Rapid nitrous oxide cycling in the suboxic ocean

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Nitrous oxide (N\textsubscript{2}O) is a powerful greenhouse gas and a major cause of stratospheric ozone depletion, yet its sources and sinks remain poorly quantified in the oceans. We used isotope tracers to directly measure N\textsubscript{2}O reduction rates in the eastern tropical North Pacific. Because of incomplete denitrification, N\textsubscript{2}O cycling rates are an order of magnitude higher than rates inferred by current models in suboxic regions, and the spatial distribution suggests strong dependence on both organic carbon and dissolved oxygen concentrations. Furthermore, N\textsubscript{2}O turnover is 20 times higher than the net atmospheric efflux. The rapid rate of this cycling coupled to an expected expansion of suboxic ocean waters implies future increases in N\textsubscript{2}O emissions.

Anthropogenically derived atmospheric N\textsubscript{2}O concentrations increased over the past century (1–3), but the natural marine sources and sinks of N\textsubscript{2}O have been difficult to quantify. Because of the paucity of direct measurements of N\textsubscript{2}O production and consumption in the ocean, current rate estimates and predictions of how the N\textsubscript{2}O budget will respond to a changing climate remain uncertain (4). The most concentrated oceanic sources of N\textsubscript{2}O to the atmosphere are the suboxic (0 to 20 μmol l\textsuperscript{-1}) waters overlying the oxygen minimum zones (OMZs), based on measurements and models of supersaturated N\textsubscript{2}O concentrations (5, 6). Furthermore, N\textsubscript{2}O is produced by both nitrification and denitrification, but the overall importance of each process is uncertain. Nitrification, the oxidation of ammonium to nitrite and further to nitrate, exhibits maximum rates just below the well-lit surface layer, where remineralization rates supplying ammonium are highest. Nitrification generates an N\textsubscript{2}O by-product (7) whose yield is enhanced by suboxic concentrations—the yield of N\textsubscript{2}O as a fraction of nitrite production, can be as high as 10% in culture (8, 9) and 0.4% in the environment (10, 11). However, at very low (less than a few micromolar) oxygen concentrations, nitrification ceases (12), and no N\textsubscript{2}O can be produced via this pathway. Denitrification, the stepwise reductions of nitrate and nitrite through NO and N\textsubscript{2}O to nitrogen gas, occurs in the ocean only when molecular oxygen is sufficiently low (less than 3 μmol l\textsuperscript{-1}) (13). This anaerobic process results in local N\textsubscript{2}O minima within the OMZ core but has the potential to be a major N\textsubscript{2}O source at the suboxic-anoxic interface (the oxycline) at the top of the OMZ. Over this narrow depth interval, N\textsubscript{2}O consumption by the nitrous oxide reductase enzyme is inhibited by O\textsubscript{2} at an extent greater than its production in the denitrification sequence (14).

Further, because the denitrification steps are predominantly heterotrophic, the rates are enhanced at shallow depths, where the supply of newly produced labile organic matter from the surface (15) is greater. Incomplete denitrification (reduction of NO\textsubscript{3} to N\textsubscript{2}O rather than to N\textsubscript{2}) may account for a flux that is ignored or not explicitly represented in most biogeochemical ocean and climate models. Indeed, in culture experiments (14, 15) and sediment incubations (16) at suboxic but nonzero O\textsubscript{2} concentrations, denitrification activity decreased as expected with increasing O\textsubscript{2} concentrations, but the N\textsubscript{2}O yield (i.e., the proportion of denitrification halting at N\textsubscript{2}O) increased to ~50% (15).

We directly measured the reduction of N\textsubscript{2}O to dinitrogen gas by using labeled isotopic (15\textsubscript{N})N\textsubscript{2}O tracer incubation experiments at three stations in the eastern tropical North Pacific (ETNP), the largest suboxic zone (17) and a major site of N\textsubscript{2}O production (18, 19). N\textsubscript{2}O reduction is the only major biological N\textsubscript{2}O consumption process; because production occurs via multiple pathways, in situ production rates via isotopic tracer techniques cannot be directly constrained (20).

The transect across the ETNP (fig. S1) showed the characteristic features associated with OMZs, namely a N\textsubscript{2}O concentration peak (~100 nmol l\textsuperscript{-1}) at the base of a steep oxygen gradient and an N\textsubscript{2}O concentration minimum in the core of the OMZ. All three sites displayed similar alignments of oxygen, N\textsubscript{2}O, and nitrite maxima and minima (Fig. 1A), indicating similar mechanisms affecting the biogeochemistry across the region. The similarity between the N\textsubscript{2}O profile at the offshore station 2 and data from a nearby site measured 12 years prior (19) (Fig. 1B) indicates long-term stability in the shape and peak magnitudes of the N\textsubscript{2}O profiles.

