Constraints on global oceanic emissions of N$_2$O from observations and models

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Abstract. We estimate the global oceanic N$_2$O flux to the atmosphere and its confidence interval using a statistical method based on model perturbation simulations and their fit to a database of ΔpN$_2$O (n=6136). We evaluate two submodels of N$_2$O production. The first submodel splits N$_2$O production into oxic and hypoxic pathways following previous publications. The second submodel explicitly represents the redox transformations of N that lead to N$_2$O production (nitrification and hypoxic denitrification) and N$_2$O consumption (suboxic denitrification), and is presented here for the first time. We perturb both submodels by modifying the key parameters of the N$_2$O cycling pathways (nitrification rates, NH$_4^+$ uptake, N$_2$O yields under oxic, hypoxic and suboxic conditions), and determine a set of optimal model parameters by minimisation of a cost function against 4 databases of N cycle observations derived from observed and model ΔpN$_2$O concentrations. Our estimate of the global oceanic N$_2$O flux resulting from this cost function minimisation is 2.4 ± 0.8 Tg N yr$^{-1}$, and is invariant to the choice of N$_2$O submodel. These estimates suggest that the currently available observational data of surface ΔpN$_2$O constrain the global N$_2$O flux to a narrower range relative to the large range of results presented in the latest IPCC report.

1 Introduction

Nitrous oxide (N$_2$O) is the third most important contributor to anthropogenic radiative forcing, after carbon dioxide (CO$_2$) and methane (CH$_4$) (Myhre et al. 2013). It also currently estimated as the dominant contributor to stratospheric ozone depletion (Portmann et al. 2012). Yet our quantitative understanding of the magnitude and processes controlling natural N$_2$O emissions from the Earth surface to the atmosphere is very poor. A range of methods have
been used to constrain total oceanic N₂O emissions, including the combination of surface ocean N₂O partial pressure anomalies with gas-exchange parameterizations (Nevison et al. 1995), empirically derived functional relationships applied to global ocean datasets (Nevison et al. 2003, Freeing et al. 2012), and ocean biogeochemistry models (Suntharalingam and Sarmiento 2000, Suntharalingam et al. 2000, Jin and Gruber 2003, Martinez-Rey et al. 2015).

In spite of the multiple methods used, the reported oceanic emissions of N₂O is still poorly constrained, ranging from 1.9 to 9.4 Tg N y⁻¹ according to the latest report of the Intergovernmental Panel on Climate Change (IPCC; Ciais et al. 2013). The uncertainty in the oceanic emissions of N₂O accounts for a large part of the total uncertainty in the natural N₂O emissions, which are approximately 11 Tg N y⁻¹ (Ciais et al. 2013).

The large uncertainty in the oceanic emissions of N₂O stems from the complexity of its production pathways. There are two main pathways of N₂O production in the ocean, nitrification and denitrification, which both stem from redox reactions of nitrogen, under oxic and hypoxic conditions, respectively (Fig. 1). N₂O is formed as a byproduct of marine nitrification of ammonium (NH₄⁺) to nitrate (NO₃⁻); N₂O is also an intermediate product of denitrification, during the reduction of NO₃⁻ to nitrogen gas (N₂) (Frame and Casciotti 2010, Loescher et al. 2012, Merbt et al. 2012). Denitrification can also consume N₂O, using extracellular N₂O, and reduce it to N₂ (Bange 2008). In the oxic part of the ocean (i.e. most of the ocean, 97% > 34 μmol O₂ L⁻¹ (using O₂ data taken from Bianchi et al. 2012)) denitrification is suppressed, and the primary formation pathway is usually ascribed to nitrification (Cohen and Gordon 1978), although there are additional pathways (Klawonn et al. 2015). Oceanic N₂O production in oxic regions is often derived from the linear relationships observed between apparent oxygen utilization (AOU) and apparent N₂O production (ΔN₂O) (e.g. Yoshinari 1976, Cohen and Gordon 1978). However, the ΔN₂O/AOU slope varies in different water masses and oceanic regions (Suntharalingam and Sarmiento 2000). Previous studies have suggested that differences in the ΔN₂O/AOU slope could be driven by changing N₂O yields under varying pressure and temperature (Butler et al. 1989) or varying O₂ concentration (Nevison et al. 2003). Additional mechanisms not yet quantified could include variations in the elemental stoichiometry of the organic matter that is being remineralised, and spatial separation of organic matter remineralisation and nitrification.

