Shifts in the Isotopic Composition of Nitrous Oxide between El Niño and La Niña in the Eastern Tropical South Pacific

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Abstract

The El Niño-Southern Oscillation (ENSO) is a natural climate phenomenon that alters the biogeochemical and physical dynamics of the Eastern Tropical Pacific Ocean. Its two phases, El Niño and La Niña, are characterized by decreased and increased coastal upwelling, respectively, which have cascading effects on primary productivity, organic matter supply, and ocean-atmosphere interactions. The Eastern Tropical South Pacific (ETSP) oxygen minimum zone (OMZ) is a source of nitrous oxide (N2O), a potent greenhouse gas, to the atmosphere. While nitrogen cycling in the ETSP OMZ has been shown to be sensitive to ENSO, we present the first study to directly compare N2O distributions during both ENSO phases using N2O isotopocule analyses. Our data show that during La Niña, N2O accumulation increased six-fold in the upper 100 m of the water column, and N2O fluxes to the atmosphere increased up to 100-fold. N2O isotopocule data demonstrated substantial increases in δ 18O up to 60.5shift in N2O cycling during La Niña in the oxycline compared to El Niño. N2O production via the hybrid pathway and incomplete denitrification with overprinting of N2O consumption are likely co-occurring to maintain the high site preference (SP) values (17previous hypotheses. Ultimately, our results illustrate a strong connection between upwelling intensity, biogeochemistry, and N2O flux to the atmosphere, and highlight the importance of repeat measurements in the same region to constrain N2O interannual variability and cycling dynamics under different climate scenarios.

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10	Keywords: Nitrous Oxide, Isotopes, El Niño, Upwelling
11	Key Points:
12 13 14 15 16	 La Niña in the Eastern Tropical South Pacific led to a six-fold increase in nitrous oxide concentrations compared to El Niño. Isotopocule analysis indicates incomplete denitrification and hybrid production both contributed to the accumulation of nitrous oxide. Numerous co-occurring production and consumption pathways likely explain the nitrous oxide
17	distributions.
18	Abstract
19	The El Niño-Southern Oscillation (ENSO) is a natural climate phenomenon that alters the
20	biogeochemical and physical dynamics of the Eastern Tropical Pacific Ocean. Its two phases, El Niño and
21	La Niña, are characterized by decreased and increased coastal upwelling, respectively, which have
22	cascading effects on primary productivity, organic matter supply, and ocean-atmosphere interactions. The
23	Eastern Tropical South Pacific (ETSP) oxygen minimum zone (OMZ) is a source of nitrous oxide (N ₂ O),
24	a potent greenhouse gas, to the atmosphere. While nitrogen cycling in the ETSP OMZ has been shown to
25	be sensitive to ENSO, we present the first study to directly compare N ₂ O distributions during both ENSO

27 six-fold in the upper 100 m of the water column, and N₂O fluxes to the atmosphere increased up to 100-

26

fold. N₂O isotopocule data demonstrated substantial increases in δ^{18} O up to 60.5‰ and decreases in $\delta^{15}N^{\beta}$

phases using N2O isotopocule analyses. Our data show that during La Niña, N2O accumulation increased

down to -10.3‰, signaling a shift in N₂O cycling during La Niña in the oxycline compared to El Niño.

- N_2O production via the hybrid pathway and incomplete denitrification with overprinting of N_2O
- 31 consumption are likely co-occurring to maintain the high site preference (SP) values (17% 26.7%),
- 32 corroborating previous hypotheses. Ultimately, our results illustrate a strong connection between
- upwelling intensity, biogeochemistry, and N_2O flux to the atmosphere, and highlight the importance of
- 34 repeat measurements in the same region to constrain N₂O interannual variability and cycling dynamics
- 35 under different climate scenarios.

36 Plain Language Summary

- 37 Nitrous oxide is a greenhouse gas that is 300 times more potent than carbon dioxide in its ability
- to warm Earth, and it can be produced and consumed through the activities of microorganisms in the
- 39 ocean. The low-oxygen waters of the Eastern Tropical South Pacific are a known global 'hotspot' for
- 40 nitrous oxide cycling, as the chemical and physical conditions there provide fuel for nitrous oxide
- 41 production. A natural climate cycle known as the El Niño-Southern Oscillation, which has a warm and
- 42 cold phase, can affect the conditions that raise or lower the speed of nitrous oxide cycling. We used
- 43 isotopes small, but measurable natural differences in the masses of molecules and atoms to understand
- 44 how nitrous oxide cycling changes during each phase. We found a decrease in nitrous oxide accumulation
- 45 during the warm phase, and enhanced production during the cold phase. This enhanced production is
- 46 connected to more nitrous oxide being released to the atmosphere from the ocean during the cold phase.

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- 54 The data reported in this study can be found in the Stanford Digital Repository
- 55 (<u>https://purl.stanford.edu/sc709fd6894</u>; Gluschankoff et al., 2022) and has been submitted to BCO-DMO.
- 56

57 1. Introduction

58 Nitrous oxide (N_2O) is a powerful greenhouse gas naturally formed in the ocean via microbial 59 processes. N₂O has a greenhouse warming potential up to 300 times that of carbon dioxide (CO_2) on a per 60 molecule basis, and is also the most prominent chemical agent contributing to the depletion of 61 stratospheric ozone (Crutzen, 1970; Ravishankara et al., 2009). Global emissions of N₂O are dominated 62 by terrestrial sources such agriculture and natural emissions from soils, however approximately 20% of 63 all N₂O emitted to the atmosphere is derived from natural processes in marine environments (Thompson 64 et al., 2014, 2019; Tian et al., 2020). Of those marine environments, regional oxygen (O₂) minimum 65 zones (OMZs) and eastern boundary upwelling systems, such as the Eastern Tropical South Pacific 66 (ETSP), are among the most significant sources of N₂O (Arévalo-Martínez et al., 2015; Nevison et al., 67 2004; Yang et al., 2020).

68 A characteristic OMZ includes a shallow, well ventilated mixed layer, underlain by a steep decreasing 69 O_2 gradient, known as the oxycline, where N_2O is rapidly produced (Farías et al., 2009; Frey et al., 2020; 70 Ji et al., 2015). Below the oxycline is the oxygen deficient zone (ODZ), a region of functional anoxia 71 where fixed nitrogen is removed by denitrification and anammox (Bourbonnais et al., 2015; Cohen & 72 Gordon, 1978; Kuypers et al., 2005; Ward et al., 2009), and N₂O is reduced to nitrogen gas (N₂) (Babbin 73 et al., 2015; Bulow et al., 2010; Sun et al., 2020). It is at the oxic-anoxic boundary found between the 74 base of the oxycline and the ODZ where the most intense N₂O cycling occurs, as N₂O can be both 75 produced by nitrification and denitrification, and also consumed by denitrification (Bourbonnais et al., 76 2017; Casciotti et al., 2018).

77 Denitrification is the anaerobic stepwise reduction of nitrate (NO_3^-) or NO_2^- to nitrogen gas (N_2) via

nitric oxide (NO) and N_2O . When the process does not go to completion, it can produce N_2O at high rates.

The enzymes responsible for each step in denitrification are increasingly sensitive to dissolved O_2

80 concentrations, thus, incomplete denitrification can produce N_2O when nitrous oxide reductase is

81 inhibited by the presence of dissolved O₂ (Bonin et al., 1989). It is thought that denitrification produces

82 N₂O at rates up to 2 orders of magnitude higher than nitrification in the suboxic ocean ($[O_2] \le 20 \mu M$;

Babbin et al., 2015; Frey et al., 2020; Ji et al., 2015). In the functionally anoxic regions ($[O_2] < 5 \mu M$) of

84 the water column, consumption of N₂O via denitrification dominates its cycling, leading to a local minima

85 in N₂O concentration, but N₂O production may continue to occur (Casciotti et al., 2018; Cohen &

86 Gordon, 1978; Elkins et al., 1978; Kelly et al., 2021; Monreal et al., 2022; Sun et al., 2020;

87 Suntharalingam & Sarmiento, 2000).

- 88 In oxic waters, N₂O production is largely linked to nitrification (Elkins et al., 1978; Nevison et al.,
- 89 2003; Yoshinari, 1976), and it is recognized that ammonia-oxidizing archaea (AOA) represent the
- 90 dominant oceanic nitrifiers and sources of N₂O in the oxygenated ocean (Francis et al., 2005; Frey et al.,
- 91 2020; Santoro et al., 2011; Toyoda et al., 2019). AOA may produce N₂O through multiple pathways,
- 92 including a putative "hybrid mechanism," combining nitrogen atoms sourced from ammonium (NH_4^+) –
- 93 derived from the degradation of organic matter and from nitrite (NO_2^{-}) to produce N_2O (Frame et al.,
- 94 2017; Frey et al., 2020; Kozlowski et al., 2016; Löscher et al., 2012; Santoro et al., 2011; Stein, 2019;
- 95 Stieglmeier et al., 2014). Rates of hybrid N₂O production appear to represent more than 70% of N₂O
- 96 produced from NH₄⁺ in OMZs (Frey et al., 2020; Ji et al., 2015; Santoro et al., 2021). Ammonia-oxidizing
- 97 bacteria (AOB) may also produce N₂O, but the role AOB play in oceanic N₂O production appears to be
- 98 small (Francis et al., 2005; Löscher et al., 2012; Santoro et al., 2010). The N₂O yields from AOA and
- AOB have been shown to increase under high NO_2^- and low O_2 concentrations (Frame & Casciotti, 2010;
- 100 Frey et al., 2020; Ji et al., 2018; Löscher et al., 2012; Santoro et al., 2021). Thus, organisms involved with
- both nitrification and denitrification can produce N_2O at significant rates in suboxic waters; however,
- their relative contributions on a global scale remain unresolved (Martinez-Rey et al., 2015).
- 103 Of the ocean's three primary OMZs, the ETSP OMZ is believed to be the single largest natural 104 oceanic source of N2O, and its biogeochemical dynamics are sensitive to interannual variability, such as 105 the El Niño-Southern Oscillation (ENSO; Ji et al., 2019; Llanillo et al., 2013; Yang et al., 2017, 2020). 106 ENSO oscillates approximately every two to seven years and shifts the spatial distribution of biologically limiting nutrients, dissolved O₂, and microbial community composition in the equatorial Pacific Ocean 107 through alterations to the dominant ocean circulation patterns (Espinoza-Morriberón et al., 2019; Llanillo 108 109 et al., 2013; Mogollón & Calil, 2017). These shifts in ocean circulation modulate the ventilation of the 110 upper ocean and organic matter supply in the tropical Pacific Ocean, which in turn, alters the cycling and emissions of N2O (Babbin et al., 2020; Espinoza-Morriberón et al., 2019; Ji et al., 2019; Mogollón & 111 Calil, 2017; Thompson et al., 2014). In climate model simulations, the more oxic conditions and 112 decreased organic matter (OM) supply in near-shore waters of the ETSP OMZ during El Niño have been 113 predicted to decrease the rates of suboxic processes like denitrification, which could decrease overall N₂O 114 115 production and consumption (Mogollón & Calil, 2017; Yang et al., 2017). The opposite scenario would be expected during La Niña, with an expanded ODZ volume and increased OM supply increasing N₂O 116 117 production and consumption in the oxycline and ODZ, respectively (Yang et al., 2017).
- Projections of increased ocean deoxygenation, as well as increased frequency and intensity of ENSO events, have significant implications for ocean biogeochemistry with potential repercussions to N₂O cycling and emissions to the atmosphere (Babbin et al., 2020; Cai et al., 2014, 2015; Horak et al.,

- 121 2016; Schmidtko et al., 2017; Stramma et al., 2008; Yang et al., 2017). The distinct oceanographic
- 122 conditions observed during both phases of ENSO can be harnessed as natural experiments of modified
- 123 ocean biogeochemistry and circulation. We hypothesized that the expanded low oxygen waters, enhanced
- upwelling, and greater substrate availability in shallower waters during La Niña, compared to El Niño,
- 125 could increase the overall production of N₂O through both denitrification and nitrification in the oxycline,
- 126 and increase the N_2O flux to the atmosphere.
- N₂O is composed of numerous isotopocules, molecules that differ only in their isotopic composition. 127 As N has two stable isotopes, ¹⁴N and ¹⁵N, and O has three stable isotopes, ¹⁶O, ¹⁷O, and ¹⁸O, the primary 128 isotopocules of N₂O are ¹⁴N-¹⁴N-¹⁶O, ¹⁵N-¹⁴N-¹⁶O, ¹⁴N-¹⁵N-¹⁶O, ¹⁴N-¹⁴N-¹⁷O, and ¹⁴N-¹⁴N-¹⁸O, where ¹⁵N-129 ¹⁴N-¹⁶O and ¹⁴N-¹⁵N-¹⁶O are also referred to as 'isotopomers', or isotopic isotomers. The stable isotope 130 ratios of nitrogen ($^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$) in N₂O, are reported relative to standards atmospheric 131 N₂ and VSMOW, respectively, using delta notation, where $\delta = (R_{N2O}/R_{std} - 1)*1000$ (‰). The bulk values 132 of δ^{15} N and δ^{18} O are affected by the substrate's isotopic composition and isotopic fractionation associated 133 with chemical or enzymatic reaction. The isotope ratios thus serve as powerful tools to elucidate the N_2O 134 135 cycling mechanisms, as each process imparts predictable isotopic fractionation on water column N_2O (Ostrom et al., 2007; Schmidt et al., 2004; Sutka et al., 2006; Toyoda, 2002; Toyoda et al., 2005). Due to 136 the asymmetrical linear geometry of N₂O, the distribution of ¹⁵N between isotopomers that contain ¹⁵N in 137 the inner (alpha: α) versus outer (beta: β) nitrogen atoms provide an independent constraint from the 138 isotopes of N₂O beyond the bulk compositions of nitrogen and oxygen isotopes (Schmidt et al., 2004; 139 Sutka et al., 2006; Toyoda et al., 2005; Toyoda & Yoshida, 1999). The difference in $\delta^{15}N$ of the inner and 140 outer atoms in N₂O is known as site preference (SP = $\delta^{15}N^{\alpha} - \delta^{15}N^{\beta}$), and this value is thought to reflect 141 142 the mechanism of N₂O production and consumption.