N\textsubscript{2}O consumption rates (Fig. 2) measured across all three profiles were up to ~35 nmol l\textsuperscript{-1} day\textsuperscript{-1}, indicating residence times as low as 1 day (calculated from the concentration divided by the biological rate). This fast turnover was observed throughout the OMZ core, presumably because of tight coupling of sequential denitrification steps. Within the oxycline, the N\textsubscript{2}O residence times increased and the reduction rates decreased sharply as O\textsubscript{2} increased. This synchronism is consistent with oxygen poisoning of the nitrous oxide reductase enzyme above the OMZ. Moreover, and of greater consequence to atmospheric N\textsubscript{2}O emissions, an estimate of the rate of production based on a one-dimensional (1D) transport-reaction balance (fig. S3) was systematically larger than that of consumption near the base of the oxycline. This 1D estimate is likely to be conservative, because the inclusion of horizontal transport terms, which act to erode the N\textsubscript{2}O peak, would require an increase in the N\textsubscript{2}O source to maintain the balance (table S2 and supplementary text). The observed near-shore (station 1) rates of N\textsubscript{2}O reduction and production decreased with depth (Fig. 2), resembling the depth-dependent power law decay of organic carbon supply (18). This organic carbon dependence of N\textsubscript{2}O cycling was also apparent from the occurrence of the highest rates near shore, where the greatest primary production occurs. These measurements highlight the large spatial heterogeneity of N\textsubscript{2}O cycling dependent on organic carbon export in the ETNP.

We investigated the broader implications of such rapid N\textsubscript{2}O cycling with a mechanistic, 1D model of OMZ biogeochemistry (supplementary materials) built on parameterizations widely adopted in ocean biogeochemical models, including biological N\textsubscript{2}O production via nitrification, enhanced at suboxic concentrations (4, 6, 21, 22), and consumption via denitrification (19). Following previous parameterizations (21), we defined an oxygen threshold of 2 μmol l\textsuperscript{-1}, above which N\textsubscript{2}O was produced and below which, consumed. However, this 1D model with N\textsubscript{2}O production from nitrification alone generated a production rate (maximum of 0.3 nmol l\textsuperscript{-1} day\textsuperscript{-1}) that was a fraction of the net production rate calculated from the measured consumption (Fig. 3A). The observed N\textsubscript{2}O concentration peaks measured here at >100 nmol l\textsuperscript{-1} (Fig. 1) are likely not reproduced in models (21), including our 1D version (which only achieves a maximum of 70 nmol l\textsuperscript{-1}), because they do not include explicit production by incomplete denitrification. The importance of denitrification to N\textsubscript{2}O production has been implicated by measurements across all three major OMZs: the ETNP (18, 23), the eastern tropical South Pacific (ETSP) (24), and the Arabian Sea (20, 25).

We expanded the 1D model to separate the N\textsubscript{2}O production and consumption terms of denitrification and allow for O\textsubscript{2}-dependent denitrification (26). With this change, denitrification became a major N\textsubscript{2}O source in the low-O\textsubscript{2} waters directly overlying the OMZ (0.3 μmol m\textsuperscript{-2} day\textsuperscript{-1}) and was comparable in size to the source from nitrification (9.1 μmol m\textsuperscript{-2} day\textsuperscript{-1}). Furthermore, the maximum modeled net N\textsubscript{2}O production rate of 0.6 nmol l\textsuperscript{-1} day\textsuperscript{-1} is consistent with our observations (Fig. 3B), with a peak concentration of >110 nmol l\textsuperscript{-1}. Such agreement could not be achieved with production via nitrification alone and suggests that denitrification constitutes a major and largely overlooked source of N\textsubscript{2}O. This conclusion also holds for a range of model parameters and formulations, including a simple.
Fig. 1. Biogeochemical measurements. (A) Depth profiles of N$_2$O (open circles), O$_2$ (solid gray line), and NO$_2^-$ (dashed line) concentrations at the three stations included in this study. (B) Comparison of N$_2$O concentration data (open circles) from station 2 collected in April 2012 with those from a previous study (19) (solid circles) of a nearby location (16°N 107°W) in spring 2000.

Fig. 2. N$_2$O cycling rates. Rates of measured N$_2$O consumption (solid squares) and calculated production (open diamonds) are shown at the three stations. Turnover times are indicated by open circles. Scaled (0 to 100% saturation) O$_2$ concentration profiles (solid gray line) are included for reference (see Fig. 1 for concentrations). Note the broken vertical axis between 250 and 500 m. N$_2$O production was calculated by using the measured consumption rates and concentration profiles and assuming a vertical balance between advection, diffusion, consumption, and production. Lateral transport processes, which would tend to erode the N$_2$O peak and thus require more production, were ignored here, making these production rates likely lower estimates (supplementary text).