Estimates of the contribution from suboxic regions of the ocean (about 3%) to the global N₂O flux vary from net depletion via denitrification (Cohen and Gordon 1978), to 33% for the total N₂O production in the suboxic ocean (Suntharalingam et al. 2012), and to more than 50% from denitrification alone (Yoshida et al. 1989). This ambiguity remains unresolved, and stems from the variation in the ΔN₂O/AOU slope from negative under suboxic conditions,
maximal under hypoxic conditions and lower under oxic conditions (e.g. 0.31 – 0.033 nmol/µmol, Law and Owens 1990).

Here, we estimate the global ocean N\textsubscript{2}O flux to the atmosphere and its confidence interval. First, we estimate N\textsubscript{2}O flux from observations only (Section 2.1). This estimate has large uncertainty. We subsequently use a statistical approach introduced by Buitenhuis et al. (2013a) to estimate the global oceanic emissions of N\textsubscript{2}O and its confidence interval by combining ocean N\textsubscript{2}O model simulations with a global database of measurements of surface ΔpN\textsubscript{2}O. This approach involves minimisation of a cost function that compares a series of model simulations with a global database of point measurements of surface ΔpN\textsubscript{2}O. To achieve this, we use 4 observational databases of the N cycle (Section 2.2). We extend the global ocean biogeochemistry model PlankTOM10 (Le Quéré et al. 2016) with additional N cycle processes, deriving the biogeochemical parameters from the observational databases (Section 2.3-2.4). Then, we describe two separate submodels of different levels of complexity that represent N\textsubscript{2}O cycling pathways (Section 2.5-2.7). Finally, estimation of the global oceanic N\textsubscript{2}O flux applying the statistical approach to the two submodels is described in Section 3, followed by a discussion of the results (Section 4).

2 Ocean N cycle

2.1 Calculation of global ocean N\textsubscript{2}O production from N cycle observations

In this section we provide an initial estimate of global marine N\textsubscript{2}O production based on observationally derived quantities characterising marine productivity and the global ocean N cycle. This follows a similar method to Cohen and Gordon (1979), who estimated ocean N\textsubscript{2}O production using ‘Redfield’ type ratios. N\textsubscript{2}O is produced either during production of NO\textsubscript{3} in NH\textsubscript{4}\textsuperscript{+}oxidation or during NO\textsubscript{3} reduction in denitrification (Fig. 1). We therefore base the N\textsubscript{2}O production on total NO\textsubscript{3} turnover, calculated from primary production times the f-ratio. Primary production (PP) was estimated at 58 ± 7 Pg C y\textsuperscript{-1} (Buitenhuis et al. 2013a). We compiled a database of uptake rates of NO\textsubscript{3}, NH\textsubscript{4}\textsuperscript{+} and urea, which gives an average f-ratio of 0.29 ± 0.18 (Fig. 2, large symbols, n=34). The globally averaged ΔN\textsubscript{2}O/AOU slope is 81.5 ± 1.4 nmol/mmol (Fig. 3). Finally, since primary production is expressed in carbon terms, and N\textsubscript{2}O production was correlated with oxygen (O\textsubscript{2}) utilization, we need to include the -O\textsubscript{2}-C ratio, which was taken from Anderson & Sarmiento (1994) as 170 ± 10 / 117 ± 14, and the molar weights of C (12) and N in N\textsubscript{2}O (28). Thus N\textsubscript{2}O production was calculated as PP *f-ratio*-O\textsubscript{2}-C *ΔN\textsubscript{2}O/AOU. Our best estimate of N\textsubscript{2}O production using this method is 58 *1000 * 0.29 * 170/117 * 8.15e-5 *28/12 = 4.6 ± 3.1 Tg N y\textsuperscript{-1}. This estimate lies in the middle of other
reported estimates (see Introduction) but the 68% confidence interval is very large. We therefore investigate the N$_2$O fluxes using a model optimized with observations in the rest of the paper.

2.2 Observational databases for model development

We used four databases to tune or optimise different aspects of the N cycle in the PlankTOM10 ocean biogeochemistry model. The number of datapoints reported for each database are after gridding to 1° × 1° × 12 months × 33 depths (World Ocean Atlas 2009). The databases used are (1) NH$_4^+$ specific nitrification rate (n=296) as described in Yool et al. (2007); (2) surface NH$_4^+$ concentration distribution (n=2713) that combines the dataset used in Paulot et al. (2015) with data held by the British Oceanographic Data Centre in January 2014 (Johnson et al. in prep., http://www.bodc.ac.uk); (3) depth-resolved N$_2$O concentration from the MEMENTO project (n=8047; https://memento.geomar.de/; Bange et al. 2009; downloaded 4 June 2014); and (4) surface partial pressure of N$_2$O (pN$_2$O) also from MEMENTO (n=6136; downloaded 16 Sept. 2015). pN$_2$O was converted to ΔpN$_2$O using atmospheric pN$_2$O:

$$p_{N_2O} = 0.000009471353376 \times Y^{33} - 0.05214713935 \times Y^{22} + 95.6806625 \times Y - 58228.4121$$ (1)

(A. Freing, pers. comm., correction to Freing et al. 2009), in which Y is the decimal year.

