Natural Variability in Eastern Tropical Pacific Nitrous Oxide Emissions

by

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1. ABSTRACT

Nitrous oxide (N$_2$O) is a powerful greenhouse gas and ozone depleting substance, but its natural sources remain poorly constrained. Marine emissions are likely much higher than IPCC estimates predict, due to unusually high emissions from the oxygen minimum zones (OMZs) in the eastern tropical Pacific and Arabian Sea that are not accounted for in assessments. Measurements of atmospheric concentrations from a selection of AGAGE stations around the Pacific Ocean were combined with back-trajectories calculated using the HYSPLIT4 atmospheric model, in order to study the relative importance of OMZs on Pacific N$_2$O emissions. Spatial and temporal variability in nitrous oxide concentrations were analyzed in order to determine potential regions of higher emissions, as well as the impacts of ENSO on biogeochemistry in the OMZs. Air parcels that passed over the oxygen minimum zone in the Eastern Tropical South Pacific were found to have N$_2$O concentrations as much as 0.5 ppb higher than average. Average concentrations over the OMZ were modulated by an additional ~0.2 ppb higher during La Niña events and ~0.2 ppb lower during El Niño periods, a deviation of the same order of magnitude as N$_2$O’s seasonal cycle. Comparisons with CFC-12 and SF$_6$ suggested strong influences on nitrous oxide concentrations in the Southern Hemisphere from stratosphere-troposphere exchange, but little influence from inter-hemispheric transport.

2. INTRODUCTION

Nitrous oxide (N$_2$O), commonly known as laughing gas, is the third most potent greenhouse gas in the atmosphere today, with a global warming potential 300 times greater than CO$_2$ (Ciais et al., 2013; Thompson et al., 2014). N$_2$O is also a concern as it is the single greatest ozone depleting substance emitted in the 21st century, and unlike many other ozone depleting chemicals, it is not currently regulated under the Montreal Protocol (Ravishankara, Daniel and Portmann, 2009). The current atmospheric concentration of nitrous oxide is ~330 parts per billion, 20% higher than pre-industrial levels, and the concentration has been increasing steadily for the past several decades (Figure 1), at a rate of 0.73 ± 0.03 ppb year$^{-1}$ (MacFarling Meure et al., 2006; AGAGE, 2017).
Nitrous oxide concentrations measured at five AGAGE stations, from 1978 to 2016. N₂O concentrations have been increasing steadily since measurements began. Higher concentrations are found at stations in the northern hemisphere than those in the southern hemisphere, and there is a small seasonal cycle at all stations. Smaller error bars after 1996 reflect a change in instrumentation to a highly improved gas chromatograph multidetector (AGAGE, 2017).

Global estimates of N₂O emissions sources have extremely high margins of uncertainty, largely because N₂O emissions are heterogeneous in space and time. The most recent IPCC report (AR5) provides magnitudes for total natural emissions from soils, ocean and atmosphere from 5.4 - 19.6 TgN (N₂O) yr⁻¹; estimates for oceanic emissions alone range from 1.8 - 9.4 Tg N yr⁻¹ (Ciais et al. 2013). The natural marine sources have proved particularly hard to quantify, due in part to the fact that there have been very few direct measurements of N₂O production and consumption (Babbin et al. 2015).

While data of marine nitrous oxide emissions remain sparse, a number of oceanographic cruises and recent modeling studies suggest that unusually high N₂O emissions occur in the Eastern Tropical North and South Pacific and Arabian Sea. These regions correspond to the locations of oxygen minimum zones (OMZs), where a combination of both biological and physical factors result in near zero oxygen concentrations at depths of around 200-1500 m. Nitrification and denitrification, critical processes in the marine nitrogen cycle, are expected to produce more nitrous oxide than usual in the steep oxycline above the OMZs, though the relative importance of each of these pathways to N₂O emission is still uncertain. Studies also suggest that emissions from these regions are further increased during periods of La Niña, as a result of increased upwelling, a shallowing of the oxycline, and enhanced primary production. Conversely, during El Niño events, decreased upwelling and low primary production should result in lower than average nitrous oxide emissions from the OMZs.

The IPCC's evaluation of marine nitrous oxide emissions does not fully account for the OMZ regions however, and as a result, their numbers for the ocean source are almost certainly an underestimate of true emissions. The range provided in the AR5 remains largely unchanged from the Second Assessment Report’s estimate, published in 1995. The SAR’s estimate in turn is only slightly increased from the first assessment report, which based its numbers on measurements taken from a
single cruise track, shown in Figure 2. This cruise occurred in the Western Pacific, far from the OMZs that are now expected to have much higher emissions rates. Furthermore, the cruise was performed during an El Niño period, when nitrous oxide emissions are expected to be even lower than average. IPCC estimates of the nitrous oxide budget therefore must be scrutinized in the face of mounting evidence of a larger role of dynamic heterogeneous marine emissions.

Figure 2: Cruise track of the Soviet research vessel, Akademik Korolev, during the SAGA II expedition, May-July 1987 (Butler et al., 1989). Data from this cruise were used to approximate marine \( \text{N}_2\text{O} \) emissions in the IPCC’s First Assessment Report, and the IPCC’s estimates have remained largely unchanged since then.

In order to better quantify the emissions of nitrous oxide from the eastern tropical Oxygen Minimum Zones and understand the natural variability in these emissions, atmospheric data from stations around the Pacific were combined with back-trajectories calculated with NOAA’s HYSPLIT model. Both the temporal and spatial patterns of \( \text{N}_2\text{O} \) concentrations over the Pacific Ocean were examined in an effort to determine to what extent air parcels emanating from the Oxygen Minimum Zones differ in nitrous oxide concentrations from those emanating from other regions of the Pacific. The seasonal and inter-annual variability in nitrous oxide concentrations are also explored in order to understand how much of the observed variability in atmospheric \( \text{N}_2\text{O} \) is due to marine biogeochemistry rather than physical transport, as well as how ENSO events impact emissions from the OMZ regions.
3. BACKGROUND
3.1 Global nitrous oxide emissions and natural variability

According to the IPCC AR5 report, it is likely that 80% of the growth in \( \text{N}_2\text{O} \) emissions is a result of agricultural expansions and increased food production in order to meet the needs of growing populations (Ciais et al., 2013). Of the anthropogenic sources of \( \text{N}_2\text{O} \), agriculture is by far the largest component (~60% of the 6.9 TgN yr\(^{-1} \)), but other key sources include fossil fuel combustion, biomass and biofuel burning, atmospheric nitrogen deposition on land and the ocean, and nitrogen leaching in coastal and estuarine regions. There are also a number of natural sources of nitrous oxide to the atmosphere, totaling ~11 TgN yr\(^{-1} \), some of which may be increasing as a result of a changing climate (in addition to the increases from anthropogenic activity). The IPCC estimates that 60% of these come from soils under natural vegetation, 35% come from the ocean, and the remaining 5% from atmospheric chemistry (such as oxidation of ammonia) (Ciais et al., 2013).

One key uncertainty in the understanding of atmospheric nitrous oxide comes from \( \text{N}_2\text{O} \)’s largely unconstrained atmospheric sink. Destruction via photolysis in the stratosphere is expected to account for about 90% of the loss, splitting \( \text{N}_2\text{O} \) into \( \text{N}_2 \) and \( \text{O}(^1\text{D}) \) (Eq. 1) (Blake et al., 2002). Photo-oxidation, the reaction of \( \text{N}_2\text{O} \) with \( \text{O}(^1\text{D}) \) to form either 2 \( \text{NO} \) or \( \text{N}_2 \) and \( \text{O}_2 \), accounts for the other 10% (Eq. 2 & 3) (Blake et al., 2002). The fraction converted to \( \text{NO} \) is of particular concern to scientists and policymakers as \( \text{NO} \) assists in the depletion of ozone.

\[
\begin{align*}
  \text{N}_2\text{O} + h\nu (\lambda = 185 - 230 \text{nm}) & \rightarrow \text{N}_2 + \text{O}(^1\text{D}) \quad (1) \\
  \text{N}_2\text{O} + \text{O}(^1\text{D}) & \rightarrow 2\text{NO} \quad (2) \\
  \text{N}_2\text{O} + \text{O}(^1\text{D}) & \rightarrow \text{N}_2 + \text{O}_2 \quad (3)
\end{align*}
\]

\( \text{N}_2\text{O} \)’s long atmospheric lifetime – 118-131 years – suggests that once nitrous oxide has entered the atmosphere it will remain there for a long period of time, and that the atmosphere should be reasonably well mixed in \( \text{N}_2\text{O} \) (Ciais et al. 2013). That said, \( \text{N}_2\text{O} \) concentrations are not globally uniform. Concentrations are 0.75 ± 0.16 ppbv higher in the Northern Hemisphere than in the Southern Hemisphere (Prinn et al., 1990). As such, interhemispheric exchange will have an impact on the concentrations measured at a particular site.

