



RESEARCH LETTER

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Key Points:

- Methane and nitrous oxide measurements conducted in the North Pacific Subtropical Gyre from 2008 to 2016
- Nitrous oxide concentrations conform to predicted values with a slight summer increase
- Methane concentrations vary over subdecadal timescales

Supporting Information:

- Supporting Information S1

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Interannual Variability of Methane and Nitrous Oxide in the North Pacific Subtropical Gyre

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Abstract The temporal variability of two important greenhouse gases, methane (CH₄) and nitrous oxide (N₂O), is reported for the upper water column at Station ALOHA in the North Pacific Subtropical Gyre. Measured concentrations of N₂O conform to predicted values with an increase in saturation during the summer period. In contrast, CH₄ is less predictable and shows an approximate 2 year transition from a state of oversaturation in surface waters to equilibrium values in 2015, implying a change in net CH₄ production. The decrease in CH₄ followed on from fluctuations in phosphate concentrations supporting the hypothesized link between microbial metabolism of phosphorus and the global biogeochemical cycle of CH₄. At this current time, future trends in the net CH₄ production in the North Pacific Subtropical Gyre are uncertain and specifically whether the surface ocean will be a net source or sink for CH₄.

1. Introduction

Quantifying the concentrations and dynamics of climate-relevant trace gases dissolved in seawater is a critical component of Earth sciences, but conducting measurements of sufficient duration to determine trends over seasonal, interannual, and decadal time frames for any marine ecosystem remains a challenging task. An oceanographic long-term monitoring station that has proven invaluable for documenting the role of oceans in relation to climate-relevant gases, namely, carbon dioxide (CO₂), is Station ALOHA, located at 22°45'N, 158°00'W, approximately 100 km north of the Hawaiian Islands (Karl & Lukas, 1996). Situated within the oligotrophic North Pacific Subtropical Gyre (NPSG), its warm, stable, isolated location minimizes the influence of episodic variability and provides the opportunity to determine long-term interannual trends in key ecosystem parameters more readily than highly variable marine environments such as coastal habitats. To date, temporal trends in the functioning of the oligotrophic NPSG as a source or sink for atmospheric CO₂ have been reported (Dore et al., 2003; Keeling et al., 2004; Winn et al., 1998). Two other important greenhouse gases are nitrous oxide (N₂O) and methane (CH₄), which are typically reported to be in excess of atmospheric equilibrium in the surface waters of the open ocean ever since their initial measurements (Lamontagne et al., 1971; Yoshinari, 1976). The oversaturation results from in situ microbial production, although the precise processes and controls for both gases remain to be fully determined. Previous estimates indicate the global oceans contribute 0.6–1.2 Tg yr⁻¹ for CH₄ and 1.2–4 Tg N yr⁻¹ for N₂O (Rhee et al., 2009). Herein, we report on the seasonal and interannual variability of N₂O and CH₄ at Station ALOHA which has been measured at near-monthly intervals since December 2008.

2. Analytical Methods

Discrete seawater samples for CH₄ and N₂O analyses were collected at Station ALOHA as part of the near-monthly Hawaii Ocean Time-series (HOT) cruises since December 2008. For the majority of this observational period, single samples were collected from eight depths (5, 25, 45, 75, 100, 125, 150, and 175 m) with collection of replicate samples on discrete occasions and periodically extending the vertical profiles to a depth of 1000 m. Sampling was conducted using 12 L Niskin-like bottles connected to a rosette with a conductivity temperature-depth (CTD) package (Sea-Bird SBE 911Plus) integrated into the system. These bottles were designed by John Bullister (NOAA Pacific Marine Environmental Laboratory (PMEL)) to specifically minimize contamination for trace gases, in particular chlorofluorocarbons and sulfur hexafluoride (Bullister & Wisegarver, 2008). Seawater was dispensed using Tygon® tubing from the bottles into the bottom of 240 mL borosilicate bottles to at least two times overflowing, ensuring the absence of bubbles. The samples were preserved using 200 μL of saturated mercuric chloride solution, crimp-sealed, and stored in the dark at

