

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

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8 **Key Points:**

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

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Abstract

Oceanic emissions of nitrous oxide (N_2O) account for roughly one-third of all natural sources to the atmosphere. Hot-spots of N_2O outgassing occur over oxygen minimum zones (OMZs), where the presence of steep oxygen gradients surrounding anoxic waters leads to enhanced N_2O production from both nitrification and denitrification. However, the relative contributions from these pathways to N_2O 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_2O production from denitrification is approximately one order of magnitude greater than nitrification within the ETSP OMZ. However, only $\sim 30\%$ of denitrification-derived N_2O production ultimately outgasses to the atmosphere in this region (contributing $\sim 34\%$ of the air-sea N_2O flux on an annual basis), while the remaining is exported out of the domain. Instead, remotely-produced N_2O advected into the OMZ region accounts for roughly half ($\sim 56\%$) of the total N_2O outgassing, with smaller contributions from nitrification ($\sim 7\%$). Our results suggests that, together with enhanced production by denitrification, upwelling of remotely-derived N_2O (likely produced via nitrification in the oxygenated ocean) contributes the most to N_2O outgassing over the ETSP OMZ.

1 Introduction

Nitrous oxide (N_2O) 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_2O budget over the decade of 2007 - 2016 suggest that anthropogenic emissions are responsible for up to 40% of total N_2O sources to the atmosphere, mostly from agriculture, whereas outgassing from the ocean accounts for roughly 20% (Canadell et al., 2021). The production of N_2O 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; Babbín et al., 2015; Ji et al., 2015; Yang et al., 2020). While in large parts of the surface ocean N_2O concentrations are close to saturation, the most intense hot-spots of N_2O 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 $\text{O}_2 < 5 \text{ mmol m}^{-3}$) 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_2O emissions (Codispoti, 2010; Arévalo-Martínez et al., 2015; Babbín 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 ($\sim 45^\circ\text{S}$) to northern Peru ($\sim 4^\circ\text{S}$) (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_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-

67 gen from the ventilated subtropical gyres to the OMZs, and leaves the relatively O₂-rich
 68 eastward tropical currents such as the Equatorial Undercurrent (EUC) and the South-
 69 ern Subsurface Countercurrents (SSCC) as the major advective sources of O₂ to the equa-
 70 torward side of the ETSP OMZ (Karstensen et al., 2008; Stramma et al., 2010). While
 71 these advective pathways are reinforced by lateral O₂ supply from mesoscale eddies (Gnanadesikan
 72 et al., 2013; Bettencourt et al., 2015), O₂ remains depleted within the OMZ core (Kwieceński
 73 & Babbin, 2021), leading to functional anoxia (Thamdrup et al., 2012), fixed nitrogen
 74 loss, a pronounced subsurface nitrite (NO₂⁻) maximum, and a strong nitrogen deficit (Kalvelage
 75 et al., 2013). An additional characteristic of the ETSP is the relatively sharp transition
 76 from anoxic to suboxic ($5 \text{ mmol m}^{-3} < \text{O}_2 < 10 \text{ mmol m}^{-3}$) waters along the OMZ bound-
 77 ary. These O₂ gradients host both aerobic (i.e., nitrification) and anaerobic (i.e., deni-
 78 trification) nitrogen cycle transformations, ultimately leading to N₂O supersaturation
 79 in the layers surrounding the anoxic core (Babbin et al., 2015; Kock et al., 2016). Up-
 80 welling of these waters to the surface likely contributes to the local hot-spot of N₂O out-
 81 gassing in the ETSP, as shown by observational and modeling studies (Arévalo-Martínez
 82 et al., 2015; Ji et al., 2018; Yang et al., 2020).

83 Nitrification is a two-step process that occurs within the oxygenated water column
 84 wherein ammonium (NH₄⁺) produced from remineralization of organic matter (pathway
 85 1 in Figure 1) is oxidized by O₂ to NO₂⁻ and subsequently to nitrate (NO₃⁻) by NH₄⁺-
 86 oxidizing bacteria and archaea and NO₂⁻-oxidizing bacteria, respectively (pathways 2 and
 87 4, respectively) (Lam & Kuypers, 2011). Nitrification-derived N₂O occurs as a byprod-
 88 uct of NH₄⁺ oxidation (pathway 3), resulting in a positive correlation between apparent
 89 oxygen utilization (AOU) and supersaturated N₂O concentrations in many areas of the
 90 ocean (Cohen & Gordon, 1978; Walter et al., 2006), a process that has been further quan-
 91 tified by active production of ¹⁵N₂O in ¹⁵N tracer incubation experiments (Yoshida et
 92 al., 1989). The ratio of N₂O yield to NO₂⁻ yield from NH₄⁺ oxidation has been observed
 93 to increase at decreasing O₂ concentrations in cultures with NH₄⁺-oxidizing bacteria and
 94 archaea (Goreau et al., 1980; Löscher et al., 2012), likely leading to enhanced nitrification-
 95 derived N₂O production within the steep suboxic gradients above and below the anoxic
 96 core of OMZs (Nevison et al., 2003; Ji et al., 2015, 2018; Santoro et al., 2021).

97 Besides N₂O production via the nitrification pathway, N₂O also forms as an inter-
 98 mediary product of step-wise denitrification (NO₃⁻ to NO₂⁻ to N₂O to N₂) under sub-
 99 oxic and anoxic conditions (pathways 5 - 7 in Figure 1). Within the anoxic core of OMZs,
 100 widespread consumption of N₂O occurs via N₂O reduction — the only known process
 101 able to remove N₂O from the water column. However, recent studies have highlighted
 102 how the different steps, each mediated by distinct enzymes and likely different microor-
 103 ganisms (Ganesh et al., 2014; Kuypers et al., 2018), are subject to variable O₂ sensitiv-
 104 ities wherein NO₃⁻, NO₂⁻, and N₂O reduction become progressively less O₂ tolerant (Körner
 105 & Zumft, 1989; Kalvelage et al., 2011; Dalsgaard et al., 2014; Babbin et al., 2015; Ji et
 106 al., 2015). Therefore, the same suboxic gradients that lead to enhanced N₂O production
 107 from nitrification can also lead to N₂O accumulation from denitrification, as NO₂⁻ re-
 108 duction proceeds while N₂O reduction is inhibited, in a process referred to as “incom-
 109 plete” denitrification (Babbin et al., 2015).

110 The coupled production of N₂O at low O₂ from nitrification and denitrification,
 111 and their shared NO₂⁻ intermediary, complicate the interpretation of in situ observations
 112 from OMZs (Ji et al., 2015, 2018; Santoro et al., 2021). Observations of N₂O and NO₂⁻
 113 in these regions typically reveal an OMZ anoxic core layer characterized by a secondary
 114 NO₂⁻ maximum and undersaturated N₂O concentrations, suggesting coupled step-wise
 115 denitrification. Supersaturated concentrations of N₂O in the bounding suboxic gradi-
 116 ents (the upper and lower oxyclines) have been linked to the enhanced production by
 117 nitrification (Cohen & Gordon, 1978). Yet, studies have noted the lack of a linear rela-
 118 tionship with AOU and high abundances of gene markers for NO₂⁻ reduction as evidence

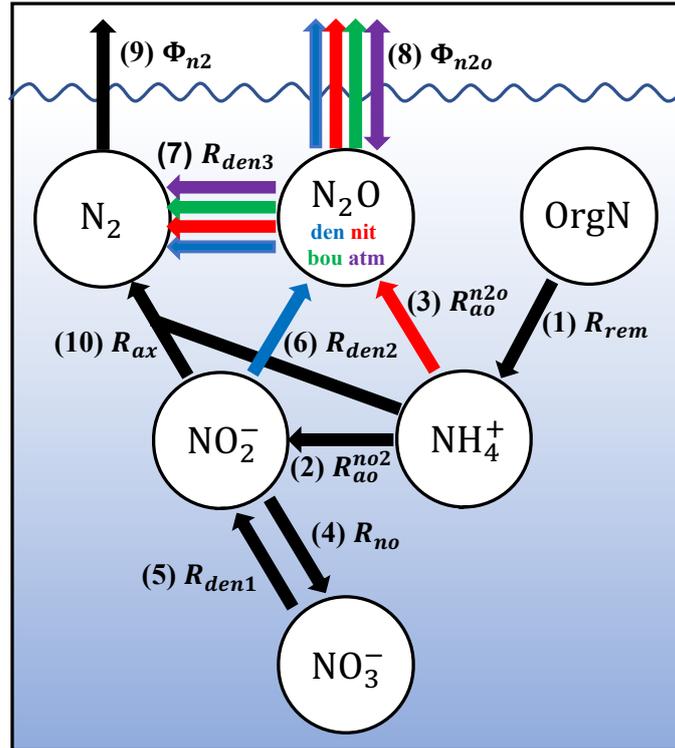


Figure 1. Schematic of the oceanic nitrogen cycle (ignoring biological uptake) as represented in ROMS. Transformation pathways include: (1, R_{rem}) oxic remineralization of nitrogen in organic matter (OrgN) to ammonium; (2, R_{ao}^{no2}) ammonium oxidation to nitrite; (3, R_{ao}^{n2o}) ammonium oxidation to nitrous oxide; (4, R_{no}) nitrite oxidation; (5, R_{den1}) nitrate reduction; (6, R_{den2}) nitrite reduction; (7, R_{den3}) decomposed nitrous oxide reduction; (8, Φ_{n2o}) decomposed nitrous oxide air-sea flux; (9, Φ_{n2}) dinitrogen air-sea flux; and (10, R_{ax}) anaerobic ammonium oxidation (anammox). Colored arrows correspond to the sources and sinks of the decomposed N_2O tracers (N_2O_{den} , N_2O_{nit} , N_2O_{bou} , and N_2O_{atm}) discussed in Section 2.4.