Several spatial scales and timescales of variability must also be addressed when examining the atmospheric data, as \( \text{N}_2\text{O} \) concentrations are affected by changes in circulation, biology and other factors that vary spatially, seasonally, and inter-annually. Studies of \( \text{N}_2\text{O} \) emissions from atmospheric measurements and model inversions have found that tropical and subtropical regions are the largest source of \( \text{N}_2\text{O} \) and South America (a region important to our analysis) contributed 13 ± 4 % of global total emissions (Figure 3) (Saikawa, Schlosser and Prinn, 2013; Thompson et al., 2014). Emissions from India and China were also found to be much higher than anticipated, perhaps due to increased use of mineral nitrogen fertilizer, and contributed 20 ± 4 % (Thompson et al., 2014). With regards to timescales, seasonal and inter-annual cycles are particularly critical to this analysis. The seasonal cycle of \( \text{N}_2\text{O} \) is on the order of 0.3-0.9 ppb, fairly large in comparison to the long-term increase rate of 0.73 ppb year\(^{-1} \) (Nevison et al., 2011). Thompson et al found with their inversions that over the period between 1999 and 2009 global emissions varied between 17.5 and 20.1 Tg year\(^{-1} \) N, while the sink only varied between 11.8-12.6 Tg year\(^{-1} \) N (Thompson et al., 2014).
Nevison et al. published studies in 2007 and 2011 that looked at correlations between inter-annual variability of N₂O with CFC-12, CFC-11 and SF₆, trace gases that do not have biological influences, to determine whether N₂O was affected by the same physical transport mechanisms (Nevison et al., 2007, 2011). Like N₂O, CFCs are long-lived and are destroyed by photochemistry in the stratosphere (Nevison et al., 2007). However, they are purely-made and current emissions are near zero. Hence CFCs can be used as indicators of two non-biological explanations of N₂O variability, tropospheric transport and the stratospheric sink (Nevison et al., 2007). SF₆ is also anthropogenic and has a very long atmospheric lifetime, but its main source is in the northern hemisphere, so it can be used as an indicator of interhemispheric exchange (Nevison et al., 2007).

Nitrous oxide’s seasonal signal was found to be strongly correlated with CFCs at the AGAGE station in American Samoa, weakly correlated at Cape Grim, Tasmania, and poorly correlated at Barbados in the Caribbean and Trinidad Head, California (Nevison et al., 2007). Stratosphere-troposphere exchange then seemed to be responsible for the CFC and N₂O minima in May for both Samoa and Tasmania (Nevison et al., 2007). Additionally, Tasmania data showed minima in CFCs and N₂O were preceded 2-3 months earlier by minimums in SF₆ (Nevison et al., 2007). This finding suggested a transport influence from the interhemispheric gradient in the southern extra-tropics as well, leading to lowest SF₆ concentrations in January or February in Tasmania (Nevison et al., 2007). No SF₆ data existed for Samoa at the time of publication so the comparison at that station could not be made; however, seasonal cycles in halocarbons at Samoa also suggested seasonal influences from interhemispheric transport (Nevison et al., 2007).

The atmospheric records from the California station and other Northern Hemisphere sites showed summertime minima in CFCs, SF₆ and N₂O, which are inconsistent with known biological cycles and suggest that the main mechanisms in this hemisphere are abiotic (Nevison et al., 2011). The Brewer-Dobson Circulation, depicted in Figure 4, brings equatorial surface air into the stratosphere and acts as a removal process for atmospheric N₂O (Laing and Evans, 2011). Stratospheric air masses, depleted in N₂O, eventually re-enter the troposphere at high latitudes. The circulation has a seasonal signal as pressure gradients increase between pole and equator during winter months when the pole becomes colder, directing the flow in the stratosphere towards the winter pole (Laing and Evans, 2011).

Using similar approaches, Thompson et al. found that in the tropics, N₂O was not correlated with CFC-12, implying that stratospheric-tropospheric exchange is not the cause of variability in the N₂O signal.
(Thompson et al., 2013). However, N₂O had a relatively strong correlation with SF₆, which is a good indicator for inter-hemispheric exchange (Thompson et al., 2013).

There are also correlations between N₂O and CFCs in inter-annual variability. The Brewer-Dobson circulation varies year-to-year as well as seasonally, and is expected to be a key source of inter-annual variability in nitrous oxide concentrations (Simmonds et al., 2013). However, this signal is somewhat obscured in the Southern Hemisphere by ocean ventilation and biology, as well as terrestrial sources (Ciais et al., 2013). The other main source of inter-annual variability is the El-Niño Southern Oscillation, which will be discussed further below.

![Brewer-Dobson circulation schematic](image)

Figure 4: Schematic of Brewer-Dobson circulation (Laing and Evans, 2011). Brewer-Dobson circulation lifts tropical surface air up into the stratosphere, where it moves poleward and descends. The circulation is strongest in the winter hemisphere, and may have strong influences on atmospheric nitrous oxide concentrations as the main sink for N₂O is in the stratosphere.

### 3.2 The Marine Nitrogen Cycle

In order to understand the oceanic source of nitrous oxide, a detailed examination of the marine nitrogen cycle is crucial. Nitrous oxide is primarily produced in the ocean through two key processes: nitrification and denitrification (Freing, Wallace and Bange, 2012), but the percentage contribution from each process to emissions remains uncertain (Babbin et al, 2015). The cycle begins when bacteria fix inorganic N₂ into ammonium (NH₄⁺), which can then be taken up by other organisms. In well-oxygenated waters, nitrification then occurs, whereby aerobic bacteria and archaea oxidize ammonium, forming first nitrite (NO₂⁻) then nitrate (NO₃⁻) (right-hand-side of Figure 5). The first process, from ammonium to nitrite, also produces a nitrous oxide by-product at a low-rate (Codispoti, 2010). Nitrification exhibits maximum rates in the region just below the well-lit surface layer, for two main reasons. First of all, the process is inhibited by light, and secondly, remineralization, which supplies ammonium, has highest rates in the region just below the well-lit surface layer (Babbin et al., 2015). N₂O production by nitrification increases
in suboxic conditions where oxygen concentrations are low but nonzero. Goreau et al found in lab experiments with cultures of chemoautotrophic nitrifying bacterium that the yields increased from 0.3% to 10% for oxygen partial pressures of 0.2 to 0.005 atm (Goreau et al., 1980). Models agree with these laboratory studies, predicting that yields of nitrous oxide to nitrate at 1% oxygen saturation are 20 times higher than at 100% oxygen saturation (Codispoti, 2010). However, because nitrification cannot be performed at concentrations of oxygen less than a few μMol, no N₂O is produced through nitrification in completely anoxic waters (Babbin et al., 2015). Despite some laboratory studies and in situ measurements, the precise oxygen sensitivity of nitrification remains poorly constrained. Additionally, oxygen contamination by short mixing events can sometimes bring enough oxygen into the anoxic regions to oxidize ammonium and nitrite, forming N₂O (Bristow et al., 2016).

Figure 5: The marine nitrogen cycle. Two key processes are nitrification, the oxidation of ammonium (NH₄⁺) to nitrite (NO₂⁻) then nitrate (NO₃⁻), and denitrification, the reduction of nitrate (NO₃⁻) to nitrous oxide (N₂O) then to dinitrogen gas (depicted on the left-hand-side). Both processes release nitrous oxide, but the relative contribution of each to global N₂O emissions remains poorly constrained. Genes sequences important to the many processes are written in italics.

Anoxic regions provide habitat for anaerobic bacteria who perform nitrifier-denitrification, whereby nitrate is reduced in another two-step process, first to N₂O, then to N₂ (Codispoti, 2010). This process is shown on the left-hand-side of the cycle in Figure 5. In completely anoxic water, denitrification is a sink for nitrous oxide, as bacteria use N₂O as a source for respiration and convert N₂O to N₂ faster than N₂O is produced (Suntharalingam, Sarmiento and Toggweiler, 2000). Because both N₂O production and consumption are high in anoxic regions, small changes to oxygen distribution can have major impacts on the net N₂O source from these areas (Suntharalingam, Sarmiento and Toggweiler, 2000). Denitrification’s
oxygen tolerance is quite low however, and the kinetics of the pathway are altered at slightly higher oxygen concentrations (Bristow et al., 2016). Incomplete denitrification may be a large source of N\textsubscript{2}O at the suboxic-anoxic interface however (Babbin et al., 2015). Here, oxygen inhibits the nitrous oxide reductase enzyme, creating a build-up of the intermediary N\textsubscript{2}O (Babbin et al., 2015). Additionally, if denitrification is performed at shallow enough depths, rates will be further enhanced due to increased supply of organic matter to the heterotrophic denitrifiers (Babbin et al., 2015). Experiments with bacterial cultures and sediment incubations have revealed that while denitrification decreases with increased oxygen concentrations, nitrous oxide yield increases in suboxic conditions (Babbin et al., 2015).

An anaerobic process commonly referred to as anammox also acts as an organic nitrogen sink, converting ammonium and nitrite, into inorganic dinitrogen (Voss et al., 2013). While the mechanisms behind this process in the ocean are still not fully resolved, it is understood that anammox short circuits nitrification and denitrification, and does not produce N\textsubscript{2}O (Babbin et al., 2014).