room temperature until analysis. Analysis of samples typically occurred 1 to 6 months after sample collection, and no differences were observed for CH₄ and N₂O for this timeframe using the bottles and stoppers as described. Analysis of CH₄ and N₂O was conducted simultaneously using a gas chromatography method as previously described (del Valle & Karl, 2014; Wilson et al., 2014). Briefly, the water sample was transferred under positive pressure supplied by helium gas from the glass vials to a purge chamber fitted with a porous frit. The sample was then purged with ultrahigh purity helium and the gas stream passed through a Nafion[®] drier (Perma Pure LLC) and a Drierite[®] trap (VWR) to remove water vapor and then passed through an Ascarite trap to remove CO₂, before being trapped on a packed sample loop (Porapak Q 80/100; Sigma-Aldrich) immersed in liquid nitrogen. After sparging for 10 min, the sample loop was heated and injected onto an analytical column (30 m × 0.32 mm GS-CarbonPLOT capillary column; J&W Scientific) within a gas chromatograph (Agilent 7890A) equipped with a flame ionization detector (FID) and an electron capture detector (ECD). The carrier flow was alternated from the FID to the ECD using a Dean's switch[®] (Agilent Technologies) which allowed the quantification of both CH₄ and N₂O from a single sample. The oven temperature was typically maintained at 38°C, although this subsequently was decreased to 30°C in August 2016 to better resolve the CH₄ peak when partial overlap with an O₂ peak occurred. The CH₄ and N₂O data sets are attached as Data Sets S1 and S2, respectively, in the supporting information and have been deposited with the Biological and Chemical Oceanography Data Management Office.

Calibration of the analytical system was conducted using gaseous standards purchased from Scott-Marin (CH₄: 20.15 ± 1% ppmv; N₂O: 4.81 ± 2% ppmv in a balance of N₂) and NOAA (CH₄: 1965.32 ppbv; N₂O: 357.56 ppbv in a balance of air). From March 2016 onward, the calibration for CH₄ and N₂O was compared against reference standards prepared by John Bullister at NOAA PMEL on behalf of SCOR Working Group #143. In all instances, standards were injected prior to the purge and trap setup and therefore passed through the purge chamber and gas drying apparatus. A linear curve was applied to the CH₄ calibration values, and a polynomial curve was fitted to the N₂O calibration values. The precision of CH₄ measurements for surface seawater with concentrations of 2.57 ± 0.07 (SD) nmol kg⁻¹ (*n* = 14), as calculated by the coefficient of variation, was 3%. The accuracy of CH₄ measurements was evaluated by analyzing filtered (0.2 μm) seawater samples that had been equilibrated with atmospheric air at a range of set temperatures between 19–27°C which were maintained using a water bath. The measured values agreed within 2.4 ± 0.9% of predicted values. The precision of N₂O measurements in surface seawater, with concentrations of 6.47 ± 0.14 (SD) nmol kg⁻¹ (*n* = 14), as calculated by the coefficient of variation, was 2%. Using the same air-equilibrated seawater setup as described for CH₄, the accuracy of N₂O measurements was 2.6 ± 1.9% of predicted values. The additional data sets required for calculation of gas concentrations and fluxes were provided by separate research programs. Water column measurements of temperature, salinity, oxygen, and phosphate were provided by the HOT program (<http://hahana.soest.hawaii.edu/hot/methods/results.html>).

The sea-air flux (F , μmol m⁻² d⁻¹) of CH₄ and N₂O was calculated as

$$F = k(C_w - C_{eq})$$

where k is the gas transfer velocity (m d⁻¹), C_w is the ambient concentration of the gas dissolved in water (μmol m⁻³), and C_{eq} is the concentration of the gas at equilibrium with the atmosphere. C_{eq} was determined from the solubility equations for N₂O (Weiss and Price, 1980) and for CH₄ (Wiesenburg & Guinasso, 1979), and using the atmospheric concentrations measured at the NOAA Mauna Loa Observatory (available online at <https://www.esrl.noaa.gov/gmd/dv/data/>) (Dlugokencky et al., 2016). The wind speed data, used to calculate k , for January 2009 to May 2016 were taken from the Woods Hole Oceanographic Institution-Hawaii Ocean Time-series Site (WHOTS) mooring available at <http://uop.whoi.edu/projects/WHOTS/whotsdata.html> and normalized to a height of 10 m above sea surface (Smith, 1988). The wind data from July–December 2016 derive from the Blended Sea Winds data product for the coordinates 22°45'N and 158°00'W (Zhang et al., 2006) (Figure S1). k was determined for each gas using the wind speed parameterization of Wanninkhof (2014) and the Schmidt numbers for each gas, calculated using the updated empirical temperature dependence formulations (Wanninkhof, 2014). To calculate the sea-air fluxes, the mean k value for the week prior to sample collection was used.