2.3 Cost Function Formulation

To parameterise the model N cycle, we use a cost function to minimize the difference between model and observations, following the methods of Buitenhuis et al. (2013a):

$$\text{cost function} = 10^\text{average}(|10^\log(model/observation)|)$$ (2)

This formulation gives equal weight to the relative correspondence between model and observations at small and large observational values. A value of 2 means that, on average, the model deviates from the observations by a factor 2 in either direction. The cost function results for the optimised simulations are summarised in Table 1.

2.4 Nitrification

Our initial biogeochemical model configuration is PlankTOM10 (Le Quéré et al. 2016), which represents growth and loss terms from ten Plankton Functional Types (PFTs), including N$_2$-fixers, picoheterotrophs (Bacteria plus Archaea) and denitrification rate, but not denitrifier biomass. A full model description and parameter values were provided in the supplementary material of Le Quéré et al. (2016). Here, we extend the model representation of redox reactions in the N cycle, to create the global biogeochemical model PlankTOM10.2. We describe the new N cycle components below.
In order to represent nitrification rate, the state variable for dissolved inorganic nitrogen was split into NO$_3^-$ and NH$_4^+$. Respiration by all PFTs produces NH$_4^+$. The parameterization for nitrification used in our model is based on the analysis of a database of NH$_4^+$-specific nitrification rates (Yool et al. 2007). Yool et al. (2007) found that observed nitrification rates are highly variable, with no obvious relationship with either latitude or depth. They therefore used a constant rate of 0.2 d$^{-1}$ throughout the ocean in their model. Implementing this rate in our model resulted in a cost function relative to the nitrification rate observations of 4.22 (Table 1). We tested if including temperature, O$_2$ or light dependence improves the ability of the model to reproduce observed nitrification rates.

Regarding the response of ammonia oxidizing Archaea (AOA), the main nitrifiers in the ocean (Francis et al. 2005, Wuchter et al. 2006, Loescher et al. 2012), to temperature, we are only aware of the measurements of Qin et al. (2014). These show a ~4-fold variation in maximum growth rate between 3 strains, which poorly constrains the temperature dependence of AOA. We therefore first used a generic Q$_{10}$ of 2 and optimised the rate at 0°C using the nitrification rate observations. This led to a slightly improved representation of the observations (cost function = 4.18). Although the response of AOA and ammonia oxidizing Bacteria (AOB) to O$_2$ has only been measured at 21-25 °C (Frame et al. 2010, Loescher et al. 2012), which limits the range of O$_2$ concentrations, there was a significant logarithmic relationship between N$_2$O yield and O$_2$ (Fig. 4). Implementing this response to O$_2$ led to a further small improvement of the model nitrification rate relative to the observations (cost=4.16). The response of AOA to light is estimated to be 50% inhibited at 5 µmol photons m$^{-2}$ s$^{-1}$. However, this estimate is not well constrained (Merbt et al. 2012). Implementing this light response did not improve the model, either in combination with the O$_2$ and temperature responses or with the temperature response only, and was subsequently omitted. The lack of improvement in nitrification rates by adding light inhibition might reflect the lower sensitivity of AOA to light found by Qin et al. (2014).

2.5 Phytoplankton $K_{15}$ for NH$_4^+$ uptake

We used the calculation of the preferential uptake of NH$_4^+$ over NO$_3^-$ by phytoplankton PFTs of Vallina and Le Quéré (2008). The $K_{15}$ of phytoplankton for NH$_4^+$ has mostly been measured based on uptake rates (syntheses by Goldman and Glibert 1983, and Killberg-Thoreson et al. 2014). Aksnes and Egge (1991) have shown a theoretical expectation of a linear increase of $K_{15}$ with cell radius. The observations are so variable that they neither confirm nor contradict such an increase. Because the model does not include a variable N quota, we need a $K_{15}$ for growth rather than for uptake. The available uptake rate data do not include the supporting data to allow conversion to the $K_{15}$ for growth.
growth. We are only aware of measurements of the $K_{\text{half}}$ for growth by Stawiarski (2014). Based on the latter values of $0.09 \pm 0.15 \mu\text{mol/L}$ for picocyanobacteria, the $K_{\text{half}}$ of phytoplankton for $\text{NH}_4^+$ was set to 0.1 to 5 $\mu\text{M}$, increasing linearly with nominal size (Buitenhuis et al. 2013b). The resulting model simulation of surface $\text{NH}_4^+$ concentration increases with latitude, consistent with the observations (Fig. 5). However, due to the highly dynamic nature of $\text{NH}_4^+$ turnover, the ability of the model to reproduce the observed $\text{NH}_4^+$ concentrations at the same times and places was relatively low (cost function=3.3).

