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Global oceanic production of nitrous oxide

Alina Freing†, Douglas W. R. Wallace‡ and Hermann W. Bange*

GEO/MAR/Helmholtz Centre for Ocean Research Kiel, 24148 Kiel, Germany

We use transient time distributions calculated from tracer data together with in situ measurements of nitrous oxide (N₂O) to estimate the concentration of biologically produced N₂O and N₂O production rates in the ocean on a global scale. Our approach to estimate the N₂O production rates integrates the effects of potentially varying production and decomposition mechanisms along the transport path of a water mass. We estimate that the oceanic N₂O production is dominated by nitrification with a contribution of only approximately 7 per cent by denitrification. This indicates that previously used approaches have overestimated the contribution by denitrification. Shelf areas may account for only a negligible fraction of the global production; however, estuarine sources and coastal upwelling of N₂O are not taken into account in our study. The largest amount of subsurface N₂O is produced in the upper 500 m of the water column. The estimated global annual subsurface N₂O production ranges from 3.1 ± 0.9 to 3.4 ± 0.9 Tg N yr⁻¹. This is in agreement with estimates of the global N₂O emissions to the atmosphere and indicates that a N₂O source in the mixed layer is unlikely. The potential future development of the oceanic N₂O source in view of the ongoing changes of the ocean environment (deoxygenation, warming, eutrophication and acidification) is discussed.

Keywords: nitrous oxide; oceanic production; nitrification; denitrification

1. INTRODUCTION

Nitrous oxide (N₂O) is an atmospheric trace gas which influences the Earth’s climate both directly and indirectly [1,2]: (i) In the troposphere, it acts as a strong greenhouse gas and (ii) owning to a relatively long atmospheric lifetime, N₂O can reach up to the stratosphere, where it acts as the major source for ozone-depleting nitric oxide radicals. Since the industrial revolution, the concentration of N₂O in the atmosphere has increased rapidly by about 18 per cent [3]. The dominant natural sources are believed to be soils and oceans, whereas anthropogenic sources mostly result from agricultural and industrial activities. N₂O is biologically produced in the ocean, and the resulting N₂O emissions play a major role for the atmospheric N₂O budget [4,5]. According to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, open ocean and coastal areas make up approximately 21 per cent and approximately 10 per cent of the total source of atmospheric N₂O of 17.7 Tg N yr⁻¹, respectively [5].

N₂O is microbially produced via nitrification (NH₄⁺ → NO₂⁻ → NO₃⁻) and denitrification (NO₃⁻ → NO₂⁻ → N₂O → N₂). They are widely accepted to be the main production mechanisms of N₂O in the ocean [6]. N₂O can occur as a by-product during nitrification and as an intermediate during denitrification. However, the exact metabolism used for N₂O production during nitrification, the net behaviour of denitrification and their respective contributions to the global N₂O inventory in the ocean remain unclear [6–9].

Here, we present an estimate of the N₂O subsurface production rates by using the transient time distribution (TTD) approach. The discrepancy between the predicted global N₂O production and ocean–atmosphere flux estimates and its potential reasons as well as implications are discussed.

2. METHODS

In Freing et al. [10], TTDs calculated from tracer data together with in situ measurements of N₂O were used to estimate the concentration of biologically produced N₂O and N₂O production rates in the central North Atlantic Ocean. This approach to estimate N₂O production rates integrates the effects of potentially varying production/decomposition mechanisms along the transport path of a water mass. A new parametrization of N₂O production during nitrification depending linearly on the apparent oxygen utilization (AOU) and exponentially on temperature/depth was developed by Freing et al. [10], which is used here together with global gridded World Ocean Atlas (WOA) temperature [11], salinity [12] and oxygen [13] data and global gridded CFC-12 (i.e. dichlorodifluoromethane, CF₂Cl₂) data from the Global Data Analysis Project (GLODAP) [14] to calculate the global annual subsurface N₂O yield. We calculated a TTD age distribution and a mean age for every grid point. Because CFC-12 concentrations in the deep Pacific are too low to allow calculation of TTDs and the highest calculated mean age is 731 years, the mean age for every grid point

* Author for correspondence (hbange@geomar.de).
† Present address: NeuroCure Clinical Research Center, Charité-Universitätsmedizin Berlin, Berlin, Germany.
‡ Present address: Oceanography Department, Dalhousie University, Halifax, Nova Scotia, Canada.

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with such a low CFC-12 concentration was set to 800 years. This choice results in a realistically smooth age distribution and is in line with the results of Matsumoto [15], who, using 14C, found the deep ocean to be characterized by centennial rather than millennial timescales.

In order to estimate the background N2O signal (N2Oeq) in the ocean from the TTD, we need to know the time-dependent history of atmospheric concentrations. We used a synthesis of ice-core and firn data [16,17] merged with more recent air measurements. The data are available at http://daac.ornl.gov [18]. We assume a constant atmospheric mixing ratio of N2O of 275 ppb prior to year 1800 and used a polynomial fit of the data from 1800 to the present day. For details on the atmospheric history of N2O used and the use of TTDs to calculate [N2O]eq see Freing et al. [10].