Through analysis of the isotopocules of N₂O, nitrate (NO₃⁻), and nitrite (NO₂⁻), in conjunction with supporting hydrographic and biogeochemical data, such as temperature, salinity, nutrient, and dissolved oxygen concentrations, we evaluated the mechanistic underpinnings of N₂O cycling in the ETSP during both ENSO states. Understanding the role ENSO has on N₂O cycling and emissions is imperative, as each ENSO event represents an altered climate-ocean dynamic that has occurred in the past or can occur in the future. To our knowledge, this work is the first to directly compare N₂O cycling under both phases of ENSO in the ETSP OMZ using isotopic measurements.



151 Figure 1: Map of stations analyzed along 10 °S (black diamonds): Station 7 (100 °W), Station 9 (90 °W), and

152 Station 11 (82.5 °W) overlain on dissolved oxygen concentrations (μM) at 250 m from World Ocean Atlas

153 2018 (WOA18), using yearly averaged data from the entire climatology, illustrated using DIVA interpolation.

154 The limit of suboxic waters ($[O_2] < 20 \mu$ M) is illustrated in a dashed white contour line, and the locations of

155 grid points from WOA18 are shown in black dots.

156 2. Materials and Methods

157 2.1 Cruise and N₂O Sampling Details

Samples for N₂O isotopes were collected from the ETSP OMZ aboard the R/V Atlantis (Cruise 158 AT15-61) from January to March 2010 and R/V Melville (Cruise MV1104) from March and April 2011 159 (Knapp et al., 2016; Santoro et al., 2021). Three stations were evaluated for this work along 10 °S: Station 160 7 (100 °W), Station 9 (90 °W), and Station 11 (82.5 °W) (Fig. 1). Each cruise collected N₂O concentration 161 and isotopocule samples at the same stations, with greater vertical sampling resolution during the 2011 162 cruise. The 2010 and 2011 cruises utilized a 24 and 36 Niskin bottle CTD rosette, respectively. N₂O 163 164 samples were collected through silicone tubing directly into Wheaton 160 mL glass serum bottles 165 (Wheaton prod. no. 223748) and overflowed twice before filling. The tubing was removed, and a 1 mL 166 headspace was introduced into each bottle before capping with a grey butyl septum (MicroLiter Analytics 167 Prod #20-0025). After collection, 100 μL of saturated mercuric chloride was added to each bottle and 168 then resealed with the grey butyl septum and an aluminum crimp seal. Samples were stored in the dark at 169 room temperature until analysis.

170 2.2 N₂O Isotopic Analysis

All 247 N₂O samples from the 2010 cruise were analyzed soon after the cruise at the Woods Hole
Oceanographic Institution in 2010 using a Thermo Fisher Scientific Delta^{PLUS} XP isotope ratio mass
spectrometer (IRMS) over approximately one month. Samples collected in the 2011 cruise were analyzed
at Stanford University over three different analytical years and with two different instruments: a Delta^{PLUS}
XP, used in 2012 and 2014, and a Thermo Fisher Scientific DeltaV Plus IRMS used in 2017. Of the 440
samples analyzed from the 2011 cruise, 324 (73.6%), 59 (13.4%), and 57 (13%) samples were analyzed in
2012, 2014, and 2017, respectively.

In all cases, samples were extracted and analyzed using a custom automated purge and trap inlet system and normalized to an injection of calibrated pure N₂O reference gas introduced prior to the elution of each sample peak (McIlvin & Casciotti, 2010). Isotope ratios were referenced initially to the calibrated N₂O reference tank to create a set of 'ratio of ratios' (${}^{31}R_{sample}/{}^{31}R_{reference}$, ${}^{45}R_{sample}/{}^{46}R_{reference}$). Next, the data were size corrected in reference to a calibrated 20 volt-second (Vs) peak area for a mass to charge ratio of 44 (m/z 44). Finally, 'scrambling coefficients' were applied to the isotopomer data to correct the measured ${}^{15}R^{\alpha}$ and ${}^{15}R^{\beta}$ for the rearrangement of nitrogen atoms in N₂O

- 185 when the gas is ionized in the mass spectrometer ion source (Frame et al., 2014; Frame & Casciotti, 2010;
- 186 Kelly et al., 2021). The isotope ratios of N and O atoms in N_2O , ${}^{15}R_{sample}$ or ${}^{18}R_{sample}$, respectively, are
- 187 expressed in delta notation (δ), where the δ^{15} N and δ^{18} O are defined relative to the isotope ratios of

188 certified standards: δ^{15} N or δ^{18} O = (R_{sample}/R_{standard} - 1) x1000. The R_{standard} values used for δ^{15} N and δ^{18} O 189 are the ratios of 15 N/ 14 N and 18 O/ 16 O in atmospheric N₂ and Vienna Standard Mean Ocean Water 190 (VSMOW), respectively. Analytical precision for δ^{15} N^{α}, δ^{15} N^{β}, SP, δ^{15} N^{bulk}, and δ^{18} O for 2010 data were 191 0.33‰, 0.39‰, 0.66‰, 0.12‰, 0.2‰, respectively, and 1.25‰, 1.03‰, 2.08‰, 0.52‰, 0.89‰ for 2011

192 data, respectively.

193 Inconsistencies in the isotopocule data between the 2010 and 2011 datasets became apparent when data interpretation began. To assess isotopic offsets between the two cruise years, deep water 194 samples (herein defined as all samples below 1000 m) for $\delta^{15}N^{\text{bulk}}$, SP, and $\delta^{18}O$ were evaluated. Samples 195 from 2010 were plotted against those from 2011 found within five meters, and deviations from a 1:1 line 196 were used to identify offsets. $\delta^{15}N^{\text{bulk}}$ values were higher in 2011 by approximately 1‰-2‰, except for 197 198 three outliers that were about 3‰-5‰ below 2010 values, but the offset varied depending on the year the 199 2011 data were analyzed. SP had more variance in both directions from the 1:1 line, and δ^{18} O was 200 consistently 2‰ higher in the 2011 samples than in 2010. Following the intercalibration methods used in 201 (Mohn et al., 2014), we identified two potential methods for post-analysis corrections for N_2O 202 isotopocules: an offset correction and a two-point correction. Ultimately, it was determined that an offset correction, using deep water isotopocule values as a comparative standard, would best serve our data 203 204 correction needs. In this correction scheme, we averaged each isotopic value of N₂O for overlapping 205 depths measured during the 2010 and 2011 cruises below 1000 m. We further broke the averages down for each analytical year for the 2011 measurements (2012, 2014, and 2017) and found the difference 206 207 between each year's deep water isotopic values and the 2010 values. The difference was then applied as 208 an offset to the 2011 cruise data to better resolve year to year differences in the N₂O isotopic 209 measurements. The exact offset correction applied to the 2011 data can be found in the supplement (Table 210 S1).

211 2.3 N₂O Concentrations

The N₂O concentration ([N₂O]) was also determined for each gas sample. The m/z 44 peak area for each sample was converted to a nmole quantity using a calibrated conversion factor between nmols of N₂O and peak area (Vs) of the mass 44 (McIlvin & Casciotti, 2010). Based on extraction system testing, the sample volume was assumed to be 153.8 ± 0.5 mL (McIlvin and Casciotti, 2010). Repeat measurements of duplicate N₂O samples yielded average [N₂O] precisions for Stations 7, 9, and 11 of 0.54 nmol/L and 2.45 nmol/L for 2010 and 2011, respectively, and were previously reported (Santoro et al., 2021)

220 2.4 N₂O Air-Sea Flux

- Air-sea N₂O flux calculations were performed for each station during both ENSO phases using
- measured average mixed layer $[N_2O]$, the expected $[N_2O]$ at equilibrium with the atmosphere, and the 10-
- 223 meter wind speed (Wanninkhof, 2014). Calculations were made using monthly averaged 10-meter wind
- speed data for the month leading up to each station's sampling date. Wind speed was derived using the
- 225 NCEP/NCAR Reanalysis 2 data product using four-time daily wind speed measurements and were
- averaged for the monthlong period (National Centers for Environmental Prediction, National Weather
- 227 Service, NOAA, U.S. Department of Commerce, 2000). Atmospheric N₂O mixing ratios were derived
- 228 from NOAA's Global Monitoring Laboratory
- 229 (https://www.esrl.noaa.gov/gmd/hats/insitu/cats/conc.php?site=mlo&gas=n2o)
- and converted to equilibrium [N₂O] using the surface salinity and temperature data derived from the CTD
- 231 (Weiss & Price, 1980). If atmospheric N₂O data were not available for the same day that the station was
- 232 occupied, then the closest date of sampling was used.

233 2.5 Isotopic Analysis of Nitrate and Nitrite

- All NO₃⁻ and NO₂⁻ isotopic analyses were performed using a Thermo Fisher Scientific Delta^{PLUS} 234 235 XP IRMS. For sample preservation, NO₃⁻ and NO₂⁻ samples were filtered at sea, and NO₂⁻ isotopic samples were treated with 2 M sodium azide in 20% acetic acid in a crimp sealed 20 mL vial (McIlvin & 236 Altabet, 2005). The NO_2^- sample preservation method, known as the "azide method," converts NO_2^- to 237 238 N₂O which can then be analyzed on an IRMS (McIlvin & Altabet, 2005). During analysis, the produced 239 N₂O was purged from the vial, cryogenically trapped, and analyzed on the IRMS. Samples were corrected against NO₂⁻ isotopic standards RSIL-N20, N7373, and N10219 made from sodium nitrite salts converted 240 in parallel at sea (Casciotti et al., 2007). Nitrite isotope samples are reported in delta notation, where 241 δ^{15} N-NO₂⁻ and δ^{18} O-NO₂⁻ are in reference to atmospheric N₂ and VSMOW, respectively. Precision for 242 δ^{15} N-NO₂⁻ and δ^{18} O-NO₂⁻ in both 2010 and 2011 were approximately 0.2‰ and 0.3‰, respectively. 243
- 244 Nitrate isotope samples for δ^{15} N and δ^{18} O were analyzed in duplicates, at minimum, using the
- 'denitrifier method' which involves the microbial reduction of NO_3^- to N_2O (Casciotti et al., 2002;
- Sigman et al., 2001). These data are also reported in delta notation in reference to atmospheric N₂ and
- 247 VSMOW, and samples were analyzed alongside reference material with known isotopic values (USGS32,
- 248 USGS34, and USGS35). Samples were treated with sulfamic acid to remove NO₂⁻, if present (Granger &
- Sigman, 2009). Analytical precisions for δ^{15} N-NO₃⁻ were 0.20‰ and 0.14 ‰ for 2010 and 2011,
- respectively, and precisions for 2010 and 2011 δ^{18} O-NO₃⁻ were 0.37‰ and 0.18‰, respectively.

