



## 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 (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O), is reported for the upper water column at Station ALOHA in the North Pacific Subtropical Gyre. Measured concentrations of N<sub>2</sub>O conform to predicted values with an increase in saturation during the summer period. In contrast, CH<sub>4</sub> 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 CH<sub>4</sub> production. The decrease in CH<sub>4</sub> followed on from fluctuations in phosphate concentrations supporting the hypothesized link between microbial metabolism of phosphorus and the global biogeochemical cycle of CH<sub>4</sub>. At this current time, future trends in the net CH<sub>4</sub> production in the North Pacific Subtropical Gyre are uncertain and specifically whether the surface ocean will be a net source or sink for CH<sub>4</sub>.

## 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 (CO<sub>2</sub>), 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 CO<sub>2</sub> have been reported (Dore et al., 2003; Keeling et al., 2004; Winn et al., 1998). Two other important greenhouse gases are nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>), 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<sup>-1</sup> for CH<sub>4</sub> and 1.2–4 Tg N yr<sup>-1</sup> for N<sub>2</sub>O (Rhee et al., 2009). Herein, we report on the seasonal and interannual variability of N<sub>2</sub>O and CH<sub>4</sub> at Station ALOHA which has been measured at near-monthly intervals since December 2008.

## 2. Analytical Methods

Discrete seawater samples for CH<sub>4</sub> and N<sub>2</sub>O 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 CH<sub>4</sub> and N<sub>2</sub>O for this timeframe using the bottles and stoppers as described. Analysis of CH<sub>4</sub> and N<sub>2</sub>O 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<sup>®</sup> drier (Perma Pure LLC) and a Drierite<sup>®</sup> trap (VWR) to remove water vapor and then passed through an Ascarite trap to remove CO<sub>2</sub>, 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<sup>®</sup> (Agilent Technologies) which allowed the quantification of both CH<sub>4</sub> and N<sub>2</sub>O 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 CH<sub>4</sub> peak when partial overlap with an O<sub>2</sub> peak occurred. The CH<sub>4</sub> and N<sub>2</sub>O 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.

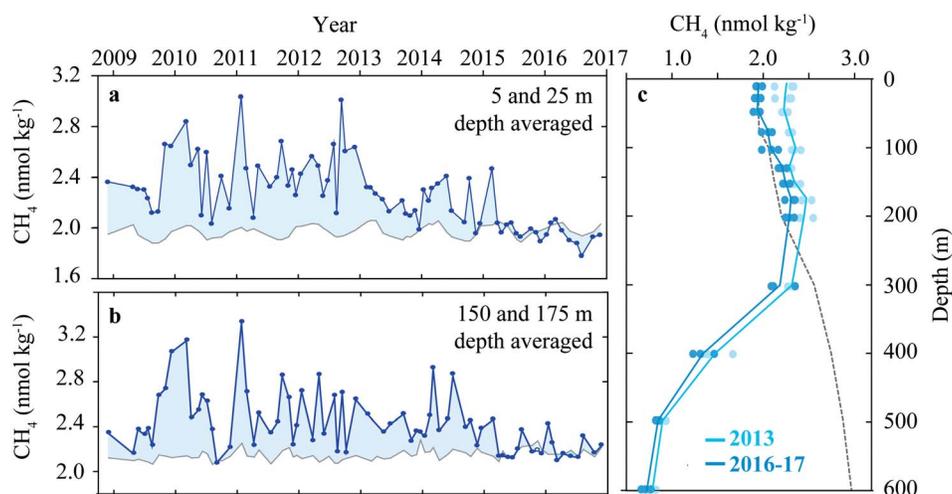
Calibration of the analytical system was conducted using gaseous standards purchased from Scott-Marine (CH<sub>4</sub>: 20.15 ± 1% ppmv; N<sub>2</sub>O: 4.81 ± 2% ppmv in a balance of N<sub>2</sub>) and NOAA (CH<sub>4</sub>: 1965.32 ppbv; N<sub>2</sub>O: 357.56 ppbv in a balance of air). From March 2016 onward, the calibration for CH<sub>4</sub> and N<sub>2</sub>O 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 CH<sub>4</sub> calibration values, and a polynomial curve was fitted to the N<sub>2</sub>O calibration values. The precision of CH<sub>4</sub> measurements for surface seawater with concentrations of 2.57 ± 0.07 (SD) nmol kg<sup>-1</sup> (*n* = 14), as calculated by the coefficient of variation, was 3%. The accuracy of CH<sub>4</sub> 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 N<sub>2</sub>O measurements in surface seawater, with concentrations of 6.47 ± 0.14 (SD) nmol kg<sup>-1</sup> (*n* = 14), as calculated by the coefficient of variation, was 2%. Using the same air-equilibrated seawater setup as described for CH<sub>4</sub>, the accuracy of N<sub>2</sub>O 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<sup>-2</sup> d<sup>-1</sup>) of CH<sub>4</sub> and N<sub>2</sub>O was calculated as

