean ocean, the mean ocean $\delta^{15}$N is very sensitive to the benthic-to-water column denitrification ratio [Brandes and Devol, 2002]. This high sensitivity makes this value a possible important constraint for relative importance of water column versus benthic denitrification. However, Deutsch et al. [2004] pointed out that this constraint is weakened by the fact that the strong regional localization of water column denitrification leads to a dilution effect, as the isotopic signal in $\text{NO}_3^-$ generated in that region will be diluted as these waters are mixed with the remainder of the ocean.

Several previous studies have determined rates of N-fixation or denitrification using either $N^*$ or $P^*$. N-fixation has been extensively investigated in the Atlantic [Michaels et al., 1996; Gruber and Sarmiento, 1997; Hansell et al., 2004; Bates and Hansell, 2004; Hansell et al., 2007], and to a lesser extent in the Pacific [Deutsch et al., 2001]. In a recent modeling
approach, Deutsch et al. [2007] estimated N-fixation rates based on the \( P^* \) tracer. \( N^* \) tracer was also used to estimate water column denitrification in the Eastern Tropical North and South Pacific and in the Arabian Sea [Deutsch et al., 2001; Codispoti et al., 2001]. In each case, the data had been used to estimate either denitrification or N-fixation, but not both processes simultaneously. In addition, very little attention was given to a full characterization of the uncertainties associated with the resulting estimates.

2.3 Methods

2.3.1 Overview

We determine the global and regional rates of N-fixation and denitrification in the water column and sediments in an inverse manner, i.e., by combining information contained in physical and biogeochemical tracers with a newly developed box model that describes the rates and pattern of ocean transport and mixing. A novel aspect of our approach is that we estimate not only the optimal value of N-fixation and denitrification, but attempt to fully describe the empirical probability density function (PDF) of these rates. Two major sources of uncertainty need to be considered when establishing the PDFs through our inverse approach: uncertainty in the data constraining the marine N-cycle and uncertainty in the rates and pattern of ocean transport and mixing.

We address these two sources of uncertainty by following a two-step process: First, we determine the transport and mixing terms of the box model by optimizing the model with primarily physical observations, taking into consideration the uncertainties in the observations using a Monte Carlo approach. This results in the generation of a suite of 2500 circulation configurations, each of which is optimally consistent with the observational constraints. In the second step, we use this suite of circulation configurations and determine the rates of the marine N-cycle again by optimally combining nutrient and isotopic observations and these models. This permits us to generate PDFs that contain not only the errors that come from the propagation of uncertainties in the data used to constrain the N-cycle, but also the errors that come from the circulation.

We follow two different strategies for determining the rates of the main sinks of fixed N (water column and benthic denitrification) and the main source (N-fixation). The denitrification rates are determined by inverting observations of nutrients and N isotopes coming from the whole water column. In contrast, N-fixation is estimated by using nutrient observations from the near surface ocean in a restoring approach. Since the inversion used to determined denitrification requires the assumption of steady-state, i.e., the existence of a globally balanced
marine N-cycle, it gives us a second estimate of N-fixation, which we then use to assess the robustness of the restoring method.

### 2.3.2 Model architecture and circulation

We constructed a new 14-box model of the global ocean consisting of an Atlantic, a Southern Ocean, and of the joint Indian and Pacific Oceans (IndoPacific) (Fig. 2.1). The Atlantic basin is divided into a northern and a low-latitude part, whereas the IndoPacific is divided into an oxic and a suboxic part. In the vertical, each (sub)basin is separated into 2 to 4 depth layers, resulting in a total of 14 boxes. The suboxic lower thermocline box represents the regions where water column denitrification occurs i.e., the Arabian Sea and the Eastern Tropical Pacific. This arrangement of boxes essentially extends the 8 box model of Deutsch et al. [2004] and combines it with elements of the Cyclops box model of Keir [1988].

We determined the water mass transport (one-way fluxes) and mixing (two-way fluxes) terms by an inversion of three tracers, i.e., \(\text{PO}_4^{3-}\), \(\text{PO}_4^{2-}\) as defined by Broecker et al. [1991]:

\[
\text{PO}_4^* = \text{PO}_4^{3-} + \frac{\text{O}_2}{175} - 1.95 \text{ } \mu \text{mol/kg,}
\]

and natural radiocarbon \(\Delta^{14}C\). Mean values and variances for each tracer and box were determined by depth and geographic-averaging climatological data from the World Ocean Atlas (WOA) (nutrients and oxygen) [Conkright et al., 2002] and from the gridded GLODAP product (natural \(\Delta^{14}C\)) [Key et al., 2004].

A simple description of the cycling of \(\text{PO}_4^{3-}\) was added, consisting of surface production of organic phosphorus, export and remineralization. Production and export was fixed for each region on the basis of the estimates provided by Dunne et al. [2007], which gives a global carbon export flux of 11.3 PgC yr\(^{-1}\), i.e., 8.9 TmolP yr\(^{-1}\). In the ocean interior, organic P is remineralized according to a power law function [Martin et al., 1987]. Following Deutsch et al. [2004] different exponents are used in the suboxic vs oxic regions (b = 0.400 and 0.858, respectively). \(\text{O}_2\) is not simulated, even though its distribution was used to construct the architecture of the model. Specifically, the volume of the suboxic box, where water column denitrification is restricted to happen, was calculated from the WOA’s climatological \(\text{O}_2\) distribution by integrating all waters with concentrations lower than \(10 \mu \text{mol kg}^{-1}\).

The inversion was performed by minimizing a least-squares type cost function that included a Bayesian component, i.e., we regularized the inversion by adding prior knowledge about the magnitude of the fluxes (see section B.1 in Appendix). The minimization was carried out by a Hessian method, which proved to be sufficient due to the near-linearity of the optimization problem. A non-negativity constraint was added, i.e., the inversion was not permitted to reverse the direction of the transport.

The prior values for each transport and mixing term were either estimated from the observed
2.3. Methods

Design of water circulation based on:
- Keir 1988
- Deutsch et al. 2004 new

Posterior (prior) water mass flux [Sv]
- Northlow-latitude
- Southern Ocean
- Oxic
- Suboxic

Export production [GtC/yr], modelled (observation)
- 18.56

PO4 [mmol/m^3] / N* [mmol/m^3] / δ¹⁵NO₃ [permil], data
- 1.78 / 0.7 / 4.0
- 1.62 / 1.3 / 4.8

Box volume [10^16 m^3], surface area [10^14 m^2]
- 18.56

Suboxic box where water column denitrification occurs

Figure 2.1  See next page for caption
vertical density gradient (mixing terms, see section B.1 in Appendix) or were taken from the literature (transport terms) [Schmitz, 1996a,b; Ganachaud and Wunsch, 2000; Deutsch et al., 2004]. The initially estimated mixing terms were then upscaled by a factor of 4 to 6 in order to obtain a realistic global export flux [Laws et al., 2000; Najjar et al., 2007] (see also discussion section). The lower bounds were set to 50% of their prior values, while the upper bounds were set equal to the square of the prior values, but at most 100 Sv. We have chosen these skewed distribution of the bounds on the basis of the fact that the posterior values must not be negative. Generally, this choice had little effect on the solutions, except for a few one-way advection fluxes (see section B.1 and Fig. B.1 in Appendix). For instance, the upwelling flux in the suboxic water column has a posterior PDF that hugs the lower boundary, indicating that the a priori chosen value for the lower bound is a stronger determinant of the magnitude of this flux than the observations.

A Markov Chain Monte Carlo (MCMC) method was used to investigate the sensitivity of the posterior transport and mixing terms toward three of the data constraints, i.e., $PO_{4}^{3-}$, $\Delta^{14}C$, and export production. For each iteration, a new set of observations was generated for each box of the model by randomly sampling the empirical probability density function of each observation, generated by assuming a normal distribution and using the mean and one standard deviation of the observations. For export production, a standard deviation of 20% was assumed. The MCMC was repeated 2500 times, which resulted in the generation of 2500 sets of observations, each of which was then used to optimize the box model. We thus obtained a suite of 2500 circulation configurations, each of which is optimally consistent with observations within the uncertainties of the observations.

In the subsequent investigations, all configurations were considered equally, i.e., no weighting was performed according to the value of their a posteriori cost function or any other criteria. However, we sometimes compare all 2500 circulation configurations with a suite of 100 configurations that have the smallest a posteriori cost function. For some specific investigations, the circulation setup with the smallest cost function was selected (displayed in Fig. 2.1).
2.3. Methods

2.3.3 Water column and benthic denitrification

We determined water column and benthic denitrification rates by considering the full marine N budget and then adjusting these rates in such a manner that the modeled distribution of $N^{+}$ and $\delta^{15}N$ are optimally consistent with the observations. This required a number of a-priori simplifications. First we assumed that water column denitrification occurs only in one location, i.e., the suboxic box within the thermocline of the IndoPacific. Additionally, since the current state of knowledge about anammox does not allow our geochemical approach to estimate the rates of anammox and canonical denitrification separately, anammox is implicitly included in our denitrification estimate. Second, we prescribed the relative distribution of benthic denitrification between the different boxes of our model, while keeping the global total adjustable. Third, for the purpose of this approach only, we imposed a steady-state on the marine N and P budgets. We ensured this by forcing global N-fixation to balance the global marine N budget. However, we kept its regional distribution adjustable, i.e., the amount of N-fixation occurring in the Atlantic relative to that in the IndoPacific. This left us with three unknowns that we solved for, i.e., the global magnitudes of water column and benthic denitrification, and the relative spatial distribution of N-fixation.

The starting points for determining these unknowns are the global marine budgets of N and P, for which we considered the following processes: Riverine input of both N and P, atmospheric deposition of N, N-fixation and denitrification for N, and finally burial at the sea-floor of N and P. We considered here primarily the budget of the open ocean, for which we assume that the human footprint has remained small. This is supported by recent modeling studies that showed relatively small changes in open ocean biogeochemistry resulting from the anthropogenic imprint [Krishnamurthy et al., 2007, 2009]. Consequently, we will be using pre-industrial flux estimates for the budget.

The pre-industrial input by riverine N and P discharge is based on the estimates from the Global Nutrient Export from WaterSheds (NEWS) model [Seitzinger and Mayorga, 2008], but scaled down to account for the significant losses of nutrients occurring in river mouths before reaching the coastal ocean. The global total N input is assumed to amount to 14 TgN yr$^{-1}$ and that of P to 2 TgP yr$^{-1}$. There is no river input into the Southern Ocean and inputs into the suboxic and oxic IndoPacific are calculated on a per-surface area basis given the integrated N and P discharge into the Indian and Pacific Oceans.

The pre-industrial N input via atmospheric deposition is prescribed based on Duce et al. [2008]. Given the negligible source of P from the atmosphere [Baturin, 2003], atmospheric P deposition is neglected. We prescribed the loss of P by burial or organic matter to exactly balance the global river input of P in order to satisfy the steady-state assumption. The spatial distribution of organic P burial in sediments is set to follow that of export production. The burial flux of organic P is implemented in the model by removing $PO_{4}^{3-}$ from the surface,
since this is where the buried P is transformed from inorganic to organic form. The relative spatial distribution of benthic denitrification is prescribed as 23% Atlantic, 69% Indo-Pacific, and 8% Southern Ocean [Christensen et al., 1987; Devol, 1991; Middelburg et al., 1996]. The fraction of benthic denitrification in each water column is defined on a per surface area, while within each water column benthic denitrification is vertically distributed based on Middelburg et al. [1996]. This gives the following relative vertical distribution (from surface box to bottom): 30%/30%/30%/10% (suboxic IndoPacific), 40%/50%/10% (oxic IndoPacific), 40%/60% (Southern Ocean), 40%/50%/10% (Low-latitude Atlantic), and 40%/60% (North Atlantic).

The cycling of $\text{NO}_3^-$ and $\text{PO}_4^{3-}$ associated with the biological loop is modeled as before, except that export production is now interactively modeled by restoring surface $\text{PO}_4^{3-}$ concentration to observations with a restoring time scale of five days. The cycling of $\text{NO}_3^-$ is then linked to that of $\text{PO}_4^{3-}$ following the C:N:P Redfield ratio of 106:16:1 [Redfield et al., 1963]. A few additional assumptions had to be made for N-fixation: While the relative distribution between the Atlantic and IndoPacific was left as an unknown, four times more N-fixation per surface area was prescribed in the suboxic column (same assumption than Deutsch et al. [2004]). In addition, 7% of the global N-fixation rate was set to occur in the Southern Ocean. In the vertical, 90% of the newly fixed N is released in the surface box, while the remaining is exported as particulate organic matter to depth where it is subject to the same remineralization rates as standard organic matter.

The cycling of $^{15}\text{N}$ was implemented to follow the cycling of total nitrogen ($^{15}\text{N} + ^{14}\text{N}$), with proper consideration of the isotopic fractionations and the different isotopic values of the external sources. The values for these fractionations and source compositions are the literature-derived values given in section 2.2.

The three unknowns, i.e., the global rates of water column and benthic denitrification, and the fraction of N-fixation occurring in the Atlantic, were determined on the basis of a standard least-squares method for each of the 2500 circulation configurations. Systematic scans over the ranges of the three parameters were done for each circulation configuration, and the parameter combination that matched best the observed $N^*$ at each box and the observed mean ocean $\delta^{15}\text{N}$ in the least-square sense was extracted. Observed $N^*$ was computed for each box from the WOA climatology [Conkright et al., 2002], except for the suboxic box, where we used a $N^*$ value of $-13.0 \text{ mmol m}^{-3}$ computed from the World Ocean Database, instead of the $N^*$ value of $-10.6 \text{ mmol m}^{-3}$ from WOA. The discrepancy comes from the smoothing performed to generate the gridded WOA product. For the global ocean mean $\delta^{15}\text{N}$, we adopted a value of 4.8‰ [Liu and Kaplan, 1989; Sigman et al., 2000]. Due to the relatively sparse $\delta^{15}\text{N}$ measurements, we decided to use the spatial distribution of the observed $\delta^{15}\text{N}$ only as a validation for the posteriori solutions, rather than using it for the
optimization. The section B.2 in Appendix provides a discussion of the misfits.

### 2.3.4 Nitrogen fixation

The primary means we use to estimate global and regional N-fixation is by diagnosing it from restoring excess $\text{PO}_4^{3-}$ relative to $\text{NO}_3^-$ in surface waters [Deutsch et al., 2007]. We will later compare the results of this approach to the N-fixation rates implied by the budget approach used above to estimate denitrification. This restoring approach uses the quasi conservative tracer $P^*$ (see Eq.(2.2)), whose variations in the surface ocean primarily reflect the balance between N-fixation that consumes $P^*$ and the transport convergence of $P^*$ that tends to increase $P^*$. Assuming that the N-cycle is in steady-state locally, i.e., within each surface box, the rate of N-fixation, $J_{\text{FIX}}(N)_i$, in box $i$ can then be diagnosed from the transport convergence $-\nabla \phi(P^*)_i$:

$$J_{\text{FIX}}(N)_i = \lambda \left[ -\nabla \phi(P^*)_i + b(P^*)_i \right]$$

with $\lambda = \frac{16}{1 - \gamma_e \left( 1 - \frac{16}{r_f} \right)}$

where $\lambda$ is a non-dimensional parameter and $\gamma_e$, prescribed to 0.1, corrects for the fraction of organic matter that sinks as particulate organic matter. $r_f$ is the N:P ratio of N-fixers, taken as 40 [Letelier and Karl, 1998; Krauk et al., 2006]. The term $b(P^*)_i$, summarizes a number of additional processes that occur with non-Redfieldian stoichiometry and thus contribute to sources or sinks of $P^*$. Ocean internal sources of $P^*$ are benthic denitrification ($B$) and sediment burial of N ($SBN$), while sediment burial of P ($SBP$) is an internal sink of $P^*$. Furthermore, atmospheric deposition of N ($AD$), and river inputs of N ($RIN$) and P ($RIP$) represent external output/input of $P^*$. Since water column denitrification is confined to a lower thermocline box that does not exchange directly with a surface box, we do not have to consider it here. This gives for $b(P^*)_i$:

$$b(P^*)_i = \sum_m \text{source}_{i,m}(P^*) - \sum_n \text{sink}_{i,n}(P^*) = \frac{1}{16} \left[ +B_i + SBN_i + RIP_i \right] - SBP_i - AD_i - RIN_i$$

All terms of $b(P^*)_i$ (Eq.2.6) were prescribed based on literature estimates. Their uncertainties are neglected and the same patterns and rates as in the budget approach are assumed (see above). Atmospheric deposition of N was set to 14 TgN yr$^{-1}$, a value of 14 TgN yr$^{-1}$, and 2 TgP yr$^{-1}$ was chosen for the river inputs of N and P, respectively, and organic N and P burial were set to 14.5 TgN yr$^{-1}$, 2 TgP yr$^{-1}$ respectively. The concentration of $P^*$ was estimated by first computing it for each grid-box of WOA using annual mean concentrations of $\text{NO}_3^-$ and
and then averaging it over each box of the model. If the diagnosed rate of N-fixation (Equ. 2.6) is negative in a basin, the rate is set to zero.

We disregard the diagnosed N-fixation rates in the Southern Ocean based on the rationale that no N-fixation in this oceanic basin is expected to occur [Deutsch et al., 2007]. Nevertheless, substantial transport convergences of $P^*$ exist in this ocean basin. We interpret this to be primarily the result of non-Redfield utilization of N and P by non-diazotrophic organisms, which have a significant impact on the upper ocean distribution of N and P in this ocean basin [Arrigo et al., 1999; Weber and Deutsch, 2010; Mills and Arrigo, 2010].

2.4 Results and discussion

2.4.1 Global denitrification rates

Our budget approach yields an empirical probability density function (PDF) of the global rates of water column and benthic denitrification (includes both canonical denitrification and anammox) with a median of 51 TgN yr$^{-1}$ and 81 TgN yr$^{-1}$, respectively (Fig. 2.2A,B). The 5th to 95th percentile range for water column denitrification goes from 39 to 66 TgN yr$^{-1}$, while that for benthic denitrification goes from 56 to 108 TgN yr$^{-1}$ (Tab. 2.1). Since the PDFs of the rates do not deviate too strongly from a normal distribution, the 5th to 95th percentile ranges are very similar to the ranges described by the mean ± two standard deviations, which are 35 TgN yr$^{-1}$ to 68 TgN yr$^{-1}$ and 51 TgN yr$^{-1}$ to 111 TgN yr$^{-1}$ respectively. As mentioned above, we regard our estimates to reflect the pre-industrial N-cycle, as we assume that the anthropogenic perturbation has not yet significantly altered the open-ocean data that we employ to diagnose the rates.

Our probabilistic estimates of the total N loss by denitrification of 132 (95 to 174) TgN yr$^{-1}$ clearly refute the high rates proposed by Codispoti et al. [2001] and Codispoti [2007] which are in excess of 400 TgN yr$^{-1}$ (Tab. 2.1). They are also lower by nearly a factor of two in comparison to several other recent estimates such as those of Gruber [2004], Deutsch et al. [2004], and Galloway et al. [2004]. Although these estimates pertain to different time-periods, i.e., pre-industrial or present-day, the human perturbation is too small to explain the difference (maximally about 20 to 30 TgN yr$^{-1}$ [Galloway et al., 2004]). Our low total denitrification rates are in line with those suggested by Gruber and Sarmiento [1997] and the very recent estimate of Sigman et al. [2009]. However, Sigman et al. [2009] noted that their model diagnosed denitrification rate may be biased low because of their unrealistically low simulated export production. Although our approach shares some similarities with that employed by Sigman et al. [2009], our median diagnosed global C export is consistent with
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Figure 2.2 Probability density function (PDF) of (A) water column denitrification, (B) benthic denitrification, (C) benthic-to-water column denitrification ratio, (D) N-fixation from the budget approach, and (E) N-fixation from the restoring approach. Red PDFs: 2500 circulation configurations. Blue PDFs: suite of 100 circulation setups with smallest cost functions. Blue PDFs have been scaled five times for the purpose of comparison with the red PDFs. Solid black line is the median, dashed lines are 5th, 95th percentile respectively.
observationally based estimates, i.e., our relatively low denitrification rates cannot be related back to such a bias.

Comparing our water column and benthic denitrification rates to the published estimates separately, it turns out that the water column denitrification rates tend to be more consistent among each other (with the notable exception of Codispoti et al. [2001] and Codispoti [2007]), and that the largest differences occur with the benthic rates. Nevertheless, also our water column denitrification rate of 51 (39 to 66) TgN yr\(^{-1}\) is at the lower end of most recent estimates.

Our water column denitrification rate depends sensitively on the size of the suboxic lower thermocline box in the IndoPacific, which constitutes the only place where water column denitrification occurs in our model. The larger the volume of this suboxic box, the more water column denitrification is diagnosed in our model in order to match the observed mean ocean \(\delta^{15}N\) and the low \(N^*\) value in this box. The size of our suboxic box was estimated by considering the oceanic volume that has oxygen concentrations lower than 10 \(\mu\)mol/kg. Since this threshold is higher than that normally associated with the onset of water column denitrification (5 \(\mu\)mol/kg) [Goering, 1968] we consider our estimate more likely to be biased high rather than biased low. Thus, this argument does not explain our relatively low water column denitrification rate.

Codispoti [2007] suggested that his large modern water column denitrification estimate, in contrast to Gruber [2004] and our new estimates, could reflect the anthropogenic perturbation. His global estimate comes from a few in-situ observations extrapolated to the global ocean, which make them sensitive to recent perturbations. However, if modern water column denitrification were as high as suggested by Codispoti [2007], i.e., above 150 TgN yr\(^{-1}\) and had been operating for at least a few decades, then this should have left an imprint on the tracers in the main denitrification zones and hence should have been detected by our approach. In addition, all modeling studies conducted so far to investigate the possible effect of the anthropogenic perturbation on the marine N-cycle identified only small changes [Krishnamurthy et al., 2007, 2009]. Thus, while we can clearly refute the very high water column denitrification rates suggested by Codispoti [2007], our rate is at the low end, but not clearly inconsistent with most recent estimates, which suggest fixed N loss rates of the order of 60 to 80 TgN yr\(^{-1}\).

Our globally integrated rate of benthic denitrification of 81 (56 to 108) TgN yr\(^{-1}\) is considerably smaller than any other recent estimate (Tab. 2.1). It is nearly 4 times smaller than the value suggested by Codispoti et al. [2001], but it is also smaller by a factor of about two compared to the estimates provided by Gruber [2004], Galloway et al. [2004] and Deutsch et al. [2004] (Tab. 2.1). Most of these estimates are based on scaling the water column denitrification rate with the ratio of benthic-to-water column denitrification. Thus, an overly
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large water column denitrification rate would immediately lead to an overestimation of benthic denitrification. This is clearly the case with Codispoti et al. [2001] estimate, but not for the others. In addition, a more direct estimate of benthic denitrification obtained by using the parameterizations of Middelburg et al. [1996] and export production estimates following the particle export database of Dunne et al. [2007] gives a global benthic denitrification rate close to 200 TgN yr\(^{-1}\), suggesting that our rate is rather on the low end. Our low rate is primarily driven by the need of the model to fit the observed global mean \(\delta^{15}N\) of \(\text{NO}_3^-\), which puts strong constraints on the ratio between benthic-to-water column denitrification. With our water column denitrification being on the low end compared to recent estimates, this ratio demands also a relatively low benthic denitrification rate. It turns out, however, that also this ratio is relatively low compared to other estimates.

The median benthic-to-water column denitrification ratio computed from all inverted configurations is 1.57 (1.38 to 1.75), (lower left PDF Fig. 2.2C). This ratio is substantially lower than the value of 2.7 found by Deutsch et al. [2004] and much lower than the originally proposed value of 4 [Brandes and Devol, 2002]. Our models estimate this low ratio while maintaining a global mean ocean \(\delta^{15}N\) of \(\text{NO}_3^-\) of 4.8\(^{\circ}/00\), which means that our models exhibit a strong dilution effect. This effect, introduced by Deutsch et al. [2004], postulates that as water column denitrification takes place in a very limited ocean volume (Arabian Sea and Eastern Tropical Pacific) with high degrees of \(\text{NO}_3^-\) loss, denitrification causes less \(^{15}N\) enrichment than would arise if this process was homogeneously distributed throughout the ocean. If the latter was the case, the benthic-to-water column denitrification ratio would be 4 in order to match a mean ocean \(\delta^{15}N\) of \(\text{NO}_3^-\) of 5\(^{\circ}/00\) [Brandes and Devol, 2002]. This is because water column denitrification has an expressed isotope effect of 25\(^{\circ}/00\), while benthic denitrification leads to no fractionation. We hypothesize that our strong dilution effect and the thus inferred low benthic-to-water column denitrification ratio is due to a larger degree of spatial separation of suboxic waters in our model. Compared to all configurations, the suite of 100 circulation setups with the smallest cost functions have a distribution slightly shifted toward a higher ratio as a consequence of higher benthic denitrification. Nevertheless, all configurations have a ratio below 2. \(\delta^{15}N\) within each box provide some confidence of this low estimate, since modeled \(\delta^{15}N\) successfully reproduce the data (see Fig. B.2 in Appendix). This validation is possible because \(\delta^{15}N\) within each box is not used to constraint the model.

2.4.2 Global N-fixation rate

The global N-fixation rate estimated by restoring surface \(P^*\) toward climatological data yields a median of 134 TgN yr\(^{-1}\) with a 5th to 95th percentile range of 117 TgN yr\(^{-1}\) to 150 TgN yr\(^{-1}\) (Fig. 2.2E). If we also considered the diagnosed N-fixation in the Southern Ocean, the global fixation rate would increase by 21 TgN yr\(^{-1}\) to 155 TgN yr\(^{-1}\) (138 to 171 TgN yr\(^{-1}\)). The global
N-fixation rate estimated by restoring $P^*$ tends to be somewhat, but not significantly, higher than that implied from the budget approach, which yields a median rate of 118 TgN yr$^{-1}$ (82 to 160 TgN yr$^{-1}$) (Fig. 2.2D). Among all 2500 circulation setups, there is no correlation between the global N-fixation rates estimated from the restoring and the budget approaches (not shown). This lack of correlation is interpreted as evidence that the two approaches are based on independent geochemical constraints. The budget approach aims to fit the mean ocean $\delta^{15}N$ and $N^*$ within each box, while the restoring approach uses $P^*$ mainly in the surface and thermocline boxes.

Our $P^*$-inferred global N-fixation rate of 134 (117 to 150) TgN yr$^{-1}$ is consistent with most recent estimates, such as those by Gruber [2004], and Galloway et al. [2004] and Deutsch et al. [2007] (Tab. 2.1). The latter estimate of 130 TgN yr$^{-1}$ is largely based on the same methodology and the same data, i.e., the analysis of the transport convergence of $P^*$, but used a full three-dimensional general circulation model coupled to a simple ecosystem model to compute this convergence. The close agreement indicates that our large set of optimized circulation configurations captures the three-dimensional transport convergence well, yet also provides us with the capability to estimate the associated uncertainties.

Our global N-fixation is, however, substantially smaller than the estimate put forward by Deutsch et al. [2004]. The latter is based on a similar box model as employed here, but did not include a separation of the ocean basins into an Atlantic and IndoPacific region. But the more important reason for the large difference is that Deutsch et al. [2004] did not include the substantial input of fixed N into the ocean by atmospheric deposition and rivers in his budget approach. Since global N-fixation is estimated by difference in this approach, the lack of consideration of this source makes their estimate by definition an overestimate.

Our approach to diagnose N-fixation depends sensitively on the assumed N:P ratio of the diazotrophic organisms. Our value, $r_f = 40$, stems largely from observations of the growth of Trichodesmium. But recent discoveries point toward a substantially greater diversity of diazotrophs that thrive under different environmental conditions [Zehr et al., 2001; Montoya et al., 2004; Moisander et al., 2010; Hamersley et al., 2011] and possibly have different N:P ratios. We cannot assess the implications of such variations well at this time, but note that the two independent geochemical approaches we used here estimate very similar global fixation rates. This suggests that our rates reflect the global N-fixation by all diazotrophs, i.e., the sum of the contribution from both Trichodesmium and unicellular diazotrophs.

### 2.4.3 State of the pre-industrial marine N-cycle

Our directly estimated rates of N-fixation and denitrification and the literature-based estimates of the other source and sink terms indicate that the pre-industrial N-cycle was bal-
2.4. Results and discussion

anced or close to being balanced (Fig. 2.3). The median of the N budget imbalance is a small excess of 16 TgN yr\(^{-1}\) with a large range (-24 to 52 TgN yr\(^{-1}\)), implying that the Null-hypothesis of a balanced pre-industrial N-cycle cannot be rejected. This conclusion hinges critically on the assumption that the source and sink estimates stem from independent approaches. With the most important loss terms, i.e., denitrification, being determined by fitting interior ocean \(N^*\) and mean ocean \(\delta^{15}N\), and the most important source term being determined by fitting a largely independent set of data, i.e., upper ocean \(P^*\), this condition is met. This is confirmed by the lack of a correlation when the global sources are plotted against the global sinks across all 2500 circulation setups (Fig. 2.3). Thus, our finding of a pre-industrial fixed N budget in the ocean close to a steady-state is not an a-priori assumption, but a result emerging from the data.

![Figure 2.3](image_url)

**Figure 2.3** Evaluation of the imbalance of the N-cycle by comparing all sources estimated by the restoring approach (diagnosed N-fixation without Southern Ocean rate, and prescribed atmospheric N deposition and riverine N discharge) with all sinks estimated from the N budget approach (determined water column and benthic denitrification, and prescribed organic N burial). Red: 2500 circulation configurations. Blue: suite of 100 circulation setups with smallest cost functions. 1-to-1 dashed line represents a balanced N budget.

Our finding of a (within the large error bars) balanced budget for the pre-industrial N-cycle clearly contrasts with Codispoti’s proposition of a modern budget with a substantial imbalance, but corroborates evidences from geological records [Kienast, 2000] that indicate essentially no substantial changes in the N-budget over the Holocene. Although we interpret
our estimates to reflect largely the pre-industrial situation, i.e., a budget without anthropogenic influences, the data underlying our results were collected in the last few decades and therefore possibly may not be entirely free of anthropogenic influences. The human alteration of the marine N-cycle consists mainly of a substantial increase of atmospheric deposition and river discharge of N [Duce et al., 2008; Seitzinger and Mayorga, 2008], amounting to an increase in the inputs of about 50 TgN yr\(^{-1}\) since 1860 [Galloway et al., 2004]. Also the sinks could have increased, in part in response to the increased input of fixed N, but perhaps mostly in response to an increase in the regions with hypoxic to anoxic conditions [Diaz and Rosenberg, 2008]. Thus, most of the additional input and losses of fixed N in the ocean occurred along the continental margins, and thus they are not expected to have altered substantially the open and deep ocean data that largely underlie our estimate. Nevertheless, this adds further uncertainty to our estimates, but we consider this additional contribution to be rather small, i.e., likely less than 10 TgN yr\(^{-1}\).

Although our estimates are limited to the pre-industrial budget, it is nevertheless tempting to investigate the consequences of our finding for the likelihood of a present imbalance in the marine N budget exceeding 100 TgN yr\(^{-1}\). One important argument speaks against this, i.e., the magnitude of the human perturbation is likely not large enough. With the anthropogenic increase in the sources amounting to about 50 TgN yr\(^{-1}\), the sinks would have had to increase by about 150 TgN yr\(^{-1}\) since pre-industrial times, which essentially requires a doubling of total marine denitrification. This largely would have to be accomplished by benthic denitrification, since the observed expansion of the oxygen minimum zones over the last 50 years [Stramma et al., 2008] is too small to have increased water column denitrification substantially. Thus, benthic denitrification would have had to triple. While oxygen minimum zones along the continental margins have increased [Diaz and Rosenberg, 2008], it is difficult to conceive such a large increase since pre-industrial times. Thus, given our refined estimate of the pre-industrial fixed N budget, it is hard to justify the strong modern imbalance suggested by Codispoti et al. [2001].

Our pre-industrial budget implies a residence time of fixed N of 4,500 yr (3,700 yr to 5,600 yr) assuming an oceanic fixed N inventory of 660,000 Tg N [Gruber, 2008]. Our residence time is at the high end of the values published in the literature (Tab. 2.1), but still shorter than the time it took for Earth to transition from the last glacial maximum into the Holocene, which took about 10,000 years [Petit et al., 1999]. Thus, our longer residence times do not refute the hypotheses that have been put forward to explain part of the atmospheric CO\(_2\) changes across glacial-interglacial transitions through transient source/sink imbalances that may have caused changes in the fixed N inventory [McElroy, 1983; Broecker and Henderson, 1998].
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2.4.4 Sensitivity analyses

While our probabilistic approach explores the uncertainties associated with our estimates already in substantial depth, there exist several additional sources of uncertainty that require attention as they have the potential to influence the results substantially. We identified the following important parameters: (i) the magnitude of vertical mixing, which we upscaled by a factor of nearly 3 relative to the initial first guesses, (ii) the value of $N^*$ in the suboxic box, (iii) the isotopic enrichment associated with water column denitrification ($\varepsilon_{\text{wcd}}$), and (iv) the two vertical mixing fluxes exchanging water to the suboxic box. We explore the impact of these properties by conducting sensitivity experiments.

To determine the sensitivity of our results to vertical mixing, we re-determined N-fixation and

![Diagram](https://via.placeholder.com/150)

**Figure 2.4** Influence of the magnitude of subsurface vertical two-way water mixing fluxes on: the global C export flux (yellow histogram), the global water column and benthic denitrification rates computed from the B budget approach, the diagnosed N-fixation rate from the restoring approach, and on the global N imbalance (N-fixation rates from restoring approach minus rates from the budget approach). All values are averages from the suite of 100 circulation setups with smallest cost functions. The literature suggests for the carbon export flux a value of about 10 Pg C yr$^{-1}$, constraining the integrated subsurface vertical water fluxes to about 300 Sv.
denitrification using the suite of 100 circulation setups with the smallest cost functions, but imposed a different value of the upscaling factor. We varied this factor between 0.5 and nearly 5, resulting in an integrated vertical exchange flux ranging from 50 Sv to 450 Sv (standard value is 300 Sv) and then diagnosed for each factor the median of the different processes. Denitrification rates are hardly sensitive to subsurface vertical mixing fluxes (Fig. 2.4 green and blue curves), because these rates are determined on the basis of $N^*$ at each box, mean ocean $\delta^{15}N$ and the circulation and mixing of the entire ocean. On the other hand, the N-fixation rate diagnosed from $P^*$ in the surface and thermocline strongly depends on subsurface vertical mixing fluxes since water masses carry the high $P^*$ concentration in the thermocline to the surface (Fig. 2.4 red curve). Thus, stronger subsurface vertical mixing fluxes bring more high $P^*$ into surface waters, generating higher rate of N-fixation in order to restore $P^*$ to its observed value. As a result of this differential behavior between the main sources and sinks of fixed N, the global marine N imbalance is strongly affected by the magnitude of vertical mixing in the models. Low vertical mixing (50 Sv) causes a deficit of 50 TgN yr$^{-1}$, while high vertical mixing (450 Sv) increases N-fixation without affecting denitrification resulting in a surplus of more than 50 TgN yr$^{-1}$.

We can use the diagnosed biological productivity as an indicator for a realistic value of this mixing flux. Since productivity is diagnosed in our model from the transport convergence of $PO_4^{3-}$, which is largely controlled by the magnitude of vertical mixing, the production and export of organic matter (carbon) increases nearly proportionally with the changes in vertical mixing (Fig. 2.4 bottom). We had used this constraint already to upscale the mixing fluxes from the initial first guess of 110 Sv to our standard case of 300 Sv, as a mixing flux of 110 Sv results in a too small C export flux of $\sim 5$ PgC yr$^{-1}$, while 300 Sv yields an export flux of $\sim 10$ PgC yr$^{-1}$, consistent with the most recent estimates [Najjar et al., 2007; Dunne et al., 2007]. This value of the vertical mixing flux yields our standard imbalance of 16 TgN yr$^{-1}$ (-24 to 52 TgN yr$^{-1}$). If we used the C export constraint less vigorously, the imbalance could be larger or smaller, but the median of the absolute imbalance will unlikely exceed 50 TgN yr$^{-1}$.

To investigate the sensitivity of the global N imbalance to the other three properties, i.e., $N^*$ assigned to the suboxic box, the isotopic enrichment associated with water column denitrification, and to the two vertical mixing fluxes of the suboxic box, we use just ten circulation configurations. We investigate the co-influence by varying two parameters simultaneously (Fig. 2.5). Varying $N^*$ in the suboxic box between $-10$ to $-16$ mmol m$^{-3}$ changes the N imbalance between 40 and 0 TgN yr$^{-1}$ (Fig. 2.5B,D). The uncertainty range of this $N^*$ concentration is difficult to estimate exactly, but we note that the standard value of $N^*$ (-13.6 mmol m$^{-3}$ according to the World Ocean Database) implies a better match to the data than when the $N^*$ value computed from the WOA ($-10.6$ mmol m$^{-3}$) is used (Fig. 2.5A,C). Varying $\varepsilon_{\text{wcd}}$ in the literature range from $-30\%$ to $-20\%$ [Altabet et al., 1999b; Brandes et al., 1998; Sigman et al., 2003] yield imbalances ranging from 0 to 50 TgN yr$^{-1}$ (Fig. 2.5D). The imbal-
Figure 2.5  See next page for caption
Figure 2.5 Parameter sensitivity (a, c) of the root mean square deviation (RMSD) between modeled and observed $N^*$ and (b, d) of the global scale N-budget imbalance. Investigated are the sensitivity of the results to changes (i) of the two vertical water mixing fluxes of the suboxic box (expressed as function of a scale-factor), (ii) of the $N^*$ value used at the suboxic box in the N-budget approach, and (iii) of the isotopic enrichment associated with water column ($\varepsilon_{\text{wcd}}$). The imbalances and the RMSD were computed from the restoring approach using ten circulation configurations without consideration of N-fixation in the Southern Ocean. Red circles show the standard case.

...ance is rather insensitive to the uncertainty of the two vertical mixing fluxes in the suboxic box. Even a doubling of the magnitudes does not alter the imbalance much. In all these cases, the primary driver for the changes in the imbalance are changes in denitrification, since N-fixation determined from the restoring approach does not depend on these values.

In summary, these sensitivity analyses performed on several key parameters confirm that the pre-industrial N-cycle was balanced within the uncertainties. They also demonstrate a relatively large robustness of the global rates of N-fixation and denitrification with changes that are smaller than the uncertainty ranges determined from the probabilistic approach.

2.4.5 Basin-scale N-fixation rates

The highest N-fixation rates from the restoring approach are found in the IndoPacific, whereas essentially no fixation is diagnosed in the Atlantic (Fig. 2.6). The median rate of N-fixation in the oxic IndoPacific is $86 \text{TgN yr}^{-1}$ ($78$ to $95 \text{TgN yr}^{-1}$), followed by the suboxic IndoPacific with a median rate of $47 \text{TgN yr}^{-1}$ ($31$ to $61 \text{TgN yr}^{-1}$). In contrast, diagnosed fixation in the Atlantic ranges only from $0$ to $3 \text{TgN yr}^{-1}$, with a median of $0 \text{TgN yr}^{-1}$. The restoring approach diagnoses a substantial amount of N-fixation in the Southern Ocean with a median rate of $21 \text{TgN yr}^{-1}$ ($20$ to $22 \text{TgN yr}^{-1}$). As discussed above, we disregard this rate, as we consider it to be caused by non-Redfieldian uptake by non-N-fixing organisms [Weber and Deutsch, 2010].

