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Nitrogen and oxygen isotopomeric constraints on the origins and sea-to-air flux of N_2O in the oligotrophic subtropical North Pacific gyre

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[1] Although the oceans are a significant source of the greenhouse gas nitrous oxide (N_2O) to the atmosphere, the magnitude and characteristics of this source are poorly constrained. We present here stable isotope and isotopomer (intramolecular distribution of ^{15}N within the linear NNO molecule) results for N_2O and oxygen stable isotopic data for dissolved O_2 from Station ALOHA in the subtropical North Pacific gyre near Hawaii. The results indicate shallow (~100–300 m) in situ N_2O production. Results of isotope mass balance models constrain the rate of N_2O production and the sea-to-air flux of N_2O. Results of an isotope mass balance model that takes into account the ratios of the vertical gradients in the isotopic abundances of N, O, N^{α} (central N) and N^{β} (terminal N) of N_2O and the measured gradients of N_2O concentration through the thermocline indicate that shallow in situ production contributed 40% to 75% of the sea-to-air flux of N_2O. This model also indicates that the net sea-to-air flux of N_2O was at least 0.4 μmol m^{-2} d^{-1} and could be as high as 1.0 μmole m^{-2} d^{-1}. These model results are not statistically different from the sea-to -air flux of N_2O calculated using an empirical relationship between wind speed and gas transfer rate (1.1 ± 0.7 μmole m^{-2} d^{-1}) derived from measured values for wind speed, temperature and the surface mixed layer concentration of N_2O. These results can be used to better constrain the global N_2O budget. *INDEX TERMS:* 4820 Oceanography: Biological and Chemical: Gases; 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 4870 Oceanography: Biological and Chemical: Stable isotopes; 9355 Information Related to Geographic Region: Pacific Ocean; *KEYWORDS:* stable isotopes, isotopomers, nitrous oxide, N_2O, sea-to-air flux, nitrification

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1. Introduction

[2] Nitrous oxide (N_2O) plays a significant role in the reduction of ozone in the stratosphere and is an atmospheric greenhouse gas in the troposphere with a concentration that is increasing at an annual rate of 0.25% [*Prinn et al.*, 1990; *Khalil and Rasmussen*, 1992; *Intergovernmental Panel on Climate Change* (*IPCC*), 2001]. At this current rate of increase, atmospheric N_2O may significantly impact global climate over the next 100 years [*Lashof and Ahuja*, 1990; *Albritton et al.*, 1995]. The oceans are considered a significant source of N_2O to the atmosphere [*Oudot et al.*, 1990; *Prather et al.*, 1995; *Nevison et al.*, 1995], even though N_2O may be reduced to N_2 in areas of low O_2 [*Cohen and Gordon*, 1978]. N_2O in the oceans is produced by nitrification and denitrification, but it is not clear which N_2O production mechanism is most important: nitrification in areally extensive oligotrophic waters where N_2O is only slightly saturated, or denitrification in areally restrictive regions with a strong O_2 minimum layer near the surface where N_2O is supersaturated. Although an observed negative correlation between concentrations of N_2O and O_2, and a positive correlation between concentrations of N_2O and NO_3^-, suggest N_2O is produced mainly by nitrification [*Yoshinari*, 1976; *Cohen and Gordon*, 1978; *Butler et al.*, 1989; *Yoshida et al.*, 1989], these correlations do not prove nitrification is the dominant mechanism [*Pierotti and Rasmussen*, 1980]

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and evidence has accumulated suggesting that denitrification may control N_2O production under certain conditions [e.g., *Jorgensen et al.*, 1984; *Yoshida et al.*, 1989].

[3] Early work at Station ALOHA in the oligotrophic subtropical North Pacific gyre near Hawaii identified near-surface waters of the subtropical North Pacific as a large source of N_2O to the atmosphere [*Dore et al.*, 1998]. While not apparent from concentration profiles of N_2O, in situ production was evident from subsurface minima (at ~100–300 m) in the $\delta^{15}N$ and $\delta^{18}O$ values of N_2O. These findings, taken in the context of the conclusions of *Dore and Karl* [1996], who documented nitrification within this depth interval using independent rate estimates, suggested that the upper ocean N_2O reservoir is probably produced by microbial nitrification. More recently, *Ostrom et al.* [2000] used the large differences between the $\delta^{18}O$ of seawater, dissolved O_2, and N_2O to clarify mechanisms of formation of N_2O at Station ALOHA. During nitrification, N_2O can be produced by the reduction of NH_2OH or the reduction of NO_2^-. The latter is often referred to as nitrifier-denitrification. The oxygen in NH_2OH is derived solely from dissolved O_2 whereas the oxygen in NO_2^- is derived from both dissolved O_2 and the oxygen atom in seawater [*Dua et al.*, 1979; *Hollocher et al.*, 1981; *Andersson and Hooper*, 1983; *Kumar et al.*, 1983]. Comparison of the $\delta^{18}O$ in O_2 and N_2O can thus indicate the relative importance of the roles of nitrification and nitrifier-denitrification in forming N_2O. *Ostrom et al.* [2000] found that the $\Delta^{18}O$ ($=\delta^{18}O_{N_2O} - \delta^{18}O_{O_2}$) values at station ALOHA were not constant with depth and that low values of $\Delta^{18}O$ between about 100 and 400 m suggested a greater contribution to N_2O of oxygen from water. This finding suggested that N_2O was derived in part from the reduction of NO_2^-, probably via nitrifier-denitrification [e.g., *Poth and Focht*, 1985].

[4] In this study, we measured (1) the natural abundance nitrogen and oxygen isotopic compositions of N_2O, (2) the oxygen isotopic composition of dissolved O_2, and (3) the isotopomers of N_2O (i.e., the intramolecular distribution of ^{15}N within the linear NNO molecule [*Yoshida and Toyoda*, 2000]) and used these results to constrain hypotheses on the origins of N_2O in seawater and estimates of the flux of N_2O to the atmosphere at Station ALOHA. We use isotope mass balance models of the N_2O isotopomeric data to constrain estimates of the net sea-to-air flux of N_2O and to estimate the proportion of shallow in situ production that contributes to that flux. We show that a comparison of the $\delta^{18}O$ of N_2O and dissolved O_2 in July 1999 is consistent with previous work that suggests that N_2O in the lower-euphotic and upper-aphotic zone is formed by ammonium oxidation using in part a nitrifier-denitrification pathway. Our isotope and isotopomer results indicate that N_2O is produced in the deep-euphotic and upper-aphotic zone (roughly 100–300 m) and that N_2O in the deep oxygen minimum has been partly reduced to N_2.