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

where  $k$  is the gas transfer velocity (m d<sup>-1</sup>),  $C_w$  is the ambient concentration of the gas dissolved in water (μmol m<sup>-3</sup>), and  $C_{eq}$  is the concentration of the gas at equilibrium with the atmosphere.  $C_{eq}$  was determined from the solubility equations for N<sub>2</sub>O (Weiss and Price, 1980) and for CH<sub>4</sub> (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) CH<sub>4</sub> concentrations. (b) Lower euphotic zone (150 and 175 m averaged) CH<sub>4</sub> concentrations. The shaded area in Figures 1a and 1b represents saturation relative to atmospheric equilibrium. (c) Vertical profiles of CH<sub>4</sub> 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 CH<sub>4</sub> 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  $0.125 \text{ kg m}^{-3}$  from the sea surface.

### 3. Results and Discussion

#### 3.1. Methane

The range of dissolved CH<sub>4</sub> concentrations reported in the surface waters of the global ocean away from coastal, benthic, or hydrothermal influences is  $2\text{--}4 \text{ nmol kg}^{-1}$ , which is broadly equivalent to  $100\text{--}220\%$  supersaturation with respect to atmospheric equilibrium (Reeburgh, 2007). Historically, the oligotrophic NPSG conformed to this global distribution pattern of CH<sub>4</sub> supersaturation with measurements prior to this current study of  $2\text{--}4 \text{ nmol kg}^{-1}$  at Station ALOHA (Holmes et al., 2000; Tilbrook & Karl, 1995) and hydrographic surveys across the NPSG measuring a mean CH<sub>4</sub> mixing ratio of  $105\%$  supersaturation (Bates et al., 1996). The ongoing CH<sub>4</sub> time series measurements at Station ALOHA likewise recorded supersaturated CH<sub>4</sub> values until  $\sim 2015$  (Figure 1). During 2009–2013, CH<sub>4</sub> concentrations (5–25 m averaged) ranged from  $2.1$  to  $3.1 \text{ nmol kg}^{-1}$  with an overall mean concentration of  $2.5 \pm 0.2$  (standard deviation: SD)  $\text{nmol kg}^{-1}$ , equivalent to a saturation value of  $105 \pm 2\%$  (Figure 1a and Table 1). However, in 2013 dissolved CH<sub>4</sub> concentrations in surface waters began to decline and in 2016 CH<sub>4</sub> concentrations at depths of 5–25 m averaged  $1.9 \pm 0.1 \text{ nmol kg}^{-1}$ , which is equivalent to a saturation value of  $97 \pm 3\%$ . These comparatively low CH<sub>4</sub> concentrations, which have been measured since 2015, are most prevalent in the upper 100 m of the water column. Below depths of 100 m, CH<sub>4</sub> concentrations increase to produce a small CH<sub>4</sub> maximum in the lower euphotic zone and the mean value of CH<sub>4</sub> at depths of 150–175 m during 2016 was  $2.2 \pm 0.2 \text{ nmol kg}^{-1}$ , equivalent to slightly supersaturated values of  $102 \pm 7\%$  (Figure 1b). Elevated CH<sub>4</sub> 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 CH<sub>4</sub> concentrations to vary from  $1.9$  to  $2.1 \text{ nmol kg}^{-1}$ , but no seasonal fluctuations were present in measured concentrations (Figure 1a). Deeper in the mesopelagic zone, CH<sub>4</sub> profiles show a rapid decrease in concentration (Figure 1c). The saturation inflection point, that is, the depth at which CH<sub>4</sub> becomes undersaturated, occurs at depths of  $300\text{--}400 \text{ m}$  as previously described in other oceanic locations (Rehder et al., 1999; Scranton & Brewer, 1977).