251 2.6 El Niño-Southern Oscillation

- 252 The warm and cold phases of the El Niño-Southern Oscillation (ENSO), known as El Niño and
- 253 La Niña, respectively, are defined through the National Oceanic and Atmospheric Administration
- 254 (NOAA) Ocean Niño Index
- 255 (https://origin.cpc.ncep.noaa.gov/products/analysis monitoring/ensostuff/ONI v5.php). ENSO events are
- determined when sea-surface temperature (SST) anomalies in the central equatorial Pacific region, known
- as Niño 3.4, are ± 0.5 °C over a 3-month running mean, using the previous 30 years as a baseline
- 258 (NOAA's Climate Prediction Center, n.d.). Using the running mean of SST anomalies for the Niño 3.4
- region for both cruise years, 2010 and 2011, they were defined as moderate El Niño and La Niña events,
- 260 respectively.
- 261 **3. Results**

262 **3.1 Study Site Characteristics**

Stations 7, 9, and 11 during both cruise years maintained ODZ-like properties, such as having two N₂O maxima separated by a local minimum in N₂O concentrations, coinciding with the lowest dissolved O₂ concentrations (Fig. 2). These stations were also characterized by sustained suboxia ($[O_2] < 20 \mu$ M) below the mixed layer into intermediate waters. Upwelling velocities, calculated using beryllium-7 (⁷Be) measurements, were high at these stations (1.09-2.95 m d⁻¹) compared to other stations measured along 20 °S (0-0.33 m d⁻¹) during the same expeditions, suggesting greater supply of "new" nutrients to the euphotic zone at 10 °S (Berelson et al., 2015; Fuenzalida et al., 2009; Haskell et al., 2015).

270 The oxycline bases for Stations 9 and 11 were found at shallower depths during La Niña (75 m -271 80 m) compared to El Nino (125 m - 200 m; Fig. 2). As a result, thicker ODZs were found during La Niña at Stations 9 and 11 compared to El Niño, and ODZ ventilation for all three stations occurred between 272 273 600 m and 700 m. At all stations during both years, a shallow N₂O concentration maximum was found at 274 the base of the oxycline, with maximal oxycline N₂O concentrations ranging from 75 nM to 145 nM (Fig. 275 2). At Station 7, the most offshore station, a larger N_2O maximum was found in the oxycline during El Niño compared to La Niña despite having comparable oxycline depths during both ENSO states (Fig. 276 277 2A). However, the impacts of ENSO do not appear to have a substantive impact on the hydrographic features at Station 7, overall. At Stations 9 and 11, the [N₂O] maximum at the base of the oxycline was 278 279 larger, and shallower, during La Niña than during El Niño.





Figure 2: Dissolved N₂O (nmol/L; solid lines) and O₂ (μmol/L; dashed lines) concentrations for A) Station 7;
B) Station 9; and C) Station 11. El Niño measurements are in shades of red, while La Niña measurements are in shades of blue.

284 A primary nitrite maximum (PNM) was observed at each station, ranging from 1 μ M – 2 μ M (Santoro et al., 2021). During El Niño, the PNM was found at greater depths moving westward, occurring 285 at 40 m at Station 11 and 150 m at Station 7, with concentrations ranging from 1.2 μ M - 1.4 μ M. During 286 287 La Niña, the PNM features were generally at lower potential density horizons and shallower depths, at 35 288 m-80 m depth, with concentrations ranging from 1 μ M - 2 μ M. A secondary nitrite maximum (SNM), 289 indicative of functional anoxia, was found at Station 11 during both years, but only during El Niño at 290 Station 9. At Station 11, the SNM reached 2.1 µM and 1.8 µM during El Niño and La Niña, respectively. A small, but measurable third nitrite peak of 0.5 μ M was observed at Station 11 at 150 m during La Niña, 291 292 where a sharp decrease in N₂O concentration was also measured. At Station 9 during El Niño, a SNM of 0.4 µM was observed at 325 m. Significant concentrations of ammonium between 1 µM-2.5 µM were 293 294 also measured at all stations in both years, however, no ammonium measurements were made at Station 7 295 during El Niño (Santoro et al., 2021).

3.2 Upper Ocean N₂O Inventory and Atmospheric Flux

297 Apparent differences in the upper ocean N₂O inventory for Station 7, 9, and 11 led us to quantify 298 the depth-integrated N_2O concentrations for comparison between stations and sampling campaigns (Fig. 299 3). Integrations were performed from 0 to 100 m at Stations 7, 9, and 11 using a trapezoidal Riemann 300 sum. Because no measurement was made at 100 m at Station 9 during El Niño, we interpolated a value at 301 100 m between measurements made at 90 m and 150 m, to make comparable interpretations. N_2O 302 accumulation was greater at every station during La Niña compared to El Niño, with Station 9 having a six-fold higher N₂O accumulation: from approximately 1 mmol/m² during El Niño to 5 mmol/m² during 303 304 La Niña. While comparable in magnitude, N₂O accumulation at Station 11 was lower than Station 9, 305 despite Station 11 being the closest station to the coast where N₂O cycling is presumably the most intense. 306 Only a minor increase in N₂O accumulation was observed at Station 7 between El Niño and La Niña, as 307 O₂ concentrations remained high during both years in the upper 100 m, thus limiting the difference in 308 N₂O production between years.



Figure 3: Depth-integrated N₂O during El Niño (red) and La Niña (blue) calculated to 100 m for Stations 7, 9,
and 11.

Given comparable winds, higher N₂O accumulation in the upper 100 m and in the mixed layer
should increase the N₂O flux to the atmosphere during La Niña relative to El Niño. Expanding on N₂O
flux estimates from 2010 reported earlier (Santoro et al., 2021), estimated N₂O fluxes were up to two

- orders of magnitude greater during La Niña than during El Niño (Table 1). Station 11 had the largest N_2O

the surface.

Year	Station	Flux (µmol/m²/d)
El Niño (2010)	7	1.5 (1.4-1.7)
	9	0.6 (0.5-0.6)
	11	4.3 (3.9-4.8)
La Niña (2011)	7	6.7 (6.1-7.5)
	9	6.5 (6.0-7.3)
	11	22.2 (20.3-24.8)

Table 1: Air-Sea fluxes of N₂O from all three stations during both ENSO phases. Surface N₂O concentrations
for flux calculations were derived using the average mixed layer N₂O concentrations. Range of uncertainty
given in parentheses is based on a 20% error associated with the Schmidt number.

321 3.3 δ^{15} N and δ^{18} O of Nitrite and Nitrate

During La Niña, trends of increasing δ^{15} N-NO₂⁻ and decreasing δ^{18} O-NO₂⁻ were observed from 322 the surface into the oxycline at Station 9 (Fig. 4A). In contrast, NO₂⁻ isotopes at Station 11 during La Niña 323 were relatively constant, ranging from -10.9% to -14.2% and 12.1% to 10.7% for δ^{15} N-NO₂⁻ and δ^{18} O-324 NO₂⁻, respectively (Fig. 4B). The one exception to this trend at Station 11 during La Niña was at 60 m 325 where the δ^{15} N-NO₂⁻ increased to -3.2‰, which could be associated with enhanced nitrite reduction, or 326 327 lower rates of nitrite oxidation. During El Niño, the lower nitrite concentrations and sampling resolution meant that only one measurement for δ^{15} N-NO₂⁻ and δ^{18} O-NO₂⁻ was made for each of Stations 9 and 11 in 328 the upper 100 m (Fig. 4, S1). The δ^{18} O-NO₂ measured during El Nino was similar to those values 329 measured during La Nina, while δ^{15} N-NO₂⁻ was higher at Station 9 and lower at Station 11 (Fig. 4, S1). 330 The vertical distributions of δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ in the upper water column were impacted 331 by ENSO in parallel with changes in chemical and physical properties, like the oxycline and density 332 layers being found shallower in the water column during La Niña (Fig. 4, Fig. S1). Station 7 NO₃ isotopes 333 were similar between ENSO events, maintaining a surface maximum followed by a general decrease with 334 depth (Fig. S2G). No changes were observed in δ^{15} N-NO₃⁻ or δ^{18} O-NO₃⁻ at ODZ depths at Station 7, 335 which is consistent with the lack of variation in N₂O concentration and isotopes between ENSO phases at 336 this station. At Stations 9 and 11, high surface δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ were found during both ENSO 337 events, however, the decrease in δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ occurred at shallower depths and followed a 338

steeper gradient during La Niña (Fig. 4B, C). In fact, the shallow NO₃⁻ isotope minimum was measured 339 340 90 m shallower at Station 9 during La Niña compared to El Niño (Fig. 4B). Both δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ were elevated within the ODZ at Stations 9 and 11 during El Niño, consistent with nitrate reduction 341 342 occurring within the ODZ. A similar level of heavy isotope enrichment was observed during La Niña at Station 11, but less so at Station 9. The depths where elevated δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ values were 343 found corresponded with the lowest $[N_2O]$ in the ODZs, supporting the impact of denitrification on water 344 column N species distributions. Though the nitrate isotope profiles shoaled during La Niña, δ^{15} N-NO₃⁻ 345 and δ^{18} O-NO₃⁻ appear to be significantly less sensitive to the contrasting biogeochemical impacts 346

imparted by each ENSO state, relative to N_2O .



Figure 4: Station 9 (A) and Station 11 (B) δ^{15} N-NO₃⁻ (filled circles, solid line), δ^{18} O-NO₃⁻ (open circles, dashed line), and δ^{15} N-NO₂⁻ (diamonds). Data from El Niño (red) and La Niña (blue).

351 3.4 Isotopic Composition of N₂O

At each station in both years, surface $\delta^{15}N^{bulk}$, closely reflected the isotopic composition of atmospheric N₂O, ranging from 5.8 - 6.8‰ (Fig. 5B). $\delta^{15}N^{bulk}$ generally decreased to subsurface minima, ranging from 2.8‰ to 5‰, coinciding with the near surface [N₂O] maxima. For Stations 9 and 11, distinct increases in $\delta^{15}N^{bulk}$ were observed from the shallow $\delta^{15}N^{bulk}$ minimum to their ODZ maxima, found between 325 - 400 m (Fig. 5). Conversely, the increase in $\delta^{15}N^{bulk}$ at Station 7 was more gradual and did not exhibit a defined peak in the ODZ (Fig. S2B). A unique shallow $\delta^{15}N^{bulk}$ maximum was found at 150 m at Station 11 during La Niña, corresponding to increases in other isotopocule measurements and a 359 decrease in N₂O concentration. This feature is sandwiched between two lower $\delta^{15}N^{bulk}$ values and larger 360 N₂O concentration measurements, thus, potentially reflecting intrusion of anoxic waters that had 361 experienced N₂O consumption.

362 Similar to δ^{15} N^{bulk}, mean δ^{18} O-N₂O values in surface waters generally reflected that of atmospheric N₂O, averaging 45.5‰ in both years (Fig. 5C). At all stations during El Niño, and Station 7 363 during La Niña, δ^{18} O-N₂O slightly decreased from the surface to 40-43‰ near 100 m, then gradually 364 increased to maximum values of 55-80‰ in the ODZ, where [N₂O] decreased (Fig. S2, S3). During La 365 Niña, δ^{18} O-N₂O initially decreased to a minimum at 50 m at Station 9 and then increased to 48.6‰ at 100 366 m, below the [N₂O] maximum at 90 m. Station 11 during La Niña demonstrated the most variability in the 367 upper 100 m, and it had the largest observed δ^{18} O-N₂O of 94‰ in the ODZ (Fig. S3). Also at Station 11 368 during La Niña, a significant near surface δ^{18} O-N₂O peak of 79.5‰ at 150 m coincided with the reduction 369 in N₂O concentration and elevated $\delta^{15}N^{\text{bulk}}$ mentioned above. 370

The distribution of $\delta^{15}N^{\alpha}$ in both years was tightly coupled to the distribution of $\delta^{15}N^{bulk}$ and $\delta^{18}O$ -N₂O (Fig. 5E). During both years, $\delta^{15}N^{\alpha}$ values decreased from near-surface values to minima (6-9.5‰) in the oxycline, above the [N₂O] maximum. Local maxima in $\delta^{15}N^{\alpha}$ occurred at 90 m at Station 9 and 150 m at Station 11 during La Niña. Subsurface $\delta^{15}N^{\alpha}$ maxima (17.3-31.6‰) coincided with water column [N₂O] minima in the anoxic core of the ODZ at Station 11 (Fig. 5). These $\delta^{15}N^{\alpha}$ maxima also coincided with elevated $\delta^{18}O$ -N₂O and $\delta^{15}N^{bulk}$, likely representing N₂O consumption.