(a) Open ocean apparent nitrous oxide production rate

The bottom depth at each grid point was determined by using the 60 s resolution Earth Topography Digital Dataset (ETOPO) global elevation map distributed with the FERRET program (information is available at http://ferret.pmel.noaa.gov/Ferret/). A grid point was defined as an open ocean grid point if its bottom depth was more than 200 m. An apparent N2O production rate for open ocean grid points was calculated in two ways (N2OPRdepth and N2OPRtemp) using the parametrizations developed by Freing et al. [10]. An apparent N2O production rate depending on an apparent oxygen utilization rate (AOUR) and depth was calculated as

$$\text{N2OPR}_{\text{depth}} = \text{AOUR} a_1 \exp \left( -\frac{z}{z_{\text{sc}}} \right) + a_2,$$

where the coefficient values for the best fit are $a_1 = 0.0658$, $a_2 = -0.0065$, $z_{\text{sc}} = 20000$, $z$ denotes the depth and AOUR $= [\text{AOU}]_{t}$, where $t$ is the mean age of the water parcel calculated using the TTD method. An apparent N2O production rate depending on AOUR and temperature was calculated as

$$\text{N2OPR}_{\text{temp}} = \text{AOUR} a_1 \exp \left( -\frac{T}{T_{\text{sc}}} \right) + a_2,$$

where the coefficient values for the best fit are $a_1 = 0.0665$, $a_2 = -0.0032$, $T_{\text{sc}} = 20000$, $T$ denotes the temperature and AOUR $= [\text{AOU}]_{t}$, where $t$ is the mean age of the water parcel calculated using the TTD method.

To exclude any undue influence of short-term seasonal variations affecting the near-surface ocean in the estimates, all production rates were calculated only for grid fields below the mixed layer. The mixed layer depth was determined by using the mixed layer climatology of de Boyer Montégut et al. [19]. The mixed layer depth is determined by an absolute change in temperature of 0.2 °C compared with the temperature at 10 m depth. This parametrization accounts only for N2O production by nitrification.

There are no CFC-12 data, and thus there is no mean age information available for the Arctic Ocean in the GLODAP dataset. A N2OPR for the Arctic Ocean (N2OPRarctic) was estimated using the 25 per-cent-quantile of the overall N2OPR. This takes into account that, in general, the relevant biological productivity is comparatively low in the Arctic Ocean.

(b) Apparent nitrous oxide production rate on the continental shelves

A grid point was defined as a shelf grid point if its bottom depth was 200 m or less. An apparent shelf N2O production rate (N2OPRshelf) was calculated using 52 shelf data points from the N2O database MEMENTO (version March 2009; see https://memento.ifm-geomar.de/) [20]. Unlike for N2OPR, there is a good correlation between N2OPRshelf/AOUR and depth but not between N2OPRshelf/AOUR and temperature. Therefore, N2OPRshelf was estimated as

$$\text{N2OPR}_{\text{shelf}} = \text{AOUR} a_1 \exp \left( -\frac{z}{z_{\text{sc}}} \right) + a_2,$$

where the coefficient values for the best fit are $a_1 = 0.1795$, $a_2 = 0.5374$, $z_{\text{sc}} = 350$ and $z$ denotes the depth. This parametrization accounts only for N2O production by nitrification. The goodness of fit is illustrated in figure 1. Owing to lack of data, we did not attempt to calculate a production rate for the shelf of the Arctic Ocean.

(c) Denitrification

Denitrification can either produce or consume N2O, depending on the surrounding conditions: it produces N2O at the interface between suboxic and anoxic waters, while it consumes N2O under (close to) anoxic conditions when the complete process of denitrification is performed [6,21].

To estimate production owing to denitrification, we used the collection of N2O depth profiles archived in MEMENTO (version March 2009; figure 2) to determine the maximal and mean N2O ($\langle N_2O_{\text{max}} \rangle$ and $\langle N_2O_{\text{mean}} \rangle$) concentration per depth and oxygen minimum zone. Following Codispoti et al. [22]...

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Figure 1. Shelf nitrous oxide (N2O) production rates (nmol kg$^{-1}$ yr$^{-1}$) calculated from N2O data versus shelf N2O production rates (nmol kg$^{-1}$ yr$^{-1}$) calculated using equation (2.3).

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and Stramma et al. [23], we defined suboxic zones as WOA fields with an oxygen content of less than 10 μmol kg$^{-1}$. This results in three main oxygen minimum zones, in the Arabian Sea, the Eastern Tropical North Pacific and the Eastern Tropical South Pacific, which is in good agreement with Paulmier et al. [24].