Our results show that the net accumulation of N$_2$O in the OMZs on the multiyear time scales dictated by ocean circulation hides the delicate balance between production and consumption that proceeds on time scales at least one order of magnitude faster. Over long time scales into the future, expanding and shoaling OMZs resulting from changes in physical circulation, widespread ocean deoxygenation (34), and increased fertilizer runoff stimulating phytoplankton blooms could exacerbate marine N$_2$O accumulation and outgassing (4, 31). This increase would be especially important given the rapid biological rates measured in the ETNP. The rapid turnover of N$_2$O in OMZs also implies that shorter time scale variations influence N$_2$O
**Fig. 3. One-dimensional model of N₂O cycling in the OMZ.**

(A) Modeled N₂O and O₂ concentrations using a mechanistic 1D model of OMZ biogeochemistry, with rates of production from nitrification (green) and consumption from denitrification (red). The net rate is given by the dashed black curve. (B) As in (A) but with an additional N₂O source from denitrification included. The third graph separates the different production and consumption terms. Points show measurements at stations 2 and 3. Model and data profiles have been shifted vertically to align the N₂O peaks to the mean model N₂O peak depth. Solid horizontal gray lines separate the layers of nitrification-dominated production, denitrification-dominated production, and net denitrification consumption. The dashed gray line shows where denitrification begins to act as a major N₂O source in the model. Envelopes in all graphs show the standard deviation from an ensemble of Monte Carlo runs (N = 5000) simultaneously varying all of the parameterizations.

### References and Notes


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### SUPPLEMENTARY MATERIALS

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Materials and Methods

Sample collection and concentration measurements

Sampling was conducted onboard the R/V Thomas G. Thompson cruise TN278 in March and April 2012 in the Eastern Tropical North Pacific (ETNP) oxygen minimum zone (OMZ) off the coast of Mexico. Depth profiles for oxygen, N\textsubscript{2}O, and nitrite concentrations were collected by multiple CTD casts (Fig. S1) using a CTD rosette with twenty-four 12 L Niskin bottles. Dissolved oxygen was measured using an in situ Seabird membrane sensor (SBE 43) attached to the CTD package, nitrite using an AutoAnalyzer with standard spectrophotometric techniques (39), and N\textsubscript{2}O with a gas chromatograph (GC) with an electron capture detector (Shimadzu) (40). Samples for N\textsubscript{2}O were collected in 160 mL serum bottles by overfilling three times and capping immediately. N\textsubscript{2}O was measured immediately by sequential head-space equilibration of equal volumes (25 mL) of seawater sample and helium (25, 41). 0.5 mL of each extraction was injected into a Shimadzu gas chromatograph Model GC–8A with an electron capture detector and a 2 m × 2.2 mm inner diameter Haysep D column (80/100 mesh). The column temperature was set to 30 °C, while the injection port and detector were maintained at 50 and 300 °C, respectively. Analyses were standardized using ambient air and a 1 ppm N\textsubscript{2}O standard (Scott Gas).

N\textsubscript{2}O reduction rate incubations

At three stations, N\textsubscript{2}O reduction rates were directly measured at 8 depths within the oxycline and the core of the anoxic water, adapting the methods of Bulow et al. (42). The three sites consisted of a coastal site “Station 1” (20.1 °N 106.0 °W; bottom depth
2200 m) and two offshore sites “Station 2” (16.5 °N 107.2 °W; bottom depth 3600 m) and “Station 3” (16.0 °N 110.0 °W; bottom depth 3300 m). Water for incubations was collected from Niskin bottles by overflowing 300 mL ground glass stoppered bottles three times before being transferred into a N₂ flushed glove bag for aliquoting into incubation vials. 12 mL Exetainers (Labco, UK) with previously degassed septa were filled with 8 mL of seawater for incubation and purged with He for 5 minutes. Doubly-labeled (¹⁵N)₂O (Cambridge Isotope) was injected after He-purging using a gas-tight syringe to a final concentration of 30 nmol L⁻¹. We assumed any preexisting N₂O was removed during the He-purging, giving a 100% isotopic label fraction. Triplicate vials were poisoned with 50% (w/v) zinc chloride at 5 time points spanning 36 hr (coastal site) or 48 hr (offshore sites) after incubation at 10 °C in the dark. Accumulation of ³⁰N₂ was measured on an isotope ratio mass spectrometer (Europa 20/20) with an in-line liquid nitrogen trap to remove excess labeled N₂O.

**Estimate of N₂O production rates**

A steady state one-dimensional advection-diffusion-reaction balance with depth (z) was developed to calculate the N₂O production rate (P) from the reduction rate (R) measurement and the structure of the N₂O concentration (C) profile:

\[ P = R - v \frac{\partial C}{\partial z} - D \frac{\partial^2 C}{\partial z^2}. \]

We assumed a constant advection coefficient (v) of 1 × 10⁻⁷ m/s, and a constant diffusivity coefficient (D) of 2 × 10⁻⁵ m²/s consistent with previous studies in the ETNP (19) as well as analogous regions in the tropics (43, 44). As both the consumption via reduction and concentration profiles were measured, the production rate is the only
calculated variable. This calculation assumes a steady state in the concentration profile and the only biological loss term of N₂O is reduction to N₂. The calculated production rates showed minimal sensitivity to the choice of upwelling, and limited sensitivity to the choice of vertical diffusion for typically observed values, as shown in Fig. S2 (top panel).

