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Nitrous Oxide in the eastern tropical North Pacific

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Nontechnical summary

Nitrous oxide (N_2O) is an important trace gas in the atmosphere that contributes to the greenhouse gas effect and influences the global distribution of ozone. The ocean is a significant natural source of N_2O. The goal of this study was to pinpoint more clearly the source and distribution of oceanic nitrous oxide in low oxygen waters of the eastern tropical North Pacific and to deduce what mechanisms control its distribution. I collected samples for nitrous oxide between 20°N and 32.5°N along the coast of Baja California aboard the R/V Thompson during March 17 – 27 2012. N_2O increased with depth at the northernmost stations with higher oxygen concentrations. In contrast, the southernmost coastal stations with high primary productivity and lower oxygen concentrations in underlying water showed a sharp N_2O peak at the upper boundary of the low oxygen water, a broad N_2O minimum in the core of the oxygen minimum zone and a secondary peak at the lower boundary. I estimated the magnitude of the flux from the ocean to the atmosphere and found that south of 22°N, the region is a significant source of N_2O to the atmosphere.

Abstract

Nitrous oxide (N_2O) is an important greenhouse gas and is currently the most important ozone-depleting anthropogenic emission. However, its atmospheric budget is not well quantified, although it is well understood that the ocean is an important natural source of N_2O to the atmosphere. Eastern-boundary ocean-upwelling zones containing large zones of oxygen-depleted intermediate waters, like the eastern tropical North Pacific (ETNP), are large sources of N_2O to the atmosphere but they have not been adequately studied. I investigated the concentration of N_2O between 20°N and 32.5°N in the ETNP aboard the R/V Thompson during March 17 – 27 2012. Surface waters were close to saturation between 22°N and 32.5°N and highly supersaturated at stations south of 22°N indicating a large source of N_2O to the atmosphere south of 22°N. I estimated an annual flux of 0.10 – 0.32 Tg N_2O yr^{-1} to the atmosphere from the ETNP, accounting for 1.7 – 5.3% of the global oceanic N_2O source. A sharp N_2O maximum in the oxycline was found at coastal stations with high primary productivity in overlying waters due to a complex interaction between nitrification and denitrification. In the core of the suboxic zone, below the primary N_2O peak, N_2O was consumed via denitrification and this low N_2O signal was advected northward by the California Undercurrent.

Introduction

One molecule of nitrous oxide (N_2O) has a global warming potential, over a 100 year time scale, about 298 times higher than one molecule of CO_2 (IPCC 2007). N_2O is also the major source of nitric oxide (NO) in the atmosphere, which is a natural agent of stratospheric ozone destruction (Yoshinari et al. 1997). N_2O is produced by both natural processes and human activities including the use of N-fertilizers in agriculture and fossil fuel combustion. Since the industrial revolution, the concentration of N_2O in the atmosphere has increased from around 270 ± 7 ppb in 1750, to 319 ± 0.12 ppb in 2005 (IPCC 2007). Natural processes in the ocean are an important part of the atmospheric N_2O budget as the ocean acts as a net source for atmospheric N_2O, providing up to 25% of emissions (Nevison et al. 2004).

In the ocean, N_2O is produced via two microbial processes: as a by-product of nitrification and as an intermediate of denitrification (Fig. 1). Denitrification occurs predominantly in oxygen depleted waters where denitrifying bacteria reduce nitrate (NO_3^-) and nitrite (NO_2^-) to the gases NO, N_2O and nitrogen ($N_{2)}$ when oxygen is limiting. The yield of N_2O from both processes is strongly dependent on local oxygen (O_2) concentrations (Bange 2008), thus O_2 is the key factor regulating N_2O production. Several studies suggest that productive regions underlain by low-O_2 and suboxic waters such as the ETNP and the Arabian Sea are major sources of oceanic N_2O (Nevison et al. 1995; Yoshinari et al. 1997; Naqvi et al. 1998). These regions with large areas of suboxic intermediate waters are often referred to as Oxygen Deficient Zones (ODZs). For the purposes of my investigation I will define the ODZ as the region in the water column, usually occurring at depths between approximately 150 m and 800 m, where oxygen concentrations are less than 0.1 µmol kg^{-1} (Cohen and Gordon 1978).

It was not until the advent of the electron capture detector (ECD) and the development of an ECD calibration technique that precise and reliable N_2O measurements were made possible (Cohen 1977). Early investigation of N_2O in the ETNP concluded that the ETNP is a source of N_2O to the atmosphere and that nitrification might be the most important mechanism for N_2O production in the ETNP (Cohen and Gordon 1978). Isotopic measurements of N_2O made by Naqvi et al. (1998) reveal that nitrification may not be the only source of N_2O in suboxic waters and that denitrification may lead to a net accumulation of N_2O under certain conditions. The authors suggest that N_2O may also be produced via coupling of nitrification and denitrification associated with the steep oxygen gradient at the top of the ODZ. There are many different methods for measuring denitrification (Groffman et al. 2006). One approach is to look for the presence of a subsurface NO_2^- maximum in suboxic waters which is characteristic of the ODZ and is associated with production by heterotrophic denitrification (Cline and Richards 1972; Groffman et al. 2006). N_2O profiles from suboxic regions tend to show a two-peak structure: maxima are found at the upper and lower boundaries of the ODZ and concentrations are considerably undersaturated in the core of the ODZ (Cohen and Gordon 1978; Bange 2008; Farias et al. 2009). Assuming an atmospheric N_2O

