Pathways of Nitrous Oxide Production in the Eastern Tropical South Pacific Oxygen Minimum Zone

Daniel McCoy¹, Pierre Damien¹, Daniel J Clements¹, Simon Yang¹, Daniele Bianchi², Annie Bourbonnais³, Laura Bristow⁴, Pearse Buchanan⁵, Phyllis Lam⁶, Andrew Babbin⁷, Emily Zakem⁸, and Colette Kelly⁹

¹UCLA
²University of California Los Angeles
³University of South Carolina
⁴University of Southern Denmark
⁵University of Liverpool
⁶University of Southampton
⁷Massachusetts Institute of Technology
⁸Carnegie Institution for Science
⁹Stanford University, Department of Earth System Science

December 9, 2022

Abstract

Oceanic emissions of nitrous oxide (N₂O) account for roughly one-third of all natural sources to the atmosphere. Hot-spots of N₂O outgassing occur over oxygen minimum zones (OMZs), where the presence of steep oxygen gradients surrounding anoxic waters leads to enhanced N₂O production from both nitrification and denitrification. However, the relative contributions from these pathways to N₂O production and outgassing in these regions remains poorly constrained, in part due to shared intermediary nitrogen tracers, and the tight coupling of denitrification sources and sinks. To shed light on this problem, we embed a new, mechanistic model of the OMZ nitrogen cycle within a three-dimensional eddy-resolving physical-biogeochemical model of the ETSP, tracking contributions from remote advection, atmospheric exchange, and local nitrification and denitrification. Our results indicate that net N₂O production from denitrification is approximately one order of magnitude greater than nitrification within the ETSP OMZ. However, only ~30% of denitrification-derived N₂O production ultimately outgasses to the atmosphere in this region (contributing ~34% of the air-sea N₂O flux on an annual basis), while the remaining is exported out of the domain. Instead, remotely-produced N₂O advected into the OMZ region accounts for roughly half (~56%) of the total N₂O outgassing, with smaller contributions from nitrification (~7%). Our results suggests that, together with enhanced production by denitrification, upwelling of remotely-derived N₂O (likely produced via nitrification in the oxygenated ocean) contributes the most to N₂O outgassing over the ETSP OMZ.
Pathways of Nitrous Oxide Production in the Eastern Tropical South Pacific Oxygen Minimum Zone

Daniel McCoy¹, Pierre Damien¹, Daniel Clements¹, Simon Yang¹, Daniele Bianchi¹

¹Department of Atmospheric and Oceanic Sciences
¹University of California – Los Angeles
¹520 Portola Plaza, Los Angeles, CA 90095, USA

Key Points:

• In the eastern tropical South Pacific Oxygen Minimum Zone, denitrification is the dominant source of N₂O production.
• Tropical subsurface currents supply N₂O to the region, fueling N₂O emissions to the atmosphere.
• Significant amounts of locally-produced N₂O escape outgassing and are exported to the subtropical gyre.

Corresponding author: Daniel McCoy, demccoy@atmos.ucla.edu
Oceanic emissions of nitrous oxide (N$_2$O) account for roughly one-third of all natural sources to the atmosphere. Hot-spots of N$_2$O outgassing occur over oxygen minimum zones (OMZs), where the presence of steep oxygen gradients surrounding anoxic waters leads to enhanced N$_2$O production from both nitrification and denitrification. However, the relative contributions from these pathways to N$_2$O production and outgassing in these regions remains poorly constrained, in part due to shared intermediary nitrogen tracers, and the tight coupling of denitrification sources and sinks. To shed light on this problem, we embed a new, mechanistic model of the OMZ nitrogen cycle within a three-dimensional eddy-resolving physical-biogeochemical model of the ETSP, tracking contributions from remote advection, atmospheric exchange, and local nitrification and denitrification. Our results indicate that net N$_2$O production from denitrification is approximately one order of magnitude greater than nitrification within the ETSP OMZ. However, only $\sim$30% of denitrification-derived N$_2$O production ultimately outgasses to the atmosphere in this region (contributing $\sim$34% of the air-sea N$_2$O flux on an annual basis), while the remaining is exported out of the domain. Instead, remotely-produced N$_2$O advected into the OMZ region accounts for roughly half ($\sim$56%) of the total N$_2$O outgassing, with smaller contributions from nitrification ($\sim$7%). Our results suggests that, together with enhanced production by denitrification, upwelling of remotely-derived N$_2$O (likely produced via nitrification in the oxygenated ocean) contributes the most to N$_2$O outgassing over the ETSP OMZ.

1 Introduction

Nitrous oxide (N$_2$O) is a powerful greenhouse gas that is roughly 300 times more potent than carbon dioxide (CO$_2$) and is projected to become the most important ozone-depleting anthropogenic emission by the end of the 21st century (Ravishankara et al., 2009; IPCC, 2013). Recent analyses of the global N$_2$O budget over the decade of 2007 - 2016 suggest that anthropogenic emissions are responsible for up to 40% of total N$_2$O sources to the atmosphere, mostly from agriculture, whereas outgassing from the ocean accounts for roughly 20% (Canadell et al., 2021). The production of N$_2$O in the ocean is linked to the remineralization of organic matter (OM) via both aerobic and anaerobic pathways, and, as a consequence, is tightly coupled to the oceanic oxygen (O$_2$) distribution (Freing et al., 2012; Arévalo-Martínez et al., 2015; Babbin et al., 2015; Ji et al., 2015; Yang et al., 2020). While in large parts of the surface ocean N$_2$O concentrations are close to saturation, the most intense hot-spots of N$_2$O air-sea flux are found in the Eastern Tropical North Pacific (ETNP), the Eastern Tropical South Pacific (ETSP), and the Arabian Sea, where high organic matter export rates and sluggish lateral circulation results in steep O$_2$ gradients that surround anoxic (here defined as O$_2$ < 5 mmol m$^{-3}$) waters also known as oxygen minimum zones (OMZs) (Codispoti, 2010; Arévalo-Martínez et al., 2015; Ji et al., 2018; Yang et al., 2020). Although OMZ regions only account for roughly 1% of the total ocean volume, the dynamic marine nitrogen cycling that occurs there results in up to 50% of total oceanic N$_2$O emissions (Codispoti, 2010; Arévalo-Martínez et al., 2015; Babbin et al., 2015; Yang et al., 2020).

The ETSP hosts the second largest OMZ by area and comprises the Humboldt Current System, one of the four major Eastern Boundary Upwelling Systems, which extends from the southern extent of Chile ($\sim$45ºS) to northern Peru ($\sim$4ºS) (Chavez & Messié, 2009; Santoro et al., 2021). While southern Chile experiences more intense upwelling during boreal summer (Pennington et al., 2006), upwelling-favorable conditions exist year-round along the Peruvian and northern Chile coastlines, fueling high rates of surface primary productivity, organic matter export (Chavez & Messié, 2009), and subsurface O$_2$ depletion. The ETSP OMZ is located in the South Pacific tropical shadow zone of the thermocline (Luyten et al., 1983), which extends westward from the eastern boundary between the equatorward edges of the subtropical gyres. This limits the supply of oxy-
gen from the ventilated subtropical gyres to the OMZs, and leaves the relatively $O_2$-rich eastward tropical currents such as the Equatorial Undercurrent (EUC) and the Southern Subsurface Countercurrents (SSCC) as the major advective sources of $O_2$ to the equatorward side of the ETSP OMZ (Karsten et al., 2008; Stramma et al., 2010). While these advective pathways are reinforced by lateral $O_2$ supply from mesoscale eddies (Gnanadesikan et al., 2013; Bettencourt et al., 2015), $O_2$ remains depleted within the OMZ core (Kwiecinski & Babbin, 2021), leading to functional anoxia (Thamdrup et al., 2012), fixed nitrogen loss, a pronounced subsurface nitrite ($NO_2^-$) maximum, and a strong nitrogen deficit (Kalvelage et al., 2013). An additional characteristic of the ETSP is the relatively sharp transition from anoxic to suboxic ($5 \text{ mmol m}^{-3} < O_2 < 10 \text{ mmol m}^{-3}$) waters along the OMZ boundary. These $O_2$ gradients host both aerobic (i.e., nitrification) and anaerobic (i.e., denitrification) nitrogen cycle transformations, ultimately leading to $N_2O$ supersaturation in the layers surrounding the anoxic core (Babbin et al., 2015; Kock et al., 2016). Uptaking of these waters to the surface likely contributes to the local hot-spot of $N_2O$ outgassing in the ETSP, as shown by observational and modeling studies (Arévalo-Martínez et al., 2015; Ji et al., 2018; Yang et al., 2020).

Nitrification is a two-step process that occurs within the oxygenated water column wherein ammonium ($NH_4^+$) produced from remineralization of organic matter (pathway 1 in Figure 1) is oxidized by $O_2$ to $NO_3^-$ and subsequently to nitrate ($NO_3^-$) by $NH_4^+$-oxidizing bacteria and archaea and $NO_2^-$-oxidizing bacteria, respectively (pathways 2 and 4, respectively) (Lam & Kuypers, 2011). Nitrification-derived $N_2O$ occurs as a byproduct of $NH_4^+$ oxidation (pathway 3), resulting in a positive correlation between apparent oxygen utilization (AOU) and supersaturated $N_2O$ concentrations in many areas of the ocean (Cohen & Gordon, 1978; Walter et al., 2006), a process that has been further quantified by active production of $^{15}N_2O$ in $^{15}N$ tracer incubation experiments (Yoshida et al., 1989). The ratio of $N_2O$ yield to $NO_2^-$ yield from $NH_4^+$ oxidation has been observed to increase at decreasing $O_2$ concentrations in cultures with $NH_4^+$-oxidizing bacteria and archaea (Goreau et al., 1980; Lösher et al., 2012), likely leading to enhanced nitrification-derived $N_2O$ production within the steep suboxic gradients above and below the anoxic core of OMZs (Nevison et al., 2003; Ji et al., 2015, 2018; Santoro et al., 2021).

Besides $N_2O$ production via the nitrification pathway, $N_2O$ also forms as an intermediary product of step-wise denitrification ($NO_3^-$ to $NO_2^-$ to $N_2O$ to $N_2$) under suboxic and anoxic conditions (pathways 5 - 7 in Figure 1). Within the anoxic core of OMZs, widespread consumption of $N_2O$ occurs via $N_2O$ reduction — the only known process able to remove $N_2O$ from the water column. However, recent studies have highlighted how the different steps, each mediated by distinct enzymes and likely different microorganisms (Ganesh et al., 2014; Kuypers et al., 2018), are subject to variable $O_2$ sensitivities wherein $NO_3^-$, $NO_2^-$, and $N_2O$ reduction become progressively less $O_2$ tolerant (Körner & Zumft, 1989; Kalvelage et al., 2011; Dalsgaard et al., 2014; Babbin et al., 2015; Ji et al., 2015). Therefore, the same suboxic gradients that lead to enhanced $N_2O$ production from nitrification can also lead to $N_2O$ accumulation from denitrification, as $NO_2^-$ reduction proceeds while $N_2O$ reduction is inhibited, in a process referred to as “incomplete” denitrification (Babbin et al., 2015).

The coupled production of $N_2O$ at low $O_2$ from nitrification and denitrification, and their shared $NO_2^-$ intermediary, complicate the interpretation of in situ observations from OMZs (Ji et al., 2015, 2018; Santoro et al., 2021). Observations of $N_2O$ and $NO_2^-$ in these regions typically reveal an OMZ anoxic core layer characterized by a secondary $NO_2^-$ maximum and undersaturated $N_2O$ concentrations, suggesting coupled step-wise denitrification. Supersaturated concentrations of $N_2O$ in the bounding suboxic gradients (the upper and lower oxyclines) have been linked to the enhanced production by nitrification (Cohen & Gordon, 1978). Yet, studies have noted the lack of a linear relationship with AOU and high abundances of gene markers for $NO_2^-$ reduction as evidence
Figure 1. Schematic of the oceanic nitrogen cycle (ignoring biological uptake) as represented in ROMS. Transformation pathways include: (1, $R_{\text{rem}}$) oxic remineralization of nitrogen in organic matter (OrgN) to ammonium; (2, $R_{\text{no}}$) ammonium oxidation to nitrite; (3, $R_{\text{no}2\text{O}}$) ammonium oxidation to nitrous oxide; (4, $R_{\text{no}}$) nitrite oxidation; (5, $R_{\text{den1}}$) nitrate reduction; (6, $R_{\text{den2}}$) nitrite reduction; (7, $R_{\text{den3}}$) decomposed nitrous oxide reduction; (8, $\Phi_{\text{n2O}}$) decomposed nitrous oxide air-sea flux; (9, $\Phi_{\text{n2}}$) dinitrogen air-sea flux; and (10, $R_{\text{ax}}$) anaerobic ammonium oxidation (anammox). Colored arrows correspond to the sources and sinks of the decomposed N$_2$O tracers (N$_2$O$_{\text{den}}$, N$_2$O$_{\text{nit}}$, N$_2$O$_{\text{bou}}$, and N$_2$O$_{\text{atm}}$) discussed in Section 2.4.

However, while progressive O$_2$ tolerances for denitrification have been documented (Dalsgaard et al., 2014), biogeochemical models predominantly employ simple parameterizations representing N$_2$O production as a function of nitrification, whereas denitrification is typically modelled with a lack of N$_2$O production or as a net sink of N$_2$O at low O$_2$ (Sutharalingam et al., 2000; Jin & Gruber, 2003; Ji et al., 2018; Battaglia & Joos, 2018). Other studies have highlighted the importance of resolving O$_2$-dependent decoupling of N$_2$O production and consumption (Babbin et al., 2015), suggesting that N$_2$O production rates from denitrification may be up to two orders of magnitude larger than those from nitrification near the core of OMZs, albeit closely balanced by N$_2$O reduction to dinitrogen gas (N$_2$). Thus, incomplete denitrification may account for a production source that is poorly represented in most biogeochemical ocean and climate models.

While the uncertainty surrounding N$_2$O production in the ocean has been reduced in recent years following improved estimates of ocean (Yang et al., 2020), terrestrial, and anthropogenic N$_2$O sources (Canadell et al., 2021; Tian et al., 2020), barriers remain in
accurately projecting future air-sea flux because of poorly constrained contributions from
the nitrification and denitrification pathways. The observed expansion of OMZs (Stramma
et al., 2008; Schmidtke et al., 2017; Oschlies et al., 2018) is expected to continue over
the 21st century, although the extent of future changes in low O₂ and anoxic water vol-
umes remain uncertain (Cabrè et al., 2015; Bianchi et al., 2018; Busecke et al., 2021).
Therefore, accurate parameterization of N₂O cycling in global ocean models is crucial
in simulating realistic future scenarios, and a better understanding of the physical and
biogeochemical mechanisms and relative contributions from both production pathways
is warranted. This is particularly critical given that OMZ regions continue to be poorly
resolved in current global Earth system models (Cabrè et al., 2015; Busecke et al., 2021;
Séférian et al., 2020), which generally struggle to capture the role of fine-scale circula-
tion such as the zonal jet systems that ventilate the tropical Ocean (Kessler, 2006; Duteil
et al., 2014; Busecke et al., 2019; Duteil et al., 2021).

To address these sources of uncertainty, we implement a new model of the OMZ
nitrogen cycle (NitrOMZ) (Bianchi et al., 2022) into an eddy-resolving three-dimensional
(3-D) regional ocean model of the ETSP that simulates local N₂O production from ni-
trification and denitrification. The new model, constrained by in situ ETSP observations
of nitrogen cycle tracers and rates, allows for an examination of the N₂O balance within
a characteristic OMZ upwelling region. To attribute the sources of N₂O outgassing flux
to different processes, we use the 3-D model to track contributions from local air-sea gas
exchange, advection into the domain from the boundaries, and production by nitrifica-
tion and denitrification. This analysis reveals the importance of incomplete denitrifica-
tion and transport of remotely-generated N₂O for air-sea fluxes, with implications for
future N₂O emissions in a changing ocean.

The rest of the paper is organized as follows: Section 2 describes the 3-D model
configuration and setup, a brief summary of N₂O production pathways in NitrOMZ, and
the N₂O tracer decomposition strategy; Section 3 provides a short validation of model
solutions, summarizes the results of the simulations, and describes the ETSP N₂O bal-
ance; Section 4 discusses the results and implications, and concludes the paper.

2 Modelling Methods and Validation

2.1 Physical Model Configuration and Forcing

The physical component of the model consists of the Regional Ocean Modeling Sys-
tem (ROMS) (Shchepetkin & McWilliams, 2005; Shchepetkin, 2015), a primitive-equation,
hydrostatic, topography-following general ocean circulation model. The model domain
extends from -111.38°W to -66.62°W and from 42.52°S to 3.41°N and is chosen to re-
solve key oceanographic features of the ETSP such as the EUC (Figure 2c), the wind-
driven South Pacific gyre (contour lines in Figure 2a and 2b), and the horizontal extent
of the OMZ (Figure 3a). Its grid consists of 402 x 502 points with a nominal resolution
of 10 kilometers and 42 topography-following vertical levels with higher resolution at the
surface and bottom. The model time-step is 800 seconds, and output is saved as monthly
means.

For this study, low-frequency interannual variability is ignored to instead focus on
a climatological steady-state. Initial conditions and monthly climatological boundary forc-
ing (applied at the northern, western, and southern boundaries) for temperature, salini-
ity, surface elevation, and horizontal velocity are taken from an existing Pacific-wide ROMS
simulation (Lemarié et al., 2012). Normal-year-forcing of daily freshwater and turbulent
heat fluxes are estimated using bulk formulae (Large, 2006) applied to ERA-interim (ERAi)
reanalysis data for the year 1979 (Simmons et al., 2006; Dee et al., 2011). Because of known
biases in ERAi shortwave (overestimate) and longwave (underestimate) fluxes (Brodeau
et al., 2010), we applied the DRAKKAR Forcing Set version 5.2 corrections to heat flux
terms (Dussin et al., 2014). Daily climatological wind stress is taken from the QuickSCAT-based Scatterometer Climatology of Ocean Winds (Risien & Chelton, 2008). The resulting simulation produces an overall similar climatological picture of the hydrographic properties, gyre circulation, and equatorial current structure of the ETSP (Figure 2a - c) when compared to validation products (Figure 2d - f).

Figure 2. (a,d) Annually averaged sea-surface temperature from ROMS model years 46 - 50 (top) and World Ocean Atlas 2018 (bottom). Contours highlight sea-surface height at 5 cm intervals, with validation data obtained by averaging AVISO data between 2000 to 2018. Dashed lines mark the transect location in panels (c) and (f). (b,e) Same as in panels (a) and (d), but for sea-surface salinity; contours highlight calculated geostrophic velocity streamlines, with validation data derived from AVISO. (c,f) Zonal velocity sections along the equator at 95°W from ROMS (top) and Johnson et al. (2002) (bottom).