The high N-fixation rate in the IndoPacific is consistent with the findings of Deutsch et al. [2007] who suggested a relatively close coupling between the regions of denitrification and N-fixation. In their standard case, they diagnosed a N-fixation rate of $117 \text{TgN yr}^{-1}$ for the IndoPacific, close to our rate of $133 \text{TgN yr}^{-1}$ ($116$ to $149 \text{TgN yr}^{-1}$). If we assume that the Indian Ocean has a similar areal fixation rate as the Pacific, we can scale up the Pacific only rate of Deutsch et al. [2001] of $59 \pm 15 \text{TgN yr}^{-1}$ to about $100 \text{TgN yr}^{-1}$, again within the range of our estimate.

But the absence of N-fixation diagnosed in the low-latitude Atlantic challenges the canonical view of a basin with substantial N-fixation as a result of high airborne rich-iron dust deposition
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[Michaels et al., 1996; Falkowski, 1997; Moore et al., 2009]. Gruber and Sarmiento [1997] calculated a N-fixation rate of 28 TgN yr$^{-1}$ north of the equator and up to 45°N using $N^*$. More recently Hansell et al. [2004] computed a 60% lower estimate, but still substantially larger than our restoring based estimate. Isotopic analyses of NO$_3^-$ suggested an Atlantic N-fixation rate of 15 to 24 TgN yr$^{-1}$ [Knapp et al., 2008] and the $P^*$ restoring approach of Deutsch et al. [2007] yielded a rate of 20 TgN yr$^{-1}$. A similar rate, at least 20 TgN yr$^{-1}$, has been inferred by direct measurements of N-fixation rates by Trichodesmium [Capone et al., 2005].

Several reasons could lead to this discrepancy between the literature based values and those from the restoring approach: (i) the coarse vertical resolution leads to the computation of too small gradients in $P^*$, and hence to a too small transport convergence, (ii) the vertical mixing is too small, or (iii) the vertical gradients in $P^*$ are too small due to either uncertainties in the data or excess smoothing in the horizontal due to the coarse horizontal resolution.

Adding an upper thermocline box in the low-latitude Atlantic to alleviate the coarse vertical resolution does not increase N-fixation in our models, it actually decreases it. This is because $P^*$ increases with depth in the low-latitude Atlantic [Gruber, 2004; Sigman et al., 2009]. As a
result the vertical splitting of the thermocline box causes the mean $P^*$ assigned to the upper thermocline to be lower than the mean $P^*$ used in the standard case with the thermocline box extending to 1500 m. As lower values of $P^*$ are mixed into surface waters, less N-fixation is diagnosed. We can also exclude a too small vertical mixing as an explanation, since a further increase in the vertical mixing terms changes increases N-fixation in our models only marginally.

In contrast, the diagnosed N-fixation in the low-latitude Atlantic is very sensitive to uncertainties and potential biases in the $P^*$ concentration assigned to the thermocline box in this region. Increasing this value by one standard deviation, i.e., from its standard value of 0.09 to 0.21 mmol m$^{-3}$ in the suite of 100 circulation setups with smallest cost functions increases the diagnosed N-fixation in this basin to 30 TgN yr$^{-1}$ (global rate without N-fixation diagnosed in the Southern Ocean increases correspondingly to 161 TgN yr$^{-1}$). This scenario brings our diagnosed rates in line with literature estimates of N-fixation rate in the Atlantic [Gruber and Sarmiento, 1997; Capone et al., 2005; Knapp et al., 2008].

One reason why our standard $P^*$ value may be too low is the coarse horizontal resolution of our model. An inherent weakness of geochemical box models is that properties are averaged over regions with substantial gradients. For instance, the surface box of the low-latitude Atlantic contains not only oligotrophic waters, but also nutrients rich waters since the box extends to the Polar Front Zone at 40°S. This is well reflected by the relatively high standard deviations of the properties in the surface and thermocline of the low-latitude Atlantic. This non-homogeneity was already noted by Deutsch et al. [2007] as they found a very patchy pattern of N-fixation in the Atlantic. It is therefore easily conceivable that our diagnosed rate of N-fixation in the Atlantic would be higher if the surface box was horizontally split in several smaller boxes.

The N budget approach reveals overall a similar spatial pattern as the restoring approach, with a substantially larger fixation occurring in the IndoPacific compared to the Atlantic. At the same time, the budget approach assigns a much larger fraction to the Atlantic, i.e., about 20 % of the global rate (median 25 TgN yr$^{-1}$), which implies similar rates on a per surface area basis in each basin (24 mmol N/m$^2$ yr$^{-1}$ in the Atlantic and 21 mmol N/m$^2$ yr$^{-1}$ in the oxic IndoPacific). Given the very high sensitivity of N-fixation in the low latitude Atlantic region to the rather uncertain gradient between the subsurface and surface $P^*$, we are slightly more confident in the N-fixation estimate from the budget approach, as this value is less sensitive to this gradient, as it incorporates more the large-scale data constraints. However, the large discrepancy between the two approaches in this ocean basin is clearly an issue that remains to be resolved.
2.4.6 Basin-scale budgets and N transport

The spatial separation of sources and sinks of fixed N in the ocean leads to basin-scale budget imbalances even in a situation where the global marine N budget is balanced. This requires a net lateral transport from one basin to another. In order to arrive at these basin-scale budgets and the corresponding fluxes, we summed all N fluxes diagnosed in the budget approach for each ocean (sub)basin. We used the N-fixation results from the budget approach rather than those from the restoring approach in order to guarantee a globally balanced budget required to compute lateral fluxes. A second reason is our slightly higher confidence in the budget approach-derived values of N-fixation in the low-latitude Atlantic.

We find the Atlantic ocean to generate a small excess of $16 \text{TgN yr}^{-1}$ (12 to 21 TgN yr$^{-1}$), while the IndoPacific has a small deficit of the same magnitude (Fig. 2.7). This small deficit within the IndoPacific is actually the sum of a very large deficit of $42 \text{TgN yr}^{-1}$ (32 to 52 TgN yr$^{-1}$) in the suboxic part and a surplus of $27 \text{TgN yr}^{-1}$ (15 to 40 TgN yr$^{-1}$) in the oxic part. This distribution is primarily a consequence of water column denitrification only occurring in the suboxic IndoPacific, since benthic denitrification, N-fixation, and the other N sources and sinks largely tend to cancel each other in each (sub)basin.

These basin-scale imbalances imply a net lateral transport of fixed N from the Atlantic, through the Southern Ocean and oxic IndoPacific into the suboxic IndoPacific (Fig. 2.7), consistent with the large scale distribution of $N^*$ [Gruber and Sarmiento, 1997; Gruber, 2004]. The excess of $16 \text{TgN yr}^{-1}$ (12 to 21 TgN yr$^{-1}$) in the Atlantic flows through the Southern Ocean, a basin with only a very small N imbalance - and enters the oxic IndoPacific, where an additional excess of $27 \text{TgN yr}^{-1}$ (15 to 40 TgN yr$^{-1}$) is added. This results in the transport of about $42 \text{TgN yr}^{-1}$ (32 to 52 TgN yr$^{-1}$) into the suboxic part of the IndoPacific. Considering the IndoPacific in a whole, the transport of fixed N entering the suboxic part of the basin mainly comes from the oxic part, while only one third of the fixed N comes from the Atlantic. This implies a relative close spatial coupling of the sources and sinks of fixed N in the marine environment, supporting the conclusions of Deutsch et al. [2007].

2.5 Summary and conclusion

We developed a new geochemical box model to determine the global rates of N-fixation and denitrification in the water column and sediments by inverting a large range of oceanic data. A special focus of our work was on the thorough assessment of the sensitivity of the global and basin-scale rates of the N sources and sinks to the uncertainties stemming from the data and ocean transport and mixing. To this end, we employed a suite of 2500 circulation
Figure 2.7 N-fluxes and imbalance (sources minus sinks) by water column and lateral transport for the suite of 2500 circulation configurations. Nitrogen fixation, water column and benthic denitrification rates are computed from the N-budget approach, while sediment burial, atmospheric deposition and river input of N are prescribed. Thickness of the arrows and the size of the symbols highlight the amplitudes of the fluxes.

Legend
- Atmospheric deposition
- Riverine input
- Sediment burial
- Benthic denitrification
- Nitrogen fixation
- Water column denitrification
- Later N transport

Samples (min, 5th, 95th percentiles)
configurations permitting us to determine the N-fixation and denitrification rates for the first time in a probabilistic manner.

We found that our diagnosed global rate of N-fixation is broadly consistent with literature estimates, while our denitrification rates are at the lower end compared to those reported in most recent studies. We are rather confident in our estimates, as they are consistent with a large number of data constraints, including nutrient anomalies such as $N^*$ and $P^*$, and $\delta^{15}N$. This is not the case for many of the previous studies, as they are largely based on a limited set of observations and a substantial amount of upscaling.

On a basin-scale, the magnitude of N-fixation occurring in the Atlantic remains an unresolved issue, as the two probabilistic approaches developed here do not agree. Nevertheless, our estimated range implies a maximum N-fixation rate in this basin that is on a per surface basin about as large as that in the IndoPacific. This makes the Atlantic, compared to the IndoPacific, a small player for the global marine N budget. Instead, the close coupling of nitrogen sources and sinks in the IndoPacific suggest that the N deficits generated in the denitrification regions are an important controlling factor for balancing the global N budget [Gruber, 2004; Deutsch et al., 2007].

Our finding of a largely balanced marine N-budget clearly argue against the proposition of Codispoti et al. [2001] and Codispoti [2007] of a large imbalance in the current budget, even though our budget is strictly speaking applicable only for the pre-industrial period. The largest difference to these imbalanced budgets is our much smaller denitrification estimate. Although our denitrification has a considerable uncertainty (about 30%), a substantially larger denitrification can be quite firmly excluded, as this would violate several important observational constraints, such as the distribution of $N^*$ and $\delta^{15}N$.

Our N budget implies a residence time of marine fixed N in the range 3,700 to 5,600 yr. This is at the high end compared to most recent literature estimates, but still within the range of the time-scale of the glacial/deglacial transition, leaving open the question whether and how much the marine N-cycle has contributed to the atmospheric CO$_2$ variations over these transitions.

Acknowledgments

We are indebted to Curtis Deutsch for sharing the code of his geochemical box model and for his help and many fruitful discussions. We thank Samuel Jaccard and Xavier Giraud for helpful discussions throughout this work. This work was supported by funds from ETH Zurich.
Abstract

We evaluate the change in the marine N inventory across the last deglaciation by determining the changes in N-fixation and denitrification in the water column and sediments required to optimally fit the temporal evolution of stable N isotope ($\delta^{15}$N) of organic matter in marine sediment from various oceanic basins. We use a previously described geochemical multi-basin box model of the marine N-cycle and incorporated climate forcings on N-fixation (through deposition of iron-rich dust and atmospheric $\text{CO}_2$), and denitrification in the water column (suboxia changes) and sediments (sea-level rise), as well as internal feedbacks. The optimization of the sediment $\delta^{15}$N records with respect to the strengths of the forcings and the sensitivities of feedbacks is performed by adopting a Genetic Algorithm. Scenarios that best match $\delta^{15}$N data indicate a large decrease of 26 to 48% in the marine N inventory across the last deglaciation. The broad range of possible N inventory decreases informs about the sensitivity of the modeled deglacial N inventory toward different weighting of the data. The decrease in the N inventory is primarily a consequence of a transient decrease in N-fixation at the beginning of the last deglaciation due to strong iron forcing, followed by a subsequent sharp increase due to a strong ocean internal N-feedback. Synchronously to the late-deglacial rebound in N-fixation, water column denitrification undergoes a strong increase as a consequence of an expansion of suboxic waters forcing, while changes in benthic denitrification are not well resolved with our model. Case studies demonstrate that the iron forcing is required to achieve simultaneously good fits of $\delta^{15}$N records from various oceanic basins. These changes in sources and sinks imply a drastic decrease in the marine N inventory.
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*N inventory across the last deglaciation, possibly implying a decrease in marine productivity across this transition. The marine N-cycle is therefore a potential candidate for explaining part of the glacial maximum-to-late Holocene decrease in atmospheric CO$_2$ level.*

3.1 Introduction

At the last glacial maximum (LGM), about 20 kyr ago, the atmospheric CO$_2$ concentration was about 100 ppm lower than in pre-industrial times [Petit et al., 1999]. The ocean is the most likely candidate for having stored majority of this 100 ppm, but the mechanism(s) that would have sequestered carbon there are elusive [Broecker, 1982b; Sigman et al., 2010]. Physical mechanisms as well as changes in biology are often invoked as potential mechanisms to lower glacial atmospheric CO$_2$ [Archer et al., 2000]. Among the various biologically-based explanations that have been put forward, several generate changes in oceanic carbon sequestration via iron fertilization from atmospheric dust deposition [Martin, 1990], variations in the N:P ratio, or changes in the nutrient content. In particular, a larger glacial marine N inventory has been proposed, which would have allowed greater biological sequestration of atmospheric CO$_2$ in the deep sea [McElroy, 1983] (see climate-N-cycle diagram in Fig. 3.1).

A larger glacial inventory of N would have been a consequence of the temporal variability of the dominant source and sink of N, i.e., N-fixation and denitrification [Capone et al., 1997; Codispoti et al., 2001], on glacial-interglacial time-scale.

Changes in the sources and sinks, however, are not well established, and as a consequence, the extent to which the global inventory of N changed across the last deglaciation remains elusive. Previous studies have suggested climate forcings on sources and sinks of N and thus on N inventories. Recent research has suggested at least four deglacial climate forcings on N-fixation, together with water column and benthic denitrification (Fig. 3.1). Each of these, or several together have been taken into consideration to assess past change in the global inventory of N, although no study has considered simultaneously all forcings.

Glacial-interglacial changes in N-fixation and denitrification in the water column and sediment can be reconstructed using stable N isotopes or atmospheric N$_2$O concentration. Stable N isotopes ($\delta^{15}$N, notation introduced in section C.2.1 in Appendix) of organic N preserved in marine sediments are commonly used as a proxy to reconstruct the past N-cycle, i.e., past variations in N-fixation [Haug et al., 1998; Ren et al., 2009], denitrification [Altabet et al., 1995; Ganeshram et al., 1995], the degree of NO$_3^-$ utilization by phytoplankton [Altabet et al., 1991; Francois et al., 1992], and the mean ocean $\delta^{15}$N related to changes in the N inventory [Kienast, 2000; Deutsch et al., 2004]. This proxy is based on the fact that N-fixation, water column and benthic denitrification, and N assimilation by phytoplankton have distinct isotopic fractionation.
Although the interpretation of sediment $\delta^{15}$N records is challenging (as variations in $\delta^{15}$N reflect changes in processes of local, basin-scale, and global origins) we nevertheless have some confidence in interpreting records from Oxygen Minimum Zone (OMZ) and oligotrophic regions. Downcore sediment $\delta^{15}$N records from OMZ (i.e., water column denitrification zones such as Arabian Sea, Eastern Tropical North and South Pacific), reveal a glacial maximum-to-late Holocene increase in $\delta^{15}$N followed by a subsequent decrease of smaller amplitude (Fig. 3.2A and references therein). Ganeshram et al. [1995] and Altabet et al. [1995] interpreted this data as evidence of reduced glacial water column denitrification. Another piece of evidence for lower glacial rate comes from ice core reconstructions of atmospheric N$_2$O (a product of water column denitrification) that reveals lower glacial level [Flückiger et al., 1999, 2002; Sowers et al., 2003; Schilt et al., 2010b]. Various candidates can explain glacial-interglacial change in water column denitrification through expansion or strengthening of OMZ (Fig. 3.1 blue forcing): changes in the physical supply of O$_2$ (for instance changes in ventilations, water circulation and winds), or changes in export production (for instance
changes in the location where organic matter is produced, exported and remineralized) [Broecker and Peng, 1982; Kennett and Ingram, 1995; Altabet et al., 1995; Ganeshram et al., 2000; Meissner et al., 2005; Matsumoto, 2007; Kwon et al., 2009].

Another piece of the puzzle comes from reconstruction of the past $\delta^{15}N$ in sites distant from OMZ. Kienast [2000] reported $\delta^{15}N$ values of downcore sediment records from the oligotrophic South China Sea that are attributed to $\delta^{15}N$ changes in the western Pacific subsurface $\text{NO}_3^-$ (Fig. 3.2B). The data shows small variability, attributed to complete consumption of $\text{NO}_3^-$ during the last glacial period. These records reveal that $\delta^{15}N$ has not changed significantly between the last glacial period and the Holocene. Deutsch et al. [2004] demonstrated that the fraction of total denitrification in the water column is the dominant control on the deep ocean $\delta^{15}N$. In order to restore glacial $\delta^{15}N$ in the Holocene, the system therefore requires that benthic denitrification follows a somewhat similar deglacial change than water column denitrification. However, similar glacial and Holocene mean ocean $\delta^{15}N$ do not imply that the mean value has not changed during the transition. Indeed, while all sediment $\delta^{15}N$ records could be questioned as to the influence of local processes or diagenesis, Altabet [2007] stated that a consistent picture is apparent in aggregate, with a glacial maximum-to-early deglacial increase in $\delta^{15}N$ of $\sim 2^{\circ}/00$ followed by a $\sim 1^{\circ}/00$ decrease to the late Holocene. This signal is absent from the sediment records from the South China Sea [Kienast, 2000] perhaps because sediment transport processes have made age model construction problematic for these records [Higginson et al., 2003].

It has been argued that benthic denitrification changed during deglaciation due to climate forcing related to sea-level rise. Sediments in shallow continental shelves are generally oxygen depleted due to the large amount of delivered organic matter, which drives intense benthic denitrification. Under glacial conditions, lower sea-level exposed much of the continental shelf. As a consequence, organic matter settled through a greater height of water column, which implies that more organic matter was remineralized there instead of in marine sediments, resulting in lower benthic denitrification rates (Fig. 3.1, green forcing) [Christensen et al., 1987]. During the deglaciation, sea-level rise flooded continental margins and could have significantly increased benthic denitrification. As a result sea-level rise is considered as a possible forcing on benthic denitrification. However, past benthic denitrification was not only determined by bathymetry, but also by the flux of organic matter to the sea floor. Organic flux to the sea floor depends on export production for which glacial-Holocene changes are not well established, aside from the Southern Ocean south of the Antarctic Polar Front where Kohfeld et al. [2005] reported higher glacial export.

On glacial-Holocene time-scale, there is no consensus on changes in N-fixation. N-fixation would have decreased across this transition according to the iron-rich dust hypothesis, or in contrast increased in order to balance deglacial changes in denitrification, and hence stabilized the N-cycle. Falkowski [1997] and Broecker and Henderson [1998] argued that glacial
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N-fixation was stronger and in turns lead to a larger glacial N inventory. The hypothesis of higher glacial fixation is based on the fact that diazotroph N-fixers *Trichodesmium* are sensitive to the dissolved iron concentration [Paerl et al., 1994] and on observation that atmospheric deposition of dust was several times larger at the LGM than in the Holocene [Martin,
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Figure 3.2 Downcore bulk and foraminifera test-bound δ¹⁵N records. Raw δ¹⁵N data of OMZ [to be compared with suboxic surface box] (A); the South China Sea [deep box of the oxic IndoPacific] (B); and the Caribbean Sea and the Gulf of Mexico [thermocline box of the low-latitude Atlantic] (C). Idealized δ¹⁵N records are generated by shifting raw data such that the current interglacial δ¹⁵N are in line with the modeled value at this time at each site (D,E,F). [Black line] moving-average with a timespan of 2 kyr, [gray zone] one sample standard deviation. References: OMZ: δ¹⁵N of bulk organic matter from sediment cores RC27-14 and RC27-23 on the Oman continental margin [Altabet et al., 2002], core 905 in the southwestern Arabian Sea [Ivanochko et al., 2005], and core GeoB 7139-2 off northern Chile [Pol-Holz et al., 2006]. Oxic IndoPacific: four downcore records of bulk sediment δ¹⁵N of the South China Sea [Kienast, 2000]. Low-latitude Atlantic: Foraminifera test-bound δ¹⁵N of O. universa from ODP 999A located in the Caribbean Sea [Ren et al., 2009] and O.universa from giant box core MD02-2550 from the Orca Basin in the Gulf of Mexico [Meckler et al., 2011].

1990; Mahowald et al., 1999] (Fig. 3.1, orange forcing). However, foraminifera test-bound δ¹⁵N from the Atlantic (Fig. 3.2C) which are assumed to be representative of the past N-cycle evolution in this oceanic basin, are best explained by less glacial N-fixation [Ren et al., 2009; Meckler et al., 2011]. Foraminifera O.universa δ¹⁵N from two sites in the Caribbean Sea [Ren et al., 2009] and the Gulf of Mexico [Meckler et al., 2011] exhibit similar values, with high δ¹⁵N at LGM, and show a small deglacial peak followed by a strong deglacial decrease. The glacial maximum-to-late Holocene decrease in δ¹⁵N of deep euphotic zone dwelling O. universa suggests a local- or region-wide increase in N-fixation induced by deglacial increase in denitrification, lowering the thermocline δ¹⁵NO₃ [Ren et al., 2009; Meckler et al., 2011]. The observed deglaciation peak in O.universa δ¹⁵N would have been influenced by variations in the mean ocean δ¹⁵NO₃. The interpretation of the foraminifera test-bound δ¹⁵N data from the Atlantic Ocean, if correct, would disprove the hypothesis that higher deposition of iron-rich dust under glacial conditions enhanced the rate of N-fixation. But dust deposition is not the only potential climate-related forcing that would have influenced N-fixers across glacial-interglacial transitions.

Several studies have shown that higher CO₂ increases growth rates and N- and C-fixation in Trichodesmium [Ramos et al., 2007; Kranz et al., 2010], and in unicellular diazotrophic cyanobacterium Crocosphaera [Fu et al., 2008] (Fig. 3.1, red forcing). As a result of carbon limitation, Hutchins et al. [2007] postulated that due to low atmospheric CO₂, growth and N-fixation by Trichodesmium were likely marginal at the LGM. The sensitivity of N-fixers to the carbon level could therefore provide a strong negative feedback to the glacial-interglacial atmospheric CO₂ increase.

Glacial-interglacial changes in the global inventory of N depends on transient imbalance between sources and sinks of N, which in turn depend on the strength of all forcings on N sources and sinks presented above and also on the sensitivity of negative feedbacks in their response to forcings. N-fixation and denitrification react to each other through two negative feedbacks involving changes in the N inventory, so the global N inventory is regulated
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[Gruber, 2004; Deutsch et al., 2004]. The first self-limiting feedback involves diazotrophic organisms (Fig. 3.1, brown feedback loop). Diazotrophs out-compete other phytoplankton when the N:P ratio is low [Niemi, 1979; Karl et al., 2002]. When the ratio decreases, diazotrophic N-fixation increases and thus the amount of newly fixed N released by N-fixers increases. This raises the N:P ratio and the competitive advantage of N-fixers is slowly removed. N-fixation process is discouraged since normal phytoplankton are again dominant. Haug et al. [1998] first reported evidences of such a feedback.

The second feedback that regulates the N inventory is based on water column and benthic denitrification [Codispoti, 1989] (Fig. 3.1, dark gray feedback loop). Two climate forcings involving suboxia changes or sea-level rise increase denitrification. They cause a decrease in the N:P ratio which is transported back to surface waters. Lower surface N:P will imply smaller export production and thus lower oxygen demand in the ocean. In the end, the oxygen demand impacts denitrification rate. As a result, denitrification is indirectly controlled by changes in N inventory during deglacial transitions. Ultimately, these two negative feedbacks that involve N-fixation and (water column and benthic) denitrification help to stabilize the N-cycle.

Despite such stabilizing feedbacks, the picture that has emerged is of a very dynamic marine N-cycle with centennial-scale oscillations between N sources exceeding or being exceeded by sinks, and ultimately of a fluctuating N inventory. As a result of spatially decoupled sources / sinks (the Atlantic Ocean is a net source of N and the IndoPacific Ocean a net sink [Eugster and Gruber, in prep] (see chapter 2), stabilizing negative feedbacks - transported by the global oceanic circulation - would readjust the cycle on the time-scale of the water circulation. Deutsch et al. [2004] addressed the question of the sensitivities of the feedbacks using a simple geochemical box model and showed that \( \delta^{15}N \) data from OMZ and the mean deep ocean are best reproduced with strong feedback, although their relative strength mostly remains unquantified. They reported that data are best reproduced with strong negative feedbacks that tend to limit excursions in the N-cycle, and in turn stabilize the glacial maximum-to-late Holocene change in the global inventory of N (glacial inventory no more than 30% larger than the Holocene). Furthermore, geologic records provide no evidence of dramatic changes in global export production between the last glacial period and the Holocene, suggesting that the glacial N inventory could not have been significantly different [Kohfeld et al., 2005]. However, so far no elaborated study has attempted to synchronously reproduce sediment \( \delta^{15}N \) records from multiple oceanic basins.

Here, we report on the change in the global inventory of N across the last glacial termination using the multi-basin geochemical box model of Eugster and Gruber [in prep] (chapter 2). The change in the global inventory of N is derived by computing deglacial rates of N-fixation and denitrification in the water column and sediment. Several sediment \( \delta^{15}N \) records from various oceanic basins are taken into consideration in an optimization procedure that varies
the strengths of the implemented climate forcings and the sensitivities of the internal stabilizing feedbacks in order to reconstruct past rates of sources and sinks of N. Finally, change in the global inventory of N between the last glacial period and the Holocene, and during the last deglaciation, is computed according to deglacial changes in rates of N-fixation and denitrification.

3.2 Method

We use the two-dimensional box model developed by Eugster and Gruber [in prep] (section 3.2.1). The circulation setup with smallest cost function derived in this previous study is adopted as well as the corresponding N-cycle computed from the budget approach (cycle in a steady-state). This N-cycle is prescribed as the Holocene cycle. Deglacial simulations include four climate forcings on N-fixation and denitrification, and three stabilizing feedbacks between $\text{NO}_3^-$ and N-fixation and denitrification (section 3.2.2). Seven parameters are introduced, which represent the strengths of the forcings and sensitivities of the feedbacks. For a set of parameters, the glacial N-cycle is computed and then the N-cycle is simulated forward in time across the entire deglaciation. Parameters are optimized in order to best fit sediment $\delta^{15}$N records (section 3.2.3). The model-data optimization is performed by adopting a Genetic Algorithm, which minimized the model-data $\delta^{15}$N misfit (section 3.2.4). The marine N-cycle with smallest cost function at the end of the optimization procedure (after 100 iterations with 100 sets of parameters) is presented (section 3.4.1).

3.2.1 Structure of the model

The model has the same structure as the geochemical 14-box model developed by Eugster and Gruber [in prep] (Fig. 3.3, and see chapter 2). Briefly, it resolves the Atlantic Ocean (divided into a northern and a low-latitude part), the Southern Ocean, and the joint Indian and Pacific Oceans (Indo-Pacific, divided into an oxic and a suboxic part - the suboxic Indo-Pacific is referred to as OMZ in the following and depicts the Arabian Sea, and the Eastern Tropical North and South Pacific). The suboxic lower thermocline box represents the suboxic sections of the Indian and Pacific Oceans. Key features of the Holocene ocean circulation are reproduced by advection and mixing water mass fluxes. Eugster and Gruber [in prep] determined in an inverse manner 2,500 circulation setups. Here, the circulation setup with the smallest cost function was selected (displayed in Fig. 3.3).

A comprehensive marine N-cycle that includes the cycling of the $^{15}$N isotope is simulated (sections C.1.1 and C.2.1 in Appendix give a mathematical description of the cycle). Only
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$\text{NO}_3^-$, the dominant fixed N pool in the ocean, is explicitly simulated, with N-fixation representing the dominant source and denitrification the dominant sink of $\text{NO}_3^-$. Water column denitrification is restricted to the suboxic box of the IndoPacific Ocean, while benthic denitrification and N-fixation may occur everywhere, although without a priori specified rates. The spatial (and temporal) separation between the major sources and sinks makes certain regions to be sources of N (low-latitude Atlantic or oxic part of the IndoPacific), whereas lots of N is lost in the OMZ water column.

The Holocene marine N-cycle for the circulation setup with smallest cost function estimated by the budget approach of Eugster and Gruber [in prep] (chapter 2) is used. This cycle is balanced: N-fixation releases 151 TgN yr$^{-1}$ newly fixed N, and water column and benthic denitrification consume 62, 102 TgN yr$^{-1}$ respectively (spatial distribution of each N flux are given in Fig. 3.3). Atmospheric N deposition and river input discharge of N bring 14 TgN yr$^{-1}$ each into the marine environment. Sediment burial is a sink of 14 TgN yr$^{-1}$.

Internal N fluxes have various isotopic fractionation, and external inputs and outputs of N supply and remove N with specific $\delta^{15}$N. Water column denitrification is implemented with a strong isotopic enrichment factor ($\epsilon_W = -25^{\%}$ [Cline and Kaplan, 1975; Brandes et al., 1998]), while benthic denitrification does not fractionate ($\epsilon_B = 0^{\%}$ [Brandes and Devol, 1997]). Isotopic fractionation through $\text{NO}_3^-$ assimilation by phytoplankton is included with $\epsilon_{Norg} = -5^{\%}$ [Sigman et al., 1999; DiFiore et al., 2010]. Nitrogen removed through sediment burial undergoes light isotopic fractionation ($\epsilon_B = 6^{\%}$) [Brandes and Devol, 2002]. Diazotrophs are assumed to release newly fixed N with an isotopic composition $\delta^{15}$N = 0$^{\%}$ [Carpenter et al., 1997]. Finally, two external inputs of N are simulated: atmospheric N deposition ($\delta^{15}$N = -4$^{\%}$) and river input discharge of N ($\delta^{15}$N = 4$^{\%}$) [Brandes and Devol, 2002].

3.2.2 Deglaciation simulations

Deglacial simulations compute the marine N-cycle across the last glacial termination for any sets of seven parameters which represent the strengths of the climate forcings and the sensitivities of the stabilizing feedbacks of the N-cycle. Four parameters represent climate forcings on N-fixation and denitrification, and three parameters stabilizing feedback between $\text{NO}_3^-$ and N-fixation and denitrification. For a given set of parameters, glacial conditions are analytically computed, and the N-cycle is simulated forward in time across the deglaciation according to equations of the time-trajectories of N-fixation and denitrification.

Our deglacial simulations differ from the Deutsch et al. [2004] simulations in that our model resolves the ocean spatially, including four distinct climate forcings on N-fixation and denitrification (Tab. 3.1), and adopts a Genetic Algorithm procedure for model-data optimization. Several assumptions were made, either to simplify the model, or because too little is known
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Figure 3.3: Design of the geochemical box model developed by Eugster and Gruber (in prep) (chapter 2) with N inputs and outputs (pre-industrial rates are specified), atmospheric deposition, and the oceanic water circulation and the export production (both are set constant across the deglaciation). Newly fixed N by N-fixers is redistributed throughout the water column. Water column denitrification is confined to the suboxic box of the suboxic Indo-Pacific, while benthic denitrification occurs in all boxes. Atmospheric and river input of N are sources of N in surface boxes only (except in the Southern Ocean), while sedimentation removes N from organic matter which is formed in the surface. N is taken up exclusively from the surface boxes.
at present.

- Modeled export production is constant across the last glacial termination because it is not clear to which extend glacial export production would have been different in each oceanic basin [Kohfeld et al., 2005].
- The marine P-cycle is constant across the deglaciation because of the 5 to 10 times larger residence time of marine P than the residence time of N [Ruttenberg, 1993; Benitez-Nelson, 2000; Codispoti et al., 2001; Eugster and Gruber, in prep].
- Glacial and Holocene N-cycles are balanced, which is justified by invoking (i) invariable $\delta^{15}$N records from the South China Sea and OMZ before the LGM, and (ii) the global rates of N-fixation and denitrification derived from probabilistic geochemical approaches [Eugster and Gruber, in prep] (chapter 2).
- Water circulation has not changed across the last deglaciation, which simplified substantially the model.
- Atmospheric deposition, river discharge, and sediment burial of N are set constant across the deglaciation.

Climate forcings on water column and benthic denitrification which took place during the last glacial termination are simulated analogous to Deutsch et al. [2004] model (Fig. 3.4). Forcing on water column denitrification, occurring through OMZ expansion, is simulated by a step function ($H(t)$) occurring at the onset of laminations in the Eastern Tropical Pacific, i.e., 15.5 kyrBP (BP: Before Present) [Deutsch et al., 2004]. The rationale for such a forcing is the abrupt increase in $\delta^{15}$N observed in OMZ cores (Fig. 3.2A) and atmospheric N$_2$O-partly produced by nitrification and denitrification in OMZ - reconstruction from the GRIP (Greenland Ice Core Project) ice core [Flückiger et al., 1999; Suthhof et al., 2001].

Benthic denitrification is assumed to be forced by deglacial sea-level rise, which is equivalent to assuming that the area of shallow sediments is the primary factor controlling global benthic denitrification. This may include also forcing elements from changes in export production. An idealized normalized sea-level rise forcing function is computed by fitting a hyperbolic tangent to sea-level data from Bard et al. [1990] and Hanebuth et al. [2000] (analogous to Deutsch et al. [2004] model, see function $L(t)$, Fig. 3.4 and right panel Fig. C.6 in Appendix). The same forcing is applied in all ocean basins, since the cumulative hypsometric profiles for the Atlantic, Indian, Pacific, and global ocean are similar (left panel Fig. C.6 in Appendix), and that they are roughly linear in the range -120 m to Holocene sea-level. Kohfeld et al. [2005] reported paleoclimatic records of productivity which indicate a mixed picture of the glacial-Holocene difference. It is therefore not clear to which extent glacial export production would have been higher in the Atlantic, Pacific or Indian Oceans. Despite these arguments,
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<table>
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<tr>
<th>N-flux</th>
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<th>Climate forcing (normalized function)</th>
<th>Forcing strength</th>
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<td>Water column denitrification</td>
<td>$\alpha$</td>
<td>suboxia changes: $H(t)$</td>
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<tr>
<td>Benthic denitrification</td>
<td>$\beta$</td>
<td>sea-level rise: $L(t)$</td>
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<tr>
<td>N-fixation</td>
<td>$\gamma$</td>
<td>dust deposition: $D(t)$</td>
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<td></td>
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<td>atmospheric $CO_2$: $C(t)$</td>
<td>$\rho_2$</td>
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</tbody>
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Table 3.1 Forcing and feedback parameters. H for hydrographic, L for sea-level, D for dust, and C for carbon.

modeled export production does not vary across the deglaciation in order to keep the model simple.

Our model includes two climate forcings on N-fixation, one through changes in deposition of iron-rich dust and one through atmospheric $CO_2$. Dust deposition forcing is constructed according to the dust concentration record from the Vostok ice core [Petit et al., 1999; Lambert...

Figure 3.4 The four climate forcings included in the model. $H(t)$: suboxia changes (forcing on water column denitrification), $L(t)$: sea-level rise (forcing on benthic denitrification), $C(t)$: atmospheric $CO_2$ (forcing on N-fixation), $D(t)$: iron-rich dust deposition (forcing on N-fixation).
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et al., 2008]. A linear decrease in dust flux is assumed (normalized function \( D(t) \)), starting 25 kyrBP and ending 15 kyrBP (Fig. 3.4). Carbon forcing is constructed based on atmospheric \( \text{CO}_2 \) reconstruction from the same ice core. We assume no forcing under glacial conditions. Forcing increases linearly starting from zero 17 kyrBP and reaches one at 10 kyrBP (normalized function \( C(t) \), Fig. 3.4).

Deglacial N-cycle is simulated taking into consideration local feedbacks of N-fixation and denitrification. Feedbacks are computed on the basis of change in N in surface water of the water column in order to reproduce the feedbacks suggested by Haug et al. [1998] and Codispoti [1989], (brown and gray feedback loops in Fig. 3.4). N-fixation and denitrification react to local changes in N:P ratio (in our case simply to change in N since the P-cycle does not change across the deglaciation). Changes in N in local surface water impact local rate of N-fixers and therefore the amount of newly fixed N released through the water column. Similarly, in each water column, changes in surface water N trigger changes in biological production, export flux, oxygen consumption, and ultimately water column and benthic denitrification. It has to be specified that even if changes in surface water N are assumed to influence export flux (and thus indirectly influence N fluxes), export flux is kept constant across the last deglaciation, in order to keep the model simple.

We are now in position to derive the equations that give rates of N-fixation and denitrification across the last deglaciation and the initial glacial conditions. Time-trajectories of N-fixation \((F)\), and water column \((W)\) and benthic \((B)\) denitrification in box \(i\) are expressed as a function of their Holocene rates (denoted by the index \(I\)). The Holocene rates are multiplied by a scaling term \(S_y\), a term related to the change in N inventory \((N^{i,s}(t) - N^{i,G})/N^{i,G})\) in surface waters of the water column to whom box \(i\) belongs to \((N^{i,s})\) and which is normalized by \(N^{i,G}\) so that this term represents the change in N relative to its initial glacial value, and normalized forcing functions \([H(t), L(t), D(t), C(t)]\). Forcing functions reach their maximum under the Holocene conditions, except that \(D\) goes the other way round: it starts from 1 under glacial conditions and reaches 0 under the Holocene conditions (Fig. 3.4). \(W\) is confined to the lower thermocline box of the suboxic water column, i.e., \(W^s(t)\) is non-zero only in the suboxic box. Forcing function \(L(t)\) affects surface boxes only. Finally, each forcing and feedback is scaled by a specific factor. Feedback sensitivity factors of water column and benthic denitrification, and N-fixation are \(\alpha, \beta, \) and \(\gamma\), respectively, and the strength of the forcing on water column and benthic denitrification, and on N-fixation (through deposition of iron-rich dust and atmospheric \(\text{CO}_2\)) are \(\lambda, \phi, \) and \(\rho_1\) and \(\rho_2\) (Tab. 3.1). Mathematically, deglacial N-fixation and
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denitrification are given by

\[ W^i(t) = W^i_I \left( S_W^i + \alpha \frac{N^{i,s}(t) - N^{i,s}_G}{N^{i,s}_G} + \lambda H(t) \right) \]

\[ B^i(t) = B^i_I \left( S_B^i + \beta \frac{N^{i,s}(t) - N^{i,s}_G}{N^{i,s}_G} + \phi L^i(t) \right) \]

\[ F^i(t) = F^i_I \left( S_F^i - \gamma \frac{N^{i,s}(t) - N^{i,s}_G}{N^{i,s}_G} \right) - F^i_I (\rho_1 (1 - D(t)) - \rho_2 C(t)) \]

where \( x (N^{i,s}(t) - N^{i,s}_G)/N^{i,s}_G \) (with \( x = \alpha, \beta, \gamma \)) represent the feedback terms.