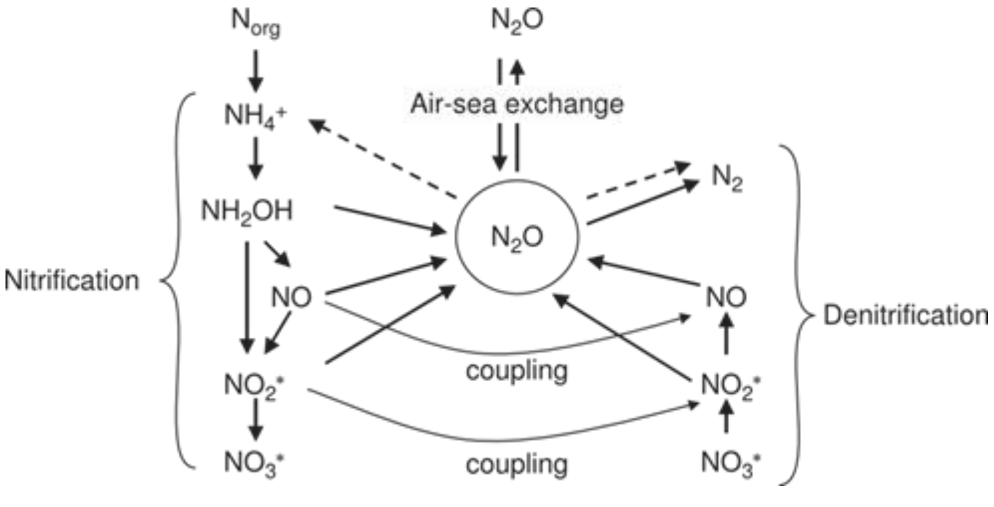

Fig. 1 Schematic of the processes which influence the distribution of N_2O in the ocean. Dashed arrows indicate N_2O reduction during nitrogen fixation. Adapted from Bange (2008).

concentration of 322 ppb, the equilibrium N_2O concentration in seawater at 20°C and salinity 34‰ is 7.57 nmol kg^{-1}. The maximum concentration of the N_2O peak at the upper boundary of the ODZ often exceeds 50 nmol kg^{-1} and can exceed 100 nmol kg^{-1} (Farias et al. 2009).

N_2O emission is currently the single most important ozone-depleting emission and is expected to remain the largest throughout the 21st century (Ravishankara et al 2009). Increasing quantities of atmospheric anthropogenic fixed nitrogen entering the open ocean through rivers and groundwater, discharge from wastewater, atmospheric deposition, and so forth, could account for the production of up to ~1.6 Tg of N_2O per year, or about a third of total oceanic N_2O emissions (Duce et al. 2008). It is important to do more research on N_2O in the ocean because although we know that the ocean is a net source for atmospheric N_2O, our understanding of the distribution and magnitude of the oceanic source term is limited. Because surface water above natural ODZs like the ETNP act as a large source of N_2O to the atmosphere, these regions are significant contributors to the global atmospheric N_2O cycle.

Net N_2O production in the ocean is $\sim 1.4 \times 10^{11}$ mol (6 Tg of N) per year (Bange 2008). About half of this production occurs in hypoxic and suboxic waters and the rest occurs in oxygenated waters (Codispoti 2010). The numbers and extent of coastal hypoxic zones caused by anthropogenic activities, such as riverine runoff of fertilizers and the burning of fossil fuels have been steadily increasing over the past few decades (Diaz and Rosenberg 2008). Because N_2O formation strongly depends on dissolved O_2 concentrations, it is important to quantify the sources of N_2O at the oxic-suboxic boundary in areas with oxygen depleted waters. It is also necessary to increase our understanding of the mechanisms contributing to N_2O production in regions with productive surface waters overlaying oxygen depleted waters as the frequency and extent coastal hypoxic zones increases (Naqvi et al. 2010). The questions I will address in this study are: What is the magnitude of the source of N_2O to the atmosphere in the ETNP? How does this atmospheric flux vary along a North-South gradient? What are the characteristics of the N_2O depth profile and in particular how do N_2O concentrations vary across the oxic-suboxic boundary?

Methods

Samples were collected at 10 depths between the surface and 1000 m at 13 stations in the ETNP (Fig. 2) Water samples were collected using Niskin bottles mounted on a CTD rosette-sampler. N_2O concentration of the samples were determined on board the ship using headspace extraction with helium followed by injection into a HP 5890 gas chromatograph with electron capture detector (Cohen 1977; Bange et al. 2001a). The gas chromatograph was standardized using N_2O standards of 0.1, 1 and 10 ppm. The relationship was nonlinear and a standard curve was determined using quadratic regression. N_2O solubility was calculated from the equation from Weiss and Price (1980) using temperature and salinity data measured during CTD sampling. Surface saturation was calculated relative to an average atmospheric N_2O concentration of 322 ppb. Oxygen concentrations were measured using a CTD mounted SBE 43 electrode and calibrated using the Carpenter modified Winkler method (Carpenter 1965).