2.2 Biogeochemical Model Configuration and Forcing

The physical model is coupled online to the Biogeochemical Elemental Cycling (BEC) model from Moore et al. (2004) using the same equations and parameter settings as in Frischknecht et al. (2017) with the exception of the nitrogen cycling component, which was expanded for the NitrOMZ model (Bianchi et al., 2022). NitrOMZ explicitly resolves the main set of nitrogen cycle transformations associated with the remineralization of sinking OM in low O₂ environments (summarized in Figure 1). These include the chemolithotrophic reactions associated with nitrification: aerobic NH₄⁺ oxidation to both N₂O (Rₕₔ), and NO₂⁻ (Rₕₒ), and aerobic NO₂⁻ oxidation to NO₃⁻ (Rₕ₃). Anaerobic NH₄⁺ oxidation with NO₂⁻ to N₂ (anammox, Rₚ₃) is also represented. Additionally, NitrOMZ partitions the OM remineralization cycle in ROMS-BEC to include three additional heterotrophic denitrification steps: NO₃⁻ reduction to NO₂⁻ (Rₚ₄), NO₂⁻ reduction to N₂O (Rₚ₅), and N₂O reduction to N₂ (Rₚ₆). The treatment of OM in the model is outlined in support-
ing information S1, with chemolithotrophic and heterotrophic reactions summarized in S2. Notably, the model expands BEC by allowing for the production of N\(_2\)O via both nitrification and incomplete denitrification pathways (Section 2.2.1).

Initial conditions and boundary forcing of biogeochemical nutrient concentrations (NO\(_3^−\), PO\(_4^{3−}\), Si(OH)\(_4^{-}\) and O\(_2\)) are taken from monthly climatological observations from the 2013 World Ocean Atlas (H. E. Garcia, Boyer, et al., 2013; H. E. Garcia, Locarnini, et al., 2013); NH\(_4^+\), NO\(_3^−\), and N\(_2\)O boundary conditions are set to 0 but adjust rapidly within the domain. Iron data were taken from the Community Earth System Model (CESM) as in Deutsch et al. (2021), and DIC/Alkalinity were extracted from GLODAP (Lauvset et al., 2016) with a reference year of 2002. Initial and monthly boundary conditions for N\(_2\)O were provided from a 3-D reconstruction based on in situ data from recent cruises to the ETSP (Kalvelage et al., 2013; Ji et al., 2015; Peng et al., 2016; Babin et al., 2017, 2020), and the MEMENTO databases (Kock & Bange, 2015) and GLODAP (Olsen et al., 2016) with a reference year of 2002. Initial and monthly boundary conditions for NO\(_2\) were taken from monthly climatological observations from the Community Earth System Model (CESM) as in Deutsch et al. (2021), and DIC/Alkalinity were extracted from GLODAP (Lauvset et al., 2016; Lauvset et al., 2016), which we extrapolate to the model domain using the same machine learning approach as described in Yang et al. (2020).

### 2.2.1 NitrOMZ N\(_2\)O Production

Production of N\(_2\)O via nitrification in NitrOMZ is modelled as a by-product of NH\(_4^+\) oxidation \((R_{\text{ao}}^{\text{n2o}}\), pathway 3 in Figure 1), with enhanced yields at lower O\(_2\) concentrations. Both nitrification steps (i.e. NO\(_2^−\) oxidation) are suppressed near the surface by light inhibition (see supporting information S4) and competition for NH\(_4^+\) and NO\(_2^−\) from phytoplankton as in Frischknecht et al. (2017). Therefore, nitrification is largely restricted to below the euphotic zone while also being suppressed at low O\(_2\). The partitioning between N\(_2\)O and NO\(_2^−\) production from \(R_{\text{ao}}\) is calculated using the function proposed by Nevison et al. (2003), derived by fitting measured N\(_2\)O and NO\(_2^−\) yields \((f_{\text{ao}}^{\text{n2o}}\) and \(f_{\text{ao}}^{\text{no2}}\), respectively) to oxygen concentrations (Goreau et al., 1980):

\[
\frac{f_{\text{ao}}^{\text{n2o}}}{f_{\text{ao}}^{\text{no2}}} = 0.01 \cdot \frac{a}{[\text{O}_2]} + b, \tag{1}
\]

Relative to the original parameterization by Nevison et al. (2003), we apply distinct values of the parameters \(a\) and \(b\) to reflect results from a series of in situ measurements of N\(_2\)O production from the ETSP and ETNP OMZs (Ji et al., 2015, 2018; Santoro et al., 2021) (see Section 2.3.1). N\(_2\)O production by nitrification, in units of mmol N m\(^{-3}\) s\(^{-1}\), is therefore represented as:

\[
R_{\text{ao}}^{\text{n2o}} = R_{\text{ao}} \cdot f_{\text{ao}}^{\text{n2o}}, \tag{2}
\]

with a similar function for NO\(_2^−\) production.

In the denitrification pathway, N\(_2\)O is produced via NO\(_2^−\) reduction at low O\(_2\):

\[
R_{\text{den}}^{\text{n2o}} = f_{\text{den2}} \cdot R_{\text{rem}}^{\text{tot}} \cdot Q_{\text{den}}^{C:N}, \tag{3}
\]

where \(f_{\text{den2}}\) is the local fraction of total OM remineralization \((R_{\text{rem}}^{\text{tot}})\) routed to NO\(_2^−\) reduction (see supporting information S2), and \(Q_{\text{den}}^{C:N}\) the carbon to nitrogen ratio from denitrification (472/2/106) following Anderson and Sarmiento (1994). Similarly, N\(_2\)O is consumed via N\(_2\)O reduction to N\(_2\) at low O\(_2\):

\[
R_{\text{den3}}^{\text{n2o}} = f_{\text{den3}} \cdot R_{\text{rem}}^{\text{tot}} \cdot Q_{\text{den}}^{C:N}. \tag{4}
\]

Net production of N\(_2\)O \((R_{\text{net}}^{\text{n2o}}\) in units of mmol N\(_2\)O m\(^{-3}\) s\(^{-1}\)) results by the combination of nitrification (equation (2)) and the residual between NO\(_2^−\) and N\(_2\)O reduction (equation (3) minus equation (4)):

\[
R_{\text{net}}^{\text{n2o}} = 0.5 \cdot (R_{\text{ao}}^{\text{n2o}} + R_{\text{den2}}^{\text{n2o}}) - R_{\text{den3}}^{\text{n2o}}. \tag{5}
\]
2.3 Biogeochemical Validation

To validate the biogeochemical tracer distributions simulated by ROMS-BEC, we gathered O$_2$, NO$_3^-$, PO$_4^{3-}$, and N$^*$ (defined as 16$\times$[NO$_3^-$] - [PO$_4^{3-}$]) reconstructions from World Ocean Atlas 2018 (H. Garcia et al., 2019a) (Figures S1 - S4); additional O$_2$ estimates were provided by Dunn (2012) and Bianchi et al. (2012). Estimates of 3-D NO$_2^-$ and N$_2$O were obtained from in situ observations (Kock & Bange, 2015; Lauvset et al., 2016), and extrapolated using a machine learning approach as outlined in Yang et al. (2020) (Figures S5 - S6). Annually averaged maps of net primary production (NPP) were obtained using three different productivity algorithms, which included the Epplery Vertically Generalized Production Model (Eppley-VGPM) (Behrenfeld & Falkowski, 1997), the updated Carbon-Based Productivity Model (CbPM2) (Behrenfeld et al., 2005) and the Carbon, Absorption, and Fluorescence Euphotic-resolving model (CAFE) (Siilbe et al., 2016) (Figure S7). Level 3 satellite chlorophyll-a concentration data were obtained from the NASA Ocean Color data center (Figure S8), with all of the satellite-based data (including NPP) obtained from the Ocean Productivity Group at Oregon State University. Additional model validation is discussed in Section 3.1.

2.3.1 Model Parameterization and Spinup

Further details on the formulation and parameterization of NitrOMZ are discussed in Bianchi et al. (2022). Briefly, we estimated uncertain model parameters by optimizing a one-dimensional version of the model against a cost functioned designed to evaluate squared errors between model estimates and local observations of tracers and N transformation rates from the ETSP (Kalvelage et al., 2013; Ji et al., 2015; Peng et al., 2016; Babbin et al., 2017, 2020). Based on the optimization, we implement a low-cost parameter set with good comparisons to observed N$_2$O and NO$_2^-$ profiles (Opt$_{sel}$ from Bianchi et al. (2022), with parameter values in Table S4) into ROMS-BEC. The model is initially run for 20 years before evaluating against the validation products discussed in Section 2.3 and in situ ETSP observations from Kalvelage et al. (2013), Cornejo and Farías (2012), and Krahmann et al. (2021).

Based on this first comparison, we applied additional tuning to (1) bring surface concentrations of NO$_2^-$ and NH$_4^+$ closer to zero and (2) increase the concentration of N$_2$O in suboxic waters to better match the magnitude of observed subsurface N$_2$O maxima in the ETSP OMZ. This was accomplished by (1) slightly increasing the maximum NH$_4^+$ and NO$_2^-$ oxidation rates ($k_{ao}$ and $k_{ano}$, respectively, see supporting information S2) and (2) slightly widening the difference between exponential O$_2$ inhibition thresholds for NO$_2^-$ and N$_2$O reduction ($K_{den2}^o$ and $K_{den3}^o$, respectively). We implement the final parameter set into ROMS-BEC and run a 50 year-long simulation to obtain a steady-state solution (Figure S9).

The choice of parameters results in a high NH$_4^+$ oxidation rate ($R_{ano}$) just below the euphotic zone that mostly produces NO$_3^-$ ($R_{ano}^{m3}$) due to high O$_2$ concentrations. As O$_2$ becomes scarce, $R_{ano}$ decreases, yet production of N$_2$O ($R_{ano}^{m2}$) relative to NO$_2^-$ increases following equations (1) and (2). Consumption of N$_2$O within anoxic waters occurs as all denitrification steps proceed without O$_2$ inhibition (consumption $>>$ production). Similar to Babbin et al. (2015) and Bianchi et al. (2022), we model a progressive O$_2$ inhibition of the three denitrification steps ($K_{den1}^{O2} > K_{den2}^{O2} > K_{den3}^{O2}$). Therefore, incomplete denitrification is allowed to occur at low but non-zero O$_2$ as NO$_3^-$ reduction and NO$_2^-$ reduction ($K_{den1}$ and $R_{den2}$, respectively) proceed while N$_2$O reduction ($R_{den3}$) is inhibited (consumption $< $ production).
2.4 $\text{N}_2\text{O}$ Balance and Tracer Decomposition

To track the evolution of $\text{N}_2\text{O}$ from different pathways, we decompose $\text{N}_2\text{O}$ into four tracers that keep track of $\text{N}_2\text{O}$ sources in the model domain:

$$\text{N}_2\text{O} = \text{N}_2\text{O}_{\text{den}} + \text{N}_2\text{O}_{\text{nit}} + \text{N}_2\text{O}_{\text{atm}} + \text{N}_2\text{O}_{\text{bou}}.$$  \hfill (6)

Each of the tracers in equation (6) follows a separate conservation equation (see supporting information S3), and is affected by a specific production process, by air-sea gas fluxes, transport from the boundaries, and destruction by the last step of denitrification ($\text{N}_2\text{O}$ reduction, $R_{\text{den}}$). By construction, the conservation equations for the individual tracers sum up to the conservation equation for $\text{N}_2\text{O}$ (equation (5)), so that equation (6) can be considered a linear tracer decomposition.

Specifically, $\text{N}_2\text{O}_{\text{nit}}$ tracks local production by nitrification ($R_{\text{as2o}}^{\text{n2o}}$, equation (2)) whereas $\text{N}_2\text{O}_{\text{den}}$ tracks production by denitrification ($R_{\text{den2o}}^{\text{n2o}}$, equation (3)) as outlined in Section 2.2.1 (pathways 3 and 6, respectively, in Figure 1). The remaining tracers, $\text{N}_2\text{O}_{\text{atm}}$ and $\text{N}_2\text{O}_{\text{bou}}$, are designed to track $\text{N}_2\text{O}$ originating from the atmosphere and from production sources outside the regional ROMS domain, respectively. Saturated $\text{N}_2\text{O}$ forced from the model boundaries (assuming an atmospheric $\text{N}_2\text{O}$ concentration of 300 ppb) can be interpreted as originating from air-sea equilibrium with the atmosphere, whereas supersaturated $\text{N}_2\text{O}$ is linked to production outside the regional model domain. We therefore split the $\text{N}_2\text{O}$ forced into the domain into a saturation component ($\text{N}_2\text{O}_{\text{atm}}$) and a supersaturation component ($\text{N}_2\text{O}_{\text{bou}}$) transported into the domain.

To close separate biogeochemical budgets for each $\text{N}_2\text{O}$ tracer, we similarly decomposed the $\text{N}_2\text{O}$ reduction rate ($R_{\text{den}}$, equation (4) and pathway 7 in Figure 1) and $\text{N}_2\text{O}$ air-sea flux ($\Phi_{\text{n2o}}$, pathway 8 in Figure 1) to track losses with respect to the decomposed $\text{N}_2\text{O}$ concentrations from within the domain:

$$R_{\text{den}} = R_{\text{den3}} + R_{\text{den3}} + R_{\text{den3}} + R_{\text{den3}}$$  \hfill (7)

$$\Phi_{\text{n2o}} = \Phi_{\text{n2o}} + \Phi_{\text{n2o}} + \Phi_{\text{n2o}} + \Phi_{\text{n2o}}$$  \hfill (8)

Here, each consumption term by denitrification is proportional to the individual tracer concentration in a linear fashion. Air-sea fluxes follow the same formulation as $\text{N}_2\text{O}$ modeled according to Wanninkhof (1992) using a constant atmospheric mixing ratio of 300 ppb, but with mixing ratios set to zero for all tracers except $\text{N}_2\text{O}_{\text{atm}}$, for which it is set to the total value. Therefore, while initially saturated at the boundaries, the concentration of $\text{N}_2\text{O}_{\text{atm}}$ can drop below saturation following consumption via $R_{\text{den}}$. When $\text{N}_2\text{O}$-undersaturated water is exposed to the surface, atmospheric in-gassing will increase $\text{N}_2\text{O}_{\text{atm}}$ until $\text{N}_2\text{O}$ reaches saturation. As such, $\text{N}_2\text{O}_{\text{atm}}$ tracks both domain ingassing of $\text{N}_2\text{O}$ and import of saturated $\text{N}_2\text{O}$ from the model boundaries, whereas $\text{N}_2\text{O}_{\text{bou}}$ exclusively tracks import of the supersaturation component. To initialize the decomposition, the initial 3-D $\text{N}_2\text{O}$ was separated into $\text{N}_2\text{O}_{\text{atm}}$ and $\text{N}_2\text{O}_{\text{bou}}$ while $\text{N}_2\text{O}_{\text{nit}}$ and $\text{N}_2\text{O}_{\text{den}}$ were set to zero everywhere; thus these tracers exclusively track production within the domain after initialization (Figure S10).

Finally, to elucidate the sources of $\text{N}_2\text{O}$ air-sea flux over the OMZ, we defined a budget domain that captures the extent of the ETSP OMZ horizontally (dashed blue box in Figure 3a) and vertically from the surface to 750 m depth. We configured ROMS output to close biogeochemical budgets within each grid cell, allowing us to scale them up to arbitrary 3-D domains within the model:

$$\frac{d[C]}{dt} = J + T - \Phi.$$  \hfill (9)

Here, $d[C]/dt$ is the climatological $\text{N}_2\text{O}$ rate of change calculated as the difference between snapshots at the beginning and end of each month; $T$ the transport component calculated as the divergence of advection/diffusion fluxes, $J$ the sum of biological sources and sinks, and $\Phi$ the air-sea flux controlled by gas exchange.
3 Results

3.1 Model Validation

Figure 3 shows the extent and thickness of the modelled OMZ from model years 46 - 50 (Figure 3a) and various validation products (Figure 3b - e). The simulated OMZ is centered offshore of the Peruvian and Ecuadorian coastline at roughly 8°S and extends from the Galapagos islands at the equator to nearly 15°S. This represents a displacement both equatorward and offshore compared to observations, which suggest a more coastal OMZ between southern Peru and Chile. The thickness of waters with less than 10 mmol O$_2$ m$^{-3}$ ranges mostly between 300 - 500 m and extends to roughly 105°W.

Considering that O$_2$ reconstructions based on spatial interpolation of in situ profiles underestimate the volume of anoxic waters (Bianchi et al., 2012), the inset bar plot in Figure 3a suggests that the ROMS simulation is overall within range of OMZ volume predictions across several thresholds ranging from 5 mmol O$_2$ m$^{-3}$ (Kwiecinski & Babbin, 2021) to 20 mmol O$_2$ m$^{-3}$ (H. Garcia et al., 2019a; Bianchi et al., 2012; Dunn, 2012).

Taking into account the slight equatorward geographic shift in the model OMZ, nitrogen tracer (NO$_3^-$, NO$_2^-$, and N$_2$O) sections at 250 m in Figure 4a - c compare well with validation products (Figure 4d - f). The simulation is able to replicate the expected draw-down of NO$_3^-$ and N$_2$O and increase in NO$_2^-$ within the core of the OMZ, characteristics of step-wise denitrification. The magnitude and spatial patterns of open ocean concentrations are similarly reproduced, such as the low NO$_3^-$ and N$_2$O concentrations observed in the subtropical gyre at 25°S. The oxic to suboxic transition zone (inshore of the 20 mmol O$_2$ m$^{-3}$ contour in Figure 4) also reveals an increase in N$_2$O concentrations that skillfully reproduces observational reconstructions discussed in Section 2.2.

The vertical subsurface structure and concentration magnitudes of nitrogen tracers in the ETSP OMZ are shown in Figure 4g - i. Model profiles centered over the OMZ.
Figure 4. (a-c) ROMS annually averaged NO$_3^-$, NO$_2^-$, and N$_2$O at 250 m from model years 46 - 50. Dashed black lines highlight the 20 mmol O$_2$ m$^{-3}$ contour. (d-f) NO$_3^-$, NO$_2^-$, and N$_2$O at 250 m from World Ocean Atlas 2018 and machine learning estimates, respectively. Grey markers show the location of shipboard samples. (g-i) Averaged profiles of NO$_3^-$, NO$_2^-$, and N$_2$O from ROMS (black curves) extracted from within the OMZ (red boxes in panels a - c). Shaded regions show the 10th/90th and 25th/75th percentiles of shipboard observations from Kalvelage et al. (2013), Cornejo and Farías (2012), and Krahmann et al. (2021) conducted within the red boxes in panels d - f. Solid blue curves show ROMS O$_2$ whereas the dashed blue curves show averaged World Ocean Atlas 2018 O$_2$ over the shipboard sampling region.

show low concentrations at the surface for NO$_3^-$, NO$_2^-$, and N$_2$O. As depth increases, local maxima in NO$_2^-$ and N$_2$O can be seen at $\sim$100 m that correspond to low but non-
zero O$_2$. Just below this depth, where O$_2$ drops further to anoxic levels, local minima in NO$_3^-$ and N$_2$O appear along with a large peak in NO$_2^-$ of roughly 3 mmol m$^{-3}$. Beneath the anoxic OMZ, a second N$_2$O peak appears of slightly greater magnitude ($\sim$60 µmol N$_2$O m$^{-3}$) to the shallower maxima ($\sim$50 µmol N$_2$O m$^{-3}$). Depth-dependent distributions from shipboard measurements (Kalvelage et al., 2013; Cornejo & Farías, 2012; Krahmann et al., 2021) through the OMZ (pink shading) generally show good agreement between model and observations as O$_2$ increases and decreases vertically. Note that the geographical location of shipboard measurements differs from the ROMS averaging box due to the equatorward and offshore OMZ shift discussed above. Despite this geographical bias, Figures 4g - i demonstrate similarity in the expression of anaerobic nitrogen cycle processes at locations with comparable O$_2$ profiles. Remaining inconsistencies, such as the shallower depth of the observed upper N$_2$O maxima, can be explained by the proximity of observations to the coast, as compared to the more offshore location used to average model profiles.