For assessing long-term hydrographic changes at Station ALOHA, ocean surface current velocities were used from the diagnostic Surface CUrrents from Diagnostic (SCUD) model which combines AVISO maps of sea level

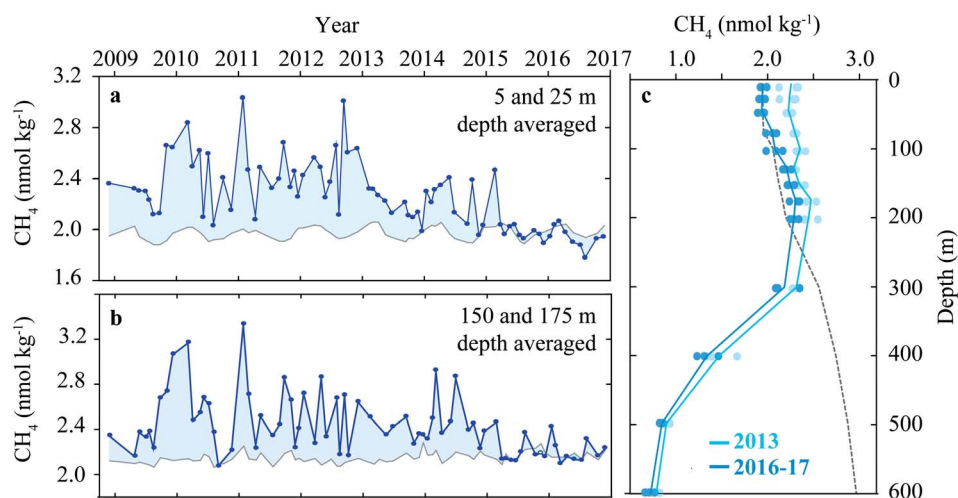


Figure 1. Methane concentrations at Station ALOHA. (a) Surface (5 and 25 m averaged) CH₄ concentrations. (b) Lower euphotic zone (150 and 175 m averaged) CH₄ concentrations. The shaded area in Figures 1a and 1b represents saturation relative to atmospheric equilibrium. (c) Vertical profiles of CH₄ concentrations between the surface and 600 m. The blue lines represent the average concentration of 3 profiles collected during 2013 and also during 2016–2017 with the individual values shown as symbols. The CH₄ concentration at atmospheric equilibrium is shown as a grey line.

anomalies and QuikSCAT surface winds (Maximenko & Hafner, 2010). The mixed layer depth was calculated based on a seawater potential density anomaly of 0.125 kg m^{-3} from the sea surface.

3. Results and Discussion

3.1. Methane

The range of dissolved CH₄ concentrations reported in the surface waters of the global ocean away from coastal, benthic, or hydrothermal influences is 2–4 nmol kg⁻¹, which is broadly equivalent to 100–220% supersaturation with respect to atmospheric equilibrium (Reeburgh, 2007). Historically, the oligotrophic NPSG conformed to this global distribution pattern of CH₄ supersaturation with measurements prior to this current study of 2–4 nmol kg⁻¹ at Station ALOHA (Holmes et al., 2000; Tilbrook & Karl, 1995) and hydrographic surveys across the NPSG measuring a mean CH₄ mixing ratio of 105% supersaturation (Bates et al., 1996). The ongoing CH₄ time series measurements at Station ALOHA likewise recorded supersaturated CH₄ values until ~2015 (Figure 1). During 2009–2013, CH₄ concentrations (5–25 m averaged) ranged from 2.1 to 3.1 nmol kg⁻¹ with an overall mean concentration of 2.5 ± 0.2 (standard deviation: SD) nmol kg⁻¹, equivalent to a saturation value of $105 \pm 2\%$ (Figure 1a and Table 1). However, in 2013 dissolved CH₄ concentrations in surface waters began to decline and in 2016 CH₄ concentrations at depths of 5–25 m averaged 1.9 ± 0.1 nmol kg⁻¹, which is equivalent to a saturation value of $97 \pm 3\%$. These comparatively low CH₄ concentrations, which have been measured since 2015, are most prevalent in the upper 100 m of the water column. Below depths of 100 m, CH₄ concentrations increase to produce a small CH₄ maximum in the lower euphotic zone and the mean value of CH₄ at depths of 150–175 m during 2016 was 2.2 ± 0.2 nmol kg⁻¹, equivalent to slightly supersaturated values of $102 \pm 7\%$ (Figure 1b). Elevated CH₄ values in the lower euphotic zone at Station ALOHA, as observed in this study, have been previously reported (Holmes et al., 2000), although this feature has not always been observed (Tilbrook & Karl, 1995). Seasonal fluctuations in sea surface temperature will cause predicted CH₄ concentrations to vary from 1.9 to 2.1 nmol kg⁻¹, but no seasonal fluctuations were present in measured concentrations (Figure 1a). Deeper in the mesopelagic zone, CH₄ profiles show a rapid decrease in concentration (Figure 1c). The saturation inflection point, that is, the depth at which CH₄ becomes undersaturated, occurs at depths of 300–400 m as previously described in other oceanic locations (Rehder et al., 1999; Scranton & Brewer, 1977).