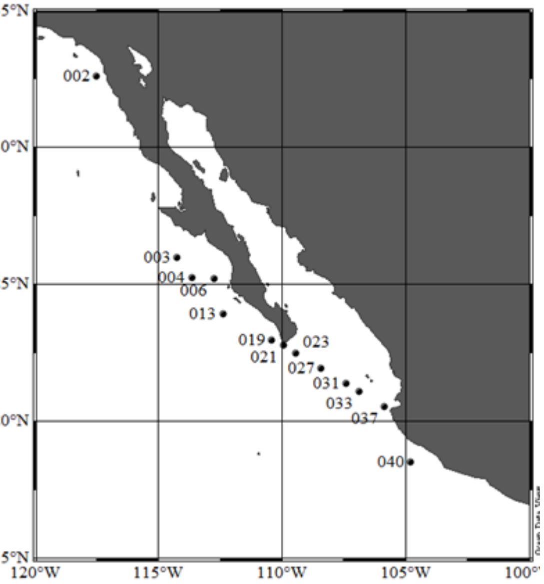

Fig. 2 Map of 13 stations sampled for N_2O along the coast of Baja California between San Diego and Manzanillo on board the R/V Thompson during March 17 – 27 2012.

Results

The N_2O per cent surface saturation ranged from 85.8 % at station 27 to 278.8 % at station 37 (Fig. 3). Stations 2 – 27, north of 21.5 N, were all between 85% and 115%. South of 21.5 N, Stations 31 – 40 were supersaturated up to 278.8% at Station 37. Chlorophyll concentrations in the upper 100 m were highest near the surface at stations 37 and 40 (Fig. 4A). The N_2O profile at stations 2, 3, 4 and 6 showed lowest concentrations at the surface, increased with depth in the oxycline in the upper 100 m and remained fairly stable below 100 m (Fig. 4B). Further south, stations 13 – 33 showed a similar increase in N_2O with depth in the upper 100 m with highest N_2O concentrations below 600 m but exhibited an N_2O minimum in the core of the suboxic zone between 150m and 600 m. This N_2O minimum extended south to stations 37 and 40 but with increased vertical extent. In the oxycline at stations 37 and 40 there were sharp N_2O maxima in the upper 100 m of 59.35 nmol L^{-1} and 71.34 nmol L^{-1} respectively which were absent at all other stations sampled. A NO_2^- maximum was observed from station 31 to station 40 in the 50 – 400 m depth range (Fig. 4C). From North to South the minimum O_2 concentration within the suboxic zone decreased while the vertical extent of the suboxic zone increased from 400 m to 800 m at the northern end of the section to 200 m to greater than 1000 m at the southern end (Fig. 4D).

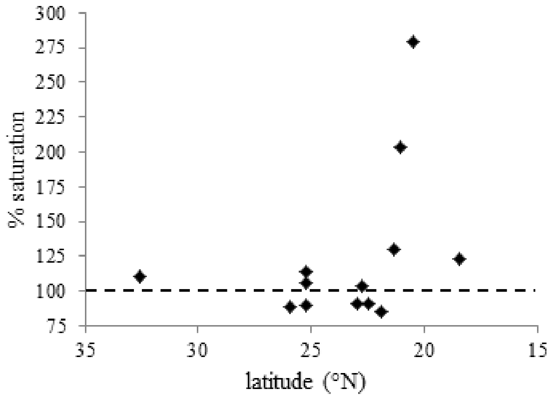

Fig. 3 Per cent N_2O saturation in surface waters in the ETNP. Values greater than 100% (dashed line) indicate flux from the ocean to the atmosphere and values less than 100% indicate flux of N_2O into the surface ocean.

Discussion

N_2O flux to the atmosphere

The per cent surface saturation (Fig. 3) of N_2O was highly supersaturated at Stations 31 – 40 indicating that this region of the ETNP is acting as a net source of N_2O to the atmosphere. Per cent surface saturation is higher for stations closer to the coast indicating that coastal upwelling processes may be enhancing the region as a source of N_2O to the atmosphere. Upwelling further north along the Pacific Northwest coast is a large source of atmospheric N_2O (Nevison et al. 2004).