### 3.3 Oxygen Minimum Zones as major sources of nitrous oxide

It is now well established that the most concentrated sources of N\textsubscript{2}O from the ocean come from the suboxic waters, containing 0 to 20 µmol l\textsuperscript{-1} of O\textsubscript{2}, above oxygen minimum zones (OMZs) (Babbin et al. 2015). The anoxic centers of OMZs are the only regions in the water column where net loss of fixed Nitrogen can occur (Voss et al. 2013). In the narrow band of the suboxic-anoxic interface above the OMZ, where oxygen inhibits the N\textsubscript{2}O reductase enzyme, nitrate reduction through denitrification remains incomplete, and results in a build-up of nitrous oxide (Babbin et al. 2015).

The three major OMZs are located in the Eastern Tropical North Pacific (ETNP), the Eastern Tropical South Pacific (ETSP), and the Arabian Sea. These are visible in purple in Figure 6. Additionally, the upwelling regions off the coasts of Namibia and Mauritania in Western Africa as well as the West Bering Sea and Gulf of Alaska in the North Pacific produce seasonal OMZs, which appear yearly for a period of time due changes in ocean circulation and productivity (Karstensen, Stramma and Visbeck, 2008; Paulmier and Ruiz-Pino, 2009). Permanent OMZs (here defined with O\textsubscript{2} < 20 µmol l\textsuperscript{-1}) are estimated to have a global surface area of 30.4 million km\textsuperscript{2} (~8% of the total oceanic area) (Paulmier and Ruiz-Pino, 2009). The exact boundaries of oxygen minimum zones are contested, however. Not only are data spatially and temporally sparse, but the debate also arises from the fact that the edges can be defined differently based on the impacts and processes under consideration. Examining just the effects on the nitrogen cycle, the critical oxygen concentration for nitrification is not the same as that for denitrification, and both numbers have large margins of uncertainty. The oxygen profiles change with depth as well (Figure 8) – so not only is it difficult to define the horizontal extents of these zones, but also the vertical ones.
Oxygen concentrations on the 1026.5 kg/m³ isopycnal surface. This density surface is that which feeds the OMZs. The three permanent OMZs, located in the Eastern Tropical North and South Pacific and Arabian Sea, show concentrations at or near zero on this isopycnal.

While the exact size of the OMZs is disputed, the mechanisms by which OMZs develop are reasonably well understood. Oxygen minimum zones are formed as a result of competing physical and biological processes. OMZs typically occur off the western coasts of continents as a result of strong wind-induced Ekman upwelling, which brings low oxygen and nutrient rich deeper water to the surface (Paulmier and Ruiz-Pino, 2009). The increased nutrients fuel high rates of primary productivity at the surface. When this newly fixed organic matter falls into the ocean interior, it enhances biological respiration and remineralization and reduces oxygen concentrations to below 10 nmol L⁻¹ (Revsbech et al., 2009; Voss et al., 2013). Although marine measurements of nitrous oxide are still fairly limited, one recent study found that N₂O was supersaturated by as much as 12,244% over atmospheric equilibrium in the ETSP off the coast of Peru, and that this region alone could account for 5–22% of previous estimates of global marine N₂O emissions (Arévalo-Martinez et al., 2015). Naqvi and Noronha also found unusually high N₂O concentrations in the Arabian Sea, resulting in a surface oversaturation of 186 ± 37% and atmospheric emissions of 4.46 ±2.60 µmol m⁻² day⁻¹ (Naqvi and Noronha, 1991). The interpolated map in Figure 7, showing the difference between atmospheric and surface ocean N₂O partial pressures, reveals ΔpN₂O values of over 60 natm in the eastern tropical Pacific, implying large fluxed from this region.
Figure 7: Difference between atmospheric and surface ocean partial pressure of N\textsubscript{2}O, derived from the Weiss et al. (1992) database (Suntharalingam and Sarmiento, 2000). ΔpN\textsubscript{2}O is unusually high in Eastern Tropical Pacific region overlying the oxygen minimum zones. These high ΔpN\textsubscript{2}O values, up to 150 natm, imply large fluxes out of the ocean in this area.

Because of the relationships between N\textsubscript{2}O and nitrite yields relative to oxygen content, nitrous oxide production is highest in hypoxic regions, where oxygen saturation is between 1 and 30% (Codispoti, 2010). At the center of the OMZs where O\textsubscript{2} is less than 1% saturated, N\textsubscript{2}O concentrations are low because N\textsubscript{2}O is quickly reduced to N\textsubscript{2}. While these regions are small on a global scale (they account for only 0.1-0.2% of ocean volume), the surrounding hypoxic waters are significantly larger (accounting for 10% of ocean volume) (Codispoti, 2010). It is in these regions on the borders of OMZs that nitrous oxide production peaks, visible in the vertical profiles from transects through the ETNP OMZ shown in Figure 8. There is also a small initial peak in nitrite at the level of the oxycline, then a much larger peak across the anoxic region (Babbin et al., 2015). Nitrous oxide reaches a maximum of ~100 nmol L\textsuperscript{-1} at the base of the oxycline, and is at a minimum in the core of the OMZ (Babbin et al., 2015). In the core, nitrous oxide exhibits low residence times and rapid turnover rates, reflecting the strong coupling of the two denitrification steps (Babbin et al., 2015). However within the oxycline region N\textsubscript{2}O residence times increase and the rate of N\textsubscript{2}O production becomes substantially faster than the rate of consumption (Babbin et al., 2015). Simple 1-D models suggest that nitrification alone cannot entirely account for the high concentrations of N\textsubscript{2}O in the suboxic layer, and that incomplete denitrification could explain the additional net N\textsubscript{2}O production here (Babbin et al., 2015).
There is concern that OMZs are now expanding dramatically as a result of climate change. The expansion is in part due to the fact that warmer water holds less dissolved oxygen, so rising global temperatures will decrease the oceans’ ability to store oxygen and extend the edges of these regions (Paulmier and Ruiz-Pino, 2009). One study found that the global oxygen content of the oceans has decreased by 2% since 1960, and estimated an additional decrease of up to 7% by the end of the century (Schmidtko, Stramma and Visbeck, 2017). The loss of oxygen in the upper water column is due to warming, which decreases the solubility of gases in the ocean, as well as biological consumption (Schmidtko, Stramma and Visbeck, 2017). A recent study which combined data from thousands of cruises worldwide found that in the past 30 years, the regions of $O_2 < 70 \mu$mol/L have increased in size by 4.5 million km², an area around half the size of the US, including Alaska (Stramma et al., 2010). It is feared that the expansion of OMZs will cause decreases in biological diversity and changes in animal distribution and ecosystem structure, in addition to higher outgassing of nitrous oxide (Stramma et al, 2010).

### 3.4 ENSO and inter-annual variability in marine nitrous oxide emission

El Niño-Southern Oscillation (ENSO) cycles alter atmospheric transport and change upwelling in the Pacific Ocean, which in turn influence nitrous oxide concentrations. The ENSO cycle is a complex coupling of feedbacks between the atmosphere and ocean, and its temporal pattern appears extremely nonlinear (Figure 9). ENSO indices, calculated from sea level pressure or sea surface temperature anomalies, show cycles range from 2-7 years. Some El Niño events are much stronger than others – the greatest departure from the mean state in the past twenty years occurred during the 1998 El Niño, followed closely by the 2015-2016 event.
Marshall and Plumb have described thoroughly how atmospheric circulation changes during El Niño and La Niña events (Marshall and Plumb, 2008). Under average conditions, the tropics experience easterly surface winds, creating a high pressure zone in the western Pacific and a low pressure zone in the east – resulting in a shallow thermocline and increased upwelling off the American coast. These dynamics also produce along the equator what is known as Walker Circulation, in which warm air rises in the western Pacific, is transported at high altitude along the equator to the eastern Pacific, and descends again. North and south of the equator, the Hadley Cells are the major circulation pattern; air descends in the mid-latitudes on the eastern side of the Pacific, and at surface level moves westward and equatorward. This pattern keeps the northern-hemisphere and the southern-hemisphere relatively isolated from mixing.

During an El Niño period however, the high pressure region moves east towards the center of the Pacific, reducing the slope of the thermocline, bringing warm surface waters eastward, and decreasing upwelling in the eastern tropics. Conversely, during a La Niña, Walker Circulation is strengthened, creating a steepened thermocline and enhanced upwelling in the eastern Pacific. Shown in Figure 10b, the oxycline in the eastern Pacific becomes shallower during La Niña periods, leading to an increase in ventilation of the subsurface and higher partial pressures of N₂O in surface waters (Nevison et al., 2011; Thompson et al., 2014). The larger gradient in dissolved gases between the air and surface ocean should result in more nitrous oxide escaping to from the ocean to the atmosphere.