It is not clear what caused a change in CH₄ production and/or loss in the surface waters of the NPSG. The near-surface local physical and biogeochemical conditions at Station ALOHA during 2009–2016 were analyzed to determine any changes to the hydrographic conditions. Climate-driven regime shifts have previously been identified in the NPSG (Karl et al., 1995), and changes in circulation patterns were

Table 1
Water Column Inventories and Flux Estimates (Mean and SD) for CH₄ and N₂O

	Methane	Methane	Nitrous oxide
	2008–14	2015–16	2008–2016
0–25 m concentration (nmol kg ⁻¹)	2.3 ± 0.2	2.0 ± 0.1	6.5 ± 0.3
0–25 m saturation (%)	120 ± 12	99 ± 6	102 ± 3
0–175 m inventory (μmol m ⁻²)	442 ± 42	366 ± 18	1243 ± 59
Sea-air flux (μmol m ⁻² d ⁻¹)	1.5 ± 1.2	-0.2 ± 0.5	0.5 ± 1.0
Number of profiles (#)	57	19	79

Note. The CH₄ measurements have been separated into two time periods to reflect the historic and current values.

evaluated as implicated in the temporal variability of dissolved inorganic carbon and pCO₂ (Keeling et al., 2004). As shown by the North Pacific Gyre Oscillation (NPGO) index, there was a strong El Niño which began in 2014 and ended in 2016 (Figure S1). The NPGO is defined as the second dominant mode of sea surface height anomalies in the central and east Pacific Ocean, and it closely tracks the second dominant mode of sea surface temperature anomalies in the North Pacific (Di Lorenzo et al., 2008). The 2014–2016 El Niño caused an oscillation in several hydrographic parameters including sea surface temperature and sea surface salinity (Figure S1). Surface current direction was also more to the southwest during 2015–2016 compared to the northwest in 2011–12 (Figure S2), although it is unclear

how a change in current direction would be associated with a decrease in CH₄ concentrations as there are no identified areas of the NPSG which have CH₄ concentrations at near-equilibrium (Bates et al., 1996; Sansone et al., 2001; Tilbrook & Karl, 1995). To better understand the possible causes of the decrease in CH₄ concentration, the mechanisms for CH₄ production in the open ocean are considered. The CH₄ in the surface ocean is of biogenic origin and most likely produced by aerobic metabolism, given the difficulty for anaerobic habitats to persist for long periods of time in the oxygenated surface waters of the open ocean (Ploug et al., 1997) and the identification of potential microbial metabolic mechanisms (Karl et al., 2008). It is now known that under phosphorus-stressed conditions, CH₄ can be produced aerobically through the degradation of methylphosphonate by a wide variety of microorganisms including cyanobacteria (Beversdorf et al., 2010) and heterotrophic bacteria (Carini et al., 2014; Repeta et al., 2016). Therefore, there exists a link between aerobic CH₄ production and phosphorus cycling (Karl et al., 2008; Metcalf et al., 2012) which has been observed in both marine (del Valle & Karl, 2014) and freshwater environments (Wang et al., 2017). Prior to the observed decline in CH₄ concentrations in surface waters of Station ALOHA, the Hawaii Ocean Time-series (HOT) program documented a twofold to threefold increase in near-surface (5 and 25 m depth-averaged) phosphate concentrations, from 55.8 ± 26.6 (SD) nmol kg⁻¹ in 2011 to 131.6 ± 30.6 (SD) nmol kg⁻¹ in 2012 (Figure 2). Phosphate concentrations subsequently declined although values in excess of 100 nmol kg⁻¹ were still being recorded in January–February 2015 and April 2016. The mean phosphate concentration at 5–25 m during 2016 was 75.3 ± 15.8 (SD) nmol kg⁻¹. We hypothesize that the decrease in net CH₄ production was associated with changes in phosphate concentrations in the surface waters. To date, investigations into the effect of phosphate availability on CH₄ production have used experi-