The difference between $[N_2O]_{\text{max}}$ and $[N_2O]_{\text{mean}}$ as well as the difference between $[N_2O]_{\text{max}}$ and the estimated $[N_2O] (= N_2O_{\text{PR}} \times t + [N_2O]_{\text{eq}})$ resulting from nitrification were used as an estimate of the total amount of $N_2O$ produced by denitrification. When $(N_2O_{\text{max}} - [N_2O])$ resulted in no $N_2O$ production via denitrification, $[N_2O]_{\text{mean}}$ and $[N_2O]_{\text{max}}$ were used as a lower and upper boundary, respectively, for the total amount of $N_2O$ produced via denitrification. The $N_2O$ production rate owing to denitrification ($N_2O_{\text{PR}}$) was then calculated as

$$N_2O_{\text{PR}} = \frac{1}{t_{\text{omz}}} (([N_2O]_{\text{max}} - [N_2O]_{\text{eq}}) - (N_2O_{\text{PR}} t + [N_2O]_{\text{eq}}))$$

where $t_{\text{omz}}$ is the average time a water parcel has already spent in the respective oxygen minimum zone [25–27] (table 1).

To estimate consumption owing to denitrification, we used the same collection of $N_2O$ depth profiles (figure 2) to determine the minimal and mean $N_2O$ ($[N_2O]_{\text{min}}$ and $[N_2O]_{\text{mean}}$) concentration per depth and oxygen minimum zone. We used an oxygen content of 4 μmol kg$^{-1}$ as a threshold for an environment supporting a denitrification sink of $N_2O$, which marks out parts of the oxygen minimum zones described above. The difference between the estimated $[N_2O]$ resulting from nitrification and $[N_2O]_{\text{mean}}$, and the difference between $[N_2O]_{\text{mean}}$ and $[N_2O]_{\text{min}}$ were used as an estimate of the total amount of $N_2O$ consumed by denitrification. When $([N_2O] - [N_2O]_{\text{min}})$ resulted in no $N_2O$ consumption via denitrification, $[N_2O]_{\text{mean}}$ and $[N_2O]_{\text{min}}$ were used as an upper and lower boundary, respectively, for the total amount of $N_2O$ consumed by denitrification. The $N_2O$ consumption rate owing to denitrification ($N_2O_{\text{OCR}}$) was then calculated as

$$N_2O_{\text{OCR}} = \frac{1}{t_{\text{omz}}} (((N_2O_{\text{PR}} t + [N_2O]_{\text{eq}}) - [N_2O]_{\text{min}})$$

$$- \frac{1}{2} ([N_2O]_{\text{mean}} - [N_2O]_{\text{min}})),$$  

(2.4)

Concentration differences in equation (2.5) indicating production were discarded for the purpose of this calculation.

### Table 1. Average time of residence (years) per oxygen minimum zone (see text for details and references).

<table>
<thead>
<tr>
<th>zone</th>
<th>average oxygen age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabian Sea</td>
<td>5</td>
</tr>
<tr>
<td>ETNP*</td>
<td>60</td>
</tr>
<tr>
<td>ETSP*</td>
<td>5</td>
</tr>
</tbody>
</table>

*ETNP and ETSP stand for eastern tropical North Pacific and eastern tropical South Pacific, respectively.

### (d) Integrated production estimates

To estimate annual production rates per square metre, the respective $N_2O_{\text{PR}}$ was integrated over the water column. To estimate the magnitude of the global annual production of $N_2O$, firstly the volume of each grid cell was determined by integrating over the three dimensions: latitude, longitude and depth. The calculated volume was then multiplied by the respective $N_2O_{\text{PR}}$ to calculate the annual $N_2O$ yield per grid cell. The sum of the annual $N_2O$ yield of all ocean grid cells was used to estimate the global annual $N_2O$ production. The integrated volume of a grid cell $V_{gc}$ in cubic metres used in our calculations can be described as

$$V_{gc} = \frac{(\varphi_2 - \varphi_1)}{3}((R_{\text{earth}} - D_1)^3 - (R_{\text{earth}} - D_2)^3)$$

$$\times (\sin(\theta_2) - \sin(\theta_1)), \tag{2.6}$$

where $\varphi_1$, $\varphi_2$ and $\theta_1$, $\theta_2$, with $\theta_2 > \theta_1$, are the longitudinal and latitudinal boundaries, respectively, of the respective grid cell in degrees, $D_1$, $D_2$, with $D_2 > D_1$, are the depth boundaries of the respective grid cell in metres and $R_{\text{earth}}$ is the radius of the Earth in metres.

### (e) Nitrous oxide concentration

$[N_2O]$ was predicted as

$$[N_2O] = [N_2O]_{\text{eq}} + N_2O_{\text{PR}} t + f ([O_2]) N_2O_{\text{OCR}} t_{\text{omz}}$$

$$- g ([O_2]),$$

(2.7)

where $f$ and $g$ are switch functions, which determine whether denitrification contributes to $[N_2O]$. They are defined as

$$f ([O_2]) = 1 \text{ for } [O_2] < 10 \text{ nmol kg}^{-1};$$

(2.8)

$$f ([O_2]) = 0 \text{ for } [O_2] \geq 10 \text{ nmol kg}^{-1};$$

and

$$g ([O_2]) = 1 \text{ for } [O_2] < 4 \text{ nmol kg}^{-1};$$

(2.9)

$$g ([O_2]) = 0 \text{ for } [O_2] \geq 4 \text{ nmol kg}^{-1}.$$
N$_2$OPR is calculated as N$_2$OPR$_{\text{depth}}$ or N$_2$OPR$_{\text{temp}}$ according to equation (2.1) or (2.2), respectively.