I calculated the N_2O exchange across the air-sea interface using a similar method to Nevison et al. (1995). The flux of N_2O across the air-sea interface can be expressed as:

$$F = k\sigma\Delta pN_2O \qquad 1)$$

where F(mol m^{-2} s^{-1}) is flux from the ocean to the atmosphere, k (m s^{-1}) is the gas transfer (or piston) velocity, σ (mol m^{-3} atm^{-1}) is the solubility of N_2O in seawater which is computed as a function of temperature and salinity (Weiss and Price 1980) and ΔpN_2O is the air-sea difference in the partial pressure N_2O. By convention, F is negative for a flux from the atmosphere to the Ocean. Several relationships have been proposed to estimate k as a function of wind speed (U_{10}). I used long term mean wind speed at 10 meters above the sea surface (NCEP reanalysis data 1948 – 2012) to and two different formulas outlined in Wanninkhof et al. (2009) to estimate k (Table 1). The formulas in Table 1 are defined for reference gases at a specific Schmidt number (Sc), the value of which is indicated on the subscript of k. For any gas, Sc is the ratio of the kinematic viscosity (v) of fresh or seawater to the molecular diffusivity (D) of the gas in that water. Sc = 660 corresponds to CO_2 in seawater at 20°C. For gases other than CO_2, Sc can be calculated using the Schmidt number scaling relationship given by

$$k_{gas} = k_{ref}\left[\frac{Sc_{gas}}{Sc_{ref}}\right]^{-\frac{1}{2}} \qquad 2)$$

For N_2O, at 20°C and a salinity of 35‰, Sc = 698 (Wanninkhoff et al. 2009). To determine the ΔpN_2O, I calculated the difference between the mean surface N_2O concentration at

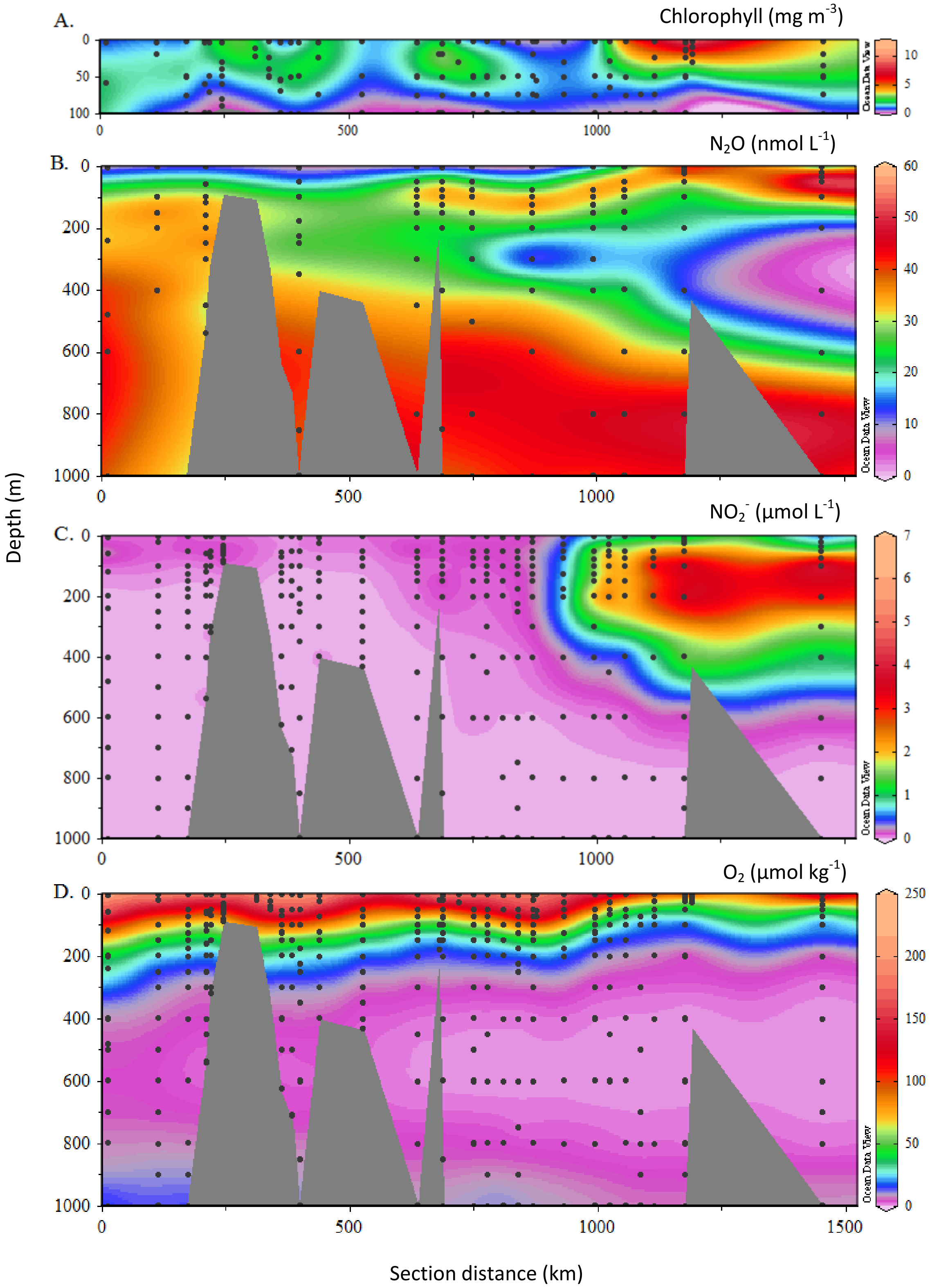

Fig. 4 Concentration of A. Chlorophyll a, B. N_2O, C. NO_2^- and D. O_2 along a north-south section from station 3 to station 40 as shown in Fig. 2. NO_2^- data was collected along the same transect from Macmillan (2012).