2. Methods

[5] Samples were collected from the Hawaii Ocean Time-series (HOT) station ALOHA (22°45′N, 158°W [*Karl and Lukas*, 1996]) during the Aka Aka Ea cruise (20–28 July 1999, *R/V Kaimikai-o-Kanaloa*). Station ALOHA is located 100 km north of the island of Oahu and has a water depth of 4700 m. This study site was chosen in part because of the large amount of ancillary biogeochemical data that is readily available (see http://hahana.soest.hawaii.edu/hot/hot_jgofs.html).

[6] Samples for stable isotope and isotopomer analyses of N_2O were taken from the same PVC water sample bottles without aeration into either 250-mL or 125-mL glass serum vials, preserved with $HgCl_2$, and sealed with a butyl rubber stopper for later laboratory analysis. The $\delta^{15}N$ and $\delta^{18}O$ of N_2O were determined at the University of Hawaii on a MAT 252 mass spectrometer. The analytical system used is a modification of that described by *Popp et al.* [1995] and *Sansone et al.* [1997], which was originally designed for analysis of $\delta^{13}C$ of dissolved CH_4 in seawater, and is described by *Dore et al.* [1998]. The $\delta^{15}N$ values are corrected for ^{17}O using the method introduced by *Craig* [1957] as modified by *Brand* [1995]. Analyses of triplicate samples yield reproducibilities of better than ±0.5‰ for $\delta^{15}N$ and ±0.8‰ for $\delta^{18}O$ of dissolved N_2O in 250 mL of near-surface waters (~6.7 nM). The isotopic composition of the laboratory standard gas was characterized using the traditional off-line analytical methods of *Yoshida and Matsuo* [1983] and *Yoshinari* [1990] and has been intercalibrated with the isotope laboratory at the Tokyo Institute of Technology. Calibration of N_2O concentration is achieved using a commercial gas mixture and quantification of the mass 44 chromatographic signals. Agreement between the two laboratories over the concentration range measured is excellent (TiTech N_2O, nM $= 1.02 \times$ UH N_2O, nM $- 1.3$, $r^2 = 0.99$, $n = 20$).

[7] Isotopomer analyses were performed at the Tokyo Institute of Technology using a MAT 252 mass spectrometer following the method of *Toyoda and Yoshida* [1999]. N_2O is an asymmetric linear molecule with one nitrogen atom at the center and another at the end or terminal position (i.e., NNO). Although 12 isotopomers are possible given this molecular structure and the possible combination of nitrogen and oxygen isotopes, only five are sufficiently abundant in nature to quantify [*Toyoda and Yoshida*, 1999]. Recently, *Yoshida and Toyoda* [2000] defined the central and end sites of N_2O as N^α and N^β, respectively, and presented a method for determining the site preference of ^{15}N in the isotopomers $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$. Thus, $\delta^{15}N^\alpha$ is a measure of ^{15}N enrichment in the central or N^α position of N_2O whereas $\delta^{15}N^\beta$ is a measure of ^{15}N enrichment in the end or N^β position of N_2O. Analyses of triplicate samples yield reproducibilities of better than ±0.9‰ for $\delta^{15}N^\alpha$, ±1.5‰ for $\delta^{15}N^\beta$, ±0.6 for $\delta^{15}N^{bulk}$, and ±0.9 for $\delta^{18}O$ of dissolved N_2O in 125 mL of near-surface waters (~6.7 nM). The greater degree of uncertainty in $\delta^{15}N^\alpha$ and $\delta^{15}N^\beta$ is derived, in part, from the requirement of two analyses to obtain bulk $\delta^{15}N$ or $\delta^{15}N^\alpha$ [*Toyoda and Yoshida*, 1999]. Characterization of the isotopomer composition of the laboratory standard gas is described in detail by *Toyoda and Yoshida* [1999].

[8] Collection of samples for determination of the isotopic composition of dissolved O_2 followed the procedure of *Emerson et al.* [1991, 1999]. The $\delta^{18}O$ of dissolved O_2 was measured using a gas chromatograph interfaced to a Prism isotope ratio mass spectrometer [*Roberts et al.*, 2000].

Reproducibility of $\delta^{18}O_{O_2}$ analysis using this method has been shown to be better than ±0.3‰ on samples ranging from 20–700 μM O_2 [*Roberts et al.*, 2000].

3. Results and Discussion

3.1. Variations in N_2O Concentration, $\delta^{15}N$ and $\delta^{18}O$

[9] Profiles of the concentration, $\delta^{15}N$, and $\delta^{18}O$ of N_2O showed variations similar to those previously observed [*Dore et al.*, 1998]. N_2O concentration ranged from near air saturation (~6.7 nM) at the surface to a maximum of approximately 50 nM within the oxygen minimum zone at 700–800 m (Figure 1). The $\delta^{15}N$ and $\delta^{18}O$ of N_2O exhibit a conspicuous minimum between 100 and 300 m (Figure 1). However, compared to historical data at station ALOHA, during July 1999 the depth of the isotopic minimum was deeper (300 m in 1999 versus 215 m in 1996) and the $\delta^{18}O$ of N_2O was lower (39.3‰ in 1999 versus 42.3‰ in 1996). The minimum $\delta^{15}N$ values of N_2O were comparable in the two studies (5.5‰ in 1999 versus 5.8‰ in 1996). Because N_2O at the isotopic minimum is depleted in both ^{15}N and ^{18}O relative to N_2O above and below this zone, N_2O at this depth cannot result from simple mixing of atmospheric N_2O with N_2O from the deep concentration maximum at ~800 m. Since consumption of N_2O is unlikely in the oxygen-rich waters at the isotopic minimum, the most likely explanation for these results is in situ production at the subsurface isotopic minimum, even though it is not apparent from the concentration profiles of N_2O.

[10] The isotopic composition of N_2O formed in the isotopic minimum layer can be constrained using an isotope mass balance [*Dore et al.*, 1998]. The $\delta^{15}N$ and $\delta^{18}O$ of N_2O in this layer is approximately a mixture of isotopically enriched N_2O diffusing upward across the thermocline and isotopically depleted N_2O produced locally. The ratios of the gradients of ^{14}N and ^{15}N and of ^{16}O and ^{18}O indicate that N_2O diffusing upward from depth has a $\delta^{15}N$ of 9.9 ± 0.4‰ and a $\delta^{18}O$ of 55 ± 1.5‰. The error in the calculated isotopic composition of N_2O diffusing across the thermocline results from uncertainty in the gradient in N and O isotopic compositions with depth. Assuming a two-component mixture, *Dore et al.* [1998] defined the fraction of N_2O contributed by shallow in situ production at the isotopic minimum:

$$f = \frac{F_{\mathrm{shallow}}}{F_{\mathrm{shallow}} + F_{\mathrm{deep}}}, \tag{1}$$