**Error estimates**

The predicted AOUR varied between 0.01 and 49 µmol kg$^{-1}$ yr$^{-1}$, with an overall mean AOUR of 2.9 ± 0.5 µmol kg$^{-1}$ yr$^{-1}$ (1σ). These values are in good agreement with measurements [28,29]. This suggests that the use of a TTD-based mean age for rate calculations yields reliable rate estimates. Additionally, Tanhua et al. [30] found TTD-based estimates of anthropogenic carbon concentrations to be in good agreement with independent methods, suggesting the use of CFC-12 as tracers is a reliable basis for water mass age and hence estimation of background concentrations such as [N$_2$O]$_{\text{eq}}$.

Figure 3, the global TTD mean age in different water depths is shown. The TTD-derived mean ages presented here are in agreement with measurements of other tracers and model results [31,32].

The CFC-12, AOU and temperature measurements originate neither from the same water mass nor necessarily even from roughly the same time. Additionally, they represent some kind of average over latitude, longitude and depth. This is likely to dominate the error in our estimates. To estimate this error, we used 5900 open ocean data points below the mixed layer and 46 shelf data points below the mixed layer from our database. Using the gridded CFC concentrations from GLODAP, we calculated the difference between the original [N$_2$O] and [N$_2$O]$_{\text{est}}$ with

$$[\text{N}_2\text{O}]_{\text{est}} = [\text{N}_2\text{O}]_{\text{eq}} + t \text{ N}_2\text{OPR},$$  

where $t$ is the mean age. The mean and median of the absolute percental differences can be found in table 2. It seems reasonable to use the median as a few very different data points can unduly influence the mean. It is likely that peculiar local conditions can lead to a
Figure 4. Section along 110°W (averaged between 100°W and 120°W). (a) Predicted [N₂O] (nmol kg⁻¹) according to N₂OPR_{depth}. (b) Predicted [N₂O] (nmol kg⁻¹) according to N₂OPR_{temp}. (c) Measured [N₂O] (nmol kg⁻¹) from Nevison et al. [33] and Farias et al. [34].

Figure 5. Global [N₂O] (nmol kg⁻¹) distribution in 200 m depth estimated using equations (2.7) with N₂OPR_{depth} (a) and equation (2.7) using N₂OPR_{temp} (b). (a,b) White areas in the Arabian Sea represent concentrations exceeding 40 nmol kg⁻¹. Annual N₂O production (μmol m⁻² yr⁻¹) via nitrification integrated over the water column estimated using (c) equation (2.1) and (d) equation (2.2).
indicating that the largest concentration of subsurface solubility and thus elevated \([N_2O]_{eq}\) highest slightly elevated, owing to the cold temperatures increase clearly displayed. Concentrations in the Antarctic are patterns. The eastern boundary upwelling systems are out in figure 5 so as not to obscure the overall qualitative which are only found in the Arabian Sea, are masked

between 4 and 31 nmol kg\(^{-1}\) differences based on temperature (see equation (2.2)) seems to do a slightly better job. The amount of \([N_2O]\) produced (consumed) by denitrification is estimated in a completely different fashion compared to nitrification rates (see §2c). Using the mean \([N_2O]\) from our database, the fraction of denitrification with regard to total annual production becomes insignificant (table 3). We therefore assume that the rate calculations based on \([N_2O]_{mean} - [N_2O]_{max} - [N_2O]_{min}\) and \([N_2O]_{max} - [N_2O]_{min}\) (cf. §2c for details) represent reasonable lower and upper boundaries.

### 3. RESULTS AND DISCUSSION

(a) Concentration and rate estimates

\([N_2O]\) varies between 0 and 3.3 nmol kg\(^{-1}\) yr\(^{-1}\) with an overall mean \([N_2O]_{opr}\) of 0.2 ± 0.04 nmol kg\(^{-1}\) yr\(^{-1}\) (1σ). Between 100 and 500 m depth, \([N_2O]_{opr}\) averages 0.4 ± 0.04 nmol kg\(^{-1}\) yr\(^{-1}\) (1σ), whereas below 500 m \([N_2O]_{opr}\) averages 0.09 ± 0.01 nmol kg\(^{-1}\) yr\(^{-1}\) (1σ), indicating that the largest concentration of subsurface \([N_2O]\) is produced in the upper 500 m of the water column. The estimates of the two parametrizations differ only in the second significant figure.