Finally, given the importance of accurately representing water column denitrification, we compared total fixed nitrogen loss in ROMS via denitrification and anammox to other ETSP estimates (Figure 5). Both processes contribute roughly 50% to OMZ N-loss throughout the year, with seasonal variability mostly driven by changes in denitrification rates (red shading). The total water-column fixed nitrogen loss in the model is 25.2 Tg N yr$^{-1}$, within the range of observational estimates for the region (Deutsch et al., 2007; Bianchi et al., 2012; DeVries et al., 2013; Yang et al., 2017). Thus, despite a geographic shift, the model produces a realistic OMZ and associated nitrogen cycle tracers and rates.
3.2 ETSP N$_2$O Production

A transect crossing the core of the model OMZ shows that N$_2$O production and consumption rates from denitrification are strongly influenced by O$_2$ concentrations (Figure 6a). Within the anoxic core, N$_2$O reduction to N$_2$ ($R_{den3}$) exceeds NO$_2^-$ reduction to N$_2$O ($R_{den2}$), causing widespread net N$_2$O consumption (red shading) of nearly 0.1 µmol N m$^{-3}$ d$^{-1}$. The resulting N$_2$O and NO$_2^-$ transects (Figure 6c and 6d) show consistent offshore subsurface N$_2$O minima coinciding with peak concentrations of NO$_2^-$ at the same depth range. These patterns suggest that all three denitrification steps proceed with minimal O$_2$ inhibition within the OMZ core, supporting a zone of active fixed N-loss.

Along the exterior of the OMZ core, O$_2$ gradients preferentially inhibit N$_2$O reduction to N$_2$ ($R_{den3}$) and allow incomplete denitrification to proceed. Accordingly, net N$_2$O consumption transitions to net production (blue shading) of a similar ~0.1 µmol N m$^{-3}$ d$^{-1}$ magnitude (Figure 6a). Beyond suboxic waters, net production from denitrification ceases. In contrast, maximum N$_2$O production from NH$_4^+$ oxidation ($R_{ao}$, Figure 6b) peaks at roughly 0.01 µmol N m$^{-3}$ d$^{-1}$ and is largely restricted to a thin, mostly oxygenated layer at roughly 100 - 150 m that mirrors vertical maxima in POC flux (not shown), with little amplification at low O$_2$.

The relative contributions from the N$_2$O tracer decomposition (Figure 6e - h) highlight the disparity between N$_2$O sources. At the surface, atmospheric ingassing allows

---

**Figure 5.** (left) Monthly averaged fixed nitrogen loss from ROMS via canonical denitrification and anammox from models year 46 - 50. (right) ETSP estimates of total annual averaged nitrogen loss from ROMS, Deutsch et al. (2007), Bianchi et al. (2012), DeVries et al. (2013), and Yang et al. (2017).
Figure 6. (a) Annually averaged net $\text{N}_2\text{O}$ production from denitrification for model years 46 - 50 along a transect from the coast at 8°S. The dotted and dashed black curves in highlight the 5 and 10 mmol O$_2$ m$^{-3}$ contours, respectively. (b-d) Same as in panel (a), but for $\text{N}_2\text{O}$ production from nitrification (b), $\text{N}_2\text{O}$ (c), and NO$^-$ (d). Panels (e) - (h) show the relative contributions to $\text{N}_2\text{O}$ for each decomposed $\text{N}_2\text{O}$ tracer ($\text{N}_2\text{O}_{\text{den}}, \text{N}_2\text{O}_{\text{nit}}$, $\text{N}_2\text{O}_{\text{bou}}$, and $\text{N}_2\text{O}_{\text{atm}}$).

saturated $\text{N}_2\text{O}$ ($\text{N}_2\text{O}_{\text{atm}}$) to dominate (Figure 6h), especially offshore. Within the anoxic OMZ core, despite vigorous net $\text{N}_2\text{O}$ consumption (Figure 6a), residual $\text{N}_2\text{O}$ concentrations of $\sim$20 mmol m$^{-3}$ persist (Figure 6e), and are nearly completely attributed to $\text{N}_2\text{O}$ denitrification ($\text{N}_2\text{O}_{\text{den}}$, Figure 6e). As O$_2$ increases beyond suboxic levels, the contribution of $\text{N}_2\text{O}_{\text{den}}$ diminishes, while contributions from supersaturated and saturated $\text{N}_2\text{O}$ from the boundaries (N$_2$O$_{\text{bou}}$ and N$_2$O$_{\text{atm}}$, respectively) account for the remainder. In contrast, $\text{N}_2\text{O}$ from nitrification ($\text{N}_2\text{O}_{\text{nit}}$, Figure 6f) does not contribute more than 10%, with a maximum at roughly 100 m depth, suggesting that incomplete denitrification is the main contributor ($\mathcal{O}$(10) times greater production) to local $\text{N}_2\text{O}$ production throughout the OMZ.

Notably, the contributions from supersaturated and saturated $\text{N}_2\text{O}$ transported into the OMZ from the model domain boundaries ($\text{N}_2\text{O}_{\text{bou}}$ and $\text{N}_2\text{O}_{\text{atm}}$, respectively) are rapidly reduced at low O$_2$, showing consumption of externally derived $\text{N}_2\text{O}$ within the OMZ core. Additionally, while production from incomplete denitrification is generally confined to
suboxic waters (Figure 6a), significant concentrations of $\text{N}_2\text{O}_{\text{den}}$ in oxygenated waters suggest export of $\text{N}_2\text{O}_{\text{den}}$ out of the OMZ. Together, these results highlight an important role for circulation in redistributing $\text{N}_2\text{O}$ within the ETSP.

3.3 Contributions of Different Processes to the $\text{N}_2\text{O}$ Balance

Figure 7 shows vertically-integrated $\text{N}_2\text{O}$ sources minus sinks ($J$ terms) over the OMZ budget region, and the annual time-series of total integrated net production for $\text{N}_2\text{O}$ and each decomposed tracer. In general, net $\text{N}_2\text{O}$ production ($J^{\text{N}_2\text{O}}_{\text{tot}}$, black line in the time-series) is positive for each month with the exception of June, and reveals higher rates beginning in August that persist through December. Production is predominantly driven by denitrification ($J^{\text{N}_2\text{O}}_{\text{den}}$, blue line), which also drives the bulk of monthly variability seen in $J^{\text{N}_2\text{O}}_{\text{tot}}$. In contrast, production from nitrification ($J^{\text{N}_2\text{O}}_{\text{nit}}$, red line) is net positive throughout the year, but only accounts for a small proportion of the $\text{N}_2\text{O}$ production. Tracers that lack domain production sources ($\text{N}_2\text{O}_{\text{bou}}$ and $\text{N}_2\text{O}_{\text{atm}}$) show consistent consumption rates throughout the year.

![Figure 7](image-url)

**Figure 7.** (top left) Vertically integrated sources-minus-sinks ($J$) for $\text{N}_2\text{O}$ from the OMZ budget domain, annually averaged from model years 46 - 50. (top right) Time-series of integrated sources-minus-sinks for $\text{N}_2\text{O}$ (black) and the decomposed $\text{N}_2\text{O}$ tracers. (bottom panels) Same as in the top left panel, but for each of the decomposed $\text{N}_2\text{O}$ tracers. Positive values (production) are shown in blue, and negative values (consumption or removal) in red.
Vertically-integrated total $N_2O$ production ($J_{tot}^{N_2O}$) and denitrification-derived production ($J_{den}^{N_2O}$) shown in Figure 7 are similar and reveal a hot-spot of vigorous net consumption (red shading) centered at roughly $8^\circ S$ and $80^\circ W$ that abruptly transitions to net production (blue shading) in the surrounding ocean. The remaining tracers reveal similar hot-spots of consumption near the coast, especially supersaturated $N_2O$ from the model boundaries ($J_{bou}^{N_2O}$). Integrated $N_2O$ consumption from nitrification ($J_{nit}^{N_2O}$) is balanced by production immediately adjacent to the coastline and in the offshore region that ultimately leads to net production within the budget domain. The region is therefore characterized by a coastal hot-spot of net $N_2O$ consumption that depletes both locally produced $N_2O$ ($N_2O_{den}$ and $N_2O_{nit}$, blue and red lines respectively) and remote $N_2O$ originating from outside the model domain ($N_2O_{bou}$ and $N_2O_{atm}$, green and purple lines respectively). Outside the coastal hot-spot, $N_2O$ production from denitrification over-compensates for the consumption at the coast and makes the OMZ a net source of $N_2O$ in all months, with the exception of June. As expected at steady-state, the divergence of advective and diffusive fluxes ($T$ terms) for each $N_2O$ tracer, shown in Figure S11, largely balances the sources minus sinks in Figure 7.

The total $N_2O$ air-sea flux ($\Phi_{tot}^{N_2O}$, black lines in Figure 8) peaks in July and is positive throughout the year, indicating the surface ocean of the ETSP OMZ as a constant source of $N_2O$ to the atmosphere with higher outgassing rates throughout upwelling season (boreal summer). The major contributing components to the flux are supersaturated $N_2O$ from the model boundaries ($\Phi_{bou}^{N_2O}$) and locally produced $N_2O$ from denitrification ($\Phi_{den}^{N_2O}$), which exhibit similar seasonal cycles as in the total flux ($\Phi_{tot}^{N_2O}$), albeit with different geographical distributions. The spatial pattern of $\Phi_{tot}^{N_2O}$ can be described as a combination of $\Phi_{bou}^{N_2O}$ and $\Phi_{den}^{N_2O}$ patterns; $\Phi_{den}^{N_2O}$ is concentrated near the coast with a structure closely mirroring the coastal hot-spot of consumption shown by Figure 7, whereas $\Phi_{bou}^{N_2O}$ takes place mostly along the northern boundary of the budget region (albeit with maximum outgassing near the coast). Since the $N_2O_{atm}$ tracer can be consumed via $N_2O$ reduction within the domain (section 2.4), $\Phi_{atm}^{N_2O}$ similarly tracks the coastal hot-spot, but reveals oceanic ingassing at the surface, peaking in July, which brings $N_2O_{atm}$ back towards saturation. Finally, the magnitude of air-sea flux from local nitrification ($\Phi_{nit}^{N_2O}$) is small but net positive, and shows a similar July maximum peaking near the coast.

3.4 $N_2O$ Balance

A schematic of the annual $N_2O$ balance (Figure 9) shows that total OMZ $N_2O$ production is dominated by incomplete denitrification (174 $Gg N y^{-1}$), whereas nitrification contributes a smaller fraction (18 $Gg N y^{-1}$). Conversely, consumption of both saturated and supersaturated $N_2O$ from the model boundaries ($N_2O_{atm}$ and $N_2O_{bou}$) drives a net $N_2O$ loss (106 and 34 $Gg N y^{-1}$ respectively). The excess production makes the OMZ a net $N_2O$ source to the atmosphere (51 $Gg N y^{-1}$). This production takes place predominantly on the fringe of the OMZ both vertically and horizontally, where thick suboxic layers support net $N_2O$ accumulation from the denitrification pathway (Figures 6 and 7).

The budget also suggests that the corresponding outgassing pathways from local production sources are somewhat inefficient; the annual export of 125 and 7 $Gg N y^{-1}$ of $N_2O_{den}$ and $N_2O_{nit}$ (respectively) suggests that $\sim$72% and $\sim$39% of their net production ($J_{den}^{N_2O}$ and $J_{nit}^{N_2O}$, respectively) ultimately avoids outgassing within the budget domain. Yet despite the surprising magnitude of these production export rates, high net import rates of $N_2O_{bou}$ and $N_2O_{atm}$ from the model boundaries (188 and 33 $Gg N y^{-1}$, respectively) drive an annual net source of 94 $Gg N y^{-1}$ into the OMZ region. Separating the advective fluxes into zonal, meridional, and vertical components reveals zonal fluxes along the western boundary of the domain as the primary interface of $N_2O$ exchange with the surrounding ocean, organized as alternating narrow bands of $N_2O$ import (Figure S12e, red shading) and export (blue shading). The net transport is driven by supersat-
urated N$_2$O (N$_2$O$_{bou}$) supplied through the boundaries (Figure S12c), with the most intense import along the equator at roughly 150 m depth (see also Figure 6g). In contrast, denitrification-driven export (Figure S12a) is focused further to the south (roughly 8°S) and at deeper depths (200 - 500 m, also evident in Figure 6e).

After accounting for boundary exchanges, local subsurface production and consumption, and periodic ingassing of N$_2$O$_{atm}$ (Figure 8), all tracers reveal net outgassing with $\Phi_{bou}$ and $\Phi_{den}$ contributing ~56% and ~34% (respectively) to the annual 152 Gg N y$^{-1}$ outgassed to the atmosphere. Thus, what emerges from the above descriptions is an ETSP OMZ that is characterized by: (1) A consistent supply of N$_2$O$_{bou}$ and N$_2$O$_{atm}$ from predominantly zonal subsurface currents in the tropical band (Figures S11, S12c, and S12e); (2) Advection of all N$_2$O tracers into a coastal hot-spot where vigorous consumption leads to significant N-loss; (3) Net N$_2$O production predominantly by denitrification within suboxic gradients surrounding the OMZ (Figure 7); (4) Significant export of N$_2$O$_{den}$ into the exterior ocean (Figures S11 and S12); (5) Consumption of locally produced and externally derived N$_2$O; and (6) Year-round air-sea flux of N$_2$O driven predominantly by imported N$_2$O$_{bou}$ and locally produced N$_2$O$_{den}$ that upwell and outgas along the northern extent of the OMZ domain and along the coast, respectively (Figure 8).
4 Discussion and Conclusions

We developed a climatological, eddy-resolving simulation of the ETSP OMZ that reproduces the main patterns in the spatial distribution of observed nitrogen tracers and transformation rates. Despite enhanced yields at low O$_2$, we find almost negligible local contributions from nitrification; rather, maximum N$_2$O production rates from NH$_4^+$ oxidation ($P_{\text{nit}}^{n_2o}$) follow vertical maxima in POC flux which occur well above the oxycline throughout much of the domain east of -90°W (Figure 6). Closer to shore, as the OMZ core shoals to ~100 m, production from nitrification ($J_{\text{nit}}^{n_2o}$ in Figure 7) suggests that N$_2$O$_{\text{nit}}$ is subsequently mixed into anoxic waters and consumed via N$_2$O reduction. The major contribution of nitrification to N$_2$O production takes place immediately adjacent to the coast, where low O$_2$ waters at shallow depths lead to enhanced production and an efficient outgassing route. As a result, the air-sea flux pattern in Figure 8 shows negligible contributions from nitrification ($P_{\text{nit}}^{n_2o}$) throughout the domain, with the exception of coastal outgassing driven by upwelling. While the contribution from nitrification to N$_2$O production in NitroOMZ is sensitive to the choice of the parameters in equation (1), the values used in this study are constrained by observations (Section 2.3.1) and fall within range of previous estimates (Ji et al., 2018; Santoro et al., 2021) which similarly suggest weak nitrification production. Therefore, similar to the results of Ji et al. (2015) and Babbin et al. (2015), our simulation suggests that local production from nitrification is not a dominant pathway for N$_2$O outgassing flux in this region.
Instead, N\textsubscript{2}O production is dominated by incomplete denitrification which takes place along the suboxic fringes of the anoxic OMZ core (Figure 6a, Figure 6e, and Figure 7), in agreement with recent studies (Babbin et al., 2015; Ji et al., 2018). In general, the three step-wise denitrification rates show a strong seasonal dependence and are primarily controlled by the timing of organic matter supply from the euphotic zone (Figure S13) rather than variability in low O\textsubscript{2} volumes throughout the year (Figure S14).

Within the anoxic core of the OMZ, rapid N\textsubscript{2}O consumption rates (Figure 6a) indicate short residence times for N\textsubscript{2}O produced via NO\textsubscript{2}\textsuperscript{-} reduction (N\textsubscript{2}O\textsubscript{den}) due to the strong coupling between denitrification steps at low O\textsubscript{2}. Significant net N\textsubscript{2}O production by denitrification (J\textsuperscript{N2Oden}) occurs where high rates of vertical POC flux overlap with an anoxic to suboxic O\textsubscript{2} gradient; there, the difference in O\textsubscript{2} tolerance thresholds leads to a relatively small residual between the large NO\textsubscript{2} and N\textsubscript{2}O reduction rates within the domain (Babbin et al., 2015). As oxic organic matter remineralization stops within the anoxic OMZ core, this leads to the characteristic double peak structure in N\textsubscript{2}O profiles (Figure 6c) bounding the OMZ throughout most of the domain.

Spatially, the vertical depth range occupied by anoxic to suboxic gradients plays a key role in determining regions of net production or consumption via the denitrification pathway. For instance, the integrated J\textsuperscript{N2Oden} in Figure 7 reveals consumption along the northern extent of the Peruvian coast at roughly 8\textdegree S; considering this pattern, Figure 6a shows relatively sharp O\textsubscript{2} gradients above and below the OMZ around -85\textdegree W, indicating that N\textsubscript{2}O consumption is particularly strong near the coast, where relatively thin but shallow suboxic layers are found. In contrast, suboxic layers become thicker further offshore, resulting in conditions more favorable to N\textsubscript{2}O production. Therefore, the high rates of coastal outgassing observed in Figure 8 are at least partially driven by net transport from more productive surrounding waters (Figure S11).

Our results demonstrate the role of advection in redistributing supersaturated N\textsubscript{2}O within the ETSP. Notably, the EUC and SSCC are revealed as zonal conduits controlling the import of supersaturated N\textsubscript{2}O (N\textsubscript{2}O\textsubscript{in}) from the boundaries (and thus, outgassing-favorable N\textsubscript{2}O) into the OMZ domain. This is demonstrated by the large fractional contributions to N\textsubscript{2}O at 150 m throughout the eastern extent of the transect in Figure 6g, which match subsurface patterns in Figure S12c. These results are consistent with those from Yang et al. (2020), who highlighted the tropics in the Eastern Pacific as an important outgassing region with seasonality driven predominantly by the timing of upwelling (May to September). While a significant fraction of the imported N\textsubscript{2}O is ultimately advected into the anoxic OMZ to be consumed (Figures 6g and 7), the remainder is responsible for the bulk (~56\%) of the outgassing flux over the OMZ domain. As the N\textsubscript{2}O budget and boundary export schematic in Figures 9 and S12 show, circulation also plays a key role in exporting the majority (roughly 72\%) of local denitrification-derived N\textsubscript{2}O production (J\textsuperscript{N2Oden}) out of the OMZ budget domain. Much of this export takes place along the western boundary (Figure S12), but at more southerly latitudes and at deeper depths compared to the import of supersaturated N\textsubscript{2}O from the boundaries (T\textsubscript{N2Oin}). Unfortunately, our regional simulations do not allow us to explore the fate of this N\textsubscript{2}O. Global or basin-wide simulations would enable tracking the interplay of N\textsubscript{2}O sources and sinks within and outside OMZs. A portion of the denitrification-derived N\textsubscript{2}O export may recirculate back into the eastward equatorial currents, or could instead add to N\textsubscript{2}O concentrations offshore waters, such as those observed by Santoro et al. (2021).