2.6 $\text{N}_2\text{O}$ production

$\text{N}_2\text{O}$ production is implemented as two distinct submodels that follow a diagnostic and a prognostic approach, respectively. The diagnostic submodel is based on observed $\Delta\text{N}_2\text{O}/\text{AOU}$ slopes and has previously been published (Suntharalingam et al. 2000, 2012). In oxic waters it uses one slope to estimate the open ocean source of $\text{N}_2\text{O}$ production. In hypoxic waters it uses a higher slope to represent the increased yield of $\text{N}_2\text{O}$ from both nitrification and denitrification in oxygen minimum zones. The hypoxic $\text{N}_2\text{O}$ yield is maximal at 1 $\mu\text{mol O}_2\text{L}^{-1}$, and decreases with an e-folding concentration of 10 $\mu\text{mol O}_2\text{L}^{-1}$ (Suntharalingam et al. 2000, 2012).

The prognostic submodel presented here is mechanistic in nature and explicitly represents the primary $\text{N}_2\text{O}$ formation and consumption pathways associated with the marine nitrogen cycle (Fig. 1). It includes the production of $\text{N}_2\text{O}$ during oxic nitrification (blue arrows in Fig. 1) and during hypoxic denitrification (red arrow in Fig. 1); and a consumption term during denitrification at even lower (suboxic) $\text{O}_2$ concentrations (yellow arrow in Fig. 1). The slopes of the three processes are globally invariant. The slopes of both submodels were optimized using the databases of observed $\text{N}_2\text{O}$ concentration and $\Delta\text{pN}_2\text{O}$ (see Sections 3.1 and 3.2).

2.7 $\text{N}_2\text{O}$ flux and simulation setup

$\text{N}_2\text{O}$ is transported like other tracers. The solubility of $\text{N}_2\text{O}$ is calculated using the formulation from Weiss and Price (1980). $\text{N}_2\text{O}$ flux (=air-sea gas exchange) is calculated with the piston velocity from Sweeney et al. (2007), which is optimised for use with the NCEP reanalysis data used here. The Schmidt number for $\text{N}_2\text{O}$ was taken from Wanninkhof et al. (1992).

The PlankTOM10.2 biogeochemical model coupled with the two $\text{N}_2\text{O}$ submodels is incorporated into the ocean general circulation model NEMO v3.1 (Madec 2008). The model resolution is 2° in longitude, on average 1.1° in latitude and has 30 vertical layers, from 10 m in the top 100 m to 5000 m. The model simulations were initialised in 1965 from observations (Le Quéré et al. 2016), with $\text{NH}_4^+$ initialised as 0, and $\text{N}_2\text{O}$ initialised from a
horizontal interpolation of the MEMENTO observations (see Section 2.2). Simulations were run to 2014, forced with daily atmospheric conditions from the NCEP reanalysis (Kalnay et al. 1996), (for details see Buitenhuis et al. 2013a). Results are reported averaged over the last 5 years.

2.8 Estimation of global \( \text{N}_2\text{O} \) flux from point measurements of \( \Delta p\text{N}_2\text{O} \)

To estimate the global air-sea flux of \( \text{N}_2\text{O} \) that best fits the \( \Delta p\text{N}_2\text{O} \) data, and its ±1-sigma (68%) confidence interval, we use the formula described in Buitenhuis et al. (2013a):

\[
\frac{\text{RSS}}{\text{RSS}_{\text{min}}} = 0.468 \times \frac{n}{(n-2)} \times \sqrt{\frac{2}{(2n-2)/(n(n-4)) + \frac{n}{(n-2)}}}
\]

in which \( \text{RSS} \) is the residual sum of squares between each model simulation and the observations, \( \text{RSS}_{\text{min}} \) is the RSS of the model simulation that is closest to the observations, and \( n \) is the number of observations.