The global distribution of predicted \([N_2O]\) varies between 4 and 31 nmol kg\(^{-1}\) and, where measurement data exist, is qualitatively very similar to the measured \([N_2O]\) of our database. Figure 4 shows a comparison of measured and predicted \([N_2O]\) along 110°W. In the oligotrophic part, the predicted concentrations agree quite well with the measured \([N_2O]\) in the suboxic zone, the predicted \([N_2O]\) clearly underestimates \([N_2O]\). This could be due to the use of annual mean dissolved \([O_2]\), which might not adequately reflect the location and extent of the oxygen minimum zone at the time of the data acquisition. Our parametrization does not account for the export of \([N_2O]_{eq}\) from highly productive regions, which might also be a reason for the underestimation shown in figure 4. Qualitative patterns are represented very well by our prediction.

Figure 5 shows the estimated \([N_2O]\) distribution in 200 m depth. Concentrations exceeding 40 nmol kg\(^{-1}\), which are only found in the Arabian Sea, are masked out in figure 5 so as not to obscure the overall qualitative patterns. The eastern boundary upwelling systems are clearly displayed. Concentrations in the Antarctic are slightly elevated, owing to the cold temperatures increasing solubility and thus elevated \([N_2O]_{eq}\). Highest concentrations, 90 nmol kg\(^{-1}\), occur in the Arabian Sea. Concentrations are also comparatively high in the North Pacific Ocean and the Bay of Bengal. Considering the parametrization was solely derived from North Atlantic data, the systematic features of \([N_2O]\) in the world ocean are remarkably well displayed.

\([N_2O]\) is almost always exclusively determined by production via nitrification and \([N_2O]_{eq}\) with the exception of the three oxygen minimum zones. In the oxygen minimum zone in the Arabian Sea, the fraction of \([N_2O]\) produced via denitrification varies between 2 per cent and 89 per cent between 200 and 900 m. In the oxygen minimum zone of the Eastern Tropical North Pacific, the average fraction of \([N_2O]\) produced via denitrification per depth varies between 2 per cent and 35 per cent between 400 and 500 m. In the oxygen minimum zone of the Eastern Tropical South Pacific, the average fraction of \([N_2O]\) produced via denitrification per depth varies between 1 per cent and 14 per cent between 150 and 400 m.

It is worth noting that the qualitative features of \([N_2O]\) are controlled not only by the qualitative features of \([N_2O]_{opr}\) but also by temperature (via solubility). \([N_2O]_{eq}\) shows patterns very similar to those displayed by \([N_2O]\). We find that \([N_2O]_{eq}\) is strongly controlled by temperature. However, the qualitative features of \([N_2O]_{opr}\) mainly reflect \([O_2]\) and not temperature.

(b) Annual subsurface nitrous oxide yield

The integrated annual \([N_2O]\) production per square metre owing to nitrification is shown in figure 5 and listed in table 3. The qualitative features are similar for both parametrizations. \([N_2O]_{opr}\) estimates a slightly bigger \([N_2O]\) yield but both parametrizations agree within the error margins. The error analysis suggests that \([N_2O]_{opr}\) estimates the production slightly more accurately (cf. §2f; table 2).

The largest amount of \([N_2O]\) per square metre and per year is produced in the North Atlantic Ocean and off Argentina, which is more likely due to a potential data mismatch between the CFC12- and \([AOU]\)-datasets in the deep rather than to truly elevated production. Profile data from the North Atlantic [35] suggest there is no significant \([N_2O]\) production this deep. However, assuming even that true North Atlantic subsurface production amounts only to half of what is predicted by our method would change the global production estimate only by approximately 5 per cent. Production is also very high in the upwelling
regions off Mauritania and Chile, and is elevated in the North Pacific Ocean, the Southern Ocean and parts of the Indian Ocean. However, even if the N$_2$O yield per square metre is relatively high in the Southern Ocean, then its overall contribution to the global annual production of N$_2$O is small owing to the small area covered. Overall, the patterns of N$_2$OPR in the deep ocean—and therefore, the patterns in the mean age in our case—govern the N$_2$O yield of the water column. Larger water depth does, however, also lead to a larger N$_2$O yield per square metre without N$_2$OPR being significantly higher for the involved grid cells.

It should be noted that areas of extensive subsurface production must not necessarily coincide with areas of large sea-to-air fluxes because of the effects of advection. In addition, the yield per square metre does not necessarily illustrate the respective contributions of the different oceanic regions to the overall N$_2$O source very well, as a high yield per square metre does not necessarily equal a large regional contribution, depending on the area of the respective region.

As denitrification is relevant only in suboxic environments, it has an impact only on the N$_2$O yield of the suboxic zones in the Arabian Sea and in the Eastern Tropical Pacific. The production yield via denitrification is badly constrained (cf. table 3) and probably also highly variable, but—despite the locally limited influence of denitrification—it yields on average approximately 7 per cent of the total amount of N$_2$O produced via nitrification (cf. table 3). However, these results are to be viewed with caution as the estimation of N$_2$OPR$^\text{denit}$ inherently depends on the predicted N$_2$OPR. Nevertheless, our estimate is considerably lower than previous estimates of the global contribution of denitrification that range from 25 to 50 per cent [7,9].