The choice of a 1–D approach is dictated here by the limited number of profiles of measured reduction rates, and the limited ability of current 3–D models in capturing the circulation, O₂ distribution and biogeochemistry of OMZ (e.g. (45)). A 1–D approach is well-suited to a process-oriented study of the OMZ, which are characterized by weak lateral circulation and large vertical gradients in chemical properties. However, because the results presented here regarding the imbalance of N₂O production and consumption depend on physical transports, we performed an additional suite of sensitivity analyses, including a parameterization of lateral transports through a restoring term (see section Parameterization of horizontal transport). This second sensitivity suite of runs shows that imbalances > 1 nmol L⁻¹ d⁻¹ are readily produced at the top of the OMZ for realistic diffusivities (> 10⁻⁵ m² s⁻¹), upwelling velocities and horizontal restoring timescale (Fig. S2).

Estimation of OMZ size

Gridded oxygen concentrations from the World Ocean Atlas 2009 dataset (46) were corrected using the method of Bianchi et al. (28). The areal expanse and volume of the ETNP were numerically integrated using the thresholds of 20 µmol L⁻¹ O₂ concentration for suboxia and 2.5 µmol L⁻¹ for anoxia.
One dimensional biogeochemistry model of the ETNP OMZ

We implemented a mechanistic 1-D model of the biogeochemistry of the ETNP OMZ that describes the cycling of organic matter, here represented by particulate organic carbon (POC), and of dissolved phosphate (PO$_4^{3-}$), nitrate (NO$_3^-$), oxygen (O$_2$), and nitrous oxide (N$_2$O). While the model includes several tracers for completeness, it is developed to explicitly target the cycling of N$_2$O along the gradients between oxygenated and anoxic waters. Models of this type have a rich history in ocean biogeochemistry, starting from the early work of Wyrtki (1947) and Munk (1948), to include recent efforts devoted to OMZ and N$_2$O dynamics, such as in Yamagishi et al. (1999). As in earlier studies, our model solves for the steady state balance between biogeochemical sources and sinks (aerobic respiration, nitrification and denitrification) and physical transport (advection, turbulent diffusion and gravitational sinking) of tracers in the water column.

The values of the parameters used are listed in Table S1. The equations are:

$$\frac{\partial (w_{\text{sink}} \cdot \text{POC})}{\partial z} = -\text{Remin} - \text{Denit}$$

$$\frac{\partial (w_{\text{up}} \cdot \text{PO}_4^{3-})}{\partial z} - \frac{\partial}{\partial z} \left( D_z \frac{\partial \text{PO}_4^{3-}}{\partial z} \right) = r_{\text{rem Po}}^{\text{C Remin}} + r_{\text{rem Po}}^{\text{C Denit}}$$

$$\frac{\partial (w_{\text{up}} \cdot \text{NO}_3^-)}{\partial z} - \frac{\partial}{\partial z} \left( D_z \frac{\partial \text{NO}_3^-}{\partial z} \right) = r_{\text{rem N}}^{\text{C Remin}} - r_{\text{rem N}}^{\text{C Denit}}$$

$$\frac{\partial (w_{\text{up}} \cdot \text{O}_2)}{\partial z} - \frac{\partial}{\partial z} \left( D_z \frac{\partial \text{O}_2}{\partial z} \right) = r_{\text{rem O}}^{\text{C Remin}}$$

$$\frac{\partial (w_{\text{up}} \cdot \text{N}_2\text{O})}{\partial z} - \frac{\partial}{\partial z} \left( D_z \frac{\partial \text{N}_2\text{O}}{\partial z} \right) = S_{\text{N}_2\text{O}}^{\text{nit}} + S_{\text{N}_2\text{O}}^{\text{den}} - S_{\text{N}_2\text{O}}^{-\text{den}}$$
In each equation, the left hand side represents the physical transport, and the right-hand side the biogeochemical sources and sinks. Here, $w_{sink}$ is the sinking speed of organic particles, $w_{up}$ is the upwelling velocity and $D_z$ is the vertical turbulent diffusion coefficient, which are in general functions of depth. The $r$ terms are stoichiometric ratios.

As discussed in the previous sections (see *Estimate of $N_2O$ production rates*), the one-dimensional framework is adequate for representing the processes that take place across the vertical biogeochemical gradients that characterize OMZ. Indeed, because of its formulation (see *Model implementation*), the 1–D model can resolve the fine-scale sharp biogeochemical transitions that characterize the oxycline, which cannot be accurately represented in the current generation of 3–D model owing to their too coarse vertical resolution. For completeness, we tested the effect of including horizontal advection and diffusion terms, as described in the section *Parameterization of horizontal transport*.