To estimate the influence that inequality of model means and the observational mean have on the validity of using equation 3, we use equation 2.1 from Donaldson (1968), with the observational database taken as the “parent” or “true” distribution:

\[
\varphi = \sqrt{n^2 \times (\text{observations} - \text{model})^2 / \text{RSS}}
\]

3 Results

3.1 \( \text{N}_2\text{O} \) production at low \( \text{O}_2 \)

The global \( \text{N}_2\text{O} \) production rate in oxygen minimum zones (OMZs) was optimized using the depth-resolved \( \text{N}_2\text{O} \) data of the MEMENTO database. As noted in previous model studies of ocean \( \text{O}_2 \), global models do not well represent the extent and intensity of OMZ regions (Bopp et al. 2013, Cocco et al. 2013, Andrews et al. 2016). The modeled OMZs in PlankTOM10 occur at greater depths than observed, resulting in unrealistic vertical distributions of \( \text{N}_2\text{O} \) (results not shown). Therefore, following Suntharalingam et al. (2012), the model was run using fixed observed \( \text{O}_2 \) concentrations (Bianchi et al. 2012), which corrected, in part, the vertical distribution of \( \text{N}_2\text{O} \) production from the two submodels, though it still occurred at too great depths (Fig. 6). In the equatorial regions and in the Pacific ocean the \( \text{N}_2\text{O} \) concentrations are underestimated between ~200 and ~1500 m. depth, and overestimated below that. This shortcoming is not significantly improved in the prognostic model (Fig. 6), even though the prognostic model represents the process of \( \text{N}_2\text{O} \) consumption at low \( \text{O}_2 \) concentrations. The depth of maximum \( \text{N}_2\text{O} \) in the model is generally deeper than observed, suggesting that organic matter remineralisation may be too low at shallow depths. This is confirmed by the depth profile of \( \text{NO}_3^- \), which is underestimated relative to the WOA2009
observations between 100 and 1500 m., and overestimated at greater depths (Fig. 7). In both submodels, the N₂O concentrations in the deep sea are also too high, but since only 5% of N₂O production occurs below 1600 m this does not have a big impact on the global N₂O fluxes. The addition of N₂O consumption in the prognostic N₂O model does result in improvement of the N₂O depth profiles in the Indian Ocean.

In order to find the optimal N₂O production that minimizes the RSS (Eq. 3), we ran a range of simulations in which the low O₂ N₂O production was varied in the diagnostic model (Fig. 8A), and a range of simulations in which both the hypoxic N₂O production and the suboxic N₂O consumption were varied in the prognostic model (Fig. 8B).

The optimum solution for the prognostic model was found at a gross production of 0.33 Tg N y⁻¹. In the diagnostic model, the derived N₂O production in low O₂ regions and its confidence interval were 0.16 ± 0.13 Tg N y⁻¹ for the diagnostic model, and 0.12 ± 0.07 Tg N y⁻¹ for the diagnostic model. In the optimized diagnostic model the hypoxic N₂O slope is 0.0017 mol N₂O/mol O₂. In the optimized prognostic model the maximum N₂O consumption slope is 0.015 mol N₂O (mol NO₃)⁻¹, decreasing to 0 above 28 µmol O₂ L⁻¹. The maximum N₂O production slope is 0.0154 mol N₂O (mol NO₃)⁻¹ decreasing to 0 above 34 µmol O₂ L⁻¹. This leads to net production that is always positive and has a maximal slope of 183 µmol N₂O (mol NO₃)⁻¹ at 10 µmol O₂ L⁻¹.

3.2 N₂O flux

We used the surface ΔpN₂O distribution to constrain the total global N₂O flux. ΔpN₂O provided a better constraint than the N₂O concentration distribution, since more N₂O production mostly leads to more N₂O outgassing to the atmosphere rather than a significant increase in shallow N₂O concentrations (data not shown). The zonal average surface ΔpN₂O distribution was well simulated by both submodels (Fig. 9D), and the model ensemble covered a wide range of global N₂O fluxes (Fig. 10). The total N₂O flux that best reproduced the ΔpN₂O distribution was 2.40 ± 0.29 Tg N y⁻¹ for the diagnostic sub-model and 2.44 ± 0.29 Tg N y⁻¹ for the prognostic sub-model (Fig. 10). In the diagnostic model, the optimized oxic ΔN₂O/AOU slope was 12.7 µmol N₂O (mol O₂)⁻¹. In the prognostic model, the optimized nitrification slope was 145 µmol N₂O (mol NH₄⁺)⁻¹.

In addition to the uncertainty that arises from the model-observations mismatch, uncertainty is contributed by the uncertainties in the N₂O solubility and the piston velocity, the two quantities that connect the measured ΔpN₂O to the estimated air-sea flux. The uncertainty in the solubility has been estimated as 3% (Cohen and Gordon 1978). The uncertainty in the piston velocity has been estimated at 32% (Sweeney et al. 2007). Uncertainties in the solubility and piston velocity are proportional to uncertainty in the optimized N₂O air-sea exchange because the
optimized N$_2$O production needs to change proportionally with solubility and piston velocity to achieve the same ΔpN$_2$O. Through error propagation, this gives a total uncertainty of 2.4 ± 0.8 Tg N yr$^{-1}$ for both sub-models.