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

121 However, while progressive O_2 tolerances for denitrification have been documented
 122 (Dalsgaard et al., 2014), biogeochemical models predominantly employ simple param-
 123 eterizations representing N_2O production as a function of nitrification, whereas denitri-
 124 fication is typically modelled with a lack of N_2O production or as a net sink of N_2O at
 125 low O_2 (Suntharalingam et al., 2000; Jin & Gruber, 2003; Ji et al., 2018; Battaglia & Joos,
 126 2018). Other studies have highlighted the importance of resolving O_2 -dependent decou-
 127 pling of N_2O production and consumption (Babbin et al., 2015), suggesting that N_2O
 128 production rates from denitrification may be up to two orders of magnitude larger than
 129 those from nitrification near the core of OMZs, albeit closely balanced by N_2O reduc-
 130 tion to dinitrogen gas (N_2). Thus, incomplete denitrification may account for a produc-
 131 tion source that is poorly represented in most biogeochemical ocean and climate mod-
 132 els.

133 While the uncertainty surrounding N_2O production in the ocean has been reduced
 134 in recent years following improved estimates of ocean (Yang et al., 2020), terrestrial, and
 135 anthropogenic N_2O sources (Canadell et al., 2021; Tian et al., 2020), barriers remain in

136 accurately projecting future air-sea flux because of poorly constrained contributions from
 137 the nitrification and denitrification pathways. The observed expansion of OMZs (Stramma
 138 et al., 2008; Schmidtko et al., 2017; Oeschies et al., 2018) is expected to continue over
 139 the 21st century, although the extent of future changes in low O₂ and anoxic water vol-
 140 umes remain uncertain (Cabr e et al., 2015; Bianchi et al., 2018; Busecke et al., 2021).
 141 Therefore, accurate parameterization of N₂O cycling in global ocean models is crucial
 142 in simulating realistic future scenarios, and a better understanding of the physical and
 143 biogeochemical mechanisms and relative contributions from both production pathways
 144 is warranted. This is particularly critical given that OMZ regions continue to be poorly
 145 resolved in current global Earth system models (Cabr e et al., 2015; Busecke et al., 2021;
 146 S ef erian et al., 2020), which generally struggle to capture the role of fine-scale circula-
 147 tion such as the zonal jet systems that ventilate the tropical Ocean (Kessler, 2006; Duteil
 148 et al., 2014; Busecke et al., 2019; Duteil et al., 2021).

149 To address these sources of uncertainty, we implement a new model of the OMZ
 150 nitrogen cycle (NitrOMZ) (Bianchi et al., 2022) into an eddy-resolving three-dimensional
 151 (3-D) regional ocean model of the ETSP that simulates local N₂O production from ni-
 152 trification and denitrification. The new model, constrained by in situ ETSP observations
 153 of nitrogen cycle tracers and rates, allows for an examination of the N₂O balance within
 154 a characteristic OMZ upwelling region. To attribute the sources of N₂O outgassing flux
 155 to different processes, we use the 3-D model to track contributions from local air-sea gas
 156 exchange, advection into the domain from the boundaries, and production by nitrifica-
 157 tion and denitrification. This analysis reveals the importance of incomplete denitrifica-
 158 tion and transport of remotely-generated N₂O for air-sea fluxes, with implications for
 159 future N₂O emissions in a changing ocean.

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

165 2 Modelling Methods and Validation

166 2.1 Physical Model Configuration and Forcing

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

177 For this study, low-frequency interannual variability is ignored to instead focus on
 178 a climatological steady-state. Initial conditions and monthly climatological boundary forc-
 179 ing (applied at the northern, western, and southern boundaries) for temperature, salin-
 180 ity, surface elevation, and horizontal velocity are taken from an existing Pacific-wide ROMS
 181 simulation (Lemari e et al., 2012). Normal-year-forcing of daily freshwater and turbulent
 182 heat fluxes are estimated using bulk formulae (Large, 2006) applied to ERA-interim (ERAi)
 183 reanalysis data for the year 1979 (Simmons et al., 2006; Dee et al., 2011). Because of known
 184 biases in ERAi shortwave (overestimate) and longwave (underestimate) fluxes (Brodeau
 185 et al., 2010), we applied the DRAKKAR Forcing Set version 5.2 corrections to heat flux

186 terms (Dussin et al., 2014). Daily climatological wind stress is taken from the QuickSCAT-
 187 based Scatterometer Climatology of Ocean Winds (Risien & Chelton, 2008). The result-
 188 ing simulation produces an overall similar climatological picture of the hydrographic prop-
 189 erties, gyre circulation, and equatorial current structure of the ETSP (Figure 2a - c) when
 190 compared to validation products (Figure 2d - f).

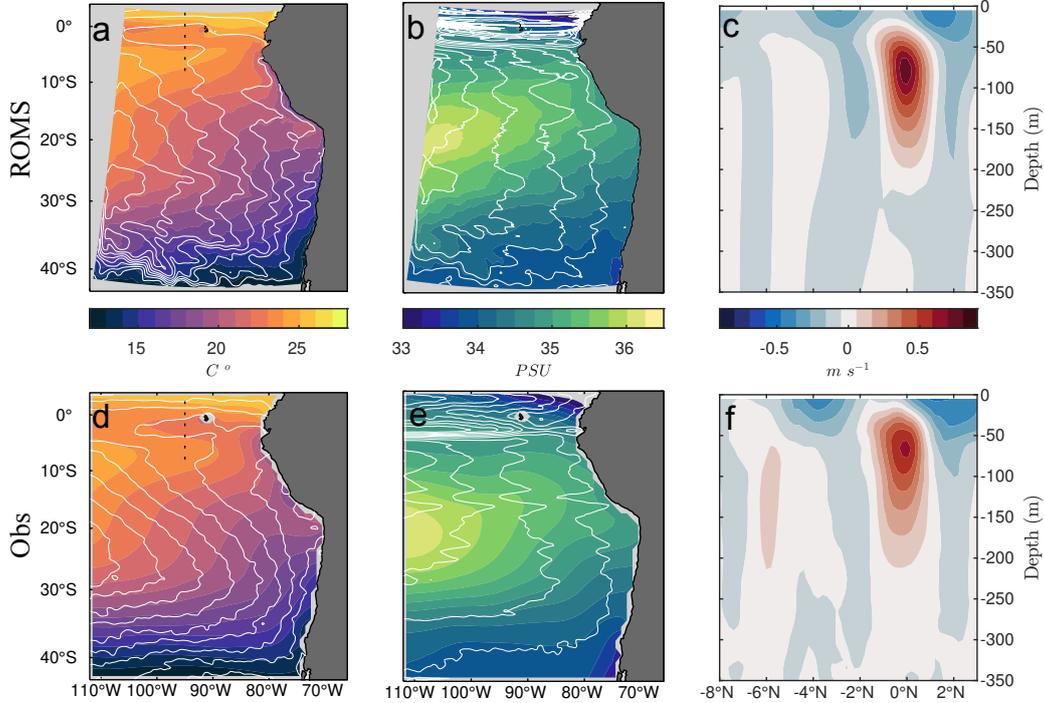


Figure 2. (a,d) Annually averaged sea-surface temperature from ROMS model years 46 - 50 (top) and World Ocean Atlas 2018 (bottom). Contours highlight sea-surface height at 5 cm intervals, with validation data obtained by averaging AVISO data between 2000 to 2018. Dashed lines mark the transect location 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).