Surface values of $\delta^{15}N^{\beta}$ were typically low, ranging between -4.5‰ and -1‰, which span the 377 expected atmospheric value of -3.3%. From there, $\delta^{15}N^{\beta}$ decreased into the [N₂O] maxima at Stations 9 378 and 11 during La Niña, whereas $\delta^{15}N^{\beta}$ values slightly increased at the [N₂O] maximum during El Niño. 379 The minima in $\delta^{15}N^{\beta}$ seen at Stations 9 and 11 corresponded with lower $\delta^{15}N^{\text{bulk}}$ and higher $\delta^{18}O-N_2O$ 380 values in the upper 100 m (Fig. 5, S3). Low $\delta^{15}N^{\beta}$ values are often observed within oxygen deficient 381 waters. Indeed, the $\delta^{15}N^{\beta}$ values reached their overall minima with the ODZ coinciding with marked 382 decreases of [N₂O] in both ENSO phases at Station 11. Thus, the $\delta^{15}N^{\beta}$ minima found in oxycline waters 383 at Stations 9 and 11 during La Niña (where high N₂O accumulation was measured) may result from a 384 different set of processes that will be further addressed below (Fig. S3). 385

Site preference (SP) values in surface waters ranged from approximately 13.8 - 21.4‰, which span the atmospheric value of 19‰ (Mohn et al., 2014). A subsurface SP minimum found near the base of the oxycline at each station ranged from 5.5 - 9.2‰, with the lowest SP observed in the oxycline at Station 11 during La Niña. During La Niña, high SP values (20 - 44‰) were found at 150 m and within the ODZ, coinciding with marked reductions in N₂O concentrations, as well as elevated δ^{18} O-N₂O and 391 $\delta^{15}N^{\text{bulk}}$ values (Fig. S3). At Station 9 in La Niña, however, the SP maximum at 90 m coincided with the 392 station's near-surface N₂O concentration maximum and corresponded with a local maximum in $\delta^{15}N^{\alpha}$ and 393 minimum in $\delta^{15}N^{\beta}$ (Fig. 5E & 5F).



394

395 Figure 5: N₂O A) concentrations (nM); B) δ^{15} N^{bulk} (‰ vs. air); C) δ^{18} O (‰ vs. VSMOW); D) SP (‰ vs. air);

396 E) δ^{15} N^α (‰ vs. air); and F) δ^{15} N^β (‰ vs. air) illustrated for Stations 9 (90 °W; dashed line) and 11 (82.5 °W;

397 solid line) during El Niño (red) and La Niña (blue).

398 4. Discussion

399 4.1 La Niña Shoaling Increased N₂O Flux and Accumulation

400 Our data demonstrated a 100-fold increase in the estimated N₂O flux to the atmosphere (Table 1) 401 and up to a six-fold increase in accumulated N₂O in the upper 100 m of the water column between El 402 Niño and La Niña (Fig. 3), as major biogeochemical features like the N₂O maximum corresponding with 403 the oxycline base were shoaled into this layer (Fig. 2). During El Niño, the trade winds weakened, 404 resulting in the return of warm, salty surface waters to the eastern Pacific, a deepening of the mixed layer, 405 and slowed coastal upwelling. The opposite occurred during La Niña, where enhanced upwelling

- transported sub-surface N₂O into shallower depths. Similarly, N₂O at shallower depths were likely
- 407 upwelled into the mixed layer leading to the increase in N₂O fluxes during La Niña. Atmospheric
- 408 backtracking demonstrated a significantly greater N₂O flux in our study region during La Niña compared
- 409 to El Niño (Babbin et al., 2020); our results provide a complementary ocean-based view of these findings.
- 410 Whether the larger accumulation of N_2O in the upper 100 m during La Niña is due to transport alone or
- 411 also due to alterations to the pathways of N_2O formation are evaluated below.

412 4.2 Limited N₂O Cycling in Surface and Oxycline Waters During El Niño

Although limited by lower sample resolution, little isotopocule heterogeneity was observed above 413 414 the oxyclines at Stations 9 and 11 during La Niña, as well as in and above the Station 9 and 11 oxyclines during El Niño (Fig. 5). In these regions, similar isotopocule values and trends indicate similar sources 415 with low N₂O production rates due to the low N₂O accumulation. Generally, N₂O in these waters had 416 lower δ^{18} O-N₂O, SP, and δ^{15} N^{α} values relative to atmospheric N₂O with increasing depth, while δ^{15} N^{β} 417 418 increased. These same isotopocules in the El Niño oxyclines of Stations 9 and 11 corresponded with lower N₂O accumulation relative to La Niña. The moderate SP (9.1‰-17.1‰; Fig. 5D) and low δ^{18} O-N₂O 419 420 (Fig. 5C) observed in the El Niño oxyclines does not point to a single specific N₂O source. While prior 421 studies have shown N₂O production rates from NH₄⁺ reached maximum values in the upper oxycline at Stations 9 and 11 during El Niño, indicating a role for hybrid N₂O production, rates of hybrid n2o 422 423 production can be up to 2 orders of magnitude lower than incomplete denitrification (Ji et al., 2015; 424 Santoro et al., 2021). It is also possible that lateral mixing from more coastal waters -- where incomplete denitrification can produce N₂O with a low SP -- is influencing the isotopic composition of N₂O we 425 426 observed in the oxyclines of Stations 9 and 11 during El Niño, as described in other work (Fig. 6; Ji et al., 427 2019). Finally, due to the significant deepening of the thermocline that occurs during El Niño, it is likely 428 that local production of N₂O was diminished in the less steep oxycline during this time. Under these conditions, consumption of NH_4^+ or organic matter would be concentrated in the upper oxycline waters 429 430 where O₂ concentrations are still high enough to maintain low N₂O yields from ammonia oxidation. Thus, 431 the combination of low N₂O accumulation and low isotopic heterogeneity in El Niño surface and oxycline 432 waters and La Niña surface waters suggest limited local cycling of N₂O.



Figure 6. N₂O Isotope mixing plot for δ¹⁸O vs SP. Stations 9 and 11 samples from both ENSO states
in the upper 100 m are illustrated. Marker sizes indicates N₂O concentration in nM ranging from
6.6 nM to 145.2 nM. Range of potential delta values for N₂O produced by AOA hybrid production
(green box) and incomplete denitrification from NO₂⁻ (left purple box) or NO₃⁻ (right purple box)
are shown. Known regression slopes for N₂O consumption from nitrite (black solid lines) and
nitrate (dashed solid lines) are also illustrated.

440 4.3 Intense N₂O Cycling Through Multiple Pathways in Oxycline Waters During La Niña

We used our measured N_2O , NO_2^- , and NO_3^- isotopic data data together with previously published SP values to examine the potential relative contributions of competing microbial N_2O production and consumption pathways (Fig. 6). The high accumulation of N_2O in the oxyclines of Stations 9 and 11 during La Niña demonstrated distinct isotopic values that point toward local production from incomplete denitrification with overprinting signals of hybrid production and/or N_2O consumption (Fig. 6). During

La Niña at Station 9, from the top of the oxycline at 50 m to the [N₂O] maximum at 90 m, increases in SP 446 and δ^{18} O-N₂O coincided with a decrease in δ^{15} N^{β} (Fig. 5C, D, F). Additionally, from 50 m to 60 m, the 447 δ^{15} N of NO₂⁻ significantly increased from -23.12% to -8.16%, corresponding with the N₂O- δ^{15} N^{β} 448 minimum found 5 m below (-7.9%; Fig. 5B). The increased δ^{15} N-NO₂⁻ indicates that NO₂⁻ reduction 449 likely superseded NO₂⁻ oxidation there, as NO₂⁻ reduction causes ¹⁵N enrichment in NO₂⁻ (Martin & 450 Casciotti, 2016), whereas NO₂⁻ oxidation exhibits an inverse isotope effect (Casciotti, 2009), thus 451 supporting a role for enhanced N₂O production from NO₂⁻. At the same time, the SP values exceed that 452 453 expected from incomplete denitrification, and suggest a role for an additional source from hybrid N₂O production (Fig. 6). Indeed, most of the points from the Station 9 La Nina oxycline fall within the mixing 454 455 space between the hybrid pathway and denitrification of NO_3 , or solely within the isotopic composition expected from hybrid N₂O production (Fig. 6). Recent modeling studies suggest that overall 456 457 denitrification increases during La Niña in the ETSP due to a shoaling and expansion of low O₂ waters 458 (Mogollón & Calil, 2017; Yang et al., 2017). Together, these effects could allow denitrifying organisms 459 to utilize organic matter closer to the surface, where there is a greater organic matter flux, resulting in 460 more production and consumption of N₂O via denitrification, thus corroborating our findings in our study.

461 Station 11 during La Niña exhibited signals of N₂O production from hybrid N₂O production and incomplete denitrification with evidence of partial N₂O consumption (Fig. 6). Consistently lower $\delta^{15}N^{bulk}$ 462 (Fig. 5B) and increased δ^{18} O-N₂O values (Fig. 5C) between the surface and the [N₂O] maximum of 463 Station 11 during La Niña reflect a low substrate δ^{15} N and significant enrichment of ¹⁸O in N₂O, 464 respectively, two indications for N_2O production from the denitrification of NO_2^- or co-occurring 465 production and consumption (Bourbonnais et al., 2017; Casciotti et al., 2018). The higher δ^{18} O-N₂O 466 467 values measured at Station 11, compared to Station 9, during La Niña could represent: 1) a greater 468 contribution of N₂O from NO₃⁻ relative to NO₂⁻ due to its larger branching isotope effects; 2) a small, but 469 significant overprinting signal of N_2O consumption, or 3) a combination of these effects.

470 Most data from Station 11 during La Niña extend from between the nitrate and nitrite bounds or 471 as a mixture of hybrid and incomplete denitrification, suggesting a potential combination of N₂O substrates and sources (Fig. 6). In particular, the low $\delta^{15}N^{\beta}$ and $\delta^{15}N^{\text{bulk}}$ values paired with the most 472 elevated δ^{18} O-N₂O point toward incomplete denitrification as a significant production mechanism. 473 474 Specifically, the low $\delta^{15}N^{\text{bulk}}$ and $\delta^{15}N^{\beta}$ values in the oxycline could represent NO₂⁻ as a key source of N₂O due to the low δ^{15} N-NO₂⁻ values measured. The δ^{15} N-NO₂⁻ values in the oxycline during La Niña 475 ranged from -38.2% to -8.16% and -14.18% to -3.22% at Stations 9 and 11, respectively (Fig. 4A, B), 476 thus representing an ¹⁵N-depleted pool that would decrease $\delta^{15}N^{\text{bulk}}$ and $\delta^{15}N^{\beta}$ values in N₂O. In contrast, 477 δ^{15} N-NO₃ values ranged from 5-20‰ over this depth range (Fig. 4). The cluster of Station 11 La Niña 478

479 data outside of the mixing bounds of the potential source boxes with δ^{18} O-N₂O > 50‰ are unique to this

- 480 station (Fig. 6). The enhancement of both δ^{18} O-N₂O and SP for these data likely results from N₂O
- $\label{eq:source} 481 \qquad \text{consumption occurring on top of the background N_2O source mixture, whereas Station 9 data points}$
- 482 during La Niña are found within the mixing bounds of hybrid production and incomplete denitrification483 sources.
- In addition to denitrification, hybrid N₂O production likely also contributed to the accumulation of N₂O at Station 11 during La Niña (Fig. 6). In prior work, a relatively high rate of N₂O production from NH₄⁺ was measured at 70 m in the Station 11 oxycline during La Niña (0.156 nmol N L⁻¹ d⁻¹; Santoro et al., 2021). Additionally, Station 11 in La Niña corresponded with the highest abundance of Water Column A ammonia monooxygenase genes (*amoA*), a genetic marker for AOA (Santoro et al., 2021). Thus, the easternmost station, where we observed the greatest variability of N₂O cycling in oxycline waters, also has a high potential for ammonia oxidation to N₂O due to an abundant AOA community.
- While mixing between N₂O production from the hybrid mechanism and incomplete 491 denitrification can partially explain the increase in SP (and δ^{18} O-N₂O) in the oxycline waters of Stations 9 492 493 and 11, modeling work has also suggested that denitrification with a positive SP (25%), which has been shown to occur for one strain of denitrifying bacteria (Toyoda et al., 2005), may play an important role in 494 495 N₂O dynamics in ODZ regions (Casciotti et al., 2018; Kelly et al., 2021; Monreal et al., 2022). In this case, denitrification could itself explain the isotopic patterns. Alternatively, hybrid N₂O production by 496 497 AOA could produce N₂O with a SP that is lower than 30‰. For example, AOA from soils were shown to produce N_2O with SP ranging from 20%-30% (Jung et al., 2014). Although the enzymology and exact 498 499 mechanism of this reaction have yet to be described, its hybrid nature implies that it could have a variable SP. This is because the δ^{15} N difference between the alpha and beta nitrogen positions could be affected by 500 501 independent variations in the oxidized and reduced substates combining to form hybrid N₂O. Thus, the 502 production of N₂O via incomplete denitrification with a site preference, or hybrid N₂O production with a 503 lower SP, cannot be excluded from consideration in the interpretation of N₂O isotopocule analysis in low 504 O₂ waters. If this is the case, they could provide an explanation for the high measured SP values coinciding with elevated δ^{18} O-N₂O and low $\delta^{15}N^{\beta}$ and $\delta^{15}N^{bulk}$ values found here. Finally, culture 505 506 experiments have also demonstrated the ability for fungi produce to N₂O with a high SP of \sim 22-37‰ 507 through a 'denitrification-like' pathway (Maeda et al., 2015; Rohe et al., 2014; Sutka et al., 2008). Indeed, fungi have been observed to account for as much as 50% of the total N₂O produced at certain depths in 508 509 the low oxygen waters of the ETSP, thus representing a significant source of N_2O and potential driver for 510 non-traditional expectations of N₂O isotopomers (Peng & Valentine, 2021).