**4 Discussion**

Cohen and Gordon (1979) estimated global N$_2$O production directly from N-cycle observations. However, they did not have information on the f-ratio, so their estimate was based on total N assimilation in primary production. Suntharalingam et al. (2012) note that N$_2$O production is proportional to export production. However, this is dependent on the model formulation, which was based on earlier studies that suggested nitrification in the ocean surface layer was light-inhibited (e.g., Horrigan, 1981). More recent analyses of nitrification, e.g., the database of Yool et al. (2007) find widespread nitrification in the upper mixed layer. In light of this, we decided to recalculate the N cycle based N$_2$O production based on currently available data. We find that we can estimate all the relevant steps in the N cycle with observational data, including their uncertainty (Section 2.1). At present this uncertainty is still fairly large, at 4.6 ± 3.1 Tg N yr$^{-1}$. The biggest contributor to this uncertainty is the f-ratio, especially in the tropics, which constitute 44% of the ocean surface area. The f-ratio data is only based on uptake of NO$_3^-$, NH$_4^+$ and urea, whereas phytoplankton can also take up NO$_2^-$ and organic N (other than urea). One of the major sources of uncertainty in using the ΔN$_2$O/AOU ratio is that it is conceptually based on the N$_2$O production during nitrification, which uses O$_2$. N$_2$O production during denitrification is spatially separated from the associated O$_2$ use that is needed to nitrify the NO$_3^-$, the electron donor in denitrification. This NO$_3^-$ is produced by nitrification, so in terms of mass balance our calculation is still valid, but this N$_2$O production would show up as a vertical increase in N$_2$O without associated increase in AOU at low O$_2$ concentrations (high AOU) in Figure 3. This estimate of global marine N$_2$O production derived from analyzing the N cycle currently has a much larger error than the N$_2$O flux derived from ΔpN$_2$O observations, but further observational constraints could further our understanding of the whole N cycle, including the option of evaluating their model representation against observations, and not just the part that N$_2$O plays in them. Such further constraints are also likely to provide the most productive way to reduce unexplained variability that is found in the observations but not in the present models.

Models of the global marine C cycle have been in use for decades, and a lot of the available information has been synthesized, cross-correlated and interpreted in detail. While actual measurements of N utilisation and transformation have also been made in abundance, the synthesis and global modelling of these data is less advanced.
In addition, N occurs in many different oxidation states in the marine environment (e.g. organic matter and NH$_4^+$ as -3, N$_2$ as 0, N$_2$O as 0 and +2, NO$_2^-$ as +3, and NO$_3^-$ as +5). Therefore, redox reactions complicate the representation of the N cycle a good deal. This lack of data synthesis and of identification of the most important controls in a complex system is reflected in a relatively low ability of the model to model observed nitrification rates and NH$_4^+$ concentrations (Table 1).

This lack of knowledge also means that partitioning the global marine N$_2$O production over the nitrification and denitrification pathways is poorly constrained. Both the diagnostic and the prognostic models assign a small percentage of the total N$_2$O production to the denitrification pathway, 6 and 4% respectively. However, because of the large bias between the observed and modeled N$_2$O concentration depth profiles (Fig. 6) these may be underestimates. Possibly because of the model bias (Fig. 6, 7), the addition of N$_2$O consumption in the prognostic submodel does not lead to a significantly better distribution of N$_2$O across depth or between different basins (Fig. 7).

As a result, the ΔpN$_2$O distributions are also quite similar (Fig. 9, 12) and the optimized N$_2$O flux and confidence intervals of the two submodels are also quite similar (Fig. 10). It should also be noted, however, that the optimization using surface ΔpN$_2$O agrees with the optimization using N$_2$O concentration that the contribution of the low O$_2$ N$_2$O production needs to be low (Fig. 10), and the error contribution from the model vs. observed ΔpN$_2$O comparison is also low with confidence intervals of 0.29 Tg N y$^{-1}$ for both submodels, confirming the visual impression that ΔpN$_2$O is equally well modelled above the low O$_2$ regions as in the rest of the ocean (Fig. 9, 12). Two complementary approaches could provide better constraints: a better representation of the vertical distribution of export and remineralisation would allow the optimization against N$_2$O concentration observations to achieve better results. But conversely, with better constraints on the physiology of nitrifiers and denitrifiers the N$_2$O concentration database could provide constraints on the representation of remineralisation.

Despite these shortcomings, the global marine N$_2$O flux is well constrained to 2.4 ± 0.8 Tg N y$^{-1}$ by both submodels (Fig. 10). This reflects the fact that the integrated effect of the different physical and biogeochemical processes determines the surface ΔpN$_2$O distribution (Fig. 9). The N$_2$O flux is at the lower end of previous estimates, and with a similar confidence interval to other recent estimates (Fig. 11). The confidence interval is dominated by uncertainty in the piston velocity (32%) rather than model-observation mismatches (12%).