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2.2 Biogeochemical Model Configuration and Forcing

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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 ($R_{ao}^{n_2o}$) and NO₂⁻ ($R_{ao}^{no_2}$), and aerobic NO₂⁻ oxidation to NO₃⁻ (R_{no}). Anaerobic NH₄⁺ oxidation with NO₂⁻ to N₂ (anammox, R_{ax}) is also represented. Additionally, NitrOMZ partitions the OM remineralization cycle in ROMS-BEC to include three additional heterotrophic denitrification steps: NO₃⁻ reduction to NO₂⁻ (R_{den1}), NO₂⁻ reduction to N₂O (R_{den2}), and N₂O reduction to N₂ (R_{den3}). The treatment of OM in the model is outlined in support-

204 ing information S1, with chemolithotrophic and heterotrophic reactions summarized in
 205 S2. Notably, the model expands BEC by allowing for the production of N₂O via both
 206 nitrification and incomplete denitrification pathways (Section 2.2.1).

207 Initial conditions and boundary forcing of biogeochemical nutrient concentrations
 208 (NO₃⁻, PO₄³⁻, Si(OH)₄ and O₂) are taken from monthly climatological observations from
 209 the 2013 World Ocean Atlas (H. E. Garcia, Boyer, et al., 2013; H. E. Garcia, Locarnini,
 210 et al., 2013); NH₄⁺, NO₂⁻, and N₂ boundary conditions are set to 0 but adjust rapidly
 211 within the domain. Iron data were taken from the Community Earth System Model (CESM)
 212 as in Deutsch et al. (2021), and DIC/Alkalinity were extracted from GLODAP (Lauvset
 213 et al., 2016) with a reference year of 2002. Initial and monthly boundary conditions for
 214 N₂O were provided from a 3-D reconstruction based on in situ data from recent cruises
 215 to the ETSP (Kalvelage et al., 2013; Ji et al., 2015; Peng et al., 2016; Babbitt et al., 2017,
 216 2020), and the MEMENTO databases (Kock & Bange, 2015) and GLODAP (Olsen et
 217 al., 2016; Lauvset et al., 2016), which we extrapolate to the model domain using the same
 218 machine learning approach as described in Yang et al. (2020).

219 **2.2.1 NitrOMZ N₂O Production**

220 Production of N₂O via nitrification in NitrOMZ is modelled as a by-product of NH₄⁺
 221 oxidation ($R_{ao}^{n_2o}$, pathway 3 in Figure 1), with enhanced yields at lower O₂ concentra-
 222 tions. Both nitrification steps (i.e. NO₂⁻ oxidation) are suppressed near the surface by
 223 light inhibition (see supporting information S4) and competition for NH₄⁺ and NO₂⁻ from
 224 phytoplankton as in Frischknecht et al. (2017). Therefore, nitrification is largely restricted
 225 to below the euphotic zone while also being suppressed at low O₂. The partitioning be-
 226 tween N₂O and NO₂⁻ production from R_{ao} is calculated using the function proposed by
 227 Nevison et al. (2003), derived by fitting measured N₂O and NO₂⁻ yields ($f_{ao}^{n_2o}$ and $f_{ao}^{no_2}$,
 228 respectively) to oxygen concentrations (Goreau et al., 1980):

$$229 \frac{f_{ao}^{n_2o}}{f_{ao}^{no_2}} = 0.01 \cdot \frac{a}{[O_2]} + b. \quad (1)$$

231 Relative to the original parameterization by Nevison et al. (2003), we apply distinct val-
 232 ues of the parameters a and b to reflect results from a series of in situ measurements of
 233 N₂O production from the ETSP and ETNP OMZs (Ji et al., 2015, 2018; Santoro et al.,
 234 2021) (see Section 2.3.1). N₂O production by nitrification, in units of $mmol\ N\ m^{-3}\ s^{-1}$,
 235 is therefore represented as:

$$236 \frac{R_{ao}^{n_2o}}{R_{ao}} = f_{ao}^{n_2o}, \quad (2)$$

238 with a similar function for NO₂⁻ production.

In the denitrification pathway, N₂O is produced via NO₂⁻ reduction at low O₂:

$$R_{den2}^{n_2o} = f_{den2} \cdot R_{rem}^{tot} \cdot Q_{den}^{C:N}, \quad (3)$$

where f_{den2} is the local fraction of total OM remineralization (R_{rem}^{tot}) routed to NO₂⁻ re-
 duction (see supporting information S2), and $Q_{den}^{C:N}$ the carbon to nitrogen ratio from
 denitrification (472/2/106) following Anderson and Sarmiento (1994). Similarly, N₂O
 is consumed via N₂O reduction to N₂ at low O₂:

$$R_{den3}^{n_2} = f_{den3} \cdot R_{rem}^{tot} \cdot Q_{den}^{C:N}. \quad (4)$$

239 Net production of N₂O ($R_{net}^{n_2o}$, in units of $mmol\ N_2O\ m^{-3}\ s^{-1}$) results by the com-
 240 bination of nitrification (equation (2)) and the residual between NO₂⁻ and N₂O reduc-
 241 tion (equation (3) minus equation (4)):

$$242 R_{net}^{n_2o} = 0.5 \cdot (R_{ao}^{n_2o} + R_{den2}^{n_2o}) - R_{den3}^{n_2}. \quad (5)$$

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2.3 Biogeochemical Validation

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To validate the biogeochemical tracer distributions simulated by ROMS-BEC, we gathered O_2 , NO_3^- , PO_4^{3-} , and N^* (defined as $16 \cdot [NO_3^-] - [PO_4^{3-}]$) 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_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 3.1.

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2.3.1 Model Parameterization and Spinup

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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_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 Farias (2012), and Krahnmann et al. (2021).

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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_{no} , respectively, see supporting information S2) and (2) slightly widening the difference between exponential O_2 inhibition thresholds for NO_2^- and N_2O reduction ($K_{den2}^{O_2}$ and $K_{den3}^{O_2}$, 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).

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The choice of parameters results in a high NH_4^+ oxidation rate (R_{ao}) just below the euphotic zone that mostly produces NO_2^- ($R_{ao}^{no_2}$) due to high O_2 concentrations. As O_2 becomes scarce, R_{ao} decreases, yet production of N_2O ($R_{ao}^{n_2o}$) 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 \gg production). Similar to Babbin et al. (2015) and Bianchi et al. (2022), we model a progressive O_2 inhibition of the three denitrification steps ($K_{den1}^{O_2} > K_{den2}^{O_2} > K_{den3}^{O_2}$). Therefore, incomplete denitrification is allowed to occur at low but non-zero O_2 as NO_3^- reduction and NO_2^- reduction (R_{den1} and R_{den2} , respectively) proceed while N_2O reduction (R_{den3}) is inhibited (consumption $<$ production).

2.4 N₂O Balance and Tracer Decomposition

To track the evolution of N₂O from different pathways, we decompose N₂O into four tracers that keep track of N₂O sources in the model domain:

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

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 (N₂O reduction, R_{den3}). By construction, the conservation equations for the individual tracers sum up to the conservation equation for N₂O (equation (5)), so that equation (6) can be considered a linear tracer decomposition.

Specifically, N₂O_{nit} tracks local production by nitrification (R_{ao}^{n2o} , equation (2)) whereas N₂O_{den} tracks production by denitrification (R_{den2}^{n2o} , equation (3)) as outlined in Section 2.2.1 (pathways 3 and 6, respectively, in Figure 1). The remaining tracers, N₂O_{atm} and N₂O_{bou}, are designed to track N₂O originating from the atmosphere and from production sources outside the regional ROMS domain, respectively. Saturated N₂O forced from the model boundaries (assuming an atmospheric N₂O concentration of 300 ppb) can be interpreted as originating from air-sea equilibrium with the atmosphere, whereas supersaturated N₂O is linked to production outside the regional model domain. We therefore split the N₂O forced into the domain into a saturation component (N₂O_{atm}) and a supersaturation component (N₂O_{bou}) transported into the domain.