511 4.4 The Dynamic Nature of N₂O at Station 11 during La Niña

512 We expanded on the results of the mixing diagram (Fig. 6) and applied an open and closed system irreversible kinetic Rayleigh model to determine what fraction of N₂O needed to be consumed via 513 denitrification to explain the elevated SP and δ^{18} O values at Station 11 during La Niña. There, data points 514 in the isotope mixing diagram were found outside of the source mixing bounds and must have incurred 515 516 N₂O consumption (Fig. 6). The open system Rayleigh model (Eq. 2) assumes steady state, meaning that 517 the N₂O we observed would be explained by the continuous balance of production and consumption 518 signals. Alternatively, the closed system Rayeligh model (Eq. 3) assumes non-steady state whereby a 519 parcel of N₂O is being consumed without replenishment.

520
$$\delta_{obs} = \delta_{predicted} + \varepsilon * [1 - f]$$
(2)

521
$$\delta_{obs} = \delta_{predicted} - \varepsilon * \ln(f)$$
(3)

522 We used measured isotopocule values within the source mixing bounds and values found outside of the source mixing bounds as our $\delta_{\text{predicted}}$ and δ_{observed} values, respectively. Depending on whether we 523 used the δ^{18} O-N₂O or SP as our isotopocule values in the models and their associated isotope effects for 524 N₂O consumption (ϵ), we calculated between 50-60% of the N₂O remained (f) after consumption using 525 526 the closed system model and 30-50% of the N₂O remained after consumption using the open system 527 model. Thus, given the cluster of Station 11 La Niña measurements found outside of the source mixing bounds with strongly negative $\delta^{15}N^{\beta}$ values, co-occurring production and consumption of N₂O must be 528 occurring there to explain the N₂O isotopic composition. While the results of both Rayleigh model 529 530 scenarios are plausible, modelling work has shown that ODZ environments may not be in steady-state, and thus, the results of closed system model may be more representative of the amount of N_2O 531 532 consumption that has occurred at Station 11 during La Niña.

533 Parallel measurements on these cruises indicate non-steady state hydrographic conditions at 534 Station 11 in 2011, during La Niña, which could explain the nature of N₂O concentrations and isotopocules measured there. For example, ⁷Be measurements were found to exceed the expected value 535 536 for water below the mixed layer, and upwelling velocities were up to an order of magnitude higher than 537 all other stations during La Niña, thus representing the potential for substantial bidirectional vertical movement (Haskell et al., 2013) (Haskell et al., 2015). Additional work from these cruises similarly found 538 high variability for ²³⁴Th measurements in the upper 100 m at Station 11 during La Niña, also indicating 539 non-steady state conditions. The "zig-zagging" nature of our N₂O isotopic profiles, such as δ^{18} O-N₂O, at 540 Station 11 during La Niña loosely mimics the variability observed in the ²³⁴Th measurements found in 541 542 Haskell 2013, potentially representing similar physical mechanisms.

543 We suggest that the variable N₂O isotopic content found at Station 11 during La Niña also 544 represents non-steady state conditions, whereby ODZ waters in which N₂O consumption via 545 denitrification has occurred have mixed into the oxycline. The notion that low-oxygen waters with partial 546 N₂O consumption may be interacting with more oxic waters during La Niña is not surprising due to the 547 higher predicted rates of denitrification and generally greater kinetic energy and stronger upwelling 548 velocities found during La Niña, which can respond rapidly depending on local fluctuations in wind 549 patterns (Mogollón & Calil, 2017).

550 4.5 The Isotopic Composition of Accumulated N₂O

To better describe the impacts ENSO has on the sources of N₂O in the upper 100 m of the water column, we calculated a depth-averaged isotope value (δ_{avg}) for the accumulated N₂O at each station:

553
$$\delta_{avg} = \frac{\sum_{i=1}^{n} \left[\left(\frac{\delta_i \times [N_2 O]_i + \delta_{i-1} \times [N_2 O]_{i-1}}{2} \right) \times (z_i - z_{i-1}) \right]}{\sum_{i=1}^{n} \left[\left(\frac{[N_2 O]_i + [N_2 O]_{i-1}}{2} \right) \times (z_i - z_{i-1}) \right]}$$
(1)

where δ_i is the isotopic composition of N₂O measured for sample i at depth z_i , and [N₂O]_i is the N₂O concentration at that depth. The sum of these concentration-weighted isotopic values is then divided by the depth-integrated N₂O concentration for the depth range under consideration (Table 2).

We initially applied a Keeling model, a commonly used isotope and mass balance equation, to 557 compute the isotopic composition of the produced N₂O from these data (Casciotti et al., 2018; Fujii et al., 558 559 2013; Yamagishi et al., 2007); however, there were evident violations of the model's assumptions, such as N₂O consumption. Comparing differences in the depth-averaged N₂O isotopic composition provides a 560 561 holistic view of the net changes in accumulated N₂O in the upper 100 m between El Niño and La Niña 562 conditions. As expected from inspection of the depth profiles (Fig. S2), the depth-averaged isotope 563 calculations at Station 7 showed no substantive changes between El Niño and La Niña (Table 2). As 564 described in Section 4.2, low N₂O accumulation coupled with low variability in the isotopocule 565 measurements suggest little change in the rates and mechanisms of N₂O production at Station 7 between 566 ENSO states. Here at Station 7, we rule out significant inputs from local denitrification as oxygen 567 concentrations are most likely too high to support reductive processes. However, the isotopocule signals 568 could be explained by a mixture of hybrid N₂O production and N₂O derived from denitrification, via long-569 range transport.

El Niño	$\delta^{15} N^{\alpha}{}_{avg}$	$\delta^{15}N^{\beta}{}_{avg}$	SPavg	$\delta^{15}N^{bulk}{}_{avg}$	$\delta^{18}O_{avg}$ -N ₂ O
Station 7	13.2 (0.1)	-1.6 (0.1)	14.8 (0.2)	5.8	45.4 (0.1)
Station 9	11.5 (0.2)	-0.9 (0.3)	12.4 (0.5)	5.3 (0)	44.2 (0.1)

Station 11	9.4 (0.1)	-0.5 (0.1)	9.9 (0.2)	4.5 (0)	41.6 (0.1)
La Niña	$\delta^{15} N^{\alpha}_{~avg}$	$\delta^{15} N^{\beta}{}_{avg}$	SPavg	$\delta^{15}N^{bulk}{}_{avg}$	$\delta^{18}O_{avg}$ -N ₂ O
Station 7	12.5 (1.1)	-0.9 (0.8)	13.4 (1.9)	5.8	44.1 (0.4)
Station 9	12.3 (1.2)	-5.2 (1.0)	17.5 (2.3)	3.6 (0.2)	46.0 (0.2)
Station 11	10.1 (0.7)	-4.1 (0.4)	14.2 (1.1)	3.0 (0.3)	51.9 (0.2)

571 Table 2: Depth-averaged N₂O isotopocule values (in ‰) for the upper 100 m. Clear increases in $\delta^{18}O_{avg}$ -N₂O 572 and SP_{avg} and decreases in $\delta^{15}N^{bulk}{}_{avg}$ and $\delta^{15}N^{\beta}{}_{avg}$ occurred at Stations 9 and 11 from El Niño to La Niña, 573 whereas, only minute changes were calculated at Station 7. Calculation uncertainties (in parantheses) were 574 based on the standard deviation of each isotopic measurement, instead of the calculated δ_{avg} -values from 575 Equation 1.

At Station 9, the depth-averaged $\delta^{15}N^{\beta}$ and $\delta^{15}N^{\text{bulk}}$ during La Niña were lower by 4.3% and 576 1.7‰, respectively, compared to El Niño. However, no significant change to $\delta^{15}N^{\alpha}$ was observed. To 577 achieve this, a source relatively depleted in ¹⁵N must be contributing to $\delta^{15}N^{\beta}$ during La Niña, while a 578 competing mechanism maintains a steady $\delta^{15}N^{\alpha}$. At the same time, there was a six-fold increase in the 579 580 overall N₂O accumulation during La Niña from the previous year's El Niño, thus N₂O production is likely 581 enhanced by the significantly steeper and shallower oxycline found during La Niña (Fig. 7). From this, we again propose N_2O production from mixed sources with the potential for NO_2^- to be an important 582 substrate of N₂O in these waters to lower the $\delta^{15}N^{\beta}$ during La Niña, while hybrid production from AOA or 583 partial N₂O consumption could be maintaining the $\delta^{15}N^{\alpha}$ values. The combined effect of these processes 584 on the isotopic composition of N₂O could support the intermediate SP and δ^{18} O-N₂O values found during 585 La Niña where N₂O accumulation was enhanced (Fig. 6). The low N₂O accumulations found at Station 9 586 587 during El Niño, as well as its isotopocule signatures, appeared to be similar to Station 7, reflecting 588 relatively low N₂O production in the upper 100 m.

589 The largest apparent difference in N₂O sources between ENSO phases occurred at Station 11. The depth-averaged δ^{18} O-N₂O during La Niña was 10‰ greater than during El Niño, indicating a greater role 590 for N₂O production and/or consumption from denitrification during La Niña. Similar to Station 9, $\delta^{15}N^{\beta}$ 591 and $\delta^{15}N^{\text{bulk}}$ values were 3.6% and 1.4% lower, respectively, during La Niña. Despite the high N₂O 592 concentrations, we believe that the higher δ^{18} O-N₂O values observed during La Niña reflect co-occurring 593 594 N₂O consumption overprinting strong production signals at Station 11 (Fig. 6). For example, at 80 m during La Niña, we observed increases in δ^{18} O-N₂O and SP concurrent with a decrease in δ^{15} N^{β}, which 595 could be indicative of simultaneous N₂O production and consumption in suboxic waters ($[O_2] = 7.2 \mu$ M) 596 597 (Fig. 5; Bourbonnais et al., 2017; Casciotti et al., 2018). These conditions contrast with the upper 100 m

- 598 during El Niño, in which [O₂] reached a minimum of ~38 μM. During El Niño, the calculated SP (9.84‰)
- and δ^{18} O-N₂O (41.38‰) achieved the lowest values observed for all stations in either ENSO event (Fig.
- S2C, D). Consequently, we suggest that hybrid N₂O formation and a lesser degree of N₂O consumption
- 601 via denitrification resulted in the depth-averaged SP and δ^{18} O-N₂O values we found during El Niño
- 602 (Bourbonnais et al., 2017; Casciotti et al., 2018; Ji et al., 2019).



Figure 7: Idealized cartoon highlighting key hydrographic and biogeochemical differences between El Niño
and La Niña. During El Niño, lower primary productivy (green phytoplankton) and organic matter (brown
circles) accompany less upwelling and a deeper oxycline (dashed line), ultimately suppressing high N2O
production. The opposite is true during La Niña, when the oxycline is upwelled and more organic matter
reaches low oxygen waters, leading to an increase in denitrification processes and greater N2O accumilation
in near-surface waters.

610 4.6 Impact of ENSO Event Intensity on N₂O Cycling

ENSO event strength (mild, moderate, or strong) has a significant influence on the net N₂O flux 611 to the atmosphere from the tropical Pacific ocean (Babbin et al., 2020). The data from the current study 612 613 allowed us to investigate how the relative intensity of an ENSO event influences the microbial sources of 614 N₂O and its accumulation from the oceanographic perspective. We did this by comparing our data to 615 other published N₂O concentrations and isotopocule data from a location approximately a half degree 616 longitude to the east of Station 11, during 2015, a strong El Niño year (Ji et al., 2019). Similarity in 617 accuracy of isotopic measurements between datasets was assessed by comparing N₂O isotopologues at 618 deepest common depth (1000 m). Measurements between datasets were comparable and any differences

619 were smaller than the difference in values between ENSO states.