Modeled ΔpN$_2$O values from the optimized simulations of the diagnostic and prognostic submodels have a small negative bias relative to the observations of -2.4 ppb for the diagnostic submodel and -2.7 ppb for the
prognostic submodel (Fig. 12). This gives a degree of inequality (φ, Eq. 4) between the means of the observations and the diagnostic submodel of 0.41 and the prognostic submodel of 0.46. This is well within the range where even much smaller sample sizes lead to negligible Type I errors and conservative Type II errors (Donaldson 1968).

We also tested how much influence sampling biases of very high supersaturation values might have on the estimated air-sea exchange. If the 40 ΔpN₂O measurements in the gridded database that are higher than 100 ppb (Fig. 12) are doubled, the optimized N₂O air-sea exchange becomes 2.9 ± 1.0 Tg N y⁻¹ for the diagnostic model and 3.0 ± 1.1 Tg N y⁻¹ for the prognostic model. If the 27 ΔpN₂O measurements in the gridded database that are higher than 140 pm are excluded, to decrease the frequency of the highly oversaturated observations down to what the diagnostic model simulates (Fig. 12), the optimized N₂O flux becomes 2.2 ± 0.7 Tg N y⁻¹ for both submodels. These results still fall within the confidence intervals of the results using the complete database.

Possible biases in ocean physical transport could in theory affect N₂O production in low O₂ regions. However the model results do not suggest strong biases in N₂O production as a result. On the one hand, if the model had too much ventilation in the OMZs, shallow N₂O concentrations would be underestimated, as they are in the model (Fig. 6), but this would also lead to ΔpN₂O overestimation in the surface areas above the OMZs, which is not the case; the high ΔpN₂O are generally lower but spread over a larger area than in the observations (Fig. 9), with a good frequency distribution of high ΔpN₂O (Fig. 12). On the other hand, if the model had too little ventilation in the OMZs, the optimization would reduce N₂O production in the OMZs in compensation, but the optimization to ΔpN₂O would then estimate a higher OMZ N₂O production than the optimization to the N₂O depth profiles to compensate for the low transport, and this is also not the case. Therefore we conclude that potential biases in ocean physical transport do not appear to have large direct impact on low N₂O production. The indirect impact of ocean physics on low N₂O production through its impact on the distribution of O₂, which Zamora and Oschlies (2014) have shown to be substantial, is not quantified here because we used observed O₂ (Bianchi et al. 2012) instead of modeled O₂.

Global oceanic N₂O emissions estimated using atmospheric inversion methods based on atmospheric N₂O concentrations tend to be higher than our results (Fig. 11). However, N₂O emissions from inversions are low in the Southern Ocean (Hirsch et al. 2006, Huang et al. 2008, Thompson et al. 2014, Saikawa et al. 2014), consistent with our results. South of 30°S, 88% of the Earth surface is ocean, resulting in a clear attribution of the atmospheric N₂O anomalies to ocean fluxes. We suggest that the higher emissions estimates from inversions could be due to a combination of overestimated priors of ocean fluxes in combination with insufficient observational constraints at
latitudes North of 30°S to allow correct partitioning between land and ocean fluxes. Results presented here are for the open and coastal ocean and do not include estuaries; fluxes from these could be as large as 2.3 – 3.6 Tg N y⁻¹ according to one estimate (Bange et al. 1996), and could be another contributing factor to the difference between our results and those of atmospheric inversions.

Acknowledgements

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References


Table, Figures and captions

Table 1: Cost function (Equation 2) for the optimisation simulations of sections 2.2-2.4, relative to the respective observational databases. The nitrification rate in bold was used in this study.