To close separate biogeochemical budgets for each N₂O tracer, we similarly decomposed the N₂O reduction rate (R_{den3} , equation (4) and pathway 7 in Figure 1) and N₂O air-sea flux (Φ^{n2o} , pathway 8 in Figure 1) to track losses with respect to the decomposed N₂O concentrations from within the domain:

$$R_{den3} = R_{den3}^{den} + R_{den3}^{nit} + R_{den3}^{bou} + R_{den3}^{atm} \quad (7)$$

$$\Phi_{n2o} = \Phi_{n2o}^{den} + \Phi_{n2o}^{nit} + \Phi_{n2o}^{bou} + \Phi_{n2o}^{atm}. \quad (8)$$

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 N₂O (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 N₂O_{atm}, for which it is set to the total value. Therefore, while initially saturated at the boundaries, the concentration of N₂O_{atm} can drop below saturation following consumption via R_{den3}^{atm} . When N₂O-undersaturated water is exposed to the surface, atmospheric in-gassing will increase N₂O_{atm} until N₂O reaches saturation. As such, N₂O_{atm} tracks both domain ingassing of N₂O and import of saturated N₂O from the model boundaries, whereas N₂O_{bou} exclusively tracks import of the supersaturation component. To initialize the decomposition, the initial 3-D N₂O was separated into N₂O_{atm} and N₂O_{bou} while N₂O_{nit} and N₂O_{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 N₂O 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:

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

Here, $d[C]/dt$ is the climatological N₂O 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 Φ 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 $8^{\circ}S$ and extends from the Galapagos islands at the equator to nearly $15^{\circ}S$. 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 $10 \text{ mmol O}_2 \text{ m}^{-3}$ ranges mostly between 300 - 500 m and extends to roughly $105^{\circ}W$. 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 $5 \text{ mmol O}_2 \text{ m}^{-3}$ (Kwiecinski & Babbín, 2021) to $20 \text{ mmol O}_2 \text{ m}^{-3}$ (H. Garcia et al., 2019a; Bianchi et al., 2012; Dunn, 2012).

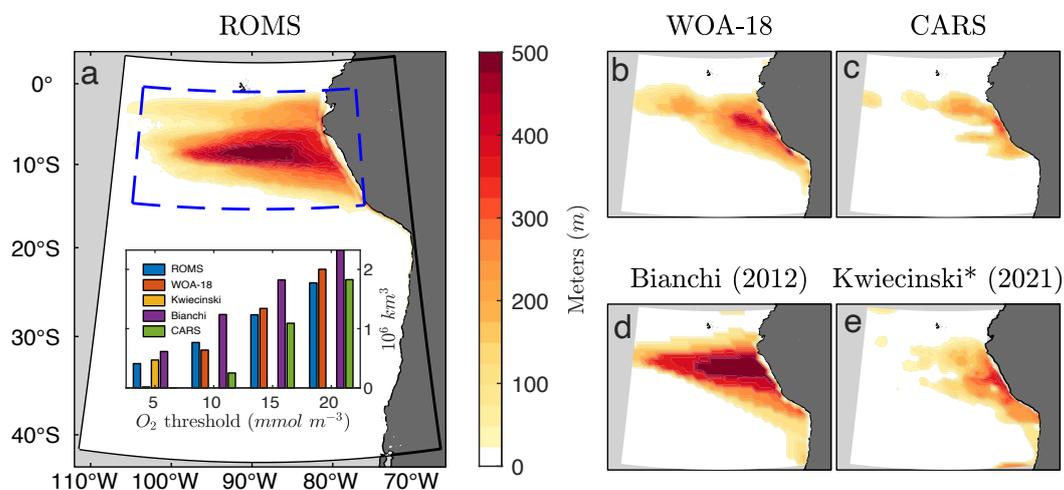


Figure 3. (a) ROMS Peru-Chile 10 km domain, with annually averaged OMZ thickness ($\text{O}_2 < 10 \text{ mmol m}^{-3}$) from model years 46 - 50. The inset bar plot shows OMZ volume from ROMS and validation products based on 5, 10, 15, and 20 mmol m^{-3} thresholds. The N_2O budget region is also shown as the area encompassed by dashed blue lines, extending vertically from the surface to 750 m. (b-d) OMZ thickness ($\text{O}_2 < 10 \text{ mmol m}^{-3}$) 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 ($\text{O}_2 < 5 \text{ mmol m}^{-3}$) from Kwiecinski and Babbín (2021).

Taking into account the slight equatorward geographic shift in the model OMZ, nitrogen tracer (NO_3^- , NO_2^- , and N_2O) 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_2O 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_2O concentrations observed in the subtropical gyre at $25^{\circ}S$. The oxic to suboxic transition zone (inshore of the $20 \text{ mmol O}_2 \text{ m}^{-3}$ contour in Figure 4) also reveals an increase in N_2O 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

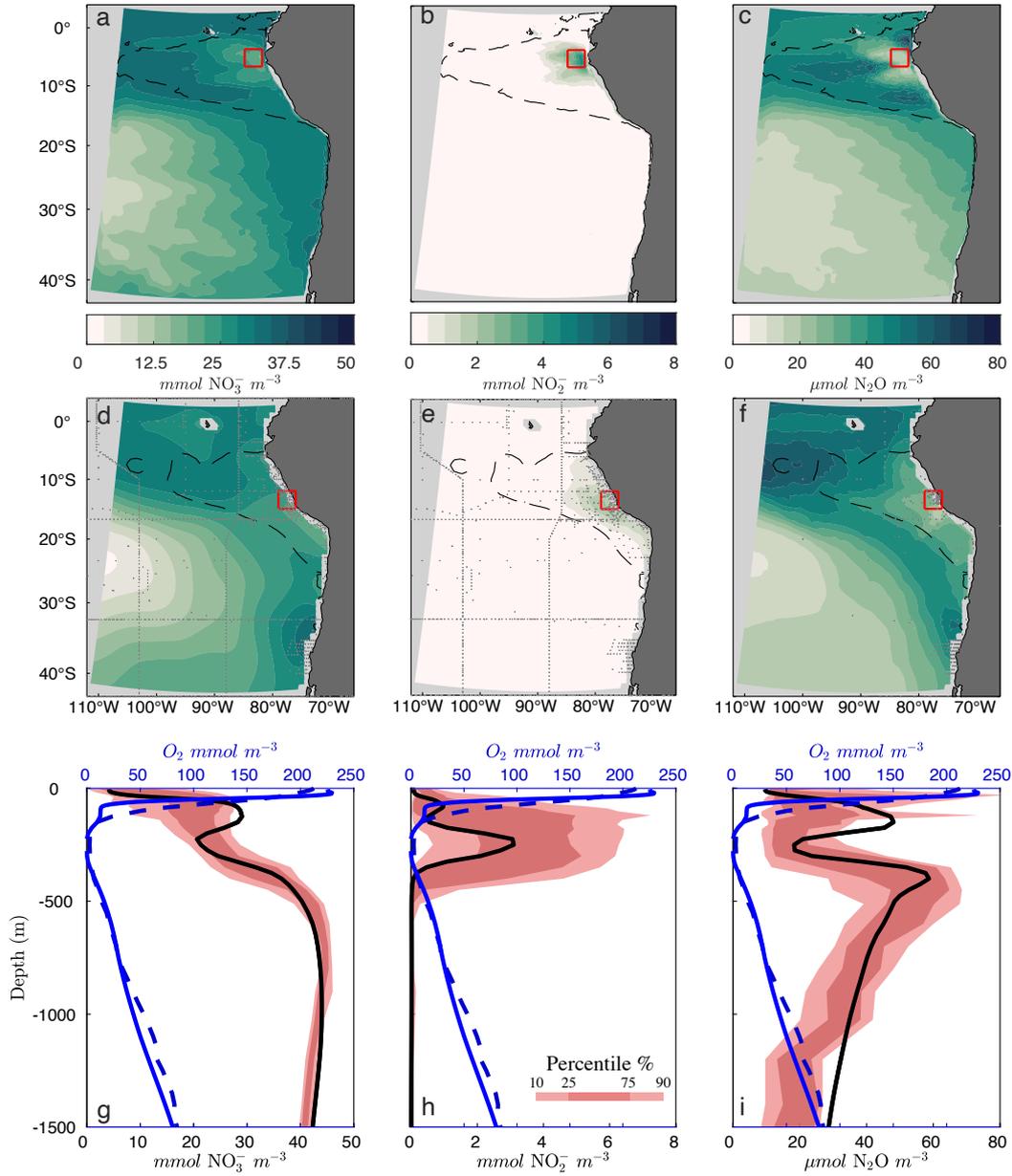


Figure 4. (a-c) ROMS annually averaged NO_3^- , NO_2^- , and N_2O at 250 m from model years 46 - 50. Dashed black lines highlight the 20 $\text{mmol O}_2 \text{ m}^{-3}$ contour. (d-f) NO_3^- , NO_2^- , and N_2O at 250 m from World Ocean Atlas 2018 and machine learning estimates, respectively. Grey markers show the location of shipboard samples. (g-i) Averaged profiles of NO_3^- , NO_2^- , and N_2O 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 Krahnemann 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.