Shelf areas account only for less than 0.5 per cent of the subsurface production of N$_2$O (table 3). This is in line with the conclusions of Bange [36] and Barnes & Upstill-Goddard [37], who suggested that N$_2$O production in coastal areas, which are not affected by upwelling, is found only in estuaries and river plumes but not on the open shelf. A large fraction of estuarine N$_2$O comes from sedimentary sources (most probably denitrification). N$_2$O production from estuaries is, therefore, an additional source of N$_2$O; however, this is not taken into account in this study.

The overall global annual subsurface production of N$_2$O amounts to $3.1 \pm 0.9$ Tg N yr$^{-1}$ ($110.1 \pm 31.8$ Gmol N yr$^{-1}$) and $3.4 \pm 0.9$ Tg N yr$^{-1}$ ($121.7 \pm 32.2$ Gmol N yr$^{-1}$), respectively, and is detailed in table 3. Our N$_2$O production estimate is in good agreement with the estimate of $3.9$ Tg N yr$^{-1}$ by Suntharalingam & Sarmiento [38], but it is lower than the estimate of $5.8 \pm 2$ Tg N yr$^{-1}$ by Nevison et al. [33].

Recent estimates based on gas-exchange parametrizations, compiled by Bange [4], estimate an oceanic source between 1.4 and 14 Tg N yr$^{-1}$ with a mean oceanic source of $6.6 \pm 3.6$ Tg N yr$^{-1}$ ($10\sigma$) based on gas-exchange parametrization, surface measurements and models. Rhee et al. [39] recently estimated global N$_2$O emissions of 0.9–1.7 Tg N yr$^{-1}$ based on extrapolation of measurements in the open Atlantic Ocean. The annual production of N$_2$O in the ocean is obviously an upper boundary for the annual ocean atmosphere flux. Our production estimate is in agreement with the global emission estimates, especially in view of the uncertainties associated with the emission estimates.

4. SUMMARY
— The predicted N$_2$O production rates owing to nitrification according to both our suggested parametrizations, N$_2$OPR$^\text{temp}$ and N$_2$OPR$^\text{depth}$, show the same qualitative features. However, overall N$_2$OPR$^\text{temp}$ estimates slightly higher production than N$_2$OPR$^\text{depth}$. N$_2$OPR in the deep ocean is comparatively uniform. The largest amount of subsurface N$_2$O is produced in the upper 500 m of the water column.

— The predicted [N$_2$O] is qualitatively very similar to measured [N$_2$O]. Concentrations in the Antarctic Ocean are slightly elevated, whereas highest concentrations occur in the northeastern Pacific Ocean. Temperature is an important control of qualitative features of [N$_2$O] due to its effect on solubility.

— Our estimates of N$_2$O production via denitrification are badly constrained, but despite its locally limited influence, the production yield via denitrification on average amounts to approximately 7 per cent of the total amount of N$_2$O produced via nitrification.

— Shelf areas may account for only less than 0.5 per cent of the global production of oceanic N$_2$O; however, potential coastal sources of N$_2$O from estuaries and upwelling areas are not taken into account in our study.

— The annual subsurface N$_2$O yield amounts to $3.1 \pm 0.9$ (N$_2$OPR$^\text{depth}$) and $3.4 \pm 0.9$ Tg N yr$^{-1}$ (N$_2$OPR$^\text{temp}$), respectively. The annual yield of N$_2$O is generally slightly larger than that of N$_2$OPR$^\text{depth}$. The error analysis suggests that N$_2$O $^\text{temp}$ estimates the production slightly more accurately.

— Our estimate of the total annual N$_2$O subsurface yield is in agreement with of recent estimates of the global N$_2$O emissions based on gas-exchange parametrization.

In summary, our findings emphasize that the marine N$_2$O cycling, production and emissions are still not well understood and still associated with a high degree of uncertainty.

5. OUTLOOK
(a) Nitrous oxide source in the mixed layer
Because the mixed layer is well oxygenated, a significant N$_2$O source in the mixed layer originating from denitrification processes seems unlikely. Until recently, nitrification was thought to be inhibited by light [40]—making it a very unlikely occurrence in the mixed layer. The results of Bange [41], who concluded that the surface layer N$_2$O concentration in the Arabian Sea is mainly controlled by gas exchange, entrainment of N$_2$O from deeper layers and variability in the sea surface temperature, are in line with this. It should be noted, however, that assuming a uniform mixed layer
depth of 50 m and a ventilation time of N2O of three weeks [42], a mixed layer source of 1 Tg N yr\(^{-1}\) would lead only to an accumulation of approximately 0.09 nmol kg\(^{-1}\) in the mixed layer. Assuming a uniform mixed layer depth of 20 m and a mixed layer source of 1 Tg N yr\(^{-1}\) would lead only to an accumulation of approximately 0.2 nmol kg\(^{-1}\) in the mixed layer. These changes could probably not be distinguished from natural variability in the surface, even if the method’s precision allowed for their detection.