Table 1. Transfer velocity formulas

Reference	*k* formula	Wind speed U_{10} m s^{-1}
Wanninkhof (2009)	$k_{660} = 0.24\,U_{10}^2$	5
Wanninkhof (2009)	$k_{660} = 3 + 0.1\langle U_{10}\rangle + 0.064\langle U_{10}^2\rangle + 0.011\langle U_{10}^3\rangle$	5

Table 2. Summary of various flux estimates for the ETNP and the Arabian Sea

Region	Area 10^6 km^2	Flux Tg N_2O yr^{-1}	Reference
ETNP			
See Fig. 5	0.8 – 2.5	0.10 – 0.32	This study
10°N – 22°N	0.8 – 2.5	0.04 – 0.11[a]	Cohen and Gordon (1978)
4°N – 20°N	–[b]	1.2	Pierotti and Rasmussen (1980)
Arabian Sea			
Central, west (>15°N)	1.6	0.22 – 0.39	Law and Owens (1990)
Central, east	6.2	0.44	Naqvi and Noronha (1991)
Central, west	6.2	0.8 – 1.5	Bange et al. (1996)
Central, east	6.2	0.56 – 1.00	Lal and Patra (1998)
Central, west	8.0	(0.41 – 0.75)[c]	Goddard et al. (1999)
Central, west	4.9	0.16 – 0.31	Bange et al (2000)
>equator	6.8	0.33 – 0.70	Bange et al. (2001b)

[a] mean flux in pg cm^{-2} s^{-1} multiplied by the surface area used in this study
[b] surface area used for flux estimate unknown
[c] semi-annual flux

stations 31 – 40 and an N_2O equilibrium concentration of 7.57 nmol kg^{-1}. The resulting flux from equation 1) was 7.86 µmol m^{-2}d^{-1}. To estimate an annual flux for the ETNP, I used two different datasets to approximate the surface area of the region of N_2O production (Fig. 5). First, I used the extent of the subsurface NO_2^- maximum (Fig. 5A; Codispoti and Richards 1976) as the boundary for my lower estimate of surface area based on the strong relationship between N_2O surface supersaturation and a subsurface NO_2^- maximum (Cohen and Gordon 1978). Second, I defined my upper estimate of surface area as the region with minimum O_2 concentrations less than 5 µmol kg^{-1} (Fig. 5B; Fiedler and Talley 2006), assuming N_2O production above suboxic waters. From these boundaries, I calculated a surface area range of 0.8 – 2.5 ×10^6 km^2 which yielded an N_2O flux of 0.10 – 0.32 Tg N_2O yr^{-1}. Given an overall oceanic flux of 6 Tg N yr^{-1}, the ETNP accounts for 1.7 – 5.3% of the total oceanic N_2O source. This flux estimate is a similar magnitude to previous estimates in the ETNP (Table 2; Cohen and Gordon 1978; Pierotti and Rasmussen 1980). Pierotti and Rasmussen (1980) estimate a flux somewhat larger than my estimate but it is likely that this difference is due to the larger size of their study region. Considering its small area, this flux indicates that the ETNP provides a significant contribution to the global oceanic N_2O budget.

N_2O distribution

For O_2 concentrations > 25 µmol kg^{-1}, there is an inverse linear relationship between N_2O and O_2 (Fig. 6). This relationship holds in the upper water column, above the suboxic zone. For low O_2 concentrations < 25 µmol kg^{-1}, the negative N_2O-O_2 correlation breaks down and in