<table>
<thead>
<tr>
<th>Database</th>
<th>Model change</th>
<th>Cost function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrification rate</td>
<td>0.2 d(^{-1})</td>
<td>4.22</td>
</tr>
<tr>
<td></td>
<td>0.1 d(^{-1}) (\times) 2(^{(T/10)})</td>
<td>4.18</td>
</tr>
<tr>
<td></td>
<td>0.79 d(^{-1}) (\times) 2(^{(T/10)})(1-0.159*ln(O(_2)))</td>
<td>4.16</td>
</tr>
<tr>
<td></td>
<td>0.58 d(^{-1}) (\times) 2(^{(T/10)})(e^{(-0.14*I)})</td>
<td>7.15</td>
</tr>
<tr>
<td></td>
<td>4.7 d(^{-1}) (\times) 2(^{(T/10)})(1-0.159<em>ln(O(_2))) (e^{(-0.14</em>I)})</td>
<td>6.87</td>
</tr>
<tr>
<td>Surface NH(_4)+ concentration</td>
<td>K(_{0.5}) estimated from observations</td>
<td>3.3</td>
</tr>
</tbody>
</table>
Figure 1: Primary biological pathways of the oceanic nitrogen cycle represented in the model simulations, along with redox states of N. Nitrification occurs in the oxic ocean (blue arrow). Denitrification yields net N$_2$O production in hypoxic conditions (red arrow) and net N$_2$O consumption in suboxic conditions (yellow arrow). Only organic nitrogen (N$_{org}$), NH$_4^+$, NO$_3^-$ and N$_2$O are represented as model state variables.
Figure 2: f-ratio \( (\rho_{\text{NO}_3^-}/(\rho_{\text{NO}_3^-}+\rho_{\text{NH}_4^+}+\rho_{\text{urea}})) \) as a function of latitude, from \(^{15}\)N uptake experiments. Small dots were estimated without measuring \( \text{NH}_4^+ \) or urea concentrations (Prakesh et al. 2008, 2015; Gandhi et al. 2010, 2012). Large dots did not give a significant linear relationship with absolute value of latitude, and were therefore averaged at \( 0.29 \pm 0.18 \) (Wafar et al. 2004, Varela et al. 2005, 2013 Joubert et al. 2011, Thomalla et al. 2011, Simpson et al. 2013).

Figure 3: Apparent \( \text{N}_2\text{O} \) production (\( \Delta\text{N}_2\text{O} \) nmol L\(^{-1}\)) as a function of apparent oxygen utilization (AOU \( \mu\text{mol L}^{-1}\)). Calculated from the MEMENTO database (Bange et al. 2009).
Figure 4: \( \text{N}_2\text{O} \) yield of nitrification (N atom:atom) as a function of \( \text{O}_2 \) concentration, filled triangles: AOA (Loescher et al. 2012), open circles: AOB at low to medium cell numbers (Frame et al. 2010, Loescher et al. 2012), crosses: marine AOB at high cell numbers (Goreau 1980, Frame et al. 2010), plusses: soil AOB at high cell numbers (Lipschultz 1981). Black line: logarithmic fit to AOA and low to medium cell number AOB (yield = 79.1-12.6·ln(\( \text{O}_2 \)) nmol N in \( \text{N}_2\text{O} \) (mol \( \text{NH}_4^+ \))⁻¹).

Figure 5: Surface \( \text{NH}_4^+ \) concentration (µmol L⁻¹). A) observations. B) model results are for the same months where there are observations, and annual averages everywhere else. C) zonal average, black) observations, red) model results. Model results are for the same months and longitudes as the observations.
Figure 6: Depth profiles of N₂O concentration (nmol L⁻¹) for different basins. Black lines: observations, Green lines: optimised diagnostic model, Red lines: optimised prognostic model.

Figure 7: Depth (m) profile of average NO₃⁻ concentration (µmol L⁻¹). Black line) WOA2009 synthesis of observations, not interpolated. Red line) Model results sampled at the places where there are observations.
Figure 8: RSS$^{0.5}$ for the two N$_2$O submodels compared to the N$_2$O concentration database as a function N$_2$O production in the low O$_2$ regions. A) diagnostic submodel, B) net production in the prognostic submodel at different gross production rates, “no c” is with no N$_2$O consumption i.e. net production = gross production.

Figure 9: Surface ΔpN$_2$O [ppb]. A) observations, B) optimised diagnostic model, C) optimised prognostic model. Model results are for the same months where there are observations, and annual averages everywhere else. D) zonal average, Black line: observations, Green dashed: diagnostic model, Red dotted: prognostic model. Model results are for the same months and longitudes as the observations.
Figure 10: RSS^{0.5} for the two N_{2}O submodels compared to the ΔpN_{2}O database as a function of global N_{2}O flux at different N_{2}O production rates in the low O_{2} regions. A) diagnostic submodel, B) prognostic submodel.

Figure 11: Published estimates of global ocean N_{2}O production or air-sea exchange. Estimates based on global observational datasets shown as boxes when ranges are given and whiskers if error estimates are given (ocean observations: Nevison et al. 1995, Nevison et al. 2003, Freing et al. 2012 (plotted in 2011), Bianchi et al. 2012, this study; atmospheric inversions: Hirsch et al. 2006, Huang et al. 2008, Thompson et al. 2014 (plotted in 2013), Saikawa et al. 2014), model estimates shown as crosses (Suntharalingam and Sarmiento 2000, Jin and Gruber 2003, Suntharalingam et al. 2012, Martinez-Rey et al. 2015).
Figure 12: Frequency distribution of $\Delta pN_2O$ in the observations (solid black), and the optimised simulations of the diagnostic submodel (green squares) and the prognostic submodel (red lines).