Surface nitrification: A major uncertainty in marine N$_2$O emissions

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Abstract
The ocean is responsible for up to a third of total global nitrous oxide (N$_2$O) emissions, but uncertainties in emission rates of this potent greenhouse gas are high (>100%). Here we use a marine biogeochemical model to assess six major uncertainties in estimates of N$_2$O production, thereby providing guidance in how future studies may most effectively reduce uncertainties in current and future marine N$_2$O emissions. Potential surface N$_2$O production from nitrification causes the largest uncertainty in N$_2$O emissions (estimated up to ~1.6 Tg N yr$^{-1}$ or 48% of modeled values), followed by the unknown oxygen concentration at which N$_2$O production switches to N$_2$O consumption (0.8 Tg N yr$^{-1}$ or 24% of modeled values). Other uncertainties are minor, cumulatively changing regional emissions by <15%. If production of N$_2$O by surface nitrification could be ruled out in future studies, uncertainties in marine N$_2$O emissions would be halved.

1. Introduction
Oceanic nitrous oxide (N$_2$O) emissions contribute 10–30% of tropospheric N$_2$O concentrations, but uncertainties in these emissions are >100% [Ciais et al., 2013]. The largest oceanic N$_2$O emissions are observed in high-productivity low-oxygen (O$_2$) regions such as the Eastern Tropical Pacific (ETP) [Nevison et al., 1995]. The microbial processes that mediate subsurface marine N$_2$O production and consumption (nitrification and denitrification) are primarily constrained by biological activity and O$_2$ concentrations. The highest N$_2$O production and consumption rates occur at low O$_2$ levels (~1–15 μM) that are difficult to measure and even more difficult to model, making it difficult to give reliable predictions of how future-predicted deoxygenation in regions like the ETP will affect regional N$_2$O emissions [Zamora et al., 2012].

Further uncertainty unaccounted for in the above estimates arises from recent work suggesting that N$_2$O may also be produced in surface waters. Surface N$_2$O production from bacteria was previously ruled out due to excessive light [Ward, 2008] and oxygen, a denitrification inhibitor [Averill and Tiedje, 1982]. However, active archaeal ammonia oxidation has recently been observed in the ETP euphotic zone [Church et al., 2010; Beman et al., 2012] and other regions [e.g., Ward, 2005; Grundle et al., 2013]. As Archaea can produce N$_2$O during ammonia oxidation [Santoro et al., 2011; Lösch et al., 2012], it has been suggested that N$_2$O may also be produced in the upper euphotic zone [Charpentier et al., 2010].

There is N$_2$O production in the lower photic zone (~100–150 m) of the North Pacific [Dore and Karl, 1996; Dore et al., 1998; Popp et al., 2002], but currently, there is no direct evidence of N$_2$O production in the upper 100 m (the region most important for air-sea gas exchange). However, upper 100 m N$_2$O production could explain discrepancies between low subsurface diapycnal N$_2$O flux and high air-sea N$_2$O flux in the South Pacific, Caribbean, and eastern tropical Atlantic [Morell et al., 2001; Charpentier et al., 2010; Kock et al., 2012]. It might also contribute to why models cannot reproduce the anomalously early seasonal peak in ventilated Southern Ocean N$_2$O [Nevison et al., 2012].

To date, there has been complete systematic testing of the various uncertainties in marine N$_2$O emissions (including N$_2$O production and consumption rates, their dependence on oxygen concentrations, and the potential for N$_2$O production by surface nitrification). Here we examine the sensitivity of N$_2$O emissions to uncertainties in six marine N$_2$O parameterizations, with a focus on the ETP. Our goals are to quantitatively estimate current uncertainties in marine N$_2$O emissions and to provide guidelines for where future research should focus in order to reduce uncertainties and improve projections of future N$_2$O emissions.
Table 1. Overview of Parameters and Values Tested