Model results by Yool et al. [43], based on nitrification measurements, suggest something very different. They suggest a significant nitrification activity in the euphotic zone. Clark et al. [44] measured NH\(_4\) and NO\(_2\) oxidation rates on a north–south transect through the Atlantic Ocean. Their data suggest that in the oligotrophic Atlantic Ocean there is nitrification in the photic zone, which is of sufficient intensity to turn over the NO\(_3\)-pool in one day. Wankel et al. [45] found that 17–25% of the nitrate-based productivity in the euphotic zone of Monterey Bay is supported by nitrification. Bianchi et al. [46] measured significant nitrification rates in the upper 100 m of the Indian sector of the Southern Ocean. The results of the studies introduced above indicate that there might be indeed significant nitrification activity in the euphotic zone on a global scale. However, there only a few studies that deal with the associated N2O yield by nitrification in the mixed layer: Dore and Karl [47] used in situ measurements of [N2O] at the ALOHA (A Long-Term Oligotrophic Habitat Assessment) station and the gas-exchange model of Wanninkhof [48] to calculate N2O ocean–atmosphere fluxes. They calculated the flux to the euphotic zone using concentration gradients and an eddy-diffusivity coefficient of 3.7 \(\times\) 10\(^{-5}\) m\(^2\) s\(^{-1}\). They used these flux estimates to calculate a net N2O production rate in the euphotic zone of 1.68–7.94 \(\mu\)mol m\(^{-2}\) d\(^{-1}\), which they attribute to in situ nitrification. Assuming a N2O yield of 0.5% per cent during nitrification, nitrification estimates derived from the N2O production rate were on the same order of magnitude as their directly measured nitrification rates. Even taking into account the probably rather large uncertainties involved in all the calculations, these results clearly point towards a significant N2O production via nitrification in the euphotic zone. Slightly larger (super-) saturations of N2O in the upper 40 m of the water column might even have suggested near-surface production. Morelli et al. [49], Charpentier et al. [50] and Law & Ling [51] calculated the air–sea N2O flux based on their data from the Atlantic Ocean/Caribbean Sea, the central and eastern South Pacific Ocean and the Australasian sector of the Southern Ocean, respectively. They also found a difference between cross-thermocline and air–sea N2O fluxes in the range of Dore & Karl [47]. They acknowledge that this difference might possibly be due to nitrification [49,51], as indicated by experimental evidence of Dore & Karl [47] and Dore et al. [52], or suggested a further hitherto unknown production process [50]. We found the cross-thermocline flux of N2O in the North Atlantic calculated from in situ N2O data to be an order of magnitude smaller than the N2O flux across the air–sea interface calculated using gas-exchange parametrizations [53].

While these results presented above seem to point towards a significant N2O production via nitrification in the euphotic zone, the probably rather large uncertainties involved in all these calculations need to be taken into account [51,54]. Air–sea fluxes are usually estimated using empirical air–sea gas-exchange parametrizations, which introduces large uncertainties into source estimates. A suite of rather different parametrizations exist, which all fit some experimental dataset, showing that gas exchange itself is highly variable and the governing mechanisms are not yet fully understood [55]: a recent study of both the N2O air–sea fluxes and the N2O diapycnal fluxes into the mixed layer revealed that, by using a common gas-exchange approach, the mean air–sea flux is about four times larger than the mean diapycnal flux into the mixed layer. Vertical advection or biological production was found not sufficient to compensate this discrepancy. Instead, flux calculations using an air–sea exchange parametrization that takes into account the effect of surfactants in the ocean surface microlayer are in good agreement with the diapycnal fluxes, indicating that surfactants, especially in areas with a high biological productivity, may have a large dampening effect on air–sea gas exchange of N2O [54].

There is, however, also an inherent problem with using any kind of gas-exchange model involving the air–sea gradient of some species to estimate long-term average fluxes. Commonly used gas-exchange parametrizations are a measure of an instant sea-to-air flux. After the transfer of molecules, the concentration gradient between the surface water and the atmosphere changes, changing the gas transfer in turn. While this is of no/little consequence to the instant/short-term flux across the air–sea interface, it becomes important when an instant gas-exchange flux is extrapolated over time. Lacking a term to account for the change in concentration over time, it is implicitly assumed in this kind of calculation that any amount of gas lost to the atmosphere from surface waters is instantly replaced from below. In addition, flux estimates based on gas-exchange calculations could be distinctly overestimated as they fail to take the annual cycle of the N2O flux across the air–sea interface into account [53]. Such an overestimation is even more likely as the underlying datasets are mostly seasonally biased. Both these effects can result in an overestimation of the sea-to-air flux, partly explaining the slight discrepancy we encountered here. Additionally, considering the nonlinear dependence on wind speed of almost all gas-exchange parametrizations, it is at least questionable if the use of averaged wind speeds results in a reasonable estimate of the average air–sea flux.