Impacts of ENSO on biogeochemistry may also be significant sources of the inter-annual variations in atmospheric N₂O (Nevison et al., 2011). La Niña brings enhanced upwelling of nutrients to the surface, thereby increasing primary production, further de-oxygenating the subsurface region, and creating more potential for denitrification and N₂O production. N₂O production is also particularly high when suboxic waters are near the surface because periodic oxygen injections will force nitrifiers to switch between oxygen and nitrogen respiration, creating a lag in their ability to reduce N₂O to N₂ (Codispoti, 2010). Conversely, during an El Niño (Figure 10a) reductions in upwelling should reduce the surface productivity in the eastern tropical Pacific, deepen the oxycline, and thereby decrease N₂O emissions from the OMZs (Babbin et al., 2015). It is difficult to deconstruct what portion of the change is due to purely physical factors versus biological ones, but Thompson et al found from studying atmospheric concentrations that over the period from 1999-2009, El Niños were indeed associated with low marine N₂O fluxes and La Niñas with high fluxes (Thompson et al., 2014).
El Niño

La Niña

Figure 10: (a) During an El Niño, the thermocline deepens and less upwelling of high nutrient, low oxygen water occurs. This process reduces primary production and the sinking of organic matter, further reducing the extent of the oxygen minimum zone and emissions of nitrous oxide. (b) Conversely, during a La Niña stronger upwelling occurs, increasing primary productivity and oxygen utilization, thereby expanding the oxygen minimum zone and increasing N₂O production. The oxycline also becomes shallower, creating a larger gradient in N₂O between atmosphere and surface waters and further enhancing emissions (Yang, Bianchi and Deutsch, 2018).

ENSO affects latitudinal atmospheric transport as well as ocean transport, and changes in tropical atmospheric circulation associated with ENSO have been strongly correlated with N₂O variability at the Samoa monitoring station (Nevison et al., 2011). During an El Niño, there is less influence of winds from the northern hemisphere and increased south-easterly winds, resulting in a relative decrease in atmospheric N₂O in the southern hemisphere (Nevison et al., 2011). Increased inter-hemispheric transport during La Niña events correspondingly increases concentrations in the southern hemisphere.

ENSO impacts are not limited to the Pacific Ocean; the inter-annual variability also causes changes to emissions of nitrous oxide from land. Thompson et al.’s atmospheric inversion study found that El Niño events in 2002 and 2007 both coincided with negative anomalies in N₂O emissions in tropical and subtropical regions (Thompson et al., 2014). They argue that these variations are not a result of atmospheric transport-related changes during El Niño and La Niña, but rather due to biological changes (Saikawa, Schlosser and Prinn, 2013; Thompson et al., 2014). During an El Niño, central South America, sub-tropical Africa and tropical and subtropical Asia become warmer and drier, suboptimal conditions for bacterial nitrification and denitrification in soils (Thompson et al., 2014). Precipitation and nitrous oxide emissions both show strong negative anomalies during the 2002 El Niño in South America and Africa, for example (Thompson et al., 2013). The correlation is not perfect however, and it may be that water deficiency must be a certain level of severity before N₂O soil production is impacted (Thompson et al., 2014).
4. METHODS

4.1 Atmospheric data and AGAGE

Very little nitrous oxide data exist from oceanographic cruises, floats, or other ocean-going platforms, particularly from the OMZ regions of interest (Freing and Bange, 2007). However, the Advanced Global Atmospheric Gases Experiment (AGAGE), has a network of stations around the world that have been monitoring atmospheric gases, including nitrous oxide, since the late 1970s. The analysis in this thesis was limited by the locations of these stations and the frequency and precision of their measurements. Several stations around the Pacific Ocean are relevant for these inquiries into OMZs and N$_2$O production: Cape Matatula in American Samoa, Trinidad Head in California and Cape Grim in Tasmania, Australia, as well as one NOAA station in Mauna Loa, Hawaii. Their locations are listed in Table 1 and marked on the map in Figure 11. Some station records for N$_2$O went back as far as the 1970s; however, the precision of the data was significantly improved in the mid-1990s with the implementation of new gas chromatograph multi-detector systems (Figure 1) (Prinn et al., 2000). Therefore, the analysis is limited to the past 20 years of data. At all AGAGE stations in the analysis, data were collected 36 times per day (a frequency of 40 minutes). The Hawaii station logged data hourly.

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Altitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trinidad Head, California</td>
<td>41.05 N</td>
<td>124.15 W</td>
<td>120 m</td>
</tr>
<tr>
<td>Mauna Loa, Hawaii</td>
<td>19.54 N</td>
<td>155.58 W</td>
<td>3397m</td>
</tr>
<tr>
<td>Cape Matatula, Samoa</td>
<td>14.24 S</td>
<td>170.57 W</td>
<td>42 m</td>
</tr>
<tr>
<td>Cape Grim, Tasmania</td>
<td>40.68 S</td>
<td>144.68 E</td>
<td>94 m</td>
</tr>
</tbody>
</table>

Table 1: Latitude, longitude and altitude of the four stations used in the analysis. Note that the Mauna Loa, Hawaii station is located at a much higher elevation than the rest.

In order to examine the overall spatial patterns and inter-annual variability in nitrous oxide measurements, the long-term trend of rising N$_2$O concentrations was removed. De-trending was achieved by finding a two-degree polynomial fit and subtracting this trend line from the concentrations (Figure 12). A de-seasonalized time-series was also produced by averaging all data by month, interpolating through these points to create a continuous sinusoidal, seasonal cycle, and subtracting this cycle from the de-trended series (Figure 13). The de-seasonalized time series will be utilized to assess inter-annual variability in the atmospheric concentrations.
Figure 12: $\text{N}_2\text{O}$ concentrations (blue) from California, Hawaii, Samoa and Australia stations plotted from 1996 to 2016, the time period of analysis. The long term trend line, which is subtracted from the data points to create the de-trended series, is plotted on top of data points in black.
Figure 13: De-trended N₂O time-series from California, Hawaii, Samoa and Australia stations (blue), overlaid with seasonal cycles (black). This seasonal cycle was subtracted to achieve the de-seasonalized series.

4.2 HYSPLIT back-trajectory modeling

In order to estimate from where air parcels arriving at the AGAGE stations originated and help determine the influence of the OMZs, NOAA’s HYSPLIT4 model was used to calculate back-trajectories from the four stations. The model uses a combination of Lagrangian and Eularian methodologies to compute air parcel trajectories, as well as more complex dispersion, atmospheric chemistry, and deposition dynamics (NOAA Air Resources Lab, 2017). Climatological data was retrieved from the NCEP/DOE reanalysis project, which uses grid cells of 2.0 degrees latitude x 1.75 degrees longitude, and temporal coverage four times daily. In setting up the model to calculate the trajectories, the latitude, longitude, and altitude of the stations were specified. Back trajectories were calculated four times a day for 20 years, from January 1, 1996 to December 31, 2016, resulting in a total of 29,208 trajectories analyzed. Each trajectory was then matched with the corresponding station’s N₂O measurement taken closest to the time at which the back-trajectory arrived at the station. Figure 14 depicts trajectories from the four stations going 5 days back for the year 2015.
Figure 14: All Hysplit back-trajectories from California, Hawaii, Samoa and Tasmania stations calculated for the year 2015, showing the first 5 days prior to arrival at the station. Trajectories are colored to facilitate visual differentiation.

It is unclear how far back in time the trajectories remain valid before inaccuracies lead to severe divergences between the calculated path and the actual one. Both errors from the climatological data and from the Hysplit model itself must be considered in evaluating the certainty of the trajectories. However, with the large number of trajectories that were calculated, certain patterns should emerge regardless of these sources of error. In order to attempt to remove any land-based sources of emissions, a filter was created to remove all trajectories that passed over continental land within the 20-day period of calculation. For island station (Hawaii and Samoa), the islands themselves were not designated as land in this filter, under the assumption that they are too small to have large impacts on N₂O atmospheric concentrations. The stations on mainland (California and Tasmania) proved slightly more difficult to filter, and local pollution events may be impacting the results of analysis at these locations. Furthermore, because N₂O has a long atmospheric lifetime it possible that emissions which entered the air more than 20 days prior to arrival at the station may still impact the measured concentration.

4.3 Defining the ENSO strength during each trajectory

The determination of which of the many ENSO indices to use as an indicator of inter-annual variability posed a challenge. Several different indices exist to measure ENSO-induced variability, and data of each is available from NOAA as monthly averages dating back to 1950. Nino 3 and Nino 3.4 are now considered to be the most accurate indicators of what stage of the cycle the Pacific is presently experiencing (Trenberth and National Center For Atmospheric Research staff, 2016). These are based on sea surface temperature anomalies along the equator between 5°S and 5°N, from 150 to 90W and from 170 to 120 W respectively (Trenberth and National Center For Atmospheric Research staff, 2016). NOAA
defines an El Niño event as Nino 3.4 > 0.4, and a La Niña event as Nino 3.4 < -0.4. Nino 1 + 2 indices are measured as differences in far the eastern tropical Pacific, but have the highest variance of the indices and is not as indicative of the inter-annual cycle. The Multivariate ENSO Index (Nino MEI) was also considered; this index is the result of a combination of 6 variables - sea-level pressure, zonal and meridional components of the surface wind, sea surface temperature, surface air temperature, and total cloudiness fraction of the sky (NOAA ESRL, 2017).

Niño indices also exhibit seasonal cycles, and were de-seasonalized by first subtracting monthly averages from the long-term series, then applying a Kolmogorov-Zurbenko (KZ) filter with 6 iterations of filters with length 2, 4, 6, 8, and 12 months to remove all variability on scales less than 1 year. The de-seasonalized indices for Nino 1, Nino 3.4, and MEI are shown superimposed on the original indices in Figure 15. Once de-seasonalized, the 3.4 and MEI indices were very similar in phase and amplitude, so ultimately the Nino 3.4 index was used for the remainder of the analysis.