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Parameter</th>
<th>Values Tested</th>
<th>Baseline Scenario</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>Atmospheric inorganic nitrogen deposition</td>
<td>not present or present</td>
<td>not applicable</td>
<td>na</td>
</tr>
<tr>
<td>CR</td>
<td>N$_2$O consumption rate at low O$_2$</td>
<td>0.01, 0.1, and 1</td>
<td>0.1</td>
<td>mmol N$_2$O m$^{-3}$ yr$^{-1}$</td>
</tr>
<tr>
<td>SSP</td>
<td>Net subsurface N$_2$O production as a function of O$_2$</td>
<td>linear and nonlinear</td>
<td>linear</td>
<td>not applicable</td>
</tr>
<tr>
<td>SP</td>
<td>Net surface N$_2$O production from nitrification</td>
<td>0.01, 1, 10, and 50</td>
<td>0</td>
<td>% produced surface NH$_4^+$ nitrified</td>
</tr>
<tr>
<td>SOV</td>
<td>Suboxic volume for the ETP</td>
<td>6.9 and 4.4</td>
<td>6.9</td>
<td>$10^{15}$ m$^3$</td>
</tr>
<tr>
<td>SW</td>
<td>O$_2$ concentration at which net N$_2$O production changes to net N$_2$O consumption</td>
<td>1, 4, 10, and 15</td>
<td>4</td>
<td>μM O$_2$</td>
</tr>
</tbody>
</table>

$a$ Zamora et al. [2012].
$b$ Suntharalingam et al. [2000], equation (3).
$c$ Same as in label d, not including deposition as the region in Figure 1.
$d$ Suntharalingam and Sarmiento (2000), Suntharalingam et al. (2012), Jin and Gruber [2003], Nevison et al. [2003], Schmittner et al. [2008], Outreuil et al. [2009], Bianchi et al. [2012], Manizza et al. [2012], Zamora et al. [2012], Gurknecht et al. [2013], and Saikawa et al. [2014].
$e$ Suboxic is defined as ≤10 μM O$_2$. ETP is defined as the region in Figure 1.
$g$ Getzlaff and Dietze [2012].
$h$ Deposition was added here similarly to Suntharalingam et al. [2012] but using inorganic nitrogen deposition from the CAM version 3.5 [Lamarque et al., 2011].

2. Methods

N$_2$O data were obtained from the MEMENTO database following Zamora et al. [2012]. Gridded oxygen values were obtained from the corrected World Ocean Atlas 2005 [Bianchi et al., 2012]. N$_2$O fluxes from the ocean to the atmosphere were calculated following Nevison et al. [1995] and using the Comprehensive Ocean-Atmosphere Data Set monthly long-term mean surface wind speeds [da Silva et al., 1994], corresponding to the location and month of each MEMENTO surface N$_2$O sample. Salinity and temperature used in determining solubility were generally measured alongside N$_2$O and are recorded in the MEMENTO database [see Zamora et al., 2012]; however, for some stations, salinity was not recorded. In these instances, the nearest salinity values from the World Ocean Atlas 2009 [Antonov et al., 2010] were used (errors resulting from this approximation are expected to be negligible). Historic atmospheric N$_2$O concentrations at the year of sampling were calculated from Meinshausen et al. [2011].

Model sensitivity analyses were conducted with the University of Victoria (UVic) Earth System Climate Model [Eby et al., 2009] version 2.9 with modifications from Keller et al. [2012]. The model was spun up following Zamora et al. [2012], running historic atmospheric N$_2$O and CO$_2$ concentrations from Meinshausen et al. [2011] up to the year 2008. We used the UVic model to assess the sensitivity of N$_2$O emissions to six parameters (described in Table 1). Several of these parameters were heavily dependent upon O$_2$ concentrations, and therefore, we provide a description of model performance for O$_2$ and N$_2$O in the Supplement. Atmospheric inorganic nitrogen deposition estimates from 1850 to 2000 were applied from the National Center for Atmospheric Research-Community Atmosphere Model (CAM) version 3.5 [Lamarque et al., 2011] (values for individual years were interpolated from the decadal data provided). Values from 2001 to 2008 were provided from their Representative Concentration Pathway (RCP) 8.5 scenario.

When available, we tested the range of published literature values for each parameter (Table 1). Our assessment of the potential importance of surface nitrification for N$_2$O production was hindered by two major uncertainties: (1) surface nitrification rates and (2) N$_2$O production rates from surface nitrification. Surface nitrification rates vary widely [Clark et al., 2008], and nitrifiers can assimilate up to 33% of surface-regenerated NH$_4^+$ [Yool et al., 2007]. Reasons for variability in surface nitrification rates are not well known, and so we assumed that a constant fraction of regenerated N would be nitrified in each sensitivity experiment (between 0 and 50%; see Table 1 and the Supplement). This wide range in surface nitrification rate scenarios was chosen in order to bracket the observed rates [Yool et al., 2007]. Although several studies have linked surface ammonium oxidation rates with light levels [Grundle et al., 2013; Ward, 2005], we did not include light as a determinant of surface nitrification, because so far, evidence does not support light being the dominant factor controlling surface nitrification [Ward, 2005], and the causal relationship between the two is still uncertain.