The residual between rapid N\textsubscript{2}O production and consumption by denitrification is heavily coupled to O\textsubscript{2} dynamics and thus a major portion of N\textsubscript{2}O outgassing in this region is likely sensitive to future changes in OMZ magnitude and geometry. Observations suggest that deoxygenation over the past 50 years has led to expansion of OMZ volumes and shoaling of the upper oxycline (Stramma et al., 2008; Schmidtke et al., 2017). Yet, whether this has caused a positive or negative impact on N\textsubscript{2}O production likely depends on the relative changes of anoxic versus suboxic volumes. If future climate change...
results in an increase in the volume of suboxic waters, as suggested by Earth system model
projections (Cabré et al., 2015; Kwiatkowski et al., 2020; Busecke et al., 2019), it would
increase production from both incomplete denitrification and nitrification, leading to a
positive climate feedback. Conversely, an increase in the volume of anoxic waters may
drive enhanced N$_2$O consumption and constitute a negative climate feedback.

Future changes in the oxycline depth via projected stratification or wind changes
(Kwiatkowski et al., 2020; Busecke et al., 2019; Bakun, 1990) may alter the coupling be-
tween local production and outgassing over OMZs, while also affecting the export of su-
persaturated N$_2$O into the nearby gyres. The lack of interannual forcing in this study
also leaves gaps in understanding ENSO impacts. OMZ geometry and total denitrifica-
tion rates are sensitive to ENSO variability (Yang et al., 2017), thus N$_2$O production and
outgassing are likely to exhibit similar year-to-year changes. Interannually forced, high-
resolution models capable of simulating both denitrification and nitrification-derived pro-
duction are needed to resolve these emerging questions.

Open Research Section

The ROMS model code used to generate the simulation (Shchepetkin & McWilliams,
2005; Shchepetkin, 2015), and the MATLAB (MATLAB, 2020) scripts and output used
to generate the figures shown in the paper, can be found at https://doi.org/10.5281/zenodo.7374360
(McCoy et al., 2022). Raw model output can be obtained from the Authors upon request.
Biogeochemical validation data were provided by the World Ocean Atlas 2018 (H. Gar-
cia et al., 2019a, 2019b), MEMENTO (Kock & Bange, 2015) and GLODAPv2 (Key et
al., 2015; Lauvset et al., 2016) databases, with additional shipboard observations from
Kalvelage et al. (2013), Cornejo and Farias (2012), and Krahmann et al. (2021). The ME-
MENTO database is administered by the Kiel Data Management Team at GEOMAR
Helmholtz Centre for Ocean Research and supported by the German BMBF project SO-
PRAN (Surface Ocean Processes in the Anthropocene, http://sopran.pangaea.de). The
database is accessible through the MEMENTO webpage (https://memento.geomar.de).
AVISO satellite data used in model validation were processed by SSALTO/DUACS and
distributed by AVISO+ at https://www.aviso.altimetry.fr with support from CNES. MODIS
L3 ocean color data were obtained from the NASA/GSFC MODAPS Service website at
https://oceancolor.gsfc.nasa.gov/l3/. The ERA-Interim dataset (Dee et al., 2011), which
was used to force the model, was obtained from the European Centre for Medium-Range
Weather Forecasts (ECMWF) at https://www.ecmwf.int. Thanks to ICDC, CEN, Uni-
versity of Hamburg for data support in obtaining ERA-Interim products.

Acknowledgments

This material is based upon work supported by the U.S. National Science Foundation
under grant OCE-1847687. D.B. acknowledges support from the Alfred P. Sloan Founda-
tion, and computational support by the Extreme Science and Engineering Discovery
Environment (XSEDE) through allocation TG-OCE17001.

References

1029/93GB03318

nitrous oxide in the eastern tropical South Pacific. Biogeosciences Discussions,
12(12), 9243–9273. doi: 10.5194/bgd-12-9243-2015


doi: 10.1016/j.pocean.2009.07.032


-22-


Large, W. B. (2006). Surface Fluxes for Practitioners of Global Ocean Data Assimilation. In E. P. Chassignet & J. Verron (Eds.), *Ocean weather forecasting:


Pathways of Nitrous Oxide Production in the Eastern Tropical South Pacific Oxygen Minimum Zone

Daniel McCoy¹, Pierre Damien¹, Daniel Clements¹, Simon Yang¹, Daniele Bianchi¹

¹Department of Atmospheric and Oceanic Sciences
¹University of California – Los Angeles
¹520 Portola Plaza, Los Angeles, CA 90095, USA

Key Points:

• In the eastern tropical South Pacific Oxygen Minimum Zone, denitrification is the dominant source of N₂O production.
• Tropical subsurface currents supply N₂O to the region, fueling N₂O emissions to the atmosphere.
• Significant amounts of locally-produced N₂O escape outgassing and are exported to the subtropical gyre.

Corresponding author: Daniel McCoy, demccoy@atmos.ucla.edu
Abstract

Oceanic emissions of nitrous oxide (N\textsubscript{2}O) account for roughly one-third of all natural sources to the atmosphere. Hot-spots of N\textsubscript{2}O outgassing occur over oxygen minimum zones (OMZs), where the presence of steep oxygen gradients surrounding anoxic waters leads to enhanced N\textsubscript{2}O production from both nitrification and denitrification. However, the relative contributions from these pathways to N\textsubscript{2}O production and outgassing in these regions remains poorly constrained, in part due to shared intermediary nitrogen tracers, and the tight coupling of denitrification sources and sinks. To shed light on this problem, we embed a new, mechanistic model of the OMZ nitrogen cycle within a three-dimensional eddy-resolving physical-biogeochemical model of the ETSP, tracking contributions from remote advection, atmospheric exchange, and local nitrification and denitrification. Our results indicate that net N\textsubscript{2}O production from denitrification is approximately one order of magnitude greater than nitrification within the ETSP OMZ. However, only ∼30% of denitrification-derived N\textsubscript{2}O production ultimately outgasses to the atmosphere in this region (contributing ∼34% of the air-sea N\textsubscript{2}O flux on an annual basis), while the remaining is exported out of the domain. Instead, remotely-produced N\textsubscript{2}O advected into the OMZ region accounts for roughly half (∼56%) of the total N\textsubscript{2}O outgassing, with smaller contributions from nitrification (∼7%). Our results suggests that, together with enhanced production by denitrification, upwelling of remotely-derived N\textsubscript{2}O (likely produced via nitrification in the oxygenated ocean) contributes the most to N\textsubscript{2}O outgassing over the ETSP OMZ.

1 Introduction

Nitrous oxide (N\textsubscript{2}O) is a powerful greenhouse gas that is roughly 300 times more potent than carbon dioxide (CO\textsubscript{2}) and is projected to become the most important ozone-depleting anthropogenic emission by the end of the 21st century (Ravishankara et al., 2009; IPCC, 2013). Recent analyses of the global N\textsubscript{2}O budget over the decade of 2007 - 2016 suggest that anthropogenic emissions are responsible for up to 40% of total N\textsubscript{2}O sources to the atmosphere, mostly from agriculture, whereas outgassing from the ocean accounts for roughly 20% (Canadell et al., 2021). The production of N\textsubscript{2}O in the ocean is linked to the remineralization of organic matter (OM) via both aerobic and anaerobic pathways, and, as a consequence, is tightly coupled to the oceanic oxygen (O\textsubscript{2}) distribution (Freing et al., 2012; Arévalo-Martínez et al., 2015; Babbin et al., 2015; Ji et al., 2015; Yang et al., 2020). While in large parts of the surface ocean N\textsubscript{2}O concentrations are close to saturation, the most intense hot-spots of N\textsubscript{2}O air-sea flux are found in the Eastern Tropical North Pacific (ETNP), the Eastern Tropical South Pacific (ETSP), and the Arabian Sea, where high organic matter export rates and sluggish lateral circulation results in steep O\textsubscript{2} gradients that surround anoxic (here defined as O\textsubscript{2} < 5 mmol m\textsuperscript{-3}) waters also known as oxygen minimum zones (OMZ) (Codispoti, 2010; Arévalo-Martínez et al., 2015; Ji et al., 2018; Yang et al., 2020). Although OMZ regions only account for roughly 1% of the total ocean volume, the dynamic marine nitrogen cycling that occurs there results in up to 50% of total oceanic N\textsubscript{2}O emissions (Codispoti, 2010; Arévalo-Martínez et al., 2015; Babbin et al., 2015; Yang et al., 2020).

The ETSP hosts the second largest OMZ by area and comprises the Humboldt Current System, one of the four major Eastern Boundary Upwelling Systems, which extends from the southern extent of Chile (∼45°S) to northern Peru (∼4°S) (Chavez & Messié, 2009; Santoro et al., 2021). While southern Chile experiences more intense upwelling during boreal summer (Pennington et al., 2006), upwelling-favorable conditions exist year-round along the Peruvian and northern Chile coastlines, fueling high rates of surface primary productivity, organic matter export (Chavez & Messié, 2009), and subsurface O\textsubscript{2} depletion. The ETSP OMZ is located in the South Pacific tropical shadow zone of the thermocline (Luyten et al., 1983), which extends westward from the eastern boundary between the equatorward edges of the subtropical gyres. This limits the supply of oxy-
gen from the ventilated subtropical gyres to the OMZs, and leaves the relatively O$_2$-rich
eastward tropical currents such as the Equatorial Undercurrent (EUC) and the Southern
Subsurface Countercurrents (SSCC) as the major advective sources of O$_2$ to the equa-
toward side of the ETSP OMZ (Karstensen et al., 2008; Stramma et al., 2010). While
these advective pathways are reinforced by lateral O$_2$ supply from mesoscale eddies (Gnanadesikan
et al., 2013; Bettencourt et al., 2015), O$_2$ remains depleted within the OMZ core (Kwiecinski
& Babin, 2021), leading to functional anoxia (Thamdrup et al., 2012), fixed nitrogen
loss, a pronounced subsurface nitrite (NO$_2^-$) maximum, and a strong nitrogen deficit (Kalvelage
et al., 2013). An additional characteristic of the ETSP is the relatively sharp transition
from anoxic to suboxic (5 mmol m$^{-3}$ < O$_2$ < 10 mmol m$^{-3}$) waters along the OMZ bound-
ary. These O$_2$ gradients host both aerobic (i.e., nitrification) and anaerobic (i.e., den-
itrification) nitrogen cycle transformations, ultimately leading to N$_2$O supersaturation
in the layers surrounding the anoxic core (Babbin et al., 2015; Kock et al., 2016). Up-
welling of these waters to the surface likely contributes to the local hot-spot of N$_2$O out-
gassing in the ETSP, as shown by observational and modeling studies (Arévalo-Martínez
et al., 2015; Ji et al., 2018; Yang et al., 2020).

Nitrification is a two-step process that occurs within the oxygenated water column
wherein ammonium (NH$_4^+$) produced from remineralization of organic matter (pathway
1 in Figure 1) is oxidized by O$_2$ to NO$_2^-$ and subsequently to nitrate (NO$_3^-$) by NH$_4^+$-
oxidizing bacteria and archaea and NO$_2^-$-oxidizing bacteria, respectively (pathways 2 and
4, respectively) (Lam & Kuypers, 2011). Nitrification-derived N$_2$O occurs as a byprod-
uct of NH$_4^+$ oxidation (pathway 3), resulting in a positive correlation between apparent
oxygen utilization (AOU) and supersaturated N$_2$O concentrations in many areas of the
ocean (Cohen & Gordon, 1978; Walter et al., 2006), a process that has been further quan-
tified by active production of $^{15}$N$_2$O in $^{15}$N tracer incubation experiments (Yoshida et
al., 1989). The ratio of N$_2$O yield to NO$_2^-$ yield from NH$_4^+$ oxidation has been observed
to increase at decreasing O$_2$ concentrations in cultures with NH$_4^+$-oxidizing bacteria and
archaea (Goreau et al., 1980; Lö scher et al., 2012), likely leading to enhanced nitrification-
derived N$_2$O production within the steep suboxic gradients above and below the anoxic
core of OMZs (Nevison et al., 2003; Ji et al., 2015, 2018; Santoro et al., 2021).

Besides N$_2$O production via the nitrification pathway, N$_2$O also forms as an inter-
mediary product of step-wise denitrification (NO$_3^-$ to NO$_2^-$ to N$_2$O to N$_2$) under sub-
oxic and anoxic conditions (pathways 5 - 7 in Figure 1). Within the anoxic core of OMZs,
widespread consumption of N$_2$O occurs via N$_2$O reduction — the only known process
able to remove N$_2$O from the water column. However, recent studies have highlighted
how the different steps, each mediated by distinct enzymes and likely different microor-
ganisms (Ganesh et al., 2014; Kuypers et al., 2018), are subject to variable O$_2$ sensitiv-
ities wherein NO$_3^-$, NO$_2^-$, and N$_2$O reduction become progressively less O$_2$ tolerant (Körner
& Zumft, 1989; Kalvelage et al., 2011; Dalsgaard et al., 2014; Babbin et al., 2015; Ji et
al., 2015). Therefore, the same suboxic gradients that lead to enhanced N$_2$O production
from nitrification can also lead to N$_2$O accumulation from denitrification, as NO$_2^-$ re-
duction proceeds while N$_2$O reduction is inhibited, in a process referred to as “incom-
plete” denitrification (Babbin et al., 2015).

The coupled production of N$_2$O at low O$_2$ from nitrification and denitrification,
and their shared NO$_2^-$ intermediary, complicate the interpretation of in situ observations
from OMZs (Ji et al., 2015, 2018; Santoro et al., 2021). Observations of N$_2$O and NO$_2^-$
in these regions typically reveal an OMZ anoxic core layer characterized by a secondary
NO$_2^-$ maximum and undersaturated N$_2$O concentrations, suggesting coupled step-wise
denitrification. Supersaturated concentrations of N$_2$O in the bounding suboxic gradi-
ents (the upper and lower oxyclines) have been linked to the enhanced production by
nitrification (Cohen & Gordon, 1978). Yet, studies have noted the lack of a linear rela-
tionship with AOU and high abundances of gene markers for NO$_2^-$ reduction as evidence
Figure 1. Schematic of the oceanic nitrogen cycle (ignoring biological uptake) as represented in ROMS. Transformation pathways include: (1, $R_{\text{rem}}$) oxic remineralization of nitrogen in organic matter (OrgN) to ammonium; (2, $R_{\text{no}}$) ammonium oxidation to nitrite; (3, $R_{\text{no}2}$) ammonium oxidation to nitrous oxide; (4, $R_{\text{no}}$) nitrite oxidation; (5, $R_{\text{den1}}$) nitrate reduction; (6, $R_{\text{den2}}$) nitrite reduction; (7, $R_{\text{den3}}$) decomposed nitrous oxide reduction; (8, $\Phi_{\text{n2o}}$) decomposed nitrous oxide air-sea flux; (9, $\Phi_{\text{n2}}$) dinitrogen air-sea flux; and (10, $R_{\text{ax}}$) anaerobic ammonium oxidation (anammox). Colored arrows correspond to the sources and sinks of the decomposed N$_2$O tracers (N$_2$O$_{\text{den}}$, N$_2$O$_{\text{nit}}$, N$_2$O$_{\text{bou}}$, and N$_2$O$_{\text{atm}}$) discussed in Section 2.4.

of simultaneous production from both nitrification and incomplete denitrification (Arévalo-Martínez et al., 2015), as further supported by isotopic evidence (Bourbonnais et al., 2017).

However, while progressive O$_2$ tolerances for denitrification have been documented (Dalsgaard et al., 2014), biogeochemical models predominantly employ simple parameterizations representing N$_2$O production as a function of nitrification, whereas denitrification is typically modelled with a lack of N$_2$O production or as a net sink of N$_2$O at low O$_2$ (Suntharalingam et al., 2000; Jin & Gruber, 2003; Ji et al., 2018; Battaglia & Joos, 2018). Other studies have highlighted the importance of resolving O$_2$-dependent decoupling of N$_2$O production and consumption (Babbin et al., 2015), suggesting that N$_2$O production rates from denitrification may be up to two orders of magnitude larger than those from nitrification near the core of OMZs, albeit closely balanced by N$_2$O reduction to dinitrogen gas (N$_2$). Thus, incomplete denitrification may account for a production source that is poorly represented in most biogeochemical ocean and climate models.

While the uncertainty surrounding N$_2$O production in the ocean has been reduced in recent years following improved estimates of ocean (Yang et al., 2020), terrestrial, and anthropogenic N$_2$O sources (Canadell et al., 2021; Tian et al., 2020), barriers remain in
accurately projecting future air-sea flux because of poorly constrained contributions from
the nitrification and denitrification pathways. The observed expansion of OMZs (Stramma
et al., 2008; Schmidtke et al., 2017; Oschlies et al., 2018) is expected to continue over
the 21st century, although the extent of future changes in low O2 and anoxic water vol-
umes remain uncertain (Cabr´e et al., 2015; Bianchi et al., 2018; Busecke et al., 2021).
Therefore, accurate parameterization of N2O cycling in global ocean models is crucial
in simulating realistic future scenarios, and a better understanding of the physical and
biogeochemical mechanisms and relative contributions from both production pathways
is warranted. This is particularly critical given that OMZ regions continue to be poorly
resolved in current global Earth system models (Cabr´e et al., 2015; Busecke et al., 2021;
S´ef´erian et al., 2020), which generally struggle to capture the role of fine-scale circula-
tion such as the zonal jet systems that ventilate the tropical Ocean (Kessler, 2006; Duteil
et al., 2014; Busecke et al., 2019; Duteil et al., 2021).

To address these sources of uncertainty, we implement a new model of the OMZ
nitrogen cycle (NitrOMZ) (Bianchi et al., 2022) into an eddy-resolving three-dimensional
(3-D) regional ocean model of the ETSP that simulates local N2O production from ni-
trification and denitrification. The new model, constrained by in situ ETSP observations
of nitrogen cycle tracers and rates, allows for an examination of the N2O balance within
a characteristic OMZ upwelling region. To attribute the sources of N2O outgassing flux
to different processes, we use the 3-D model to track contributions from local air-sea gas
exchange, advection into the domain from the boundaries, and production by nitrifica-
tion and denitrification. This analysis reveals the importance of incomplete denitrifica-
tion and transport of remotely-generated N2O for air-sea fluxes, with implications for
future N2O emissions in a changing ocean.

The rest of the paper is organized as follows: Section 2 describes the 3-D model
configuration and setup, a brief summary of N2O production pathways in NitrOMZ, and
the N2O tracer decomposition strategy; Section 3 provides a short validation of model
solutions, summarizes the results of the simulations, and describes the ETSP N2O bal-
ance; Section 4 discusses the results and implications, and concludes the paper.

2 Modelling Methods and Validation

2.1 Physical Model Configuration and Forcing

The physical component of the model consists of the Regional Ocean Modeling Sys-
tem (ROMS) (Shchepetkin & McWilliams, 2005; Shchepetkin, 2015), a primitive-equation,
hydrostatic, topography-following general ocean circulation model. The model domain
extends from -111.38°W to -66.62°W and from 42.52°S to 3.41°N and is chosen to re-
solve key oceanographic features of the ETSP such as the EUC (Figure 2c), the wind-
driven South Pacific gyre (contour lines in Figure 2a and 2b), and the horizontal extent
of the OMZ (Figure 3a). Its grid consists of 402 x 502 points with a nominal resolution
of 10 kilometers and 42 topography-following vertical levels with higher resolution at the
surface and bottom. The model time-step is 800 seconds, and output is saved as monthly
means.