The key N_2O concentration difference between the strong 2015 El Niño and the moderate 2010 El Niño is that in 2010, the $[N_2O]$ maximum started at 100 m and stayed roughly at the same concentration (within 10 nM) until 200 m, where it then matched the 2015 data. In the upper 60 m of the water column, N₂O concentrations in the 2015 El Niño were more similar to our higher La Niña measurements than our 2010 El Niño measurements (Fig. S4A). The comparatively shallow oxycline in the 2010 El Niño likely allowed for N₂O production to occur closer to the surface, whereas the significantly depressed isopycnals and oxycline in 2015 (not shown) likely prevented strong N₂O production occurring in the upper 100 m.

627 The N₂O isotopic measurements during the strong El Niño followed similar trends to our 628 moderate El Niño measurements in the upper 100 m at Station 11, although the values were offset. Generally, during both El Niño events, δ^{18} O-N₂O values were low (<45‰) and SP values decreased from 629 the surface to 100 m (Fig. S4B). The Keeling model result (SPprod) from the previous study in the 'N2O 630 peak' (45-500 m, 5-20 μ M O₂, and NO₂⁻ < 1 μ M) for all of their stations was also within 2‰ of our El 631 Niño depth-integrated SP from 0-100 m and yielded the same δ^{18} O-N₂O as ours. Thus, we propose that 632 lateral mixing from the more coastal OMZ where N2O is being produced from denitrification is a more 633 likely candidate for the low SP, in addition to an overprinting signal of local hybrid N₂O production, 634 which would maintain the low δ^{18} O-N₂O (Fig. 6). This is in agreement with the findings from the earlier 635 636 study (Ji et al., 2019). In contrast, incomplete denitrification and N₂O consumption likely contribute to the accumulation of N₂O in oxycline waters at Station 11 during La Niña, based on the elevated δ^{18} O-N₂O 637 coincident with low $\delta^{15} N^{\text{bulk}}$ and $\delta^{15} N^{\beta}$ values. Comparing these findings with the results from a moderate 638 and strong El Niño supports the hypothesis that denitrification plays a more significant role in the local 639 640 cycling of N₂O during La Niña relative to El Niño.

641 Finally, it is noteworthy to highlight the global impact that enhanced upwelling, manifested 642 through varying physical mechanisms, has on N_2O cycling. Here, we found mixed N_2O sources partially 643 derived from NO_2 to play a substantial role, likely due to the shallower oxycline interacting with a greater 644 organic matter supply to fuel greater nitrification and denitrification rates (Fig. 7; Yang et al., 2017). 645 Similarly, Babbin et al. (2021) found enhanced upwelling during La Niña in the South Pacific to expand 646 the total volume of suboxic waters, leading to large increases to the region's overall N₂O flux to the 647 atmosphere. Other recent studies in the Eastern Tropical North Pacific ODZ (Kelly et al., 2021; Monreal 648 et al., 2022) and in the Tropical North Atlantic (Grundle et al., 2017) found the shoaling effects of eddies 649 to increase total N₂O accumulation, with isotopocule signatures also pointing toward incomplete denitrification as a significant source. Further, the hypothesized upwelling of N2O to more oxygenated 650 651 waters from waters that previously experienced strong denitrification, were used to explain dramatic increases in δ^{18} O-N₂O and decreases in δ^{15} N^{β}, of similar magnitudes to those observed in our study 652

(Bourbonnais et al., 2017). Thus, the interpreted effects of La Niña (or El Niño) on N₂O cycling and
accumulation could be extended to other marine environments where extended periods of altered
upwelling can occur.

656 **5.** Conclusion

657 Measurements of N₂O concentrations and isotopocules from the strong oxygen gradients in the 658 ETSP demonstrate distinct sources of N₂O between moderate El Niño and La Niña events. During El Niño, increasing $\delta^{15}N^{\beta}$ and decreasing $\delta^{18}O-N_2O$ and SP values throughout the top 100 m at Station 7 and 659 660 above the oxyclines at Stations 9 and 11 suggest a role for hybrid N₂O in local N₂O production, 661 overprinting a remote denitrification signal. In contrast, La Niña oxycline waters had marked decreases in $\delta^{15}N^{\beta}$ and increases in $\delta^{18}O-N_2O$ and point toward incomplete denitrification as a significant source. 662 663 Again, if non-traditional isotopic assumptions are introduced into our interpretation, such as N₂O production from incomplete denitrification having a positive SP or hybrid production having a lower SP, 664 665 then the significantly enhanced N_2O accumulation could also be explained via those mechanisms (Casciotti et al., 2018; Kelly et al., 2021; Monreal et al., 2022). Isotope mixing models and Rayleigh 666 models also indicate that N₂O consumption must be taking place at Station 11 during La Niña, but are not 667 necessary at the other stations during either ENSO event. Our interpretations of N₂O cycling during a 668 669 moderate El Niño were also tested against a strong El Niño, where findings were quite similar: N₂O in the 670 oxycline and peak was being produced at low rates likely from a hybrid mechanism, but with other 671 potential overprinting signals such as mixing from allochthonous sources from more coastal waters. 672 Ultimately, during El Niño, we found significantly reduced N₂O accumulation at Stations 9 and 11 and 673 atmospheric fluxes up to two orders of magnitude lower, as all water column properties were subducted, 674 and lower rates of N₂O production were occurring in the upper 100 m. This work highlights the power of 675 repeat measurements in the same region to resolve N₂O dynamics in distinct climate scenarios, such as 676 the El Niño-Southern Oscillation, and the need to continue such work to better understand the response of 677 N₂O cycling to climactically relevant alterations to ocean biogeochemistry and circulation. Through this 678 exercise, we strongly recommend that future investigations also consider a range of potential SP values 679 from incomplete denitrification and hybrid production, as sources of N₂O.



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682 Figure S1: δ^{15} N-NO₂⁻ (squares) and δ^{18} O-NO₂⁻ (diamonds) at Station 9 (A) and Station 11 (B). El Niño (red) 683 and La Niña (blue).



686Figure S2: Station 7 El Niño (red) and La Niña (blue) N2O A) concentrations (nM); B) $\delta^{15}N^{bulk}$ (‰ vs. air); C)687 $\delta^{18}O-N_2O$ (‰ vs. VSMOW); D) SP (‰ vs. air); E) $\delta^{15}N^{\alpha}$ (‰ vs. air); F) $\delta^{15}N^{\beta}$ (‰ vs. air); G) $\delta^{15}N-NO_3^-$ (filled688circles, solid line) and $\delta^{18}O-NO_3^-$ (open circles, dashed line); and H) $\delta^{15}N-NO_2^-$ (filled squares) and $\delta^{18}O-NO_2^-$ 689(filled diamonds) illustrated.





691 Figure S3: δ¹⁸O-N₂O versus [N₂O] plotted for all Stations 7, 9, and 11 measurements. Marker color is a

692 function of $\delta^{15}N^{\beta}$ and marker size is a function of $\delta^{15}N^{\text{bulk}}$.



695Figure S4: N₂O A) concentrations (nM); B) δ^{18} O-N₂O (‰ vs. VSMOW); C) δ^{15} N^β (‰ vs. air); D) SP (‰ vs.696air) illustrated for Station 11 and nearby station from Ji et al. (2019). Our data from a moderate El Niño697(red) and La Niña (blue) are shown along with the strong 2015 El Niño N₂O data (black; Ji et al., 2019). Most698apparent differences between values occur from the oxycline (50 m) into the ODZ (200 m) from both El Niño699events, compared to the La Niña.

Offset Correction (%)	$\delta^{15}N^{\alpha}$	$\delta^{15}N^{\beta}$	SP	$\delta^{15}N^{bulk}$	δ^{18} O-N ₂ O
2012	-0.37	-0.20	-0.17	-0.28	-1.65
2014	-0.25	-0.96	0.71	-0.61	-0.29
2017	-1.37	-1.53	0.16	-1.35	-1.80

Table S1: Offset correction performed on 2011 dataset using differences against 2010 deep water (1000 m3000 m). Individual corrections were made for each isotopic variable of N₂O for a given analysis year due to
annual variability.

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711 6. Reference	es
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- Arévalo-Martínez, D. L., Kock, A., Löscher, C. R., Schmitz, R. A., & Bange, H. W. (2015). Massive
 nitrous oxide emissions from the tropical South Pacific Ocean. *Nature Geoscience*, 8(7), 530–
 533. https://doi.org/10.1038/ngeo2469
- Babbin, A. R., Bianchi, D., Jayakumar, A., & Ward, B. B. (2015). Rapid nitrous oxide cycling in the
 suboxic ocean. *Science*, *348*(6239), 1127–1129. https://doi.org/10.1126/science.aaa8380

Babbin, A. R., Boles, E. L., Mühle, J., & Weiss, R. F. (2020). On the natural spatio-temporal

- heterogeneity of South Pacific nitrous oxide. *Nature Communications*, *11*(1), 3672.
 https://doi.org/10.1038/s41467-020-17509-6
- 720 Berelson, W. M., Haskell, W. Z., Prokopenko, M., Knapp, A. N., Hammond, D. E., Rollins, N., &
- 721 Capone, D. G. (2015). Biogenic particle flux and benthic remineralization in the Eastern Tropical
- South Pacific. *Deep Sea Research Part I: Oceanographic Research Papers*, 99, 23–34.
- 723 https://doi.org/10.1016/j.dsr.2014.12.006
- Bonin, P., Gilewicz, M., & Bertrand, J. C. (1989). Effects of oxygen on each step of denitrification on
 Pseudomonas nautica. Canadian Journal of Microbiology, *35*(11), 1061–1064.
- 726 https://doi.org/10.1139/m89-177
- 727 Bourbonnais, A., Altabet, M. A., Charoenpong, C. N., Larkum, J., Hu, H., Bange, H. W., & Stramma, L.
- 728 (2015). N-loss isotope effects in the Peru oxygen minimum zone studied using a mesoscale eddy
- as a natural tracer experiment. *Global Biogeochemical Cycles*, 29(6), 793–811.
- 730 https://doi.org/10.1002/2014GB005001

731	Bourbonnais, A., Letscher, R. T., Bange, H. W., Échevin, V., Larkum, J., Mohn, J., Yoshida, N., &
732	Altabet, M. A. (2017). N $_2$ O production and consumption from stable isotopic and concentration
733	data in the Peruvian coastal upwelling system: N $_2$ O Production and Consumption off Peru.
734	Global Biogeochemical Cycles, 31(4), 678–698. https://doi.org/10.1002/2016GB005567
735	Bulow, S. E., Rich, J. J., Naik, H. S., Pratihary, A. K., & Ward, B. B. (2010). Denitrification exceeds
736	anammox as a nitrogen loss pathway in the Arabian Sea oxygen minimum zone. Deep Sea
737	Research Part I: Oceanographic Research Papers, 57(3), 384–393.
738	https://doi.org/10.1016/j.dsr.2009.10.014
739	Cai, W., Borlace, S., Lengaigne, M., van Rensch, P., Collins, M., Vecchi, G., Timmermann, A., Santoso,
740	A., McPhaden, M. J., Wu, L., England, M. H., Wang, G., Guilyardi, E., & Jin, FF. (2014).
741	Increasing frequency of extreme El Niño events due to greenhouse warming. Nature Climate
742	Change, 4(2), 111–116. https://doi.org/10.1038/nclimate2100
743	Cai, W., Wang, G., Santoso, A., McPhaden, M. J., Wu, L., Jin, FF., Timmermann, A., Collins, M.,
744	Vecchi, G., Lengaigne, M., England, M. H., Dommenget, D., Takahashi, K., & Guilyardi, E.
745	(2015). Increased frequency of extreme La Niña events under greenhouse warming. Nature
746	<i>Climate Change</i> , 5(2), 132–137. https://doi.org/10.1038/nclimate2492
747	Casciotti, K. L. (2009). Inverse kinetic isotope fractionation during bacterial nitrite oxidation. Geochimica
748	et Cosmochimica Acta, 73(7), 2061–2076. https://doi.org/10.1016/j.gca.2008.12.022
749	Casciotti, K. L., Böhlke, J. K., McIlvin, M. R., Mroczkowski, S. J., & Hannon, J. E. (2007). Oxygen
750	Isotopes in Nitrite: Analysis, Calibration, and Equilibration. Analytical Chemistry, 79(6), 2427-
751	2436. https://doi.org/10.1021/ac061598h
752	Casciotti, K. L., Forbes, M., Vedamati, J., Peters, B. D., Martin, T. S., & Mordy, C. W. (2018). Nitrous
753	oxide cycling in the Eastern Tropical South Pacific as inferred from isotopic and isotopomeric
754	data. Deep Sea Research Part II: Topical Studies in Oceanography, 156, 155–167.
755	https://doi.org/10.1016/j.dsr2.2018.07.014