where F_{shallow} is the rate of formation of N_2O in the deep-euphotic and shallow-aphotic zone between 100 and 300 m and F_{deep} is the upward flux of N_2O from deeper water. The isotopic composition of N_2O formed in situ at the shallow isotopic minimum ($\delta_{\mathrm{shallow}}$) is unknown, but it can be calculated for a two-component mixture for any given f:

$$\delta_{\mathrm{shallow}} = \frac{\delta_{\mathrm{total}} - (1-f)\delta_{\mathrm{deep}}}{f}, \tag{2}$$

where δ_{total} is the lowest measured δ value of N_2O at the isotopic minimum ($\delta^{15}N$ = 5.5‰, $\delta^{18}O$ = 42.3‰), δ_{deep} is the isotopic composition of N_2O diffusing upward from depth calculated from the vertical gradients of $\delta^{15}N$ and $\delta^{18}O$, and f is defined in equation (1). The calculated values for $\delta_{\mathrm{shallow}}$ vary widely (Table 1), and it is readily apparent that when f is small, $\delta_{\mathrm{shallow}}$ must be extremely depleted in ^{15}N and ^{18}O. *Dore et al.* [1998] suggested that the lower limit of f could be constrained by assuming that $\delta_{\mathrm{shallow}}$ had a $\delta^{18}O$ value that was no less than that measured in a wastewater treatment plant characterized by extremely high rates of NH_4^+ oxidation and N_2O formation ($\delta^{18}O \approx 21$‰ versus VSMOW [*Yoshinari and Wahlen*, 1985]). A lower limit of f can also be estimated by assuming that $\delta_{\mathrm{shallow}}$ had a $\delta^{15}N$ equal to the lowest value measured in the ocean (Arabian Sea, ~1‰ versus AIR [*Naqvi et al.*, 1998]). Accepting these lower limits implies that shallow in situ production contributed 40–50% of the N_2O in the isotopic minimum layer (Table 1). Assuming that two-component vertical mixing between microbiologically produced N_2O and atmospheric N_2O defines the gradients in N_2O concentration, $\delta^{15}N$ and $\delta^{18}O$ between ~300 and 100 m (i.e., from the depth of N_2O in situ production to approximately the base of the mixed layer), the *y* intercept of a plot of isotopic values versus inverse N_2O concentration (Figure 2) should yield an estimate of $\delta_{\mathrm{shallow}}$ [*Toyoda et al.*, 2002]. Because upward diffusion of enriched N_2O across the thermocline also contributes to the $\delta^{15}N$ and $\delta^{18}O$ of N_2O in this layer, $\delta_{\mathrm{shallow}}$ values estimated from Figure 2 can be considered maximum values. These results suggest that the in situ source had $\delta^{15}N$ and $\delta^{18}O$ values of 3.7 ± 0.9‰ and 37.2 ± 1.9‰, respectively. If we accept these upper limits for $\delta_{\mathrm{shallow}}$, it implies that the shallow in situ production contributed 70–75% of the N_2O in the isotopic minimum layer (Table 1). Our estimate of f is limited by the relatively small change in bulk $\delta^{15}N$ and $\delta^{18}O$ of N_2O with depth and uncertainty in the possible values of $\delta_{\mathrm{shallow}}$.

3.2. N_2O Isotopomer Variations

[11] Although the isotopomer results are more variable than the bulk $\delta^{15}N$ values, a minimum was observed in the isotopic composition of the central or N^{α} position of N_2O at station ALOHA (Figure 3). In the surface-most water sample at station ALOHA, both $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ values appear to be nearly in equilibrium with N_2O in the troposphere [cf. *Yoshida and Toyoda*, 2000]. There is a minimum in $\delta^{15}N^{\alpha}$ between about 100 and 300 m and, as with bulk $\delta^{15}N$, $\delta^{15}N^{\alpha}$ values increase with depth from 300 m to 600–800 m (Figure 3). In contrast, there is a small maximum in $\delta^{15}N^{\beta}$ values between about 50 and 300 m and the values decrease with depth to 600 to 800 m (Figure 3). The N_2O site preference ($\equiv \delta^{15}N^{\alpha} - \delta^{15}N^{\beta}$) in the surface mixed layer (18.3‰ at 25 m) is within the range of values found for tropospheric N_2O (18.7 ± 2.2‰ [*Yoshida and Toyoda*, 2000]). The site preference trend with depth is similar to the bulk $\delta^{15}N$ and $\delta^{15}N^{\alpha}$ values: Minimum values exist from about 100 to 300 m and then increase with depth to about 800 m (Figure 3). On the basis of the same reasoning as above, it is logical to conclude that shallow in situ production of N_2O with a low site preference is responsible for the minimum between 100 and 300 m. A low site preference is consistent with formation of N_2O via nitrification (see *Yoshida and Toyoda* [2000] and below) and also has been observed in near-surface water at the Kyodo North Pacific Ocean Time series, station KNOT (44°N, 155°E [*Toyoda et*

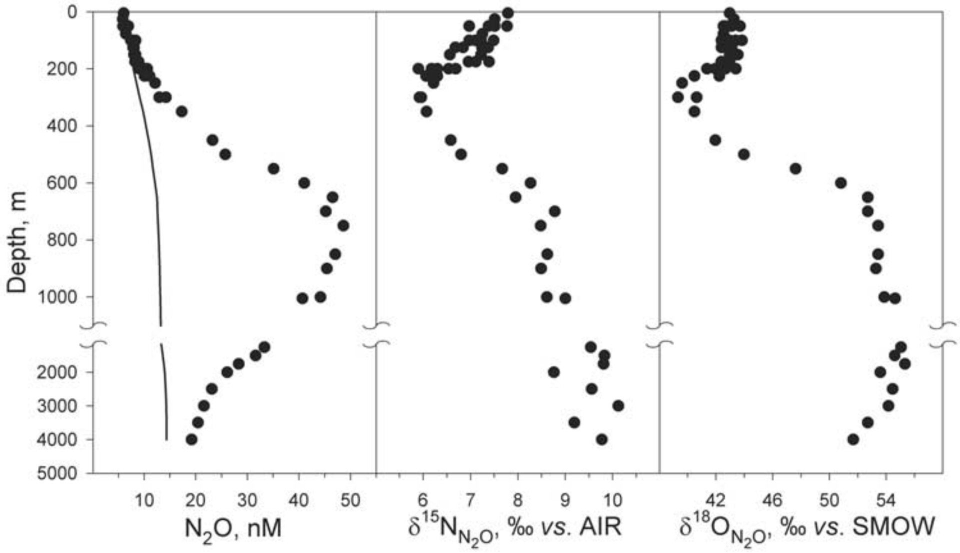

Figure 1. Depth profiles of (left) concentration, (middle) nitrogen isotopic composition, and (right) oxygen isotopic composition of N_2O at station ALOHA during July 1999. Solid line in left panel indicates hypothetical N_2O concentration at 100% air saturation.

al., 2002]). At station KNOT, a minimum in site preference (~13‰) is present in the upper 100 m [*Toyoda et al.*, 2002].