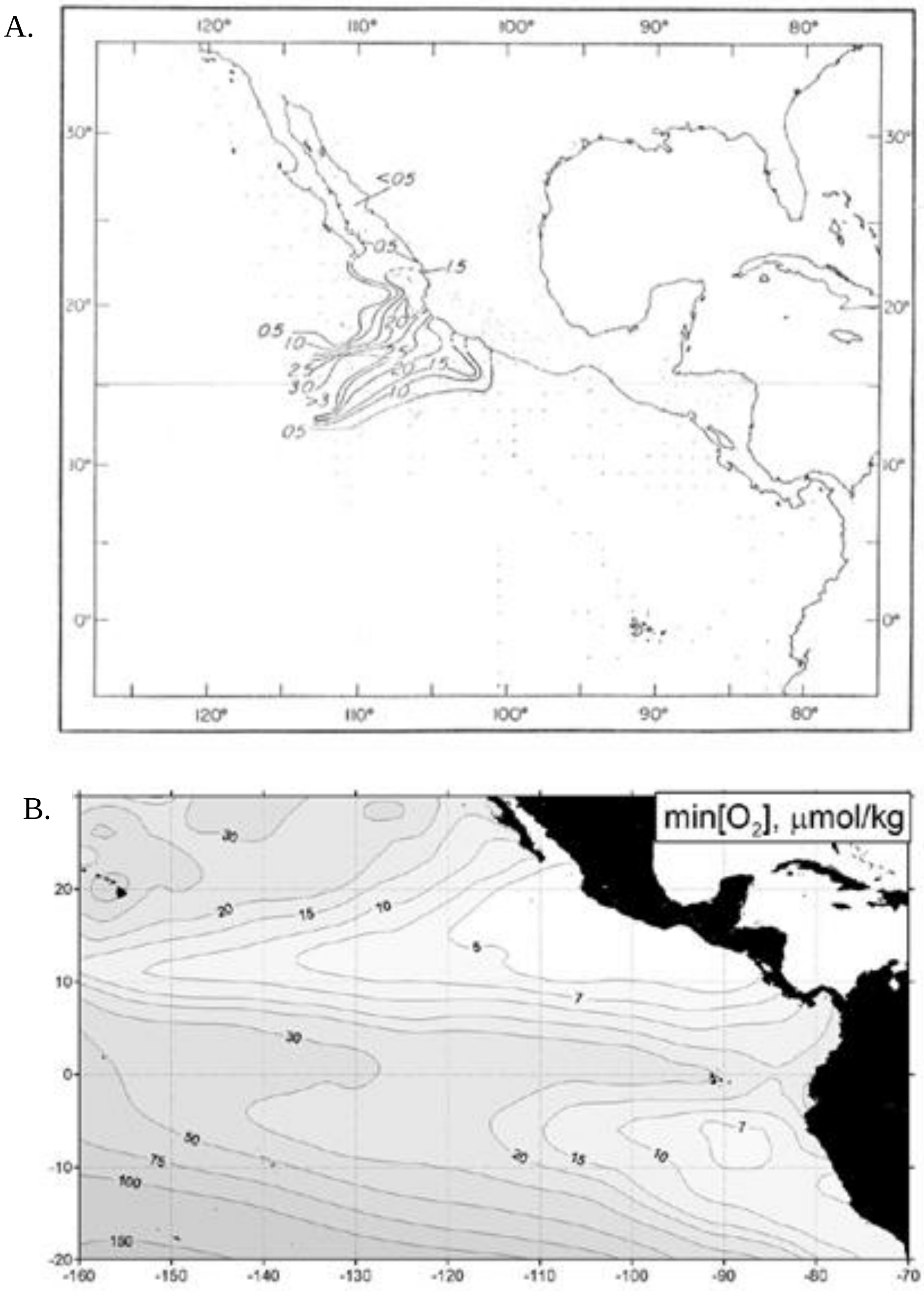

Fig. 5 A. NO_2^- (µg-atoms L^{-1}) on the 26.4 potential density surface in the ETNP. For the purposes of my flux calculations, I defined my lower estimate of the surface area of the N_2O producing region of the ETNP as the region enclosed by the NO_2^- = 1 µg-atoms L^{-1} contour line. Adapted from Codispoti and Richards (1976). B. Minimum dissolved O_2 concentration (µmol kg^{-1}) from WOD01 CTD and bottle data. I defined the upper estimate of the surface area of the N_2O source as the region enclosed by the O_2 = 5 µmol kg^{-1} contour line. Adapted from Fiedler and Talley (2006).

upper 100 m, there is a net production of N_2O. Below 100 m, there is net consumption of N_2O which is strongest at the core of the suboxic zone from around 200 m to 600 m. The breakdown in the N2O-O_2 relationship at low O_2 concentrations is due to net production or consumption of N_2O by either nitrification or denitrification or an interaction between the two processes at different depths.

The strong N_2O maximum observed between 50 – 100 m at Stations 37 and 40 which is absent at stations further north (Fig. 4B) was caused by accumulation of N_2O due to intense nitrification. These two coastal stations were in the region with the highest chlorophyll a concentration highest productivity along the transect. As oxygen decreased below the chlorophyll maximum, remineralization of organic nitrogen to ammonium (NH_4^+) increased, presumably leading to high rates of nitrification. Nitrification is an aerobic process, however, under low-O_2 conditions N_2O yields are enhanced (De Bie et al. 2002; Goreau et al. 1980). Nitrification oxidizes NH_4^+ to NO_3^-, producing N_2O as an intermediate (Fig. 1). As there was no mechanism to consume N_2O at the same rate, N_2O production via nitrification accumulated in the oxycline, forming a sharp peak. Isotopic analyses of N_2O in the ETNP and the Arabian Sea have indicated that the N_2O peak above the suboxic zone may be produced by a coupled nitrification-denitrification pathway where NO is formed during nitrification, reducing to N_2O during denitrification (Naqvi et al. 1998; Yoshinari et al. 1997). When denitrifying bacteria switch from oxic to nitrogen respiration, they experience a lag in their ability to reduce N_2O to N_2 (Codispoti 2010). Therefore, conditions are favourable for N_2O production when suboxia occurs close enough to the sea surface to allow periodic O_2 injections. At stations 37 and 40, the upper boundary of the suboxic zone is significantly shallower than the other stations, at 20 – 30 m, and may provide ideal conditions for production of N_2O via denitrification. The broad subsurface NO_2^- maximum extends from as shallow as 50 m at these southern stations, indicating that denitrification is likely occurring at these depths which coincide with the production of N_2O. Without isotopic analyses of my data, I cannot confirm the possibility that the observed N_2O peak at stations 37 and 40 may have resulted from a complex interaction between nitrification and denitrification. However, the enhanced chlorophyll concentration and inferred productivity overlying the N_2O maximum may be sufficient to explain the intensity of the N_2O maximum relative to stations