364 show low concentrations at the surface for NO_3^- , NO_2^- , and N_2O . As depth increases,
 365 local maxima in NO_2^- and N_2O can be seen at $\sim 100 \text{ m}$ that correspond to low but non-

366 zero O_2 . Just below this depth, where O_2 drops further to anoxic levels, local minima
367 in NO_3^- and N_2O appear along with a large peak in NO_2^- of roughly $3\text{ mmol } m^{-3}$. Be-
368 neath the anoxic OMZ, a second N_2O peak appears of slightly greater magnitude (~ 60
369 $\mu\text{mol } N_2O\text{ } m^{-3}$) to the shallower maxima ($\sim 50\text{ }\mu\text{mol } N_2O\text{ } m^{-3}$). Depth-dependent dis-
370 tributions from shipboard measurements (Kalvelage et al., 2013; Cornejo & Farias, 2012;
371 Krahmann et al., 2021) through the OMZ (pink shading) generally show good agreement
372 between model and observations as O_2 increases and decreases vertically. Note that the
373 geographical location of shipboard measurements differs from the ROMS averaging box
374 due to the equatorward and offshore OMZ shift discussed above. Despite this geograph-
375 ical bias, Figures 4g - i demonstrate similarity in the expression of anaerobic nitrogen
376 cycle processes at locations with comparable O_2 profiles. Remaining inconsistencies, such
377 as the shallower depth of the observed upper N_2O maxima, can be explained by the prox-
378 imity of observations to the coast, as compared to the more offshore location used to av-
379 erage model profiles.

380 Finally, given the importance of accurately representing water column denitrifica-
381 tion, we compared total fixed nitrogen loss in ROMS via denitrification and anammox
382 to other ETSP estimates (Figure 5). Both processes contribute roughly 50% to OMZ N-
383 loss throughout the year, with seasonal variability mostly driven by changes in denitri-
384 fication rates (red shading). The total water-column fixed nitrogen loss in the model is
385 $25.2\text{ TgN } yr^{-1}$, within the range of observational estimates for the region (Deutsch et
386 al., 2007; Bianchi et al., 2012; DeVries et al., 2013; Yang et al., 2017). Thus, despite a
387 geographic shift, the model produces a realistic OMZ and associated nitrogen cycle trac-
388 ers and rates.

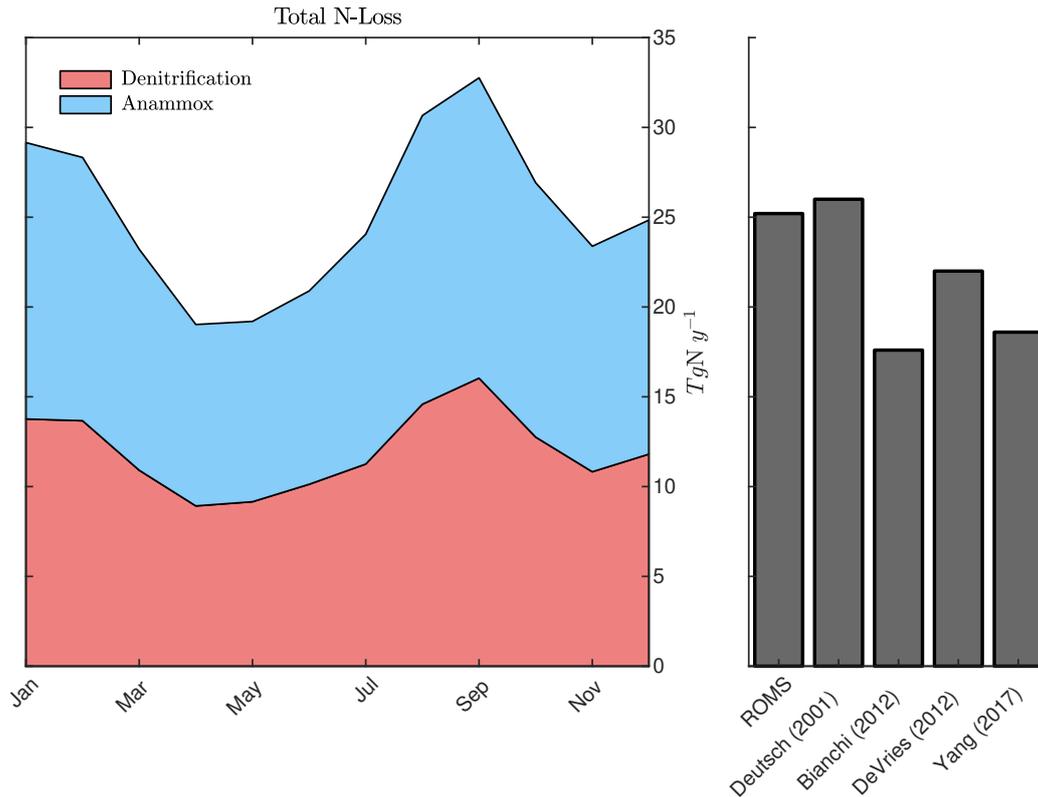


Figure 5. (left) Monthly averaged fixed nitrogen loss from ROMS via canonical denitrification and anammox from models year 46 - 50. (right) ETSP estimates of total annual averaged nitrogen loss from ROMS, Deutsch et al. (2007), Bianchi et al. (2012), DeVries et al. (2013), and Yang et al. (2017).

389 3.2 ETSP N₂O Production

390 A transect crossing the core of the model OMZ shows that N₂O production and
 391 consumption rates from denitrification are strongly influenced by O₂ concentrations (Fig-
 392 ure 6a). Within the anoxic core, N₂O reduction to N₂ ($R_{den3}^{n_2}$) exceeds NO₂⁻ reduction
 393 to N₂O ($R_{den2}^{n_2o}$), causing widespread net N₂O consumption (red shading) of nearly 0.1
 394 $\mu\text{mol N m}^{-3} \text{d}^{-1}$. The resulting N₂O and NO₂⁻ transects (Figure 6c and 6d) show con-
 395 sistent offshore subsurface N₂O minima coinciding with peak concentrations of NO₂⁻ at
 396 the same depth range. These patterns suggests that all three denitrification steps pro-
 397 ceed with minimal O₂ inhibition within the OMZ core, supporting a zone of active fixed
 398 N-loss.

399 Along the exterior of the OMZ core, O₂ gradients preferentially inhibit N₂O reduc-
 400 tion to N₂ ($R_{den3}^{n_2}$) and allow incomplete denitrification to proceed. Accordingly, net N₂O
 401 consumption transitions to net production (blue shading) of a similar $\sim 0.1 \mu\text{mol N m}^{-3}$
 402 d^{-1} magnitude (Figure 6a). Beyond suboxic waters, net production from denitrification
 403 ceases. In contrast, maximum N₂O production from NH₄⁺ oxidation ($R_{ao}^{n_2o}$, Figure 6b)
 404 peaks at roughly $0.01 \mu\text{mol N m}^{-3} \text{d}^{-1}$ and is largely restricted to a thin, mostly oxy-
 405 genated layer at roughly 100 - 150 m that mirrors vertical maxima in POC flux (not shown),
 406 with little amplification at low O₂.

407 The relative contributions from the N₂O tracer decomposition (Figure 6e - h) high-
 408 light the disparity between N₂O sources. At the surface, atmospheric ingassing allows