[12] A two-component mixing model can be used with the isotopomer results to further constrain the proportion of N_2O formed in the isotopic minimum layer. Use of this model requires knowledge of δ_{shallow}. The δ_{shallow} (either $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, or site preference) can be estimated using the isotopic composition of the N_2O precursor molecules (e.g., NH_4^+, NH_2OH, NO_2^-, NO, NO_3^-) and the isotopic fractionation factor associated with N_2O formation. Unfortunately, these precursor molecules are at very low concentrations in the deep euphotic and shallow aphotic zone at station ALOHA (e.g., see http://hahana.soest.hawaii.edu/hot/hot_jgofs.html). As a consequence, no isotopic data are available for any of these species, and thus it is impossible to construct a mixing model based on the profile of $\delta^{15}N^{\alpha}$ or $\delta^{15}N^{\beta}$. However, since possible precursors of N_2O in the ocean are molecules containing only one nitrogen atom, the site preference should be mainly dependent on production processes rather than the $\delta^{15}N$ of the precursors [*Toyoda et al.*, 2002]. The site preference for N_2O formed in situ at the shallow isotopic minimum can be calculated for a two-component mixture for any given *f* using equation (2) as well as the lowest measured site preference (8‰, see Figure 3) and the site preference for

Table 1. Constraints on Formation of N_2O From Shallow In Situ Source, as Indicated by Stable Isotope and Isotopomer Results at Station ALOHA

Fraction of N_2O Contributed to Mixture by Shallow Source,[a] %	$\delta^{15}N$ of Shallow N_2O Source,[b] ‰ Versus AIR	$\delta^{18}O$ of Shallow N_2O Source,[b] ‰ Versus VSMOW	Site Preference of Shallow N_2O Source,[b] ‰	Magnitude of Shallow N_2O Source,[c] $\mu mol\ m^{-2}\ d^{-1}$	Magnitude of Net Sea-to-Air N_2O Flux,[c] $\mu mol\ m^{-2}\ d^{-1}$
95	5.3 ± 0.1	41.6 ± 0.1	7.2 ± 0.1	4.5 ± 3.2	4.8 ± 3.3
90	5.0 ± 0.1	40.9 ± 0.2	6.2 ± 0.3	2.1 ± 1.5	2.4 ± 1.7
85	4.7 ± 0.1	40.1 ± 0.3	5.2 ± 0.4	1.3 ± 0.9	1.6 ± 1.1
80	4.4 ± 0.1	39.2 ± 0.4	4.0 ± 0.6	1.0 ± 0.7	1.2 ± 0.8
75	4.0 ± 0.1	38.1 ± 0.5	2.7 ± 0.8	0.7 ± 0.5	1.0 ± 0.7
70	3.6 ± 0.2	36.9 ± 0.6	1.1 ± 1.1	0.6 ± 0.4	0.8 ± 0.6
65	3.1 ± 0.2	35.5 ± 0.8	−0.6 ± 1.3	0.4 ± 0.3	0.7 ± 0.5
60	2.5 ± 0.3	33.9 ± 1.0	−2.7 ± 1.7	0.4 ± 0.3	0.6 ± 0.4
50	1.1 ± 0.4	29.7 ± 1.5	−8.0 ± 2.5	0.2 ± 0.2	0.5 ± 0.3
40	−1.2 ± 0.6	23.4 ± 2.3	−16.0 ± 3.8	0.2 ± 0.1	0.4 ± 0.3
30	−4.9 ± 0.9	12.9 ± 3.5	−29.3 ± 5.8	0.1 ± 0.1	0.3 ± 0.2
20	−12.3 ± 1.6	−8.1 ± 6.0	−56.0 ± 10.0	0.1 ± 0.0	0.3 ± 0.2
10	−34.4 ± 3.6	−71.0 ± 13.5	−137.0 ± 22.5	0.0 ± 0.0	0.3 ± 0.2
5	−78.8 ± 7.6	−196.9 ± 28.5	−296.0 ± 47.5	0.0 ± 0.0	0.3 ± 0.2

[a] N_2O at the isotopic minimum ($\delta^{15}N = 5.5‰$, $\delta^{18}O = 42.3‰$, site preference = 8‰) was modeled as a two-component mixture of N_2O diffusing upwards from deep water ($\delta^{15}N = 9.9‰$, $\delta^{18}O = 55‰$, site preference = 24‰), and N_2O produced in situ using equation (1).

[b] A given fractional contribution from in situ production to the mixture yields these possible values for the isotopic composition of the shallow source (see equation (2)). Error estimates are based on the uncertainty in δ_{deep} or on site preference of the vertical flux of N_2O from deep water.

[c] The magnitude of in situ production and net sea-to-air flux were calculated for a given fractional contribution using equation (3) and a vertical flux from deep water of 0.24 ± 0.13 $\mu mol\ m^{-2}\ d^{-1}$.