- Casciotti, K. L., Sigman, D. M., Hastings, M. G., Böhlke, J. K., & Hilkert, A. (2002). Measurement of the
 Oxygen Isotopic Composition of Nitrate in Seawater and Freshwater Using the Denitrifier
 Method. *Analytical Chemistry*, 74(19), 4905–4912. https://doi.org/10.1021/ac020113w
- 759 Cohen, Y., & Gordon, L. I. (1978). Nitrous oxide in the oxygen minimum of the eastern tropical North
- 760 Pacific: Evidence for its consumption during denitrification and possible mechanisms for its
- 761 production. Deep Sea Research, 25(6), 509–524. https://doi.org/10.1016/0146-6291(78)90640-9
- 762 Crutzen, P. J. (1970). The influence of nitrogen oxides on the atmospheric ozone content. *Quarterly* 763 *Journal of the Royal Meteorological Society*, 96(408), 320–325.
- 764 https://doi.org/10.1002/qj.49709640815
- Elkins, J. W., Wofsy, S. C., McElroy, M. B., Kolb, C. E., & Kaplan, W. A. (1978). Aquatic sources and
 sinks for nitrous oxide. *Nature*, 275(5681), Article 5681. https://doi.org/10.1038/275602a0
- 767 Espinoza-Morriberón, D., Echevin, V., Colas, F., Tam, J., Gutierrez, D., Graco, M., Ledesma, J., &
- Quispe-Ccalluari, C. (2019). Oxygen Variability During ENSO in the Tropical South Eastern
 Pacific. *Frontiers in Marine Science*, *5*, 526. https://doi.org/10.3389/fmars.2018.00526
- Farías, L., Castro-González, M., Cornejo, M., Charpentier, J., Faúndez, J., Boontanon, N., & Yoshida, N.
- 771 (2009). Denitrification and nitrous oxide cycling within the upper oxycline of the eastern tropical
- South Pacific oxygen minimum zone. *Limnology and Oceanography*, *54*(1), 132–144.
- 773 https://doi.org/10.4319/lo.2009.54.1.0132
- Frame, C. H., & Casciotti, K. L. (2010). Biogeochemical controls and isotopic signatures of nitrous oxide
 production by a marine ammonia-oxidizing bacterium. *Biogeosciences*, 7(9), 2695–2709.
- 776 https://doi.org/10.5194/bg-7-2695-2010
- Frame, C. H., Deal, E., Nevison, C. D., & Casciotti, K. L. (2014). N2O production in the eastern South
- 778 Atlantic: Analysis of N2O stable isotopic and concentration data. *Global Biogeochemical Cycles*,
- *28*(11), 1262–1278. https://doi.org/10.1002/2013GB004790

780	Frame, C. H., Lau, E., Nolan, E. J. I., Goepfert, T. J., & Lehmann, M. F. (2017). Acidification Enhances
781	Hybrid N2O Production Associated with Aquatic Ammonia-Oxidizing Microorganisms.
782	Frontiers in Microbiology, 7. https://doi.org/10.3389/fmicb.2016.02104
783	Francis, C. A., Roberts, K. J., Beman, J. M., Santoro, A. E., & Oakley, B. B. (2005). Ubiquity and
784	diversity of ammonia-oxidizing archaea in water columns and sediments of the ocean.
785	Proceedings of the National Academy of Sciences, 102(41), 14683–14688.
786	https://doi.org/10.1073/pnas.0506625102
787	Frey, C., Bange, H. W., Achterberg, E. P., Jayakumar, A., Löscher, C. R., Arévalo-Martínez, D. L., León-
788	Palmero, E., Sun, M., Sun, X., Xie, R. C., Oleynik, S., & Ward, B. B. (2020). Regulation of
789	nitrous oxide production in low-oxygen waters off the coast of Peru. <i>Biogeosciences</i> , 17(8),

- 790 2263–2287. https://doi.org/10.5194/bg-17-2263-2020
- Fuenzalida, R., Schneider, W., Garcés-Vargas, J., Bravo, L., & Lange, C. (2009). Vertical and horizontal
 extension of the oxygen minimum zone in the eastern South Pacific Ocean. *Deep Sea Research*

Part II: Topical Studies in Oceanography, *56*(16), 992–1003.

- 794 https://doi.org/10.1016/j.dsr2.2008.11.001
- Fujii, A., Toyoda, S., Yoshida, O., Watanabe, S., Sasaki, K., & Yoshida, N. (2013). Distribution of
- nitrous oxide dissolved in water masses in the eastern subtropical North Pacific and its origin
 inferred from isotopomer analysis. *Journal of Oceanography*, 69(2), 147–157.
- 798 https://doi.org/10.1007/s10872-012-0162-4
- Granger, J., & Sigman, D. M. (2009). Removal of nitrite with sulfamic acid for nitrate N and O isotope
 analysis with the denitrifier method. *Rapid Communications in Mass Spectrometry*, 23(23), 3753–
 3762. https://doi.org/10.1002/rcm.4307
- 802 Grundle, D. S., Löscher, C. R., Krahmann, G., Altabet, M. A., Bange, H. W., Karstensen, J., Körtzinger,
- A., & Fiedler, B. (2017). Low oxygen eddies in the eastern tropical North Atlantic: Implications
- for N2O cycling. *Scientific Reports*, 7(1), 4806. https://doi.org/10.1038/s41598-017-04745-y

D = 110 D D = 100 D D D D D D D D D D D D D D D D D D	805	Haskell, W. Z.	., Berelson,	W. M.	Hammond	D. E.	. & Ca	pone,]	D. G. ((2013)). Particle	sinking	dynam	ics
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- and POC fluxes in the Eastern Tropical South Pacific based on 234Th budgets and sediment trap
 deployments. *Deep Sea Research Part I: Oceanographic Research Papers*, *81*, 1–13.
- 808 https://doi.org/10.1016/j.dsr.2013.07.001
- 809 Haskell, W. Z., Kadko, D., Hammond, D. E., Knapp, A. N., Prokopenko, M. G., Berelson, W. M., &
- Capone, D. G. (2015). Upwelling velocity and eddy diffusivity from 7Be measurements used to
 compare vertical nutrient flux to export POC flux in the Eastern Tropical South Pacific. *Marine*
- 812 *Chemistry*, *168*, 140–150. https://doi.org/10.1016/j.marchem.2014.10.004
- 813 Horak, R. E. A., Ruef, W., Ward, B. B., & Devol, A. H. (2016). Expansion of denitrification and anoxia
- 814 in the eastern tropical North Pacific from 1972 to 2012. *Geophysical Research Letters*, 43(10),
 815 5252–5260. https://doi.org/10.1002/2016GL068871
- Ji, Q., Altabet, M. A., Bange, H. W., Graco, M. I., Ma, X., Arévalo-Martínez, D. L., & Grundle, D. S.
 (2019). Investigating the effect of El Niño on nitrous oxide distribution in the eastern tropical
- 818 South Pacific. *Biogeosciences*, *16*(9), 2079–2093. https://doi.org/10.5194/bg-16-2079-2019
- Ji, Q., Babbin, A. R., Jayakumar, A., Oleynik, S., & Ward, B. B. (2015). Nitrous oxide production by
- 820 nitrification and denitrification in the Eastern Tropical South Pacific oxygen minimum zone:
- 821 NITROUS OXIDE PRODUCTION IN OMZ. Geophysical Research Letters, 42(24), 10,755-
- 822 10,764. https://doi.org/10.1002/2015GL066853
- Ji, Q., Buitenhuis, E., Suntharalingam, P., Sarmiento, J. L., & Ward, B. B. (2018). Global Nitrous Oxide
 Production Determined by Oxygen Sensitivity of Nitrification and Denitrification. *Global*
- 825 *Biogeochemical Cycles*, *32*(12), 1790–1802. https://doi.org/10.1029/2018GB005887
- 826 Jung, M.-Y., Well, R., Min, D., Giesemann, A., Park, S.-J., Kim, J.-G., Kim, S.-J., & Rhee, S.-K. (2014).
- 827 Isotopic signatures of N2O produced by ammonia-oxidizing archaea from soils. *The ISME*
- 828 *Journal*, 8(5), Article 5. https://doi.org/10.1038/ismej.2013.205

- 829 Kelly, C. L., Travis, N. M., Baya, P. A., & Casciotti, K. L. (2021). Quantifying Nitrous Oxide Cycling
- Regimes in the Eastern Tropical North Pacific Ocean With Isotopomer Analysis. *Global Biogeochemical Cycles*, *35*(2), e2020GB006637. https://doi.org/10.1029/2020GB006637
- 832 Knapp, A. N., Casciotti, K. L., Berelson, W. M., Prokopenko, M. G., & Capone, D. G. (2016). Low rates
- of nitrogen fixation in eastern tropical South Pacific surface waters. *Proceedings of the National Academy of Sciences*, *113*(16), 4398–4403. https://doi.org/10.1073/pnas.1515641113
- Kozlowski, J. A., Kits, K. D., & Stein, L. Y. (2016). Comparison of Nitrogen Oxide Metabolism among
 Diverse Ammonia-Oxidizing Bacteria. *Frontiers in Microbiology*, 7, 1090.
- 837 https://doi.org/10.3389/fmicb.2016.01090
- 838 Kuypers, M. M. M., Lavik, G., Woebken, D., Schmid, M., Fuchs, B. M., Amann, R., Jørgensen, B. B., &
- Jetten, M. S. M. (2005). Massive nitrogen loss from the Benguela upwelling system through
- 840 anaerobic ammonium oxidation. *Proceedings of the National Academy of Sciences*, 102(18),
- 841 6478–6483. https://doi.org/10.1073/pnas.0502088102
- Llanillo, P. J., Karstensen, J., Pelegrí, J. L., & Stramma, L. (2013). Physical and biogeochemical forcing
- 843 of oxygen and nitrate changes during El Niño/El Viejo and La Niña/La Vieja upper-ocean phases
- in the tropical eastern South Pacific along 86° W. *Biogeosciences (BG)*, 10, 6339–6355.
- 845 https://doi.org/10.5194/bg-10-6339-2013
- Löscher, C. R., Kock, A., Könneke, M., LaRoche, J., Bange, H. W., & Schmitz, R. A. (2012). Production
- 847 of oceanic nitrous oxide by ammonia-oxidizing archaea. *Biogeosciences*, 9(7), 2419–2429.
 848 https://doi.org/10.5194/bg-9-2419-2012
- 849 Maeda, K., Spor, A., Edel-Hermann, V., Heraud, C., Breuil, M.-C., Bizouard, F., Toyoda, S., Yoshida,
- N., Steinberg, C., & Philippot, L. (2015). N2O production, a widespread trait in fungi. *Scientific Reports*, 5(1), 9697. https://doi.org/10.1038/srep09697
- Martin, T. S., & Casciotti, K. L. (2016). Nitrogen and oxygen isotopic fractionation during microbial
 nitrite reduction. *Limnology and Oceanography*, *61*(3), 1134–1143.
- 854 https://doi.org/10.1002/lno.10278

- 855 Martinez-Rey, J., Bopp, L., Gehlen, M., Tagliabue, A., & Gruber, N. (2015). Projections of oceanic
- N<sub>2</sub>O emissions in the 21st century using the IPSL Earth system model. *Biogeosciences*, *12*(13), 4133–4148. https://doi.org/10.5194/bg-12-4133-2015
- 858 McIlvin, M. R., & Altabet, M. A. (2005). Chemical conversion of nitrate and nitrite to nitrous oxide for
- nitrogen and oxygen isotopic analysis in freshwater and seawater. *Analytical Chemistry*, 77(17),
 5589–5595. https://doi.org/10.1021/ac050528s
- McIlvin, M. R., & Casciotti, K. L. (2010). Fully automated system for stable isotopic analyses of
 dissolved nitrous oxide at natural abundance levels. *Limnology and Oceanography: Methods*,
 863 8(2), 54–66. https://doi.org/10.4319/lom.2010.8.54
- 864 Mogollón, R., & Calil, P. H. R. (2017). On the effects of ENSO on ocean biogeochemistry in the
- Northern Humboldt Current System (NHCS): A modeling study. *Journal of Marine Systems*, *172*,
 137–159. https://doi.org/10.1016/j.jmarsys.2017.03.011
- 867 Mohn, J., Wolf, B., Toyoda, S., Lin, C.-T., Liang, M.-C., Brüggemann, N., Wissel, H., Steiker, A. E.,
- B68 Dyckmans, J., Szwec, L., Ostrom, N. E., Casciotti, K. L., Forbes, M., Giesemann, A., Well, R.,
- B69 Doucett, R. R., Yarnes, C. T., Ridley, A. R., Kaiser, J., & Yoshida, N. (2014). Interlaboratory
- assessment of nitrous oxide isotopomer analysis by isotope ratio mass spectrometry and laser
- 871 spectroscopy: Current status and perspectives: Interlaboratory assessment of nitrous oxide
- isotopomer analysis. *Rapid Communications in Mass Spectrometry*, 28(18), 1995–2007.
- 873 https://doi.org/10.1002/rcm.6982
- 874 Monreal, P. J., Kelly, C. L., Travis, N. M., & Casciotti, K. L. (2022). Identifying the Sources and Drivers
- of Nitrous Oxide Accumulation in the Eddy-Influenced Eastern Tropical North Pacific Oxygen-
- 876 Deficient Zone. *Global Biogeochemical Cycles*, *36*(6), e2022GB007310.
- 877 https://doi.org/10.1029/2022GB007310
- 878 National Centers for Environmental Prediction, National Weather Service, NOAA, U.S. Department of
- 879 Commerce. (2000). *NCEP/DOE Reanalysis 2 (R2)*. Research Data Archive at the National Center