For this study, low-frequency interannual variability is ignored to instead focus on
a climatological steady-state. Initial conditions and monthly climatological boundary forc-
ing (applied at the northern, western, and southern boundaries) for temperature, salini-
ity, surface elevation, and horizontal velocity are taken from an existing Pacific-wide ROMS
simulation (Lemarié et al., 2012). Normal-year-forcing of daily freshwater and turbulent
heat fluxes are estimated using bulk formulae (Large, 2006) applied to ERA-interim (ERAi)
reanalysis data for the year 1979 (Simmons et al., 2006; Dee et al., 2011). Because of known
biases in ERAI shortwave (overestimate) and longwave (underestimate) fluxes (Brodeau
et al., 2010), we applied the DRAKKAR Forcing Set version 5.2 corrections to heat flux
terms (Dussin et al., 2014). Daily climatological wind stress is taken from the QuickSCAT-based Scatterometer Climatology of Ocean Winds (Risien & Chelton, 2008). The resulting simulation produces an overall similar climatological picture of the hydrographic properties, gyre circulation, and equatorial current structure of the ETSP (Figure 2a - c) when compared to validation products (Figure 2d - f).

![Figure 2](image)

**Figure 2.** (a,d) Annually averaged sea-surface temperature from ROMS model years 46 - 50 (top) and World Ocean Atlas 2018 (bottom). Contours highlight sea-surface height at 5 cm intervals, with validation data obtained by averaging AVISO data between 2000 to 2018. Dashed lines mark the transect location in panels (c) and (f). (b,e) Same as in panels (a) and (d), but for sea-surface salinity; contours highlight calculated geostrophic velocity streamlines, with validation data derived from AVISO. (c,f) Zonal velocity sections along the equator at 95°W from ROMS (top) and Johnson et al. (2002) (bottom).

### 2.2 Biogeochemical Model Configuration and Forcing

The physical model is coupled online to the Biogeochemical Elemental Cycling (BEC) model from Moore et al. (2004) using the same equations and parameter settings as in Frischknecht et al. (2017) with the exception of the nitrogen cycling component, which was expanded for the NitrOMZ model (Bianchi et al., 2022). NitrOMZ explicitly resolves the main set of nitrogen cycle transformations associated with the remineralization of sinking OM in low O$_2$ environments (summarized in Figure 1). These include the chemolithotrophic reactions associated with nitrification: aerobic NH$_4^+$ oxidation to both N$_2$O ($R_{n2o}^{an}$) and NO$_2^-$ ($R_{n2o}^{an}$), and aerobic NO$_2^-$ oxidation to NO$_3^-$ ($R_{no2}^{an}$). Anaerobic NH$_4^+$ oxidation with NO$_2^-$ to N$_2$ (anammox, $R_{ax}$) is also represented. Additionally, NitrOMZ partitions the OM remineralization cycle in ROMS-BEC to include three additional heterotrophic denitrification steps: NO$_3^-$ reduction to NO$_2^-$ ($R_{den1}$), NO$_2^-$ reduction to N$_2$O ($R_{den2}$), and N$_2$O reduction to N$_2$ ($R_{den3}$). The treatment of OM in the model is outlined in support-
ing information S1, with chemolithotrophic and heterotrophic reactions summarized in S2. Notably, the model expands BEC by allowing for the production of N$_2$O via both nitrification and incomplete denitrification pathways (Section 2.2.1).

Initial conditions and boundary forcing of biogeochemical nutrient concentrations (NO$_3^-$, PO$_4^{3-}$, Si(OH)$_4$ and O$_2$) are taken from monthly climatological observations from the 2013 World Ocean Atlas (H. E. Garcia, Boyer, et al., 2013; H. E. Garcia, Locarnini, et al., 2013); NH$_4^+$, NO$_2^-$, and N$_2$O boundary conditions are set to 0 but adjust rapidly within the domain. Iron data were taken from the Community Earth System Model (CESM) as in Deutsch et al. (2021), and DIC/Alkalinity were extracted from GLODAP (Lauvset et al., 2016) with a reference year of 2002. Initial and monthly boundary conditions for N$_2$O were provided from a 3-D reconstruction based on in situ data from recent cruises to the ETSP (Kalvelage et al., 2013; Ji et al., 2015; Peng et al., 2016; Babbin et al., 2017, 2020), and the MEMENTO databases (Kock & Bange, 2015) and GLODAP (Olsen et al., 2016) with a reference year of 2002. Initial and monthly boundary conditions for N$_2$O were extrapolated to the model domain using the same machine learning approach as described in Yang et al. (2020).

### 2.2.1 NitrOMZ N$_2$O Production

Production of N$_2$O via nitrification in NitrOMZ is modelled as a by-product of NH$_4^+$ oxidation ($R_{a_{no}}^{\text{no}}$, pathway 3 in Figure 1), with enhanced yields at lower O$_2$ concentrations. Both nitrification steps (i.e. NO$_2^-$ oxidation) are suppressed near the surface by light inhibition (see supporting information S4) and competition for NH$_4^+$ and NO$_2^-$ from phytoplankton as in Frischknecht et al. (2017). Therefore, nitrification is largely restricted to the euphotic zone while also being suppressed at low O$_2$. The partitioning between N$_2$O and NO$_2^-$ production from $R_{a_{o}}$ is calculated using the function proposed by Nevison et al. (2003), derived by fitting measured N$_2$O and NO$_2^-$ yields ($f_{a_{o}}^{\text{no}}$ and $f_{a_{o}}^{\text{no}}$, respectively) to oxygen concentrations (Goreau et al., 1980):

$$
\frac{f_{a_{o}}^{\text{no}}}{f_{a_{o}}^{\text{no}}} = 0.01 \cdot \frac{a}{[O_2]} + b, \quad (1)
$$

Relative to the original parameterization by Nevison et al. (2003), we apply distinct values of the parameters $a$ and $b$ to reflect results from a series of in situ measurements of N$_2$O production from the ETSP and ETNP OMZs (Ji et al., 2015, 2018; Santoro et al., 2021) (see Section 2.3.1). N$_2$O production by nitrification, in units of mmol N m$^{-3}$ s$^{-1}$, is therefore represented as:

$$
R_{a_{o}}^{\text{no}} = R_{a_{o}} \cdot f_{a_{o}}^{\text{no}}, \quad (2)
$$

with a similar function for NO$_2^-$ production.

In the denitrification pathway, N$_2$O is produced via NO$_2^-$ reduction at low O$_2$:

$$
R_{\text{den}}^{\text{no}} = f_{\text{den}2} \cdot R_{\text{rem}}^{\text{tot}} \cdot Q_{\text{den}}^{C:N}, \quad (3)
$$

where $f_{\text{den}2}$ is the local fraction of total OM remineralization ($R_{\text{rem}}^{\text{tot}}$) routed to NO$_2^-$ reduction (see supporting information S2), and $Q_{\text{den}}^{C:N}$ the carbon to nitrogen ratio from denitrification (472/2/106) following Anderson and Sarmiento (1994). Similarly, N$_2$O is consumed via N$_2$O reduction to N$_2$ at low O$_2$:

$$
R_{\text{den}3}^{\text{n2}} = f_{\text{den}3} \cdot R_{\text{rem}}^{\text{rem}} \cdot Q_{\text{den}}^{C:N}, \quad (4)
$$

Net production of N$_2$O ($R_{\text{net}}^{\text{n2}}$, in units of mmol N$_2$O m$^{-3}$ s$^{-1}$) results by the combination of nitrification (equation (2)) and the residual between NO$_2^-$ and N$_2$O reduction (equation (3) minus equation (4)):

$$
R_{\text{net}}^{\text{n2}} = 0.5 \cdot (R_{a_{o}}^{\text{no}} + R_{\text{den}2}^{\text{n2}}) - R_{\text{den}3}^{\text{n2}}. \quad (5)
$$
2.3 Biogeochemical Validation

To validate the biogeochemical tracer distributions simulated by ROMS-BEC, we gathered $O_2$, $NO_3^-$, $PO_4^{3-}$, and $N^*$ (defined as $16[NO_3^-] - [PO_4^{3-}]$) reconstructions from World Ocean Atlas 2018 (H. Garcia et al., 2019a) (Figures S1 - S4); additional $O_2$ estimates were provided by Dunn (2012) and Bianchi et al. (2012). Estimates of 3-D $NO_3^-$ and $N_2O$ were obtained from in situ observations (Kock & Bange, 2015; Lauvset et al., 2016), and extrapolated using a machine learning approach as outlined in Yang et al. (2020) (Figures S5 - S6). Annually averaged maps of net primary production (NPP) were obtained using three different productivity algorithms which included the Eppley Vertically Generalized Production Model (Eppley-VGPM) (Behrenfeld & Falkowski, 1997), the updated Carbon-Based Productivity Model (CbPM2) (Behrenfeld et al., 2005) and the Carbon, Absorption, and Fluorescence Euphotic-resolving model (CAFE) (Silsbe et al., 2016) (Figure S7). Level 3 satellite chlorophyll-a concentration data were obtained from the NASA Ocean Color data center (Figure S8), with all of the satellite-based data (including NPP) obtained from the Ocean Productivity Group at Oregon State University. Additional model validation is discussed in Section S.1.

2.3.1 Model Parameterization and Spinup

Further details on the formulation and parameterization of NitrOMZ are discussed in Bianchi et al. (2022). Briefly, we estimated uncertain model parameters by optimizing a one-dimensional version of the model against a cost function designed to evaluate squared errors between model estimates and local observations of tracers and N transformation rates from the ETSP (Kalvelage et al., 2013; Ji et al., 2015; Peng et al., 2016; Babbin et al., 2017, 2020). Based on the optimization, we implement a low-cost parameter set with good comparisons to observed $N_2O$ and $NO_3^-$ profiles (Opt$_{sel}$ from Bianchi et al. (2022), with parameter values in Table S4) into ROMS-BEC. The model is initially run for 20 years before evaluating against the validation products discussed in Section 2.3 and in situ ETSP observations from Kalvelage et al. (2013), Cornejo and Farías (2012), and Krahmann et al. (2021).

Based on this first comparison, we applied additional tuning to (1) bring surface concentrations of $NO_2^-$ and $NH_4^+$ closer to zero and (2) increase the concentration of $N_2O$ in suboxic waters to better match the magnitude of observed subsurface $N_2O$ maxima in the ETSP OMZ. This was accomplished by (1) slightly increasing the maximum $NH_4^+$ and $NO_2^-$ oxidation rates ($k_{ao}$ and $k_{ano}$, respectively, see supporting information S2) and (2) slightly widening the difference between exponential $O_2$ inhibition thresholds for $NO_2^-$ and $N_2O$ reduction ($K_{den2}^{oa}$ and $K_{den3}^{oa}$, respectively). We implement the final parameter set into ROMS-BEC and run a 50 year-long simulation to obtain a steady-state solution (Figure S9).

The choice of parameters results in a high $NH_4^+$ oxidation rate ($R_{ano}$) just below the euphotic zone that mostly produces $NO_3^-$ ($R_{ano}^{no}$) due to high $O_2$ concentrations. As $O_2$ becomes scarce, $R_{ano}$ decreases, yet production of $N_2O$ ($R_{ano}^{no}$) relative to $NO_2^-$ increases following equations (1) and (2). Consumption of $N_2O$ within anoxic waters occurs as all denitrification steps proceed without $O_2$ inhibition (consumption $>>$ production). Similar to Babbin et al. (2015) and Bianchi et al. (2022), we model a progressive $O_2$ inhibition of the three denitrification steps ($K_{den1}^{O2} > K_{den2}^{O2} > K_{den3}^{O2}$). Therefore, incomplete denitrification is allowed to occur at low but non-zero $O_2$ as $NO_3^-$ reduction and $NO_2^-$ reduction ($K_{den1}$ and $R_{den2}$, respectively) proceed while $N_2O$ reduction ($R_{den3}$) is inhibited (consumption $<$ production).
2.4 N$_2$O Balance and Tracer Decomposition

To track the evolution of N$_2$O from different pathways, we decompose N$_2$O into four tracers that keep track of N$_2$O sources in the model domain:

$$N_2O = N_2O_{den} + N_2O_{nit} + N_2O_{atm} + N_2O_{bou}.$$  \hspace{1cm} (6)

Each of the tracers in equation (6) follows a separate conservation equation (see supporting information S3), and is affected by a specific production process, by air-sea gas fluxes, transport from the boundaries, and destruction by the last step of denitrification (N$_2$O reduction, $R_{den3}$). By construction, the conservation equations for the individual tracers sum up to the conservation equation for N$_2$O (equation (5)), so that equation (6) can be considered a linear tracer decomposition.

Specifically, N$_2$O$_{nit}$ tracks local production by nitrification ($R_{n2o}^{nit}$, equation (2)) whereas N$_2$O$_{den}$ tracks production by denitrification ($R_{n2o}^{den}$, equation (3)) as outlined in Section 2.2.1 (pathways 3 and 6, respectively, in Figure 1). The remaining tracers, N$_2$O$_{atm}$ and N$_2$O$_{bou}$, are designed to track N$_2$O originating from the atmosphere and from production sources outside the regional ROMS domain, respectively. Saturated N$_2$O forced from the model boundaries (assuming an atmospheric N$_2$O concentration of 300 ppb) can be interpreted as originating from air-sea equilibrium with the atmosphere, whereas supersaturated N$_2$O is linked to production outside the regional model domain. We therefore split the N$_2$O forced into the domain into a saturation component (N$_2$O$_{atm}$) and a supersaturation component (N$_2$O$_{bou}$) transported into the domain.

To close separate biogeochemical budgets for each N$_2$O tracer, we similarly decomposed the N$_2$O reduction rate ($R_{den3}$, equation (4) and pathway 7 in Figure 1) and N$_2$O air-sea flux ($\Phi_{n2o}$, pathway 8 in Figure 1) to track losses with respect to the decomposed N$_2$O concentrations from within the domain:

$$R_{den3} = R_{den3}^{den} + R_{den3}^{Nit} + R_{den3}^{bou} + R_{den3}^{atm}, \hspace{1cm} (7)$$

$$\Phi_{n2o} = \Phi_{n2o}^{den} + \Phi_{n2o}^{Nit} + \Phi_{n2o}^{bou} + \Phi_{n2o}^{atm}.$$ \hspace{1cm} (8)

Here, each consumption term by denitrification is proportional to the individual tracer concentration in a linear fashion. Air-sea fluxes follow the same formulation as N$_2$O (modeled according to Wanninkhof (1992) using a constant atmospheric mixing ratio of 300 ppb), but with mixing ratios set to zero for all tracers except N$_2$O$_{atm}$, for which it is set to the total value. Therefore, while initially saturated at the boundaries, the concentration of N$_2$O$_{atm}$ can drop below saturation following consumption via $R_{den3}^{atm}$. When N$_2$O undersaturated water is exposed to the surface, atmospheric in-gassing will increase N$_2$O$_{atm}$ until N$_2$O reaches saturation. As such, N$_2$O$_{atm}$ tracks both domain ingassing of N$_2$O and import of saturated N$_2$O from the model boundaries, whereas N$_2$O$_{bou}$ exclusively tracks import of the supersaturation component. To initialize the decomposition, the initial 3-D N$_2$O was separated into N$_2$O$_{atm}$ and N$_2$O$_{bou}$ while N$_2$O$_{nit}$ and N$_2$O$_{den}$ were set to zero everywhere; thus these tracers exclusively track production within the domain after initialization (Figure S10).

Finally, to elucidate the sources of N$_2$O air-sea flux over the OMZ, we defined a budget domain that captures the extent of the ETSP OMZ horizontally (dashed blue box in Figure 3a) and vertically from the surface to 750 m depth. We configured ROMS output to close biogeochemical budgets within each grid cell, allowing us to scale them up to arbitrary 3-D domains within the model:

$$\frac{d[C]}{dt} = J + T - \Phi.$$ \hspace{1cm} (9)

Here, $d[C]/dt$ is the climatological N$_2$O rate of change calculated as the difference between snapshots at the beginning and end of each month; $T$ the transport component calculated as the divergence of advection/diffusion fluxes, $J$ the sum of biological sources and sinks, and $\Phi$ the air-sea flux controlled by gas exchange.
3 Results

3.1 Model Validation

Figure 3 shows the extent and thickness of the modelled OMZ from model years 46 - 50 (Figure 3a) and various validation products (Figure 3b - e). The simulated OMZ is centered offshore of the Peruvian and Ecuadorian coastline at roughly 8°S and extends from the Galapagos islands at the equator to nearly 15°S. This represents a displacement both equatorward and offshore compared to observations, which suggest a more coastal OMZ between southern Peru and Chile. The thickness of waters with less than 10 mmol O$_2$ m$^{-3}$ ranges mostly between 300 - 500 m and extends to roughly 105°W.

Considering that O$_2$ reconstructions based on spatial interpolation of in situ profiles underestimate the volume of anoxic waters (Bianchi et al., 2012), the inset bar plot in Figure 3a suggests that the ROMS simulation is overall within range of OMZ volume predictions across several thresholds ranging from 5 mmol O$_2$ m$^{-3}$ (Kwiecinski & Babbin, 2021) to 20 mmol O$_2$ m$^{-3}$ (H. Garcia et al., 2019a; Bianchi et al., 2012; Dunn, 2012).

Taking into account the slight equatorward geographic shift in the model OMZ, nitrogen tracer (NO$_3^-$, NO$_2^-$, and N$_2$O) sections at 250 m in Figure 4a - c compare well with validation products (Figure 4d - f). The simulation is able to replicate the expected draw-down of NO$_3^-$ and N$_2$O and increase in NO$_2^-$ within the core of the OMZ, characteristics of step-wise denitrification. The magnitude and spatial patterns of open ocean concentrations are similarly reproduced, such as the low NO$_3^-$ and N$_2$O concentrations observed in the subtropical gyre at 25°S. The oxic to suboxic transition zone (inshore of the 20 mmol O$_2$ m$^{-3}$ contour in Figure 4) also reveals an increase in N$_2$O concentrations that skillfully reproduces observational reconstructions discussed in Section 2.2.