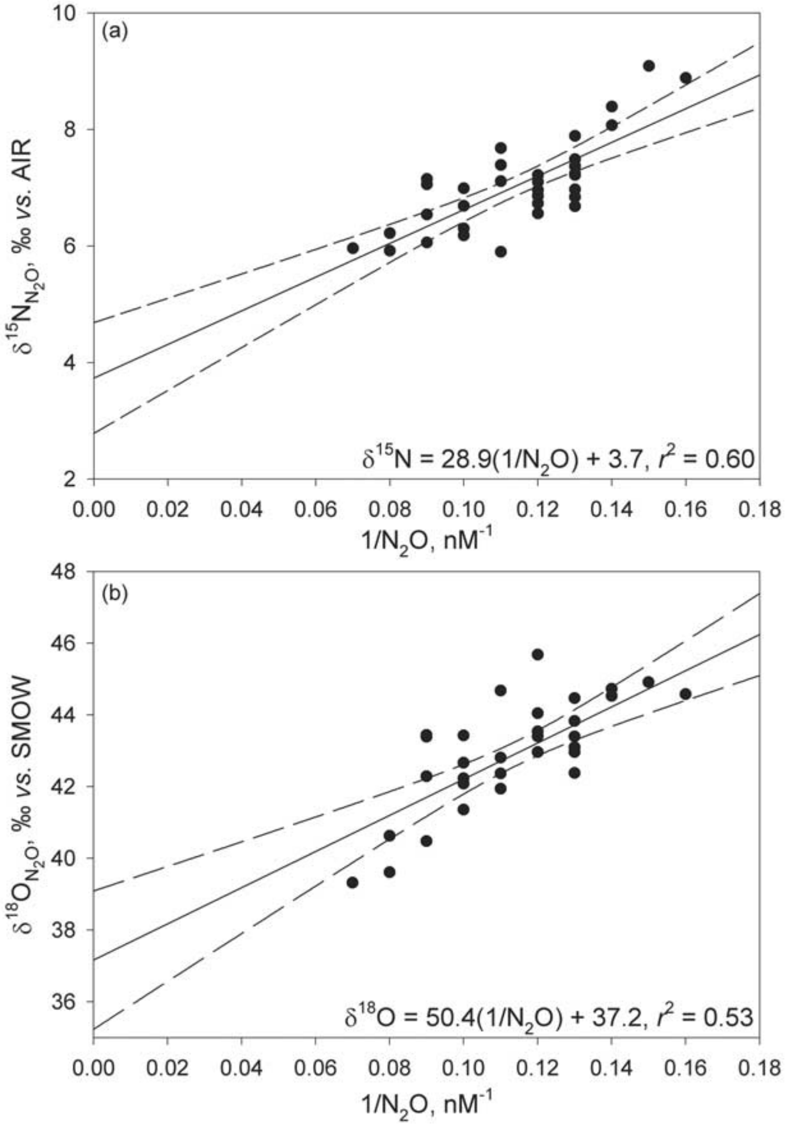

Figure 2. Mixing diagrams for (a) nitrogen and (b) oxygen isotopic composition of N_2O between ~300 and 100 m at station ALOHA during July 1999. Solid lines show results of regression analysis and dotted line shows 95% confidence limits of analysis.

N_2O diffusing upward across the thermocline (Table 1). A site preference of 24 ± 2‰ was determined for N_2O diffusing upward across the thermocline using a one-dimensional diffusion model and the ratio of the gradients of $^{14}N^{\alpha}$ and $^{15}N^{\alpha}$ and of $^{14}N^{\beta}$ and $^{15}N^{\beta}$.

[13] The site preference for N_2O formed in the shallow isotopic minimum layer is unknown; however, it can be constrained. The site preference of N_2O formed in situ should be no larger than the lowest site preference measured (∼8‰ versus AIR at 250 m). The minimum value for the site preference can be estimated based on consideration of equilibrium isotope effects. Calculations by *Yung and Miller* [1997] determined that the ground state zero point vibrational energy (ZPE) for $^{14}N^{15}N^{16}O$ was less than that for $^{15}N^{14}N^{16}O$. The result of these calculations indicates that exchange of ^{15}N between the α and β sites of N_2O lowers the energy level of the molecule. Therefore, under equilibrium conditions, formation of $^{14}N^{15}N^{16}O$ is favored over $^{15}N^{14}N^{16}O$. In other words, the heavy isotope is concentrated at the site where nitrogen is most strongly bonded (i.e., the central position where N^{α} is bonded to both N^{β} and O). Therefore, if the nitrogen atoms forming N_2O have similar $\delta^{15}N$ values, consideration of equilibrium isotope effects dictates that the N^{α} site should be enriched in ^{15}N relative to the N^{β} site (i.e., site preference > 0‰, as much as +45‰ at 25°C [see *Richet*, 1976]).

[14] The minimum value for the site preference can also be estimated based on consideration of kinetic isotope effects. Kinetic isotope effects in the enzyme-catalyzed reactions forming N_2O are not well known but can also yield a positive site preference. The N_2O formed within the isotopic minimum at station ALOHA is derived from both NH_4^+ oxidation

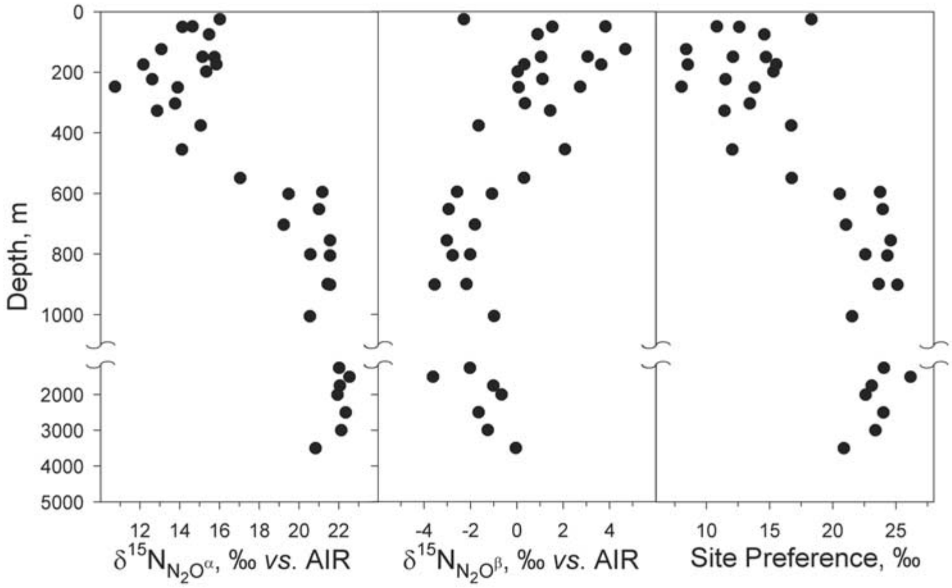

Figure 3. Depth profiles of nitrogen isotopic composition at (left) N^α-site of N_2O and (middle) at the N^β-site of N_2O, and (right) site preference ($\delta^{15}N^\alpha - \delta^{15}N^\beta$) at station ALOHA during July 1999.

and reduction of NO_2^- [*Dore et al.*, 1998; *Ostrom et al.*, 2000] (see section 3.4). Isotopic fractionation governed by kinetic isotope effects should occur during the reaction sequences $NH_4^+ \rightarrow NH_2OH \rightarrow NOH \rightarrow NO \rightarrow N_2O$ and $NH_4^+ \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O$. Oxidation of NOH does not involve a primary kinetic isotope effect and thus should not markedly affect site preference. Because the ^{14}N-^{16}O bond is weaker than the ^{15}N-^{16}O bond, reduction of $^{16}O^{14}N^{16}O$ to $^{14}N^{16}O$ is favored over reduction of $^{16}O^{15}N^{16}O$ to $^{15}N^{16}O$. However, this process does not necessarily affect the site preference of the N_2O eventually formed, since two NO molecules may react to form N_2O. N_2O formed from reduction of NO should produce enrichment in ^{15}N at the N^α position. Reduction of NO is thought to involve an intermediate, hyponitrite ($^-O\text{-}N = N\text{-}O^-$) that is considered to exist as a free species or a complex with an enzyme [*Aerssens et al.*, 1986; *Toyoda et al.*, 2002]. Regardless of the intermediate involved, reduction of NO (or the intermediate $^-O\text{-}N =N\text{-}O^-$) favors cleavage of ^{14}N-^{16}O bonds over cleavage of ^{15}N-^{16}O bonds. Consequently, if two NO molecules react (or $^-O\text{-}N = N\text{-}O^-$ breaks down) to form N_2O, the N_2O produced should show enrichment in ^{15}N at the N^α position (i.e., site preference > 0).