Given a set of factors \([\alpha, \beta, \gamma, \lambda, \phi, \rho_1, \rho_2]\), glacial boundary conditions (i.e., glacial global rates and distributions of N-fixation and denitrification, and N inventories in each box) are computed in such a way that Holocene fluxes and inventories are reached when the model is run forward in time across the deglaciation. An analytical expression that gives changes in N between the LGM and the Holocene in each box is derived (sections C.1.1 and C.2.1 in Appendix describe the derivation of these equations):

\[ \Delta N^{i,s} = -\lambda W^i_I + \phi B^i_I + (\rho_1 - \rho_2) F^i_I - \Delta Q^i \]

This expression is a function of the current interglacial N fluxes \((W^i_I, B^i_I, F^i_I)\), forcing and feedback factors \([\alpha, \beta, \gamma, \lambda, \phi, \rho_1, \rho_2]\), and changes in N fluxes carried by physical transport \((m)\) from/to box \(i\) to/from neighbored boxes \((\Delta Q^i = Q^i_I - Q^i_G,\) with \(Q^i(t) = \sum_j m^{ij} N^j(t) - \sum_j m^{ji} N^i(t))\). It means that the global change in N inventory between the last glacial period and the Holocene is directly related to the ratio of “forcings” (minus changes in \(Q\)) over “feedbacks”. For any set of parameters \([\alpha, \beta, \gamma, \lambda, \phi, \rho_1, \rho_2]\), a quadratic system of 14 equations (Equ.3.2 applied in each 14 boxes of the model) is solved by gradient methods for the 14 unknowns \(N^{i,s}_G\). Together with Equ.3.1, which scaling term \(S_x^2\)-terms are provided by evaluating Equs.3.1 at \(t = I\) (see section C.1.2 in Appendix), the N-cycle under glacial conditions is derived. Starting with these initial conditions, the N-cycle as well as \(\delta^{15}N\) are simulated forward in time across the deglaciation. The parameters which represents the strengths of forcings and sensitivities of the feedbacks are optimized in order to best fit sediment \(\delta^{15}N\) records (see section 3.2.4).

3.2.3 Data constraints

Simulated \(\delta^{15}N\) are compared with records in three sites: the OMZ, the oxic IndoPacific, and the low-latitude Atlantic. Four downcore sediment \(\delta^{15}N\) records from the Eastern Tropical South Pacific (ETSP) and from the Arabian Sea are used as constraints of past \(\delta^{15}N\) in
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surface waters of OMZ (Fig. 3.2A). Four downcore records of bulk sediment $\delta^{15}$N of the South China Sea [Kienast, 2000] are used as constraints for the oxic IndoPacific Ocean (Fig. 3.2B). Foraminifera test-bound $\delta^{15}$N data of deep euphotic zone dwelling O. universa from the Caribbean Sea [Ren et al., 2009] and from the Gulf of Mexico [Meckler et al., 2011] are used as constraints for the low-latitude Atlantic (Fig. 3.2C).

Idealized $\delta^{15}$N records are generated from all records taken into consideration in each site (Fig. 3.2D,E,F). Holocene $\delta^{15}$N values in the Arabian Sea are lower than those in the ETSP [Altabet et al., 2002; Ivanochko et al., 2005; Pol-Holz et al., 2006] as a consequence of the localization of the sediment cores and stronger water column denitrification in the ETSP. Previous simulations using our box model showed that the N-cycle that best fit pre-industrial $N^* = NO_3^- - 16 PO_4^{3-} + 2.9 \text{ mmol m}^{-3}$, cf. Gruber and Sarmiento [1997]) and $\delta^{15}$N data suggests a value of $\delta^{15}$N in the surface box of the suboxic region very similar to the value of 12.5‰ of Pol-Holz et al. [2006] [Eugster and Gruber, in prep] (see chapter 2). Given these arguments, all OMZ records are shifted such that the pre-industrial $\delta^{15}$N are in line with the modeled value at this time. The moving average ($\mu$) with a timespan of 2 kyr, as well as the sample standard deviation - defined as $s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (d_i - \mu)^2}$ (n: number of data points d) - are computed on the basis of the shifted records (Fig. 3.2D). The same approach is applied to the records from the Southern China Sea and the low-latitude Atlantic (Fig. 3.2E,F).

The three idealized $\delta^{15}$N records are used as constraints for the $\delta^{15}$N modeled in three distinct boxes. The idealized suboxic $\delta^{15}$N record is assigned as constraint for $\delta^{15}$N modeled in the suboxic surface box (Fig. 3.3). The idealized record of the South China Sea is related to $\delta^{15}$NO$_3$ of the North Pacific Intermediate Water, i.e., the deep box of the oxic IndoPacific. Foraminifera test-bound $\delta^{15}$N data are from the Caribbean Sea [Ren et al., 2009] and from the Gulf of Mexico [Meckler et al., 2011], two sites located along the same path of surface and intermediate waters from the tropical to the subtropical North Atlantic. The idealized record stemming from these two cores is therefore used to constrain $\delta^{15}$NO$_3$ modeled in the thermocline box of the low-latitude Atlantic.

3.2.4 Optimization

A Genetic Algorithm is adopted to perform the optimization of the seven feedback sensitivity and forcing strength factors $[\alpha, \beta, \gamma, \lambda, \phi, \rho_1, \rho_2]$ (Tab. 3.1) with regard to $\delta^{15}$N records. The algorithm is a heuristic method inspired by natural evolution (a detailed description of the optimization is provided in section C.3 in Appendix and the flowchart in Fig. C.1). Briefly, an initial set of 100 deglacial scenarios is randomly generated. The fitness of the $\delta^{15}$N deglacial trajectories of each scenario is evaluated by comparing to sediment $\delta^{15}$N records at each site...
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\[ s: \]
\[ j_s = \frac{1}{n_s} \sum_{k=1}^{n_s} \frac{|\delta^{15}N_{data}^k - \delta^{15}N_{model}^k|}{\sigma_{data}^k} \]  \hspace{1cm} (3.3)

where \( n_s \) is the number of data points in \( \delta^{15}N \) record located in site \( s \) (OMZ surface waters, thermocline low-latitude Atlantic, deep oxic IndoPacific). A specific weighting factor is introduced, that allows to give more weight to the OMZ (see section 3.4.2) in the computation of the global cost function: \( J_{glob} = \sum_{s=1}^{3} \gamma_s j_s / 3 \). Then, a new set of scenarios is produced by combining scenarios according to their cost functions. Randomly, some parameters of several new scenarios are altered to be sure to fully explore the defined domain. The global cost function of the new scenarios are computed for the purpose of selecting scenarios that best reproduce the data. The algorithm is repeated 100 times until termination.

### 3.3 Comparison with Deutsch’s model

We aim to repeat and compare the best scenario that stems from our model with the best scenario from Deutsch et al. [2004] (comparison and detailed discussion in section C.4 in Appendix). For the purpose of this comparison, iron and carbon forcings on N-fixation are switched off, and only sediment \( \delta^{15}N \) records assigned to the OMZ (that is the suboxic IndoPacific surface box) and the oxic IndoPacific (considered as mean ocean in Deutsch et al. [2004] model) timeseries are fitted.

The global marine N inventory decreases between the last glacial period and the Holocene (-19%), and N-fixation, water column and benthic denitrification increase (12, 34, and 3% respectively) (Fig. C.2 in Appendix). The deglacial decrease in the N inventory is larger than that reported by Deutsch et al. [2004] while the model simulates glacial-Holocene increase in N-fixation, water column and benthic denitrification of smaller amplitudes than Deutsch et al. [2004] (40, 32, and 41%).

Our model is capable of reproducing reasonably well sediment \( \delta^{15}N \) records from the OMZ, and to a lesser extent from the oxic IndoPacific, whereas simulated \( \delta^{15}N \) in the thermocline of the low-latitude Atlantic, which site is not a constraint in this comparison simulation, do not match the observations (Fig. C.2A,B in Appendix). We suspect that including low-latitude Atlantic \( \delta^{15}N \) data as a constraint in the optimization procedure will improve modeled values, especially in this basin, with respect to paleoceanographic reconstruction. The implementation of new climate forcings on N-fixation through deposition of iron-rich dust and atmospheric \( CO_2 \) might also help to improve the quality of the fits.
3.4 Global and basin-scale deglacial changes in the N-cycle

We first report on changes in global and basin-scale N inventories and N-fixation and denitrification in the water column and sediment across the last glacial termination from a standard case with all forcing and feedback active (section 3.4.1). Then, we present several sensitivity analyses (section 3.4.2) and case studies with either the iron or the carbon forcing on N-fixation turned off (section 3.4.3). Finally, in light of the presented and discussed sensitivity analyses and case studies, we propose a scenario to explain the dynamics of N-fixation across the last glacial termination and draw concluding remarks (section 3.5).

3.4.1 Standard case

In the standard case, N fluxes and inventories are computed while fitting $\delta^{15}$N data from the OMZ, the oxic IndoPacific, and the low-latitude Atlantic. The OMZ site is given twice the weight of the two other sites in order to take into consideration the higher confidence we have in this data (see rationale in section 3.4.2). All seven parameters are switched on, i.e., four climate forcings may alter the N-cycle, and three feedbacks between $\ce{NO_3^-}$, N-fixation and denitrification are possible (Fig. 3.1, Tab. 3.1).

Global deglacial N-cycle

Our model suggests a dramatic decrease in the global inventory of N across the last glacial termination (Fig. 3.5D). Across the transition, the N inventory monotonously decreases by roughly 45% during about 10 kyr, and the current interglacial N inventory is reached in the early Holocene, i.e., $\sim10$ kyrBP.

The change in the global inventory of N is controlled by a large transient source-sink imbalance, which results from weaker N-fixation and stronger water column denitrification that last over several thousand of years (Fig. 3.5E). N-fixation first starts to steadily decrease 25 kyrBP due to strong iron forcing ($\rho_1$) that represents a decrease in deposition of iron-rich dust (Fig. 3.4). The next forcing that affects the cycle is sea-level rise, with an onset at 20 kyrBP. The optimized model suggests that the strength of this forcing is very weak, i.e., sea-level rise forcing is quasi-inoperative in the model. In addition to the strength of the forcing affecting benthic denitrification, the sensitivity of the internal feedback associated with this sink is also weak, and therefore this sink stayed constant across the deglaciation. N-fixation decreased by 34% until $\sim15.5$ kyrBP with the onset of a sharp late deglacial increase in N-fixation. This
late deglacial increase in N-fixation of 63% (relative to the lowest rate reached) is primarily due to a strong sensitivity of the feedback associated with N-fixation (\(\gamma\)) which responds to a major step function jump in water column denitrification (\(\lambda\)). This step function is due to the idealized changes in suboxia taken as forcing affecting this sink (Fig. 3.4) and to the previously generated imbalance between sources and sinks of N. This imbalance results from the prior decrease in N-fixation, and to a lesser extent the carbon forcing (\(\rho_2\)). In the end, N-fixation increases only slightly (7%) between the last glacial period and the Holocene.

The very small glacial-Holocene change in N-fixation contradicts the hypothesis of higher glacial N-fixation. Reconstruction of the past level of atmospheric CO\(_2\) compared to records of past rates of dust deposition led Broecker and Henderson [1998] to promote the Falkowski [1997] hypothesis of higher glacial N-fixation due to higher deposition rate of iron-rich dust. Although our results support strong iron forcing on N-fixation and substantially reduced N-fixation at the beginning of the deglaciation, they do not support larger glacial N-fixation. The early deglacial decrease in N-fixation is over-compensated for by a strong feedback so that Holocene N-fixation is of the same order of magnitude as that during the glacial period (Fig. 3.5E). The robustness of these results with respect to the strong iron forcing and feedback of N-fixation is evaluated later (section 3.4.3).

The weak carbon forcing of N-fixation has direct implications on the question of whether the glacial N inventory was larger than that during the Holocene or not. The carbon forcing is the only one of the four implemented forcings that has the potential to increase the global inventory of N between the last glacial period and the Holocene because it drives an increase in N-fixation during the transition (see climate-N-cycle diagram in Fig. 3.1 and the forcing functions implemented in the model in Fig. 3.4). The two denitrification forcings generate an increase in those sinks, and the iron forcing generates a decrease in N-fixation, which in turn results in a transient imbalance with sinks exceeding sources and therefore a deglacial decrease in the global N inventory. The weak strength of the carbon forcing compared to the strength of the other forcings explains the deglacial decrease in the N inventory. These findings does not depend on the sensitivities of the stabilizing feedbacks, since the feedbacks cannot overcompensate imbalances between sources and sinks of N but at most completely damp them out, implying a constant global inventory of N.

The model broadly captures \(\delta^{15}\)N features across the last deglaciation in all three sites, providing a degree of confidence in the estimated glacial-Holocene changes in the global inventory and fluxes of N (see detailed discussion about the validation of the optimization and \(\delta^{15}\)N diagnostic analysis in section C.5 and Fig. C.4 in Appendix). OMZ data is well reproduced. Modeled \(\delta^{15}\)N in the oxic IndoPacific shows a small deglacial peak which is nearly in the range of the moving average plus/minus 1 sample standard deviation of deglacial invariable \(\delta^{15}\)N records from the South China Sea [Kienast, 2000]. Altabet [2007] stated that such a deglacial peak is apparent in all sediment \(\delta^{15}\)N records. We, however, decided to use Kienast
3.4. Global and basin-scale deglacial changes in the N-cycle

Figure 3.5 The global N inventory (D), N-fixation, water column and benthic denitrification trajectories across the last glacial termination (E) for the standard case (100 iterations, 100 scenarios, OMZ site weighted twice as much as each of the two others). Circles depict equilibrium rates in the Holocene. $\delta^{15}$N constraints are OMZ (A), deep oxic IndoPacific (B), and low-latitude Atlantic thermocline (C).
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[2000] records because they are from a region where consumption of $\text{NO}_3^-$ during primary production was complete on a glacial-interglacial time-scale and we aimed to have data to be fitted in the oxic IndoPacific. Nevertheless, if a small deglacial peak is considered there - as simulated in the standard case - it would be roughly in the range of the data moving average plus/minus 1 sample standard deviation (shown by the gray band in Fig. 3.2E). The model largely captures the deglacial $\delta^{15}N$ in the low-latitude Atlantic, with the exception of slightly underestimated glacial $\delta^{15}N$ as a result of the inability of the model to simulate higher $\delta^{15}N$ in the low-latitude Atlantic than in the oxic IndoPacific (see discussion in section C.5 in Appendix). It is unlikely that basin-specific forcings would resolve this issue; however a variable deglacial export productivity specific to each oceanic basin could help to resolve this issue (section C.6 in Appendix).

Deglacial N-cycle on a basin-scale

The spatial aspect of our geochemical box model allows evaluation of basin-scale changes in N-fixation and benthic denitrification across the last deglaciation (water column denitrification is not examined since it is restricted to one water column, the OMZ). However, one should be cautious here because of the constant simulated water circulation across the deglaciation. Glacial-Holocene estimates of global-scale change in the inventory and fluxes of N are less sensitive to this simplifying assumption than basin-scale estimates of changes.

N-fixation and benthic denitrification show specific glacial-Holocene changes (Fig. 3.6A,B). Irrespective of the oceanic basin, N-fixation increases by no more than 20% between the last glacial period and the Holocene, with the exception of the Southern Ocean where it decreases by $\sim$30%.

Analogous to Eugster and Gruber [in prep] (chapter 2) we have little confidence in the N-fixation rate in the Southern Ocean because the pre-industrial rate was estimated under the assumption that phytoplankton take up N and P following the Redfield ratio, although Weber and Deutsch [2010] reported that non-N-fixing organisms uptake is non-Redfieldian there. This result, in turn, implies that the estimate of the rate of N-fixation in this region is likely biased.

Relative changes in the basin-scale inventory of N between the last glacial period and the Holocene are directly correlated to transient deviations of regional source-sink imbalances (Fig. 3.6C). Similarly to deglacial change in the global N inventory, inventories decrease by 30 to 60% in all water columns across the transition. In the extreme are the two smallest oceanic basins, i.e., the OMZ looses the least N (30%), and the North Atlantic looses the most (60%).
Reproducing a glacial-Holocene $\delta^{15}$N decrease from 6‰ to $\sim$3‰ in the thermocline low-latitude Atlantic (Fig. 3.2F) requires deglacial increase in light N input compared to heavy isotopes. Ren et al. [2009] and Meckler et al. [2011] suggested a regional glacial-Holocene increase in N-fixation which would disprove the hypothesis of higher deposition of dust that would have allowed diazotrophs to fix more N at that time [Falkowski, 1997; Broecker and Henderson, 1998]. The simulated N-fixation rate does not substantial change in the low-latitude Atlantic between the last glacial period and the Holocene (Fig. 3.6A). This contrasts with the Ren et al. [2009] estimation of a regional glacial rate of N-fixation of 20% of the pre-industrial. Within the deglaciation, the feedback-related sharp increase in N-fixation subsequent to the early deglacial iron-related decrease in N-fixation, corroborates the hypothesis of Meckler et al. [2011] that N-fixation in the Gulf of Mexico would have started to increase a short time after water column and benthic denitrification are thought to start increasing. A strong feedback on N-fixation had been suggested that would prevent a large change in the global marine N budget. A similar strong N-fixation feedback is suggested by our modeling approach (Fig. 3.5, $\gamma$).

### 3.4.2 Sensitivity analyses

In this section, we evaluate and discuss the key aspects of the optimization procedure (section 3.4.2) and the sensitivity of the deglacial N-cycle toward the weighting of the data sources (section 3.4.2).
Confidence interval on the change in the global inventory of N between the last glacial period and the Holocene

Investigations of the statistical error on the basis of the scenarios with smallest cost functions gives a sense of the confidence interval on the change in the global inventory of N, N-fixation, water column and benthic denitrification. The ten deglacial scenarios with smallest cost functions derived in the standard case not only show similar deglaciation features, but also similar changes in the magnitudes of N inventory (decreases by 44.8 to 45.1%) and fluxes between the last glacial period and the Holocene (Fig. C.5 in Appendix). This suggests that the optimization algorithm is consistently reaching the same solution.

Sensitivity of the standard case to OMZ weighting

We hypothesize that the weighting of the OMZ site relative to the two other sites is a key parameter which significantly affects the fit. Several high resolution $\delta^{15}$N records are available in OMZs, therefore the idealized $\delta^{15}$N record generated on the basis of these records is a fairly good representation of past local changes in water column denitrification. We test how changing the weight given to the OMZ data relative to the other data affects the simulated N-cycle.

In the standard case, the OMZ site is given twice the weight of the two other sites. OMZ cover relatively small regions with many high resolution $\delta^{15}$N sediment records. The idealized $\delta^{15}$N record, generated on the basis of four sediment $\delta^{15}$N records from the Arabian Sea and Eastern Tropical Pacific, is therefore a fairly good representation of past changes in OMZ $\delta^{15}$N (section 3.2.3 and Fig. 3.2D). In contrast, less weight is given to data assigned to the oxic IndoPacific due to potential diagenetic influences and other contrasting records (see discussion in section C.5 in Appendix). The low-latitude Atlantic site is also downweighted since the idealized record has been generated according to two low-resolution $\delta^{15}$N records from the same region. For the purpose of simplifying the model, the same weighting factor is used for the oxic IndoPacific and the low-latitude Atlantic, and hence one factor describes the relative contributions of the OMZ versus oxic IndoPacific and low-latitude Atlantic to the objective function. In the standard case, we aim to slightly upweight the OMZ by assigning them twice as much weight as the two other sites, i.e., a weighting factor of 2.0.

The sensitivity of the deglacial N-cycle toward the weighting factor is examined by comparing the best scenario of five simulations with OMZ weighting factors ranging from 0.5 to 10.0. The weighting factor only slightly influences modeled $\delta^{15}$N across the last deglaciation in the three sites. Modeled OMZ $\delta^{15}$N reproduce the associated data reasonably well (Fig. 3.7E). In the low-latitude Atlantic, the glacial $\delta^{15}$N is always underestimated and the late deglacial
3.4. Global and basin-scale deglacial changes in the N-cycle

Figure 3.7 Sensitivity analysis of N-fixation (A), water column (B) and benthic (C) denitrification, and the global inventory of N (D) toward OMZ-site weighing (weighting factor of 0.5 to 10.0 as compared to the two other sites). $\delta^{15}$N constraints are OMZ (E), low-latitude Atlantic thermocline (F) and deep oxic IndoPacific (G).
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$\delta^{15}$N decrease is not sufficiently abrupt (Fig. 3.7F). All models fitted with changed weighting factors simulate a deglacial $\delta^{15}$N peak in the oxic IndoPacific (Fig. 3.7G).

N-fixation, and water column denitrification show similar deglacial behavior, with lower glacial rates but different amplitude of changes, whereas deglacial behavior of benthic denitrification is very sensitive to the weighting factor (Fig. 3.7A,B,C). The amplitude of changes in these fluxes between the last glacial period and the Holocene are monotonously related to the weighting factor. The less weight assigned to the OMZ, the lower the glacial N-fixation, and thus the larger the glacial-Holocene increase (Fig. 3.7A). During the early phase of the deglaciation, N-fixation steadily decreases by 33 to 35% depending on the weighting factor, with a subsequent sharp increase of 40 to 136% compared to the minimum rate reached $\sim 15.5$ kyrBP. Water column denitrification increase between the last glacial period and the Holocene is correlated to the weighting factor, and ranges from 4 to 56% (Fig. 3.7B). A fraction of the increase in water column denitrification is explained by changes in the suboxia forcing. Before this stepwise increase, a slight decrease is observed due to negative feedback on N inventory which decreased because of lower rates of N-fixation.

Deglacial benthic denitrification is not well constrained by the paleoceanographic $\delta^{15}$N data used in this model (Fig. 3.7C). A small weighting factor implies that benthic denitrification increases between the last glacial period and the Holocene (47% increase for a factor of 0.5). In contrast, a strong factor implies a glacial-Holocene decrease of this sink (12% decrease for a factor of 10.0).

The larger the weighting factor, the larger the glacial inventory of N, i.e., more N is lost across the deglaciation (Fig. 3.7D). The N inventory decreases by 26 to 48%. This fairly high sensitivity of the N inventory to the weighting factor is a consequence of the wide confidence interval on N-fixation, but also of the confidence intervals of water column and benthic denitrification.

For a given OMZ weighting factor, we have shown that the change in the global inventory of N is relatively well defined (section 3.4.2). However, this change is sensitive to the weighting factor (section 3.4.2). Nevertheless, irrespective of whether the weighting factor is set to 0.5 (OMZ downweighted with respect to the other sites) or to 10.0 (OMZ strongly upweighted), our results indicate that the global inventory of N decrease by 26 to 48% between the last glacial period and the Holocene, which strengthens the hypothesis that deglacial changes in this inventory may explain part of the decrease in the atmospheric CO$_2$ level over this period.
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3.4.3 Case studies

The robustness of our findings and the mechanisms underlying changes in the deglacial N-cycle are examined by turning off the iron forcing (section 3.4.3) or the carbon forcing (section 3.4.3) affecting N-fixation. The importance of the data constraint across the transition is also evaluated by fitting glacial and Holocene data only (section 3.4.3).

1st Case study: no iron forcing on N-fixation

In contrast to the strong evidence of varying water column denitrification across deglaciation (from sediment $\delta^{15}$N records or atmospheric $N_2O$ reconstruction for instance), the hypothesis that N-fixation varied over this time-scale is mainly based on changes in factors that are believed to be limiting for Trichodesmium (e.g. iron, via a change in deposition of iron-rich dust or carbon through change in atmospheric $CO_2$ level). Here, we evaluate how well our model can reproduce $\delta^{15}$N data with the iron forcing turned off, in order to test the importance of this forcing with regard to the standard case (all forcings active). The previously popular iron-rich dust hypothesis of Falkowski [1997] and Broecker and Henderson [1998] is strengthened if the model cannot capture $\delta^{15}$N data. Should the opposite occur, it implies that the model does not have the potential to resolve the question of whether N-fixation or denitrification is the key driver across deglaciation.

The model is not able to reproduce $\delta^{15}$N data in the three sites when the iron forcing affecting N-fixation is turned off and the OMZ data are weighted twice as much as the others. The deglacial $\delta^{15}$N decrease in the low-latitude Atlantic is too smooth, and the glacial oxic IndoPacific $\delta^{15}$N is overestimated (Fig. 3.8B,C). The N inventory decreases by 32% between the last glacial period and the Holocene, and N-fixation, water column and benthic denitrification increase by 13, 15, and 20% respectively (Fig. 3.8D,E). The major differences in term of the strengths of the forcings and feedbacks with the standard case are stronger forcing and feedback of benthic denitrification (see table in Fig. 3.8).

In order to better understand the role of the iron forcing on fixation and on the deglacial N-cycle, the optimization is forced to better reproduce OMZ $\delta^{15}$N. This is achieved by weighting the OMZ data 10 times more than the others. In this case, $\delta^{15}$N data from the OMZ and oxic IndoPacific are well reproduced, while modeled glacial $\delta^{15}$N in the low-latitude Atlantic strongly underestimates the data (Fig. 3.8A,B,C). The deglacial decrease in the global inventory of N is smaller (21%) and N-fixation, water column and benthic denitrification increase with larger amplitudes (36, 57, and 23% respectively) (Fig. 3.8D,E), implying a more dynamic N-cycle, than in the case where the OMZ data are weighted twice as much as the others and without the iron forcing.
Figure 3.8  Sensitivity analyses toward the iron forcing affecting N-fixation with OMZ weighting factor of 2 and 10, and without data constraint during deglaciation (the best scenario of the last iteration from simulations with 100 iterations, 100 scenarios, OMZ site weighted twice as much as each of the two others if nothing else specified). $\delta^{15}$N constraints are OMZ (A), deep oxic IndoPacific (B), and low-latitude Atlantic thermocline (C). The global inventory of N (D), N-fixation, water column and benthic denitrification across the last deglaciation (E).
3.4. Global and basin-scale deglacial changes in the N-cycle

Model/data $\delta^{15}$N comparisons suggest that the iron forcing is required to achieve simultaneously good fits in the OMZ, the oxic IndoPacific, and the low-latitude Atlantic. The direct implication of an active iron forcing is that N-fixation is the driver across deglaciation, i.e., N-fixation is altered before denitrification during deglaciation. The early deglacial decrease in deposition of iron-rich dust leads to a decrease in N-fixation, which slightly increases $\delta^{15}$N in all oceanic basins (Fig. 3.5A,B,C). This increase in modeled $\delta^{15}$N is observed in the low-latitude Atlantic, which permits the glacial/early deglacial model/data discrepancy to be decreased (Fig. 3.5C). In addition, it seems that the model needs low N-fixation in the mid-deglaciation so that this source of low $\delta^{15}$N can then abruptly increase - but without reaching higher rate in the Holocene than under glacial conditions - and in turn decrease $\delta^{15}$N in the low-latitude Atlantic in order to reproduce the sharp late deglacial decrease in $\delta^{15}$N observed in this basin (see also the discussion on the deglacial N-cycle on a basin-scale in section 3.4.1). In conclusion, when the iron forcing is turned off and the OMZ site is weighted twice as much as the other two sites, the model optimization procedure is not able to reproduce sediment $\delta^{15}$N records from all sites because of the required timing of change in $\delta^{15}$N source-sink in the low-latitude Atlantic versus oxic IndoPacific and OMZ.

2nd Case study: no carbon forcing on N-fixation

When the carbon forcing affecting N-fixation is turned off, a deglacial N-cycle similar to the cycle that emerges from the standard case is simulated, aside from variation in water column denitrification (not shown). The global inventory of N decreases by 47%, N-fixation exhibits a large transient decrease and a glacial-Holocene increase of 5%, and benthic denitrification increases by 1%. On the other hand, water column denitrification is more dynamic than in the standard case due to strong feedback and forcing. Before the onset of suboxia changes, it decreases from its glacial rate of 55 TgN yr$^{-1}$ to 27 TgN yr$^{-1}$ as a consequence of a strong negative response to decrease in N-fixation. Water column denitrification is also strongly affected by changes in suboxia and hence increases to 81 TgN yr$^{-1}$ before decreasing to the Holocene rate of 62 TgN yr$^{-1}$. We suspect that this strong increase in water column denitrification is required, together with strong sensitivity of the N-fixation feedback, so that N-fixation sharply increases during the late deglaciation in order to compensate for the deactivated carbon forcing. This case study shows good data fits at all sites. In conclusion, the carbon forcing plays a minor role since this case study shows a deglacial N-cycle very similar to the one stemming from the standard case, aside from stronger forcing and feedback strength of water column denitrification.
Chapter 3. Large Decrease in the N Inventory across the Last Deglaciation

3rd Case study: glacial and Holocene data constraints only

We test the role of the data constraint during the transition by fitting the glacial period and the Holocene only, i.e., without including deglacial data (no data constraint between 20 and 5 kyrBP). The deglacial N-cycle is similar to the standard case, with a decrease in the global inventory of N of 52%, and N-fixation, water column and benthic denitrification changing by 1, 11, -4% respectively (Fig. 3.8). The transient decrease in N-fixation is of larger amplitude, due to a stronger iron forcing, than in the standard case. The model captures reasonably well the data in the OMZ and low-latitude Atlantic, while a large deglacial peak is simulated in the oxic IndoPacific.

Turning off the data constraint during the transition gives a similar decrease in the global inventory of N than computed in the standard case. However, the $\delta^{15}$N data are better reproduced in the standard case, implying that transient data help to constrain the model, especially in the oxic IndoPacific.

3.5 Discussion and conclusions

We used the geochemical box model developed by Eugster and Gruber [in prep] (chapter 2) to perform deglacial simulations of the marine N-cycle. Various climate forcings are included in simulations of the last glacial termination to examine the marine N-cycle, with particular emphasis on the variation in the global inventory of N. For the first time, a modeling approach incorporates simultaneously opposing climate forcings affecting N-fixation through the effect of change in deposition of iron-rich dust and atmospheric $CO_2$, climate forcing affecting water column denitrification through suboxia changes, and climate forcing affecting benthic denitrification through variation in sea-level. Other innovative aspects of this study are: (i) its spatial dimension since it attempts to reconstruct simultaneously sediment $\delta^{15}$N records from several sites located in different oceanic basins, (ii) the powerful optimization approach adopted, and (iii) the evaluation of the sensitivity of the deglacial N-cycle toward various weighting of the paleoceanographic data. The model makes several simplifying assumptions: the global export production, the marine P-cycle, water circulation, and atmospheric and river input of N are considered constant on glacial-interglacial time-scale.

An important simplifying assumption we make is that the global export production of organic matter is constant across the last deglaciation. This assumption is probably the most appropriate since global and local changes in export production are not well established. Kohfeld et al. [2005] reported paleoclimatic records of productivity which indicate a mixed picture of the glacial-Holocene difference aside from lower glacial export production in the Southern
Ocean south of the Antarctic Polar Front. Therefore, even if changes in export production across the last deglaciation might have altered $\delta^{15}\text{NO}_3^-$, and thus the $\delta^{15}$N observed in marine sediments, as a consequence of isotopic fractionation during N assimilation by phytoplankton, the simulated export production is constant.

The marine P-cycle was set to be temporarily constant in the box model. The current scientific paradigm states that on the time-scale of the last glacial-interglacial transition (few thousands of years), the marine P-cycle was not particularly dynamic when compared to the N-cycle. This is due to the fact that P has a large residence time of 20 to 30 kyr in the marine environment [Ruttenberg, 1993; Delaney, 1998; Benitez-Nelson, 2000], which is 5 to 10 times larger than the residence time of N [Gruber and Sarmiento, 1997; Codispoti et al., 2001; Eugster and Gruber, in prep]. This means that changes in the P-cycle could not have been fast enough to affect the N-cycle on glacial-Holocene time-scales. However, Wallmann [2010] reported a residence time of P of only a few kyr based on the most recent estimates of P removal fluxes. He predicted that the P-cycle is more dynamic than previously thought, and that it could be possible that the $\text{PO}_4^{3-}$ and phosphorus budgets were not in a steady-state during the pre-industrial period [Wallmann, 2010]. A number of recent studies also suggested that the LGM inventory of P was much higher than the pre-industrial inventory [Ganeshram et al., 2002; Filippelli et al., 2007; Tamburini and Foellmi, 2009]. These variations in the P-cycle could have affected N-fixation through changes in the specific growth requirements for diazotrophs and other phytoplankton (N:P ratio), since these variations would have altered the competitive success patterns of N-fixers. Denitrification might also have been altered through changes in export production and hence rates of remineralization and O$_2$ consumption in the deep ocean. This downward revision of the residence time of P raises the question as to whether N or P was the limiting factor during this period. Due to the ability of diazotrophs to bring newly fixed N into the cycle, Tyrrell [1999] suggested that N is the proximate limiting nutrient and P the ultimate limiting nutrient over geological time-scales. The implications of a constant glacial-Holocene marine P-cycle for the rates of N-fixation and denitrification reported here cannot be foreseen since the sign, the amplitude, and the spatial changes in $\text{PO}_4^{3-}$ across the last deglaciation remain elusive.

Our model simulates a global N inventory decreasing by 26 to 48% across the last glacial termination. This substantial decrease is a consequence of deglacial changes in N-fixation and denitrification which are required to best fit sediment $\delta^{15}$N records from various sites in different oceanic basins. The inventory decrease is a consequence of a transient decrease in N-fixation (-33 to -35%) at the beginning of the deglaciation, followed by a sharp increase (40 to 136%) so that glacial rate of N-fixation is roughly restored in the Holocene. The fact that N-fixation hardly changes between the last glacial period and the Holocene contradicts the hypothesis of higher glacial rates of N-fixation [Falkowski, 1997; Broecker and Henderson, 1998]. The global rate of water column denitrification increases by 4 to 56% across
the transition compared to the glacial rate, while the change in the global rate of benthic denitrification cannot be resolved with our model (it can either increase, +47%, or decrease -12%).

The general picture that emerges is that the iron and the changes in suboxia are the dominant forcings, and that the feedback with strongest sensitivity involves N-fixation. In combination with strong sensitivity of the feedback, N-fixation only slightly changes between the last glacial period and the Holocene, although the model reveals that the iron forcing is strong and generates a substantial transient imbalanced N-cycle with sinks exceeding sources. The imbalance starts to be reduced as a consequence of the strong sensitivity of the N-fixation feedback at the time of the synchronous stop in the iron forcing and the step function increase in water column denitrification due to changes in suboxia. The cumulative effect of transient weaker N-fixation and later adjustment of a balanced N-cycle implies a transient imbalance with sinks exceeding sources and hence a glacial-Holocene decrease in the global inventory of N.

We propose a scenario to explain the dynamics of N-fixation across the last deglaciation (Fig. 3.9). Variation of three potential limiting factors of diazotroph included in the model are taken into consideration: $N^*$ (that is change in the N:P ratio, described by the feedback term in the model, see Equ.3.1), the iron availability (via the atmospheric deposition of iron-rich dust), and the carbon level (via atmospheric $CO_2$). Here, we assume that the iron control on diazotrophs is influenced by the carbon level. A higher carbon level would weaken the diazotrophs requirement for iron. Under glacial conditions the iron input is large due to large rates of dust deposition and the atmospheric $CO_2$ level is low. This would favor N-fixation [Paerl et al., 1994]. During the early deglaciation, rates of dust deposition decrease (negative influence on N-fixation) and the atmospheric $CO_2$ level remains constant, N-fixation is therefore reduced (see Fig. 3.9). The abrupt changes in suboxia 15.5 kyrBP reduces $N^*$ and hence favors N-fixation (stabilizing feedback, cf. Haug et al. [1998]). Simultaneously, the decrease in rates of dust deposition stops and the level of atmospheric $CO_2$ starts to increase. Both low $N^*$ and increasing carbon level strongly favor N-fixation. Consequently, rates of N-fixation increase to values close to those found under glacial conditions.

There are direct important biogeochemical implications of a doubled glacial inventory of N compared to the current interglacial inventory for the past atmospheric $CO_2$ evolution. Since N is the major limiting nutrient in the modern ocean, a 30 to 50% increase in the global inventory of N would cause a 30 to 80 ppm change in the atmospheric $CO_2$ level [Archer and Johnson, 2000; Sigman and Boyle, 2000]. Taking into account the estimated sensitivity of the N inventory to the atmospheric $CO_2$ level, and assuming a more conservative glacial maximum-to-late Holocene decrease in the global inventory of N of one third (see section 3.4.2), we argue that in contrast to the conclusions of Deutsch et al. [2004], the marine N-cycle could have played a major role in the evolution of past atmospheric $CO_2$. 
3.5. Discussion and conclusions

Figure 3.9  Proposed scenario to explain the dynamics of N-fixation across the last deglacial- tion. N-fixation was influenced by $N^*$, the input of iron from atmospheric dust deposition and atmospheric CO$_2$. The last glacial termination is divided into a glacial, an early deglacial, a late deglacial, and the current interglacial (Holocene) periods. Changes in $N^*$, iron input, and carbon level (upper part of the figure) and how these factors favor (⊕) or restrict (⊖) N-fixation (middle part). Variation in N-fixation depends on the individual participation of $N^*$, the iron input, and the atmospheric CO$_2$, with the assumption that carbon has the potential to influence the iron requirement of diazotroph (lower part).

Acknowledgments

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Chapter 4

Implementing N Isotopes in the BEC Model

4.1 Introduction

N-fixation and denitrification are the main source and sink of N in the marine environment [Capone et al., 1997; Gruber, 2008]. Nitrogen enters the marine N-cycle mainly through N-fixation by diazotrophic organisms (see section 1.2.2 and Fig. 1.2). These organisms, found in warm surface waters [Capone et al., 1997; Karl et al., 2002], are the only phytoplankton that are capable of converting $N_2$ into organic forms of N. This source of N is roughly balanced by denitrification which is the dominant sink for N [Gruber and Sarmiento, 1997; Codispoti et al., 2001]. Denitrification is a bacterial process in which $NO_3^-$ is used as the terminal electron acceptor and $N_2$ is ultimately produced (see section 1.2.3). This sink of N is found in waters with low oxygen concentration, either within the water column in the so-called Oxygen Minimum Zones (OMZs) or in marine sediments.

N-fixation, denitrification, as well as $NO_3^-$ and $NH_4^+$ uptake by phytoplankton, zooplankton excretion, and nitrification (the sequential oxidation of $NH_4^+$ to $NO_3^-$) have specific isotopic fractionation, i.e., these processes discriminate between the two stable isotopes of nitrogen, $^{14}N$ and $^{15}N$ (see section A.3 and Tab. A.1 in Appendix). The specific enrichment factors associated with these processes were determined in previous studies. This, in turn, provides a mean of studying N-fixation and denitrification.

In a recent modeling approach, Eugster and Gruber [in prep] (chapter 2) used N isotopes and deviations of the canonical N:P ratio to reconstruct rates and distributions of N-fixation and denitrification in a probabilistic approach, and they addressed the question whether the pre-industrial marine N-cycle was balanced or not. They reported pre-industrial global rates of N-fixation, water column and benthic denitrification of 120 TgN yr$^{-1}$ (85 to 160 TgN yr$^{-1}$, 5th to 95th percentile), 50 TgN yr$^{-1}$ (40 to 65 TgN yr$^{-1}$) and 80 TgN yr$^{-1}$ (55 to 110 TgN yr$^{-1}$) which yield a N-cycle that is balanced to within 15 TgN yr$^{-1}$ ($-25$ to 50 TgN yr$^{-1}$).