The vertical subsurface structure and concentration magnitudes of nitrogen tracers in the ETSP OMZ are shown in Figure 4g - i. Model profiles centered over the OMZ

---

**Figure 3.** (a) ROMS Peru-Chile 10 km domain, with annually averaged OMZ thickness (O$_2$ < 10 mmol m$^{-3}$) from model years 46 - 50. The inset bar plot shows OMZ volume from ROMS and validation products based on 5, 10, 15, and 20 mmol m$^{-3}$ thresholds. The N$_2$O budget region is also shown as the area encompassed by dashed blue lines, extending vertically from the surface to 750 m. (b-d) OMZ thickness (O$_2$ < 10 mmol m$^{-3}$) from World Ocean Atlas 2018, CSIRO Atlas of Regional Seas (CARS), and the Objective mapping 2 product from Bianchi et al. (2012). (e) OMZ thickness (O$_2$ < 5 mmol m$^{-3}$) from Kwiecinski and Babbin (2021).
Figure 4.  (a-c) ROMS annually averaged NO$_3^-$, NO$_2^-$, and N$_2$O at 250 m from model years 46 - 50. Dashed black lines highlight the 20 mmol O$_2$ m$^{-3}$ contour.  (d-f) NO$_3^-$, NO$_2^-$, and N$_2$O at 250 m from World Ocean Atlas 2018 and machine learning estimates, respectively. Grey markers show the location of shipboard samples. (g-i) Averaged profiles of NO$_3^-$, NO$_2^-$, and N$_2$O from ROMS (black curves) extracted from within the OMZ (red boxes in panels a - c). Shaded regions show the 10th/90th and 25th/75th percentiles of shipboard observations from Kalvelage et al. (2013), Cornejo and Farías (2012), and Krahmann et al. (2021) conducted within the red boxes in panels d - f. Solid blue curves show ROMS O$_2$ whereas the dashed blue curves show averaged World Ocean Atlas 2018 O$_2$ over the shipboard sampling region.

show low concentrations at the surface for NO$_3^-$, NO$_2^-$, and N$_2$O. As depth increases, local maxima in NO$_2^-$ and N$_2$O can be seen at ~100 m that correspond to low but non-
zero \(O_2\). Just below this depth, where \(O_2\) drops further to anoxic levels, local minima in \(\text{NO}_3^-\) and \(\text{N}_2\text{O}\) appear along with a large peak in \(\text{NO}_3^-\) of roughly 3 \(\text{mmol} \ \text{m}^{-3}\). Beneath the anoxic OMZ, a second \(\text{N}_2\text{O}\) peak appears of slightly greater magnitude (\(~60 \ \text{µmol} \ \text{N}_2\text{O} \ \text{m}^{-3}\)) to the shallower maxima (\(~50 \ \text{µmol} \ \text{N}_2\text{O} \ \text{m}^{-3}\)). Depth-dependent distributions from shipboard measurements (Kalvelage et al., 2013; Cornejo & Farías, 2012; Krahmann et al., 2021) through the OMZ (pink shading) generally show good agreement between model and observations as \(O_2\) increases and decreases vertically. Note that the geographical location of shipboard measurements differs from the ROMS averaging box due to the equatorward and offshore OMZ shift discussed above. Despite this geographical bias, Figures 4g - i demonstrate similarity in the expression of anaerobic nitrogen cycle processes at locations with comparable \(O_2\) profiles. Remaining inconsistencies, such as the shallower depth of the observed upper \(\text{N}_2\text{O}\) maxima, can be explained by the proximity of observations to the coast, as compared to the more offshore location used to average model profiles.

Finally, given the importance of accurately representing water column denitrification, we compared total fixed nitrogen loss in ROMS via denitrification and anammox to other ETSP estimates (Figure 5). Both processes contribute roughly 50% to OMZ N-loss throughout the year, with seasonal variability mostly driven by changes in denitrification rates (red shading). The total water-column fixed nitrogen loss in the model is 25.2 \(TgN \ \text{yr}^{-1}\), within the range of observational estimates for the region (Deutsch et al., 2007; Bianchi et al., 2012; DeVries et al., 2013; Yang et al., 2017). Thus, despite a geographic shift, the model produces a realistic OMZ and associated nitrogen cycle tracers and rates.
Figure 5. (left) Monthly averaged fixed nitrogen loss from ROMS via canonical denitrification and anammox from models year 46 - 50. (right) ETSP estimates of total annual averaged nitrogen loss from ROMS, Deutsch et al. (2007), Bianchi et al. (2012), DeVries et al. (2013), and Yang et al. (2017).

3.2 ETSP N$_2$O Production

A transect crossing the core of the model OMZ shows that N$_2$O production and consumption rates from denitrification are strongly influenced by O$_2$ concentrations (Figure 6a). Within the anoxic core, N$_2$O reduction to N$_2$ ($R_{den3}$) exceeds NO$_2^-$ reduction to N$_2$O ($R_{den2}$), causing widespread net N$_2$O consumption (red shading) of nearly 0.1 $\mu$mol N m$^{-3}$ d$^{-1}$. The resulting N$_2$O and NO$_2^-$ transects (Figure 6c and 6d) show consistent offshore subsurface N$_2$O minima coinciding with peak concentrations of NO$_2^-$ at the same depth range. These patterns suggest that all three denitrification steps proceed with minimal O$_2$ inhibition within the OMZ core, supporting a zone of active fixed N-loss.

Along the exterior of the OMZ core, O$_2$ gradients preferentially inhibit N$_2$O reduction to N$_2$ ($R_{den3}$) and allow incomplete denitrification to proceed. Accordingly, net N$_2$O consumption transitions to net production (blue shading) of a similar $\sim$0.1 $\mu$mol N m$^{-3}$ d$^{-1}$ magnitude (Figure 6a). Beyond suboxic waters, net production from denitrification ceases. In contrast, maximum N$_2$O production from NH$_4^+$ oxidation ($R_{a0}^{ox}$, Figure 6b) peaks at roughly 0.01 $\mu$mol N m$^{-3}$ d$^{-1}$ and is largely restricted to a thin, mostly oxygenated layer at roughly 100 - 150 m that mirrors vertical maxima in POC flux (not shown), with little amplification at low O$_2$.

The relative contributions from the N$_2$O tracer decomposition (Figure 6e - h) highlight the disparity between N$_2$O sources. At the surface, atmospheric ingassing allows...
Figure 6. (a) Annually averaged net N\textsubscript{2}O production from denitrification for model years 46-50 along a transect from the coast at 8\textdegree S. The dotted and dashed black curves in highlight the 5 and 10 mmol O\textsubscript{2} m\textsuperscript{-3} contours, respectively. (b-d) Same as in panel (a), but for N\textsubscript{2}O production from nitrification (b), N\textsubscript{2}O (c), and NO\textsubscript{2} (d). Panels (e) - (h) show the relative contributions to N\textsubscript{2}O for each decomposed N\textsubscript{2}O tracer (N\textsubscript{2}O\textsubscript{den}, N\textsubscript{2}O\textsubscript{nit}, N\textsubscript{2}O\textsubscript{bou}, and N\textsubscript{2}O\textsubscript{atm}).

saturated N\textsubscript{2}O (N\textsubscript{2}O\textsubscript{atm}) to dominate (Figure 6h), especially offshore. Within the anoxic OMZ core, despite vigorous net N\textsubscript{2}O consumption (Figure 6a), residual N\textsubscript{2}O concentrations of \textasciitilde 20 µmol m\textsuperscript{-3} persist (Figure 6e), and are nearly completely attributed to N\textsubscript{2}O denitrification (N\textsubscript{2}O\textsubscript{den}, Figure 6e). As O\textsubscript{2} increases beyond suboxic levels, the contribution of N\textsubscript{2}O\textsubscript{den} diminishes, while contributions from supersaturated and saturated N\textsubscript{2}O from the boundaries (N\textsubscript{2}O\textsubscript{bou} and N\textsubscript{2}O\textsubscript{atm}, respectively) account for the remainder. In contrast, N\textsubscript{2}O from nitrification (N\textsubscript{2}O\textsubscript{nit}, Figure 6f) does not contribute more than 10%, with a maximum at roughly 100 m depth, suggesting that incomplete denitrification is the main contributor (\textasciitilde 10 times greater production) to local N\textsubscript{2}O production throughout the OMZ.

Notably, the contributions from supersaturated and saturated N\textsubscript{2}O transported into the OMZ from the model domain boundaries (N\textsubscript{2}O\textsubscript{bou} and N\textsubscript{2}O\textsubscript{atm}, respectively) are rapidly reduced at low O\textsubscript{2}, showing consumption of externally derived N\textsubscript{2}O within the OMZ core. Additionally, while production from incomplete denitrification is generally confined to
suboxic waters (Figure 6a), significant concentrations of $N_2O_{den}$ in oxygenated waters suggest export of $N_2O_{den}$ out of the OMZ. Together, these results highlight an important role for circulation in redistributing $N_2O$ within the ETSP.

### 3.3 Contributions of Different Processes to the $N_2O$ Balance

Figure 7 shows vertically-integrated $N_2O$ sources minus sinks ($J$ terms) over the OMZ budget region, and the annual time-series of total integrated net production for $N_2O$ and each decomposed tracer. In general, net $N_2O$ production ($J_{n2o}^{tot}$, black line in the time-series) is positive for each month with the exception of June, and reveals higher rates beginning in August that persist through December. Production is predominantly driven by denitrification ($J_{n2o}^{den}$, blue line), which also drives the bulk of monthly variability seen in $J_{n2o}^{tot}$. In contrast, production from nitrification ($J_{n2o}^{nit}$, red line) is net positive throughout the year, but only accounts for a small proportion of the $N_2O$ production. Tracers that lack domain production sources ($N_2O_{bou}$ and $N_2O_{atm}$) show consistent consumption rates throughout the year.

**Figure 7.** (top left) Vertically integrated sources-minus-sinks ($J$) for $N_2O$ from the OMZ budget domain, annually averaged from model years 46 - 50. (top right) Time-series of integrated sources-minus-sinks for $N_2O$ (black) and the decomposed $N_2O$ tracers. (bottom panels) Same as in the top left panel, but for each of the decomposed $N_2O$ tracers. Positive values (production) are shown in blue, and negative values (consumption or removal) in red.
Vertically-integrated total \(N_2O\) production (\(J_{tot}^{N_2O}\)) and denitrification-derived production (\(J_{den}^{N_2O}\)) shown in Figure 7 are similar and reveal a hot-spot of vigorous net consumption (red shading) centered at roughly 8°S and 80°W that abruptly transitions to net production (blue shading) in the surrounding ocean. The remaining tracers reveal similar hot-spots of consumption near the coast, especially supersaturated \(N_2O\) from the model boundaries (\(J_{bou}^{N_2O}\)). Integrated \(N_2O\) consumption from nitrification (\(J_{nit}^{N_2O}\)) is balanced by production immediately adjacent to the coastline and in the offshore region that ultimately leads to net production within the budget domain. The region is therefore characterized by a coastal hot-spot of net \(N_2O\) consumption that depletes both locally produced \(N_2O\) (\(N_2O_{den}\) and \(N_2O_{nit}\), blue and red lines respectively) and remote \(N_2O\) originating from outside the model domain (\(N_2O_{bou}\) and \(N_2O_{atm}\), green and purple lines respectively). Outside the coastal hot-spot, \(N_2O\) production from denitrification over-compensates for the consumption at the coast and makes the OMZ a net source of \(N_2O\) in all months, with the exception of June. As expected at steady-state, the divergence of advective and diffusive fluxes (\(T\) terms) for each \(N_2O\) tracer, shown in Figure S11, largely balances the sources minus sinks in Figure 7.

The total \(N_2O\) air-sea flux (\(\Phi_{atm}^{N_2O}\), black lines in Figure 8) peaks in July and is positive throughout the year, indicating the surface ocean of the ETSP OMZ as a constant source of \(N_2O\) to the atmosphere with higher outgassing rates throughout upwelling season (boreal summer). The major contributing components to the flux are supersaturated \(N_2O\) from the model boundaries (\(\Phi_{bou}^{N_2O}\)) and locally produced \(N_2O\) from denitrification (\(\Phi_{den}^{N_2O}\)), which exhibit similar seasonal cycles as in the total flux (\(\Phi_{tot}^{N_2O}\)), albeit with different geographical distributions. The spatial pattern of \(\Phi_{tot}^{N_2O}\) can be described as a combination of \(\Phi_{bou}^{N_2O}\) and \(\Phi_{den}^{N_2O}\) patterns; \(\Phi_{den}^{N_2O}\) is concentrated near the coast with a structure closely mirroring the coastal hot-spot of consumption shown by Figure 7, whereas \(\Phi_{bou}^{N_2O}\) takes place mostly along the northern boundary of the budget region (albeit with maximum outgassing near the coast). Since the \(N_2O_{atm}\) tracer can be consumed via \(N_2O\) reduction within the domain (section 2.4), \(\Phi_{atm}^{N_2O}\) similarly tracks the coastal hot-spot, but reveals oceanic ingassing at the surface, peaking in July, which brings \(N_2O_{atm}\) back towards saturation. Finally, the magnitude of air-sea flux from local nitrification (\(\Phi_{nit}^{N_2O}\)) is small but net positive, and shows a similar July maximum peaking near the coast.

### 3.4 \(N_2O\) Balance

A schematic of the annual \(N_2O\) balance (Figure 9) shows that total OMZ \(N_2O\) production is dominated by incomplete denitrification (174 \(Gg\,N\,y^{-1}\)), whereas nitrification contributes a smaller fraction (18 \(Gg\,N\,y^{-1}\)). Conversely, consumption of both saturated and supersaturated \(N_2O\) from the model boundaries (\(N_2O_{atm}\) and \(N_2O_{bou}\)) drives a net \(N_2O\) loss (106 and 34 \(Gg\,N\,y^{-1}\) respectively). The excess production makes the OMZ a net \(N_2O\) source to the atmosphere (51 \(Gg\,N\,y^{-1}\)). This production takes place predominantly on the fringe of the OMZ both vertically and horizontally, where thick oxic layers support net \(N_2O\) accumulation from the denitrification pathway (Figures 6 and 7).

The budget also suggests that the corresponding outgassing pathways from local production sources are somewhat inefficient; the annual export of 125 and 7 \(Gg\,N\,y^{-1}\) of \(N_2O_{den}\) and \(N_2O_{nit}\) (respectively) suggests that \(\sim72\%\) and \(\sim39\%\) of their net production (\(J_{den}^{N_2O}\) and \(J_{nit}^{N_2O}\), respectively) ultimately avoids outgassing within the budget domain. Yet despite the surprising magnitude of these production export rates, high net import rates of \(N_2O_{bou}\) and \(N_2O_{atm}\) from the model boundaries (188 and 38 \(Gg\,N\,y^{-1}\), respectively) drive an annual net source of 94 \(Gg\,N\,y^{-1}\) into the OMZ region. Separating the advective fluxes into zonal, meridional, and vertical components reveals zonal fluxes along the western boundary of the domain as the primary interface of \(N_2O\) exchange with the surrounding ocean, organized as alternating narrow bands of \(N_2O\) import (Figure S12e, red shading) and export (blue shading). The net transport is driven by supersat-
urated N\textsubscript{2}O (N\textsubscript{2}O\textsubscript{bou}) supplied through the boundaries (Figure S12c), with the most intense import along the equator at roughly 150 m depth (see also Figure 6g). In contrast, denitrification-driven export (Figure S12a) is focused further to the south (roughly 8°S) and at deeper depths (200 - 500 m, also evident in Figure 6e).

After accounting for boundary exchanges, local subsurface production and consumption, and periodic ingassing of N\textsubscript{2}O\textsubscript{atm} (Figure 8), all tracers reveal net outgassing with \( \Phi_{\text{n}_2\text{O}_{\text{bou}}} \) and \( \Phi_{\text{n}_2\text{O}_{\text{den}}} \) contributing \( \sim \)56\% and \( \sim \)34\% (respectively) to the annual 152 Gg N yr\textsuperscript{-1} outgassed to the atmosphere. Thus, what emerges from the above descriptions is an ETSP OMZ that is characterized by: (1) A consistent supply of N\textsubscript{2}O\textsubscript{bou} and N\textsubscript{2}O\textsubscript{atm} from predominantly zonal subsurface currents in the tropical band (Figures S11, S12c, and S12e); (2) Advection of all N\textsubscript{2}O tracers into a coastal hot-spot where vigorous consumption leads to significant N-loss; (3) Net N\textsubscript{2}O production predominantly by denitrification within suboxic gradients surrounding the OMZ (Figure 7); (4) Significant export of N\textsubscript{2}O\textsubscript{den} into the exterior ocean (Figures S11 and S12); (5) Consumption of locally produced and externally derived N\textsubscript{2}O; and (6) Year-round air-sea flux of N\textsubscript{2}O driven predominantly by imported N\textsubscript{2}O\textsubscript{bou} and locally produced N\textsubscript{2}O\textsubscript{den} that upwell and outgas along the northern extent of the OMZ domain and along the coast, respectively (Figure 8).
Figure 9. Schematic of the ETSP OMZ N$_2$O budget, with calculated averages (Gg N yr$^{-1}$) of net air-sea flux ($\Phi$), advection ($T$), and sources-minus-sinks ($J$) from model years 46 - 50. Bar plots indicate both the direction of, and relative magnitude of, budget averages.

4 Discussion and Conclusions

We developed a climatological, eddy-resolving simulation of the ETSP OMZ that reproduces the main patterns in the spatial distribution of observed nitrogen tracers and transformation rates. Despite enhanced yields at low O$_2$, we find almost negligible local contributions from nitrification; rather, maximum N$_2$O production rates from NH$_4^+$ oxidation ($P_{\text{nit}}^{n2o}$) follow vertical maxima in POC flux which occur well above the oxycline throughout much of the domain east of -90°W (Figure 6). Closer to shore, as the OMZ core shoals to ~100 m, production from nitrification ($J_{\text{nit}}^{n2o}$ in Figure 7) suggests that N$_2$O$_{\text{nit}}$ is subsequently mixed into anoxic waters and consumed via N$_2$O reduction. The major contribution of nitrification to N$_2$O production takes place immediately adjacent to the coast, where low O$_2$ waters at shallow depths lead to enhanced production and an efficient outgassing route. As a result, the air-sea flux pattern in Figure 8 shows negligible contributions from nitrification ($\Phi_{\text{nit}}^{n2o}$) throughout the domain, with the exception of coastal outgassing driven by upwelling. While the contribution from nitrification to N$_2$O production in NitrOMZ is sensitive to the choice of the parameters in equation (1), the values used in this study are constrained by observations (Section 2.3.1) and fall within range of previous estimates (Ji et al., 2018; Santoro et al., 2021) which similarly suggest weak nitrification production. Therefore, similar to the results of Ji et al. (2015) and Babbin et al. (2015), our simulation suggests that local production from nitrification is not a dominant pathway for N$_2$O outgassing flux in this region.
Instead, N$_2$O production is dominated by incomplete denitrification which takes place along the suboxic fringes of the anoxic OMZ core (Figure 6a, Figure 6e, and Figure 7), in agreement with recent studies (Babbin et al., 2015; Ji et al., 2018). In general, the three step-wise denitrification rates show a strong seasonal dependence and are primarily controlled by the timing of organic matter supply from the euphotic zone (Figure S13) rather than variability in low O$_2$ volumes throughout the year (Figure S14).

Within the anoxic core of the OMZ, rapid N$_2$O consumption rates (Figure 6a) indicate short residence times for N$_2$O produced via NO$_2^-$ reduction (N$_2$O$_{den}$) due to the strong coupling between denitrification steps at low O$_2$. Significant net N$_2$O production by denitrification (J$_{den}$) occurs where high rates of vertical POC flux overlap with an anoxic to suboxic O$_2$ gradient; there, the difference in O$_2$ tolerance thresholds leads to a relatively small residual between the large NO$_2^-$ and N$_2$O reduction rates within the domain (Babbin et al., 2015). As oxic organic matter remineralization stops within the anoxic OMZ core, this leads to the characteristic double peak structure in N$_2$O profiles (Figure 6c) bounding the OMZ throughout most of the domain.

Spatially, the vertical depth range occupied by anoxic to suboxic gradients plays a key role in determining regions of net production or consumption via the denitrification pathway. For instance, the integrated J$_{den}$ in Figure 7 reveals consumption along the northern extent of the Peruvian coast at roughly 8°S; considering this pattern, Figure 6a shows relatively sharp O$_2$ gradients above and below the OMZ around -85°W, indicating that N$_2$O consumption is particularly strong near the coast, where relatively thin but shallow suboxic layers are found. In contrast, suboxic layers become thicker further offshore, resulting in conditions more favorable to N$_2$O production. Therefore, the high rates of coastal outgassing observed in Figure 8 are at least partially driven by net transport from more productive surrounding waters (Figure S11).