Figure 15: Nino 3.4 (blue), Nino MEI (green) and Nino 1 (orange) indices plotted over time. Thin lines represent raw data from NOAA, while thick lines are indices that have been de-seasonalized by subtracting monthly averages and applying a KZ filter. The de-seasonalized series were used in comparing nitrous oxide emissions to ENSO states.

In determining the best metric of ENSO to use, it was also necessary to consider how biological productivity and nitrous oxide were expected to respond to climatic variability. It seemed reasonable that there could be a lag between changes in climate and the biological response, though it was unclear how long that lag would be. Another consideration was that perhaps the biological response was proportional to the integral of the ENSO index rather than the index itself. This proposition comes from the consideration that a long El Niño period, for example, may have longer lasting additive impacts on oxygen minimum zones and productivity than a short one, and so the “cumulative state” of the Pacific should be considered rather than discrete time points.

Preliminary comparisons of atmospheric data from Samoa and ENSO indices suggest that it may be necessary to incorporate this lag or integration into the analyses. The best fit for the de-seasonalized Nino 3.4 index to the Samoa data was determined to be a three-month shift (Figure 16b). The integral of the Nino 3.4 index, calculated with a cumulative trapezoidal numerical integral and then re-normalized,
also seems to fit the N$_2$O data surprisingly well (Figure 16c). Ultimately the shifted Nino 3.4 index was chosen for analysis, and was associated by date with atmospheric concentrations and trajectories.

![Figure 16: De-seasonalized N$_2$O monthly averages from Samoa plotted in blue against various Nino indices. (a) De-seasonalized Nino 3.4 index. (b) Nino 3.4 de-seasonalized and shifted forward 3 months. (c) Integrated Nino 3.4. Both N$_2$O and Nino indices have been normalized here to have an oscillation amplitude of 1 and mean 0 for visual comparison. Ultimately the shifted Nino 3.4 index was used for comparison.]

4.4 Defining marine oxygen concentrations

Dissolved oxygen concentrations were taken from the second version of the Global Ocean Data Analysis Program (GLODAP v2), which is an accumulation of data from 45,306 stations around the world, collected from cruises undertaken between 1972 to 2013 (Olsen et al., 2016). The oxygen content along the isopycnal surface with $\sigma_0 = 26.5$ kg/m$^3$ (Figure 6) was used to evaluate the relationship between nitrous oxide emissions and oxygen content; this value is commonly taken in literature to define the location of the oxygen minimum in the Eastern Pacific (Karstensen, Stramma and Visbeck, 2008). Oxygen concentrations were then gridded across the Pacific in boxes of 2 degrees latitude by 2 degrees longitude, and trajectory endpoints were associated with the oxygen values of the water below them.
5. RESULTS

5.1 Exploring spatial patterns in atmospheric trajectories and nitrous oxide concentrations

Once trajectories were combined with atmospheric concentrations, the spatial distribution of concentrations, as well as the seasonal and inter-annual variability in these distributions, could be examined. As evidenced in Figure 17, no clear spatial patterns were found in the concentrations from California, Hawaii, or Tasmania more than a few days prior. Trajectories from Samoa however, when combined with concentrations, revealed anomalously high nitrous oxide arriving from the tropical eastern Pacific, and lower than average from the Southern Ocean.

Figure 17: Trajectories from California, Hawaii, Samoa, and Tasmania stations, with all trajectories passing over land within the past 20 days removed. For each station, locations of air parcels are plotted 1, 5, 10, 15, and 20 days prior to arrival at station. De-trended nitrous oxide measurements are represented by the color of the corresponding dot, as anomalies relative to the mean at each station. Higher than average concentrations appear red and lower than average are blue. No spatial patterns are visible in California, Hawaii, and Tasmania concentrations 5 days prior and beyond. However, Samoa data maintain a clear spatial divergence for the full 20-day period, with much higher concentrations arriving from the eastern tropical Pacific, and much lower concentrations from the west and Southern Ocean.
Northern Hemisphere stations in Figure 17 show no clear spatial signal in the nitrous oxide concentrations after more than a few days. The data from California may be contaminated by a regional pollution source; in the 1-day prior figure, concentrations are higher near the shore and to the north (see Figure 21 for a seasonal break-down of the local emissions here). This source could potentially be obscuring other spatial trends, though when parcels traveling through this region are removed there is still no spatial pattern in the resulting maps. Hawaii data are less likely to suffer from anthropogenic pollution as the island is so small, so it is unlikely that local pollution is the cause of the jumbled concentrations here. The measurements of atmospheric concentrations have much higher variance at the Hawaii station, and considering that the station is owned by NOAA rather than AGAGE and uses different instrumentation, it may be that the instrumentation has a lower degree of accuracy at Hawaii that is obscuring any spatial patterns. The Hawaii station is also located at a much higher altitude than the other stations, at over 3000 m elevation, so it may also experience different atmospheric dynamics and feel less of the effects of surface emissions than the other stations. That all said, considering that both northern hemisphere stations show little in the way of spatial variation in nitrous oxide concentrations, the lack of spatial signal may just exemplify the fact that the hemisphere is very well-mixed on the timescales analyzed here.

Examining trajectories from Tasmania in Figure 17, higher concentrations are visible 1-day prior around the South-Eastern side of Tasmania, reflecting a similar local pollution event as in California. Removing trajectories that pass over land, this local signal disappears. However, trajectories that remain near Tasmania for a few days prior are generally higher in concentration than those that move westward very quickly. Tasmania data do not show any obvious spatial trends after 10, reflecting the influence of rapid sub-polar winds that quickly mix air at high latitudes.

Contrary to all the other stations, Samoa concentrations maintain a visible spatial gradient in nitrous oxide for the entire 20 days. A divergence in concentrations is visible just one-day prior, with higher concentrations arriving from the north of the island than from the south. This pattern remains moving further back in time; the highest concentrations arrive from the eastern tropical Pacific, while the lowest come from the west in the Southern Ocean. The pattern becomes slightly less well-defined between 15 and 20 days-prior, as parcels with high concentrations spread out along the Western coast of North and South America.

In studying the spatial dispersion of parcels alone, there is significant meridional spreading visible from all stations – ranging from the equator all the way past 70 degrees or south. It is important to note however that trajectories mostly remain confined to the hemispheres in which they originated. Samoa is the only station from which a significant number of parcels show movement across the equator within the 20-day timeframe (see Figure 18 for an enlarged view of concentrations 15 and 20 days prior). These come almost exclusively from the eastern Pacific, traveling down the North American coast before turning towards the west. It is not apparent from the data however that the parcels that came from the northern hemisphere have markedly higher N_2O concentrations, despite the Northern Hemisphere being comparatively enriched in N_2O. Figure 18 shows that many high concentration trajectories travel across the Isthmus of Panama from the Caribbean. However, 20-days prior there are still a large number of high concentration trajectories in the southern hemisphere, which travel northward off the coast of South America before arriving at Samoa. Also worth noting is that very few trajectories actually cross over the South American continent; most are deflected either north or south along its western edge. As a result, it is unlikely that land emissions of N_2O from South America have a large impact on the visible spatial signal.
Figure 18: Samoa back trajectories 15 and 20 days prior, including those that pass over land. Highest concentrations arrive from the region of the Eastern Tropical Pacific. Many cross over the equator into the southern hemisphere, some traveling down the North American coast and some arriving from the Caribbean. However, interhemispheric transport does not appear to be the sole reason for high concentrations in this region, as many air parcels enriched in nitrous oxide also move northward up the west coast of South America into the tropics (visible in the 20 days prior), then ultimately southwest to the Samoa station.

Strong polar westerlies are visible in the trajectories from both Tasmania and Samoa, which push the parcels towards the east (Figure 17). Even within 10 days, Tasmania trajectories have circumnavigated the globe. The effect of these high latitude westerlies is also visible in the Samoa trajectories that come from the south-west. Those from California also mostly arrive from the west, experiencing similar westerlies in the northern high latitudes, and some air parcels that arrive at California from farther north have also circumnavigated the globe within 10 days. Hawaii, located farther south, does not show quite as strong westerlies; there appears to be a more even zonal spread east and west, and it takes at least 15 days for any trajectories to circumnavigate the globe.

Studying the trajectories’ vertical positions also reveals valuable insights into the atmospheric dynamics at play (Figure 19). For both northern hemisphere stations, air parcels coming from farther north also tend to come from higher altitudes. The reverse is true in the southern hemisphere – parcels from lower latitudes come from higher in the atmosphere. Figure 19 appears to show that the northern hemisphere trajectories do gain as much altitude as the ones in the southern hemisphere. This asymmetry between hemispheres in the figure is misleading however, because the trajectories that reach high altitudes in the northern hemisphere as they also tend to move more rapidly in the zonal direction, pass over land, and are removed with the land filter. There is simply less land in the southern hemisphere so fewer trajectories from these stations are filtered out. All stations show many trajectories reach at least 10 km altitude, which is the height of the tropopause and the top of the Hysplit model. At low latitudes, this pattern is surely a result of the Hadley Cells, which bring air from high altitudes down to the surface around 30° North and South, then thrust it equatorward. Samoa plots show that concentrations that remain nearer the surface of the earth have higher concentrations than those that come from higher...
altitudes, though this does not seem to be true for California, Hawaii, or Tasmania (except perhaps 1-day prior here).