There is much interest in incorporating a N isotope model in finer resolution and higher
complexity ecosystem models embedded in ocean Global Circulation Models (GCMs). The recent development of high-resolution and complex biogeochemical model holds great potential for examining the marine N-cycle with particular emphasis on its dynamics and its sensitivity to climate forcings. The previous studies based on a geochemical box model allow numerous sensitivity analyses over thousand of years but with coarse resolution (see chapters 2 and 3). In contrast, complex biogeochemical models included in GCMs, which have high resolution, allow to take advantage of localized geochemical data. The finer resolution and high complexity of these models is to the detriment of the computation power they require, and hence long time-scale simulations cannot be envisaged. Intermediate complexity ecosystem models included in GCMs also permit a finer examination of the N-cycle since they simulate several N pools and N exchanges between the pools.

So far, only one study included a dynamic N isotope model within a GCM [Somes et al., 2010b]. This study addressed the effect of various fractionating processes on the distribution of $\delta^{15}$NO$_3$ ($\delta^{15}$N = ($R/R_{atm} - 1) \cdot 1000/0$, with $R$ and $R_{atm}$ the isotope ratios $^{15}$N/$^{14}$N in the sample and in the atmosphere, which is taken as reference, i.e., $R_{atm} = 0.3663/99.633$, respectively). Water column denitrification, N-fixation, and NO$_3^-$ uptake by phytoplankton were reported to have the strongest effects on $\delta^{15}$NO$_3$. Zooplankton excretion was a secondary control on N isotopes. However, the ecosystem model used by Somes et al. [2010b] was relatively simple. This model contained only one general NO$_3^-$ assimilating phytoplankton class. Additionally, it did not include NH$_4^+$, and thus did not simulate nitrification, although this process has a rather strong enrichment factor and is the most important source of NO$_3^-$ for benthic denitrification.

Here we report on the implementation of a complex dynamic N isotope model and benthic denitrification into the intermediate complexity multiple limiting nutrients Biogeochemical Elemental Cycling (BEC) model which is run within the Community Climate System Model (CCSM) Parallel Ocean Program module [Collins et al., 2006] (section 4.2). A detailed description of the implemented benthic denitrification model is provided with a comparison of simulated rates with data-based estimates (section 4.3). Technical aspects on the incorporation of the marine N isotope module are presented (section 4.4). First millennium-scale equilibrium runs are reported with pre-industrial boundary conditions (section 4.5). The equilibrium run which best match observations (mean ocean $\delta^{15}$NO$_3$ and the global export flux of POC) is discussed in detail and model validation is started (section 4.6). We summarize the most important findings, present an outlook of future goals and envisaged simulations using this model (section 4.7). Model equations of N and $^{15}$N and parameter values are provided at the end of the thesis (section D.1 in Appendix).
4.2 The model

4.2.1 Description of the CCSM

The CCSM is a three dimensional coupled climate model that simulates the Earth's climate system [Collins et al., 2006]. This project is a cooperative effort among climate researchers, centered at the National Center for Atmospheric Research (NCAR, USA). The CCSM is one of the world's most powerful climate models used to conduct fundamental research on the past, present and future. It consists of four fully coupled dynamical components that simulate the atmosphere, the ocean, the land surface and sea ice. The ocean component contains the BEC model we focus on.

4.2.2 Description of the Biogeochemical Elemental Cycling model

The BEC model is a global marine ecosystem model with several phytoplankton functional groups. It is an adaptation of the ecosystem model of Doney et al. [1996]. We use BEC model Version 1.25, the version used in Moore et al. [2004], coupled to a modified version of the OCMIP-2 biogeochemistry model [Doney et al., 2003]. A water column denitrification scheme has been added to this model (see section D.1.7 in Appendix). The physical model is the coarse-resolution POP ocean component of the NCAR CCSM [Collins et al., 2006]. The BEC model has previously been described by Moore et al. [2002] and Moore et al. [2004]. It simulates the biogeochemical cycling of C, O, N, P, Fe, Si, and alkalinity. These nutrients, e.g. $\text{NO}_3^-$, $\text{NH}_4^+$, $\text{PO}_4^{3-}$ and Fe, can regulate the growth rates of the various phytoplankton groups.

Three functional groups of phytoplankton are included: small phytoplankton (nano- and picoplankton), diazotrophs (N-fixers), and diatoms (large silicifying phytoplankton) (Fig. 4.1). Coccolithophores (calcifying phytoplankton) are included implicitly as a variable fraction of the small phytoplankton. Phytoplankton functional groups have specific growth parameters and nutrient and light requirements. Small phytoplankton class can be limited by available N ($\text{NO}_3^-$ and $\text{NH}_4^+$), P, Fe, and light levels, while diatoms are also limited by Si. Under strongly nutrient limiting conditions, small phytoplankton tend to dominate. In contrast, diatoms are very abundant under nutrient rich conditions and high photosynthetically available radiation. Diazotrophs are the only organisms capable of N-fixation of $\text{N}_2$ into bioavailable N compounds. The growth rates of Trichodesmium may be limited by P, Fe, and light levels (see section 1.2.2).

There are various phytoplankton mortality/loss terms in the BEC model: grazing losses, losses due to non-grazing mortality, and losses due to aggregation (Fig. 4.1, see detailed
description in Moore et al. [2002] and Moore et al. [2004]). The routing of biomass between particulate organic matter (POM), dissolved organic matter (DOM), and $\text{NH}_4^+$ depends on the type of phytoplankton and loss process. None of the diazotroph non-grazing mortality is routed to POM and since it is assumed that diazotrophs cannot sink out of the surface waters, they do not have aggregation losses. Conversely, small phytoplankton and diatoms...
aggregation losses go exclusively into POM.

A single zooplankton class is incorporated in the model. It was decided to simulate only one grazer because this makes the BEC model more stable than a system with multiple zooplankton functional types. Zooplankton graze on small phytoplankton, diatoms, and diazotrophs (Fig. 4.1). Even though there is only one zooplankton class, grazing and growth characteristics depend on the food source (Tab. 4.1). 30% of organic matter grazed by diatoms and small phytoplankton is incorporated into zooplankton biomass, while a smaller fraction of grazed diazotrophs is routed to new zooplankton biomass. Non-assimilated grazed material mostly represents excretion by the zooplankton, even though a small fraction would account for sloppy feeding (K. Moore personal communication). There is no zooplankton mortality routed to POM and respiration is neglected.

<table>
<thead>
<tr>
<th>Grazed organic matter goes to</th>
<th>Diazotrophs</th>
<th>Small phytoplankton</th>
<th>Diatoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assimilated (biomass)</td>
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<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>PON (partly excretion)</td>
<td>0.00</td>
<td>0.34 · γsp</td>
<td>0.26</td>
</tr>
<tr>
<td>DON (partly excretion)</td>
<td>0.24</td>
<td>0.34 · (1 − γsp)</td>
<td>0.13</td>
</tr>
<tr>
<td>NH₄⁺ (partly excretion)</td>
<td>0.55</td>
<td>0.36</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 4.1 Details of grazing losses. Grazed material routed to PON, DON and NH₄⁺ mostly represent excretion (non-assimilated nutrients). Fraction of grazed small phytoplankton routed to POM, γsp, depends on CaCO₃ and C biomass levels.

The fraction of biomass routed through remineralization pathways and the detrital pools depends on the type of phytoplankton eaten (Tab. 4.1). The detrital pools consist of one non-sinking pool, which largely represents DOM, and one large particulate detrital pool, which represents POM and sinks out of the mixed layer.

Nitrogen enters the marine cycle through N-fixation by diazotrophs and is removed by denitrification. N-fixers have been modeled after *Trichodesmium*, since the datasets existing for them are the most robust ones in terms of biomass and diazotrophic activity. *Trichodesmium* was reported to release N in the form of DON and NH₄⁺ [Capone et al., 1994; Mulholland et al., 2004] (Fig. 4.1). According to studies about *Trichodesmium*, diazotrophs exude 30% of the fixed N fixed from N₂ as DON (see related ¹⁵N equations in section D.1.6 in Appendix), and it is assumed that all N required by diazotrophs is met through N-fixation, hence the N supply can not be growth-limiting. However, *Trichodesmium* have been found to take up NO₃⁻ and NH₄⁺ to a lesser extent. The diazotrophic C:N:P elemental ratios are set at 365:50:1 (P:C ratio is 0.002735 and C:N ratio is 16), that is C:N are set to Redfield values and the N:P ratio is higher than Redfield, according to Letelier and Karl [1998]. The C:N ratio of non-sinking detritus is not kept constant at 117:16, but rather varies, since additional extra DON
Chapter 4. Implementing N Isotopes in the BEC Model

is excreted by diazotrophs.

Nitrogen forms released by diazotrophs are ultimately consumed by small phytoplankton and diatoms. DON released by diazotrophs is remineralized and nitrification oxidizes \( \text{NH}_4^+ \) to \( \text{NO}_3^- \). This N released by diazotroph organisms is essential for the growth of small phytoplankton and diatoms because \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) can limit their growth. Small phytoplankton and diatoms have fixed C:N:P ratios of 117:16:1 (based on Anderson and Sarmiento [1994]). The same elemental ratios are assumed for zooplankton. The C:N ratio of POM is also 117:16 because POM comes from aggregation, non-grazing mortality, and zooplankton grazing on small phytoplankton and diatoms, which have the same elemental ratio. It is assumed that the initial C:N ratio of POM is conserved through the water column settling.

Organic matter is decomposed either through the consumption of \( \text{O}_2 \) (aerobic remineralization) or through the consumption of \( \text{NO}_3^- \) (denitrification). The aerobic remineralization does not consume any forms of N, while denitrification takes up \( \text{NO}_3^- \) instead of \( \text{O}_2 \). In 2005, a water column denitrification scheme was added to the BEC model (described in [Moore and Doney, 2007]). When \( \text{O}_2 \) is below 4 nmol/cm\(^3\), and if \( \text{NO}_3^- \) is available, organic matter is remineralized through water column denitrification. Moore and Doney [2007] set a \( \text{NO}_3^- \) threshold of 32 mmol/m\(^3\) below which water column denitrification does not occur. The threshold was adjusted so that water column denitrification was roughly equal to N-fixation, which in turn implies that the marine N inventory does not drift to an unrealistic state during millennium-scale simulations. In the present study, this \( \text{NO}_3^- \) threshold is adjusted to avoid large drifts in the global N budget and the export flux of POC for simulations over time-scales of millennia (with benthic denitrification, see section 4.5). Organic matter that reaches the marine sediment is instantaneously remineralized and released as inorganic N in the bottom layer, through aerobic remineralization or through benthic denitrification (Tab. 4.2). The incorporation of benthic denitrification is detailed below (section 4.3).

4.2.3 N-fixation and denitrification

In the following, we focus on the global rates and patterns of N-fixation and water column denitrification (from BEC model version 1.25) [Moore and Doney, 2007]. In a later section, we present simulations with N fluxes that deviate from these original rates as a consequence of the incorporation of benthic denitrification and the adjustment of several parameters related to diazotroph organisms and denitrification (section 4.6.2). Adjustments aim to reproduce a realistic mean ocean \( \delta^{15}\text{NO}_3^- \) and to minimize drifts in the global \( \text{NO}_3^- \) budget and export flux of POC during millennium-scale equilibrium runs that include benthic denitrification.

The original BEC model broadly captures the spatial distribution and global rates of diazotrophs [Moore et al., 2004]. A global N-fixation rate of 62.8 TgN yr\(^{-1}\) was reported. This
### in each grid-cell

<table>
<thead>
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<th>state variable</th>
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<th>bottom cell (sea floor)</th>
<th>no bottom cell</th>
<th>bottom cell (sea floor)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>only aerobic remineralization (no isotopic fractionation)</td>
<td>partly benthic denitrification (no isotopic fractionation)</td>
<td>water column denitrification (does fractionate)</td>
<td>partly benthic denitrification (no isotopic fractionation)</td>
</tr>
<tr>
<td>water column denitrification</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>benthic denitrification</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2$</td>
<td>$J_{\text{poc}} - R_{\text{C:N}}^{\text{fbd}} \text{BD} + \text{rem}_{\text{dom}} \text{DOC}$</td>
<td>$J_{\text{poc}}/R_{\text{C:N}}^{\text{fbd}} \text{BD} / R_{\text{C:O}}^{\text{p}} + \text{rem}<em>{\text{dom}} \text{DOC} / R</em>{\text{C:O}}^{\text{C}}$</td>
<td>$0$</td>
<td>$J_{\text{poc}} / R_{\text{C:N}}^{\text{fbd}} \text{BD} / R_{\text{C:N}}^{\text{fbd}} \text{BD} / R_{\text{C:O}}^{\text{p}} + \text{rem}<em>{\text{dom}} \text{DOC} / R</em>{\text{C:O}}^{\text{C}}$</td>
</tr>
<tr>
<td>$NO_3$</td>
<td>$0$</td>
<td>$J_{\text{poc}}/R_{\text{C:N}}^{\text{fbd}} \text{BD} / R_{\text{C:N}}^{\text{fbd}} \text{BD} / R_{\text{C:O}}^{\text{p}} + \text{rem}<em>{\text{dom}} \text{DOC} / R</em>{\text{C:O}}^{\text{C}}$</td>
<td>$0$</td>
<td>$J_{\text{poc}} / R_{\text{C:N}}^{\text{fbd}} \text{BD} / R_{\text{C:N}}^{\text{fbd}} \text{BD} / R_{\text{C:O}}^{\text{p}} + \text{rem}<em>{\text{dom}} \text{DOC} / R</em>{\text{C:O}}^{\text{C}}$</td>
</tr>
</tbody>
</table>

| if $O_2 > S_{O}^{\text{wcd}}$ | | | | |
| if $O_2 \leq S_{O}^{\text{wcd}}$ | | | | |

Table 4.2 Details of aerobic remineralization and water column (WCD) and benthic (BD) denitrification with their respective $O_2$ and $NO_3^-$ consumption (terms defined in section D.1 in Appendix). All organic matter remineralized in a grid-cell undergoes water column denitrification if $O_2 < S_{O}^{\text{wcd}}$ and $NO_3^- > S_{NO_3}^{\text{bd}}$. Organic matter entering a bottom cell is instantaneously remineralized (global remineralized flux: $J_{\text{poc}}^r$) through a mix of benthic denitrification, and aerobic remineralization and water column denitrification according to $O_2$. Aerobic remineralization and $J_{\text{poc}}^r$ are expressed in [mmol C/m$^3$/sec]. WCD and BD are in [mmol N/m$^3$/sec] and $O_2$ and $NO_3^-$ in [mmol/m$^3$].
is at the lower range of literature estimates (Tab. 1.3) possibly due to unresolved eddies, storms and others mesoscale processes that are sources of nutrients in tropical and subtropical regions [Moore et al., 2004]. The model has a low N-fixation rate in regions with low dissolved Fe, indicating that Fe strongly limits diazotroph growth rates (for instance, fixation is more abundant in the Western Pacific where the atmospheric deposition of Fe is greater, see Fig. 4.8A). N-fixation is widely spread in surface warm waters, especially in the Indian Ocean (with 43% of global N-fixation in this basin). One deficiency of the model is the low rates in the subtropical North Atlantic where strong P-limitation restricts the growth of all phytoplankton groups. High N-fixation is sometimes observed here [Capone et al., 2005], likely fueled in part by dissolved organic P and mesoscale eddies, processes not included in the model [Moore and Doney, 2007]. Additionally, and in contrast to the findings of Deutsch et al. [2007], Moore and Doney [2007] found less N-fixation within the upwelling zones, and substantial N-fixation rates located to the south of the High Nutrient Low Chlorophyll region.

A rate of water column denitrification of 64.8 TgN yr$^{-1}$ is simulated with reasonable spatial distribution compared to in situ studies, although it is under-predicted in the Arabian Sea and over-predicted in the Bay of Bengal (Fig. 4.8B). Like in other coarse resolution GCMs, the OMZs in the Eastern Tropical North and South Pacific are merged in the BEC. This results from excessive amounts of nutrients upwelled in these regions, which contribute to high rates of denitrification. Low $O_2$ are also observed in waters off South-West Africa [Calvert and Price, 1971].

### 4.3 Implementation of benthic denitrification

Denitrification is a microbially facilitated process in which $NO_3^-$ is used as the terminal electron acceptor and $N_2$ is ultimately produced through a series of intermediate N products. This sink of $NO_3^-$ occurs in environment with low dissolved oxygen concentrations, e.g. in the OMZs or in marine sediments. Since denitrification in the benthos represents a substantial loss term in the N-cycle and plays a dominant role for $\delta^{15}N$ of $NO_3^-$, we have incorporated this sink in the BEC model. In this section, the incorporation of benthic denitrification is presented (section 4.3.1), and simulated rates and patterns are compared with data-based estimates (section 4.3.2).
4.3. Implementation of benthic denitrification

4.3.1 Coding and technical aspects

Benthic denitrification (BD) is implemented on the basis of two metamodels [Middelburg et al., 1996]. These metamodels are based on a mechanistic diagenetic model of benthic biogeochemical processes calibrated against observations. A metamodel has the advantage that it can easily be incorporated into a GCM. The first relationship is a function of the labile carbon (C) flux that settles onto marine sediments only (Middelburg 1). The second relationship depends on the labile C flux that reaches sediments, depth, and local $O_2$ and $NO_3^-$ (Middelburg 2). This parameterization better predicts benthic denitrification ($r^2 = 0.976$, and $s^2 = 0.019$, see Middelburg et al. [1996]). In both cases, $NO_3^-$ has to be positive so benthic denitrification can occur:

\[
\begin{align*}
BD_1^C &= 10^\left[-0.9543 + 0.7662 \log_{10} J_{poc}' - 0.2350 \log_{10} \left(J_{poc}'\right)^2\right] \quad \text{(Middelburg 1)} \\
BD_2^C &= 10^\left[-2.2567 - 0.1850 \log_{10} J_{poc}' - 0.2210 \log_{10} \left(J_{poc}'\right)^2\right] - 0.3995 \log_{10} NO_3^- \cdot \log_{10} O_2 + 1.2500 \log_{10} NO_3^- \\
&\quad + 0.4721 \log_{10} O_2 - 0.0996 \log_{10} z + 0.4256 \log_{10} J_{poc}' \cdot \log_{10} O_2 \\
\end{align*}
\]  

(4.1)

$BD_i^C$ is in [$\mu$molC/cm$^2$/day], $NO_3^-$ and $O_2$ in [$\mu$mol/m$^3$], water depth ($z$) in [m], and the labile C flux that reaches the sea floor ($J_{poc}'$) in [$\mu$molC/cm$^2$/day]. $J_{poc}'$ is computed as the sum of the soft (associated reactive organic carbon) and hard flux (associated inert organic carbon) of POC that leave the grid-cell (Fig. 4.2 and see detailed description in section D.1.8 in Appendix).

All organic matter that reaches the oceanic sea floor, i.e., the bottom cells of the model, is instantaneously remineralized. This means setting the outgoing organic flux to zero. The fraction of organic matter that is denitrified consumes $NO_3^-$ with a stoichiometry of $R_{C:N}^d = 117 : 136$ (same C:N ratio than for water column denitrification) and does not remove $O_2$ (Tab. 4.2 and Equs.D.1 and D.16 in section D.1.4 in Appendix). In contrast, the fraction of organic matter that undergoes aerobic remineralization consumes $O_2$ with a C:O stoichiometry $R_{C:O}^p = 117 : 170$.

By default, the second metamodel of Middelburg, ($BD_2^C$ in Equ.4.1), is used to compute benthic denitrification. However, if $J_{poc}'$ is zero, benthic denitrification is set to zero. If $O_2 \leq 0$ then $BD^C$ is computed on the basis of Middelburg’s first metamodel ($BD_1^C$ in Equs.4.1). When $NO_3^- \leq 0$, $BD^C$ is set to zero.
Chapter 4. Implementing N Isotopes in the BEC Model

Figure 4.2  Schematic of the particulate matter cycling (sinking detritus pool) in the BEC model (terms defined in section D.1 in Appendix). Soft and hard C fluxes (\(J_{\text{soft}}\) \(J_{\text{hard}}\)) refer to the reactive, inert part of POM respectively. Incoming soft and hard C fluxes are assumed to be the outgoing fluxes from the previous level. Organic matter is instantaneously remineralized or denitrified in the bottom cell (implemented by setting the outgoing flux to zero). A fraction of the C flux that reaches the sea floor (\(J_{\text{b}}\)) is denitrified (BD) based on Middelburg Metamodels (Equs.4.1) and consumes \(\text{NO}_3^-\), while the rest requires \(\text{O}_2\) to be remineralized. PON15 cycling is implicitly computed according to POC since the PON cycling is not explicitly simulated (see equations in section D.1.5 in Appendix).

4.3.2 Deficiency of the BEC model in computing the C flux that reaches the sea floor

The modeled C flux that reaches the oceanic sea floor is compared to a data-based estimate of this flux. Data-based C flux is derived from the particulate export (PE) database of Dunne.
et al. [2007], and the C flux that reaches the sea floor is computed assuming that remineralization follows a power law function (uniform factor $b = 0.858$ is assumed) [Martin et al., 1987]) and according to bathymetry [ETOPO5, 1988]. A land mask from the POP model is applied to the data in order to keep exactly the same land and oceanic regions as in the CCSM-BEC model to allow for model-data inter-comparisons. The modeled integrated C flux that reaches the sea floor is 3 to 4 times smaller than the data-based flux (Tab. 4.3, Fig. 4.3 upper panel). In a spatial dimension, the simulated C flux is generally too low in shallow continental margins when compared to data (Fig. 4.3 lower panel), while the Sunda Shelf is the major region where the simulated C flux exceeds the data-based estimate. North of $60^\circ$N, the data-based C flux is substantially larger than the simulated flux. We hypothesize that this results from an over estimation of the particulate export flux.

Modeled global rates of benthic denitrification are more than a factor of five smaller than data-based estimates, independently of the assumed parameterization. Assuming a C:N

![Observation-based C flux that reaches the sea floor [molC/m²/yr]](image1)

![Model-data misfit of the C flux that reaches the sea floor [molC/m²/yr]](image2)

**Figure 4.3** C flux that reaches the sea floor. **Upper panel:** C flux computed using the particulate export database of Dunne et al. [2007], and a uniform Martin Curve ($b = 0.858$). **Lower panel:** Model-data misfit (from yr2000, millennium-scale equilibrium run 4, see Tab. 4.4).
ratio of 117:136, the global rates of observation-based benthic denitrification, derived from the first or second metamodel of Middelburg et al. [1996] (Equ.4.1) result in a large $\text{NO}_3^-$ flux removal of 197, 183 TgN yr$^{-1}$ respectively. The simulated rates of benthic denitrification computed offline from the modeled C flux are smaller (35 and 25 TgN yr$^{-1}$) than the global rates calculated from the data. This is because the simulated C flux is four times lower than the data-based flux.

Compared to the global estimates of rates found in the literature (Tab. 1.3), the data-based estimates of benthic denitrification are smaller than the estimates by Middelburg et al. [1996] and Codispoti et al. [2001], but of the same order of magnitude as reported by Gruber [2004] and Eugster and Gruber [in prep] (chapter 2). Modeled estimates are at least two times smaller than observational and model estimates of rates reported in the literature. Both Somes et al. [2010b] and this study underestimate the global rate of benthic denitrification, even though our integrated rate is three to four times larger than the rate they found. By multiplying benthic denitrification by a constant factor of 4.5, Somes et al. [2010b] reported a global rate of benthic denitrification of only 38 TgN yr$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>Data-based</th>
<th>BEC model spin-up 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>C flux that reaches the sea floor [molC/yr]</td>
<td>14.85 $\cdot 10^{13}$</td>
<td>3.58 $\cdot 10^{13}$</td>
</tr>
<tr>
<td>Benthic denitrification (Middelburg 1) [TgN yr$^{-1}$]</td>
<td>197</td>
<td>35</td>
</tr>
<tr>
<td>Benthic denitrification (Middelburg 2) [TgN yr$^{-1}$]</td>
<td>183</td>
<td>25</td>
</tr>
</tbody>
</table>

**Table 4.3** Data- and model-based global C flux that reaches the sea floor and global rate of benthic denitrification from the two parameterizations of Middelburg et al. [1996]. Parameterization function of the C flux only (Middelburg 1), and function of the C flux, depth, and local $\text{O}_2$ and $\text{NO}_3^-$ (Middelburg 2). Modeled values from yr2000, millennium-scale equilibrium run 4 (see section 4.5).

Benthic denitrification is the highest in shallow continental margins as a consequence of the high organic C flux in these areas (Fig. 4.4 upper panel). On the other hand, the only region where the modeled rates of benthic denitrification overestimate the observation-based rates is the Sunda Shelf in Indonesia because the modeled C fluxes at the sea floor are larger than observation-based fluxes (see Fig. 4.3 lower panel).

On the global scale, the model deficiencies in reproducing data-based estimates of the C flux that reaches the sea floor can be explained by invoking the poor resolution of continental shelves, which in turn implies
4.3. Implementation of benthic denitrification

**Figure 4.4** Benthic denitrification rate computed from Middelburg 2 (Equ.4.1). **Upper panel:** Data-based benthic denitrification rate computed on the basis of data-based C flux (see Fig. 4.3 top). **Lower panel:** Model-data misfit (from yr2000, millennium-scale equilibrium run 4, see Tab. 4.4).

1. an underestimation of the coastal upwelling which leads to an underestimated export production, and

2. that the depth of the bottom box is deeper than real bathymetry (Fig. 4.2).

Modeled rates of benthic denitrification are upscaled by including a uniform scaling factor since the model clearly underestimates the global rate of benthic denitrification, but the spatial distribution seems reasonable compared to data. The scale factor is one of the few parameters of the BEC model which is tuned to fit geochemical properties, e.g. mean ocean δ¹⁵NO₃, and to prevent excessive drifts in the global N budget and export flux of POC during century- to millennium-scale equilibrium simulations (see section 4.5).
4.4 Implementation of N isotopes

4.4.1 Coding and technical aspects

Exchanges of $^{15}$N between the various N pools is tracked separately in order to model variations in $\delta^{15}$N. The addition of $^{15}$N state variables for each N component yields a substantial increase in the number of biological variables (from 24 to 31). Seven prognostic variables of $^{15}$N have been embedded in the BEC model for all species containing N, i.e., NO$_3^-$, NH$_4^+$, small phytoplankton, diatoms, diazotrophs, zooplankton, DON (small detritus), and the implicit PON pool (large detritus) (Fig. 4.1, all equations are given in section D.1 in Appendix). The N pools of small phytoplankton, diatoms, diazotrophs and zooplankton are not explicitly formulated but can be derived from their C pools assuming a constant N:C ratio. The transfers of $^{15}$N between the $^{15}$N pools are followed independently of the transfer of N. It follows that the concentration of $^{14}$N is computed from the total N (C multiplied by N:C ratio for pools without explicit N formulation) and $^{15}$N concentrations in a given pool since N = $^{14}$N + $^{15}$N. The $^{15}$N fluxes exchange $^{15}$N from source pool (s) to product pool (p) taking into consideration the N flux and isotopic enrichment factor ($\epsilon$) associated with the process:

$$^{15}J_{s\rightarrow p}(^{15}N) = J_{s\rightarrow p}(N) r (1 + \epsilon_{s\rightarrow p}/1000)$$

(4.2)

where $r$ is the fractional abundance, i.e., $r = \frac{^{15}N}{^{15}N + ^{14}N}$ (more technical details on the coding can be found in section D.2 in Appendix).

4.4.2 Simulated isotope effects

Water column denitrification, nutrient uptake by phytoplankton, zooplankton excretion, and nitrification are the various pathways that enable isotopic N differentiation in the model. Water column denitrification causes a high enrichment factor ($\epsilon_{wcd} = -25/00$) [Brandes et al., 1998; Sigman et al., 2003], while benthic denitrification does not fractionate ($\epsilon_{bd} = 0/00$) [Brandes and Devol, 2002]. Small phytoplankton and diatom discriminate against $^{15}$N during NO$_3^-$ and NH$_4^+$ uptake with $\epsilon_{sp, no3} = \epsilon_{diat, no3} = \epsilon_{sp, nh4} = \epsilon_{diat, nh4} = -5/00$ [Sigman et al., 1999; DiFiore et al., 2006]. The enrichment factor assigned to nitrification is set to 10/00 [Brandes and Devol, 1997; Casciotti et al., 2003].

Checkley and Miller [1989] reported that some zooplankton (Neocalanus) preferably keep $^{15}$N, and that their excretion is enriched in $^{14}$N, when compared to the isotopic composition of the body. NH$_4^+$ is the principal remineralized compound excreted by zooplankton [Biggs, 1977] but DON is also released (Fig. 4.1, Tab. 4.1). The excreted NH$_4^+$ has been shown
to be depleted in $^{15}$N compared to the food source of zooplankton [Checkley and Miller, 1989]. Zooplankton tissues and wastes are therefore about 3\% higher in $\delta^{15}$N than their food sources. This enrichment process is responsible for the stepwise enrichment of $^{15}$N along the trophic chain [Minagawa and Wada, 1984].

The BEC model only simulates one zooplankton pool. Since a 3 to 3.5\% $\delta^{15}$N enrichment per trophic level is commonly assumed [Minagawa and Wada, 1984; Post, 2002], simulating only one trophic level likely leads to a discrepancy between simulated and observed $\delta^{15}$N of zooplankton. As a result, we first prescribe an enrichment factor for zooplankton excretion $\epsilon_{\text{excr}} = -6\%_0$. In future runs, this parameter may be adjusted to simulate a $\delta^{15}$N zooplankton enriched by about 3\% relative to small phytoplankton and diatoms.

Finally, diazotrophs release newly fixed N with an isotopic composition $\delta^{15}$N = 0\% as a consequence of very little to no fractionation [Carpenter et al., 1997] and POM sinks and remineralizes without isotopic fractionation.

### 4.4.3 Testing the new model

The model was carefully tested with zero fractionation in order to check the isotopes implementation. In case of zero fractionation, the outputs of N and $^{15}$N have to be the same. For this purpose, all enrichment factors ($\epsilon$) were set to 0\%$_0$, and the isotopic fraction of atmospheric N$_2$ gas ($r_{\text{atm}}$) to one. The simulation was initialized from a previous equilibrium run from X. Giraud at ETH Zürich (without N isotopes and without benthic denitrification) and with $^{15}$N pools initialized with their N pools. The outputs confirmed that $^{15}$N and N pools were the same, while time-average outputs show that $^{15}$N slightly deviated from N. In contrast, the $^{15}$N- N discrepancy from time-average outputs is interpreted by invoking issues of numerical stability. The discrepancy depends on the computation time but does not increase with the simulated time-scale. This demonstrated that N isotopes were correctly implemented.

### 4.5 Millennium-scale equilibrium runs

#### 4.5.1 Adjusted parameters

We conducted several millennium-scale equilibrium runs of 2,000 years that include N isotopes and benthic denitrification (Tab. 4.4, and Fig. 4.5). Five parameters related to N-fixation or denitrification were adjusted in order to reproduce a mean ocean $\delta^{15}$NO$_3$ value of 5\%$_0$ [Liu and Kaplan, 1989; Sigman et al., 2000]. Furthermore, parameters were also tuned
Chapter 4. Implementing N Isotopes in the BEC Model

so that the global NO$_3^-$ budget and the POC export flux do not drift to unrealistic states during the time it takes to reach equilibrium. Realistic mean ocean $\delta^{15}$NO$_3$ is chosen between 4.0 and 6.0‰, and global POC export flux should not deviate by more than 10% from the initial flux. In practice, this was accomplished by adjusting five parameters (see Tab. 4.4):

- the scaling factor for benthic denitrification ($f^{bd}$),
- the minimum NO$_3^-$ needed for water column denitrification ($S^{wcd}_N$),
- the length-scale of remineralization ($l_{diss}^{poc}$),
- the initial slope of photosynthesis versus irradiance curve for diazotrophs ($a_{diaz}$),
- and the diazotroph Fe half saturation coefficient ($K_{Fe}^{diaz}$).

These parameters were selected based on previous works by Moore and Doney [2007], which included an arbitrary and unrealistic constraint ($S^{wcd}_N$) deemed necessary to prevent excessive drift in the N inventory after the incorporation of water column denitrification, and works by Krishnamurthy et al. [2007] who changed $l_{diss}^{poc}$, $a_{diaz}$, and $K_{Fe}^{diaz}$ to improve simulation results of atmospheric inorganic N deposition on marine biogeochemistry (see rationale for adjusting these parameters in Krishnamurthy et al. [2007] and additional references therein). $f^{bd}$ is also adjusted, since benthic denitrification is underestimated if this scaling term is not introduced (section 4.3.2). Here, we present four millennium-scale equilibrium runs, which show different drifts in the mean ocean $\delta^{15}$NO$_3$ and changes in export flux of POC.

4.5.2 Setup of millennium-scale equilibrium runs

We use a climatological data atmospheric model, a standard data land model, a fully active ocean model, a standard data ice model, and the coupler (see Vertenstein et al. [2004] and references therein). A relatively coarse grid is adopted in order to keep the model light (100 longitudes, 116 latitudes, and 25 vertical levels) (more technical aspects of the initialization of simulations are provided in section D.3.1 in Appendix).

Millennium-scale equilibrium runs are started from an initial spin-up without N isotopes and without benthic denitrification performed by X. Giraud at ETH Zürich. $^{15}$N pools are initialized according to their respective N pools assuming uniform $\delta^{15}$N of 5‰, except for the diazotroph pool which has a $\delta^{15}$N of 0‰ (described in more detail in section D.3.2 in Appendix). The model is spun up to approximately steady-state within 2,000 yr. Decadal time-averaged outputs are generated and mean ocean $\delta^{15}$NO$_3$, global NO$_3^-$ budget, and export flux of POC are computed through time and compared between the equilibrium runs.
### Table 4.4
Compilation of the various millennium-scale equilibrium runs. Five parameters related to N-fixation or denitrification are adjusted so to best fit mean ocean $\delta^{15}$NO$_3$ and to minimize drift in global NO$_3^-$ budget.

### 4.5.3 Comparison of equilibrium runs

Four millennium-scale equilibrium runs with several sets of model parameters are presented (Tab. 4.4, tuned parameters see section 4.5.1).

- Run 1 represents a weak N-cycle. This is because the global rate of N-fixation is small (small $a_{\text{diaz}}$) and high $K_{\text{Fe}}^{\text{diaz}}$. Furthermore, the global rate of benthic denitrification is low ($f_{\text{bd}}$ set to 1).
Run 2 shows a large drift in the mean ocean $\delta^{15}\text{NO}_3$ toward a higher value and a strong decrease in the global inventory of $\text{NO}_3^-$ and in the global export flux of POC. This is due to a large global rate of water column denitrification ($\text{low } S_{\text{Nwcd}}^\text{recd}$) while the global rate of benthic denitrification is relatively large ($f_{\text{bd}}$ set to 4).

Run 3 has the smallest mean ocean $\delta^{15}\text{NO}_3$ and a strong decrease in the global inventory of $\text{NO}_3^-$ and in the global export flux of POC. This is due to a large benthic-to-water column denitrification ratio. The global rate of benthic denitrification is large ($f_{\text{bd}}$ set to 5), while the global rate of water column denitrification is small (high $S_{\text{Nwcd}}^\text{recd}$).

Run 4 has the highest export flux of POC. This might be due to the large rate of N-fixation (very high $a_{\text{diaz}}$) and a relatively small imbalance between sources and sinks of N.

In all simulations, the marine N-cycle does not reach a quasi steady-state even after a 2,000 yr spin up simulation. This is a consequence of drifts in N-fixation and denitrification in the water column and sediment (Fig. 4.5A,B,C), and hence in the $\text{NO}_3^-$ budget, as well as in the export flux of POC and mean ocean $\delta^{15}\text{NO}_3$ (Fig. 4.5D,E,F). All equilibrium runs show the same tendency to drift in mean ocean $\delta^{15}\text{NO}_3$, global inventory of $\text{NO}_3^-$ and export flux of POC, but with different amplitudes.

The global inventory of $\text{NO}_3^-$ decreases as a result of sinks larger than sources due to the newly incorporated benthic denitrification sink, and modified model parameters. The rate of N-fixation, which is the only source of N in the BEC model, does not balance water column and benthic denitrification at the beginning of the equilibrium runs since these runs are started from a spin-up without benthic denitrification (Fig. 4.5A,B,C,D). Diazotrophs respond slowly to the imbalance between sources and sinks of N, with time-scale of thousand of years. This response is not a consequence of an explicit assumption about the influence of the N:P ratio on diazotrophs, which is not included, but rather results from ecological competition between diazotrophs and other phytoplankton. The competition is due to the specific requirement of diazotrophs and other phytoplankton [Moore and Doney, 2007]. However, larger N sinks than sources tend to lower the N:P ratio in surface waters and ultimately increase the competitiveness of the diazotrophs as a consequence of their ability to take up $\text{N}_2$.

The adjustment of model parameters does not permit drifts to be avoided in the mean ocean $\delta^{15}\text{NO}_3$, in the $\text{NO}_3^-$ budget and in the export flux of POC, even though specific parameters permit the control of either N-fixation or denitrification in the water column or sediment. This is a consequence of the millennial time-scale for sources of N to react to changes in sinks of N. Increasing $a_{\text{diaz}}$ can relax the light-limitation of diazotrophs in parts of the tropical and subtropical oceans. Furthermore, decreasing $K^{\text{diaz}}_{\text{Fe}}$ permits N-fixation to be increased, and
4.5. Millennium-scale equilibrium runs

Figure 4.5  Global (A) N-fixation, (B) water column and (C) benthic denitrification, (D) NO$_3^-$ budget, (E) global export flux of POC at 92 m depth, and (F) mean ocean $\delta^{15}$NO$_3^-$ for four millennium-scale equilibrium runs with diverse tuning of parameters (see Tab. 4.4). Original values from BEC model version 1.25 are shown with dashed lines.
thus to minimize the drift in the global inventory of $\text{NO}_3^-$ and export flux of POC (Run 4 versus Run 1). Water column denitrification can be controlled by adjusting $S_{\text{nwd}}^N$, and benthic denitrification is controlled by $f^{bd}$ (see section 4.3).

At the beginning of the equilibrium run, the export flux of POC is larger in Runs 2, 3, and 4 compared to Run 1 (Fig. 4.5E). We hypothesize that this is due to modification in parameters related to diazotrophs. For instance, the relaxation in the Fe limitation permits diazotroph growth to be enhanced and hence the global rate of N-fixation as well (Fig. 4.5A). However, diazotroph growth is only enhanced briefly. The enhanced diazotroph growth is a consequence of the system not being in a steady-state at the beginning of the simulation. However, this much higher diazotroph growth cannot be sustained over time, because other factors might become limiting. Consequently, diazotroph growth and thus the global rate of N-fixation sharply decrease at the beginning of the simulation. This hypothesis will need to be tested.