The biogeochemical sources and sinks are modeled as described in the following sections.

**Remineralization:**

$$\text{Remin} = k_{\text{rem}} \cdot \frac{O_2}{O_2 + K_{O_2}} \cdot \text{POC}$$

Aerobic remineralization and nitrification processes are modeled as a first order reaction depending on the concentration of POC, and modulated by the dissolved $O_2$ according to a Michaelis–Menten formulation, in agreement with the oxygen response of nitrifying communities described in Martens-Habbema et al. (12).
Denitrification:

\[
\text{Denit} = k_{\text{den}} \cdot \frac{\text{NO}_3^-}{\text{NO}_3^- + K_{\text{NO}_3^-}} \cdot e^{-\frac{O_2}{k_{\text{O}_2}^\text{den}}} \cdot \text{POC}
\]

The denitrification term describes the set of anaerobic reactions that reduce \(\text{NO}_3^-\) to \(\text{N}_2\text{O}\) and \(\text{N}_2\). We assume that denitrification is an overall heterotrophic process fueled by organic matter, hence the first order dependence on POC. Two limitation factors are introduced: a Michaelis–Menten dependence on dissolved \(\text{NO}_3^-\), and an exponential inhibition by dissolved oxygen, in agreement with the results of Dalsgaard et al. (26).

\(\text{N}_2\text{O}\) production by nitrification:

\[
S_{\text{N}_2\text{O}}^{+\text{nit}} = H\left(O_2 - K_{O_2}^\text{Nev}\right) \cdot \left(\frac{a_1}{O_2} + b_1\right) \cdot r_{\text{N:C}}^{\text{rem}} \cdot \text{Remin}
\]

The production of \(\text{N}_2\text{O}\) by nitrification is modeled as described in Nevison et al. (21) and in agreement with the experimental data of Goreau et al. (8) Following Nevison et al. (21), the production of \(\text{N}_2\text{O}\) by nitrification is set to zero below an oxygen threshold \(O_2 = K_{O_2}^\text{Nev}\), using an oxygen-dependent Heaviside step function \(H\).

\(\text{N}_2\text{O}\) production by denitrification:

\[
S_{\text{N}_2\text{O}}^{+\text{den}} = \frac{1}{2} \cdot r_{\text{N:C}}^{\text{den}} \cdot \text{Denit}
\]

Here we assume that \(\text{N}_2\text{O}\) is an obligate intermediate of denitrification that can escape to the water column, where it can be taken up again and reduced to \(\text{N}_2\) by denitrifiers, as described by the next term. This parameterization is only incorporated into the second version of the model.
\[ S^{-\text{den}}_{\text{N}_2\text{O}} = k_{\text{N}_2\text{O}} \cdot N_{\text{2O}} \cdot e^{\frac{O_2}{K_{\text{O}_2}}} \]

The reduction of \( \text{N}_2\text{O} \) to \( \text{N}_2 \) during the final step of denitrification follows the simple approach described in Yamagishi et al. (19), and we model \( \text{N}_2\text{O} \) reduction as a first order reaction, equivalent to assuming that organic matter is not a limiting substrate. In addition, we introduce an exponential oxygen-dependent inhibition factor after Dalsgaard et al. (26) to represent oxygen poisoning of denitrification.

Anaerobic respiration processes other than denitrification (e.g. sulfate reduction) are not explicitly represented in the model. However, \( \text{NO}_3^- \) is never consumed to completion in the experiments described, in agreement with observations. Furthermore, we do not explicitly model the cycling of \( \text{NH}_4^+ \) and \( \text{NO}_2^- \) (including anammox), and we assume that the cycling of these tracers is rapid, and their reservoirs small compared to \( \text{NO}_3^- \).

**Model implementation**

Rather than simulating primary production in the upper layers, we impose a constant flux of organic particles (\( \Phi_{\text{POC}} = w_{\text{sink}} \text{POC} \)) as the upper boundary condition for POC (13). We impose Dirichlet boundary conditions (fixed concentrations) at the top and bottom of the water column for the remaining dissolved tracers, using values from literature (49). We assume constant sinking and upwelling velocities \( w_{\text{sink}} \) and \( w_{\text{up}} \), and a depth-dependent vertical diffusion profile \( D_z \) that includes a high-diffusion mixed layer that quickly transitions to a low-diffusion water column interior. The model equations are reduced to a first-order nonlinear system by recasting them in terms of the first
derivatives of each variable. The system is solved by a finite difference algorithm using
the three-stage Lobatto IIIa formula, as implemented in the MATLAB function \textit{bvp4c}.
This formulation allows for an increased vertical resolution in regions of sharp variation,
and produces continuous differentiable solutions. For example, considering the
conservation equation for $O_2$, an auxiliary equation is introduced for the first derivative in
the vertical direction, and the equation is split into a system of two equations:

$$
y_1 = O_2
$$

$$
y_2 = \frac{\partial O_2}{\partial z}
$$

In this way that the conservation equations can be written as a first-order non-linear
system:

$$
\frac{\partial y_1}{\partial z} = y_2
$$

$$
\frac{\partial y_2}{\partial z} = \frac{1}{D_z} \left[ \left( w_{\text{up}} - \frac{\partial D_z}{\partial z} \right) \cdot y_2 + \frac{\partial w_{\text{up}}}{\partial z} \cdot y_1 - \text{SMS}(y_1) \right]
$$

To prevent non-physical negative solutions, the absolute value of each variable is used in
the numerical implementation the model.

**Model parameters and boundary condition values**

We chose the model parameters from the existing literature, or estimated by
applying physical and biogeochemical scaling arguments. As with many biogeochemical
models, some tuning was required for the parameters not drawn from literature, and we
used the observed tracer profiles as our tuning target. A list of the parameter values and
the corresponding references is provided in Table S1.
Model sensitivity analysis

To estimate the errors associated with this one-dimensional representation of the biogeochemistry of the OMZ, we ran a full set of Monte Carlo simulations ($N = 5000$) perturbing each parameter (Table S1) simultaneously. The new parameters are chosen randomly from a Gaussian or gamma (chosen when the parameters cannot be negative) distribution, with the same mean of the baseline run and a standard deviation equal to 25% of the parameter value. The 25% uncertainty is arbitrarily selected, but we chose such a large value to conservatively account for the range of variability. The output was aligned at the depth of the N$_2$O concentration peak in order to avoid over-smoothing of features that occurs when maxima are spatially separated.

We further sought to assess the 1-D simplification ignoring horizontal terms in modeling the OMZ by including an additional N$_2$O restoration parameter to represent horizontal advection and diffusion. The term is implemented as a restoration to a “far-field” N$_2$O concentration (a typical mean profile outside the OMZ, with a subsurface peak $\sim$50 nmol L$^{-1}$ at $\sim$500 m depth (50)). The timescale for this restoring function was estimate with scaling arguments for typical horizontal advection and turbulent diffusion terms (described in section Parameterization of horizontal transport), and is 1.2 yr in the baseline run. The effect of this restoration is a sink of N$_2$O around the peak, and a source at depth.

A third run that looks solely at the uncertainties of the biogeochemical N$_2$O production terms $K_{O_2}^N,K_{O_2}^{Nev},a_1,b_1,k_{fast}^{N_2O},k_{den}^{N_2O},k_{sink}^{N_2O}$ to separate biological production from physical redistribution of N$_2$O. The results of these three runs in affecting the N$_2$O concentration and production profiles are summarized in Table S2. These runs
consistently indicate a deeper net N$_2$O production rate maximum than concentration maximum, with an oxygen concentration at the N$_2$O concentration peak $\sim$3–10 µmol L$^{-1}$, but 1.5 µmol L$^{-1}$ at the net production rate maximum.

**Parameterization of horizontal transport**

Because the one-dimensional framework does not include explicit horizontal / isopycnal advection and diffusion, we included a parameterization of these horizontal terms based on physical scaling arguments. Assuming the N$_2$O concentration has a subsurface peak within the OMZ that is affected by a far-field N$_2$O distribution outside the OMZ ($N_2O^{out}$) by horizontal advection through the peak and outward diffusion, the horizontal terms in the N$_2$O conservation equation can be approximated by:

$$\nabla \cdot (\bar{u} N_2O) \approx \frac{U}{\Delta x} \left( N_2O^{out} - N_2O \right) \text{ (advection)}$$

$$\nabla \cdot K_h \nabla N_2O \approx \frac{2K_h}{\Delta x^2} \left( N_2O^{out} - N_2O \right) \text{ (diffusion)}$$

Here $U$ is the scale for horizontal advection into the OMZ (0.01 m/s), $\Delta x$ the horizontal distance for typical horizontal gradients around the N$_2$O peak (500 km), $K_h$ a typical eddy horizontal diffusion (1000 m$^2$/s). The constant 2 in the diffusive term is a geometric factor that arises from assuming diffusion outwards of the N$_2$O peak in the $x$ direction, and homogeneity in the $y$ direction. This geometric factor could be different for different geometric assumptions and remains irrelevant the purpose of the scaling.