mental incubations with variability in CH₄ concentrations observed after a period of 1–3 days (Beversdorf et al., 2010; Carini et al., 2014; Repeta et al., 2016). The increased phosphate observed in the NPSG in 2012 was not immediately followed by a suppression of net CH₄ production, and an ~3 year lag time was observed between peak phosphate concentrations and the period when CH₄ concentrations reached values equivalent to equilibrium with the atmosphere. For context, a cessation in CH₄ production with a standing stock of 2.3 nmol kg⁻¹ and a sea-air flux of 1.5 μmol m⁻² d⁻¹ (Table 1) would cause CH₄ concentrations to reach saturation in approximately 2 weeks. The lag time could potentially be explained by the availability of inorganic and organic phosphorus in the upper water column. It is conceivable that the more rapid cycling of inorganic phosphate, with a peak concentration in 2012, was replaced with followed by a much slower cycling of the dissolved organic phosphorus pool, which is known to represent a much larger pool of phosphate (Karl, 2014). An increase in organic phosphorus relative to other years might be expected to increase CH₄ production if there is increased availability of methylphosphonate. However, it is the availability of methylphosphonates relative to other organic forms of phosphorus, for example, phosphoesters, nucleotide triphosphates, polyphosphatase

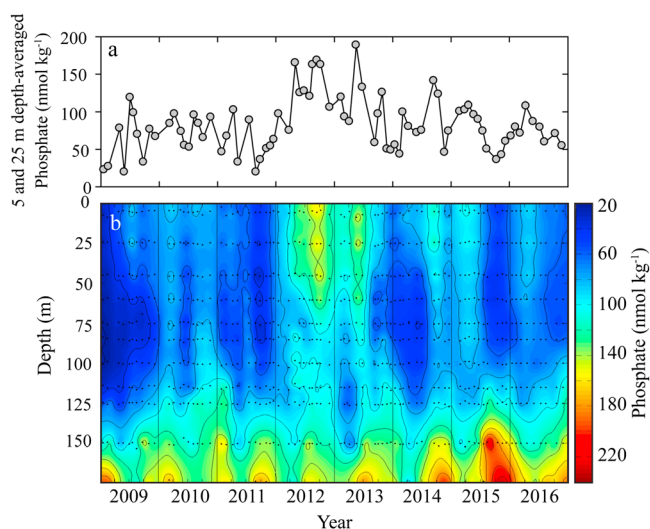


Figure 2. Phosphate concentrations at Station ALOHA. (a) Depth-averaged (5 and 25 m) phosphate concentrations. (b) Contour plot of phosphate concentrations in the upper 175 m at Station ALOHA between 2009 and 2016. The pulse of elevated phosphate in the surface waters is evident during 2012–2014.