### 4.6 Best millennium-scale equilibrium run

In this section, we examine the distribution of $\delta^{15}\text{NO}_3$ in more detail, and describe the global and basin-scale rates of N-fixation and denitrification in the water column and sediment of one equilibrium run. The equilibrium run 4 is selected because it shows a good compromise between the deviation in export flux of POC from the initial value and the mean ocean $\delta^{15}\text{NO}_3$ (Fig. 4.5E,F). In this simulation, the Fe limitation of diazotrophs is decreased and the initial slope of P-I curve has been substantially increased (Tab. 4.5).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
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<td>new $f^{bd}$</td>
<td>3</td>
<td>unitless</td>
<td>scaling factor for benthic denitrification</td>
</tr>
<tr>
<td>changed $S_{\text{nwd}}^N$</td>
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<td>mmol/m$^3$</td>
<td>minimum $\text{NO}_3^-$ needed for water column denitrification</td>
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<td>$p_{\text{poc diss}}$</td>
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<td>m</td>
<td>length-scale of remineralization</td>
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<td>$a_{\text{diaz}}$</td>
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<td>mmolC/cm$^2$/ngChlWday</td>
<td>initial slope of P versus I curve for diazotrophs</td>
</tr>
<tr>
<td>$K_{\text{diaz Fe}}$</td>
<td>0.06</td>
<td>nM Fe</td>
<td>diazotrophs Fe half saturation coefficient</td>
</tr>
</tbody>
</table>

Table 4.5  New parameters and parameter changes for the millennium-scale equilibrium run 4 relative to BEC model version 1.25.
4.6. Best millennium-scale equilibrium run

4.6.1 Model evaluation

Despite the relatively small number of $\delta^{15}$NO$_3$ observations, Somes et al. [2010b] constructed a global database of $\delta^{15}$NO$_3$ measurements which were used to evaluate our model. Because of the poor temporal coverage, seasonal biases in the annually averaged data exist for several regions. So far, the performance of the model has been evaluated by comparing (i) the spatial distribution of $\delta^{15}$NO$_3$ at various depths and (ii) $\delta^{15}$NO$_3$ in suboxic waters, to the observations.

The model successfully captures the general distribution of $\delta^{15}$NO$_3$ at 100 and 600 m depth (Fig. 4.6). High values are simulated in OMZ and low values in the Eastern Tropical North Pacific appear to be fairly consistent with observations. Very low, or even negative, $\delta^{15}$NO$_3$ values are simulated at 100 m depth in the subtropical gyres, where NO$_3^-$ is low (Fig. 4.10A). We hypothesize that these negative $\delta^{15}$N are a consequence of low N and $^{15}$N values and inaccuracies of the advection scheme.

Globally, the model performance for $\delta^{15}$NO$_3$ is evaluated by computing the Pearson product-moment correlation coefficient ($r$). Negative modeled values of $\delta^{15}$NO$_3$, for instance in the low-latitude Atlantic (Fig. 4.6B) are not taken into consideration in the calculation of $r$ (see model-observation comparison in Fig. 4.7). A correlation coefficient $r = 0.605$ is computed. It is very likely that if the model were able to simulate the Indian OMZ in the Arabian Sea instead of having this OMZ localized in the Bay of Bengal, the correlation coefficient would be higher.

4.6.2 N-fixation and denitrification in the water column and sediment

Global rates

Global integrals of the rates of N-fixation, water column and benthic denitrification are 95.6, 30.4, and 85.4 TgN yr$^{-1}$, respectively, at yr2000. The magnitudes of these rates imply that the cycle is still in an imbalance of $\sim$ 40 TgN yr$^{-1}$ after a spin up time of 2,000 yr. Rates of N-fixation and water column denitrification diverge from original rates computed from BEC model version 1.25 (62.8, 64.8, and 0 TgN yr$^{-1}$) because of the newly incorporated benthic denitrification sink and parameter adjustments (Tab. 4.5).

A benthic-to-water column denitrification ratio of 3.1 is calculated, which implies a weaker dilution effect compared to values reported by recent modeling studies (e.g. Somes et al. [2010b] and Eugster and Gruber [in prep], see chapter 2). Deutsch et al. [2004] introduced the concept of the dilution effect. This effect refers to the fact that since water column den-
Chapter 4. Implementing N Isotopes in the BEC Model

Figure 4.6 δ¹⁵N of a global database of measurements and BEC model at 100 and 600 m depth. Annual δ¹⁵N from Somes et al. [2010b] database at 100 m (A) and 600 m depth (B). Modeled δ¹⁵N of NO₃ from equilibrium run 4 (C) and 600 m depth (D).
itrification leads to locally high $\delta^{15}\text{NO}_3$ values in low $\text{NO}_3^-$ concentration waters, when they transport out of the denitrification zone and mix with water with much higher $\text{NO}_3^-$, the high $\delta^{15}\text{NO}_3$ values are largely diluted away. This dilution comes from the fact that the resulting $\delta^{15}\text{NO}_3$ values are weighted toward the water parcel with more $\text{NO}_3^-$. This effect implies that a mean ocean $\delta^{15}\text{NO}_3$ of 5‰ is achieved with a benthic-to-water column denitrification ratio lower than the ratio expected, if water column denitrification was spread homogeneously throughout the ocean (ratio of 4 assuming $\epsilon_{wcd} = -25$‰, $\epsilon_{bd} = 0$‰ and a mean ocean $\delta^{15}\text{NO}_3$ of 5‰ [Brandes and Devol, 2002]). Here, we find a ratio of 3.1, which highlights a weaker dilution effect than the ratio of 1.6 reported by Eugster and Gruber [in prep] (chapter 2) and of 0.6 reported by Somes et al. [2010b]. Somes et al. [2010b] reported a large dilution effect with roughly twice as much water column denitrification as benthic denitrification to reach a mean ocean $\delta^{15}\text{NO}_3$ of 5‰. They interpreted this large dilution effect as a consequence of an important and overestimated $\text{NO}_3^-$ consumption via water column denitrification in the Eastern Tropical North Pacific (ETNP) compared to observations. They reported a $\text{NO}_3^-/16\text{PO}_4^{3-}$ ratio of up to 0.3 in the ETNP. In comparison, the millennium-scale equilibrium run 4 shows lower $\text{NO}_3^-$ consumption, with values that hardly go below $\text{NO}_3^-/16\text{PO}_4^{3-} = 0.6$ (Fig. 4.11). We interpret our lower $\text{NO}_3^-$ deficit by invoking lower rates of water column denitrification ($\sim 40$ TgN yr$^{-1}$), when compared to Somes et al. [2010b] (101 TgN yr$^{-1}$). This lower $\text{NO}_3^-$ deficit explains our weaker dilution effect.

**Figure 4.7** Measure of $\delta^{15}\text{NO}_3$ model performance. Modeled $\delta^{15}\text{NO}_3$ (equilibrium run 4, yr2000) versus database of $\delta^{15}\text{NO}_3$ measurements from Somes et al. [2010b].
Figure 4.8  Vertically integrated rates of (A) N-fixation, and (B) water column and (C) benthic denitrification from equilibrium run 4, yr2000.
4.6. Best millennium-scale equilibrium run

The spatial distribution and basin-scale rates of N-fixation and to a lesser extent water column denitrification are different to those of the original BEC model version 1.25. Basin-scale rates of N-fixation and denitrification in the water column and sediment are calculated from yr2000 of the equilibrium run 4. Additionally, spatial distributions of vertically integrated rates of N-fixation and benthic denitrification from yr2000 are compared to the rates computed from the original model (Figs. 4.8, and 4.9).

In contrast to the original model, whose highest integrated rate of N-fixation is located in the Indian Ocean (43% of the global rate), it is the Pacific Ocean that presents the highest integrated rate of N-fixation (53%) in the new model (Fig. 4.8A). N-fixation is higher throughout the Pacific Ocean compared to the original model (Fig. 4.9A). Moore et al. [2004] reported that low dissolved Fe concentrations strongly limit diazotroph growth rates in the equatorial
Figure 4.10  \( \text{NO}_3^- \) and export flux of POC in BEC model version 1.25 and with benthic denitrification implemented (equilibrium run 4, yr2000).  \( \text{NO}_3^- \) and export flux of POC from yr2000 of equilibrium run 4 (A, B). Absolute change in \( \text{NO}_3^- \) and export flux of POC between the original model and equilibrium run 4 (B, D).
4.6. Best millennium-scale equilibrium run

Pacific. We find that the relaxation in the Fe limitation of diazotrophs ($K_{diaz}^{Fe}$ is adjusted from original value of 0.10 to 0.06 nM Fe) can explain the increase in N-fixation in this oceanic basin. This hypothesis is supported by the other millennium-scale equilibrium runs that show that N-fixation is very sensitive to $K_{diaz}^{Fe}$ (Tab. 4.5). The N-fixation rate in the Atlantic Ocean hardly changed compared to the original model (12 TgN yr$^{-1}$ compared to 14 TgN yr$^{-1}$ in the original model). However, within this basin, the distribution of N-fixation is changed: we find less fixation at low-latitudes and higher rates at high latitudes. Conversely, N-fixation has not changed in the subtropical North Atlantic, with low rates due to strong P-limitation (Figs. 4.8A, 4.9A) [Moore et al., 2004]. A higher initial slope of the P-I curve for diazotrophs ($a_{diaz}$) is invoked to explain higher N-fixation at high latitudes. The original value of $a_{diaz}$ of 0.036 nmolC/cm$^2$/ngChlWday is increased to 0.15 nmolC/cm$^2$/ngChlWday in the equilibrium run 4. This implies that the ecological niche for diazotrophs can spread to higher latitudes. A similar pattern exists in the Indian Ocean, with more N-fixation at high latitudes in the new model.

The basin-scale rates of water column denitrification are similar to those in the original model, and all OMZs show a uniform decrease in integrated rates of denitrification. Roughly 65% of the global water column denitrification occurs in the Pacific Ocean. The Indian Ocean follows with 22% denitrification. Our low global rate of ~30 TgN yr$^{-1}$, compared to ~65 TgN yr$^{-1}$ in the original model, implies that the vertically integrated rates of water column denitrification are lower everywhere, except close to the boundaries of the Eastern Tropical Pacific OMZ (Fig. 4.9B).

Benthic denitrification is higher in shallow continental margins (see section 4.3.2), and integrated basin-scale rates are roughly proportional to the surface area of the basins. Most benthic denitrification occurs in the Pacific Ocean (46% of the total). In general, benthic denitrification is mainly a high-latitude process (Fig. 4.8C).

Although the global NO$_3^-$ budget and the export flux of POC do not substantially change in the new model (see values at $t = 0$ for equilibrium run 4 in Fig. 4.5D,E), their spatial distributions are non-uniformly changed compared to their original distributions. Surface NO$_3^-$ is slightly higher in the Pacific Ocean, has not changed in the Atlantic, and is lower at high latitudes compared to the original model (Fig. 4.10B). A strong correlation between changes in annual mean surface NO$_3^-$ and changes in the N-fixation is observed (Figs. 4.9A and 4.10B). One consequence of higher NO$_3^-$ is that the export flux of POC is higher in the Pacific subtropical gyres (Fig. 4.10D).

Relative close coupling between the sources and sinks of N

N-fixation and denitrification are relatively well coupled (Fig. 4.8). N-fixation and water column denitrification are found at low-latitudes, although water column denitrification is not
widely spread, but confined to small regions. In contrast, benthic denitrification is mainly a high-latitude process. The spatial distribution of these sources and sinks of N ultimately control the stability of the N-cycle via negative sources-sinks feedbacks.

We hypothesize that the relative spatial decoupling between benthic denitrification and N-fixation might imply a marine N-cycle with weaker sensitivities of the internal N-feedbacks, and thus a cycle which is less stable than previously reported. Using the original version of this model, Moore and Doney [2007] reported strong negative feedbacks between denitrification and N-fixation, which stabilize the N-cycle over time-scales of circa 100 yr. The inclusion of benthic denitrification, which is relatively well decoupled from regions of N-fixation (Fig. 4.8A,C), would promote a more dynamic cycle, since a longer time-scale would be required for changes in benthic denitrification to be balanced by opposing changes in N-fixation, and vice versa. We plan to test this hypothesis and investigate the dynamics of the cycle in future applications of this model.

### 4.7 Conclusions and outlook

A dynamic N isotope model and benthic denitrification were embedded in the BEC model. Various isotopic fractionating processes were included: water column denitrification, nutrient uptake by phytoplankton, zooplankton excretion, and nitrification. Benthic denitrification does not fractionate and is implemented following Middelburg et al. [1996]'s parameterization.
Middelburg et al. [1996]'s parameterizations lead to a clear underestimation of the integrated benthic denitrification rate compared to literature estimates. The CCSM-BEC model simulates a benthic denitrification rate of $\sim 30 \, \text{TgN yr}^{-1}$, while the smallest estimates from the literature articulate rates of at least $50 \, \text{TgN yr}^{-1}$ (e.g. Gruber and Sarmiento [1997] and Eugster and Gruber [in prep], see chapter 2). The underestimation is explained by invoking the poor resolution of continental shelves which in turn implies that (i) coastal upwelling is underestimated and hence export production is too low, and (ii) the depth of the bottom box is deeper than real bathymetry. To correct for these deficiencies, a constant scaling factor that multiplies the benthic denitrification equations is introduced.

The model successfully reproduces the available $\delta^{15}\text{NO}_3$ from Somes et al. [2010b]'s database. This demonstrates that N isotopes can be used to constrain sources and sinks of N. Global rates of N-fixation, water column and benthic denitrification are $\sim 95$, $\sim 30$, and $\sim 85 \, \text{TgN yr}^{-1}$. These rates are at the lower end of ranges given in the literature (see Tab. 1.3). The benthic-to-water column denitrification ratio is 3.1 which implies a weaker dilution effect compared to estimates by Somes et al. [2010b] and Eugster and Gruber [in prep] (see chapter 2) likely due to low $\text{NO}_3^-$ deficit in suboxic waters.

Sources and sinks of N show relative close spatial coupling. Diazotrophs inhabit low-latitude waters and water column denitrification is confined to a few regions at low-latitudes. Benthic denitrification is a high latitude process. This, in turn, implies that sources and sinks of N are spatially decoupled which would induce relatively weak sources-sinks feedbacks. The spatial decoupling between sources and sinks is invoked to explain the long time-scale required for millennium-scale equilibrium runs to reach a quasi steady-state. Several equilibrium runs have been started that span so far over 2 to 3 kyr. Clearly, a longer time-scale than 2 to 3 kyr is required for the marine N-cycle to reach a quasi-steady-state.

Although model evaluation has been started by evaluating drifts in the global $\text{NO}_3^-$ budget, the export flux of POC, the mean ocean $\delta^{15}\text{NO}_3$ and the spatial distribution of $\delta^{15}\text{NO}_3$, additional model evaluation is necessary. For example, one should:

- perform statistical comparison of modeled $\delta^{15}\text{NO}_3$ with the database of Somes et al. [2010b], e.g. by drawing Taylor diagrams,
- compare $N^*$ stemming from modeled N and P with $N^*$ computed from climatology (World Ocean Atlas [Conkright et al., 2002]),
- compare vertical $\delta^{15}\text{NO}_3$ profiles with available data in regions contained in the database of Somes et al. [2010b], e.g. in OMZs, the Sargasso Sea, and the Southern Indian-Pacific Ocean.

We are confident that drifts in the global $\text{NO}_3^-$ budget and in the export flux of POC could be
minimized by incorporating new sources of N, e.g. the atmospheric deposition of N. This implementa-
tion would be based on the atmospheric deposition of dust and on previous studies on the impact of atmospheric N deposition on the marine biogeochemistry by Krishnamurthy et al. [2007].

Future applications of this model will include centennial- to millennial-scale simulations of abrupt climate events, e.g. Dansgaard-Oeschger events. These events will be reproduced by simulating a large release of cold water in the North Atlantic, which will decease the North Atlantic Deep Water formation and generate a global scale decrease in nutrient concentrations in the surface ocean and in biological productivity. Consequently, OMZs will be reduced and denitrification will decrease. The direct comparison of simulated $\delta^{15}NO_3$ with sediment $\delta^{15}N$ records will permit the model results to be validated. This will also allow to better understand the spatial characteristics of sediment $\delta^{15}N$ records and could strengthen their interpretation. Ultimately, these simulations will provide insight into mechanisms controlling past changes in ocean circulation, productivity and nutrient cycling, and may be useful to better understand and quantify past changes in the N-cycle. This might provide insights into the dynamics of the (future) N-cycle and also its past changes across glacial-interglacial transitions. It would be of interest to perform the investigations suggested previously using two different setups of the marine N-cycle, for example one with a weak N-cycle (equilibrium run 1) and one with a more vigorous cycle (equilibrium run 3).
Chapter 5

Conclusions and Outlook

5.1 Summary of the thesis

This thesis shows that stable N isotopes can be used to constrain the N-cycle in two different types of models. Stable N isotopes can be used to estimate the rates of N-fixation, and of water column and benthic denitrification, as well as to investigate the dynamics of the marine N-cycle. At the beginning of this thesis, I asked the following main questions: “Do pre-industrial estimates of rates of N-fixation and denitrification yield a balanced marine N-cycle?” and: “How did the marine N-cycle, and particularly the N inventory, evolve across the last glacial termination?” I successfully developed a geochemical box model and started to use the CCSM-BEC model to address these two questions. In the following, I summarize and present my key findings regarding these two questions.

5.1.1 Do pre-industrial estimates of rates of N-fixation and denitrification yield a balanced marine N-cycle?

During my Ph.D., I used a geochemical box model to determine global and basin-scale rates of N-fixation and denitrification, and their associated uncertainties under pre-industrial conditions (chapter 2). The use of observed distributions of stable N isotopes (see chapter A in Appendix) and nutrients (e.g. $N^*$) helped to overcome the sampling bias due to the fact that these tracers integrate the signal of sources and sinks of N in space and time. For the first time, a probabilistic approach was adopted to determine the uncertainties in the rate estimates, arising primarily from the poorly known ocean circulation and mixing fields. A strength of this probabilistic approach is the large number of data constraints (e.g. $N^*$, $P^*$, and $\delta^{15}N$) that can be used to determine the rates of N-fixation and denitrification in the water column and sediments.

My modeling studies revealed that the estimates of pre-industrial rates of N-fixation and denitrification yield a marine N-cycle close to balance. In more detail, my results indicate that:
• The pre-industrial marine N-cycle was balanced to within 16 TgN yr\(^{-1}\) (-24 to 52 TgN yr\(^{-1}\), 5th and 95th percentile) according to the ranges of estimates of globally integrated rates of N-fixation and denitrification (see Tab. 1.3). This range implies that it is not unlikely that the pre-industrial N-cycle was in a slight imbalance, but excludes a large imbalance between sources and sinks of N.

• Under pre-industrial conditions, the balance in the marine N budget results from global rates of N-fixation which are broadly consistent with literature estimates, whereas the rates of water column and benthic denitrification are at the lower end of the range of estimates reported in recent studies (see rate estimates and references in Tab. 1.3).

• Under pre-industrial conditions, both the box model and the CCSM-BEC model simulate most of the N-fixation in the Indian and Pacific Ocean, suggesting a relatively close spatial coupling between sources and sinks of N. In the Atlantic Ocean, the maximum rate of N-fixation, which is computed by the box model on the basis of two different approaches, supports at most a basin-scale rate that is roughly as large as the rate of the IndoPacific, when compared on a per surface area basis.

5.1.2 How did the marine N-cycle, and particularly the N inventory, evolve across the last glacial termination?

The box model was then used to determine the dynamics of the N-cycle across the last glacial termination. In particular, I estimated the variation in the global N inventory, which results from changes in the magnitude of rates of N-fixation and denitrification over this time-scale (chapter 3). For the first time, a modeling approach incorporated several types of climate forcings simultaneously: the effect of different climate forcings influencing N-fixation through changes in deposition of iron-rich dust and atmospheric CO\(_2\), the effect of a climate forcing affecting water column denitrification through changes in suboxia, and the effect of a climate forcing affecting benthic denitrification through variations in the sea-level. Other innovative aspects of this study include: its attempt to simultaneously reconstruct sediment \(\delta^{15}\)N records from several sites located in different oceanic basins, the \(\delta^{15}\)N model-data optimization attained by adopting a genetic algorithm, and the evaluation of the sensitivity of the deglacial N-cycle towards different weighting of the \(\delta^{15}\)N data from OMZs.

I found that the global inventory of N decreased substantially across the last glacial termination, as a result of a large millennium-scale transient decrease in the amplitude of the N-fixation rate. More specifically, the results I presented using the geochemical box model indicate that:

• The global inventory of N steadily decreased by 26 to 48% across the last glacial ter-
• The marine N-cycle was very dynamic across the last glacial termination. This is a consequence of strong climate forcings affecting N-fixation and water column denitrification, as well as weak sensitivities of the negative feedbacks between N-fixation and denitrification. This, in turn, implies that the feedbacks do not tend to strongly limit excursions in the N-cycle. Weak sensitivities of the feedbacks are also suggested by the fact that CCSM-BEC model requires long time periods (millennial-scale) to reach a steady-state.

• The bioavailability of Fe was a very important control for the rate of N-fixation across the last glacial termination. The decrease in the atmospheric deposition of iron-rich dust at the beginning of the last glacial termination implied a transient decrease in the rate of N-fixation of \( \sim 35\% \).

### 5.1.3 Exploring the marine N-cycle with the CCSM-BEC model

Another project of this thesis was to incorporate a complex dynamic N isotope model into a global biogeochemical ocean model embedded into a GCM (BEC-CCSM) (chapter 4). In addition, benthic denitrification was implemented on the basis of two metamodels. Millennium-scale equilibrium runs have been started, as well as an initial model validation. Finer resolved ocean dynamics and a higher complexity in the ecosystem model have great potential for examining the marine N-cycle with a particular emphasis on its dynamics and its sensitivity to climate forcings. The high resolution of the GCMs allows us to take advantage of localized geochemical data. The preliminary results presented in this thesis show that the CCSM-BEC model reproduces the mean ocean \( \delta^{15}\text{N} \) of \( \text{NO}_3^- \) and the magnitude of global export flux of POC reasonably well, and, to a lesser extent, the distribution of \( \delta^{15}\text{NO}_3^- \) in different oceanic basins. Even though the millennium-scale runs presented here do not reach a steady-state, the preliminary results show that a close to steady-state cycle can reproduce geochemical data.

### 5.1.4 Implications of my simplifications and assumptions for the results

The development of the geochemical box model and the incorporation of a complex dynamic N isotope model in the CCSM-BEC model required several assumptions to be made (e.g.
not including the simulation of anammox or unicellular diazotrophs, since they remain poorly understood as of yet). I also decided to simplify some aspects of the models as much as possible, while nevertheless keeping enough detail to permit the relevant questions to be addressed (e.g. restricting the number of boxes in the box model to the minimum, and keeping water circulation, export production, atmospheric deposition and river inputs of N constant across the last glacial termination). Below, I discuss in more detail the major underlying assumptions and simplifications which were made, and their implications for the results. All of the first five items of this list are related to the pre-industrial investigations while some of them refer to glacial-Holocene simulations as well. The subsequent four items are related exclusively to simulations of the N-cycle across the last glacial termination.

- The number of boxes in the box model was restricted to a minimum of 14 boxes. This allows for enough detail in the model to permit a thorough investigation of the marine N-cycle. Nevertheless, not all OMZs could be explicitly represented in the box model due to the restricted number of boxes. The joint Indian and Pacific Ocean was divided into an oxic and a suboxic part, of which the latter is assumed to contain all OMZs. The eastern tropical South Atlantic is also an OMZ, where N is lost [Kuypers et al., 2005]. While this low oxygen region is captured in the CCSM-BEC model, it was neglected in the box model, since it represents only a minor sink of N [Calvert and Price, 1971; Tyrrell and Lucas, 2002]. Another reason for neglecting this suboxic region is that the box model was designed to be as simple as possible, so as to permit multiple sensitivity analyses and millennium-scale simulations. Hence, the rate of water column denitrification may be slightly underestimated due to the fact that the eastern tropical South Atlantic OMZ was neglected.

- The N:P elemental ratio of non N-fixing organisms was set to the Redfield ratio of 16:1. A variable ratio was not implemented in the box model. On a regional-scale it was found that non N-fixing organisms do not follow Redfield dynamics. For instance, the relatively low observed N:P ratio in the Southern Ocean is due to the dominance of diatoms with a low N:P ratio of $\sim 11:1$ [Kopczynska et al., 1986; Weber and Deutsch, 2010]. Neglecting non-Redfield dynamics of non-N-fixing organisms leads to an overestimation of rates of N-fixation [Mills and Arrigo, 2010]. I hypothesize that the substantial rate of N-fixation I found in the Southern Ocean is partly explained by the fact that the N:P ratio prescribed in the model is too high for regions dominated by diatoms. Preliminary results demonstrate that by assigning an N:P ratio of 8:1 in the Southern Ocean, only half of the rate of N-fixation diagnosed in the standard case (N:P ratio of 16:1) is computed. I therefore disregarded the large rate of N-fixation diagnosed in this basin. This decision is also motivated by the fact that N-fixation is not expected to occur in high-latitude waters, as conditions considered necessary to sustain N-fixers are not found in these latitudes (see section 1.2.2). Interestingly, in an early version of the CCSM-BEC model, the N:P
ratios of phytoplankton were variable. However, in the version used here (version 1.25 [Moore and Doney, 2007]) these ratios were set to fixed values in order to make the model computationally less intensive and simpler, and because modeling flexible ratios added too much uncertainty to the model [Moore et al., 2002, 2004].

- **N-fixation** is simulated in both models according to factors that control the growth of *Trichodesmium*. However, recent discoveries pointed towards a larger diversity of diazotrophs that thrive under different environmental conditions [Zehr et al., 2001; Montoya et al., 2004; Moisander et al., 2010; Hamersley et al., 2011]. Although environmental factors that control N-fixers are not well known, and *Trichodesmium* and unicellular diazotrophs are likely to have distinct physiological and growth requirements, N-fixers are nevertheless simulated on the basis of the best studied N-fixer *Trichodesmium* in the box model. We cannot well assess the implications of such variations at this time. Nonetheless, confidence in the pre-industrial estimates of rates of N-fixation comes from the fact that the two independent geochemical approaches I developed estimate very similar global rates of N-fixation. This suggests that our rates reflect the global N-fixation by all diazotrophs, i.e., the sum of the contributions from both *Trichodesmium* and unicellular diazotrophs.

- **Anammox** is neglected in this study [Thamdrup and Dalsgaard, 2002; Kuypers et al., 2003; Dalsgaard et al., 2003; Lam and Kuypers, 2011]. In both the box model and the CCSM-BEC model, N sinks in suboxic environments are simulated based on our knowledge about canonical denitrification. Until the community acquires a more complete understanding of anammox through observational and laboratory studies, it will not be possible to include this sink in ecosystem models, despite the fact that it has been confirmed to be significant. Moreover, the isotopic enrichment factor for processes associated with anammox is not known yet. Nevertheless, the enrichment factor of water column denitrification used in this thesis implicitly includes anammox, because the isotopic enrichment factor is derived from field studies in which the isotope effect is estimated from the total N loss. Therefore, my pre-industrial estimates of integrated rates of denitrification implicitly include the loss of N through anammox.

- **Data collected** during the last decades, which were used to constrain the models, were assumed to be representative for pre-industrial conditions. However, these data have likely been altered by the ongoing anthropogenic perturbation. For instance, present-day river discharge and atmospheric deposition of N are substantially larger than under pre-industrial conditions [Seitzinger and Mayorga, 2008; Duce et al., 2008; Baker et al., 2010]. I therefore prescribed pre-industrial estimates of rates of river discharge and atmospheric deposition of N in the box model. Present-day nutrient fields (e.g. $N^*$) were used to constrain both models, although they have been affected by the anthropogenic perturbation. Human activities have not only affected these nutrient fields
Chapter 5. Conclusions and Outlook

through larger river discharge and atmospheric deposition of N, but also through the expansion of OMZs [Naqvi et al., 2000]. This expansion implies an increase in water column denitrification, which has likely affected the data used in this study. However, not only surface data but also data from the deep ocean, which are expected to have been unaltered by the anthropogenic perturbation so far, were used as constraints. I therefore assume that the data mainly represent a pre-industrial N-cycle. Nevertheless, it cannot be excluded that the reported rates of N-fixation and denitrification partially correspond to rates of a transient cycle due to consideration of present-day data taken during a transient period.

- Export production is constant in the glacial-Holocene box model. There is, nevertheless, paleoceanographic evidence that export production changed between the last glacial period and the Holocene [Kohfeld et al., 2005]. However, there is no observational consensus on the size of glacial-Holocene changes in export production on the basin-scale. In contrast, the most detailed study so far [Kohfeld et al., 2005] reported that, in the Southern Ocean south of the Antarctic Polar Front, glacial export production was higher than the export production under Holocene conditions. Even though a variable export production would affect the simulated N-cycle, the export production is constant across the last deglaciation due to the lack of consistency in information. It cannot be predicted how the simulated glacial-Holocene N-cycle would be altered by a variable export production, since the alterations would depend on the sign, the magnitude and the spatial changes in export production.

- The marine P-cycle was set to be temporarily constant in the box model. The current scientific paradigm states that on the time-scale of the last glacial-interglacial transition (few thousands of years), the marine P-cycle was not particularly dynamic when compared to the N-cycle. This is due to the fact that P has a large residence time of 20 to 30 kyr in the marine environment [Ruttenberg, 1993; Delaney, 1998; Benitez-Nelson, 2000], which is 5 to 10 times larger than the residence time of N [Gruber and Sarmiento, 1997; Codispoti et al., 2001; Eugster and Gruber, in prep]. This means that changes in the P-cycle could not have been fast enough to affect the N-cycle on glacial-Holocene time-scales. However, Wallmann [2010] reported a residence time of P of only a few kyr based on the most recent estimates of P removal fluxes. He predicted that the P-cycle is more dynamic than previously thought, and that it could be possible that the \( \text{PO}_4^{3-} \) and phosphorus budgets were not in a steady-state during the pre-industrial period [Wallmann, 2010]. A number of recent studies also suggested that the LGM inventory of P was much higher than the pre-industrial inventory [Ganeshram et al., 2002; Filippelli et al., 2007; Tamburini and Foellmi, 2009]. These variations in the P-cycle could have affected N-fixation through changes in the specific growth requirements for diazotrophs and other phytoplankton (N:P ratio), since these variations would have altered
the competitive success patterns of N-fixers. Denitrification might also have been altered through changes in export production and hence rates of remineralization and $O_2$ consumption in the deep ocean. Additionally, a variable marine P-cycle across the last deglaciation would have consequences for the use of geochemical tracers (e.g. $N^*$) as proxies for the reconstruction of sources and sinks of N. Finally, this downward revision of the residence time of P raises the question as to whether N or P was the limiting factor during this period. Due to the ability of diazotrophs to bring newly fixed N into the cycle, Tyrrell [1999] suggested that N is the proximate limiting nutrient and P the ultimate limiting nutrient over geological time-scales. The implications of a constant glacial-Holocene marine P-cycle for the rates of N-fixation and denitrification reported here cannot be foreseen since the sign, the amplitude, and the spatial changes in $PO_4^{3-}$ across the last deglaciation remain elusive.

- Oceanic water circulation, atmospheric deposition and river inputs of N were set constant across the deglaciation. Simulating a dynamic water circulation would require detailed knowledge of the oceanic water circulation during the last glacial period. This reconstruction is difficult to conceive since available nutrient-based proxies are lacking (e.g. $PO_4^{3-}$ or $PO_4$ across the last deglaciation would be convenient since $PO_4^{3-}$ is included in the box model). A recent study by Negre et al. [2010] reported that the reconstruction of the oceanic water circulation in the North Atlantic Ocean during the LGM remains controversial. Moreover, the reconstruction of the dynamics of the circulation during the glacial-Holocene transition would be very uncertain, given the lack of proxies that could be used to constrain the model. The inputs of N through atmospheric deposition and river discharge were set constant as well. Although it is not well established how their rates changed across deglaciation, the fact that their rates are secondary compared to rates of N-fixation allow these rates to be assumed constant. Constant river input and atmospheric deposition of N also made the model more simple. The implications of neglecting potential glacial-Holocene changes in atmospheric deposition and river inputs of N for the rates of sources and sinks of N are likely negligible. In contrast, the implication of prescribing a constant oceanic water circulation for the simulated N-cycle could be of importance on a local or regional scale.

- A steady-state N-cycle was prescribed in the Holocene for the subsequent investigations conducted across the last glacial termination. I demonstrated that the pre-industrial marine N budget was nearly balanced. Additionally, the absence of long-term drifts in the oceanic $^{15}NO_3$ and atmospheric $CO_2$ [Gruber and Sarmiento, 1997; Kienast, 2000; Gruber, 2008] further support the theory of a nearly-balanced pre-industrial marine N-cycle. This evidence, combined with my geochemical findings, support my decision to prescribe a balanced N-cycle in the Holocene in order to perform simulations across the last glacial termination.
5.2 Challenges for future research on the marine N-cycle

In this thesis, I encountered many open questions concerning the marine N-cycle, which go far beyond the scope of my thesis. For instance, isotopic enrichment factors associated with N processes need to be better evaluated (e.g., the enrichment factor associated with anammox not being established yet, I did not implement this sink of N in the box model). Moreover, the role of Fe limitation for N-fixation remains elusive, and estimates of changes in the global inventory of marine N cannot easily be converted into changes in atmospheric levels of CO$_2$. I will discuss some of these open questions here. The first four items concern pre-industrial and glacial-Holocene simulations, and the following four items concern more specifically the N-cycle across the last glacial termination.

- The isotopic enrichment factors of anammox and benthic denitrification need to be constrained. In fact, the enrichment factor of anammox first needs to be established. It will be very instructive to incorporate anammox into ecosystem models as soon as the parameterization and the enrichment factor of anammox are better understood. For the purpose of simulating anammox, dissimilatory nitrate reduction to ammonium will likely need to be implemented as well (see section 1.2.3). Furthermore, the enrichment factor associated with benthic denitrification has become a matter of concern. Granger et al. [2010a] reported surprisingly elevated enrichment factors associated with benthic denitrification, ranging between -6.2$^{\%o}$ and -8.1$^{\%o}$. These values are surprisingly high compared to previous observations of little to no isotope enrichment during this process [Brandes and Devol, 1997]. There is thus a significant ongoing need for future evaluations of isotopic enrichment factors.

- Only little N-fixation was simulated by the two models in the Atlantic Ocean. This, in turn, disproves the canonical view that this basin is a region with substantial N-fixation as a result of high atmospheric iron-rich dust deposition [Michaels et al., 1996; Falkowski, 1997; Moore et al., 2009] or as inferred from $N^*$-based methods [Gruber and Sarmiento, 1997] or from the supply of physical transport of $P^*$ into the subtropical gyre [Palter et al., 2011]. The fraction of the global N-fixation computed in the Atlantic Ocean differs between the approaches used (see Tab. 1.1). In the box model, the budget approach simulates $\sim$20% of the global rate of N-fixation in the Atlantic Ocean (chapter 2). The CCSM-BEC model simulates roughly the same distribution, with 14% of the global rate of N-fixation in this ocean basin (Tab. 1.1). Conversely, the restoring approach of the box model diagnosed no N-fixation in the Atlantic Ocean. I demonstrated that the diagnosed N-fixation in this basin is very sensitive to uncertainties and potential biases in the $P^*$ concentrations assigned to the thermocline box. However, the large discrepancy between this restoring approach and the budget approach/CCSM-BEC simulations remains to be resolved. In any case, these various approaches demonstrate that the
Atlantic Ocean is not the basin with the highest rate of N-fixation, as has long been assumed (see section 1.2.2). Furthermore, it remains to be clarified why my estimates of rates of N-fixation in the Atlantic Ocean are at the lower end of literature estimates. Is this because N-fixation rates were simulated according to factors that control the growth of *Trichodesmium*, despite the fact that unicellular diazotrophs also exist? Beside the large diversity of diazotrophs, which is neglected in my models, specific limiting factors may control the growth of diazotrophs in different oceanic basins. For instance, Moore and Doney [2007] reported that Fe strongly limits diazotroph growth rates in all ocean basins, with the exception of the subtropical North Atlantic where strong P limitation restricts their growth. In a recent study, Palter et al. [2011] quantified the effect of physical transport of $P^*$ into the subtropical gyre in order to infer a gyre-integrated rate of N-fixation of $\sim\!5\,\text{TgN}\,\text{yr}^{-1}$. This $P^*$ supply explains how N-fixation can be maintained in this region despite low $\text{PO}_4^{3-}$ concentrations. In conclusion, the magnitude of the rates of N-fixation occurring in the Atlantic Ocean remains an unresolved issue.

- The role of Fe limitation for N-fixation remains debated. Literature suggests that Fe is probably the most important overall control on N-fixation (see section 1.2.2), which is precisely what the box model simulations showed across the last deglaciation. The iron forcing strongly affected my rates of N-fixation on this time-scale (chapter 3). However, the high sensitivity of N-fixation toward the iron forcing conflicts with box model simulations of pre-industrial N-fixation. Only little N-fixation was found in the Atlantic Ocean under pre-industrial conditions, despite large atmospheric input of Fe in this ocean basin (chapter 2). These low rates of N-fixation under pre-industrial conditions would contradict a strong Fe control on diazotrophs, except if another factor limits diazotroph growth in the Atlantic Ocean (section 1.2.2). It has been reported that, *Trichodesmium* are more P limited in the North Atlantic than in the North Pacific, while Fe could potentially control N-fixation in the Pacific Ocean [Sohm et al., 2008, 2011]. Hence, different limiting factors might be invoked to explain the current basin-scale rates of N-fixation. Conversely, one could question the strong sensitivity of N-fixation arising from the iron forcing I reported in the glacial-Holocene simulations. The box model shows that an early deglaciation decrease in N-fixation is required to best fit the $\delta^{15}\text{N}$ data in all oceanic basins (see section 3.4). Case studies showed that the iron forcing has the potential to generate such a decrease in N-fixation. The assumption that the Fe control on diazotroph growth is not so strong would therefore require finding another climate forcing which would have the potential to strongly affect N-fixation during the early deglaciation. I could not find such an alternative forcing, and thus concluded that the iron forcing existed at that time, and that Fe is one of the most, if not The most, important overall control on N-fixation.
• There is need to incorporate unicellular diazotrophs in ecosystem models. Models will be able to give a more realistic representation of diazotrophs (magnitude of rates and spatial distributions) when they will incorporate not only *Trichodesmium* but also unicellular diazotrophs. This step will be possible once our gaps in the understanding and knowledge of the large diversity of N-fixers will be filled (see also the third item in section 5.1.4).