Combination of the advective and diffusive terms produces a typical restoring timescale for the N$_2$O profile given by:

$$\tau = \left( \frac{U}{\Delta x} + \frac{2K_h}{\Delta x^2} \right)^{-1}$$
By using the typical values above, the timescale $\tau$ becomes $\sim 1.1$ yr, and appears to be dominated by advective terms (timescale of $\sim 1.6$ yr) rather than diffusive (timescale $\sim 4$ yr). Note that the scale of $U$ chosen is probably large for the OMZ, and $\Delta x$ relatively small, meaning that $\tau$ is likely a conservative low estimate, and restoring timescales of several years could be possible.

Following this analysis, we tested the influence of the horizontal restoring term of the form:

$$\text{restoring} \approx \tau^{-1}(N_2O^{\text{out}} - N_2O)$$

in both the $N_2O$ production estimate from observations (see Estimate of $N_2O$ production rates) and the 1D biogeochemical model (see One dimensional biogeochemistry model of the ETNP OMZ).

We found that in both cases the impact on the net production rates is minimal (Fig. S3). While smaller than the vertical terms, the horizontal terms provide an additional $N_2O$ sink around the peak so that, to maintain the observed $N_2O$ concentration magnitude, these terms must be balanced by an increased net (biological) source. Thus, excluding the horizontal terms provides a lower estimate of the cycling rates around the $N_2O$ peak.

Lastly, a full sensitivity analysis of the three physical representations included in the model – vertical diffusion, upwelling, and horizontal restoration – was performed by varying the vertical advection velocity, diffusion coefficient, and horizontal restoring timescale (Table S2, Fig. S2). Station 3 is displayed, but all three stations show the same trends. These figures show the magnitude of the maximum imbalance in $N_2O$ production at the top of the OMZ. By this analysis, (1) vertical diffusion should dominate both other
terms, and has to be very low to reduce the imbalance to less than 1 nmol L⁻¹ d⁻¹, and (2) the horizontal terms are negligible unless restoring scales are reduced to < 1 yr, at which point this acts as a net sink of N₂O and requires an increase of the net imbalance rate to reproduce concentration observations.
Fig. S1. ETNP biogeochemistry.
Biogeochemical section for (top) oxygen, (middle) N$_2$O, and (bottom) NO$_2^-$ concentrations. Inset shows map of stations along with waypoints A–E corresponding to sections as shown. Filled points denote concentration sampling sites and orange asterisks indicate the 3 stations at which rate experiments were conducted.
Fig. S2. Model sensitivity of Sta. 3 imbalance of sources and sinks to physical parameters.
The N₂O imbalance (nmol L⁻¹ d⁻¹) at the peak N₂O concentration are shown for varying vertical diffusion and (top) upwelling velocities and (bottom) horizontal restoration time scales. Vertical diffusion is the overwhelmingly important term, and, for commonly observed diffusivity values, a net source > 1 nmol L⁻¹ d⁻¹ can be generated regardless of upwelling velocity or horizontal physics.
Fig. S3. 1–D profiles of modeled sources and sinks.
Average contributions to overall N₂O sources (src) and sinks via biology and physics for the model runs that include a parameterization of horizontal transport and vertical advection and diffusion.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>$w_{\text{sink}}$</td>
<td>Particulate sinking velocity</td>
<td>$1.2 \times 10^{-4}$ m s$^{-1}$</td>
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<tr>
<td>$w_{\text{up}}$</td>
<td>Upwelling velocity</td>
<td>$8 \times 10^{-7}$ m s$^{-1}$</td>
</tr>
<tr>
<td>$D_z$</td>
<td>Turbulent diffusivity</td>
<td>$4 \times 10^{-5}$ m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$r_{\text{P}:\text{C}}^{\text{rem}}$</td>
<td>Redfield stoichiometry (51)</td>
<td>1/106</td>
</tr>
<tr>
<td>$r_{\text{P}:\text{C}}^{\text{den}}$</td>
<td>Redfield stoichiometry (51)</td>
<td>1/106</td>
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<tr>
<td>$r_{\text{N}:\text{C}}^{\text{rem}}$</td>
<td>Redfield stoichiometry (51)</td>
<td>16/106</td>
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<td>Anderson denit. stoichiometry (52, 53)</td>
<td>104/106</td>
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<tr>
<td>$r_{\text{O}_2:\text{C}}^{\text{rem}}$</td>
<td>Anderson stoichiometry (52)</td>
<td>150/106</td>
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<tr>
<td>$k_{\text{rem}}$</td>
<td>Remineralization rate constant</td>
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<tr>
<td>$K_{\text{O}_2}$</td>
<td>Nitrification O$_2$ half saturation constant (12)</td>
<td>$4$ µmol L$^{-1}$</td>
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<td>$K_{\text{N}_2\text{O}}^{\text{Nev}}$</td>
<td>Nitrification O$_2$ threshold</td>
<td>$2^\dagger$ µmol L$^{-1}$</td>
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<td>$a_1$</td>
<td>Nevison nitrification O$_2$ parameter (21)</td>
<td>0.26 µmol L$^{-1}$</td>
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<tr>
<td>$b_1$</td>
<td>Nevison nitrification parameter (21)</td>
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<td>Denitrification rate constant</td>
<td>$1.9 \times 10^{-7}$ s$^{-1}$</td>
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<td>$K_{\text{NO}_3^-}$</td>
<td>Denitrification NO$_3^-$ half saturation constant</td>
<td>$5$ µmol L$^{-1}$</td>
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<td>$k_{\text{N}_2\text{O}}^{\text{Yam}*}$</td>
<td>N$_2$O consumption constant (19)</td>
<td>$6.0 \times 10^{-9}$ s$^{-1}$</td>
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<tr>
<td>$k_{\text{N}_2\text{O}}^{\text{fast}*}$</td>
<td>N$_2$O consumption to match observations</td>
<td>$1.8 \times 10^{-6}$ s$^{-1}$</td>
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<td>$K_{\text{O}_2}^{\text{den}}$</td>
<td>N$_2$O production O$_2$ poisoning (26)</td>
<td>$1$ µmol L$^{-1}$</td>
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<td>$K_{\text{O}_2}^{\text{sink}}$</td>
<td>N$_2$O consumption O$_2$ poisoning (26)</td>
<td>$0.3$ µmol L$^{-1}$</td>
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**Table S1. Parameters used in 1D model.**