(b) Nitrous oxide and deoxygenation of the ocean

Stramma et al. [23] showed that the oxygen minimum zones of the intermediate layers (300–700 m water depth) in various regions of the ocean are expanding and have been losing oxygen during the past 50 years. This would result in an expansion of the zones
supporting denitrification, which would probably have an impact on the production and decomposition of N₂O. Whether it would have a net positive or net negative effect on N₂O production remains unclear as the net behaviour of denitrification and its controlling mechanisms are not yet fully understood [21]. As N₂O yields during both bacterial and archaeal nitrification have been found to be enhanced under low oxygen conditions in laboratory studies [56,57], this increase in volume will probably also lead to increased production of N₂O owing to nitrification. Please note that Frame and Casciotti [58] recently showed that the bacterial N₂O production via nitrification seems to be less sensitive to [O₂] than previously thought [56]. This is in line with the results of two recent studies by Löschler et al. [57] and Santoro et al. [59] which indicate that oceanic N₂O production is dominated by archaeal nitrification which, in turn, showed a considerably stronger [O₂] sensitivity in culture experiments [57].

(c) Nitrous oxide from anammox
The traditional view that denitrification is the dominant process in suboxic oxygen minimum zone has been challenged by the finding that in the oxygen minimum zone of the Eastern Tropical South Pacific and off Namibia the N₂ loss might be almost exclusively performed by bacterial anammox (i.e. anaerobic ammonia oxidation: NO₂⁻ + NH₄⁺ → N₂) [60,61]. However, so far, N₂O has only been found to be produced during anammox in relatively small quantities during nitric oxide detoxification (NO₂ → NO → N₂O), which seems to be performed by the anammox bacterium *Kuenenia stuttgartiensis* as a side reaction [62]. Thus, the role of marine anammox bacteria in N₂O cycling in suboxic oxygen minimum zones remains to be verified.

(d) Nitrous oxide from coastal hypoxia
Estuaries and nitrogen rich coastal zones probably contribute to a significant degree to the total oceanic emissions of N₂O [63,64]. Estuaries and their adjacent regions are fertilized via an increasing degree by river run-off carrying a high load of organic nitrogen. This fertilization may lead to enhanced primary production and thus enhanced nitrification and N₂O formation in an increasing number of [O₂] depleted (i.e. hypoxic) coastal areas [65]. Additionally, the changing flux of organic material reaching the sediments might change O₂ concentrations in the sediment, changing N₂O production in turn. And, unlike in the open ocean, the shallow depths of coastal regions allow for N₂O produced in the sediments to reach the atmosphere.

(e) Warming of the ocean
There is evidence that the oceans are warming [66,67]. As marine autotrophic and heterotrophic processes display sensitivities to temperature (to varying degrees), ocean warming might result in changes of the bacterial community structure and hence in changes of N₂O production. Changes in ocean temperature also affect the solubility of N₂O. Rising ocean temperature implies that the N₂O long-term storage capacity of the deep ocean will be reduced. Additionally, this effect will temporarily strengthen the N₂O source, as apparent supersaturations created by warming water masses after their last contact with the atmosphere will increase the ocean–atmosphere gradient when these water masses finally get into contact with the atmosphere again. This strengthening effect will disappear again once the temperature change levels off and the system reaches equilibrium again. In addition, non-uniform warming could induce enhanced stratification of the water column. This could potentially diminish the oceanic N₂O source by keeping N₂O-rich water from intermediate depths from reaching the air–sea interface.

(f) Ocean acidification
The ongoing increase of CO₂ in the atmosphere also causes a decrease of the oceanic pH (i.e. ocean acidification). This, in turn, results in a shift of the NH₄⁺−NH₃ equilibrium towards NH₃. In a recent study by Beman et al. [68], it was shown that nitrification rates decreased significantly when the pH was lowered to values expected to occur in the future ocean. (One explanation for the pH sensitivity of nitrification rates is that the ammonia monoxygenase enzyme uses NH₃ rather than NH₄⁺ as substrate in the first step of the nitrification sequence [69].) On the basis of these results, it was suggested by Beman et al. [68] that future oceanic N₂O production during nitrification should be decreased as well. However, this scenario might be not that straightforward: nitrification is part of organic matter remineralization (i.e. oxidation of organic matter with O₂ to CO₂). Therefore, both pH and O₂ are decreasing during organic matter remineralization. However, it is well known that decreasing O₂ concentrations lead to increasing N₂O production during nitrification [57] and obviously there seems to be only a minor effect of decreasing pH on N₂O production during nitrification as part of the organic matter remineralization process. Laboratory experiments to verify the effect of ocean acidification on N₂O production via nitrification are missing.

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REFERENCES
3 Forster, P. et al. 2007 Changes in atmospheric constituents and in radiative forcing. In Climate change 2007: the physical science basis. Contribution of working group I