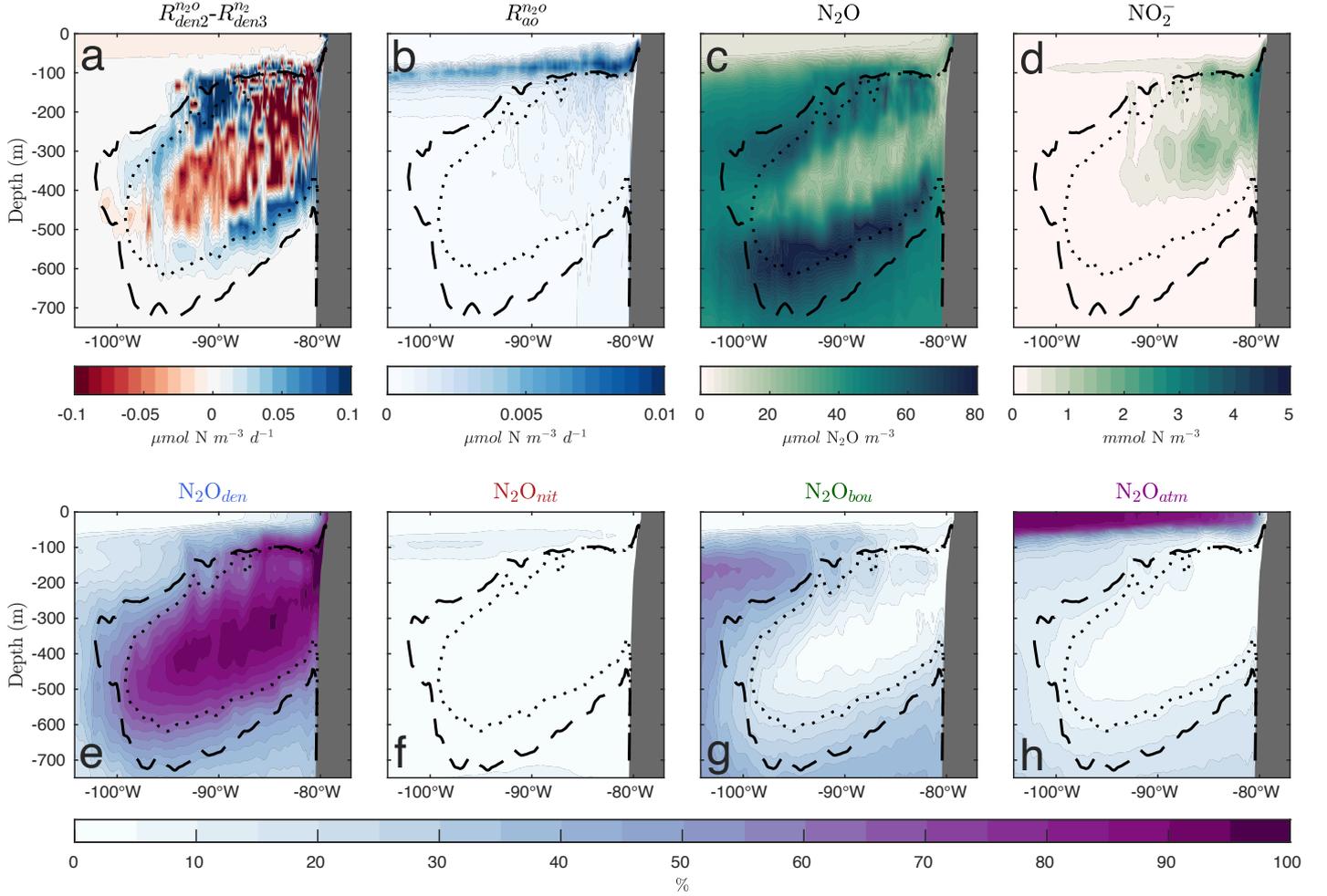


Figure 6. (a) Annually averaged net N₂O production from denitrification for model years 46 - 50 along a transect from the coast at 8°S. The dotted and dashed black curves in highlight the 5 and 10 mmol O₂ m⁻³ contours, respectively. (b-d) Same as in panel (a), but for N₂O production from nitrification (b), N₂O (c), and NO₂⁻ (d). Panels (e) - (h) show the relative contributions to N₂O for each decomposed N₂O tracer (N₂O_{den}, N₂O_{nit}, N₂O_{bou}, and N₂O_{atm}).

409 saturated N₂O (N₂O_{atm}) to dominate (Figure 6h), especially offshore. Within the anoxic
 410 OMZ core, despite vigorous net N₂O consumption (Figure 6a), residual N₂O concentra-
 411 tions of $\sim 20 \mu\text{mol m}^{-3}$ persist (Figure 6c), and are nearly completely attributed to N₂O
 412 denitrification (N₂O_{den}, Figure 6e). As O₂ increases beyond suboxic levels, the contri-
 413 bution of N₂O_{den} diminishes, while contributions from supersaturated and saturated N₂O
 414 from the boundaries (N₂O_{bou} and N₂O_{atm}, respectively) account for the remainder. In
 415 contrast, N₂O from nitrification (N₂O_{nit}, Figure 6f) does not contribute more than 10%,
 416 with a maximum at roughly 100 m depth, suggesting that incomplete denitrification is
 417 the main contributor ($\mathcal{O}(10)$ times greater production) to local N₂O production through-
 418 out the OMZ.

419 Notably, the contributions from supersaturated and saturated N₂O transported into
 420 the OMZ from the model domain boundaries (N₂O_{bou} and N₂O_{atm}, respectively) are rapidly
 421 reduced at low O₂, showing consumption of externally derived N₂O within the OMZ core.
 422 Additionally, while production from incomplete denitrification is generally confined to

423 suboxic waters (Figure 6a), significant concentrations of N_2O_{den} in oxygenated waters
 424 suggest export of N_2O_{den} out of the OMZ. Together, these results highlight an impor-
 425 tant role for circulation in redistributing N_2O within the ETSP.

426 3.3 Contributions of Different Processes to the N_2O Balance

427 Figure 7 shows vertically-integrated N_2O sources minus sinks (J terms) over the
 428 OMZ budget region, and the annual time-series of total integrated net production for
 429 N_2O and each decomposed tracer. In general, net N_2O production ($J_{tot}^{n_2o}$, black line in
 430 the time-series) is positive for each month with the exception of June, and reveals higher
 431 rates beginning in August that persist through December. Production is predominantly
 432 driven by denitrification ($J_{den}^{n_2o}$, blue line), which also drives the bulk of monthly vari-
 433 ability seen in $J_{tot}^{n_2o}$. In contrast, production from nitrification ($J_{nit}^{n_2o}$, red line) is net posi-
 434 tive throughout the year, but only accounts for a small proportion of the N_2O produc-
 435 tion. Tracers that lack domain production sources (N_2O_{bou} and N_2O_{atm}) show consist-
 436 ent consumption rates throughout the year.

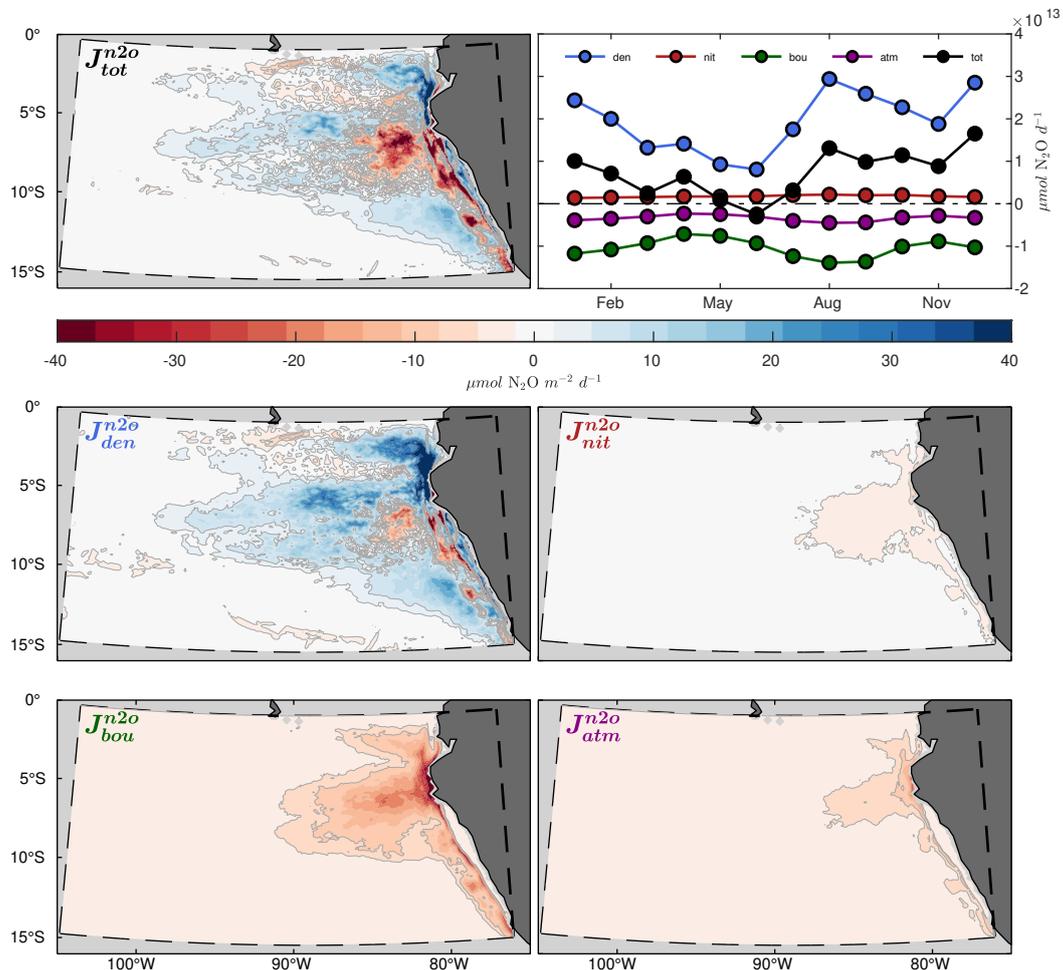


Figure 7. (top left) Vertically integrated sources-minus-sinks (J) for N_2O from the OMZ budget domain, annually averaged from model years 46 - 50. (top right) Time-series of integrated sources-minus-sinks for N_2O (black) and the decomposed N_2O tracers. (bottom panels) Same as in the top left panel, 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 overcompensates 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 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-