Models incorporated values as shown, with references where appropriate. $^\dagger$We used a lower nitrification cutoff than $4$ µmol L$^{-1}$ O$_2$ per Nevison et al. (21), to be more in line with observations by Martens-Habbena et al. (12). *Original model used a slower N$_2$O consumption rate parameterized as in Yamagishi et al. (19) as a net rate, but the new model required a faster consumption term to match observed rates.
<table>
<thead>
<tr>
<th>Model</th>
<th>Baseline</th>
<th>With horizontal restoration</th>
<th>Varying BGC parameters only</th>
<th>No denitrification production</th>
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<tr>
<td>$[\text{N}<em>2\text{O}]</em>{\text{max}}$ (nM)</td>
<td>113 ± 34</td>
<td>96 ± 26</td>
<td>120 ± 34</td>
<td>74 ± 26</td>
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<tr>
<td>$z_{[\text{N}<em>2\text{O}]</em>{\text{max}}}$ (m)</td>
<td>133 ± 24</td>
<td>156 ± 35</td>
<td>135 ± 5</td>
<td>128 ± 23</td>
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<tr>
<td>SMS$\text{max}$ (nM/d)</td>
<td>0.62 ± 0.27</td>
<td>0.68 ± 0.29</td>
<td>0.65 ± 0.23</td>
<td>0.26 ± 0.13</td>
</tr>
<tr>
<td>$z_{\text{SMS}}$ (m)</td>
<td>162 ± 31</td>
<td>168 ± 33</td>
<td>163 ± 6</td>
<td>158 ± 31</td>
</tr>
<tr>
<td>$\Delta z$ offset (m)</td>
<td>29 ± 9</td>
<td>13 ± 17</td>
<td>29 ± 5</td>
<td>30 ± 9</td>
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<tr>
<td>$[\text{O}_2]$ @ $[\text{N}<em>2\text{O}]</em>{\text{max}}$ (µM)</td>
<td>10.1 ± 2.7</td>
<td>3.4 ± 1.7</td>
<td>9.1 ± 2.6</td>
<td>14.6 ± 2.5</td>
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<tr>
<td>$[\text{O}_2]$ @ SMS$\text{max}$ (µM)</td>
<td>1.6 ± 0.6</td>
<td>1.4 ± 0.6</td>
<td>1.5 ± 0.7</td>
<td>2.5 ± 0.5</td>
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Table S2. $\text{N}_2\text{O}$ profile characteristics under different modeling schemes.
Concentration and net sources minus sinks (SMS) peak characteristics for each of the Monte Carlo run types are shown. Brackets indicate concentrations of parameters, SMS the net $\text{N}_2\text{O}$ production rate, $z$ the depth, and $\Delta z$ offset indicates how much deeper the SMS rate maximum is compared with the $\text{N}_2\text{O}$ concentration maximum. The baseline model is the 1–D model used throughout the paper and described in the SOM. Model changes are included as headers, with BGC an abbreviation for biogeochemistry.
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<th>Sta.</th>
<th>Depth (m)</th>
<th>[N₂O] (nM)</th>
<th>[NO₂⁻] (µM)</th>
<th>R* (nM/d)</th>
<th>P* (nM/d)</th>
<th>Net (nM/d)</th>
<th>Turnover (d)</th>
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</table>

**Table S3. Biogeochemical measurements in the ETNP**

Concentration and reduction rate (R) measurements from the 3 stations in the ETNP. Calculated production rates (P) and the net (P – R) are included. The turnover time is calculated as the N₂O concentration divided by the reduction rate if net N₂O sink or by the production rate if net source.
References