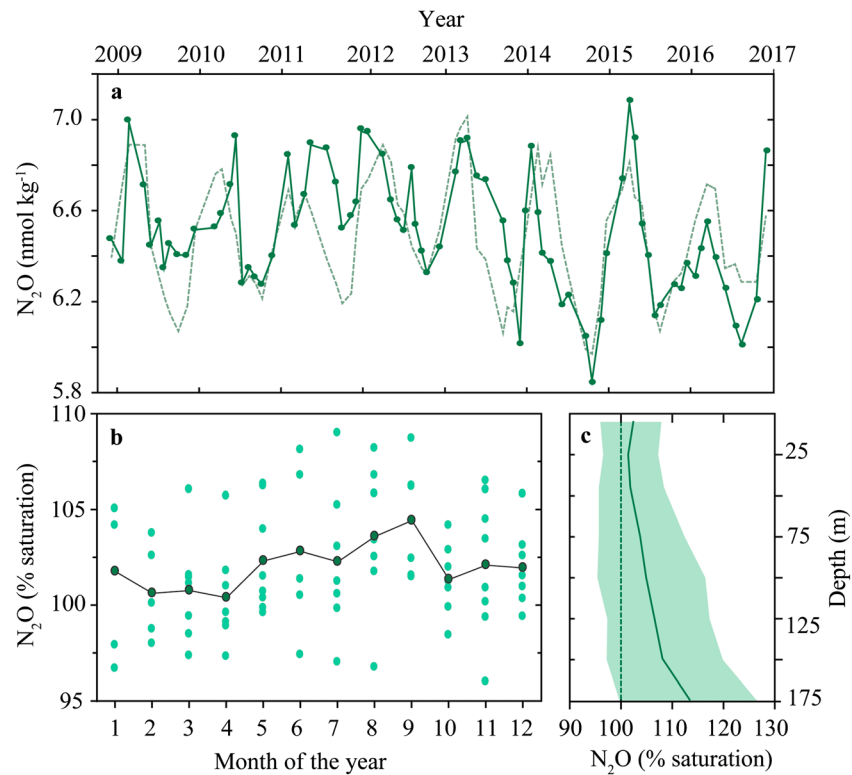


Figure 3. Nitrous oxide at Station ALOHA. (a) Surface (5 and 25 m averaged) N_2O concentrations (solid line) compared with the predicted N_2O values when the ocean is in equilibrium with the atmosphere (dashed line). (b) Monthly aggregated values of N_2O saturation with the mean (green line and symbols) and the individual data points. (c) Vertical profiles (5–175 m) of N_2O saturation at Station ALOHA from December 2008 to December 2016 with the mean (solid line) and the 5th to 95th percentile (shaded area) ($n = 77$). The dashed line distinguishes the 100% saturation.

(Dyrman et al., 2007; Karl & Björkman, 2015), and the microbial demand for phosphorus, that will influence CH_4 production. Dissolved organic phosphorus measurements were not conducted at Station ALOHA during 2008–2016 and therefore changes in the magnitude and the composition are unknown. In addition to the production of CH_4 , loss processes including microbial oxidation and sea-air fluxes also determine the net concentration of CH_4 . Due to the effect of temperature on microbial CH_4 oxidation (Bussman et al., 2015), an increase in the rate of CH_4 oxidation could have occurred during the period of elevated sea surface temperature (Figure S1). However, the interannual differences in temperature are much smaller than the seasonal fluctuations in seawater temperature of 3–4°C at Station ALOHA and there is no observed seasonal cycle in CH_4 concentrations (Figure 1). Furthermore, the rates of oxidation reported to date are much lower compared to the loss of CH_4 to the overlying atmosphere (Ward et al., 1987).

3.2. Nitrous Oxide

The temporal trends of dissolved N_2O concentrations are very different from those described for CH_4 . During 2008–2016, near-surface (5 and 25 m averaged) concentrations of N_2O ranged from 5.9–7.4 nmol kg^{-1} with an overall mean concentration of 6.5 ± 0.3 (SD) nmol kg^{-1} , which is equivalent to a saturation value of $102 \pm 3\%$ (Figure 3a). The mean saturation state for N_2O during 2008–2016 is in agreement with the $\sim 103\%$ supersaturation previously reported using shipboard automated measurements (Nevison et al., 1995; Weiss et al., 1992). Because N_2O is approximately 20 times more soluble than CH_4 , dissolved N_2O concentrations are more heavily influenced by seasonal and interannual temperature oscillations. During 2008–2016, seasonal changes in surface seawater temperature ranged from 23 to 27°C which is sufficient to cause a variance of 1 nmol kg^{-1} in predicted N_2O concentrations based on atmospheric equilibrium. The time series measurements at Station ALOHA reflected this predicted variability with the lowest concentrations of N_2O (5.9 nmol kg^{-1}) occurring during the warm summer in 2014 when the 2014–2016 El Niño was developing (Figure 3a). By aggregating the measurements into a single year, it is evident that supersaturation