Samoa is likely affected by the northern hemisphere Hadley Cell as well as the southern Hadley Cell. In Figure 19’s depiction of Samoa trajectories 20-days prior, trajectories beyond 20°N curve upwards again. It is also interesting to note that the trajectories farthest north mostly have lower concentrations than those remaining in the equatorial region 20 days prior, despite typically higher concentrations in the northern hemisphere. It is also probable that the much lower concentration at high latitude and altitude are a result of Brewer-Dobson circulation, which brings N_2O depleted air down from the stratosphere near the pole.

The local pollution event near the California station is also more apparent in this projection. See highest concentrations are visible towards the north in Figure 19’s depiction of California trajectories 1-day prior, but this latitudinal signal disappears in the plots for 5-days prior and beyond. The vanishing signal supports the idea of a localized source of emissions – perhaps from land (though no trajectories that pass directly over land are plotted) or coastal estuary emissions.

In order to get a better idea of how the concentrations and circulation patterns compare across stations, average monthly concentrations from each station in January 2005 (chosen as a mid-point in our time-series) were added back to the de-trended data. Figure 20 below shows sea-going trajectories for all four stations plotted 20-days prior, colored with this new N_2O variable. The difference in N_2O concentrations between hemispheres is particularly apparent here. The northern hemisphere also shows more homogenous concentrations, whereas there is a clear latitudinal gradient in the low to mid-latitudes of the southern hemisphere. Very little inter-hemispheric transport occurs in the west or central Pacific. The eastern Pacific sees much more movement across the equator, and there is a fairly smooth transition in this region between the higher concentrations in the northern hemisphere and the lower ones in the southern. However there still appears to be a region in the eastern Pacific, centered around the equator and extending southward along the Peruvian and Chilean coasts, where concentrations are consistently and anomalously high.
Figure 19: Trajectories from all four stations 1, 5, 10, 15 and 20-days prior, plotted with altitude vs. latitude and with colors representing de-trended N₂O data. Trajectories that pass over land are not depicted. Few patterns emerge from California, Hawaii and Tasmania concentrations. Trajectories from Samoa that arrive from the north remain close to land and have high N₂O concentrations, while those arriving from farther south come from high altitudes and have low N₂O.
Figure 20: Trajectory positions 20 days prior, with (a) viewed from above and (b) altitude vs. latitude. All trajectories over continental land have been removed. N₂O values are de-trended, with the monthly average value from January 2005 for individual stations added back into the time series to allow for comparison between stations. The northern hemisphere has much higher concentrations of N₂O than the southern hemisphere, and where interhemispheric transport occurs in the eastern Pacific, there is a gradient in concentrations. However, particularly high concentrations are still visible in (b) in the region near the equator and below 2000 m, and appear distinct from the northern hemisphere concentrations.
5.2 Seasonal variability in atmospheric transport and N$_2$O

While the time series of the N$_2$O data in Figure 13 made it evident that seasonal signals existed at California, Samoa and Tasmania, separating trajectories by month helps establish the source of the seasonal variability. No seasonal signal was observed from Mauna Loa, and concentrations from California and Tasmania stations show overall seasonal variations but no spatial differences in these variations. Once again, Samoa is the only station from which spatial variation observed in both concentrations and parcel trajectories.

California shows a strong local source of seasonal variability, resulting in much higher N$_2$O concentrations recorded on the coast in the spring and summer (Figure 21a). The seasonal timing of this signal suggests a biological source from increased agriculture during the summertime. Removing all trajectories passing over land in the last 2 days, and thus any local land emissions source, the sea-going trajectories actually have significantly lower concentrations in summertime and highest concentrations in the wintertime (Figure 21b). Winter trajectories also experience faster westerlies and summer trajectories experience the slowest – this makes sense as the jet stream is strengthened by the larger thermal gradient between equator and pole during the wintertime. No spatial pattern in the N$_2$O concentrations is visible in sea-going trajectories however.
Figure 21: California back-trajectories separated into four seasons: December-February, March-May, June-August, and September-November. (a) Positions 1-day prior with all trajectories included, revealing a local emissions source that is highest in spring and summertime. (b) Positions of trajectories 15 days prior with the local emissions source removed, revealing lowest concentrations in the summertime and highest in winter.

Hawaii concentrations exhibit no clear seasonal signal in N₂O concentrations (Figure 22); again, this may be a result of different atmospheric dynamics at the altitude of this station located high on a volcano, or a difference in instrumentation. The only visible seasonal signal is that, as in the case of the California back-trajectories, the westerly winds appear to be faster in the winter months.
There are clear seasonal patterns in both dynamics and N₂O at Samoa however (Figure 23). In the austral summer (December-February) very few trajectories come from the Southern Ocean, though during all other months northward trajectories are common. There is also significantly more inter-hemispheric transport in the eastern Pacific from December to May than the rest of the year; almost no inter-hemispheric transport occurs June through August. Concentrations are highest in the Eastern Tropical Pacific in the period when interhemispheric transport is strongest. However, the concentrations from this region are still relatively higher compared to the rest of the Pacific year-round, even when there is no visible interhemispheric transport, as is the case in June-August. This pattern suggests that while interhemispheric transport has an impact on concentrations in the southern hemisphere, there are likely other forces at play as well. It is also noteworthy that a significant number of parcels arriving from the Northern Hemisphere have lower than average N₂O concentrations. Especially visible in the December-February vertical plot (Figure 22b), the highest concentrations are in the region from 0-20°S – not north of the equator. We would expect to see greatest N₂O emissions from the oxygen minimum zone during December through February because in the austral summer, productivity is higher in the southern hemisphere. There should therefore be more oxygen utilization, lower oxygen concentrations in the OMZ region, and increased anaerobic denitrification during this time of year. However, it could also be the result of higher emissions from land sources during austral summer, just as there were higher land emissions at the California station in the summertime. Figure 22b also makes evidence the seasonal
Brewer-Dobson signal, which brings more high altitude, N₂O deficient air down to the surface in the austral summer than in the wintertime.

Figure 23: Samoa back-trajectories separated into four seasons: December-February, March-May, June-August, and September-November. (a) Positions of all trajectories 15-days prior, revealing more transport from the eastern tropical Pacific and northern hemisphere as well as higher N₂O concentrations in austral summer and fall. (b) Positions 15-days prior plotted by altitude and longitude. In winter and spring more air parcels come from the polar regions and high latitudes, and have lower N₂O concentrations. However, those that come from the eastern tropical Pacific during these months still show higher than average N₂O.

At the Tasmania station, local emissions are visible in 1-day prior positions of trajectories when those that pass over land are included (Figure 24a). The area just north of the station is has anomalously high N₂O concentrations year round, though these are slightly lower during austral winter. This signal may reflect a biological source from land, as agricultural emissions should be lowest in wintertime. Once these land trajectories are removed a seasonal signal emerges however, the lowest concentrations occurring in March through May, and the highest in September through December (Figure 24b). No spatial patterns are visible horizontally or vertically in the physical dynamics of the trajectories (Figure 24 b & c). One might expect that austral winter months would show parcels coming from higher altitudes, since Brewer-Dobson is strongest in the winter hemisphere, and that the concentrations would be correspondingly low, but this does not appear to be the case. Trajectories may travel slightly higher in June through August, but the minimum in concentrations comes earlier in the year.
It is curious that while trajectories from Samoa that come from the sub-polar region are consistently low in nitrous oxide, those from Tasmania show such clear seasonal variability. The discrepancy between the two stations may imply that the seasonal cycle near Tasmania is obscured by larger scale variations only visible from Samoa.

5.3 ENSO inter-annual variability and effects on OMZ emissions

Marine nitrous oxide emissions are expected to respond quickly to ENSO changes, as a result of both changes to upwelling of nutrients and to concentrations of oxygen. As theory suggests, nitrous oxide concentrations from Samoa were found to be largest over the OMZ during La Niña events and lowest during El Niños.
In order to compare concentrations between different ENSO periods, N₂O concentrations were gridded by placing all air parcel positions from 15-days prior in cells of 5° latitude by 5° longitude, and averaging over the N₂O concentrations corresponding to the air parcels found in each grid cell. The concentration of N₂O in each cell is therefore the average concentration of all air parcels that were in that cell 15 days prior. Individual grids were made for four ranges of ENSO – “Strong Niña,” corresponding to an index smaller than -0.4, “Weak Niña” with an index between -0.4 and 0, “Weak Niño” with an index between 0 and 0.4, and “Strong Niño” with an index greater than 0.4. In order to account for different spatial transport patterns in the different periods of the ENSO cycle, the average field was created by weighting each of the four grids by the number of trajectories in this grid cell in each of the four ENSO periods. Then the average field was subtracted from the four ENSO period fields in order to distinguish between variations in the mean state.