• Glacial-Holocene global and local changes in export production are not well established (sixth item in section 5.1.4). Kohfeld et al. [2005] reported no significant global-scale / basin-scale changes in export production, aside from a lower glacial export production in the Southern Ocean south of the Antarctic Polar Front. The box model simulated a decrease in the global inventory of N of 26 to 48% across the last glacial-Holocene transition. Did this large decrease in the inventory of N affect the global export production, and in turn lead to a fraction of the decrease in the atmospheric CO$_2$ level over this transition? Perhaps. Since N is the major limiting nutrient in the modern ocean, it is likely that a decrease of this magnitude would decrease the global export production, especially in regions of excess PO$_4^{3-}$. The fact that paleoceanographic data does not reveal significant changes in the global export production between the LGM and the Holocene does not mean that the global export production did not change. It is conceivable that we are not yet able to detect a slightly higher global export production at the LGM compared to the Holocene in the data. This would mean that the simulated large decrease in the global inventory of N could have reduced the global export production and in turn played a role in the increase of the past atmospheric CO$_2$ level across the last deglaciation. Or perhaps the large decrease in the global inventory of N across the deglaciation did not cause a decrease in the global export production because of changes in the surface-ocean nutrient limitation. It cannot be excluded that the surface-ocean nutrient limitation increased under glacial conditions, even though the global inventory of N was larger. This is because regionally-variable rates of nutrient resupply to the euphotic zone would have affected primary production and would have caused changes in the export production. Consequently, the decrease in the global inventory of N reported in this thesis would not have affected the global export production and hence would not have played a significant role for the past evolution of the atmospheric CO$_2$ level. I would tend to prefer the scenario with larger global export production under glacial conditions given the simulated large magnitude of the decrease in the global inventory of N.

• The sensitivities of the negative feedbacks between N-fixation and denitrification are weak, despite a relatively close coupling between sources and sinks of N. The pre-industrial box model simulates the largest rates of N-fixation and the whole water column denitrification in the Indian and Pacific Ocean (chapter 2). This relatively close
sources-sinks coupling would promote rather strong sensitivities of the feedbacks (see sections 1.2.4 and 1.2.5). However, the box model simulates weak sensitivities of the feedbacks across the last glacial termination (chapter 3). Millennium-scale simulations with the CCSM-BEC model strengthened the findings of such weak sensitivities of the feedbacks. The CCSM-BEC model simulates a rather good spatial coupling of N-fixation and denitrification, however, several thousand years of simulation were required for sources to roughly balance sinks (chapter 4). So, why are the sensitivities of the stabilizing feedbacks so weak, while sources and sinks of N are relatively closely coupled? One explanation for these weak sensitivities of the feedbacks could be that the sensitivities do not only depend on the time required for water to transport the signal of changes in sources (sinks) of N to regions of sinks (sources) of N, but also on the ability of the sinks (sources) to respond to the signal, which may be slowed down depending on limiting factors.

- Past reconstruction of the marine N-cycle would be facilitated if more widely distributed high resolution $\delta^{15}$N records were available. GCM simulations will permit us to take full advantage of these sediment records. However, the fact that the $O_2$ concentration is poorly simulated in the current version of the CCSM-BEC model will limit the $\delta^{15}$N model-data comparison. The lowest concentrations simulated in the Indian Ocean OMZ are mostly confined to the Bay of Bengal and not the Arabian Sea. Consequently, high $\delta^{15}$NO$_3$ values are not simulated in the right place, and as a consequence, a model-data inter-comparison for $\delta^{15}$N will present a large model-data misfit.

- It is not well established how a given change in the global inventory of N would affect the atmospheric $CO_2$ level. A larger glacial inventory of N does not imply that the strength of the glacial biological pump was strong enough to sequester a major fraction of the extra interglacial 100 ppm $CO_2$ found in the atmosphere (see also above discussion about the impact of a change in the global inventory of N on the global export production). The impact of changes in the marine N inventory on the atmospheric $CO_2$ level is tricky to quantify. Such a quantification requires assumptions about (i) the limiting factors for biological production (is it N, P, Fe?), and (ii) how a given change in the inventory of N quantitatively affects the atmospheric $CO_2$ level. GCMs can be used to address these questions. The CCSM could be used in this regard. However, to investigate this question, the fully-coupled version of the CCSM would need to be used.

### 5.3 My future goals

Based on the contribution of my thesis to our knowledge of the marine N-cycle, I am convinced that, in order to continue my work, use should be made not only of my box model,
but also of more complex ecosystem models such as the CCSM-BEC model. This means (i) performing additional sensitivity analyses and investigations of underlying mechanisms using the glacial-Holocene box model and (ii) using the CCSM-BEC model to address the dynamics of the N-cycle at a finer resolution than that of the box model. In the following, I discuss which issues I would like to address next. The first two issues, organized in order of importance, concern future simulations using the glacial-Holocene box model. The subsequent three issues concern the future development of and simulations with the CCSM-BEC model.

- The mechanisms underlying the strong transient decrease in N-fixation at the beginning of the last deglaciation will be investigated in more detail. Simulations without iron forcing, and thus without an early deglacial decrease in N-fixation, show that the $\delta^{15}N$ data from the Atlantic Ocean cannot be reproduced. It is hypothesized that the deglacial decrease in $\delta^{15}N$ in the thermocline of the low-latitude Atlantic is a consequence of the strong iron forcing affecting N-fixation. This forcing might generate specific basin-scale changes in the imbalances between sources and sinks of N and of $^{15}N$ across the last deglaciation. This hypothesis will be tested by computing the changes in isotopic weighted source-sink imbalances across the deglaciation on a basin-scale. Since the process that fractionates the most, i.e., water column denitrification, is restricted to the IndoPacific, glacial-Holocene changes in this sink would affect $\delta^{15}N$ mainly in this basin. In other words, a given absolute change in the basin-scale imbalance between sources and sinks of N would affect $\delta^{15}N$ differently in the low-latitude Atlantic than in the IndoPacific Ocean. This would explain why $\delta^{15}N$ records from the low-latitude Atlantic can be reasonably well reproduced with glacial-Holocene changes in basin-scale imbalances between sources and sinks, and without substantial changes in N-fixation between the last glacial period and the Holocene.

- The sensitivity of the glacial-Holocene changes in inventories, sources and sinks of N towards the onset and the end of the climate forcings needs to be evaluated (Fig. 3.4). Here, the idea is to use a Markov Chain Monte Carlo method to investigate this sensitivity. Probability density functions of the timing of the start/end of each climate forcing will be generated, assuming a normally distributed environment of parameters and using the start/end time from the standard case as a mean value. This sensitivity analysis will be useful to test the robustness of the results, especially since three climate forcings, i.e., the atmospheric $CO_2$, changes in suboxia and the deposition of iron-rich dust forcings, start or end within a time-span of less than $\sim$2 kyr (between 17 and 15.5 kyrBP). Hence, shifting their start/end timing randomly might change the order in which they are activated/deactivated, i.e., they impact the system, and hence affect modeled deglacial $\delta^{15}N$, and finally the change in inventory across the transition.
5.3. My future goals

- A comprehensive, quantitative validation of the CCSM-BEC model is necessary. I suggest performing a statistical comparison of modeled $\delta^{15}\text{NO}_3$ with the database of Somes et al. [2010b]. An additional comparison of $N^*$ stemming from modeled $\text{N}$ and $\text{P}$ with $N^*$ computed from a climatology (World Ocean Atlas [Conkright et al., 2002]), as well as a comparison of vertical $\delta^{15}\text{NO}_3$ profiles with data available for the regions of the Somes et al. [2010b] database might be used to validate the model.

- It may be relevant to incorporate an atmospheric deposition of $\text{N}$ into the CCSM-BEC model. The model version I used did not simulate atmospheric deposition of $\text{N}$. Nevertheless, the preliminary results presented in this thesis show that the CCSM-BEC model broadly captures the mean ocean $\delta^{15}\text{N}$ of $\text{NO}_3^-$, the magnitude of global export flux of POC, and to a lesser extent the distribution of $\delta^{15}\text{NO}_3$ in different oceanic basins, despite small amplitude drifts in the global export flux of POC and the global inventory of $\text{NO}_3^-$. Including atmospheric deposition of $\text{N}$ will decrease these drifts since this input will permit the imbalance between sources and sinks of $\text{N}$ to be decreased. Atmospheric deposition of $\text{N}$ can affect diazotrophs, since this external input will change the ecological competition between diazotrophs and other phytoplankton due to their specific growth requirements [Moore and Doney, 2007]. The implementation of $\text{N}$ deposition could be based on the atmospheric deposition of dust and on a previous study by Krishnamurthy et al. [2007] on the impact of atmospheric $\text{N}$ deposition on the marine biogeochemistry.

- The dynamics and sensitivity of the $\text{N}$-cycle could be addressed by simulating abrupt climate events (Dansgaard-Oeschger events) using the CCSM. Dansgaard-Oeschger events could be reproduced by simulating a large release of cold water into the North Atlantic. This release of cold water would decrease the North Atlantic Deep Water formation and generate a global-scale decrease in nutrient concentrations in the surface ocean and in biological productivity. Consequently, OMZs would be reduced and denitrification would decrease. The direct comparison of simulated $\delta^{15}\text{NO}_3$ with sediment $\delta^{15}\text{N}$ records would permit the validation of the model results, and might help to better understand the spatial characteristics of sediment $\delta^{15}\text{N}$ records and their interpretation. Ultimately, these simulations will provide insight into mechanisms controlling past changes in ocean circulation, productivity and nutrient cycling, and may be useful to better understand and quantify past changes in the N-cycle. This might provide insights into the dynamics of the (future) $\text{N}$ cycle and also its past changes across glacial-interglacial transitions.
5.4 Final remarks

The marine N-cycle is an exciting, complex cycle. Even though this cycle has been studied extensively over the last decades, recent major findings revealed that some aspects of this cycle remain poorly understood. These recent findings involve the discovery of novel organisms capable of N-fixation, but also novel N removal processes (anammox), the important role of Fe-limitation for *Trichodesmium*, and the implications of a potential large decrease in the N inventory for the atmospheric CO$_2$ level between glacial and interglacial periods.

I think that several types of models should continuously be used to study the present and past marine N-cycle. Given their simplicity, box models have the advantage of being suitable for various sensitivity analyses. In contrast, more complex ecosystem models coupled to GCMs are a promising tool for getting a detailed insight into the mechanisms driving the marine N-cycle. On the observation side, the more complex the models become, the more data will be required for their validation. Clearly, in the case of the N-cycle across the last glacial termination, paleoceanographic data from more sites, located throughout the entire ocean, would be valuable.

Finally, there is increasing need to better understand biogeochemical mechanisms and interactions in the present ocean, among others those of the marine N-cycle. This need has become more important as the anthropogenic perturbation has started to widely affect the marine environment. Human activities have altered the amount of fixed N in the Earth’s ecosystem [Gruber and Galloway, 2008] through combustion of fossil fuels and N-based fertilizers used in agriculture and industry [Galloway et al., 2008] which has resulted in a doubling of the input of fixed N to the marine environment. On the global scale, there is at present little evidence of a perturbation of the marine N-cycle due to human activities. In contrast, many coastal systems have already been seriously impacted. For instance, eutrophication has been reported to have intensified and extended [Naqvi et al., 2000; Diaz and Rosenberg, 2008]. Eutrophication induces two significant environmental problems: the increased occurrence of blooms of harmful algae, and the generation of hypoxic water. Another concern is river discharge of N and P and atmospheric deposition of N. Both inputs of N to the ocean have substantially increased since the onset of the anthropogenic perturbation [Seitzinger and Mayorga, 2008; Duce et al., 2008; Baker et al., 2010]. Human activities have also led to the expansion of OMZs [Naqvi et al., 2000] which, in turn, implies an increase in water column denitrification. Larger rates of denitrification would lead to changes in the amount of available fixed N in the ocean, and changes in marine productivity, the biological pump, and the flux of N$_2$O into the atmosphere. The consequences and impacts of all these pressing issues will need to be addressed soon. In this regard, comparing the modern marine N cycle to the glacial cycle may help to gain insight into the consequences and impacts of the anthropogenic perturbation on this cycle.
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Appendix A

Stable N isotopes

This appendix shows how stable N isotopes can be used as geochemical tracers to investigate the sources and sinks of N in the marine environment. The definition of the isotopic composition of a N pool is provided (section A.2). The definition of the isotopic enrichment factor of a reaction is given and the main fractionation processes of the marine N cycle are listed with their specific enrichment factors (section A.3). The Rayleigh and steady-state models frequently used to interpret N isotope data are briefly presented (section A.4). Finally, a brief discussion of sediment $\delta^{15}$N records closes this chapter (section A.5).

A.1 Nitrogen isotopes in nature

The natural distribution of stable N isotopes has been extensively used to trace the inputs and fate of N in the marine environment. Two stable isotopes of N are found in the nature. The light isotope, $^{14}$N, is by far the most common (99.635% of the atoms). By contrast, $^{15}$N is a minor isotope constituting 0.365% of the global N pool. Both isotopes behave chemically the same way in each process within the marine N-cycle. However, the heavier isotope reacts at a slightly slower rate than the light, producing a kinetic isotopic fractionation which reflects the difference in reaction rate for molecules containing the two isotopes of N, in many biological reactions.

A.2 Isotopic composition of a pool

As natural variations of $^{15}$N are small, it is more convenient to quantify the isotopic ratio of N between two samples than to measure the absolute isotopic composition of one pool, and the $\delta$ convention for expressing the isotopic composition of sample with regard to a standard reference is commonly used:

$$\delta^{15}\text{N} = \left( \frac{R_{\text{sample}}}{R_{\text{ref}}} - 1 \right) \cdot 1000 \text{%}$$

(A.1)
$R_{\text{sample}}$ and $R_{\text{ref}}$ are the isotope ratios $^{15}\text{N}/^{14}\text{N}$ in the sample and the reference respectively. The N isotopic composition of the atmosphere is commonly taken as the reference, since it represents a large enough reservoir and since it has not changed over the past tens of thousands of years.

The mean ocean $\delta^{15}\text{N}$ diverges from the atmospheric value (the reference) as a consequence of processes of the marine N-cycle that fractionate. The mean ocean $\delta^{15}\text{N}$ is $\sim 5\permil$ [Liu and Kaplan, 1989; Sigman et al., 2000]. This value, assuming a steady-state cycle, is largely dependent on the relative contributions of water column and benthic denitrification: A strong isotopic discrimination effect is associated with the former sink, while the latter sink hardly fractionates (see next section and Tab. A.1). The isotopic effect of water column denitrification is recorded in the high $\delta^{15}\text{N}$ of $\text{NO}_3^-$ measured in OMZs (see values in the Eastern Tropical North Pacific and Arabian Sea in Figs. A.1 and A.2).

### A.3 Isotopic enrichment associated with a reaction

The isotopic fractionation is the partition of isotopes between two pools of the same element, but with different isotopic signatures. It reflects the difference in the probability of reaction of the light versus heavy particles of a reaction. Let’s assume the following kinetic reaction:
A.3. Isotopic enrichment associated with a reaction

that is: \( r \rightarrow p \). The degree of isotopic fractionation associated with this reaction is expressed by the kinetic fractionation factor \( \alpha \):

\[
\alpha = \frac{15^k}{14^k}
\]  
(A.2)

with \( 14^k \) and \( 15^k \) the rate constants for \( ^{14}\text{N} \) and \( ^{15}\text{N} \) respectively. This factor describes the preference of a process for the light isotope. Since \( \alpha \) falls for most reactions between 0.97 and 1.00, it is convenient to introduce a finer isotopic factor, the isotopic enrichment, \( \epsilon \), expressed in per mil (‰):

\[
\epsilon = (\alpha - 1) \cdot 1000^{\%}_{\text{oo}}
\]  
(A.3)

It has to be mentioned that some authors use a different sign convention of \( \epsilon \), i.e., \( \epsilon = (1 - \alpha) \cdot 1000^{\%}_{\text{oo}} \).

Several biogeochemical relevant processes within the marine N cycle (see Fig. 1.2 and section 1.1) fractionate, e.g. \( \text{NO}_3^- \) uptake by phytoplankton, N-fixation, water column denitrification, nitrification, sediment burial, and zooplankton excretion (see how some of these processes affect the \( \delta^{15}\text{N} \) of \( \text{NO}_3^- \) and the \( \text{NO}_3^- \) pool in Fig. A.3, Tab. A.1 and the isotopic imprint of N-fixation and water column denitrification on \( \text{NO}_3^- \) in Figs. A.1 and A.2).
Appendix A. Stable N isotopes

<table>
<thead>
<tr>
<th>Process</th>
<th>( \epsilon [%o] )</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>N uptake by phytoplankton</td>
<td>-4 to -10</td>
<td>Sigman et al. [1999], Granger et al. [2010b], DiFiore et al. [2010]</td>
</tr>
<tr>
<td>N-fixation</td>
<td>0 to -2</td>
<td>Wada and Hattori [1991], Carpenter et al. [1997]</td>
</tr>
<tr>
<td>Water column denitrification</td>
<td>-20 to -30</td>
<td>Cline and Kaplan [1975], Brandes et al. [1998], Voss et al. [2001]</td>
</tr>
<tr>
<td>Benthic denitrification</td>
<td>0</td>
<td>Brandes and Devol [1997]</td>
</tr>
<tr>
<td>Nitrification</td>
<td>-7</td>
<td>Brandes and Devol [1997], Casciotti et al. [2003]</td>
</tr>
<tr>
<td>Sediment burial</td>
<td>+ 6</td>
<td>Brandes and Devol [2002]</td>
</tr>
<tr>
<td>Zooplankton excretion</td>
<td>-3.5</td>
<td>Checkley and Miller [1989]</td>
</tr>
<tr>
<td>Enrichment per trophic position</td>
<td>-3 to -3.5</td>
<td>Minagawa and Wada [1984], Post [2002]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pool</th>
<th>( \delta^{15}N [%o] )</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>Mean ocean</td>
<td>+4.8 ± 0.2</td>
<td>Liu and Kaplan [1989], Sigman et al. [2000]</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>-4 ± 5</td>
<td>Brandes and Devol [2002]</td>
</tr>
<tr>
<td>River input</td>
<td>+4 ± 5</td>
<td>Brandes and Devol [2002]</td>
</tr>
</tbody>
</table>

Table A.1 Isotopic enrichment factors (\( \epsilon \)'s) associated with N processes, and \( \delta^{15}N \) of several N pools. The isotopic effect of anammox, recently discovered in the marine environment [Kuyper et al., 2003; Dalsgaard et al., 2003], is included in the isotopic effect assigned to canonical denitrification (called simply denitrification in this thesis).

A.4 Two isotopic models

Two models are commonly used to interpret oceanic N isotope data. The first model, called Rayleigh model, is a closed model that assumes no import or export of \( \text{NO}_3^- \) during N utilization [Mariotti et al., 1981]. The second model is an alternative to the Rayleigh model, it is the steady-state model in which continuous N supply balances consumption [Sigman and Casciotti, 2001].

A.4.1 Rayleigh model

The Rayleigh model assumes a closed system (see e.g. Mariotti et al. [1981] or Sigman and Casciotti [2001]). This model would be an adequate description of basins that occasionally undergo complete flushing, i.e., resetting the composition of the water to \( \delta^{15}\text{NO}_3^- \text{init} \) and \( \text{NO}_3^- \text{init} \). Consequently, this model is used to describe the uptake of \( \text{NO}_3^- \) by phytoplankton during a bloom (\( \text{NO}_3^- \) is taken up to produce biomass). The \( \delta^{15}N \) of the reactant (\( \delta^{15}N_r \)), the instantaneous product (\( \delta^{15}N_{pi} \)), and the integrated product (\( \delta^{15}N_{int} \)) are:

\[
\begin{align*}
\delta^{15}N_r &= \delta^{15}N_{\text{init}} + \epsilon \ln f \\
\delta^{15}N_{pi} &= \delta^{15}N_r + \epsilon \\
\delta^{15}N_{int} &= \delta^{15}N_{\text{init}} + \epsilon \frac{f}{1 - f} \ln f
\end{align*}
\] (A.4)
A.4. Two isotopic models

Figure A.3 Plot showing how marine N processes affect the $\delta^{15}$N of NO$_3^-$ and the NO$_3^-$ pool (figure adapted from Gruber [2004]). The isotopic changes associated with each process from an initial pool with $\delta^{15}$NO$_3^-$ = 5‰ is shown. Instantaneous isotopic fractionation factor are provided (references for the isotopic enrichments are given in Tab. A.1). Anammox can be implicitly included in the enrichment factor of water column denitrification because the factors are derived from field studies in which the isotope effect is estimated from the total N loss [Galbraith et al., 2008].

with $f$ the fraction of reactant pool remaining at time $t$ defined as $f = N/N_{init}$, $\epsilon$ the isotopic enrichment factor, and $\delta^{15}N_{init}$ the isotopic composition of the initial reactant pool.

In the example of NO$_3^-$ uptake by phytoplankton, the NO$_3^-$ pool is the reactant, and the produced biomass is the product. The isotopic composition of infinitesimally produced biomass is referred by the instantaneous product, and the accumulated produced biomass is the integrated product. During NO$_3^-$ uptake by phytoplankton, the remaining NO$_3^-$ pool gets enriched in the heavy isotope as a consequence of a positive isotopic enrichment factor ($\epsilon$) (see Fig. A.4 which displays the $\delta^{15}$N of the reactant pool, the instantaneous product and the integrated product versus $f$). The instantaneous product has an isotopic composition which differs from the composition of the remaining NO$_3^-$ pool by $\epsilon$ at any time. The isotopic composition of the integrated product increases as well.

If the reactant N pool is completely consumed and converted into the product N pool, the isotopic signature of the product pool is equal to the signature of the original reactant pool.
i.e., $\delta^{15}\text{N}_{\text{int}} = \delta^{15}\text{N}_{\text{init}}$. This is because the reactant pool is completely consumed, hence as indicated by Equ.A.4 with $f = 0$ there is no fractionation. For instance, in the previous example, if there is complete $\text{NO}_3^-$ consumption by phytoplankton, i.e., waters depleted in $\text{NO}_3^-$, like in oligotrophic regions of the Atlantic, the isotopic effect of $\text{NO}_3^-$ uptake by phytoplankton does not occur any longer. This is because the uptake of $\text{NO}_3^-$ cannot discriminate against $^{15}\text{N}$ anymore since all $^{14}\text{N}$ and $^{15}\text{N}$ of $\text{NO}_3^-$ are consumed (see Fig. A.4). An other example is benthic denitrification. Its enrichment factor is close to zero (Tab. A.1) as a consequence of $\text{NO}_3^-$ supply limitation, i.e., $\text{NO}_3^-$ is almost completely consumed in benthic layer [Brandes and Devol, 1997; Sigman et al., 2001]. In conclusion, isotopic fractionation is only observable under conditions of partial consumption of the reactant pool.

### A.4.2 The steady-state model

In the steady-state model, the reactant N pool is continuously supplied and partially consumed [Sigman and Casciotti, 2001]. The supply of reactant N equals the sum of the product N and residual reactant N. Here, the equations that apply for the $\delta^{15}\text{N}$ of the reactant pool ($\delta^{15}\text{N}_r$) and product pool ($\delta^{15}\text{N}_p$) are:
A.5 Sediment $\delta^{15}$N records

\[
\begin{align*}
\delta^{15}N_r &= \delta^{15}N_{init} - \epsilon (1 - f) \\
\delta^{15}N_p &= \delta^{15}N_{init} + \epsilon f
\end{align*}
\]  \hspace{1cm} (A.5)

with $f$ the fraction of reactant pool remaining at time $t$ defined as $f = N/N_{init}$, $\epsilon$ the isotopic enrichment factor, and $\delta^{15}N_{init}$ the $\delta^{15}$N of the initial reactant pool. This model is used to quantify uptake processes where supply and uptake of N are simultaneous. For instance, the consumption of $\text{NO}_3^-$ by denitrification is well described by these equations.

In the BEC model, $\delta^{15}\text{NO}_3$ and the $\text{NO}_3^-$ deficits in suboxic waters ($O_2 < 4$ nmol/cm$^3$) show that these regions follow a steady-state model (see Fig. 4.11 in section 4.6.2). In these suboxic regions, water column denitrification strongly affects the $\delta^{15}$N of $\text{NO}_3^-$ with an enrichment factor $\epsilon_{wd}$ set to $-25/00$. $\delta^{15}$N of $\text{NO}_3^-$ is higher with a stronger $\text{NO}_3^-$ deficit expressed as $f = \text{NO}_3^-/(16\text{PO}_4^3-)$. We demonstrate that the suboxic regions follow a steady-state model by assuming such a model and showing that the enrichment factor that is derived from Equ. A.5 matches the factor prescribed in the BEC model. The enrichment factor is derived from a linear regression of the modeled $\delta^{15}\text{NO}_3$ versus modeled $f$ (see Fig. 4.11 in section 4.6.2).

We derive an enrichment factor associated with water column denitrification of $-20.3/00$ assuming a steady-state model. The prescribed factor is $-25/00$. This good match demonstrates that a steady-state model well describe the suboxic environment in the BEC model.

A.5 Sediment $\delta^{15}$N records

The $\delta^{15}$N of marine sediments is commonly used to reconstruct the history of the marine N-cycle and its processes on glacial-interglacial time-scales. Sediment $\delta^{15}$N records show past changes in the $\delta^{15}$N of sinking particles, which values reflect the $\delta^{15}\text{NO}_3$ in the upper water column. Values in the upper water column are controlled by local as well as remote processes. Therefore, past changes in the degree of $\text{NO}_3^-$ utilization by phytoplankton [Altabet et al., 1991; Francois et al., 1992], in water column denitrification [Altabet et al., 1995; Ganeshram et al., 1995] and N-fixation [Haug et al., 1998; Ren et al., 2009], as well as changes in the mean ocean $\delta^{15}$N [Kienast, 2000] and N inventory [Deutsch et al., 2004] affect $\delta^{15}\text{NO}_3$ and are recorded in marine sediments. But diagenetic (link to marine sediments) processes can also alter the isotopic signature recorded in the sediments (e.g. Freudenthal et al. [2001], Moebius et al. [2011]). In order to avoid measuring a $\delta^{15}$N signal that partly contains the diagenetic effect from the sediment and from the settling of organic matter through the water column, foraminifera-bound $\delta^{15}$N can be measured [Ren et al., 2009; Meckler et al., 2011]. This signal was not affected by diagenetic effect because the organic matrix laid down in foraminiferal tests is physically protected by the test.
Appendix B

A Probabilistic Estimate of Global Marine N-fixation and Denitrification

This appendix provides details on two issues that are only briefly discussed in the main part of the paper, i.e., (i) the determination of the circulation and mixing fields of the box model (section B.1), and (ii) the evaluation and validation of the box model results with data (section B.2). Parameter values of the model are given in section B.3.
Appendix B. A Probabilistic Estimate of N source/sink

B.1 Water circulation inversion

Three types of processes need to be considered for each box of a box model: (i) One-way (advective) fluxes that provide a box with the tracer concentrations of the box where they come from; (ii) Two-way (mixing) fluxes that mix the concentrations between two adjacent boxes; and (iii) internal sources and sinks due to biological or chemical processes that affect the tracer concentrations in each box. All these processes are included in a tracer conservation equation that is established for each tracer in each box $i$:

$$\frac{dC_i}{dt} = \sum_j u_{ij}C_j + \sum_j k_{ij} \cdot (C_i - C_j) + SMS_i$$

(B.1)

where $C$ is the concentration, $u_{ij}$ is the one-way advective flux between box $j$ and box $i$, $k_{ij}$ is the two-way mixing flux between box $j$ and box $i$, and $SMS$ represents the sources minus sinks. Assuming a steady-state ocean, equations for all boxes form a linear system of equations which is expressed in a matrix notation as $A \cdot \vec{m} = \vec{d}$. In our case, the matrix $A$ consists of tracer concentrations. $A$ has as many rows as equations in the system of equations and as many columns as unknowns, i.e., the water mass fluxes $\vec{m}$ consisting of $u_{ij}$ and $k_{ij}$. Vector $\vec{d}$ contains all sinks minus sources of each tracer, and $m$ corresponds to a vector of all water mass fluxes. This means that the advection and mixing water mass fluxes multiplied by the output box tracer concentrations have to exactly balance the internal sinks minus sources ($\vec{d}$) related to the considered tracer in the considered box.

In a Bayesian approach, the inversion is constrained on the one hand by first-guess values, also called prior values (water mass fluxes $\vec{m}$ in the present case), and on the other hand by observations, i.e., tracer concentrations. Mathematically, a cost function $J$ is defined and has to be minimized for $\vec{m}$:

$$J(\vec{m}) = \frac{1}{2}[(A\vec{m} - \vec{d})^T C(\vec{d})^{-1}(A\vec{m} - \vec{d}) + (\vec{m} - \vec{m}_p)^T C(\vec{m}_p)^{-1}(\vec{m} - \vec{m}_p)]$$

(B.2)

$C(\vec{d})$ and $C(\vec{m}_p)$ are the error or uncertainty covariance matrices of $\vec{d}$ and of $\vec{m}_p$, respectively. $C(\vec{d})$ is computed assuming an arbitrary 10% uncertainty of each source and sink term belonging to $\vec{d}$. $C(\vec{m}_p)$ is arbitrarily chosen as the square of the value of $\vec{m}_p$ but at most as 100 Sv. This means that the set of water mass fluxes which is the solution of the problem represents an optimal balance between two requirements:

1. optimized, or posterior, water mass fluxes ($\vec{m}$) should be as close as possible to prior fluxes ($\vec{m}_p$);

2. measurement values (sinks minus sources) that would result from the inversion-derived posterior fluxes ($A \cdot \vec{m}$) should agree as closely as possible with the actual computed $\vec{d}$. 


Two kinds of water mass fluxes are considered: (1) one-way advection fluxes (simple arrows in Fig. 2.1) and (2) two-way mixing fluxes (double arrows in Fig. 2.1). Water mass fluxes between adjacent boxes are prescribed based on Deutsch et al. [2004] (suboxic water column), and on observations [Schmitz, 1996a,b; Ganachaud and Wunsch, 2000; Keir, 1988] (all other water columns). In contrast to the Cyclops model [Keir, 1988], mixing fluxes are added between the Southern Ocean and the Atlantic and IndoPacific basins at surface and intermediate boxes in order to better depict the intricate circulation pattern around Antarctica (see Fig. 2.1). There are also direct water mass fluxes from the surface and intermediate layers of the IndoPacific to the low-latitude Atlantic to represent the Agulhas Current.

Prior values of water mass fluxes either come from literature or are estimated analytically. Prior values of advection fluxes are taken from observations [Schmitz, 1996a,b; Ganachaud and Wunsch, 2000], except the prior value of the upwelling flux within the suboxic column which is based on Deutsch et al. [2004] model. Prior values of two-way mixing fluxes are estimated analytically using eddy-mixing coefficients [Lane et al., 2006]. Distances between box centers are taken as typical length-scales and interfaces are those in between two adjacent boxes.

All prior vertical two-way mixing fluxes are increased in order to get a realistic global export flux [Laws et al., 2000] when restoring surface \( \text{PO}_4^{3-} \) toward observed concentrations (see discussion in section 2.4.4 and Fig. 2.4). The requirement to upscale water mass fluxes to reach realistic modeled export fluxes has been discussed by Matsumoto et al. [2002] (and references there cited). In our model, we multiply all prior values of vertical mixing fluxes assigned to surface boxes by 4.2, while other deeper prior vertical mixing fluxes are upscaled by 6.0.

Three tracers are used: \( \text{PO}_4^{3-}, \text{PO}_4^*, \) and natural pre-nuclear radiocarbon \( \Delta^{14} \text{C} \). \( \text{PO}_4^{3-} \) and \( \text{PO}_4^* \) are only affected by biology and water circulation. On the contrary, \( \Delta^{14} \text{C} \) is not only affected by isotopic fractionation associated with photosynthetic carbon uptake, but also by radioactive decay of \( ^{14} \text{C} \) (half-life: 5730 years). Mean \( \text{PO}_4^{3-} \) and \( \text{O}_2 \) values are determined for each box of the model by depth- and geographic-averaging the annual mean climatological data of the World Ocean Atlas (WOA) [Conkright et al., 2002], while pre-nuclear bomb radiocarbon values are computed from gridded GLODAP natural \( \Delta^{14} \text{C} \) [Key et al., 2004].

Water mass conservation equations are also required within each box with more than one input or output flux. Additionally, equations that preclude large net lateral transport of \( \text{PO}_4^{3-} \) from one water column to another are taken into account. Therefore, our system of equations contains: 14 equations related to \( \text{PO}_4^{3-} \) and \( \text{PO}_4^* \) conservation (one per box), and 14 related to \( \Delta^{14} \text{C} \), 6 water mass conservation equations, and 5 equations related to the lateral transport of \( \text{PO}_4^{3-} \) between the water columns. It ensues a system of 53 equations with 30 unknown water mass fluxes. Additional information comes from first estimation of the water mass
fluxes. This is a classical Bayesian approach in which all parameters are expressed as statistical probability distributions.

First-guess of the export fluxes of organic matter are required to perform the inversion. Organic matter export represents a sink of $\text{PO}_4^{3-}$ in surface water through nutrient uptake by phytoplankton, and a source of $\text{PO}_4^{3-}$ in the ocean interior due to organic matter remineralization. Spatially, the pattern of export fluxes is prescribed for each water column according to the Dunne et al. [2007] particle export database. Based on Deutsch et al. [2004], export flux in the suboxic water column is specified to be about four times the global areal mean export flux. The fraction of export production in dissolved form is considered to be 25% [Najjar et al., 2007] and is assumed to be homogeneous throughout the ocean. Given this ratio, the prior global particulate plus dissolved export production is 11.3 PgC/yr.

The minimization of the cost function is carried out using a Hessian method. We add non-negativity constraints to all posterior fluxes. The rationale is that negative values of posterior mixing fluxes would not have any physical significance, even though they do mathematically. In the case of advection fluxes, we do not want negative values of posterior advection fluxes, which would mean water fluxes flowing in the direction opposite to the prior. We even go one step further by prescribing that posterior values of advection fluxes have to be at least half of their prior values. Finally, we test whether the minimization reaches a global minimum.

The PDFs of most of the posterior two-way mixing fluxes are in good agreement with the prior values (Fig. B.1). One exception is flux 8 (lateral mixing flux between the suboxic IndoPacific deep box and the oxic IndoPacific thermocline box). Its PDF is narrow and close to zero, which is due to the non-negativity constraint added to the inversion. Several PDFs of two-way mixing fluxes show similar behavior, even though they are not restricted to 0 Sv but to 50% of their prior values as a result of the additional constraint that posterior advection fluxes cannot be smaller than half their prior values. Advection fluxes 7, 13, 18, and 20 show such behavior. Particularly interesting is the case of advection 7, the suboxic water column upwelling flux. The inversion sets its value to the minimum allowed, meaning that a smaller value would have decreased the cost function more. The issue of the suboxic upwelling flux is related to mixing flux 8 whose posterior value is zero. We suspect that this is a consequence of the tracer gradient between box 8 and box 12. A reverse gradient would likely help the inversion. It has to be noted that we did not force prior values of advection fluxes within a box to be conserved; for example, flux 7 does not balance flux 12 plus flux 13. This non-conservation of mass is due to the fact that prior values of advection fluxes come from various sources, e.g. Schmitz [1996a,b]; Ganachaud and Wunsch [2000]; Deutsch et al. [2004].

Posterior fluxes of the circulation setup with smallest cost function (circulation displayed in Fig. 2.1) are generally close to prior values. In the opposite case, posterior values are
B.2 Assessment of the optimization

To assess the degree to which the optimized model is capable of matching the observations, we compare the modeled $\text{NO}_3^-$, $\text{PO}_4^{3-}$, $N^*$, and $\delta^{15}N$ in each box with the observations using

Figure B.1 PDF of each water mass flux of a suite of 2500 circulation configurations. Green lines: prior values. Red dots: posterior fluxes for the circulation setup with smallest cost function. Bottom right sketch shows labeling of the water mass fluxes used in PDFs.

close to the median of the PDF (for instance water mass fluxes 3, 7, 12, 13, 19) (Fig. B.1). According to all PDFs, we are confident that the circulation setup with smallest cost function well describes the set of 2500 configuration setups.

B.2 Assessment of the optimization

To assess the degree to which the optimized model is capable of matching the observations, we compare the modeled $\text{NO}_3^-$, $\text{PO}_4^{3-}$, $N^*$, and $\delta^{15}N$ in each box with the observations using
Figure B.2 Comparison of modeled and data for NO$_3^-$, PO$_4^{3-}$, $N^*$, and $\delta^{15}N$ in each box (SRF: surface, THC: thermocline, UT: upper thermocline, LT: lower thermocline, DP: deep ocean). Modeled values computed by N budget approach for the circulation setup with smallest cost function (circulation configuration shown in Fig. 2.1). Observed PO$_4^{3-}$ and NO$_3^-$ in each box are given with mean plus/minus one standard deviation computed from the WOA over the box. Modeled $N^*$ are compared to $N^*$ computed from WOA mean PO$_4^{3-}$ and mean NO$_3^-$ in each box. Observed $\delta^{15}N$ are based on a global database of $\delta^{15}NO_3$ measurements [Somes et al., 2010b]. Red and blue bold lines highlight boxes where model values overestimate, underestimate respectively, climatology or observed value. Grey errorbars represent one standard deviation (due to the sparsity of the $\delta^{15}NO_3$ data, uncertainties are not computed).

the circulation configuration with the smallest cost function as an example (Fig. B.2). For this particular circulation configuration, all modeled NO$_3^-$ and PO$_4^{3-}$ concentrations, with the exception of those in the lower thermocline and the deep ocean boxes of the suboxic Indo-Pacific, are in agreement with the climatological mean plus/minus one standard deviation computed over each box. Largest NO$_3^-$ and PO$_4^{3-}$ residuals are found in the low-latitude and deep water Atlantic, although the modeled values are within the range given by plus/minus one standard deviation. Also the model-optimized $N^*$ concentrations match the observa-
B.2. Assessment of the optimization

tions quite well, with the largest $N^*$ residuals found in the upper thermocline of the suboxic IndoPacific and in the low-latitude Atlantic. Modeled $N^*$ in the deep suboxic IndoPacific matches the data much better than either $\text{NO}_3^-$ or $\text{PO}_4^{3-}$, since their discrepancies cancel each other.