To describe N$_2$O production rates in the surface, we made a second major assumption: that there are similar relationships between nitrification-derived N$_2$O production and O$_2$ consumption in the surface and subsurface (we used the subsurface relationship described by Zamora et al. [2012]; see the Supplement). Given that the
surface N₂O production rates from nitrification have not yet been quantified in field studies, this assumption represents our best guess of actual rates. However, due to the large uncertainties in surface nitrification and its relationship to N₂O, this study cannot quantitatively describe the impact of surface nitrification on marine N₂O emissions. Instead, we seek to merely assess the potential importance of this process.

To compare the sensitivity analyses, one combination of parameters, labeled as the “baseline scenario,” was chosen to represent our best guess for N₂O model parameterizations (described in Table 1, with reasoning and documentation for the selection of baseline scenario parameters provided in the Supplement). From the baseline scenario, we altered six parameters, one or two at a time. In this way, the effect of individual parameter changes on simulated oceanic N₂O emissions were assessed, as well as some of the major interactions between parameters. Individual uncertainties derived from sensitivity analyses were then added together to produce one total uncertainty range relative to the baseline scenario that pertains to the parameters tested.

The six parameters tested are not comprehensive of all potential parameters which might affect N₂O emissions; for example, we assumed that the impacts of temperature and depth on subsurface N₂O production were negligible [Zamora et al., 2012], and the surface mediation of fluxes from surfactants [Kock et al., 2012] had no effect. Although the effect of air-sea gas exchange parameterization should not have large effects on the relative importance of the various uncertainties tested here, it could affect total emissions to the atmosphere.

3. Results and Discussion

Figure 1 summarizes the changes in N₂O emissions (globally and within the ETP) caused by uncertainty in model parameterizations. Based on the UVic model, the greatest uncertainties in global N₂O emissions were caused by nitrification-derived surface production of N₂O (abbreviated as SP). SP is not likely to interact with
most other parameters that are primarily sensitive to O₂ concentrations (e.g., subsurface N₂O production (SSP), the N₂O consumption rate at low O₂ (CR), suboxic volume (SOV), and the unknown oxygen concentration at which net N₂O production switches to net N₂O consumption (SW)). The exception was the potential impact of atmospheric inorganic nitrogen deposition (AD) on N₂O emissions, as AD may spur surface water production of N₂O. However, the interactions between SP and AD were tested and found to be negligible (Figure 1), in good agreement with previous work finding that AD is not a major contributor to global N₂O emissions [Sintharalingam et al., 2012].

SW was the second largest uncertainty in global N₂O emissions. Unlike with SP, the SW might have an effect on the simulated importance of other subsurface parameters, because it affects the volume of O₂ that is relevant for the other parameterizations. Therefore, we simulated the change in N₂O emissions for all other parameters at the two SW values considered as the best estimates (i.e., 4 and 10 μM O₂). The exception is SSP because the study upon which the severely nonlinear parameterization is based precludes a SW of 10 μM [Goreau et al., 1980; Sintharalingam et al., 2000].

Figure 2. Modeled regional N₂O profiles of the ETP (nM) (defined as region in Figure 1) for the baseline scenario with 0, 10, and 50% surface nitrification. Differences in the upper 100 m are small (<1 and 5 nM for surface nitrification of 10 and 50%, respectively).

However, marine global N₂O emissions were relatively insensitive to most of the other parameters tested, independent of SW value (Figure 1). The other parameterizations, including the effect of reduced SOV had minor (<15%) impacts on N₂O emissions globally and within the ETP.

We found that the ETP had higher relative uncertainties in N₂O emissions than globally because of the regional importance of oxygen minimum zones and the high-surface water productivity (both factors related to the most important uncertainties in N₂O production). SP contributed a large portion of the total uncertainty in the ETP, along with the SW. Within the ETP alone, there also appeared to be relatively high uncertainty caused by assuming a severely nonlinear SSP parameterization (Figure 1). Note however that the nonlinear SSP parameterization [Sintharalingam et al., 2000] is not likely to be realistic for the ETP, because this parameterization had a poor fit to the regional data [Zamora et al., 2012]. We show the effect of the widely referred to SSP severely nonlinear parameterization only to indicate that while it had a relatively minor net impact on global emissions, it could have important consequences on modeled emissions in the ETP, leading to unrealistically large regional N₂O emissions in our model. Uncertainties in the linear SSP parameterization itself were small, altering ETP N₂O flux by ~7% (Figure 1).