[15] At the moment it is not known what controls the site preference of oceanic N_2O. However, given that both equilibrium and kinetic isotope effects associated with the direct formation of N_2O favor enrichment of ^{15}N at the N^α position, it is not likely that the series of reactions forming N_2O in the oceans would result in a site preference ≤ 0‰. Assuming that N_2O in the isotopic minimum is a two-component mixture of in situ production and N_2O diffusing upward across the thermocline, and that the site preference of N_2O produced locally is equal to 0‰, a minimum contribution of the N_2O in situ source can be calculated. These results indicate that shallow in situ production contributed at least 65% of the N_2O in the isotopic minimum layer (Table 1) and suggest that N_2O formed in situ at the isotopic minimum had values of $\delta^{15}N$ of at least 3.1‰ (versus AIR) and $\delta^{18}O$ of 35.5‰ (versus VSMOW) (Table 1). These estimates for the $\delta^{15}N$ and $\delta^{18}O$ of N_2O formed in situ at the isotopic minimum agree well with a two-component mixing model between microbiologically produced N_2O and atmospheric N_2O (see section 3.1 and Figure 2).

3.3. Sea-to-Air Flux of N_2O

[16] The sea-to-air flux of any slightly soluble gas can be estimated from the air-water concentration differences in the gas and the relationship between gas transfer velocity and wind speed [e.g., *Liss and Merlivat*, 1986; *Erickson*, 1989; *Tans et al.*, 1990; *Wanninkhof*, 1992]. We estimated the sea-to-air flux of N_2O using the empirical relationship between wind speed and gas transfer of *Wanninkhof* [1992] with measured values for wind speed, temperature, and concentration of N_2O. During the Aka Aka Ea cruise, temperature (25.40 ± 0.10°C) and N_2O concentration (6.65 ± 0.36 nM, $n = 9$) varied little within the mixed layer (upper ~50 m). This concentration of N_2O was oversaturated (103%, Figure 1) with respect to the atmosphere [*Weiss and Price*, 1980] assuming an atmospheric N_2O concentration of 315 ppmv [*IPCC*, 2001]. Wind speed was not measured during the Aka Aka Ea cruise but is available for Hawaii Ocean Time-series cruise HOT-106 (12–16 July 1999) and from the National Oceanic and Atmospheric Administration northwest Hawaii weather buoy 51001 (23.40°N, 162.27°W). Average wind speed on HOT 106 (8.4 ± 1.7 m s^{-1}; $n = 15$) agrees well with the hourly wind speed records from buoy 51001 for 20–28 July 1999 (8.4 ± 1.2 m s^{-1}). Using this average wind speed, the calculated N_2O sea-to-air flux was 1.1 μmol m^{-2} d^{-1} (standard error 0.7 μmol m^{-2} d^{-1}). The large uncertainty in the calculated sea-to-air flux results from the variability in measured mixed layer N_2O concentration. This flux estimate agrees well with previous estimates at station ALOHA

Table 2. Summary of Calculated Sea-to-Air Flux of N_2O and Proportion of Sea-to-Air Flux Contributed by In Situ Shallow Ocean Production of N_2O

Model	Data Used	N_2O Sea-to-Air Flux, μmol m^{-2} d^{-1}	Contribution by In Situ Production, %
Vertical flux	$\delta^{18}O$	0.4 ± 0.3	40
Across thermocline	$\delta^{15}N$	0.5 ± 0.3	50
	site preference	0.7 ± 0.5	65
Air-sea exchange	ΔN_2O, wind speed	1.1 ± 0.7	–

indicating N_2O sea-to-air flux significantly greater than zero [*Dore et al.*, 1998] and long-term measurements of N_2O concentration (see http:// hahana.soest.hawaii.edu/hot/hot_jgofs.html).

[17] The vertical flux of N_2O from deep water and the rate of shallow in situ N_2O production can also be used to constrain the sea-to-air flux of N_2O. The vertical flux of N_2O from deep water can be calculated using one-dimensional diffusion models [*Ledwell et al.*, 1993; *Jørgensen*, 1979] and the measured gradients of N_2O concentration through the thermocline. Assuming an eddy diffusion coefficient of 0.37 cm^2 s^{-1} [*Lewis et al.*, 1986], these calculations yield an upward N_2O flux of 0.24 ± 0.13 μmol m^{-2} d^{-1}, a value similar to that previously determined for this site (0.26 μmol m^{-2} d^{-1} [*Dore et al.*, 1998]). Our error in the calculated flux assumes an uncertainty of ±0.26 cm^2 s^{-1} in the vertical eddy-diffusion coefficient. Estimates of the average long-term vertical mixing coefficient for the oceanic thermocline range from 0.11–0.15 cm^2 s^{-1} [*Ledwell et al.*, 1993] to 1.7 cm^2 s^{-1} [*Li et al.*, 1984]. Since the isotope mass balance above constrained production of N_2O in the isotopic minimum layer to 40–75% of the total (Figures 1 and 2, Table 1), the vertical flux of N_2O from depth is only partly responsible for the net sea-to-air flux of N_2O.

[18] *Dore et al.* [1998] suggested that the contribution of shallow in situ N_2O production to the net sea-to-air flux of N_2O could be constrained by using an isotope mass balance of the $\delta^{15}N$ and $\delta^{18}O$ of N_2O. Rearrangement of equation (1) allows calculation of F_{shallow} for a two-component mixture for any given *f*:

$$F_{\text{shallow}} = F_{\text{deep}} \frac{f}{(1-f)}. \tag{3}$$

Consideration of the $\delta^{15}N$ and $\delta^{18}O$ results above suggests that in situ shallow production of N_2O contributed at least 40% and as much as 75% of the N_2O exchanging with the atmosphere (Table 1); therefore the sea-to-air flux of N_2O ($F_{\text{shallow}} + F_{\text{deep}}$) during July 1999 ranged from 0.4 to 1.0 μmol m^{-2} d^{-1} depending on the choice of $\delta^{18}O_{\text{shallow}}$ and $\delta^{15}N_{\text{shallow}}$ (Table 1).