An independent validation of the optimization is possible by confronting modeled $\delta^{15}\text{N}$ of each box with in-situ $\delta^{15}\text{N}$ measurements (bottom right graph Fig. B.2). Deep boxes have small $\delta^{15}\text{N}$ residuals, and modeled $\delta^{15}\text{N}$ in the surface Atlantic is too high compared to observations. Modeled $\delta^{15}\text{N}$ in the upper thermocline of the suboxic zone is too low compared to data. Deutsch et al. [2004] noticed the same shift and explained it by invoking denitrification reaching these waters. $\delta^{15}\text{N}$ modeled in the surface box of the suboxic water column is higher than in the suboxic box (Fig. B.2), which is a result of isotopic preference during $\text{NO}_3^-$ uptake. Sensitivity analyses show that modeled surface $\delta^{15}\text{N}$ matches $\delta^{15}\text{N}$ data better if $\alpha_{\text{Norg}}$ is set to 0.997 (standard case: $\alpha_{\text{Norg}} = 0.995$). $\alpha_{\text{Norg}}$ strongly impacts $\delta^{15}\text{N}$ in all surface boxes as a consequence of non-complete nutrient utilization. This allows $\text{NO}_3^-$ effective isotopic enrichment, while it does not impact deep water $\delta^{15}\text{N}$, and weakly impacts thermocline $\delta^{15}\text{N}$. In the real ocean, some low-latitude surface waters show seasonal complete N utilization: surface water in the Arabian Sea for instance is nutrient depleted in spring and summer. This prevents isotopic enrichment via $\text{NO}_3^-$ uptake. In our model, export fluxes are computed by restoring annualized nutrient concentrations. As a consequence, surface waters are never nutrient depleted and fractionation occurs and enriches surface $\delta^{15}\text{N}$ of $\text{NO}_3^-$ to values higher than the $\delta^{15}\text{N}$ data. The same reason can explain the large $\delta^{15}\text{N}$ residual in the surface Atlantic. Our primary goal is to evaluate the rates of N-fixation and denitrification which are hardly impacted by $\alpha_{\text{Norg}}$. We therefore do not aim to best simulate surface water $\delta^{15}\text{N}$, and prescribe the isotopical preference of $\text{NO}_3^-$ uptake to 0.995, a conservative literature estimate [Sigman et al., 1999]. Finally, $\text{NO}_3^-$, $\text{PO}_4^{3-}$, $N^*$, and $\delta^{15}\text{N}$ do not present structural biases, i.e., the model does not weaken climatological tracer gradients between boxes (Fig. B.2). In conclusion, the model well captures $\text{NO}_3^-$, $\text{PO}_4^{3-}$, $N^*$, and $\delta^{15}\text{N}$ observations even if it shows limitations in matching $\delta^{15}\text{N}$ and $N^*$ in the Atlantic surface waters.
### Appendix B. A Probabilistic Estimate of N source/sink

#### B.3 Parameters used to construct the pre-industrial box model

<table>
<thead>
<tr>
<th>Symbol (in the code)</th>
<th>Description</th>
<th>Model value (standard case)</th>
<th>Units</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>atm</td>
<td>atmospheric deposition of N</td>
<td>14</td>
<td>TgN yr$^{-1}$</td>
<td>Duce et al. [2008]</td>
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<tr>
<td>rin</td>
<td>riverine input of N</td>
<td>14</td>
<td>TgN yr$^{-1}$</td>
<td>Seitzinger and Mayorga [2008]</td>
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<tr>
<td>rip</td>
<td>riverine input of P</td>
<td>2</td>
<td>TgN yr$^{-1}$</td>
<td>Seitzinger and Mayorga [2008]</td>
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<td>alphaNorg</td>
<td>isotopic effect of N uptake by phyto.</td>
<td>0.995</td>
<td>%/00</td>
<td>Sigman et al. [1999], DiFiore et al. [2006]</td>
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<td>alphaa</td>
<td>isotopic composition of riverine N</td>
<td>0.996</td>
<td>%/00</td>
<td>Brandes and Devol [2002]</td>
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<tr>
<td>alphab</td>
<td>isotopic effect of sediment burial</td>
<td>1.006</td>
<td>%/00</td>
<td>Brandes and Devol [2002]</td>
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<td>alphar</td>
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</tr>
<tr>
<td>alphas</td>
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<td>%/00</td>
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<td>%/00</td>
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<td>meandel_obs</td>
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<td>Rair</td>
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<td>%/00</td>
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<tr>
<td>nfdon</td>
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<td>unitless</td>
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<td>rf</td>
<td>N:P ratio of the bulk of N-fixers</td>
<td>40</td>
<td>unitless</td>
<td>Letelier and Karl [1998], Krauk et al. [2006]</td>
</tr>
</tbody>
</table>

**Table B.1** List of parameters used in the pre-industrial box model.
Appendix C

N Isotopes Suggest a Large Decrease in the Marine N Inventory across the Last Deglaciation

This appendix provides:

- a detailed mathematical description of the N and $^{15}$N models (sections C.1 and C.2),
- a brief description of the optimization procedure (section C.3 and flowchart in Fig. C.1),
- additional information on the comparison of our model with the model of Deutsch et al. [2004] (section C.4),
- details on the optimization procedure with special emphasis on the convergence of the optimization approach and on the quality of fit in all three sites (section C.5),
- a brief discussion justifying the uniform influence of climate forcings on N-fixation and denitrification in the water column and sediment (section C.6), and
- a list of the parameter values of the deglacial simulations (section C.7).
C.1 N model

C.1.1 N trajectories

The rate of change in the N inventory in box $i$ depends on:

- the inputs and outputs of N carried by advection and mixing water mass fluxes ($m$) to/from box $i$ ($N(t)$ always refer to inventory, $V$: box volume, $m_{ij}$: water mass flux from box $i$ to box $j$):

$$Q^i(t) = \sum_j m_{ij} N^j(t)/V_j - \sum_j m_{ji} N^i(t)/V_i$$  \hspace{1cm} (C.1)

In other words, $Q^i(t)$ is the net transport convergence of N resulting from all physical transport processes into and out of box $i$,

- newly fixed N released by N-fixers ($F$), N consumed by water column ($W$) and benthic denitrification ($B$). $W$, $B$, and $F$ are computed at each time-step according to Equ.C.4,

- diverse sources and sinks of N which are set constant across the deglaciation: N uptake by biological production ($J_p$), N release by organic matter remineralization ($J_r$), atmospheric deposition of N ($AD$), river input of N ($RI$), and sediment burial of N ($SB$).

All terms that do not depend on local N are included in $b^i$:

$$b^i(t) = J^i_r - J^i_p + F^i(t) + AD^i + RI^i - (W^i(t) + B^i(t) + SB^i)$$  \hspace{1cm} (C.2)

Finally, combining Equ.C.1 and Equ.C.2, the rate of change of N is given by:

$$\frac{\Delta N^i}{\Delta t} = Q^i(t) + b^i(t)$$  \hspace{1cm} (C.3)

Glacial-Holocene trajectories are computed using a stiff solver. It is variable order solver based on the numerical differentiation formulas.

C.1.2 Glacial boundary conditions of N

Glacial-Holocene trajectories of N-fixation and denitrification in the water column and sediment in box $i$ can be stated as a function of:

- scaling terms [$S^i_W$, $S^i_B$, $S^i_F$] that express the rates of these fluxes under glacial conditions as a function of their Holocene rates (i.e., $W^i_I$, $B^i_I$, and $F^i_I$),
the seven positive factors $[α, β, γ, λ, φ, ρ_1, ρ_2],$

- the inventory of N in surface water of the water column to whom box $i$ belongs to ($N_{i,s}^{l,s}$ under glacial conditions and $N_{i}^{l,s}$ under the current interglacial conditions, i.e., the Holocene conditions). Relative change in surface N corresponds to the internal feedback $((N_{i,s}^{l,s}(t) - N_{G}^{l,s})/N_{G}^{l,s}),$

- the forcing functions $[H(t), L(t), D(t), C(t)]$ normalized to one and which reach their maximum under the current interglacial conditions, except $D$ that goes the other way round: it starts with one under glacial conditions and reaches zero under the current interglacial conditions (Fig. 3.4). $L(t)$ affects benthic denitrification in surface boxes only, i.e., $L_i^s(t)$ is zero function if $i$-box is not in the surface, while if $i$-box is a surface box, $L_i^s(t)$ is defined as a hyperbolic tangent.

Mathematically:

$$W^i(t) = W_i^I \left( S_W^i + \frac{\alpha N_{i,s}^{l,s}(t) - N_{G}^{l,s}}{N_{G}^{l,s}} + \lambda H(t) \right)$$

$$B^i(t) = B_i^I \left( S_B^i + \beta \frac{N_{i,s}^{l,s}(t) - N_{G}^{l,s}}{N_{G}^{l,s}} + \phi L^s_i(t) \right)$$

$$F^i(t) = F_i^I \left( S_F^i - \gamma \frac{N_{i,s}^{l,s}(t) - N_{G}^{l,s}}{N_{G}^{l,s}} \right) - F_i^I (ρ_1 (1 - D(t)) - ρ_2 C(t))$$

(C.4)

Note that $W$ is confined to the lower thermocline box of the suboxic water column of the IndoPacific.

The scaling terms $[S_W^i, S_B^i, S_F^i]$ can be expressed as function of the current interglacial N inventory and N-fixation and denitrification in the water column and sediment. For that purpose, Equus.C.4 are evaluated at $t = I$ (note that $H(t = I) = L(t = I) = C(t = I) = 1$, and $D(t = I) = 0$, see Fig. 3.4):

$$W^i(t = I) = W_i^I \left( S_W^i + \frac{\Delta_{IG}N_{i,s}^{l,s}}{N_{G}^{l,s}} + \lambda \right)$$

$$B^i(t = I) = B_i^I \left( S_B^i + \beta \frac{\Delta_{IG}N_{i,s}^{l,s}}{N_{G}^{l,s}} + \phi \right)$$

$$F^i(t = I) = F_i^I \left( S_F^i - \gamma \frac{\Delta_{IG}N_{i,s}^{l,s}}{N_{G}^{l,s}} - (ρ_1 - ρ_2) \right)$$

(C.5)

where the change in the inventory of N in surface water between the current interglacial and glacial is $\Delta_{IG}N_{i,s}^{l,s} = N_{i,s}^{l,s} - N_{G}^{l,s}$. From Equus.C.5 it is straightforward to extract the scaling term.
Appendix C. Large Decrease in the N Inventory across the Last Deglaciation

\[ [S_{Wi}, S_{Bi}, S_{Fi}]: \]

\[
S_{Wi}^i = 1 - \alpha \frac{\Delta IG N_{i,s}^{G}}{N_{i,s}^{G}} - \lambda \\
S_{Bi}^i = 1 - \beta \frac{\Delta IG N_{i,s}^{G}}{N_{i,s}^{G}} - \phi \\
S_{Fi}^i = 1 + \gamma \frac{\Delta IG N_{i,s}^{G}}{N_{i,s}^{G}} + (\rho_1 - \rho_2) \\
\text{(C.6)}
\]

The terms \([S_{Wi}, S_{Bi}, S_{Fi}]\) are simply scaling terms that express N-fixation and denitrification under glacial conditions as function of their interglacial rates:

\[
W^i_G = S_{Wi} W^i_I \\
B^i_G = S_{Bi} B^i_I \\
F^i_G = S_{Fi} F^i_I \\
\text{(C.7)}
\]

We are now in position to derive an expression for the glacial N inventory in each box as a function of the current interglacial cycle and the prescribed strengths of the forcings and sensitivities of the feedbacks. We start by writing down the equation of the change in N in box \(i\) at any time \(t\) (N conservation equation, see Equs.C.2 and C.3):

\[
\frac{dN^i(t)}{dt} = F^i(t) - (B^i(t) + W^i(t)) + Q^i(t) + SMS^i(t) + (J^i_r(t) - J^i_p(t)) \\
\text{(C.8)}
\]

with \(Q^i(t)\) the transport convergence of N defined in Equ.C.1. Secondary sources and sinks are combined in \(SMS^i\): \(SMS^i = AD^i + RI^i - SB^i\) (\(AD^i\): atmospheric deposition of N, \(RI^i\): river input of N, \(SB^i\): sediment N burial). Equ.C.8 is evaluated at \(t = G\) and at \(t = I\) assuming steady-state N-cycles under glacial and interglacial conditions:

\[
\begin{align*}
F^i_G - (B^i_G + W^i_G) + Q^i_G + SMS^i_G + (J^i_r,G - J^i_p,G) &= 0 \\
F^i_I - (B^i_I + W^i_I) + Q^i_I + SMS^i_I + (J^i_r,I - J^i_p,I) &= 0
\end{align*}
\]

\text{(C.9)}

Substituting \([W^i_G, B^i_G, F^i_G]\) from Equ.C.7 in Equ.C.9 at \(t = G\) gives:

\[
S_{Fi}^i F^i_I - (S_{Bi}^i B^i_I + S_{Wi}^i W^i_I) + Q^i_G + SMS^i_G + (J^i_r,G - J^i_p,G) = 0 \\
\text{(C.10)}
\]
The scaling terms \([S_W, S_B, S_F]\) can be expressed in terms of \(N\) under glacial and current interglacial conditions according to Equs.C.6, hence Eq.C.10 becomes:

\[
\begin{align*}
&\left(1 + \gamma \frac{\Delta IG N_{i,s}^{ls}}{N_{i}^{ls}} + (\rho_1 - \rho_2)\right) F_i^i \\
&- \left(1 - \beta \frac{\Delta IG N_{i,s}^{ls}}{N_{i}^{ls}} - \phi\right) B_i^i - \left(1 - \alpha \frac{\Delta IG N_{i,s}^{ls}}{N_{i}^{ls}} - \lambda\right) W_i^i \\
&+ Q_G^i + SMS_G^i + (J_{r,G}^i - J_{p,G}^i) = 0
\end{align*}
\] (C.11)

Subtracting Eq.C.9 at \(t = I\) from Eq.C.11, and assuming that biological production and remineralization fluxes do not change across the last deglaciation, i.e., \(J_{r,G}^i = J_{r,I}^i\) and \(J_{p,G}^i = J_{p,I}^i\), we find:

\[
\begin{align*}
\gamma \frac{\Delta IG N_{i,s}^{ls}}{N_{i}^{ls}} F_i^i + (\rho_1 - \rho_2) F_i^i + \beta \frac{\Delta IG N_{i,s}^{ls}}{N_{i}^{ls}} B_i^i + \phi B_i^i \\
+ \alpha \frac{\Delta IG N_{i,s}^{ls}}{N_{i}^{ls}} W_i^i + \lambda W_i^i + (Q_G^i - Q_I^i) \\
+ (SMS_G^i - SMS_I^i) = 0
\end{align*}
\] (C.12)

Finally, the expression is rearranged as follows:

\[
\frac{\Delta IG N_{i,s}^{ls}}{N_{i}^{ls}} = - \frac{\lambda W_i^i + \phi B_i^i + (\rho_1 - \rho_2) F_i^i - \Delta IG Q_i^i - \Delta IG SMS_i^i}{\alpha W_i^i + \beta B_i^i + \gamma F_i^i}
\] (C.13)

with \(\Delta IG Q_i^i = Q_I^i - Q_G^i\) and \(\Delta IG SMS_i^i = SMS_I^i - SMS_G^i\).

C.2 15N model

C.2.1 15N trajectories

Equations for 15N are similar to the equations for N, except that some processes in the marine N-cycle present N isotopic fractionation, expressed by fractionation factors \(\alpha\) defined as \(\alpha = 1 + \epsilon/1000\) (see Appendix A). The processes which affect 15N in box \(i\) are:

- the inputs and outputs of 15N carried by water mass fluxes \((m)\) to/from box \(i/j\):

\[
15Q_i^i(t) = \sum_j m_j^{ij} \frac{15N_j^i(t)}{V_j} - \sum_j m_j^{ij} \frac{15N_j^i(t)}{V_i}
\] (C.14)
Appendix C. Large Decrease in the N Inventory across the Last Deglaciation

- the biological production taking up N, and remineralization releasing nitrogen. Uptake is function of local surface N and $^{15}$N, and nitrogen uptake by phytoplankton has a non-zero fractionation factor $\alpha_{N_{\text{org}}}$ (see Tab. A.1 in Appendix). As a consequence, biological uptake and remineralization of nitrogen affect $^{15}$N in box $i$ as follows:

$$^{15}J_{i}^{b}(t) = \alpha_{N_{\text{org}}}(J_{r}^{i} - J_{p}^{i})^{15}N_{i,s}^{j}(t)$$

(C.15)

- the $^{15}$N consumption by $W$ (with the isotopic fractionation factor $\alpha_{W}$, see section A.3 in the Appendix) and $B$ (fractionation factor $\alpha_{B}$), both depending on local N and $^{15}$N values. $W$ and $B$ are computed at each time-step according to Equs.C.4. Sediment burial of N, even if constant across the last deglaciation, is also a sink of N that depends on local N and $^{15}$N (fractionation factor $\alpha_{S}$). Eventually, the change in $^{15}$N in box $i$ due to $W$, $B$, and $S$ is:

$$^{15}J_{\text{int}}^{i}(t) = - (\alpha_{W} W^{i}(t) + \alpha_{B} B^{i}(t) + \alpha_{S} S^{i})^{15}N_{i}^{j}(t)$$

(C.16)

- the release of newly fixed $^{15}$N by N-fixers with a $\delta^{15}$N of zero. $^{15}$N flux released by N-fixers is thus given by $R_{\text{air}}F^{i}(t)$. $F$ is computed at each time-step according to Eq.C.4,

- the atmospheric deposition ($AD$) and the river input of N ($RI$). $AD$ and $RI$, which are set constant across the deglaciation, bring $^{15}$N according to their specific $\delta^{15}$N. These two inputs of $^{15}$N as well as the flux of $^{15}$N released by N-fixers in box $i$ are included in the vector $^{15}b^{i}$:

$$^{15}b^{i}(t) = R_{\text{air}} (F^{i}(t) + \alpha_{A} A^{i} + \alpha_{R} R^{i})$$

(C.17)

All terms described above are combined to give the change in $^{15}$N in box $i$:

$$\frac{\Delta^{15}N^{i}(t)}{\Delta t} = ^{15}Q^{i}(t) + ^{15}J_{s}^{i}(t) + ^{15}J_{\text{int}}^{i}(t) + ^{15}b^{i}(t)$$

(C.18)

C.2.2 Glacial boundary conditions of $^{15}$N

The goal is to derive the equations which give the inventories of $^{15}$N under glacial conditions ($^{15}N_{G}$). We start from the differential equation that describes the temporal change in $^{15}$N, $^{15}n$ ($^{15}n^{i} = ^{15}N^{i}/V^{i}$, i.e., the concentration in box $i$), written using a matrix notation:

$$\frac{\partial^{15}n}{\partial t} = ^{15}A(t)^{15}n + ^{15}b(t)$$

(C.19)

All $^{15}$N processes that are $^{15}$N-dependent are included in the 14x14 matrix $^{15}A$ (this squared matrix has a size of 14 which corresponds to the number of boxes of the model). Row $i$ of
C.3. Genetic algorithm

$^{15}A(t)$ is related to box $i$:

$$^{15}A(t)[i,:]=\sum_j m^{ji} - \sum_j m^{ij} + \frac{\alpha_{N,\text{org}}}{n^i(t)}(J_r^i - J_p^i) - \frac{1}{n^i(t)}(\alpha_W W^i(t) + \alpha_B B^i(t) + \alpha_S S^i) \quad (C.20)$$

with $n^i = N_i/V^i$. The vector $^{15}b(t)$ contains $^{15}N$ processes that are not function of $^{15}N$ (see Equ.C.17).

The system of equations C.19 is evaluated under glacial conditions assuming a steady-state N-cycle. This implies that $\frac{\partial^{15}n_G}{\partial t} = 0$. The right-hand member of Equ.C.19 becomes:

$$^{15}A(t = G)^{15}n_G + ^{15}b(t = G) = 0 \quad (C.21)$$

this linear system of 14 equations is solved for $^{15}n_G$:

$$^{15}n_G = \left(^{15}A(t = G)\right)^{-1}^{15}b(t = G) \quad (C.22)$$

Finally the inventory of $^{15}N_G$ in box $i$ is $^{15}N_G^i = ^{15}n_G^i \cdot V^i$.

C.2.3 $\delta^{15}N$ notation

According to modeled N and $^{15}N$ it is straightforward to compute $\delta^{15}N$ trajectory in box $i$ since:

$$\delta^{15}N^i = \left(\frac{R_i}{R_{\text{air}}} - 1\right) \cdot 1000 \% \quad (C.23)$$

with $R_x = ^{15}N/^{14}N$. In this $\delta^{15}N$ definition, the isotopic ratio is compared with a reference ratio taken as the ratio found in the air ($R_{\text{air}} = ^{15}N_{\text{air}}/^{14}N_{\text{air}} = 0.3663/99.6337 \approx 0.3676\%$).

C.3 Genetic algorithm

A Genetic Algorithm is adopted to solve the optimization of sediment $\delta^{15}N$ records with respect to the seven sensitivities of the feedbacks and strengths of the forcings [$\alpha, \beta, \gamma, \lambda, \phi, \rho_1, \rho_2$]. The algorithm is a heuristic method used to solve problems in a wide variety of domains. It involves technics inspired by natural evolution such as selection, mating, recombination processes and mutations (the Genetic Algorithm method is schematized in Fig. C.1 in Appendix).

The first step is to choose an initial population of chromosomes, in our case a set of deglacial scenarios with various feedback sensitivity and forcing strength (Tab. 3.1). Our initial popu-
Appendix C. Large Decrease in the N Inventory across the Last Deglaciation

is randomly generated according to the search space. Minimum and maximum boundaries of the search space of each parameter are set in a way that does not constrain the optimization procedure. All feedback sensitivity and forcing strength factors \([\alpha, \beta, \gamma, \lambda, \phi, \rho_1, \rho_2]\) are restricted to be positive. An initial population is generated based on a uniform distribution \(N_{\text{init}} = 100\) chromosomes. We assume that the population covers the entire range of possible solutions, i.e., the search space.

Chromosomes that belong to the initial or previous pool are selected to breed a new generation. The fitness of each initial chromosome is first evaluated by computing a cost function of modeled deglacial \(\delta^{15}N\) vs sediment \(\delta^{15}N\) records at each site \(s\) (e.g. OMZ, oxic IndoPacific, and low-latitude Atlantic):

\[
j_s = \frac{1}{n_s} \sum_{k=1}^{n_s} \frac{|\delta^{15}N^\text{data}_k - \delta^{15}N^\text{model}_k|}{\sigma^\text{data}_k}\tag{C.24}
\]

\(n_s\) is the number of data points in \(\delta^{15}N\) record located in site \(s\) (OMZ surface waters, thermocline low-latitude Atlantic, deep oxic IndoPacific). A specific weighting factor is introduced, that allows more weight to be given to the OMZ (see section 3.4.2) in the computation of the global cost function: \(J_{\text{glob}} = \sum_{s=1}^{3} \gamma_s j_s / 3\). From the initial population, pairs of chromosomes are chosen randomly for the reproduction of offsprings. This genetic operator, called crossover, occurs with a rate \(r_c = 0.8\), that is 80% of the chromosomes mate. The two parent chromosomes are then split at the same point and one part of each parent is combined together to generate the offspring. The present reproduction and recombination process is called single point crossover. Since the recombination process cannot explore sections of the search space that are not represented in the initial population, the algorithm can guide the search into a local rather than the global minimum with respect to the cost function. That is why genetic algorithm usually perform random mutations.

The mutation operator introduces new genetic structures in the chromosome population by randomly changing some of the seven feedback and forcing factors. Mutation is implemented by altering a random factor from \(N_{\text{init}}(1 - r_c) = 100(1 - 0.8) = 20\) chromosomes, that is from as many chromosomes that have not mated. Since the mutation operation is totally random, it creates different genetic structures related to sections of the search space that were not present in the genetic structure of the previous generation. Mutation and crossover will ultimately result in the next generation of chromosomes.

The evaluation of the fitness of offspring chromosomes is required to select the next population. The fitness of each individual offspring is evaluated by computing a cost function the same way than for their parents. Parents and offsprings fitnesses are then sorted in order to select the next parent generation. Selection is done by elitism, i.e., only the fittest chromosomes among parents and offsprings are kept (steady-state approach). By selecting the
C.3. Genetic algorithm

Evaluate (fitness)
Compute cost function at each three sites
Generate global cost function

Selection, mating
1-point crossover and recombination
Parents chosen randomly
Crossover rate: \( r_c = 0.8 \)
(80 offsprings scenarios)

Mutation
Number of mutating chromosomes: \((1 - r_c)N \)
(20 deglaciation scenarios)

Offspring population
Number of chromosomes: \( N_{\text{offsprings}} \)
(80 deglaciation scenarios)

Evaluate (fitness)
Compute cost function at each three sites
Generate global cost function

Choose best ever
Selection among parents and offsprings
Sort by fitness

New population
Steady-state approach
(\( N_{\text{offsprings}} = N_{\text{offsprings}} \))
(100 deglaciation scenarios)

Parents population
New population becomes new generation of parents
(100 deglaciation scenarios)

Termination?
Number of iterations: \( N_{\text{iter}} = 100 \)

Figure C.1 Flowchart depicting the genetic algorithm developed to generate solutions to the model-data \( \delta^{15}N \) optimization across the last glacial termination.
fittest 100 chromosomes, the initial population size is conserved. Generally, the averaged fitness of the new generation will have increased as compared to the previous generation since only the fittest chromosomes are selected.

The generational algorithm is repeated until a fixed number of generations is reached. In our case, we perform 100 iterations until termination.

C.4 Comparison with Deutsch’s model

We aim to repeat and compare the best scenario that stems from our model with the best scenario from Deutsch et al. [2004], although the two models have some differences. Forcing strength and feedback sensitivity of Deutsch et al. [2004] model were tuned by trial and error, while our model includes a genetic algorithm optimization approach. Another difference between the two models comes from their architectures. The former model has no spatial dimension, the ocean is split into a suboxic and an oxic water column, while the later model fully resolves diverse oceanic basins (Fig. 3.3). For the purpose of this comparison, the iron and the carbon forcings affecting N-fixation are switched off, and like the Deutsch et al. [2004] model we only aim to best fit sediment δ¹⁵N records assigned to the OMZ (that is the suboxic IndoPacific surface box) and the oxic IndoPacific (considered as mean ocean in Deutsch et al. [2004] model). The scenario with smallest cost function at the end of 100 iterations with 100 scenarios is compared to the Deutsch et al. [2004] best scenario.

Prescribing the Deutsch et al. [2004] setup, our model is capable of reproducing reasonably well sediment δ¹⁵N records from the OMZ, and to a lesser extent records from the oxic IndoPacific (Fig. C.2A,B in Appendix). Glacial and Holocene modeled OMZ δ¹⁵N match the data very well, and the deglacial transition is precisely reproduced (2.8‰ increase followed by a 0.2‰ decrease until the current interglacial equilibrium). In the oxic IndoPacific, glacial δ¹⁵N data are slightly underestimated and a small amplitude deglacial peak is simulated (0.8‰ increase followed by a 0.9‰ decrease until the current interglacial equilibrium).

Feedback and forcing factors of our model (see Tab. 3.1) show similar relative strength to that reported by Deutsch et al. [2004]. We find \([\alpha, \beta, \gamma, \lambda, \phi] = [0.30, 0.08, 0.22, 0.41, 0.17]\) while Deutsch et al. [2004] reported \([\alpha, \beta, \gamma, \lambda, \phi] = [9, 1, 9, 0.6, 0.3]\). We suspect that the higher values of the later study compared to the former are due to the different implementation of feedback mechanisms. In the Deutsch et al. [2004] model, feedbacks are constructed based on change in global N relative to the initial glacial value, while the parameterization of the feedbacks in the former model are function of change in N in the surface boxes. Like the former study, we found that stronger forcings affecting water column denitrification (λ) than affecting benthic denitrification (φ) require higher feedback sensitivities of water column
C.4. Comparison with Deutsch’s model

Figure C.2 Reproducing Deutsch et al. [2004] model, i.e., without N-fixation forcings, δ15N constraints from OMZ (A) and oxic IndoPacific (B) only. Modeled δ15N in low-latitude Atlantic is displayed (dashed curve) although this site is not used as a constraint. (A and B): sediment δ15N records ([black curve] 2 kyr moving average, [gray zone] one sample standard deviation) and modeled δ15N [red curve]. (C) simulated global N inventory. (D) N-fixation (F), and water column (W) and benthic (B) denitrification.

denitrification (α) than of benthic denitrification (β). This requirement is necessary so as to satisfy the condition that the Holocene benthic-to-water column denitrification ratio has to be restored close to its glacial value in order to simulate constant glacial-Holocene mean ocean δ15N (oxic IndoPacific δ15N in our model).

Similarly to the Deutsch et al. [2004] findings, the global inventory of N decreases across the deglaciation, and N-fixation and denitrification rates increase (Fig. C.2C,D). The N inventory decreases by 19% as a consequence of weak negative feedbacks from N-fixation and denitrification, whereas the Deutsch et al. [2004] best scenario shows almost no change in the N
inventory. Conversely, our model simulates a glacial-Holocene increase in N-fixation, water column and benthic denitrification of 12, 34, and 3% respectively, which diverge from those reported by Deutsch et al. [2004] (40, 32, and 41%).

The optimization procedure does not aim to best fit $\delta^{15}$N in the thermocline of the low-latitude Atlantic, although it is instructive to inspect simulated values there. $\delta^{15}$N hardly changes between the last glacial period and the Holocene, and a small amplitude deglacial peak is simulated (Fig. C.2B dashed curve). Sediment $\delta^{15}$N reconstruction for this site reveals that the model strongly underestimates glacial data (Fig. 3.2F). This indicates that without iron and carbon forcings on N-fixation and using only the OMZ and oxic Indo-Pacific sites as constraints do not allow the model to simultaneously reproduce $\delta^{15}$N records from the OMZ, the oxic Indo-Pacific, and the low-latitude Atlantic.

C.5 Optimization validation and $\delta^{15}$N diagnostic analysis

This section provides details on the optimization procedure with special emphasis on the convergence of the optimization approach, on the quality of fit in all three sites, and on the consequences of prescribing constant export production on glacial-interglacial time-scales.

Global and site-specific cost functions reach stable minima, and all seven parameters (see Tab. 3.1) converge reasonably well within the 100 iterations performed by the Genetic Algorithm (Fig. C.3 in Appendix). Sensitivity of N-fixation feedback ($\gamma$) and iron forcing strength ($\rho_1$) converge the fastest, while the sensitivity of water column denitrification feedback ($\alpha$) and forcing strength on benthic denitrification ($\phi$) convergences are slower. Although until the last iteration, the suite of 100 scenarios does not show perfect convergence of these two parameters, these parameters are invariable for the scenario with smallest global cost function of each of the last 40 iterations. This invariability is interpreted as evidence of an acceptable stability of these parameters, although the weak convergence suggests that these two parameters are not well constrained by data.

The model broadly captures the last deglaciation $\delta^{15}$N features in the OMZ, the oxic Indo-Pacific, and the low-latitude Atlantic (Fig. C.4 in Appendix). $\delta^{15}$N diagnostic analysis reveals that the model does not systematically under- or overestimate $\delta^{15}$N data in any site, although there is a small tendency for data overestimation in the OMZ and oxic Indo-Pacific under glacial conditions (Fig. C.4 in Appendix). $\delta^{15}$N data in the OMZ are successfully reproduced with a glacial to early deglacial increase of $\sim 4\%_o$ and an early deglacial to Holocene decrease of $\sim 1\%_o$. In the oxic Indo-Pacific, the model simulates a glacial-Holocene decrease in $\delta^{15}$N of $0.7\%_o$, with a transient deglacial peak ($1.1\%_o$ increase with a subsequent $1.8\%_o$ decrease), even though the $\delta^{15}$N data used as constraint do not reveal corresponding variation.
C.5. Optimization validation and $\delta^{15}$N diagnostic analysis

Figure C.3  Convergence of the cost functions and optimized parameters in the standard case. Cost functions and parameters of each of the 100 scenarios at each of the 100 iterations are displayed. **Upper panels:** global, OMZ, oxic IndoPacific, and low-latitude Atlantic cost functions. **Middle panels:** sensitivities of the feedback of water column ($\alpha$) and benthic ($\beta$) denitrification, and N-fixation ($\gamma$). **Lower panels:** strengths of the forcings on water column ($\lambda$, suboxia changes) and benthic denitrification ($\phi$, sea-level rise), and on N-fixation ($\rho_1$, iron-rich dust deposition; $\rho_2$, atmospheric CO$_2$). Red dots show the setups of the scenarios with smallest global cost function at each time-step. Dashed blue lines show the minimum and maximum boundaries that define the search space of each parameters.

during the transition. In the low-latitude Atlantic $\delta^{15}$N data is underestimated by the model and show a smoother deglacial decrease than the data.

Sediment $\delta^{15}$N records from the South China Sea [Kienast, 2000] are assigned as a model constraint to the oxic IndoPacific, although there is debate in the literature about the interpretation of these invariable records [Higginson et al., 2003; Kienast et al., 2005]. Altabet [2007] stated that, while all sediment $\delta^{15}$N records could be questioned as to the influence of local processes or diagenesis, a consistent picture is apparent in aggregate, with a glacial maximum-to-late Holocene increase in $\delta^{15}$N of 2 to $3^{\%}_o$ followed by a 1 to $2^{\%}_o$ decrease.
Figure C.4  $\delta^{15}N$ diagnostic in each three sites: data $\delta^{15}N$ moving average [black curve] with confidence interval of $+/−1$ std [gray zone], and modeled $\delta^{15}N$ for scenario with smallest cost function at the end of the last iteration of the standard case run (A,B,C). Model - data $\delta^{15}N$ residual in each site (D,E,F). A positive (negative) residual means that modeled $\delta^{15}N$ overestimate (underestimate) the data. Data $\delta^{15}N$ as a function of the modeled value highlights systematic $\delta^{15}N$ deviation of the model to higher (lower) value, i.e., dots below (above) 1:1 line [dashed line] (G,H,I).
Figure C.5  Confidence interval for the marine N-cycle across the last deglaciation for the standard case (100 iterations, 100 scenarios, OMZ site weighted twice as much as each of the two others). Changes in N-fixation (A), water column (B) and benthic (C) denitrification, and in the global inventory of N (D) for the suite of 10 scenarios with smallest cost functions.

to the late Holocene. However, we assume that the South China Sea records are the best reconstruction of the past oxic IndoPacific, whereas, even if a small deglacial peak might be considered there, it would be in the range of the data moving average plus/minus 1 sample standard deviation (the gray band in Fig. 3.2E).

The deglacial peak simulated in the oxic IndoPacific can be seen to be in reasonable agreement with records reported in literature. Although the deglacial peak is not revealed in South China Sea measurements, its amplitude exceeds the moving average plus one standard deviation value. In addition to the fact that too little is known at present about whether or not a deglacial $\delta^{15}N$ peak has to be assigned to the oxic IndoPacific, and if yes its amplitude, we conclude that the modeled $\delta^{15}N$ is in broad agreement with data.

The underestimated glacial $\delta^{15}N$ in the low-latitude Atlantic stems from overestimation of $\delta^{15}N$ data in the oxic IndoPacific and the inability of the model in simulating higher glacial $\delta^{15}N$ in the low-latitude compared to the oxic IndoPacific. Higher glacial $\delta^{15}N$ in the low-latitude At-
Appendix C. Large Decrease in the N Inventory across the Last Deglaciation

Atlantic compared to the oxic IndoPacific can only be achieved with relatively higher inputs of heavy isotopes in the Atlantic, and respectively smaller outputs of light isotopes. Water column denitrification is by far the dominant fractionating process but is strictly confined to the OMZ where water masses can only communicate with the Atlantic through the oxic Indo-Pacific (Fig. 3.3). This sink can therefore not aid in reproducing higher glacial $\delta^{15}$N in the Atlantic than in the oxic IndoPacific. Alternatives would be by invoking basin-scale specific river input, atmospheric deposition or sediment burial of N since all these minor sources and sinks alter the isotopic composition of N. Given the opposite effect of river input and atmospheric deposition, and the fact that these inputs and outputs are rather uniformly distributed under pre-industrial (see input rates in Fig. 3.3) and likely also during glacial conditions, it is hardly conceivable to invoke these processes to explain the model/data $\delta^{15}$N discrepancy in the oxic Indo-Pacific and low-latitude Atlantic. Additionally, deglacial change in export production could alter $\delta^{15}$N on a basin-scale and hence help to resolve this issue.

An important simplifying assumption we made is that the export production of organic matter is constant across the last deglaciation. This assumption is probably the most appropriate since global and local change in export production are not well established, aside from lower glacial export production in the Southern Ocean south of the Antarctic Polar Front [Kohfeld et al., 2005]. But, assuming higher glacial export production in the Atlantic and a deglacial decrease would affect the $\delta^{15}$N in the thermocline. Relatively higher export productivity in the Atlantic compared to the IndoPacific might help to increase modeled $\delta^{15}$N in the low-latitude Atlantic as a consequence of isotopic fractionation during N assimilation by phytoplankton. However, this hypothesis will not hold depending on how the regional degree of N utilization will have changed and imprinted $\delta^{15}$N over the past. In conclusion, it may be that prescribing a constant export production on glacial-interglacial time-scale prevents the model from fully restoring glacial $\delta^{15}$N data in the oxic Indo-Pacific and low-latitude Atlantic.

Additionally, basin-scale changes in export productivity would have specifically affected benthic denitrification and thus $\delta^{15}$N in each basin. Here, we hypothesize on the effect of distinct changes in export productivity on $\delta^{15}$N in the oxic Indo-Pacific and low-latitude Atlantic, although it is not known how export productivity changed in these basins between the last glacial period and the Holocene [Kohfeld et al., 2005]. A deglacial constant export productivity in the Pacific and decrease in the Atlantic would tend to decrease benthic denitrification in the later basin since benthic denitrification is related to the C flux that reaches the sea floor. As a consequence, deglacial basin-scale changes in export productivity would imply a larger increase in the imbalance between sources and sinks of N in the Atlantic, which implies a lightening of $\delta^{15}$N and therefore might help to resolve the glacial model/data $\delta^{15}$N discrepancy in the oxic Indo-Pacific and low-latitude Atlantic (see also section 3.4.1 and Fig. 3.5).
C.6 Justifying uniform influence of climate forcings on N fluxes

In this section, we justify why uniform forcing strength of each climate forcing can be assumed, i.e., what the rationale is for prescribing the same strength of each climate forcing in all oceanic basins. Water column denitrification is restricted to a single oceanic basin, i.e., the OMZ, and it thus makes sense to use a unique forcing strength on this sink.

The issue of the sea-level rise forcing on benthic denitrification on a basin-scale is more challenging to address since it involves changes in sea-level, vertical hypsometric profile and export production. The forcing is based on the fact that lower sea-level exposes much of the global shelf area where substantial benthic denitrification occurs, which implies that organic matter settles through a greater height of water column and in turn a larger fraction is oxidized there instead of in marine sediments. The issue of changes in export production across the last deglaciation is discussed above (see section C.5 in Appendix) and reveals that it is not clear to what extent glacial export productivity would have been different than the export productivity under the current interglacial conditions [Kohfeld et al., 2005]. On a basin-scale, the Atlantic and Pacific vertical profiles in the upper 120 m are quite similar (Fig. C.6 in Appendix), and it is assumed that sea-level rise was uniform in all basins. In conclusion, there is no clear evidence for considering benthic denitrification forcing strength separately for each basin.