- for Atmospheric Research, Computational and Information Systems Laboratory.
- 881 https://doi.org/10.5065/KVQZ-YJ93
- Nevison, C. D., Butler, J. H., & Elkins, J. W. (2003). Global distribution of N₂ O and the ΔN₂ O-AOU
 yield in the subsurface ocean. *Global Biogeochemical Cycles*, 17(4), n/a-n/a.
- 884 https://doi.org/10.1029/2003GB002068
- Nevison, C. D., Lueker, T. J., & Weiss, R. F. (2004). Quantifying the nitrous oxide source from coastal
 upwelling: N₂ O FROM COASTAL UPWELLING. *Global Biogeochemical Cycles*, *18*(1), n/an/a. https://doi.org/10.1029/2003GB002110
- 888 NOAA's Climate Prediction Center. (n.d.). NOAA's Climate Prediction Center. Retrieved November 21,
- 889 2021, from https://origin.cpc.ncep.noaa.gov/products/analysis_monitoring/ensostuff/ONI_v5.php
- 890 Ostrom, N. E., Pitt, A., Sutka, R., Ostrom, P. H., Grandy, A. S., Huizinga, K. M., & Robertson, G. P.
- 891 (2007). Isotopologue effects during N₂ O reduction in soils and in pure cultures of denitrifiers.
 892 *Journal of Geophysical Research*, *112*(G2), G02005. https://doi.org/10.1029/2006JG000287
- Peng, X., & Valentine, D. L. (2021). Diversity and N2O Production Potential of Fungi in an Oceanic
 Oxygen Minimum Zone. *Journal of Fungi*, 7(3), Article 3. https://doi.org/10.3390/jof7030218
- 895 Ravishankara, A. R., Daniel, J. S., & Portmann, R. W. (2009). Nitrous Oxide (N2O): The Dominant
- 896 Ozone-Depleting Substance Emitted in the 21st Century. *Science*, *326*(5949), 123–125.
- 897 https://doi.org/10.1126/science.1176985
- Rohe, L., Anderson, T.-H., Braker, G., Flessa, H., Giesemann, A., Lewicka-Szczebak, D., WrageMönnig, N., & Well, R. (2014). Dual isotope and isotopomer signatures of nitrous oxide from
- 900 fungal denitrification a pure culture study. *Rapid Communications in Mass Spectrometry*,
- 901 28(17), 1893–1903. https://doi.org/10.1002/rcm.6975
- 902 Santoro, A. E., Buchwald, C., Knapp, A. N., Berelson, W. M., Capone, D. G., & Casciotti, K. L. (2021).
- 903 Nitrification and Nitrous Oxide Production in the Offshore Waters of the Eastern Tropical South
- 904 Pacific. *Global Biogeochemical Cycles*, 35(2), e2020GB006716.
- 905 https://doi.org/10.1029/2020GB006716

- 906 Santoro, A. E., Buchwald, C., McIlvin, M. R., & Casciotti, K. L. (2011). Isotopic Signature of N₂ O
- 907 Produced by Marine Ammonia-Oxidizing Archaea. *Science*, *333*(6047), 1282–1285.
 908 https://doi.org/10.1126/science.1208239
- Santoro, A. E., Casciotti, K. L., & Francis, C. A. (2010). Activity, abundance and diversity of nitrifying
 archaea and bacteria in the central California Current. *Environmental Microbiology*, *12*(7), 1989–
 2006. https://doi.org/10.1111/j.1462-2920.2010.02205.x
- 912 Schmidt, H.-L., Werner, R. A., Yoshida, N., & Well, R. (2004). Is the isotopic composition of nitrous
- 913 oxide an indicator for its origin from nitrification or denitrification? A theoretical approach from
- 914 referred data and microbiological and enzyme kinetic aspects. *Rapid Communications in Mass*

915 Spectrometry, 18(18), 2036–2040. https://doi.org/10.1002/rcm.1586

- Schmidtko, S., Stramma, L., & Visbeck, M. (2017). Decline in global oceanic oxygen content during the
 past five decades. *Nature*, 542(7641), 335–339. https://doi.org/10.1038/nature21399
- 918 Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., & Böhlke, J. K. (2001). A
- Bacterial Method for the Nitrogen Isotopic Analysis of Nitrate in Seawater and Freshwater.

920 *Analytical Chemistry*, 73(17), 4145–4153. https://doi.org/10.1021/ac010088e

- Stein, L. Y. (2019). Insights into the physiology of ammonia-oxidizing microorganisms. *Current Opinion in Chemical Biology*, 49, 9–15. https://doi.org/10.1016/j.cbpa.2018.09.003
- 923 Stieglmeier, M., Mooshammer, M., Kitzler, B., Wanek, W., Zechmeister-Boltenstern, S., Richter, A., &
- 924 Schleper, C. (2014). Aerobic nitrous oxide production through N-nitrosating hybrid formation in
 925 ammonia-oxidizing archaea. *The ISME Journal*, 8(5), 1135–1146.
- 926 https://doi.org/10.1038/ismej.2013.220
- 927 Stramma, L., Johnson, G. C., Sprintall, J., & Mohrholz, V. (2008). Expanding Oxygen-Minimum Zones
 928 in the Tropical Oceans. *Science*, *320*(5876), 655–658. https://doi.org/10.1126/science.1153847
- 929 Sun, X., Jayakumar, A., Tracey, J., Wallace, E., Kelly, C., Casciotti, K., & Ward, B. (2020). Microbial

930 N2O consumption in and above marine N2O production hotspots. *The ISME Journal*.

931 https://doi.org/10.1038/s41396-020-00861-2

- 932 Suntharalingam, P., & Sarmiento, J. L. (2000). Factors governing the oceanic nitrous oxide distribution:
- 933 Simulations with an ocean general circulation model. *Global Biogeochemical Cycles*, *14*(1), 429–
 934 454. https://doi.org/10.1029/1999GB900032
- 935 Sutka, R. L., Adams, G. C., Ostrom, N. E., & Ostrom, P. H. (2008). Isotopologue fractionation during
- N2O production by fungal denitrification. *Rapid Communications in Mass Spectrometry*, 22(24),
 3989–3996. https://doi.org/10.1002/rcm.3820
- 938 Sutka, R. L., Ostrom, N. E., Ostrom, P. H., Breznak, J. A., Gandhi, H., Pitt, A. J., & Li, F. (2006).
- 939 Distinguishing Nitrous Oxide Production from Nitrification and Denitrification on the Basis of
- 940 Isotopomer Abundances. *Applied and Environmental Microbiology*, 72(1), 638–644.
- 941 https://doi.org/10.1128/AEM.72.1.638-644.2006
- 942 Thompson, R. L., Chevallier, F., Crotwell, A. M., Dutton, G., Langenfelds, R. L., Prinn, R. G., Weiss, R.
- 943 F., Tohjima, Y., Nakazawa, T., Krummel, P. B., Steele, L. P., Fraser, P., O'Doherty, S., Ishijima,
- 944 K., & Aoki, S. (2014). Nitrous oxide emissions 1999 to 2009 from a global atmospheric
- 945 inversion. Atmospheric Chemistry and Physics, 14(4), 1801–1817. https://doi.org/10.5194/acp-
- 946 14-1801-2014
- 947 Thompson, R. L., Lassaletta, L., Patra, P. K., Wilson, C., Wells, K. C., Gressent, A., Koffi, E. N.,
- 948 Chipperfield, M. P., Winiwarter, W., Davidson, E. A., Tian, H., & Canadell, J. G. (2019).
- Acceleration of global N2O emissions seen from two decades of atmospheric inversion. *Nature Climate Change*, 9(12), 993–998. https://doi.org/10.1038/s41558-019-0613-7
- 951 Tian, H., Xu, R., Canadell, J. G., Thompson, R. L., Winiwarter, W., Suntharalingam, P., Davidson, E. A.,
- 952 Ciais, P., Jackson, R. B., Janssens-Maenhout, G., Prather, M. J., Regnier, P., Pan, N., Pan, S.,
- 953 Peters, G. P., Shi, H., Tubiello, F. N., Zaehle, S., Zhou, F., ... Yao, Y. (2020). A comprehensive
- 954 quantification of global nitrous oxide sources and sinks. *Nature*, *586*(7828), 248–256.
- 955 https://doi.org/10.1038/s41586-020-2780-0

- 956 Toyoda, S. (2002). Production mechanism and global budget of N₂ O inferred from its isotopomers in the
- 957 western North Pacific. *Geophysical Research Letters*, 29(3), 1037.

958 https://doi.org/10.1029/2001GL014311

- 959 Toyoda, S., Mutobe, H., Yamagishi, H., Yoshida, N., & Tanji, Y. (2005). Fractionation of N2O
- isotopomers during production by denitrifier. *Soil Biology and Biochemistry*, *37*(8), 1535–1545.
- 961 https://doi.org/10.1016/j.soilbio.2005.01.009
- 962 Toyoda, S., & Yoshida, N. (1999). Determination of Nitrogen Isotopomers of Nitrous Oxide on a

963 Modified Isotope Ratio Mass Spectrometer. *Analytical Chemistry*, 71(20), 4711–4718.

- 964 https://doi.org/10.1021/ac9904563
- 965 Wanninkhof, R. (2014). Relationship between wind speed and gas exchange over the ocean revisited.
- 966 *Limnology and Oceanography: Methods*, *12*(6), 351–362.
- 967 https://doi.org/10.4319/lom.2014.12.351
- 968 Ward, B. B., Devol, A. H., Rich, J. J., Chang, B. X., Bulow, S. E., Naik, H., Pratihary, A., & Jayakumar,
- 969 A. (2009). Denitrification as the dominant nitrogen loss process in the Arabian Sea. *Nature*,
- 970 *461*(7260), 78–81. https://doi.org/10.1038/nature08276
- 971 Weiss, R. F., & Price, B. A. (1980). Nitrous oxide solubility in water and seawater. *Marine Chemistry*,

972 8(4), 347–359. https://doi.org/10.1016/0304-4203(80)90024-9

- 973 Yamagishi, H., Westley, M. B., Popp, B. N., Toyoda, S., Yoshida, N., Watanabe, S., Koba, K., &
- 974 Yamanaka, Y. (2007). Role of nitrification and denitrification on the nitrous oxide cycle in the
- 975 eastern tropical North Pacific and Gulf of California. *Journal of Geophysical Research:*
- 976 *Biogeosciences*, *112*(G2). https://doi.org/10.1029/2006JG000227
- 977 Yang, S., Chang, B. X., Warner, M. J., Weber, T. S., Bourbonnais, A. M., Santoro, A. E., Kock, A.,
- 978 Sonnerup, R. E., Bullister, J. L., Wilson, S. T., & Bianchi, D. (2020). Global reconstruction
- 979 reduces the uncertainty of oceanic nitrous oxide emissions and reveals a vigorous seasonal cycle.
- 980 Proceedings of the National Academy of Sciences, 117(22), 11954–11960.
- 981 https://doi.org/10.1073/pnas.1921914117

- 982 Yang, S., Gruber, N., Long, M. C., & Vogt, M. (2017). ENSO-Driven Variability of Denitrification and
- 983 Suboxia in the Eastern Tropical Pacific Ocean: ENSO, DENITRIFICATION AND SUBOXIA.
- 984 *Global Biogeochemical Cycles*, *31*(10), 1470–1487. https://doi.org/10.1002/2016GB005596
- 985 Yoshinari, T. (1976). Nitrous oxide in the sea. *Marine Chemistry*, 4(2), 189–202.
- 986 https://doi.org/10.1016/0304-4203(76)90007-4