[19] The isotopomer results further constrain the contribution of the shallow in situ N_2O production to the net sea-to-air flux of N_2O. Assuming that the minimum value of the site preference of N_2O produced locally is 0‰ (see section 3.2), the isotopomer results indicate that shallow in situ production contributed at least 65% of the N_2O in the isotopic minimum layer, yielding a N_2O sea-to-air flux of 0.7 μmol m^{-2} d^{-1} (Table 1). Using these mass balances, the isotope and isotopomer results suggest that the net sea-to-air flux of N_2O during July 1999 was at least 0.4 μmol m^{-2} d^{-1} and most likely exceeded 0.7 μmol m^{-2} d^{-1} (see Tables 1 and 2). The N_2O sea-to-air flux calculated using these isotope mass balance models (0.4–1.0 μmol m^{-2} d^{-1}) agrees well with the flux derived from the wind-driven mixing model (1.1 ± 0.7 μmol m^{-2} d^{-1}).

[20] Assuming that the area of the North Pacific subtropical gyre is ~26.3 × 10^6 km^2 (the area between 15°N-40°N and 120°W–130°E) and that our limited estimates of N_2O flux based on isotopic mass balance are representative of temporal and spatial variations in the North Pacific subtropical gyre, then this area is an atmospheric source of at least 0.11–0.26 Tg N yr^{-1}. According to our estimate, this oceanic region can represent ~4–9% of the global oceanic N_2O emission [*IPCC*, 2001].

3.4. Mechanisms of N_2O Formation

[21] N_2O in the oceans is produced by nitrification and denitrification, but it is not known which mechanism is more important in controlling the sea-to-air flux of N_2O. Nitrification is an aerobic process known to occur within the upper ocean [*Wada and Hattori*, 1972; *Cohen and Gordon*, 1978; *Ward et al.*, 1982; *Ward and Zafiriou*, 1988], and N_2O produced by nitrifiers is depleted in ^{15}N relative to its initial substrate ammonium [*Yoshida*, 1988; *Wada et al.*, 1996]. Thus the negative shift in $\delta^{15}N$ between 100 and 300 m is consistent with this process (Figure 1) and is in agreement with previous work at this site [*Dore and Karl*, 1996].

[22] Comparison of the $\delta^{18}O$ of seawater, dissolved O_2, and N_2O can provide further insight into the pathways of N_2O production because it can trace the origins of oxygen in N_2O [*Ostrom et al.*, 2000]. The $\delta^{18}O$ of seawater at station ALOHA is close to 0‰ versus VSMOW and varies by less than 1‰ throughout the water column [*Ostrom et al.*, 2000]. In contrast, the isotopic composition of O_2 is enriched in ^{18}O relative to surface seawater by about 24–26‰ and ranges from about 25‰ versus VSMOW at the surface to 35‰ versus VSMOW in the oxygen minimum (Figure 4). The oxygen isotopic composition of N_2O is enriched in ^{18}O relative to seawater by about 40–55‰ (Figures 1 and 3). The profile of $\Delta^{18}O$ $\left(= \delta^{18}O_{N_2O} - \delta^{18}O_{O_2}\right)$ is similar to that of the $\delta^{15}N$, $\delta^{18}O$, and the site preference of N_2O (Figure 4). Throughout most of the water column, $\Delta^{18}O$ is reasonably constant with values ranging from 18 to 22‰. A conspicuous minimum in $\Delta^{18}O$ is present between about 200 and 500 m and indicates that either the source of oxygen in N_2O or the magnitude of oxygen isotope discrimination associated with N_2O formation is distinct over this depth interval. A greater contribution of oxygen from water would result in lower $\Delta^{18}O$ values. These results, in the context of the conclusions of *Dore and Karl* [1996] and interpretation of the $\delta^{15}N$ of N_2O in the isotopic minimum, are consistent with the

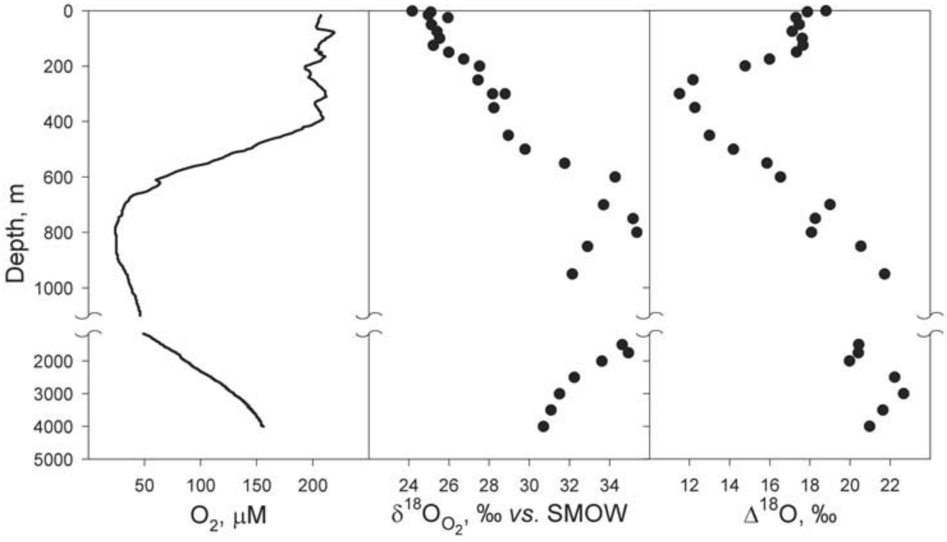

Figure 4. Depth profiles of (left) concentration and (middle) oxygen isotopic composition of dissolved O_2 and (right) difference between the oxygen isotopic composition of dissolved O_2 and N_2O $(\Delta^{18}O = \delta^{18}O_{N_2O} - \delta^{18}O_{O_2})$ at station ALOHA during July 1999. Concentration of O_2 is from sensor on CTD that was calibrated against discrete O_2 concentrations analyzed by Winkler titration.

interpretation that N_2O is derived in part from the reduction of NO_2^- via nitrifier-denitrification [e.g., *Poth and Focht*, 1985].

[23] Since the site preference should be mainly dependent on production processes rather than the $\delta^{15}N$ of the precursors, consideration of the isotopomer results can further constrain the mechanisms responsible for N_2O formation at station ALOHA. The general trends in $\Delta^{18}O$ and site preference are similar, showing minimum values in the lower-euphotic and upper-aphotic zone and maximum values in the oxygen minimum. Taken together, these results indicate that the cycling of N_2O is distinct within these two depth zones of the water column. We argued above that processes responsible for in situ N_2O formation in the isotopic minimum had a site preference between about 0 and 8‰. Although the isotopomer results are consistent with formation of N_2O by nitrification, they do not provide new information to determine if N_2O is derived in part from the reduction of NO_2^- via nitrifier-denitrification.