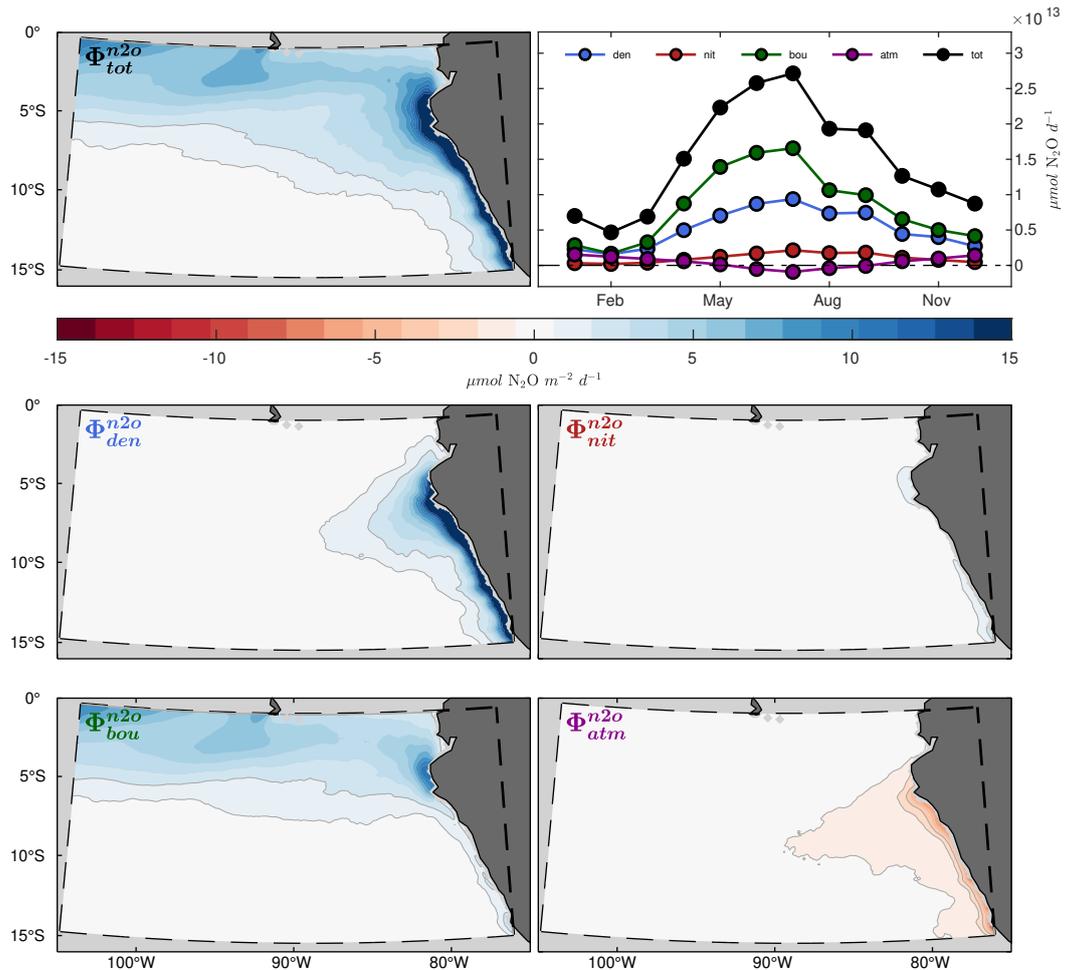


Figure 8. Same as in Figure 7, but for air-sea flux (Φ) of N_2O

489 urated N_2O (N_2O_{bou}) supplied through the boundaries (Figure S12c), with the most intense
 490 import along the equator at roughly 150 m depth (see also Figure 6g). In contrast,
 491 denitrification-driven export (Figure S12a) is focused further to the south (roughly 8°S)
 492 and at deeper depths (200 - 500 m , also evident in Figure 6e).

493 After accounting for boundary exchanges, local subsurface production and consumption,
 494 and periodic ingassing of N_2O_{atm} (Figure 8), all tracers reveal net outgassing with
 495 $\Phi_{bou}^{n_2o}$ and $\Phi_{den}^{n_2o}$ contributing $\sim 56\%$ and $\sim 34\%$ (respectively) to the annual 152 Gg N y^{-1}
 496 outgassed to the atmosphere. Thus, what emerges from the above descriptions is an ETSP
 497 OMZ that is characterized by: (1) A consistent supply of N_2O_{bou} and N_2O_{atm} from pre-
 498 dominantly zonal subsurface currents in the tropical band (Figures S11, S12c, and S12e);
 499 (2) Advection of all N_2O tracers into a coastal hot-spot where vigorous consumption leads
 500 to significant N-loss; (3) Net N_2O production predominantly by denitrification within
 501 suboxic gradients surrounding the OMZ (Figure 7); (4) Significant export of N_2O_{den} into
 502 the exterior ocean (Figures S11 and S12); (5) Consumption of locally produced and exter-
 503 nally derived N_2O ; and (6) Year-round air-sea flux of N_2O driven predominantly by
 504 imported N_2O_{bou} and locally produced N_2O_{den} that upwell and outgas along the north-
 505 ern extent of the OMZ domain and along the coast, respectively (Figure 8).

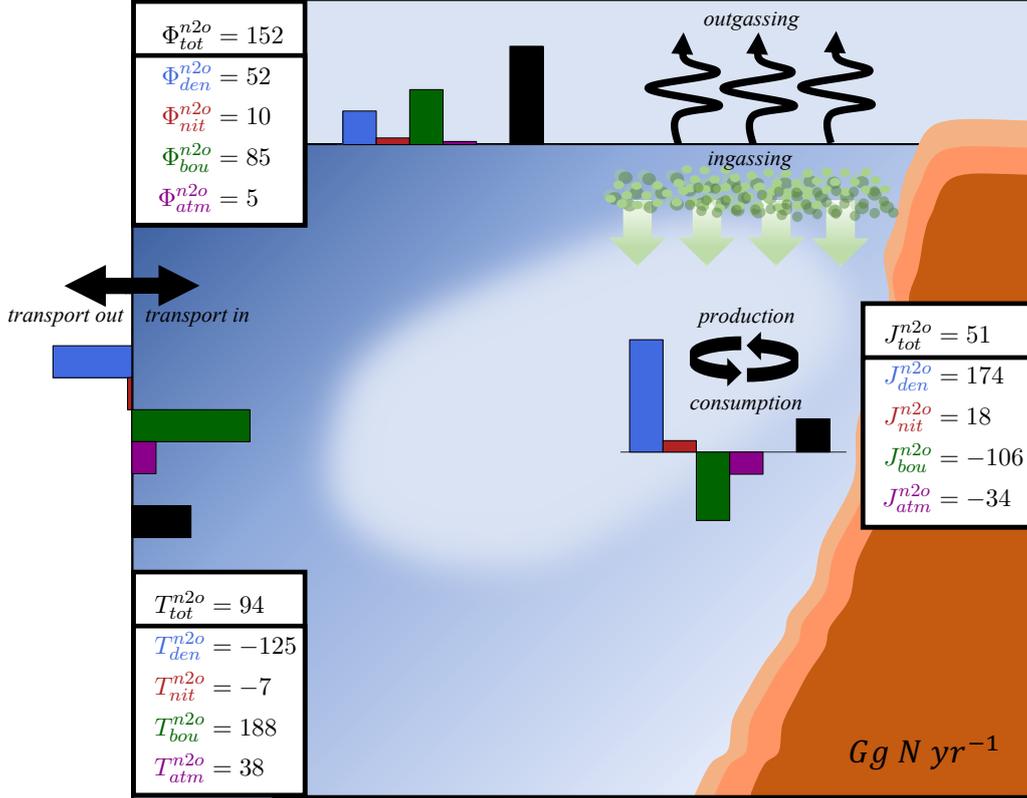


Figure 9. Schematic of the ETSP OMZ N₂O budget, with calculated averages ($Gg N y^{-1}$) of net air-sea flux (Φ), advection (T), and sources-minus-sinks (J) from model years 46 - 50. Bar plots indicate both the direction of, and relative magnitude of, budget averages.