of N_2O is significantly higher (t test, $p < 0.05$) during May–September ($103 \pm 3.5\%$) than October–April ($101 \pm 2.8\%$) (Figure 3b). A contributing factor to N_2O supersaturation during May–September is the warming of the surface seawater if it occurs at a more rapid rate than the ventilation of N_2O to the atmosphere. Such conditions are facilitated during summer by the calm conditions and stratified water column. Moreover, the steady increase of N_2O supersaturation during May–September coincides with the increase of new production (Böttjer et al., 2017) and the buildup of particulate nitrogen during the summer period at Station ALOHA. Increased nitrogen availability would presumably favor nitrification, the metabolic process responsible for N_2O production in the surface waters at Station ALOHA (Dore et al., 1998; Dore & Karl, 1996). An estimate of N_2O production can be calculated from the difference between the upward flux from the lower euphotic zone (Figure 3c) and sea-air gas exchange (Table 1). The lower euphotic zone (i.e., depths of 100–175 m) has higher concentrations of N_2O in excess of the values predicted for atmospheric equilibrium (Figure 4). The depth-related changes between the upper and lower euphotic zone are subtle with an increase of approximately 1.5 nmol kg^{-1} occurring gradually across a 150 m depth horizon. The shallow vertical gradient in N_2O concentrations throughout the euphotic zone results in an upward flux to the near-surface waters which can be calculated using the N_2O concentration gradient across the base of the mixed layer as defined by an offset of 0.125 in potential density anomaly (σ_θ) and applying an eddy diffusivity coefficient of $1.5 \text{ cm}^2 \text{ s}^{-1}$ which is applicable for these depths in the water column at Station ALOHA (Emerson et al., 1995). The resulting upward flux of 0.15 ± 0.17 (SD) $\text{nmol N}_2\text{O m}^{-2} \text{ d}^{-1}$ into the mixed layer is exceeded by loss of N_2O to the atmosphere via sea-air gas exchange which is calculated at 0.5 ± 0.9 (SD) $\mu\text{mol N}_2\text{O m}^{-2} \text{ d}^{-1}$ (Table 1). The difference between the upward flux and sea-air gas exchange of $0.35 \mu\text{mol N}_2\text{O m}^{-2} \text{ d}^{-1}$ indicates that the majority of N_2O in the surface waters results from in situ production assuming steady state conditions and no horizontal advection.

Acknowledgments

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4. Conclusions

In summary, near-monthly measurements of CH_4 and N_2O during 2008–2016 have yielded new insights into the cycling of these trace gases in the euphotic zone of the oligotrophic ocean. We show that CH_4 concentrations in the surface ocean have declined since 2013 and are now at atmospheric equilibrium, indicating decreased in situ net CH_4 production. The decline in CH_4 concentrations is a rare observation of long-term persistent changes in the surface waters of the open ocean. Temporal variability has been reported over shorter timescales of days (Weller et al., 2013) and seasons (Bates et al., 1996); however, persistent long-term trends in the open ocean are both unique and unexpected. We hypothesize that the long-term decrease in water column CH_4 inventories was triggered by the elevated phosphate that occurred during 2012–2013. It is now imperative to determine how far the decline in CH_4 extends across the NPSG and to continue the long-term observations to document further changes in the water column CH_4 inventory. Temporal fluctuations of surface phosphate concentrations are known to occur in the NPSG on subdecadal timescales (Karl et al., 1995), and conducting the relevant biogeochemical measurements of sufficient resolution might provide a mechanistic explanation for variability in the net balance of CH_4 fluxes in the NPSG. In contrast to CH_4 , N_2O concentrations are more predictable in the NPSG. Lower seasonal variability is observed in the NPSG compared to other oceanic environments (Farias et al., 2015); however, increased supersaturation of N_2O is evident during the months of May–September. The comparability of CH_4 and N_2O measurements being conducted at disparate time series sites, hydrographic survey lines and discrete oceanographic expeditions is being improved through an ongoing global intercalibration effort being led by Scientific Commission on Oceanic Research (SCOR) Working Group #143. This coordinated effort will greatly facilitate resolving the temporal and spatial variability associated with CH_4 and N_2O across the global oceans and thereby help to determine the hydrographic and biogeochemical factors that influence their ambient concentrations.

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