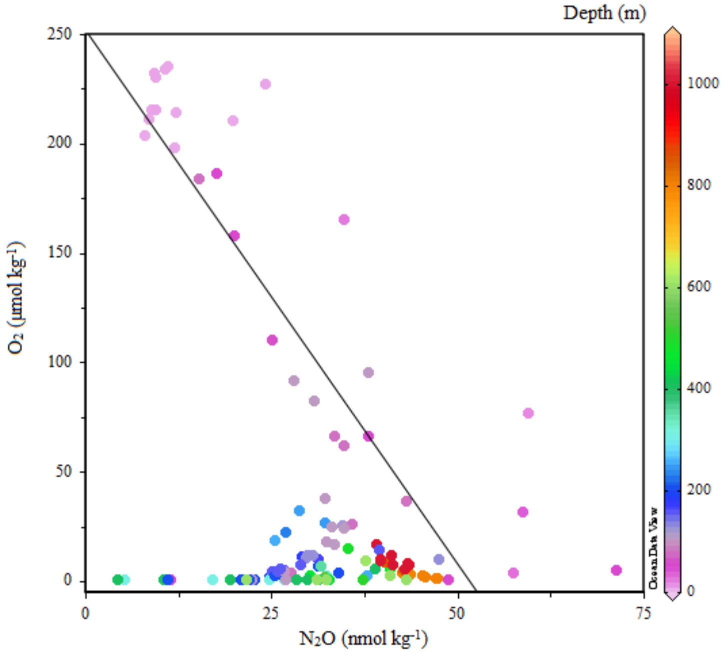

Fig. 6 N_2O-O_2 relationship in the ETNP. For samples with $O_2 > 25$ µmol kg^{-1}, the solid black line was fitted by least squares linear regression and has r = -0.81.

further north via nitrification alone.

Sharp N_2O maxima at the upper oxic-suboxic boundary were absent at all the other stations sampled due to low surface productivity indicating less nitrification in the upper 100 m of the water column (Fig. 4). At the northern stations 2 – 6, oxygen decreased gradually with depth in the upper 500 m causing nitrification to occur deeper in the water column. Nitrification at depth leads to accumulation of N_2O at depth and thus the lowest N_2O concentrations were observed at the surface and then increased with depth to 1000 m. Increasing N_2O with depth in the upper 1000 m is consistent with what has been observed in oligotrophic regions of the open ocean where there is no suboxic zone (Walter et al. 2006).

Below the upper N_2O peak at Stations 37 and 40 is a broad N_2O minimum where N_2O is consumed by denitrification (Fig. 4; Fig. 6). Low N_2O concentrations less than 10 nmol L^{-1} in the 200 – 600 m range correspond to the subsurface NO_2^- maximum from 50 – 500 m (Fig. 4C). Therefore, N_2O was likely consumed by heterotrophic denitrification to produce N_2 gas in the high NO_2^- region from 50 m to 400 m. Further northward, stations 31 and 33 also exhibited an N_2O minimum in the core of the suboxic zone as a result of denitrification, corresponding to the NO_2^- maximum. The slightly increased N_2O at 300 m depth around station 33 is likely an artifact of the data interpolation and I would expect N_2O concentrations to remain low between 400 m and 600 m at this station. The appearance of low N_2O water at intermediate depths at stations 13, 19, 21, 23, and 27, north of the high NO_2- region (Fig. 4C), indicates that denitrification was not responsible for the production of N_2O at these stations. Instead, this low N_2O water was likely advected northward at depth via the California undercurrent. Along the same transect the California current was observed with a northward flow with an average velocity of 0.5 – 1 m s^{-1} with the strongest at 100 – 300 m depth which agrees with the location of the low N_2O signal (Spencer 2012). Bacterial samples were collected along the same transect to look for the *nirS* gene, which encodes the enzyme nitrite reductase, and is present in all denitrifying bacteria (Geurtsen 2012). Geurtsen (2012) found the *nirS* gene present from 50 – 300 m close to station 23 and from 160 – 300 m at station 6. However, the lack of an NO_2^- signal in these regions indicates that although the genes are present, the bacteria are not actively denitrifying and are most likely not responsible for the N_2O minimum observed at these northern stations. The *nirS* may also have been advected northward via the California Undercurrent, similar to the N_2O. At all stations with a N_2O minimum in the core of the suboxic zone, the N_2O peak at the lower boundary of the suboxic zone is formed by nitrification. This is similar to the deep water at the northern stations which lack an intermediate low N_2O signal.