[24] Primary kinetic isotope effects associated with reduction of N_2O should result in a high site preference and elevated $\delta^{18}O$ values in the residual N_2O. The ZPE of $^{14}N^{14}N^{16}O$ is higher than the ZPE of all heavy isotopomers of this molecule. Therefore, reduction of N_2O to N_2 should occur preferentially at ^{14}N-^{16}O bonds and thus favor production of $^{14}N_2$, leaving the residual N_2O pool enriched in ^{18}O and in ^{15}N, especially at the N^{α} position. If the high site preference and enrichment of ^{18}O in N_2O in the oxygen minimum relative to shallower depths results from reduction of N_2O, then the depth where reduction of N_2O is greatest corresponds with maximum concentration of N_2O at station ALOHA (Figure 1). This suggests either high rates of simultaneous production and consumption of N_2O in the oxygen minimum or advection of preformed N_2O into this region. Reduction of N_2O at these oxygen concentrations is unlikely unless it occurs within anoxic microsites in particles [*Alldredge and Cohen*, 1987; *Paerl and Prufert*, 1987]. In addition, the constant $\Delta^{18}O$ values throughout most of the water column are consistent with production of N_2O in the oxygen minimum. However, advection of preformed N_2O from the eastern tropical North Pacific is possible. The importance of denitrification in the ETNP has been recognized for many years on the basis of N-O-P stoichiometric relationships, the existence of a nitrite maximum within the O_2 minimum [e.g., *Brandhorst*, 1959; *Thomas*, 1966; *Cline and Richards*, 1972], and observations of apparent N_2O consumption in the O_2 minimum [*Cohen and Gordon*, 1978]. Recently, *Castro et al.* [2001] predicted and *Lukas and Santiago-Mandujano* [2001] documented probable advection of a mesoscale eddy from eastern tropical North Pacific waters to station ALOHA. Isotopic and isotopomer studies between station ALOHA and the eastern tropical North Pacific are required to test whether the high site preference and elevated $\delta^{18}O$ values are results of advection of a pool of partly reduced N_2O into this region. If preformed N_2O was transported to station ALOHA, interpretation of the $\Delta^{18}O$ values in the O_2 minimum could be misleading. Since O_2 is a more reactive gas than N_2O, the $\delta^{18}O$ of O_2 is likely to have been affected more than that of N_2O during the time it took to transport the water mass from the eastern tropical North Pacific to station ALOHA. On the basis of the isotopic and isotopomeric results, the processes affecting the pool of N_2O in the deep oxygen minimum are different than those that affect N_2O in the lower-euphotic and upper-aphotic zones.

3.5. Implications for Global Isotope Mass Balance of N_2O

[25] Our results have implications for the global budget of N_2O. *Kim and Craig* [1993] suggested that the stable isotopic compositions of tropospheric N_2O results from the

flux-weighted mixing of three major reservoirs: (1) tropical soil N_2O emissions, (2) return flux of N_2O from the stratosphere, and (3) a hypothesized near-surface oceanic N_2O source. They postulated that an oceanic source must exist because isotopic compositions of tropospheric N_2O lie off a conservative mixing line between the stratospheric and soil-gas end-members. Although the exact isotopic compositions of stratospheric samples of *Kim and Craig* [1993] have been recently questioned [*Rahn and Wahlen*, 1997; *Toyoda et al.*, 2002], it appears that the isotopic compositions of tropospheric N_2O are still influenced by these three sources. The recent global isotope mass balance model of *Rahn and Wahlen* [2000] indicated that the isotopic end-member values suggested by *Dore et al.* [1998] for the open ocean surface waters were consistent with the flux-weighted average values recently found for terrestrial sources [*Perez et al.*, 2000]. If we accept that the site preference of the shallow open ocean source of N_2O was between 0 and 8‰, then the $\delta^{15}N$ and $\delta^{18}O$ values must fall in the range ~3.5–5.5‰ versus AIR and ~35.5–41.5‰ versus VSMOW (~11.7–17.5 versus AIR), respectively. Given the extreme variation in the terrestrial isotopic signatures [*Perez et al.*, 2000], the isotopic values found in the present study are also consistent with a global isotope mass balance model considering only back-fluxing of N_2O from the stratosphere, terrestrial, and upper oceanic sources of N_2O to the atmosphere. Our proposed oceanic values are well within the estimated range of values *Yoshida and Toyoda* [2000] calculated for the flux-weighted average of the oceanic and terrestrial sources. The potential to better constrain the global N_2O budget will depend on how well our data are representative of the processes controlling the isotopic and isotopomer compositions of global oceanic N_2O.

4. Conclusions

[26] Observations of isotopic and isotopomer N_2O variations at station ALOHA in the oligotrophic subtropical North Pacific gyre are consistent with previous observations suggesting in situ N_2O production primarily within the deep euphotic and shallow aphotic zone (~100–300 m). The isotopic results can be modeled as a two-component mixture of isotopomerically enriched N_2O diffusing upward across the thermocline and isotopomerically depleted N_2O produced locally. These model results indicate that approximately 40–75% of the net flux of N_2O to the atmosphere is produced from water depth between about 100 and 300 m. Our estimates of the sea-to-air flux of N_2O based on the isotopomeric models ($0.4-1.0\ \mu\text{mol m}^{-2}\ \text{d}^{-1}$) are in good agreement with the sea-to-air flux of N_2O calculated using an empirical relationship between wind speed and gas transfer with measured values for wind speed, temperature, and the surface mixed layer concentration of N_2O ($1.1 \pm 0.7\ \mu\text{mol m}^{-2}\ \text{d}^{-1}$). If these estimates are representative of the temporal and spatial variations in the oligotrophic subtropical North Pacific gyre, then this in situ production supports an annual sea-to-air N_2O flux for this region of $0.11-0.26$ Tg N yr^{-1}. Our results suggest that the site preference of the in situ source of N_2O was likely between 0 and 8‰ and that the $\delta^{15}N$ and $\delta^{18}O$ values are in the range ~3.5–5.5‰ versus AIR and ~35.5–41.5‰ versus VSMOW (~11.7–17.5 versus AIR), respectively. The negative shift in $\delta^{15}N$ and the low site preference of N_2O between 100 and 300 m is consistent with historical studies of ammonium oxidation and suggests that N_2O within this depth range is formed in part by nitrification. Comparison of the oxygen isotopic composition of dissolved O_2 and N_2O is consistent with the interpretation that N_2O between 100 and 300 m is also derived from the reduction of NO_2^- via nitrifier-denitrification. The high site preference and enrichment of ^{18}O in N_2O in the deep oxygen minimum relative to shallower depths indicates that at least a part of the N_2O pool has been reduced to N_2. These results suggest either a high rate of simultaneous production and consumption of N_2O in the deep oxygen minimum or advection into this region of preformed N_2O that has previously undergone a significant amount of reduction.

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