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 O₂, we find almost negligible local contributions from nitrification; rather, maximum N₂O production rates from NH₄⁺ oxidation (R_{ao}^{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_{nit}^{n2o} in Figure 7) suggests that N₂O_{nit} is subsequently mixed into anoxic waters and consumed via N₂O reduction. The major contribution of nitrification to N₂O production takes place immediately adjacent to the coast, where low O₂ 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 (Φ_{nit}^{n2o}) throughout the domain, with the exception of coastal outgassing driven by upwelling. While the contribution of nitrification to N₂O 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 Babbitt et al. (2015), our simulation suggests that local production from nitrification is not a dominant pathway for N₂O outgassing flux in this region.

526 Instead, N_2O production is dominated by incomplete denitrification which takes
 527 place along the suboxic fringes of the anoxic OMZ core (Figure 6a, Figure 6e, and Fig-
 528 ure 7), in agreement with recent studies (Babbin et al., 2015; Ji et al., 2018). In general,
 529 the three step-wise denitrification rates shows a strong seasonal dependence and are pri-
 530 marily controlled by the timing of organic matter supply from the euphotic zone (Fig-
 531 ure S13) rather than variability in low O_2 volumes throughout the year (Figure S14).
 532 Within the anoxic core of the OMZ, rapid N_2O consumption rates (Figure 6a) indicate
 533 short residence times for N_2O produced via NO_2^- reduction (N_2O_{den}) due to the strong
 534 coupling between denitrification steps at low O_2 . Significant net N_2O production by den-
 535 itrification (J_{den}^{n2o}) occurs where high rates of vertical POC flux overlap with an anoxic
 536 to suboxic O_2 gradient; there, the difference in O_2 tolerance thresholds leads to a rel-
 537 atively small residual between the large NO_2^- and N_2O reduction rates within the do-
 538 main (Babbin et al., 2015). As oxic organic matter remineralization stops within the anoxic
 539 OMZ core, this leads to the characteristic double peak structure in N_2O profiles (Fig-
 540 ure 6c) bounding the OMZ throughout most of the domain.

541 Spatially, the vertical depth range occupied by anoxic to suboxic gradients plays
 542 a key role in determining regions of net production or consumption via the denitrifica-
 543 tion pathway. For instance, the integrated J_{den}^{n2o} in Figure 7 reveals consumption along
 544 the northern extent of the Peruvian coast at roughly 8°S ; considering this pattern, Fig-
 545 ure 6a shows relatively sharp O_2 gradients above and below the OMZ around -85°W , in-
 546 dicated that N_2O consumption is particularly strong near the coast, where relatively
 547 thin but shallow suboxic layers are found. In contrast, suboxic layers become thicker fur-
 548 ther offshore, resulting in conditions more favorable to N_2O production. Therefore, the
 549 high rates of coastal outgassing observed in Figure 8 are at least partially driven by net
 550 transport from more productive surrounding waters (Figure S11).

551 Our results demonstrate the role of advection in redistributing supersaturated N_2O
 552 within the ETSP. Notably, the EUC and SSCC are revealed as zonal conduits control-
 553 ling the import of supersaturated N_2O (N_2O_{bou}) from the boundaries (and thus, outgassing-
 554 favorable N_2O) into the OMZ domain. This is demonstrated by the large fractional con-
 555 tributions to N_2O at 150 *m* throughout the eastern extent of the transect in Figure 6g,
 556 which match subsurface patterns in Figure S12c. These results are consistent with those
 557 from Yang et al. (2020), who highlighted the tropics in the Eastern Pacific as an impor-
 558 tant outgassing region with seasonality driven predominantly by the timing of upwelling
 559 (May to September). While a significant fraction of the imported N_2O is ultimately ad-
 560 vected into the anoxic OMZ to be consumed (Figures 6g and 7), the remainder is respon-
 561 sible for the bulk ($\sim 56\%$) of the outgassing flux over the OMZ domain. As the N_2O bud-
 562 get and boundary export schematic in Figures 9 and S12 show, circulation also plays a
 563 key role in exporting the majority (roughly 72%) of local denitrification-derived N_2O pro-
 564 duction (J_{den}^{n2o}) out of the OMZ budget domain. Much of this export takes place along
 565 the western boundary (Figure S12), but at more southerly latitudes and at deeper depths
 566 compared to the import of supersaturated N_2O from the boundaries (T_{bou}^{n2o}). Unfortu-
 567 nately, our regional simulations do not allow us to explore the fate of this N_2O . Global
 568 or basin-wide simulations would enable tracking the interplay of N_2O sources and sinks
 569 within and outside OMZs. A portion of the denitrification-derived N_2O export may re-
 570 circulate back into the eastward equatorial currents, or could instead add to N_2O con-
 571 centrations in offshore waters, such as those observed by Santoro et al. (2021).

572 The residual between rapid N_2O production and consumption by denitrification
 573 is heavily coupled to O_2 dynamics and thus a major portion of N_2O outgassing in this
 574 region is likely sensitive to future changes in OMZ magnitude and geometry. Observa-
 575 tions suggest that deoxygenation over the past 50 years has led to expansion of OMZ
 576 volumes and shoaling of the upper oxycline (Stramma et al., 2008; Schmidtke et al., 2017).
 577 Yet, whether this has caused a positive or negative impact on N_2O production likely de-
 578 pends on the relative changes of anoxic versus suboxic volumes. If future climate change

579 results in an increase in the volume of suboxic waters, as suggested by Earth system model
 580 projections (Cabr e et al., 2015; Kwiatkowski et al., 2020; Busecke et al., 2019), it would
 581 increase production from both incomplete denitrification and nitrification, leading to a
 582 positive climate feedback. Conversely, an increase in the volume of anoxic waters may
 583 drive enhanced N₂O consumption and constitute a negative climate feedback.

584 Future changes in the oxycline depth via projected stratification or wind changes
 585 (Kwiatkowski et al., 2020; Busecke et al., 2019; Bakun, 1990) may alter the coupling be-
 586 tween local production and outgassing over OMZs, while also affecting the export of su-
 587 persaturated N₂O into the nearby gyres. The lack of interannual forcing in this study
 588 also leaves gaps in understanding ENSO impacts. OMZ geometry and total denitrifica-
 589 tion rates are sensitive to ENSO variability (Yang et al., 2017), thus N₂O production and
 590 outgassing are likely to exhibit similar year-to-year changes. Interannually forced, high-
 591 resolution models capable of simulating both denitrification and nitrification-derived pro-
 592 duction are needed to resolve these emerging questions.

593 Open Research Section

594 The ROMS model code used to generate the simulation (Shchepetkin & McWilliams,
 595 2005; Shchepetkin, 2015), and the MATLAB (MATLAB, 2020) scripts and output used
 596 to generate the figures shown in the paper, can be found at <https://doi.org/10.5281/zenodo.7374360>
 597 (McCoy et al., 2022). Raw model output can be obtained from the Authors upon request.
 598 Biogeochemical validation data were provided by the World Ocean Atlas 2018 (H. Gar-
 599 cia et al., 2019a, 2019b), MEMENTO (Kock & Bange, 2015) and GLODAPv2 (Key et
 600 al., 2015; Lauvset et al., 2016) databases, with additional shipboard observations from
 601 Kalvelage et al. (2013), Cornejo and Far as (2012), and Krahnmann et al. (2021). The ME-
 602 MENTO database is administered by the Kiel Data Management Team at GEOMAR
 603 Helmholtz Centre for Ocean Research and supported by the German BMBF project SO-
 604 PRAN (Surface Ocean Processes in the Anthropocene, <http://sopran.pangaea.de>). The
 605 database is accessible through the MEMENTO webpage (<https://memento.geomar.de>).
 606 AVISO satellite data used in model validation were processed by SSALTO/DUACS and
 607 distributed by AVISO+ at <https://www.aviso.altimetry.fr> with support from CNES. MODIS
 608 L3 ocean color data were obtained from the NASA/GSFC MODAPS Service website at
 609 <https://oceancolor.gsfc.nasa.gov/l3/>. The ERA-Interim dataset (Dee et al., 2011), which
 610 was used to force the model, was obtained from the European Centre for Medium-Range
 611 Weather Forecasts (ECMWF) at <https://www.ecmwf.int>. Thanks to ICDC, CEN, Uni-
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