While the largest uncertainties in global N₂O emissions come from SP, it is unfortunately very difficult to verify the amount of N₂O actually produced in the upper 100 m. One study indicates that up to 18–33% of surface water NH₄⁺ is nitrified [Yool et al., 2007]. Our model indicated that even low-surface nitrification levels (10% of surface water NH₄⁺) can increase N₂O emissions to the atmosphere by 50%, assuming similar N₂O production from nitrification as in the subsurface. However, N₂O production in the upper 100 m from 10% nitrification levels would be very difficult to actually observe. First, rapid air-sea gas exchange could mask even large N₂O sources [Ward, 2011]. In Figure 2, we show that modeled ETP surface water N₂O profiles in the upper 100 m at 10% nitrification would produce less than a 1 nM difference in N₂O concentrations compared to a simulation without any N₂O production in the euphotic zone—a difference that is barely, if at all, measurable (note that the signal from SP would be higher in the ETP than globally due to the high regional primary production). Second, fast rates of phytoplankton NH₄⁺ assimilation prevent an accumulation of surface water NH₄⁺ and an accurate measurement of nitrification [Ward, 2011]. Finally, it is difficult to distinguish upwelling-driven N₂O emissions from SP-derived N₂O emissions caused by upwelling-driven production. Although we have not tested different air-sea gas parameterizations in this work, air-sea gas exchange parameterization should not affect...
Oceanic N₂O emissions are an important source of N₂O to the atmosphere. If surface nitrification, which accounts for huge potential ranges in marine N₂O emissions. Because it is difficult to assess the likelihood of N₂O production from surface nitrification based on chemical assessments alone, there might be much larger marine N₂O emissions to the atmosphere than previously assumed.

The next most significant uncertainty in N₂O emissions was the O₂ concentration at which net N₂O production switches to net N₂O consumption. The range of values considered possible here (1–15 μM O₂) caused an 81% change in ETP N₂O emissions. Because it becomes increasingly difficult to accurately assess the differences between observations and models at low O₂ concentrations (especially at ≤4 μM O₂), our findings quantitatively support previous work, suggesting that accurate determination of suboxic volume is vital to determining N₂O emissions (e.g., Codispoti, 2010).

Surface nitrification-derived N₂O production (SP) is a possible pathway of N₂O into the atmosphere. As this pathway is yet unverified but even small amounts could account for large N₂O emissions, the potential for SP should be studied in further detail, particularly because SP might be susceptible to global changes in primary production and acidification (Dore et al., 1998; Law, 2008; Beman et al., 2012). To constrain these estimates, more investigations on the emissions of marine N₂O to the atmosphere are needed, as are biological studies assessing the potential for N₂O emissions from surface waters.

References

Figure 3. Estimates of global marine N₂O emissions from the ocean to the atmosphere, based on data-interpolation methods and models. Uncertainty ranges due to various SP parameterizations are shown for our model.

4. Conclusions
We assessed six of the major uncertainties in the marine N₂O emissions using an Earth system climate model with a focus on the eastern tropical Pacific. By far, the largest uncertainty is the potential for surface N₂O production from nitrification, which accounts for huge potential ranges in marine N₂O emissions. Because it is difficult to assess the likelihood of N₂O production from surface nitrification based on chemical assessments alone, there might be much larger marine N₂O emissions to the atmosphere than previously assumed.

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Oceanic N₂O emissions are an important source of N₂O to the atmosphere. If surface nitrification does not occur, our study suggests a large reduction in the uncertainty range in previous ocean emissions: from ∼7.6 Tg N yr⁻¹ (Clais et al., 2013) to 1.6 Tg N yr⁻¹. This reduction in uncertainty is based on a more thorough testing of literature values for N₂O marine emission uncertainties. However, assuming that 10% of surface remineralized N is nitrified and that similar amounts of N₂O produced in the surface as in the subsurface from nitrification, the uncertainty range in marine N₂O emissions goes back up to 3.3 Tg N yr⁻¹.

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