![Graphs showing normalized basin-scale hypsometric profiles and sea-level rise data.](image)

**Figure C.6** Left panel: Normalized basin-scale hypsometric profiles from 120 m depth (LGM sea-level) to 0 m (pre-industrial sea-level). Data: ETOPO5 [1988]. Right panel: sea-level rise reconstruction data from Bard et al. [1990] and Hanebuth et al. [2000]. Idealized normalized sea-level rise is computed by fitting a hyperbolic tangent to the data.
We have good arguments in favor of setting global-scale iron and carbon forcings affecting N-fixation. Change in dust deposition between glacial-Holocene periods have been reported as a global-scale phenomenon with larger glacial deposition observed not only in the Vostock ice core [Petit et al., 1999] but also in several marine sediment cores (see Kohfeld et al. [2005] SOM and references therein). Therefore, a global-scale forcing parameterization with one global forcing strength factor is incorporated in the model. The carbon forcing affecting diazotrophs is assumed homogeneous because the same atmospheric $CO_2$ level is found everywhere and it is assumed that the same mix of diazotrophic communities are found in each oceanic basin.
## C.7 Parameters used in box model simulations across the last glacial termination

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Model value (standard case)</th>
<th>Units</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>atm</td>
<td>atmospheric deposition of N</td>
<td>14</td>
<td>TgN yr(^{-1})</td>
<td></td>
</tr>
<tr>
<td>rin</td>
<td>riverine input of N</td>
<td>14</td>
<td>TgN yr(^{-1})</td>
<td></td>
</tr>
<tr>
<td>rip</td>
<td>riverine input of P</td>
<td>2</td>
<td>TgN yr(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>
| alphaNorg  | isotopic effect of N uptake by phyto.             | 0.995                       | \%/yr        | Sigman et al. [1999]
|            |                                                  |                             |              | DiFiore et al. [2006]                            |
| alphaa     | isotopic composition of riverine N               | 0.996                       | \%/yr        | Brandes and Devol [2002]                         |
| alphab     | isotopic effect of sediment burial               | 1.006                       | \%/yr        | Brandes and Devol [2002]                         |
| alphar     | isotopic composition atm. depos. of N            | 1.004                       | \%/yr        | Brandes and Devol [2002]                         |
| alphas     | isotopic effect of sediment denitrif             | 1.000                       | \%/yr        | Brandes et al. [1998]                            |
| alphaw     | isotopic effect of water col denitrif            | 0.975                       | \%/yr        |                                                  |
| meandel_obs| mean ocean \(\delta^{15}\)N                     | 4.800                       | \%/yr        | Liu and Kaplan [1989]                            |
|            |                                                  |                             |              | Sigman et al. [2000]                            |
| Rair       | isotopic composition of atm. N (reference)       | 0.3663                      | \%/yr        |                                                 |
| nfdon      | fraction of organic matter remin. in surface     | 0.9                         | unitless     |                                                 |
| frac_bur_surf| fraction N and P buried in surface box         | 0.5                         | unitless     |                                                 |
| nn         | N:P redfield ratio                               | 16                          | unitless     |                                                 |
| sites      | site optimizex (1:OMZ, 2:LLA, 3:IPO)             | [1 2 3]                     | unitless     |                                                 |
| weight_omz | OMZ weighting factor (standard case)             | 2                           | unitless     |                                                 |
| n_chr      | number of chromosomes                            | 100                         | unitless     |                                                 |
| n_iter     | number of iterations                             | 50                          | unitless     |                                                 |
| n_cross    | number of chromosomes that mate                  | 80                          | unitless     |                                                 |
| n_mutant   | number of chromosomes that mutate                | 20                          | unitless     |                                                 |
| min_bnd    | lower boundaries search space                    | seven times 0.01            | unitless     |                                                 |
| max_bnd    | upper boundaries search space                    | [50 50 50 10 10 10 10]      | unitless     |                                                 |
| tstart     | start simulation                                 | -30000                      | yr           |                                                 |
| tend       | end simulation                                   | 0                           | yr           |                                                 |
| tba1       | start/end suboxia expansion (step function)      | -15500                      | yr           |                                                 |
| dust_start | start decrease in dust flux                      | -25000                      | yr           |                                                 |
| dust_end   | end decrease in dust flux                        | -15000                      | yr           |                                                 |
| crb_start  | start increase in atm. \(\text{CO}_2\)          | -17000                      | yr           |                                                 |
| crb_end    | end increase in atm. \(\text{CO}_2\)            | -10000                      | yr           |                                                 |

Table C.1 List of parameters used in simulations across the last glacial termination.
Appendix D

Implementing N Isotopes in the BEC Model

This appendix provides details on:

- the equations and parameters values associated with the N-cycle (section D.1),
- the coding of the implementation of the N isotopes in the BEC model (section D.2), and
- the initialization of simulations with the CCSM-BEC model (section D.3).
Appendix D. Implementing N Isotopes in the BEC Model

D.1 Model equations and parameter values

D.1.1 Ecosystem parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$dps$</td>
<td>$1/86400$</td>
<td>number of days in a second (d/sec)</td>
</tr>
<tr>
<td>$r_{atm}$</td>
<td>$0.003663$</td>
<td>isotopic fraction of atmospheric $N_2$ gas (reference)</td>
</tr>
<tr>
<td>$Q_{N:C}$</td>
<td>$0.137$</td>
<td>ratio of N:C in small phytoplankton, diatoms, diazotrophs, zooplankton and sinking detritus</td>
</tr>
<tr>
<td>$R_{C:N}^{d}$</td>
<td>$117/136$</td>
<td>C:N ratio for water column and benthic denitrification</td>
</tr>
<tr>
<td>$R_{C:O}^{d}$</td>
<td>$117/170$</td>
<td>ratio of dissolved matter C:O</td>
</tr>
<tr>
<td>$R_{C:O}^{p}$</td>
<td>$117/170$</td>
<td>ratio of particulate matter C:O</td>
</tr>
<tr>
<td>$R_{C:O}^{diaz}$</td>
<td>$117/150$</td>
<td>ratio of diazotroph C:O</td>
</tr>
<tr>
<td>$S_{wcd}$</td>
<td>$35$</td>
<td>minimum $NO_3^-$ needed for water column (long equil. run 4) denitrification (standard case) (mmol/m$^3$)</td>
</tr>
<tr>
<td>$S_{bd}$</td>
<td>$0.0$</td>
<td>minimum $NO_3^-$ needed for benthic denitrification (mmol/m$^3$)</td>
</tr>
<tr>
<td>$S_{wcd}$</td>
<td>$4.0$</td>
<td>maximum $O_2$ for water column denitrification (nmol/cm$^3$)</td>
</tr>
<tr>
<td>$rem_{dom}$</td>
<td>$0.01 \cdot dps$</td>
<td>remineralization rate of small detrital (1/sec)</td>
</tr>
<tr>
<td>$f^{bd}$</td>
<td>$3$</td>
<td>scaling factor for benthic denitrification (long equil. run 4)</td>
</tr>
</tbody>
</table>

Fractionation and isotopic enrichment factors ($\alpha_x = 1.0 + \epsilon_x/1000$)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{nit}$</td>
<td>$-10.0%_{oo}$</td>
<td>nitrification</td>
</tr>
<tr>
<td>$\epsilon_{wcd}$</td>
<td>$-25.0%_{oo}$</td>
<td>water column denitrification</td>
</tr>
<tr>
<td>$\epsilon_{bd}$</td>
<td>$0.0%_{oo}$</td>
<td>benthic denitrification</td>
</tr>
<tr>
<td>$\epsilon_{sp,no3}$</td>
<td>$-5.0%_{oo}$</td>
<td>nitrate uptake by small phytoplankton</td>
</tr>
<tr>
<td>$\epsilon_{diat,no3}$</td>
<td>$-5.0%_{oo}$</td>
<td>nitrate uptake by diatoms</td>
</tr>
<tr>
<td>$\epsilon_{sp,nh4}$</td>
<td>$-5.0%_{oo}$</td>
<td>ammonium uptake by small phytoplankton</td>
</tr>
<tr>
<td>$\epsilon_{diat,nh4}$</td>
<td>$-5.0%_{oo}$</td>
<td>ammonium uptake by diatoms</td>
</tr>
<tr>
<td>$\epsilon_{diaz}$</td>
<td>$0.0%_{oo}$</td>
<td>N-fixed by diazotrophs</td>
</tr>
<tr>
<td>$\epsilon_{zoo}$</td>
<td>$-6.0%_{oo}$</td>
<td>zooplankton excretion</td>
</tr>
</tbody>
</table>
D.1.2 Nitrogen pools variables with initial values

\[ \begin{align*}
\text{NO}_3 & \quad \text{from restart file} \\
\text{\textsuperscript{15}NO}_3 & \quad \text{according to } \delta_{\text{\textsuperscript{15}NO}_3} = 5 \% \\
\text{NH}_4 & \quad \text{from restart file} \\
\text{\textsuperscript{15}NH}_4 & \quad \text{according to } \delta_{\text{\textsuperscript{15}NH}_4} = 5 \% \\
\text{spN} & \quad \text{from restart file} \\
\text{sp\textsuperscript{15}N} & \quad \text{according to } \delta_{\text{\textsuperscript{15}spN}} = 5 \% \\
\text{diatN} & \quad \text{from restart file} \\
\text{diat\textsuperscript{15}N} & \quad \text{according to } \delta_{\text{\textsuperscript{15}diatN}} = 5 \% \\
\text{diazN} & \quad \text{from restart file} \\
\text{diaz\textsuperscript{15}N} & \quad \text{according to } \delta_{\text{\textsuperscript{15}diazN}} = 0 \% \\
\text{zooN} & \quad \text{from restart file} \\
\text{zoo\textsuperscript{15}N} & \quad \text{according to } \delta_{\text{\textsuperscript{15}zooN}} = 5 \% \\
\text{DON} & \quad \text{from restart file} \\
\text{DON\textsuperscript{15}} & \quad \text{according to } \delta_{\text{\textsuperscript{15}DON}} = 5 \%
\end{align*} \]

\[ \begin{align*}
\text{nitrate (mmol/m}^3 & \text{)} \\
\text{\textsuperscript{15}N nitrate (mmol/m}^3 & \text{)} \\
\text{ammonium (mmol/m}^3 & \text{)} \\
\text{\textsuperscript{15}N ammonium (mmol/m}^3 & \text{)} \\
\text{small phytoplankton (mmol/m}^3 & \text{)} \\
\text{\textsuperscript{15}N small phytoplankton (mmol/m}^3 & \text{)} \\
\text{diatoms (mmol/m}^3 & \text{)} \\
\text{\textsuperscript{15}N diatoms (mmol/m}^3 & \text{)} \\
\text{diazotrophs (mmol/m}^3 & \text{)} \\
\text{\textsuperscript{15}N diazotrophs (mmol/m}^3 & \text{)} \\
\text{zooplankton (mmol/m}^3 & \text{)} \\
\text{\textsuperscript{15}N zooplankton (mmol/m}^3 & \text{)} \\
\text{dissolved organic nitrogen (mmol/m}^3 & \text{)} \\
\text{\textsuperscript{15}N dissolved organic nitrogen (mmol/m}^3 & \text{)}
\end{align*} \]

D.1.3 Local variables and constants

\[ \text{Isotopic fraction } (r = \frac{\text{\textsuperscript{15}N}_{\text{x}}}{\text{\textsuperscript{15}N}_{\text{x}} + \text{\textsuperscript{14}N}_{\text{x}}}) \]

\[ \begin{align*}
r_{\text{no3}} & \quad \text{isotopic fraction of nitrate} \\
r_{\text{nh4}} & \quad \text{isotopic fraction of ammonium} \\
r_{\text{sp}} & \quad \text{isotopic fraction of small phytoplankton} \\
r_{\text{diat}} & \quad \text{isotopic fraction of diatoms} \\
r_{\text{diaz}} & \quad \text{isotopic fraction of diazotrophs} \\
r_{\text{zoo}} & \quad \text{isotopic fraction of zooplankton} \\
r_{\text{don}} & \quad \text{isotopic fraction of small detritus} \\
J_{\text{zoo}} & \quad \text{fraction of zooplankton routed to POM in mortality losses (-)}
\end{align*} \]

[see model equations by Lima, 2010]
$J_{\text{sp}, \text{no3}}^i$, nitrate uptake by small phytoplankton (mmol N/m$^3$/sec)
$J_{\text{sp}, \text{nh4}}^i$, ammonium uptake by small phytoplankton (mmol N/m$^3$/sec)
$J_{\text{diat}, \text{no3}}^i$, nitrate uptake by diatoms (mmol N/m$^3$/sec)
$J_{\text{diat}, \text{nh4}}^i$, ammonium uptake by diatoms (mmol N/m$^3$/sec)

$J_{\text{sp}}^g$, grazing loss for small phytoplankton (mmol C/m$^3$/sec)
$J_{\text{sp}, \text{dic}}^g$, grazed small phytoplankton routed to DIC (mmol C/m$^3$/sec)
$J_{\text{sp}, \text{doc}}^g$, grazed small phytoplankton routed to DOC (mmol C/m$^3$/sec)
$J_{\text{sp}, \text{poc}}^g$, grazed small phytoplankton routed to POC (mmol C/m$^3$/sec)
$J_{\text{sp}, \text{zoo}}^g$, grazing loss for small phytoplankton routed to new zoo biomass (mmol C/m$^3$/sec)

$J_{\text{diat}}^g$, grazing loss for diatoms (mmol C/m$^3$/sec)
$J_{\text{diat}, \text{dic}}^g$, grazed diatoms routed to DIC (mmol C/m$^3$/sec)
$J_{\text{diat}, \text{doc}}^g$, grazed diatoms routed to DOC (mmol C/m$^3$/sec)
$J_{\text{diat}, \text{poc}}^g$, grazed diatoms routed to POC (mmol C/m$^3$/sec)
$J_{\text{diat}, \text{zoo}}^g$, grazed diatoms routed to new zoo biomass (mmol C/m$^3$/sec)

$J_{\text{diaz}}^g$, grazing loss for diazotrophs (mmol C/m$^3$/sec)
$J_{\text{diaz}, \text{dic}}^g$, grazed diazotrophs routed to DIC (mmol C/m$^3$/sec)
$J_{\text{diaz}, \text{doc}}^g$, grazed diazotrophs routed to DOC (mmol C/m$^3$/sec)
$J_{\text{diaz}, \text{poc}}^g$, grazed diazotrophs routed to POC (mmol C/m$^3$/sec)
$J_{\text{diaz}, \text{zoo}}^g$, grazed diazotrophs routed to new zoo biomass (mmol C/m$^3$/sec)

$J_{\text{sp}}^l$, aggregation loss of small phytoplankton (mmol C/m$^3$/sec)
$J_{\text{sp}, \text{dic}}^l$, non-grazing mortality of small phytoplankton routed to DIC (mmol C/m$^3$/sec)
$J_{\text{sp}, \text{doc}}^l$, non-grazing mortality of small phytoplankton routed to DOC (mmol C/m$^3$/sec)
$J_{\text{sp}, \text{poc}}^l$, non-grazing mortality of small phytoplankton routed to POC (mmol C/m$^3$/sec)
$J_{\text{sp}}^l$, aggregation loss of small phytoplankton (mmol C/m$^3$/sec)
$J_{\text{diat}}^l$, non-grazing mortality of diatoms (mmol C/m$^3$/sec)
$J_{\text{diat}, \text{dic}}^l$, non-grazing mortality of diatoms routed to DIC (mmol C/m$^3$/sec)
$J_{\text{diat}, \text{doc}}^l$, non-grazing mortality of diatoms routed to DOC (mmol C/m$^3$/sec)
$J_{\text{diat}, \text{poc}}^l$, non-grazing mortality of diatoms routed to POC (mmol C/m$^3$/sec)

$J_{\text{diaz}}^l$, non-grazing mortality of diazotrophs (mmol C/m$^3$/sec)
$J_{\text{diaz}, \text{dic}}^l$, non-grazing mortality of diazotrophs routed to DIC (mmol C/m$^3$/sec)
$J_{\text{diaz}, \text{doc}}^l$, non-grazing mortality of diazotrophs routed to DOC (mmol C/m$^3$/sec)
$J_{\text{zoo}}^l$, zooplankton mortality (mmol C/m$^3$/sec)
$J_{\text{zoo}, \text{dic}}^l$, zooplankton mortality routed to DIC (mmol C/m$^3$/sec)
$J_{\text{zoo}, \text{doc}}^l$, zooplankton mortality routed to DOC (mmol C/m$^3$/sec)
D.1. Model equations and parameter values

NIT  amount of NH$_4^+$ converted to nitrate by nitrification (mmol N/m$^3$/sec)

WCD  amount of NO$_3^-$ converted to N$_2$ by water column denitrification (mmol N/m$^3$/sec)

BD   amount of NO$_3^-$ converted to N$_2$ by benthic denitrification (mmol N/m$^3$/sec)  
     \hspace{1cm} (normalized by grid-cell height)

$J_p$  amount of large detritus C produced (mmol C/m$^3$/sec)

$J_{pon15}$ amount of large detritus $^{15}$N produced (mmol N/m$^3$/sec)

$J'_p$  amount of large detritus C remineralized (mmol C/m$^3$/sec)

$J'_{pon15}$ amount of large detritus $^{15}$N remineralized (mmol N/m$^3$/sec)

$J_b$   amount of C in large detritus at the sea floor (mmol C cm/m$^3$/sec), 
        \hspace{1cm} (C flux that reaches the sea floor divided by grid-cell height)

$J'_b$  amount of C in large detritus at the sea floor ($\mu$molC/cm$^2$/day)

$J_{soft}$ incoming reactive (soft) C flux (mmol C cm/m$^3$/sec)

$J_{soft,pon15}$ incoming reactive (soft) $^{15}$N flux (mmol N cm/m$^3$/sec)

$J_{hard}$ incoming inert (hard) C flux (mmol C cm/m$^3$/sec)

$J_{hard,pon15}$ incoming inert (hard) $^{15}$N flux (mmol N cm/m$^3$/sec)

$J_{photoN}$ N$_2$-fixed and assimilated to diazotroph biomass (mmol N/m$^3$/sec)

$J_{Nfix}$ total N-fixation by diazotrophs (mmol N/m$^3$/sec)

$J_{photo15N}$ $^{15}$N-fixed and assimilated to diazotrophs biomass (mmol/m$^3$/sec)

$J_{15Nfix}$ total $^{15}$N-fixation by diazotrophs (mmol/m$^3$/sec)

$J_{15Nexcr}$ $^{15}$N fixed and then excreted as DON by diazotroph (mmol/m$^3$/sec)

[see model equations by Lima, 2010]
D.1.4 Model equations

\[
\frac{d}{dt} (\text{NO}_3) = \text{NIT} - \text{WCD} - f^{\text{bel}} \text{BD} \\
- J_{\text{diat,no3}}^u - J_{\text{sp,no3}}^u \tag{D.1}
\]

\[
\frac{d}{dt} (^{15}\text{NO}_3) = \alpha_{\text{nit, nh4}} \text{NIT} - \alpha_{\text{wcd, no3}} \text{WCD} - \alpha_{\text{bd, no3}} f^{\text{bel}} \text{BD} \\
- \alpha_{\text{diat, no3}} r_{\text{no3}} J_{\text{diat,no3}}^u - \alpha_{\text{sp, no3}} r_{\text{no3}} J_{\text{sp,no3}}^u \tag{D.2}
\]

\[
\frac{d}{dt} (\text{NH}_4) = Q_{\text{N:C}} J_{\text{poc}}^r + \text{rem}_{\text{dom}} \text{DON} \\
+ Q_{\text{N:C}} \left( J_{\text{diat,dic}}^l + J_{\text{sp,dic}}^l + J_{\text{diaz,dic}}^l + J_{\text{zoo,dic}}^l \right) \\
+ Q_{\text{N:C}} \left( J_{\text{diat,dic}}^g + J_{\text{sp,dic}}^g + J_{\text{diaz,dic}}^g \right) \\
- \text{NIT} - J_{\text{diat,nh4}}^u - J_{\text{sp,nh4}}^u \tag{D.3}
\]

\[
\frac{d}{dt} (^{15}\text{NH}_4) = J_{\text{pon15}}^r + \text{rem}_{\text{dom}} r_{\text{don}} \text{DON} \\
+ Q_{\text{N:C}} \left( r_{\text{diat}} J_{\text{diat,dic}}^l + r_{\text{sp}} J_{\text{sp,dic}}^l + r_{\text{diaz}} J_{\text{diaz,dic}}^l + r_{\text{zoo}} J_{\text{zoo,dic}}^l \right) \\
+ \alpha_{\text{zoo}} r_{\text{zoo}} Q_{\text{N:C}} \left( J_{\text{diat,dic}}^g + J_{\text{sp,dic}}^g + J_{\text{diaz,dic}}^g \right) \\
- \alpha_{\text{nit}} r_{\text{nh4}} \text{NIT} \\
- \alpha_{\text{diat,nh4}} r_{\text{nh4}} J_{\text{diat,nh4}}^u - \alpha_{\text{sp,nh4}} r_{\text{nh4}} J_{\text{sp,nh4}}^u \tag{D.4}
\]

\[
\frac{d}{dt} (\text{spC}) = \frac{1}{Q_{\text{N:C}}} \left( J_{\text{sp,no3}}^u + J_{\text{sp,nh4}}^u \right) \\
- \left( J_{\text{sp}}^l + J_{\text{sp}}^g + J_{\text{sp}}^a \right) \tag{D.5}
\]

\[
\frac{d}{dt} (\text{sp}^{15}\text{N}) = \alpha_{\text{sp,no3}} r_{\text{no3}} J_{\text{sp,no3}}^u + \alpha_{\text{sp,nh4}} r_{\text{nh4}} J_{\text{sp,nh4}}^u \\
- r_{\text{sp}} Q_{\text{N:C}} \left( J_{\text{sp}}^g + J_{\text{sp}}^l + J_{\text{sp}}^a \right) \tag{D.6}
\]
\[
\frac{d}{dt}(\text{diatC}) = \frac{1}{Q_{N:C}} \left( J_{\text{diat,no3}}^u + J_{\text{diat,nh4}}^u \right) - \left( J_{\text{diat}}^g + J_{\text{diat}}^l + J_{\text{diat}}^a \right)
\]  
(D.7)

\[
\frac{d}{dt}(\text{diat}^{15}\text{N}) = \alpha_{\text{diat,no3} r_{\text{no3}}} J_{\text{diat,no3}}^u + \alpha_{\text{diat,nh4} r_{\text{nh4}}} J_{\text{diat,nh4}}^u - r_{\text{diat}} Q_{N:C} \left( J_{\text{diat}}^g + J_{\text{diat}}^l + J_{\text{diat}}^a \right)
\]  
(D.8)

\[
\frac{d}{dt}(\text{diazC}) = \frac{1}{Q_{N:C}} J_{\text{diaz}}^{\text{photoN}} - \left( J_{\text{diaz}}^g + J_{\text{diaz}}^l \right)
\]  
(D.9)

\[
\frac{d}{dt}(\text{diaz}^{15}\text{N}) = J_{\text{diaz}}^{\text{photo15N}} - r_{\text{diaz}} Q_{N:C} \left( J_{\text{diaz}}^g + J_{\text{diaz}}^l \right)
\]  
(D.10)

\[
\frac{d}{dt}(\text{zooC}) = \left( J_{\text{sp,zoo}}^g + J_{\text{diat,zoo}}^g + J_{\text{diaz,zoo}}^g \right) - J_{\text{zoo}}^l
\]  
(D.11)

\[
\frac{d}{dt}(\text{zoo}^{15}\text{N}) = Q_{N:C} \left[ r_{\text{sp}} J_{\text{sp}}^g - \alpha_{\text{zoo} r_{\text{zoo}}} \left( J_{\text{sp}}^g - J_{\text{sp,zooc}}^g \right) \right] + Q_{N:C} \left[ r_{\text{diat}} J_{\text{diat}}^g - \alpha_{\text{zoo} r_{\text{zoo}}} \left( J_{\text{diat}}^g - J_{\text{diat,zooc}}^g \right) \right] + Q_{N:C} \left[ r_{\text{diaz}} J_{\text{diaz}}^g - \alpha_{\text{zoo} r_{\text{zoo}}} \left( J_{\text{diaz}}^g - J_{\text{diaz,zooc}}^g \right) \right] - r_{\text{zoo}} Q_{N:C} \left( J_{\text{zoo,doc}}^l + J_{\text{zoo,doc}}^l + J_{\text{zoo,doc}}^l \right)
\]  
(D.12)

\[
\frac{d}{dt}(\text{DOC}) = \left( J_{\text{sp,doc}}^l + J_{\text{diat,doc}}^l + J_{\text{diaz,doc}}^l + J_{\text{zoo,doc}}^l \right) + \left( J_{\text{sp,doc}}^g + J_{\text{diat,doc}}^g + J_{\text{diaz,doc}}^g \right) - \text{rem}_{\text{dom}} \text{DOC}
\]  
(D.13)
\[ \frac{d}{dt} (\text{DON}) = Q_{\text{N:C}} \left( J_{\text{sp,doc}}^l + J_{\text{diat,doc}}^l + J_{\text{zoo,doc}}^l \right) + Q_{\text{N:C}} \left( J_{\text{sp,doc}}^g + J_{\text{diat,doc}}^g + J_{\text{zoo,doc}}^g \right) + \left( J_{\text{diaz}}^{\text{Nfix}} - J_{\text{diaz}}^{\text{photoN}} \right) - \text{rem}_{\text{dom}} \text{ DON} \]  

(D.14)

\[ \frac{d}{dt} (\text{DON}^{15}) = Q_{\text{N:C}} \left( r_{\text{sp}} J_{\text{sp,doc}}^l + r_{\text{diat}} J_{\text{diat,doc}}^l + r_{\text{zoo}} J_{\text{zoo,doc}}^l + J_{\text{sp,doc}}^{15g} + J_{\text{diat,doc}}^{15g} + J_{\text{zoo,doc}}^{15g} \right) + \alpha_{\text{zoo}} r_{\text{zoo}} Q_{\text{N:C}} \left( J_{\text{g,doc}}^{15g} + J_{\text{g,doc}}^{15g} + J_{\text{g,doc}}^{15g} \right) + \left( J_{\text{diaz}}^{15\text{Nfix}} - J_{\text{diaz}}^{15\text{photoN}} \right) - \text{rem}_{\text{dom}} r_{\text{don}} \text{ DON} \]  

(D.15)

\[
\frac{d}{dt} (\text{O}_2) = \begin{cases} 
\frac{1}{Q_{\text{N:C}} R_{\text{C:O}}^{\text{RD}}} \left( J_{\text{sp,na}}^u + J_{\text{sp,na}}^u + J_{\text{sp,na}}^u + J_{\text{sp,na}}^u \right) + \frac{1}{Q_{\text{N:C}} R_{\text{C:O}}^{\text{RD}}} J_{\text{diaz}}^{\text{photoN}}, & \text{if } O_2 < S_{\text{wcd}} \\
\frac{1}{Q_{\text{N:C}} R_{\text{C:O}}^{\text{RD}}} \left( J_{\text{sp,na}}^u + J_{\text{sp,na}}^u + J_{\text{sp,na}}^u + J_{\text{sp,na}}^u \right) + \frac{1}{Q_{\text{N:C}} R_{\text{C:O}}^{\text{RD}}} J_{\text{diaz}}^{\text{photoN}}, & \text{if } O_2 > S_{\text{wcd}} \\
- \frac{1}{R_{\text{C:O}}} \left( J_{\text{poc}} - R_{\text{C:N}}^{\text{bd}} f^{\text{bd}} \text{ BD} \right) - \frac{1}{R_{\text{C:O}}} \text{rem}_{\text{dom}} \text{ DOC} \\
- \frac{1}{R_{\text{C:O}}} \left( J_{\text{zoo,dic}}^l + J_{\text{sp,dic}}^l + J_{\text{diaz,dic}}^l + J_{\text{diaz,dic}}^l \right) \end{cases}
\]  

(D.16)

D.1.5 Implicit particulate C and N terms

First of all, we set all particulate C terms (production, remineralization, and reactive and inert C fluxes) that are relevant for incorporating the particulate $^{15}$N cycling. The amount of POM
that is produced is:

\[ J_{\text{poc}} = (J_{\text{sp,poc}}^g + J_{\text{diat,poc}}^g + J_{\text{diaz,poc}}^g) + (J_{\text{sp}}^a + J_{\text{diat}}^a) \]

\[ + (J_{\text{sp,poc}}^l + J_{\text{diat,poc}}^l + f_{\text{zoo}}^d J_{\text{zoo}}^l) \]

(D.17)

Remineralization is calculated from conservation of mass as function of depth (z):

\[ J'_{\text{poc}} = J_{\text{poc}}^p(\bar{z}) + \frac{d}{d\bar{z}} \left( J_{\text{poc}}^{\text{soft}}(\bar{z}) + J_{\text{poc}}^{\text{hard}}(\bar{z}) \right) \]

(D.18)

And the particulate \textsuperscript{15}N terms are:

\[ J_{\text{pon15}}^p = \alpha_{\text{zoo}} r_{\text{zoo}} Q_{\text{N:C}} \left( J_{\text{sp,poc}}^g + J_{\text{diat,poc}}^g + J_{\text{diaz,poc}}^g \right) \]

\[ + r_{\text{sp}} Q_{\text{N:C}} \left( J_{\text{sp,poc}}^l + J_{\text{sp}}^a \right) + r_{\text{diat}} Q_{\text{N:C}} \left( J_{\text{diat,poc}}^l + J_{\text{diat}}^a \right) \]

\[ + r_{\text{zoo}} Q_{\text{N:C}} f_{\text{zoo}}^d J_{\text{zoo}}^l \]

(D.19)

\[ J_{\text{pon15}}^p \] is vertically redistributed to all grid-cells at greater depths following \( J'_{\text{poc}} \):

\[ J'_{\text{pon15}} = Q_{\text{N:C}} r_{\text{pon}} J'_{\text{poc}} \]

(D.20)

where the isotopic fraction of large detritus is:

\[ r_{\text{pon}} = \frac{J_{\text{pon15}}^p + J_{\text{pon15}}^{\text{soft}} + J_{\text{pon15}}^{\text{hard}}}{Q_{\text{N:C}} \left( J_{\text{poc}}^p + J_{\text{poc}}^{\text{soft}} + J_{\text{poc}}^{\text{hard}} \right)} \]

(D.21)

with

\[ J_{\text{pon15}}^{\text{soft}} = Q_{\text{N:C}} r_{\text{pon}} J_{\text{poc}}^{\text{soft}} \]

\[ J_{\text{pon15}}^{\text{hard}} = Q_{\text{N:C}} r_{\text{pon}} J_{\text{poc}}^{\text{hard}} \]

(D.22)

D.1.6 Diazotrophs and N-fixation

\[ J_{\text{diaz}}^{15\text{Nfix}} = \alpha_{\text{diaz}} r_{\text{atm}} J_{\text{diaz}}^{\text{Nfix}} \]

(D.23)
Appendix D. Implementing N Isotopes in the BEC Model

\[ J_{\text{diaz}}^{\text{photo15N}} = \alpha_{\text{diaz}} r_{\text{atm}} J_{\text{diaz}}^{\text{photoN}} \]  \hspace{1cm} (D.24)

\[ J_{\text{diaz}}^{15\text{Nexcr}} = J_{\text{diaz}}^{15\text{Nfix}} - J_{\text{diaz}}^{\text{photo15N}} \]  \hspace{1cm} (D.25)

D.1.7 Water column denitrification

\[ \text{WCD} = \begin{cases} \frac{1}{R_{\text{EC:N}}} (J_{\text{poc}}^r + \text{rem}_{\text{dom}} \text{ DOC}) - f^{\text{bd}} \text{ BD}, & \text{if } O_2 < S_{\text{wcd}} \text{ and } \text{NO}_3^- > S_N^{\text{wcd}} \\ 0, & \text{if } O_2 > S_{\text{wcd}} \text{ or } \text{NO}_3^- < S_N^{\text{wcd}} \end{cases} \]  \hspace{1cm} (D.26)

D.1.8 Benthic denitrification

The amount of large detritus C at the sea floor is the sum of the soft and hard flux of POC that leave the grid-cell (bottom cell):

\[ J_{\text{poc}}^b = (J_{\text{poc}}^{\text{hard}} + J_{\text{poc}}^{\text{soft}}) \]  \hspace{1cm} (D.27)

\[ J_{\text{poc}}^b \] has units of [mmol C cm/m³/sec]. This flux is expressed in [µmolC/cm²/day] in the parameterizations of Middelburg et al. [1996] (named \( J_{\text{poc}}^b \)).

All organic matter is remineralized in the bottom cell, either through aerobic remineralization (takes up \( O_2 \)) or through benthic denitrification (takes up \( \text{NO}_3^- \)). The amount of organic matter remineralized through benthic denitrification is computed using both Middelburg et al. [1996]'s metamodels which give the amount of organic C decomposed through denitrification (BD^C in [µmolC/cm²/day]). There are two parameterizations, one is a function of the labile C flux that reaches the sea floor only \( J_{\text{poc}}^b \) (Equ.D.27), in [µmolC/cm²/day]), the other is a function of the C flux that reaches the sea floor, the depth (\( z \) in [m]), and \( \text{NO}_3^- \) and \( O_2 \) (both
in [$\mu$mol/m$^3$]):

$$BD^C = \begin{cases} 
10^{[-0.9543 +0.7662 \log_{10} J_{\text{poc}}^b ' -0.2350 \log_{10} \left( J_{\text{poc}}^b \right)^2]} 
& \text{for all } J_{\text{poc}}^b ' > 0, \ NO_3^- > S_N^{\text{bd}}, \text{ and } O_2 \leq 0 \\
10^{[-2.2567 -0.1850 \log_{10} J_{\text{poc}}^b ' -0.2210 \log_{10} \left( J_{\text{poc}}^b \right)^2 -0.3995 \log_{10} \NO_3^- \cdot \log_{10} \text{O}_2 +1.2500 \log_{10} \NO_3^- +0.4721 \log_{10} \text{O}_2 -0.0996 \log_{10} \text{z}} \\
& +0.4256 \log_{10} J_{\text{poc}}^b ' \cdot \log_{10} \text{O}_2] 
& \text{for all } J_{\text{poc}}^b ' > 0, \ NO_3^- > S_N^{\text{bd}}, \text{ and } O_2 > 0 
\end{cases}$$

(D.28)

It is assumed that the organic matter which is not remineralized through benthic denitrification is aerobically remineralized (see Tab. 4.2). The amount of organic C that undergoes aerobic remineralization in marine sediments is $J_{r\text{poc}} - R_{C:N}^{\text{bd}}BD + rem_{\text{dom}}\text{ DOC}$.

### D.2 Detailed description of the coding of the implementation of N isotopes

Coding of the ratio $r$ has to be done very carefully. Although $r$ ranges between 0.00366 and 0.00374 (Fig. D.2) in the marine environment, the range of modeled $r$ is broader since the BEC can simulate zero or negative N and $^{15}$N (Figs. D.1 and D.2). Sometimes the model simulates negative values for some biological state variables due to the advection scheme (for example diazC and diaz$^{15}$N are negative in the ocean interior). State variables can even
change from negative to positive value through time, due to seasonality for example.

The ratio $r$ is computed at the beginning of each time-step. In the computation of $r$, local copies of N and $^{15}$N are used, which values are set to zero if the state variable N or $^{15}$N is negative. If N > 0 then $r = ^{15}$N/N, while if the local copy of N is zero, $r$ is not defined and thus set to zero (see $r$ in lower table in Fig. D.2). A non-zero condition on N is therefore included. In order to avoid an unrealistic concentration of $^{15}$N greater than that of N, $r$ is forced to one whenever $^{15}$N ≥ N (see Fig. D.1).
D.2. Detailed description of the coding of the implementation of N isotopes

We compute the $\delta^{15}N$ of each seven prognostic N pools in order to compare simulation outputs with $\delta^{15}N$ data. The $\delta^{15}N$ convention for expressing the isotopic composition of a sample with regard to a standard reference is:

$$\delta^{15}N = \left( \frac{R}{R_{atm}} - 1 \right) \cdot 1000\%_{oo}$$ (D.29)

$R$ and $R_{atm}$ are the isotope ratios $^{15}N/^{14}N$ in the sample and in the atmosphere respectively. The N isotopic composition of the atmosphere is commonly taken as a reference ($R_{atm} =$...
0.3663/99.6337), since it represents a large enough N reservoir and since it has not changed during the investigated time-scale. $\delta^{15}\text{N}$ depends on $R$, which is computed offline on the basis of the state variables $N$ and $^{15}\text{N}$. In case $^{14}\text{N} = N - ^{15}\text{N}$ is zero, that is all N is found as $^{15}\text{N}$, not a number (NaN) is assigned to $R$. Outputs are either instantaneous history files ("snapshots") or time-averaged files in which state variables have been averaged throughout the selected time-period.

$\delta^{15}\text{N}$ is computed offline and depends on $R$. If $N$ or $^{15}\text{N}$ is not strictly positive, $\delta^{15}\text{N}$ is set to NaN (Fig. D.1 and D.2). $\delta^{15}\text{N}$ behavior as a function of $r$ presents a singularity at $N = ^{15}\text{N}$, i.e., at $r = 1.0$ (Fig. D.1), and $\delta^{15}\text{N}$ is therefore not computed. Mean ocean $\delta^{15}\text{NO}_3$ is also computed offline on the basis of total NO$_3$ and total $^{15}\text{NO}_3$ budgets.

### D.3 Simulations with the CCSM-BEC model

#### D.3.1 Technical specificities

We use the CCSM version 3.0 (ID on passive tracers: v 1.1.4.7.10.22005/11/17) with the coarse resolution Parallel Ocean Program (POP) model (version POP1.4), in order to keep the model computationally efficient. The grid has a longitudinal resolution of 3.6° and variable latitudinal resolution (116 latitudes), from 2.0° at high latitudes to finer resolution near the equator. The ocean-model is divided in 25 vertical layers with a monotonically increasing level thickness from approximately 12 to 450 m. The upper 100 m include 8 vertical layers.

#### D.3.2 Initial conditions for simulations with N isotopes

Our model simulations are initialized with a millennium-scale equilibrium run without isotopes and without benthic denitrification. We restart from a 2,200 years equilibrium run for pre-industrial conditions from X. Giraud at ETH Zürich. Physics and standard biogeochemistry are from an equilibrium run from I. Lima (personal communication). The $^{15}\text{N}$ pools of small phytoplankton, diatoms, zooplankton are initialized according to their respective C pools and assuming $\delta^{15}\text{N} = 5^{\circ}$/oo and a C:N ratio of 0.137. This in turn implies a C:$^{15}\text{N}$ scale factor of 0.000504330918179. The initial $^{15}\text{N}$ pools of NO$_3$, NH$_4$, and DON are initialized on the basis of their N pools and assuming $\delta^{15}\text{N} = 5^{\circ}$/oo. It follows a N:$^{15}\text{N}$ scale factor of 0.003681247577951. In contrast, initial diazotroph $^{15}\text{N}$ is computed assuming a $\delta^{15}\text{N} = 0^{\circ}$/oo isotopic value. The rationale is that diazotrophs take up N$_2$ with the same isotopic ratio than the atmospheric, i.e., the reference value. With a C:N ratio of bulk diazotroph of 0.137 the scale factor is 0.000501831000000.
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A la mémoire de ma mère.
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Articles published in reviewed journals


Articles in preparation


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<td>2010</td>
<td>Eugster O. and N. Gruber</td>
<td>Determination of the main sources and sinks of marine nitrogen</td>
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