Our results demonstrate the role of advection in redistributing supersaturated N$_2$O within the ETSP. Notably, the EUC and SSCC are revealed as zonal conduits controlling the import of supersaturated N$_2$O (N$_2$O$_{in}$) from the boundaries (and thus, outgassing-favorable N$_2$O) into the OMZ domain. This is demonstrated by the large fractional contributions to N$_2$O at 150 m throughout the eastern extent of the transect in Figure 6g, which match subsurface patterns in Figure S12c. These results are consistent with those from Yang et al. (2020), who highlighted the tropics in the Eastern Pacific as an important outgassing region with seasonality driven predominantly by the timing of upwelling (May to September). While a significant fraction of the imported N$_2$O is ultimately advected into the anoxic OMZ to be consumed (Figures 6g and 7), the remainder is responsible for the bulk (~56%) of the outgassing flux over the OMZ domain. As the N$_2$O budget and boundary export schematic in Figures 9 and S12 show, circulation also plays a key role in exporting the majority (roughly 72%) of local denitrification-derived N$_2$O production (J$_{den}$) out of the OMZ budget domain. Much of this export takes place along the western boundary (Figure S12), but at more southerly latitudes and at deeper depths compared to the import of supersaturated N$_2$O from the boundaries (J$_{in}$). Unfortunately, our regional simulations do not allow us to explore the fate of this N$_2$O. Global or basin-wide simulations would enable tracking the interplay of N$_2$O sources and sinks within and outside OMZs. A portion of the denitrification-derived N$_2$O export may recirculate back into the eastward equatorial currents, or could instead add to N$_2$O concentrations in offshore waters, such as those observed by Santoro et al. (2021).

The residual between rapid N$_2$O production and consumption by denitrification is heavily coupled to O$_2$ dynamics and thus a major portion of N$_2$O outgassing in this region is likely sensitive to future changes in OMZ magnitude and geometry. Observations suggest that deoxygenation over the past 50 years has led to expansion of OMZ volumes and shoaling of the upper oxycline (Stramma et al., 2008; Schmidtko et al., 2017). Yet, whether this has caused a positive or negative impact on N$_2$O production likely depends on the relative changes of anoxic versus suboxic volumes. If future climate change
results in an increase in the volume of suboxic waters, as suggested by Earth system model projections (Cabré et al., 2015; Kwiatkowski et al., 2020; Busecke et al., 2019), it would increase production from both incomplete denitrification and nitrification, leading to a positive climate feedback. Conversely, an increase in the volume of anoxic waters may drive enhanced N\textsubscript{2}O consumption and constitute a negative climate feedback.

Future changes in the oxycline depth via projected stratification or wind changes (Kwiatkowski et al., 2020; Busecke et al., 2019; Bakun, 1990) may alter the coupling between local production and outgassing over OMZs, while also affecting the export of supersaturated N\textsubscript{2}O into the nearby gyres. The lack of interannual forcing in this study also leaves gaps in understanding ENSO impacts. OMZ geometry and total denitrification rates are sensitive to ENSO variability (Yang et al., 2017), thus N\textsubscript{2}O production and outgassing are likely to exhibit similar year-to-year changes. Interannually forced, high-resolution models capable of simulating both denitrification and nitrification-derived production are needed to resolve these emerging questions.

Open Research Section

The ROMS model code used to generate the simulation (Shchepetkin & McWilliams, 2005; Shchepetkin, 2015), and the MATLAB (MATLAB, 2020) scripts and output used to generate the figures shown in the paper, can be found at https://doi.org/10.5281/zenodo.7374360 (McCoy et al., 2022). Raw model output can be obtained from the Authors upon request. Biogeochemical validation data were provided by the World Ocean Atlas 2018 (H. Garcia et al., 2019a, 2019b), MEMENTO (Kock & Bange, 2015) and GLODAPv2 (Key et al., 2015; Lauvset et al., 2016) databases, with additional shipboard observations from Kalvelage et al. (2013), Cornejo and Farias (2012), and Krahmann et al. (2021). The MEMENTO database is administered by the Kiel Data Management Team at GEOMAR Helmholtz Centre for Ocean Research and supported by the German BMBF project SOPRAN (Surface Ocean Processes in the Anthropocene, http://sopran.pangaea.de). The database is accessible through the MEMENTO webpage (https://memento.geomar.de). AVISO satellite data used in model validation were processed by SSALTO/DUACS and distributed by AVISO+ at https://www.aviso.altimetry.fr with support from CNES. MODIS L3 ocean color data were obtained from the NASA/GSFC MODAPS Service website at https://oceancolor.gsfc.nasa.gov/l3/. The ERA-Interim dataset (Dee et al., 2011), which was used to force the model, was obtained from the European Centre for Medium-Range Weather Forecasts (ECMWF) at https://www.ecmwf.int. Thanks to ICDC, CEN, University of Hamburg for data support in obtaining ERA-Interim products.

Acknowledgments

This material is based upon work supported by the U.S. National Science Foundation under grant OCE-1847687. D.B. acknowledges support from the Alfred P. Sloan Foundation, and computational support by the Extreme Science and Engineering Discovery Environment (XSEDE) through allocation TG-OCE17001.

References


-21-


–22–
doi: 10.1002/2013GL058888


ceedings of the National Academy of Sciences of the United States of America, 117(22). doi: 10.1073/pnas.1921914117


Supporting Information for "Pathways of Nitrous Oxide Production in the Eastern Tropical South Pacific Oxygen Minimum Zone"
Daniel McCoy¹, Pierre Damien¹, Daniel Clements¹, Simon Yang¹, Daniele Bianchi¹

¹Department of Atmospheric and Oceanic Sciences

¹University of California – Los Angeles

¹520 Portola Plaza, Los Angeles, CA 90095, USA

Contents of this file
1. Text S1 to S4
   • S1: Treatment of Organic Matter
   • S2: NitrOMZ Nitrogen Cycle
   • S3: NitrOMZ Tracer Sources-and-sinks
   • S4: Light Inhibition
2. Tables S1 to S5
3. Figures S1 to S14

Corresponding author: Daniel McCoy, Department of Atmospheric and Oceanic Sciences, University of California – Los Angeles, 520 Portola Plaza, Los Angeles, CA 90095, USA. (demccoy@atmos.ucla.edu)
**S1: Treatment of Organic Matter** In the model, remineralization of sinking particulate OM follows the formulation of Moore, Doney, and Lindsay (2004), where sinking is implicit and based on the ballast model from Armstrong, Lee, Hedges, Honjo, and Wakeham (2001). Particulate organic carbon (POC) in BEC is produced at each time-step following:

\[ R_{\text{prod}}^{\text{poc}}(z) = (R_{\text{graze,poc}}^{\text{sp}}(z) + R_{\text{graze,poc}}^{\text{diat}}(z) + R_{\text{graze,poc}}^{\text{diaz}}(z)) + (R_{\text{agg}}^{\text{sp}}(z) + R_{\text{agg}}^{\text{diat}}(z) + R_{\text{agg}}^{\text{diaz}}(z)) + \\
R_{\text{loss,poc}}^{\text{sp}}(z) + R_{\text{loss,poc}}^{\text{diat}}(z) + R_{\text{loss,poc}}^{\text{diaz}}(z) + \int R_{\text{zoo}}^{\text{d}} R_{\text{zoo}}^{\text{l}}(z) dz. \]

See Table S1 for descriptions of each rate; further details can be found in Deutsch et al. (2021). POC production is then partitioned into a free and mineral component:

\[ R_{\text{prod}}^{\text{poc}}(z) = R_{\text{prod}}^{\text{free,poc}}(z) + R_{\text{prod}}^{\text{min,poc}}(z). \]  

Following equation (1), both free and mineral POC is instantaneously distributed in the water column following one-dimensional steady-state production-remineralization equations. The vertical profile of free POC flux (\( \Phi_{\text{poc}} \)) is calculated as:

\[ \Phi_{\text{free,poc}}(z) = \Phi_{\text{free,poc}}(z_o) e^{-\frac{1}{\lambda_{\text{poc}}}(z-z_o)} + \int_{z_o}^{z} R_{\text{prod}}^{\text{free,poc}}(z) e^{-\frac{1}{\lambda_{\text{poc}}}(z-z_o)} dz. \]

Here, \( \lambda_{\text{poc}} \) is a discretized exponential scale length computed from an initial scale length \( \gamma_{\text{poc}} \) that is modified by both the local \( O_2 \) concentration of layer \( z \):

\[ \gamma_{\text{poc}} = \begin{cases} 
\gamma_{\text{poc}} \ast 3.3 & \text{where } O_2 < 5 \text{ mmol/m}^3 \\
\gamma_{\text{poc}} \ast (1 + (3.3 - 1)(40 - o_2)/35) & \text{where } 5 \text{ mmol/m}^3 < O_2 < 40 \text{ mmol/m}^3 \\
\gamma_{\text{poc}} & \text{elsewhere}
\end{cases} \]
and its thickness $dz$:

$$\lambda_{\text{poc}} = \begin{cases} 
\gamma_{\text{poc}} \ast (1.0), & \text{where } dz < 100m \\
\gamma_{\text{poc}} \ast (1.0 \ast (2.9 - 1.0) \ast (-dz - 1.0)/(2.9 - 1.0)), & \text{where } 100m < dz < 250m \\
\gamma_{\text{poc}} \ast (2.9 \ast (5.6 - 2.9) \ast (-dz - 2.9)/(5.6 - 2.9)), & \text{where } 250m < dz < 500m \\
\gamma_{\text{poc}} \ast (5.6 \ast (5.7 - 5.6) \ast (-dz - 5.6)/(5.7 - 5.6)), & \text{where } 500m < dz < 700m \\
\gamma_{\text{poc}} \ast (5.7), & \text{elsewhere}
\end{cases}$$

(4)

See Table S2 for parameter values.

The vertical profile of POC flux for each mineral is calculated as the sum of a soft and hard component (where the hard component is a fraction of the total based on $f_{\text{peaco}}$, $f_{\text{psio}}$, and $f_{\text{dust}}$, respectively, see Table S2). The soft component for CaCO$_3$, SiO$_2$, and dust follow similar remineralization processes as in equation (2), whereas the hard components remineralize according to $\lambda_{\text{hard}}$ and $\lambda_{\text{hard,dust}}$ (for dust). The fluxes of each mineral are then summed in C units:

$$\Phi_{\min,poc}(z) = \rho_{\text{peaco}}(\Phi_{\text{peaco}}^{\text{soft}}(z) + \Phi_{\text{peaco}}^{\text{hard}}(z)) +$$

$$\rho_{\text{psio}}(\Phi_{\text{psio}}^{\text{soft}}(z) + \Phi_{\text{psio}}^{\text{hard}}(z)) +$$

$$\rho_{\text{dust}}(\Phi_{\text{dust}}^{\text{soft}}(z) + \Phi_{\text{dust}}^{\text{hard}}(z))$$

Remineralization at each vertical level is then calculated as the divergence of the POC flux:

$$R_{\text{rem}}^{\text{poc}}(z) = R_{\text{prod}}^{\text{poc}}(z) + \frac{d}{dz}(\Phi_{\text{free,poc}}(z) + \Phi_{\min,poc}(z))$$

(5)

In contrast, dissolved organic carbon (DOC) is an explicit ROMS-BEC tracer and is remineralized ($R_{\text{rem}}^{\text{doc}}$) based on a timescale of 15 years with a sharp decrease (6.85%) applied below the euphotic zone as in Frischknecht, Münnich, and Gruber (2017). Local OM remineralization in the water column ($R_{\text{rem}}^{\text{tot}}$) is calculated as the sum of POC and DOC remineralization:

$$R_{\text{rem}}^{\text{tot}}(z) = R_{\text{rem}}^{\text{poc}}(z) + R_{\text{rem}}^{\text{doc}}(z).$$

(6)
**S2: NitrOMZ Nitrogen Cycle** The NitrOMZ model expands BEC by including, along with aerobic remineralization ($R_{rem}$), additional heterotrophic denitrification steps under low-O$_2$ conditions (Bianchi et al., 2022): NO$_3^-$ reduction ($R_{den1}$), NO$_2^-$ reduction ($R_{den2}$), and N$_2$O reduction ($R_{den3}$). In order to preserve BEC OM cycle, $R_{rem}^{tot}$ (equation (6)) is partitioned into four possible components at each vertical level and time-step:

$$R_{rem}^{tot}(z) = R_{rem}(z) + R_{den1}(z) + R_{den2}(z) + R_{den3}(z) = \sum_{n=1}^{4} R_{i}(z),$$

where $i$ represents one of the four respiration pathways. In practice, we calculate the contribution to total remineralization by each pathway $i$ as:

$$R_{i}(z) = f_{i}(z) \cdot R_{rem}^{tot}(z),$$

where $f_{i}$ is the relative fraction of remineralization carried out by the process $i$. The individual depth-dependent fractions are calculated as:

$$f_{i}(z) = \frac{r_{i}(z)}{\sum_{i=1}^{4} r_{i}(z)},$$

where $r_{i}$ is the specific heterotrophic respiration rate of the reaction, calculated based on a maximum remineralization rate modulated by a Michaelis-Menten function of the oxidant utilized (O$_2$, NO$_3^-$, NO$_2^-$, and N$_2$O for $R_{rem}$, $R_{den1}$, $R_{den2}$, and $R_{den3}$, respectively) and an exponential inhibition by oxygen (ignored for aerobic respiration):

$$r_{i}(z) = k_{i} \cdot \frac{[X](z)}{K_{i}^{X} + [X](z)} \cdot e^{-\frac{O_2(z)}{K_{O_2}^{i}}}.$$  

Here, $k_{i}$ represents the maximum respiration rate for each reaction, $K_{i}^{X}$ is the half saturation constant for oxidant $[X]$ uptake, and $K_{O_2}^{i}$ is the scale for inhibition by oxygen.

The chemolithotrophic rates of NH$_4^+$ oxidation ($R_{ao}$), NO$_2^-$ oxidation ($R_{no}$), and anaerobic NH$_4^+$ oxidation (anammox, $R_{ax}$) are represented in NitrOMZ using Michaelis-Menten
functions for both the oxidants (O$_2$, O$_2$, and NO$_2^-$ for $K_{ao}$, $K_{no}$, and $K_{ax}$, respectively) and reductants (NH$_4^+$, NO$_2^-$, and NH$_4^+$, respectively). The general form for $R_{ao}$ and $R_{no}$ is:

$$R_i(z) = k_i \cdot \frac{[X](z)}{K_X^i + [X](z)} \cdot \frac{[Y](z)}{K_Y^i + [Y](z)}.$$  \hspace{1cm} (11)

Here, $k_i$ represents the maximum respiration rate for each reaction, and $K_X^i$ and $K_Y^i$ are the half saturation constants for oxidant [X] and reductant [Y] uptake, respectively. Both $R_{ao}$ and $R_{no}$ are also inhibited by light, outlined in 1. The rate of anammox follows a similar calculation, but with an additional rate-specific exponential $O_2$ inhibition ($K_{o2}^a$) term applied, similar to the heterotrophic denitrification steps in equation (10). See Table S4 for parameter values used in this study.
S3: NitrOMZ Tracer Sources-and-sinks

NitrOMZ represents six major components of the marine nitrogen cycle: N₂, NO₃⁻, NO₂⁻, N₂O, NH₄⁺, and organic nitrogen, which is linked to POC and DOC via fixed stoichiometry. The biogeochemical sources and sinks for each of the remaining tracers (in units of mmol m⁻³) are:

\[
\frac{d}{dt}(N₂) = (Q_{den}^{C:N} \cdot R_{den3}) + R_{ax} + (0.5 \cdot R_{sed}) \tag{12}
\]

\[
\frac{d}{dt}(NO₃⁻) = R_{no} - (Q_{den}^{C:N} \cdot R_{den1}) - R_{den}^{sed} - R_{up,nos}^{up} - R_{sp}^{up} - R_{diaz}^{up} \tag{13}
\]

\[
\frac{d}{dt}(NO₂⁻) = R_{ao}^{no2} - R_{no} + Q_{den}^{C:N}(R_{den1} - R_{den2}) - R_{ax} - R_{up,nos}^{up} - R_{sp}^{up} - R_{diaz}^{up} \tag{14}
\]

\[
\frac{d}{dt}(N₂O) = 0.5(R_{ao}^{no2} + (Q_{den}^{C:N} \cdot R_{den2})) - (Q_{den}^{C:N} \cdot R_{den3}) \tag{15}
\]

\[
\frac{d}{dt}(NH₄⁺) = DON(\tau^{DON}) + DONr(\tau^{DONr}) - R_{ao} - R_{ax} + Q_{rem}^{C:N}(R_{loss,dic}^{up} + R_{diaz,dic}^{up} + R_{loss,dic}^{up}) \tag{16}
\]

\[
+ Q_{rem}^{C:N}(R_{graze,dic}^{up} + R_{diaz,dic}^{up} + R_{loss,dic}^{up})
\]

\[
+ Q_{rem}^{C:N}(R_{poc}^{up} (1 - Q^{DONr})) - (R_{up,nh4}^{sp} + R_{up,nh4}^{diaz} + R_{up,nh4}^{diaz}) \tag{17}
\]

Here the symbol \(d/dt\) denotes the sum of the local time derivative and the physical transport, and \(Q_{rem}^{C:N}\) and \(Q_{den}^{C:N}\) represent the approximate carbon to nitrogen ratio from remineralization (16/117) and denitification (472/2/106), respectively, following Anderson and Sarmiento (1994). The sedimentary denitification rate \(R_{sed}^{den}\) follows the same formulation as in Deutsch et al. (2021).

Following the N₂O tracer and N₂O reduction rate decomposition described in Section 2.4, the equations for each of the N₂O tracers (in units of mmol N₂O m⁻³) are represented...
as:

\[
\frac{d}{dt}(N_2O_{den}) = Q^{C:N}_{den} \left(0.5 \cdot R_{den}^2 - R_{den}^3\right),
\]

(18a)

\[
\frac{d}{dt}(N_2O_{nit}) = \left(0.5 \cdot R_{ao}^{n2o}\right) - \left(Q^{C:N}_{den} \cdot R_{den}^{nit}\right),
\]

(18b)

\[
\frac{d}{dt}(N_2O_{bou}) = -Q^{C:N}_{den} \cdot R_{den}^{bou},
\]

(18c)

\[
\frac{d}{dt}(N_2O_{atm}) = -Q^{C:N}_{den} \cdot R_{den}^{atm}.
\]

(18d)

(18e)

Descriptions of each nitrogen cycle tracer are presented in Table S5.
**S4: Light Inhibition** In NitrOMZ, rates of both $\text{NH}_4^+$ and $\text{NO}_2^-$ oxidation ($R_{ao}$ and $R_{no}$, respectively) are photo-inhibited by photosynthetically available radiation (PAR) near the surface, modelled in ROMS-BEC using the same formulation as in Frischknecht et al. (2017). Surface PAR ($\text{PAR}_{in}$) is attenuated with depth via a discretized exponential scale length parameter ($\lambda_{par}$) computed from an initial surface value ($\lambda_{par,i}$):

$$\lambda_{par,i} = \max(0.02, \text{Chl}_{tot}),$$  \hspace{1cm} (19)

where $\text{Chl}_{tot}$ is the sum of community chlorophyll from diatoms ($\text{Chl}_{diat}$), diazotrophs ($\text{Chl}_{diaz}$), and small phytoplankton ($\text{Chl}_{sp}$). The attenuation coefficient is then further modified depending on the initial value of $\lambda_{par,i}$:

$$\lambda_{par}(z) = \begin{cases} 0.0919 \cdot (\lambda_{par})^{0.3536} \cdot dz & \text{where } \lambda_{par,i} < 0.13224, \\ 0.1131 \cdot (\lambda_{par})^{0.4562} \cdot dz & \text{where } \lambda_{par,i} \geq 0.13224. \end{cases}$$  \hspace{1cm} (20)

In the initial surface grid cell, attenuation of $\text{PAR}_{in}$ from the top of the cell over the cell thickness ($m$) is calculated as:

$$\text{PAR}_{out}(z) = \text{PAR}_{in}(z) \cdot e^{-\lambda_{par}(z)}.$$  \hspace{1cm} (21)

For each cell, if both $\text{PAR}_{in}(z)$ and $\text{PAR}_{out}(z)$ are less than the PAR limitation for either rate ($\text{PAR}_{lim}^{ao}$ and $\text{PAR}_{lim}^{no}$, here both set to 1 W m$^{-2}$), then photo-inhibition is avoided and the rates are calculated via equation (11). If only $\text{PAR}_{in}(z)$ exceeds PAR limitation, each rate is attenuated via:

$$R_{ao}(z) = R_{ao}(z) \cdot \log\left(\frac{\text{PAR}_{out}(z)/\text{PAR}_{lim}^{ao}}{-\lambda_{par}(z)}\right)$$  \hspace{1cm} (22)

$$R_{no}(z) = R_{no}(z) \cdot \log\left(\frac{\text{PAR}_{out}(z)/\text{PAR}_{lim}^{no}}{-\lambda_{par}(z)}\right).$$  \hspace{1cm} (23)

Following the calculation, $\text{PAR}_{out}(z)$ is set to $\text{PAR}_{in}(z)$ for the cell below and iterated over the number of depths.
Table S1. Organic matter cycle rates.