The distribution and magnitude of concentrations of N_2O observed in the ODZ agree with previous observations in the same region (Cohen and Gordon 1978; Yoshida et al. 1984; Yoshinari et al. 1997). The inverse N_2O-O_2 relationship I observed (Fig. 6) is very similar to that identified by Cohen and Gordon (1978) although they did not find N_2O concentrations above 40 nmol L^{-1} in the ETNP. More recent studies have found N_2O concentrations above 70 nmol L^{-1} (Yoshinari et al. 1997) similar to my observations but these maxima occurred below the suboxic zone. The peaks observed at the upper oxic-suboxic boundary are weaker than my observations and this is most likely due to higher surface productivity along the coast where I observed the strongest N_2O peak. The production of N_2O via nitrification is probably highly variable because of its dependence on the productivity of the overlying oxic water. The depth of the primary N_2O peak also appears shallower in my data than in previous observations corresponding to a shallower oxycline.

Comparisons with other major ODZs

There are two other major ODZs in the global ocean: the Arabian Sea and the Eastern tropical South Pacific (ETSP). These regions have also been the focus of much N_2O research. A similar characteristic double peak structure to that observed at stations 37 and 40 in this study has been observed consistently in low oxygen regions of the Arabian Sea and the ETSP (Bange et al. 2001a; Yoshinari et al 1997; Farias et al. 2009). The range of N_2O concentrations in the Arabian Sea is similar to those found in the ETNP ranging from 10 – 60 nmol L^{-1} in one study (Bange et al.

2001a) and up to 80 nmol L^{-1} in another (Yoshinari et al. 1997). The authors found significantly different isotopic enrichment of N_2O in the Arabian Sea compared to the ETNP. The cause of this difference requires further study but it is possible that higher productivity in the Arabian Sea may support more intense denitrification (Yoshinari et al. 1997). In the ETSP the N_2O maxima in the oxycline are of a similar magnitude but have been found above 100 nmol L^{-1} (Farias et al. 2009). The magnitude of the flux of N_2O to the atmosphere from the ETNP is similar to estimates made in the Arabian Sea (Table 2). My estimates are similar to the lower end of estimates from the Arabian Sea, but taking into account the relatively small surface area used for my flux estimate suggests that the magnitude of the flux in the ETNP is comparable to upper estimates for the Arabian Sea. To directly compare the N_2O distribution and flux with greater accuracy, it would be necessary to standardize the flux parameterization and the criteria for determining the area of N_2O production in different regions. This is beyond the scope of this study, but warrants further investigation.

Conclusions

1. South of 22°N, the ETNP is a significant source of N_2O to the atmosphere with an annual flux of 0.10 – 0.32 Tg N_2O yr^{-1}. This flux accounts for approximately 1.7 – 5.3% of the global oceanic N_2O source.

2. A sharp N_2O peak observed in the oxycline underlying a highly productive coastal region was likely produced by intense nitrification but may be the result of a complex interaction between nitrification and denitrification.

3. The broad N_2O minimum observed in the core of the suboxic zone below the primary N_2O peak was consumed at depth via heterotrophic bacterial denitrification south of Station 31 and this low N_2O was advected northward via the California Undercurrent.

Future research directions

There are a number of broad, important questions about the global N_2O budget and the ocean's role in N_2O production that remain unanswered: Is the global N_2O budget balanced? Is nitrification or denitrification the dominant N_2O formation process in the ocean and how do these production mechanisms interact? Constraining the magnitude and spatial variability of the air-sea N_2O flux is necessary is a priority to understand the global N_2O budget. This is important because the Ocean is a net source of atmospheric N_2O (Bange 2008). About half of this production occurs in hypoxic and suboxic waters, although they only make up ~10% of the ocean's volume (Codispoti 2010). Therefore, these regions, particularly the ETNP, ETSP and Arabian Sea, should continue to be the focus of research as recent observations suggest that marine suboxic regions are likely to expand and shoal (Stramma et al. 2008) which may lead to enhanced N_2O accumulation at the oxic-suboxic boundary. Future work should pay more attention to N_2O pathways in coastal areas such as estuaries, mangroves, upwelling areas etc. since it is evident that a significant portion of the oceanic flux to the atmosphere comes from coastal areas (Nevison et al. 2004; Naqvi et al. 2005; Codispoti 2010) and that anthropogenic sources have increased the incidence of coastal hypoxia (Diaz and Rosenberg 2008).

Also, future work on oceanic N_2O should focus on using isotopic measurements of N_2O and NO_2^- to help decipher the formation pathways of N_2O production. However, isotopic measurements in some cases are difficult to explain and can even lead to contradicting results (Bange 2008). We need to learn more about the N_2O forming pathways and the resulting signatures of the different types of N_2O producing organisms. The isolation of NH_4^+ oxidizing archaea raises the possibility that N_2O forming organisms other than bacteria have been overlooked. Unknown N_2O formation pathways may be identified with the help of further N_2O isotopic studies.

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