In the mean field shown in Figure 25a, parcels with higher N₂O concentrations arrive from the Eastern Tropical Pacific – directly overlapping the region of the oxygen minimum zone. The Niño Index anomaly fields in Figure 25b reveal that even higher than average concentrations in the eastern tropical Pacific during strong La Niñas, though the Western Pacific tends to have lower than average concentrations during this period. During strong El Niños, there are lower than average concentrations over the entire eastern Pacific. Weak Niña and Niño fields show less clear spatial divergence, though the weak Niño field already shows decreases in N₂O in the far eastern tropical Pacific.
Figure 25: Gridded N\textsubscript{2}O concentrations from Samoa trajectory positions 15 days prior. (a) Mean field, averaged over all four ENSO ranges. Concentrations are significantly higher over the OMZ region in the eastern tropical Pacific. (b) Anomalies in N\textsubscript{2}O from mean grid during the four ranges of ENSO, using the shifted Nino 3.4 index and bounds of +/- 0.4 to define strong versus weak ENSO events. Strong La Niñas show above average concentrations over the OMZ and strong El Niño shows below average concentrations in the same region.

Plotting nitrous oxide values from these grid cells against the dissolved oxygen concentrations on the \(\sigma = 26.5\) isopycnal surface in the Pacific illustrates how nitrous oxide values change with proximity to the OMZ (Figure 26). Overall, N\textsubscript{2}O concentrations increase with decreasing oxygen concentrations. N\textsubscript{2}O
values also increase more rapidly at low oxygen concentrations, particularly below 50 μmol O₂ kg⁻¹. There
is also an apparent difference between N₂O concentrations with relation to oxygen during different ENSO
periods. The running averages of the gridded N₂O concentrations, shown in Figure 26b, show the trends
most clearly. In the waters with high oxygen concentrations far away from the OMZ, N₂O concentrations
are nearly identical between strong La Niña and El Niño periods. However, over waters with low oxygen
concentrations, N₂O is much higher during La Niñas than during El Niños. The difference is up to 0.35 ppb
difference in the anomaly between Strong La Niñas and El Niños for oxygen concentrations of less than
10 μmol kg⁻¹.

Figure 26: De-seasonalized N₂O plotted versus oxygen concentration on the σ = 26.5 isopycnal. (a) Each
grid cell is represented by four dots, the averaged N₂O concentrations in that grid cell during each of the
four ENSO index ranges. The corresponding ENSO range (Strong/Weak Niña/Niño) is reflected in the
color of the dot. (b) Running average de-seasonalized N₂O, with each line corresponding to a different
ENSO index range. While concentrations are similar between all ENSO ranges in regions of high oxygen
content, as oxygen concentrations approach zero concentrations during La Niña and El Niño diverge
significantly.

5.4 Determining the source of inter-annual variability: comparisons of N₂O with CFC-12 and SF₆

While the analysis supports the hypothesis that higher nitrous oxide emissions occur in the
eastern tropical Pacific OMZs and that the emissions from OMZs are higher during La Niña events, it is
difficult to ascertain from looking at nitrous oxide data alone to what extent non-biological factors could
be influencing the spatial and temporal signals of nitrous oxide concentrations as well. In order to
determine how interhemispheric transport and stratosphere-troposphere exchange may be affecting the
inter-annual cycles, CFC-12 and SF₆ were also combined with back-trajectories, and the resulting spatial
patterns were compared to those of N₂O. CFC-12 and N₂O are found to be strongly correlated both
spatially and temporally, implying a strong influence from stratosphere-troposphere exchange. SF₆’s
distribution is dissimilar to N₂O however, suggesting that interhemispheric transport is not as important
in explaining N₂O concentrations.

CFC-12 data were de-trended and de-seasonalized in the same way as the N₂O data, with one
caveat. The long-term trend in CFC-12 is very different from that of N₂O; concentrations increase through
the end of the 1990s, remain stable for several years, then begin to decrease again around 2006 and have been on a steady decline since that time (Figure 27). Several fit equations were attempted to de-trend the whole curve, but was unable to find a satisfactory fit that removed the long-term trend while leaving inter-annual variability. This difficulty is due to the fact that when the Montreal Protocol came into effect banning the use of CFCs it caused a rapid shift to near zero emissions, which cannot be accounted for in a simple one or two-degree polynomial curve. Instead, the time series was separated into two sections, which were then de-trended separately with a two-degree polynomial fit. The sections used were 1996 to 1999 and 2006 to 2016 (the period between 1999 and 2006 was not included).

Figure 27: CFC-12 concentrations measured at 7 AGAGE stations. The Montreal Protocol, which came into effect in 1989, banned CFCs and caused atmospheric concentrations to stabilize, then begin to decrease. Concentrations are higher in the northern hemisphere than in the southern hemisphere in the 1980s-90s, but since emissions ceased, the interhemispheric mixing has brought the values asymptotically close together.

SF₆ emissions continue today, and atmospheric concentrations have been growing nearly constantly since the AGAGE record began in 2001. SF₆ data were also de-trended in the same manner as N₂O. While concentrations do not show much seasonal or inter-annual variability at individual stations, the difference in concentrations between northern hemisphere stations and southern hemisphere ones is very apparent in the long-term trends. This discrepancy should therefore allow SF₆ to act as a good indicator for inter-hemispheric transport.
Figure 28: SF$_6$ concentrations measured at 7 AGAGE stations. These have increased consistently over the period of measurement, and show markedly higher values at northern hemisphere stations than southern hemisphere ones.

Figure 29 provides the seasonal cycles in CFC-12 at the four stations. California CFC-12 shows maxima during winter and minima during summer, just like N$_2$O. Similarly, Tasmania reveals an overall seasonal cycle of CFC-12 that is the same as that of N$_2$O: values peak in September through November, and are minimal in March through May. Unlike with N$_2$O, no regional source of CFC-12 is visible in 1 day back-trajectories from Tasmania or California, as is expected considering that emissions ceased in the 1990s. Hawaii experiences almost no variability in space or time for CFC-12, again as was the case with the N$_2$O data. Samoa CFC-12 measurements have a similar spatial pattern to nitrous oxide. Higher concentrations arrive from the north east, with significantly higher values in austral summer and autumn. The finding that CFC-12 and N$_2$O are strongly correlated is not a surprise; it follows from research by Nevison et al. and Thompson et al. showing that N$_2$O is affected by the same physical processes as CFC-12, specifically stratosphere-troposphere exchange. The question becomes whether it is possible to determine any signal in the N$_2$O data that is separate from that of CFC-12.
Figure 29: Seasonal cycles of CFC-12 at the four stations, with all trajectories plotted 20 days prior. The seasonal cycles and spatial patterns in CFC-12 are very similar to those of N\textsubscript{2}O at all stations.

The gridded concentrations of CFC-12 from Samoa, separated for the four ENSO periods, exhibit a very similar distribution to those of nitrous oxide as well. In the average field, higher concentrations of CFC-12 come from the ETSP, and lower concentrations from the South-Western Pacific. Strong La Niña periods experience higher than average concentrations of CFC-12 from the eastern Pacific, and strong El Niño periods experience lower than average concentrations from the same region. During weak Niña/Niño periods, the spatial trend is less clear, though lower-than-average concentrations do seem to come from the far East Pacific right along the equator in both cases.
Figure 30: Gridded CFC-12 concentrations from Samoa trajectory positions 15 days prior. (a) Mean field, averaged over all four ENSO ranges; (b) anomalies in CFC-12 from mean grid during the four ranges of ENSO, using the shifted Nino 3.4 index and bounds of +/- 0.4 to define strong versus weak ENSO events. Both CFC-12 mean field and ENSO fields show similar spatial patterns to those of N2O.

The CFC-12 distribution with relation to marine oxygen content is correspondingly similar to that of N2O. All ENSO periods show highest CFC-12 concentrations over low oxygen water, and the anomalies are higher during strong La Niña periods than strong El Niño ones (Figure 31a). The percentage of grid boxes overlying low-oxygen waters that have higher than average CFC-12 concentrations is more similar
between La Niña and El Niño for than it was for N₂O however (Figure 31b). The greater number of grid boxes with high CFC-12 concentrations in the OMZ region during Strong El Niño suggest that while the anomaly is positive, it remains small.

Figure 31: De-seasonalized CFC-12 plotted versus oxygen concentration on the $\sigma = 26.5$ isopycnal, as depicted for N₂O in Figure 26bc. The running average of de-seasonalized CFC-12 for each ENSO range is taken, revealing trends very similar to those of N₂O.

Examining these results, stratosphere-troposphere exchange likely plays a leading role in determining the overall spatial signal in nitrous oxide concentrations and seasonal variability. The changes in vertical transport also seem to correlate with ENSO events, leading to positive anomalies in both CFC-12 and N₂O in the eastern Pacific during strong La Niña periods, and negative anomalies during strong El Niño periods. The inter-annual correlation is in line with the findings of Simmonds et al. 2013, but this analysis provides a spatial interpretation of their regression analysis.

While measured concentrations of CFC-12 in the northern hemisphere were higher than those in the southern hemisphere during the 1990s, ever since emissions ceased at the end of the century, the northern hemisphere and southern hemisphere have had roughly equivalent concentrations. Considering just data from after the Montreal Protocol, the signal of much higher concentrations from the equatorial region therefore cannot be due to inter-hemispheric transport. Gridding only the CFC-12 concentrations from 2006 to the present (once hemispheres were roughly equilibrated), the spatial signal appears roughly identical to that in Figure 30a.