<table>
<thead>
<tr>
<th>Rates</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{sp\text{graze, poc}}$</td>
<td>Grazing loss for small phytoplankton routed to POC</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{diat\text{graze, poc}}$</td>
<td>Grazing loss for diatoms routed to POC</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{diaz\text{graze, poc}}$</td>
<td>Grazing loss for diazotrophs routed to POC</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{sp\text{agg}}$</td>
<td>Aggregation loss of small phytoplankton</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{diat\text{agg}}$</td>
<td>Aggregation loss of diatoms</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{diaz\text{agg}}$</td>
<td>Aggregation loss of diazotrophs</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{sp\text{loss,poc}}$</td>
<td>Non-grazing mortality of small phytoplankton routed to POC</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{diat\text{loss,poc}}$</td>
<td>Non-grazing mortality of diatoms routed to POC</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{diaz\text{loss,poc}}$</td>
<td>Non-grazing mortality of diazotrophs routed to POC</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{\text{prod}\text{poc}}$</td>
<td>Amount of particulate organic C produced</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{\text{prod}\text{free,poc}}$</td>
<td>Amount of non-mineral particulate organic C produced</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{\text{prod}\text{min,poc}}$</td>
<td>Amount of mineral particulate organic C produced</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$R_{\text{rem,poc}}$</td>
<td>Amount of particulate organic C remineralized</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$\Phi_{\text{poc}}$</td>
<td>Incoming particulate C-flux</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$\Phi_{\text{free,poc}}$</td>
<td>Incoming non-mineral particulate C-flux</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$\Phi_{\text{min,poc}}$</td>
<td>Incoming mineral particulate C-flux</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$\Phi_{\text{soft,paco}}$</td>
<td>Incoming soft CaCO$_3$ particulate flux</td>
<td>mmol CaCO$_3$/m$^3$/s</td>
</tr>
<tr>
<td>$\Phi_{\text{soft,psio}}$</td>
<td>Incoming soft SiO$_2$ particulate flux</td>
<td>mmol SiO$_2$/m$^3$/s</td>
</tr>
<tr>
<td>$\Phi_{\text{soft,dust}}$</td>
<td>Incoming soft dust flux</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$\Phi_{\text{hard,paco}}$</td>
<td>Incoming hard CaCO$_3$ particulate flux</td>
<td>mmol CaCO$_3$/m$^3$/s</td>
</tr>
<tr>
<td>$\Phi_{\text{hard,psio}}$</td>
<td>Incoming hard SiO$_2$ particulate flux</td>
<td>mmol SiO$_2$/m$^3$/s</td>
</tr>
<tr>
<td>$\Phi_{\text{hard,dust}}$</td>
<td>Incoming hard dust flux</td>
<td>mmol C/m$^3$/s</td>
</tr>
</tbody>
</table>
### Table S2. Organic matter cycle parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{\text{pcaco}}$</td>
<td>Associated molar ratio of CaCO$_3$ to POC</td>
<td>0.417</td>
<td>mol CaCO$_3$/mol POC</td>
</tr>
<tr>
<td>$\rho_{\text{psio}}$</td>
<td>Associated molar ratio of SiO$_2$ to POC</td>
<td>0.250</td>
<td>mol SiO$_2$/mol POC</td>
</tr>
<tr>
<td>$\rho_{\text{dust}}$</td>
<td>Associated molar ratio of dust to POC</td>
<td>4163.197</td>
<td>mol dust/mol POC</td>
</tr>
<tr>
<td>$\gamma_{\text{poc}}$</td>
<td>Initial length scale for remineralization of POC</td>
<td>88</td>
<td>m</td>
</tr>
<tr>
<td>$\gamma_{\text{pcaco}}$</td>
<td>Length scale for remineralization of CaCO$_3$</td>
<td>150</td>
<td>m</td>
</tr>
<tr>
<td>$\gamma_{\text{psio}}$</td>
<td>Length scale for remineralization of SiO$_2$</td>
<td>250</td>
<td>m</td>
</tr>
<tr>
<td>$\gamma_{\text{dust}}$</td>
<td>Length scale for remineralization of dust</td>
<td>200</td>
<td>m</td>
</tr>
<tr>
<td>$\lambda_{\text{hard}}$</td>
<td>Length scale for remineralization of hard subclass</td>
<td>40</td>
<td>km</td>
</tr>
<tr>
<td>$\lambda_{\text{hard,dust}}$</td>
<td>Length scale for remineralization of hard dust subclass</td>
<td>125</td>
<td>km</td>
</tr>
<tr>
<td>$f_{\text{poc}}$</td>
<td>Fraction of POC routed to hard subclass</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
<td>$f_{\text{pcaco}}$</td>
<td>Fraction of CaCO$_3$ routed to hard subclass</td>
<td>0.3</td>
<td>N/A</td>
</tr>
<tr>
<td>$f_{\text{psio}}$</td>
<td>Fraction of SiO$_2$ routed to hard subclass</td>
<td>0.03</td>
<td>N/A</td>
</tr>
<tr>
<td>$f_{\text{dust}}$</td>
<td>Fraction of dust routed to hard subclass</td>
<td>0.97</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Table S3. Nitrogen cycle rates

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{rem}$</td>
<td>Remineralized particulate organic C</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{no}$</td>
<td>Rate of NH$_4^+$ oxidation to NO$_2^-$</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{n2o}$</td>
<td>Rate of NH$_4^+$ oxidation to N$_2$O</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{n2}$</td>
<td>Rate of NO$_2$ oxidation to NO$_3^-$</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{den1}$</td>
<td>Rate of NO$_3^-$ reduction to NO$_2$</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{den2}$</td>
<td>Rate of NO$_2$ reduction to N$_2$O</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{den3}$</td>
<td>Rate of N$_2$O reduction to N$_2$</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{ax}$</td>
<td>Rate of NO$_2^-$ and NO$_3^-$ loss to N$_2$ via anammox</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{den}$</td>
<td>Rate of sedimentary denitrification</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{loss,dic}$</td>
<td>Non-grazing mortality of small phytoplankton routed to DIC</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{loss,dic}$</td>
<td>Non-grazing mortality of diatoms routed to DIC</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{loss,dic}$</td>
<td>Non-grazing mortality of diazotrophs routed to DIC</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{zoop}$</td>
<td>Zooplankton mortality routed to DIC</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{graze,dic}$</td>
<td>Grazed mortality of small phytoplankton routed to DIC</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{graze,dic}$</td>
<td>Grazed mortality of diatoms routed to DIC</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{graze,dic}$</td>
<td>Grazed mortality of diazotrophs routed to DIC</td>
<td>mmol C/m³/s</td>
</tr>
<tr>
<td>$R_{up,nh}$</td>
<td>Uptake of NH$_4^+$ by small phytoplankton</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{up,nh}$</td>
<td>Uptake of NH$_4^+$ by diatoms</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{diaz}$</td>
<td>Uptake of NH$_4^+$ by diazotrophs</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{ap,nh}$</td>
<td>Uptake of NO$_3^-$ by small phytoplankton</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{ap,nh}$</td>
<td>Uptake of NO$_3^-$ by diatoms</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{ap,nh}$</td>
<td>Uptake of NO$_3^-$ by diazotrophs</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{ap,nh}$</td>
<td>Uptake of NO$_3^-$ by small phytoplankton</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{ap,nh}$</td>
<td>Uptake of NO$_3^-$ by diatoms</td>
<td>mmol N/m³/s</td>
</tr>
<tr>
<td>$R_{ap,nh}$</td>
<td>Uptake of NO$_3^-$ by diazotrophs</td>
<td>mmol N/m³/s</td>
</tr>
</tbody>
</table>
Table S4. Nitrogen cycle parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{rem}$</td>
<td>Maximum respiration rate</td>
<td>9.259E-7</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$k_{ao}$</td>
<td>Maximum NH$_4^+$ oxidation rate</td>
<td>5.787E-7</td>
<td>mmol N/m$^3$/s</td>
</tr>
<tr>
<td>$k_{no}$</td>
<td>Maximum NO$_2^-$ oxidation rate</td>
<td>5.787E-7</td>
<td>mmol N/m$^3$/s</td>
</tr>
<tr>
<td>$k_{den1}$</td>
<td>Maximum NO$_3^-$ reduction rate</td>
<td>1.852E-7</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$k_{den2}$</td>
<td>Maximum NO$_2^-$ reduction rate</td>
<td>9.259E-8</td>
<td>mmol C/m$^3$/s</td>
</tr>
<tr>
<td>$k_{den3}$</td>
<td>Maximum N$_2$O reduction rate</td>
<td>5.741E-7</td>
<td>mmol N/m$^3$/s</td>
</tr>
<tr>
<td>$k_{ax}$</td>
<td>Maximum anaerobic NH$_4^+$ oxidation rate</td>
<td>5.105E-6</td>
<td>mmol N/m$^3$/s</td>
</tr>
<tr>
<td>$K_{o2_{rem}}$</td>
<td>Respiration half-saturation constant for O$_2$ uptake</td>
<td>1.000</td>
<td>mmol O$_2$/m$^3$</td>
</tr>
<tr>
<td>$K_{o2_{ao}}$</td>
<td>NH$_4^+$ oxidation half-saturation constant for O$_2$ uptake</td>
<td>0.333</td>
<td>mmol N/m$^3$</td>
</tr>
<tr>
<td>$K_{o2_{no}}$</td>
<td>NO$_2^-$ oxidation half-saturation constant for O$_2$ uptake</td>
<td>0.778</td>
<td>mmol N/m$^3$</td>
</tr>
<tr>
<td>$K_{o2_{den1}}$</td>
<td>NO$_3^-$ reduction half-saturation constant for NO$_3^-$ uptake</td>
<td>1.000</td>
<td>mmol N/m$^3$</td>
</tr>
<tr>
<td>$K_{o2_{den2}}$</td>
<td>NO$_2^-$ reduction half-saturation constant for NO$_2^-$ uptake</td>
<td>0.010</td>
<td>mmol N/m$^3$</td>
</tr>
<tr>
<td>$K_{o2_{den3}}$</td>
<td>N$_2$O reduction half-saturation constant for N$_2$O uptake</td>
<td>0.159</td>
<td>mmol N/m$^3$</td>
</tr>
<tr>
<td>$K_{no_{ax}}$</td>
<td>NH$_4^+$ oxidation half-saturation constant for NH$_4^+$ uptake</td>
<td>0.230</td>
<td>mmol N/m$^3$</td>
</tr>
<tr>
<td>$K_{no_{ax}}$</td>
<td>NH$_4^+$ oxidation half-saturation constant for NO$_3^-$ uptake</td>
<td>0.010</td>
<td>mmol N/m$^3$</td>
</tr>
<tr>
<td>$a$</td>
<td>O$_2$-dependent coefficient (Nevison et al., 2003)</td>
<td>0.300</td>
<td>N/A</td>
</tr>
<tr>
<td>$b$</td>
<td>Background coefficient (Nevison et al., 2003)</td>
<td>0.100</td>
<td>N/A</td>
</tr>
<tr>
<td>$K_{o2_{den1}}$</td>
<td>O$_2$ poisoning constant for NO$_3^-$ reduction</td>
<td>6.000</td>
<td>mmol O$_2$/m$^3$</td>
</tr>
<tr>
<td>$K_{o2_{den2}}$</td>
<td>O$_2$ poisoning constant for NO$_2^-$ reduction</td>
<td>2.300</td>
<td>mmol O$_2$/m$^3$</td>
</tr>
<tr>
<td>$K_{o2_{den3}}$</td>
<td>O$_2$ poisoning constant for N$_2$O reduction</td>
<td>0.506</td>
<td>mmol O$_2$/m$^3$</td>
</tr>
<tr>
<td>$K_{o2_{ax}}$</td>
<td>O$_2$ poisoning constant for anammox</td>
<td>6.000</td>
<td>mmol O$_2$/m$^3$</td>
</tr>
<tr>
<td>$\tau_{DON}$</td>
<td>Semi-labile DON remineralization inverse timescale</td>
<td>1.826E-4</td>
<td>1/s</td>
</tr>
<tr>
<td>$\tau_{DONr}$</td>
<td>Refractory DON remineralization inverse timescale</td>
<td>2.884E-7</td>
<td>1/s</td>
</tr>
<tr>
<td>$Q_{DONr}$</td>
<td>Fraction of DON to refractory pool</td>
<td>0.0115</td>
<td>N/A</td>
</tr>
<tr>
<td>$PAR_{ao_{lim}}$</td>
<td>PAR limitation for NH$_4^+$ oxidation</td>
<td>1.000</td>
<td>W/m$^2$</td>
</tr>
<tr>
<td>$PAR_{no_{lim}}$</td>
<td>PAR limitation for NO$_2^-$ oxidation</td>
<td>1.000</td>
<td>W/m$^2$</td>
</tr>
<tr>
<td>Name</td>
<td>Description</td>
<td>Units</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>DON</td>
<td>Dissolved organic nitrogen</td>
<td>mmol N/m³</td>
<td></td>
</tr>
<tr>
<td>DONr</td>
<td>Refractory dissolved organic nitrogen</td>
<td>mmol N/m³</td>
<td></td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>Ammonium</td>
<td>mmol N/m³</td>
<td></td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>Nitrite</td>
<td>mmol N/m³</td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>Nitrate</td>
<td>mmol N/m³</td>
<td></td>
</tr>
<tr>
<td>N₂O</td>
<td>Nitrous oxide</td>
<td>mmol N/m³</td>
<td></td>
</tr>
<tr>
<td>N₂O&lt;sub&gt;den&lt;/sub&gt;</td>
<td>Nitrous oxide sourced from denitrification</td>
<td>mmol N/m³</td>
<td></td>
</tr>
<tr>
<td>N₂O&lt;sub&gt;nit&lt;/sub&gt;</td>
<td>Nitrous oxide sourced from nitrification</td>
<td>mmol N/m³</td>
<td></td>
</tr>
<tr>
<td>N₂O&lt;sub&gt;atm&lt;/sub&gt;</td>
<td>Saturated nitrous oxide sourced from boundaries and ingassing</td>
<td>mmol N/m³</td>
<td></td>
</tr>
<tr>
<td>N₂O&lt;sub&gt;bou&lt;/sub&gt;</td>
<td>Supersaturated nitrous oxide sourced from boundaries</td>
<td>mmol N/m³</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>Dinitrogen</td>
<td>mmol N/m³</td>
<td></td>
</tr>
</tbody>
</table>

Table S5. Nitrogen cycle tracers
Figure S1. 0, 150, 300, and 450 m annually averaged $O_2$ from (top) ROMS model years 46 - 50, (middle) World Ocean Atlas 2018 $O_2$ (Garcia et al., 2019), and (bottom) their differences (ROMS - WOA18).
Figure S2. Same as in Figure S1, but for nitrate + nitrite ($\text{NO}_x$).
Figure S3. Same as in Figure S1, but for phosphate (PO$_4^{3-}$).
Figure S4. Same as in Figure S1, but for $N^*$ (here defined as $16\cdot[\text{NO}_3^-] - [\text{PO}_4^{3-}]$).
Figure S5. Same as in Figure S1, but for NO$_2^-$ comparisons against machine learning estimates.
**Figure S6.** Same as in Figure S1, but for N₂O comparisons against machine learning estimates.
Figure S7. Annually averaged net Primary Production (NPP) from (top left) ROMS model years 46 - 50, (top right) the Eppley Vertically Generalized Production Model (Eppley-VGPM, Behrenfeld and Falkowski (1997)), (bottom left) the updated Carbon-Based Productivity Model (CbPM, Behrenfeld et al. (2005)), and (bottom right) the Fluorescence Euphotic-resolving model (CAFE, Silsbe et al. (2016)).
Figure S8. Annually averaged surface chlorophyll-A (chlA) from (left) ROMS model years 46 - 50 and (right) MODIS-Aqua.
Figure S9. Integrated $O_2$, $NO_3^-$, $NO_2^-$, and $N_2O$ tracers within the OMZ budget domain for model years 0 - 50.
**Figure S10.** Integrated $N_2O_{nit}$, $N_2O_{den}$, $N_2O_{bou}$, and $N_2O_{atm}$ tracers within the OMZ budget domain for model years 0 - 50.
Figure S11. (top left) Vertically integrated divergence of advective and diffusive fluxes ($T$) for N$_2$O from the OMZ budget domain, annually averaged from model years 46 - 50. (top right) Time-series of integrated divergence of advective and diffusive fluxes for N$_2$O (black) and the decomposed N$_2$O tracers. (bottom panels) Same as in the top left panel, but for each of the decomposed N$_2$O tracers. Positive values are shown in blue, and negative values in red.
Figure S12. Annually averaged zonal N\textsubscript{2}O transport from the western boundary of the OMZ budget domain (roughly 105\textdegree W) from model years 46 - 50 for (a) N\textsubscript{2}O\textsubscript{den}, (b) N\textsubscript{2}O\textsubscript{nit}, (c) N\textsubscript{2}O\textsubscript{bou}, (d) N\textsubscript{2}O\textsubscript{atm}, and (e) N\textsubscript{2}O.
Figure S13. Integrated net N$_2$O production rate from denitrification ($J^\text{N}_2\text{O}_{\text{den}}$), integrated NO$_2^-$ reduction rate ($R^\text{N}_2\text{O}_{\text{den}}$), integrated N$_2$O reduction rate of denitrification-sourced N$_2$O ($R^\text{N}_2\text{O}_{\text{den3}}$), and vertical POC flux ($\Phi_{\text{poc}}$) at 100m from the OMZ budget domain for ROMS model years 46 - 50.
**Figure S14.** Volume of the OMZ budget domain occupied by various O$_2$ thresholds (0 - 5, 5 - 10, 10 - 15, and 15 - 20 mmol O$_2$ m$^{-3}$) for ROMS model years 46 - 50.
References


December 7, 2022, 8:52pm