Although CFC-12 and N₂O have similar spatial patterns, their resemblance is not necessarily indicative of N₂O concentrations being predominantly a function of atmospheric transport. CFC-12 also exists dissolved in the ocean, and exhibits higher concentrations in the Southern Ocean, where the water is colder and thus can hold more gases. These CFC-12 enriched waters sink as they move northward. Data from a meridional transect west of South America (around longitude 86W) reveal that there are slightly higher concentrations of the compound 50-100 m down than at the surface in the region of the Oxygen Minimum Zone. If there were enhanced upwelling, as during a La Niña event, one might then expect to see higher than average CFC-12 concentrations at the surface and higher CFC-12 emissions from the ocean as well.
Figure 32: CFC-12 concentrations from transect P19 in the Pacific, just offshore of South America, retrieved from GLODAPv2. CFC-12 concentrations are higher near the pole. It may be that water with higher dissolved CFC-12 concentrations is upwelling in the OMZ region, resulting in emissions of CFC-12 similarly to $N_2O$.

The $SF_6$ data should provide a better indication of the effects of inter-hemispheric transport. Samoa trajectories combined with $SF_6$ and separated by season show no spatial or seasonal variations (Figure 33). While the overall variations in $SF_6$ concentrations are very small (on the order of $10^{-2}$ parts per trillion), the mean field actually shows that on average, lower concentrations come from the region of the OMZ, while higher concentrations arrive from further south (Figure 34a). Furthermore, during strong La Niña periods the concentrations from the OMZ show either no change or are even lower than average for the region (Figure 34b). Interhemispheric transport therefore must not play a significant role in explaining why there are higher concentrations coming from the Eastern Tropical Pacific, and why these are even higher during La Niña events. The other ENSO periods do not have such clear spatial patterns in $SF_6$, though Weak Niño periods show the highest overall concentrations, and weak Niño the lowest overall concentrations. The finding that inter-hemispheric transport does not play a leading role in explaining $N_2O$ concentrations at Samoa may seem surprising, but referring back to Figure 18, it was not clear that parcels crossing the equator had higher concentrations. Many air parcels that were farther south along the Chilean coast 20-days prior and passed through the OMZ before arriving at Samoa had anomalously high concentrations as well.

![Figure 33](image)

Figure 33: Seasonal cycles of $SF_6$ with de-trended data from Samoa and all trajectories plotted 20 days prior. Unlike $N_2O$ and CFC-12, $SF_6$ shows no clear spatial or seasonal signal in concentrations.
Figure 34: Gridded SF$_6$ concentrations from Samoa trajectory positions 15 days prior. (a) Mean field, averaged over all four ENSO ranges; (b) anomalies in SF$_6$ from mean grid during the four ranges of ENSO, using the shifted Nino 3.4 index and bounds of +/- 0.4 to define strong versus weak ENSO events.
6. DISCUSSION AND CONCLUSIONS

While California, Hawaii and Tasmania stations do no reveal any influence from OMZs on nitrous oxide concentrations, the Samoa station measurements demonstrate a surge in N₂O from the region of the eastern tropical Pacific OMZ. Trajectories that pass through the ETSP OMZ on their way to Samoa have higher than average concentrations year round; air parcels located over the core of the OMZ 15-days prior have concentrations averaging more than 0.5 ppb higher than the mean, which is quite significant considering that the seasonal cycle in nitrous oxide at Samoa has an amplitude of only 0.33 ppb. The strong signal is evidence for the OMZ region being a key source of nitrous oxide. Furthermore, trajectories from the OMZ region had even higher than average concentrations during La Niña events, supporting the hypothesis that stronger upwelling of nutrients and low oxygen concentrations results in higher nitrous oxide emissions from the OMZs. The difference between concentrations over the OMZ between La Niña and El Niño was found to be ~0.4 ppb. A next step in this analysis would be to produce a simple 1D vertical model combining air-sea exchange, physical transport and biological productivity to determine how nitrous oxide production within the suboxic layer above the OMZs would have to vary in order to produce the observed differences in atmospheric concentrations.

Recent modeling work by Curtis Deutsch at the University of Washington showed that nitrous oxide emissions from the ETSP OMZ were on average 1 Tg N year⁻¹, and accounted for 16-25% of total marine N₂O flux (Yang, Bianchi and Deutsch, 2018). The models showed that ENSO drove large changes in emissions from the OMZ region (Figure 35). Emissions from the OMZ increased nearly doubled during the strong La Niña in 1999 and decreased similarly during the preceding El Niño, just as the analysis of atmospheric data in this paper suggests.

Figure 35: Spatially integrated N₂O emissions in the region above the OMZ (red) and the full domain of the eastern Pacific Ocean (black) from a regional ocean model (Yang, Bianchi and Deutsch, 2018). The emissions rate from the OMZ is nearly 0.5 Tg yr⁻¹ higher during the La Niña in 1999 than the preceding El Niño.
Both seasonal and inter-annual variability in the concentrations are likely influenced by other factors however, and the 0.5 ppb anomaly observed over the ETSP cannot be entirely attributed to microbial nitrification and denitrification within the OMZ. CFC-12 concentrations, when mapped over the back-trajectories, also reveal higher than average concentrations from the region of the OMZ, reflecting an influence from stratosphere-troposphere exchange on spatial variation in both trace gases. CFC-12 concentrations have at most a +1.3 ppt anomaly in this region, also substantially higher than their seasonal 0.55 ppt amplitude cycle. SF6, a potential indicator of inter-hemispheric transport, shows only very small deviations from the mean. Anomalies are actually negative in the OMZ region, with the largest deviation at -0.022 ppt (0.32% of the average SF6 concentration over the period of measurement). This finding suggests that despite higher N2O concentrations coming from near the equator, mixing from the northern hemisphere is not the cause of this variability. It is also possible that higher emissions from the tropical region of South America might influence measurements of N2O at Samoa, but distinguishing between marine and land emissions using only 20-day back-trajectories proved difficult. That said, considering that most trajectories were deflected around South America instead of over it, it seems likely that land emissions are not the dominant factor explaining the observed variability. While the data from the other stations do not show any obvious spatial trends, it is probable that regional sources and rapid atmospheric mixing distort influences from the OMZ. The development of an inversion model would be valuable in helping determine the key drivers of variability more conclusively.

One or multiple new AGAGE stations located in the eastern tropical Pacific would greatly improve our analysis and ability to constrain the dynamic emissions patterns within OMZs. Using HYSPLIT, back-trajectories were calculated from three islands in the region that are readily accessible for installation and maintenance of the instrumentation. Easter Island was attempted first, but back-trajectories here arrive almost exclusively from the South Pacific and do not pass through the OMZ (Figure 36a). A station within the Galapagos archipelago also poses a similar problem, with the majority of trajectories arriving from the South Pacific as well (Figure 36b). However, because the Galapagos station would be located right at the center of the ETSP OMZ, seasonal and inter-annual variability in the nitrous oxide emissions from the OMZ should be visible here, and examining how this signal evolves with ENSO would provide valuable insights into nitrogen cycling in the suboxic waters. In fact, because the direction of the trajectories is so consistent, this station may provide an even better understanding of the biological impacts on atmospheric nitrous oxide, without influences from physical transport. If stations were built on both Easter Island and the Galapagos, these would function as valuable comparisons of concentrations within and immediately outside of the OMZ. Another promising option for a new station is Clipperton Island, a small coral atoll and French territory located 10 degrees north of the equator within the Eastern Tropical North Pacific OMZ. Some trajectories arrive here from the North, while others cross the equator from the South Pacific, and still others traverse Central America from the Caribbean Sea (Figure 36c). Exploring how concentrations vary between parcels arriving from these different directions would provide insight as to how concentrations are affected by proximity to Oxygen Minimum Zones, or other influences like inter-hemispheric transport or agricultural emissions. That said, Clipperton Island has little land area and is at near zero elevation, so building a monitoring station there may prove difficult.
Another helpful tool for improving our understanding of the emissions from OMZs is a site preference instrument, which measures the relative abundance of two $^{15}$N isotopomers in a sample of nitrous oxide. Site preference varies depending on the source of the $N_2O$; it will have a different value if the $N_2O$ has been formed through nitrification rather than denitrification, or nitrifier-denitrification (Santoro et al., 2011). This instrument has been used for example to determine that ammonia oxidation by archaeal enrichment cultures taken from the Pacific Ocean also produces $N_2O$, and could account for a large percentage of the marine nitrous oxide source (Santoro et al., 2011). Incorporating such an instrument into AGAGE stations’ measurements would allow scientists to determine the processes creating the nitrous oxide in the atmosphere, and better quantify their relative importance.

The analysis of atmospheric concentrations reveals that emissions are likely significantly higher from the Eastern Tropical South Pacific Oxygen Minimum Zone than most of the Pacific Ocean, and that emissions from these regions are further enhanced during La Niña events. However, much work remains to be done to quantify these emissions precisely and understand the root source of the higher emissions from OMZs. A better understanding of the nitrification and denitrification pathways and how they are modified in the suboxic regions overlying the OMZs is crucial to constraining marine emissions, and therefore the overall atmospheric nitrous oxide budget. Particularly as climate change causes OMZs to expand and ENSO events to become more extreme, it will be ever more important to understand the source of emissions from these regions and the extent of their natural variability.
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