It is not clear what caused a change in CH<sub>4</sub> 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 CH<sub>4</sub> and N<sub>2</sub>O

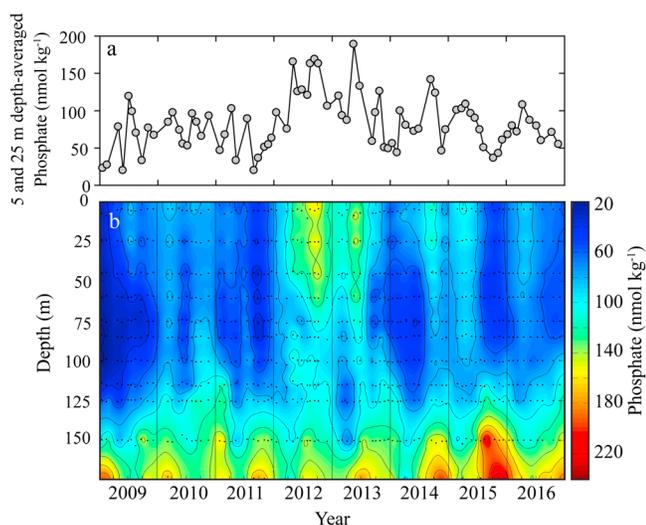
	Methane	Methane	Nitrous oxide
	2008–14	2015–16	2008–2016
0–25 m concentration (nmol kg <sup>-1</sup> )	2.3 ± 0.2	2.0 ± 0.1	6.5 ± 0.3
0–25 m saturation (%)	120 ± 12	99 ± 6	102 ± 3
0–175 m inventory (μmol m <sup>-2</sup> )	442 ± 42	366 ± 18	1243 ± 59
Sea-air flux (μmol m <sup>-2</sup> d <sup>-1</sup> )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

Note. The CH<sub>4</sub> measurements have been separated into two time periods to reflect the historic and current values.

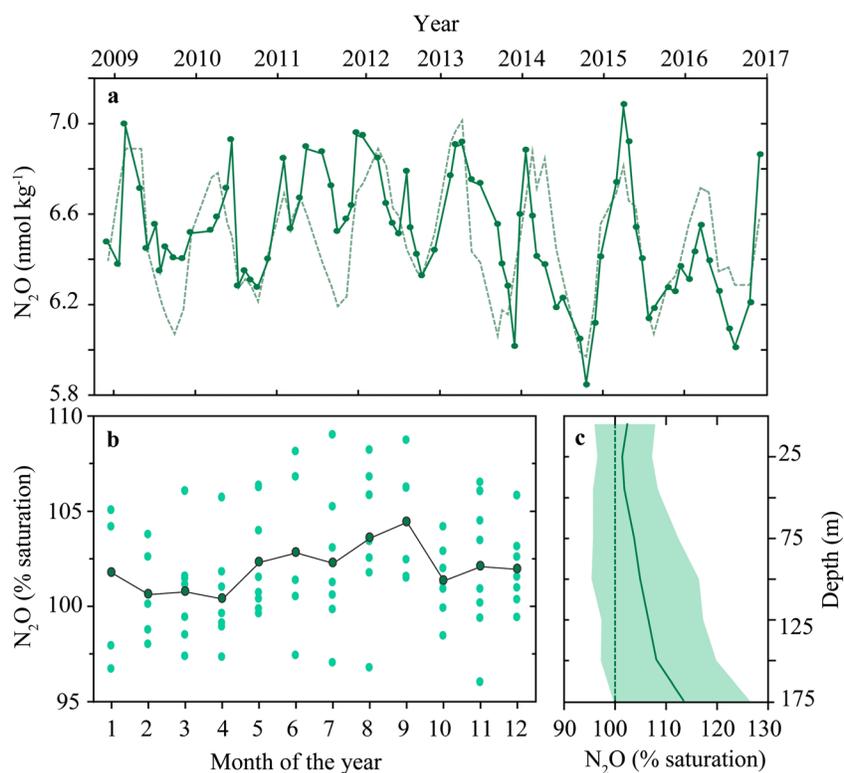
evaluated as implicated in the temporal variability of dissolved inorganic carbon and pCO<sub>2</sub> (Keeling et al., 2004). As shown by the North Pacific Gyre Oscillation (NPGO) index, there was a strong El Niño which began in 2014 and ended in 2016 (Figure S1). The NPGO is defined as the second dominant 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 CH<sub>4</sub> concentrations as there are no identified areas of the NPSG which have CH<sub>4</sub> 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 CH<sub>4</sub> concentration, the mechanisms for CH<sub>4</sub> production in the open ocean are considered. The CH<sub>4</sub> 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, CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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<sup>-1</sup> in 2011 to 131.6 ± 30.6 (SD) nmol kg<sup>-1</sup> in 2012 (Figure 2). Phosphate concentrations subsequently declined although values in excess of 100 nmol kg<sup>-1</sup> 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<sup>-1</sup>. We hypothesize that the decrease in net CH<sub>4</sub> production was associated with changes in phosphate concentrations in the surface waters. To date, investigations into the effect of phosphate availability on CH<sub>4</sub> production have used experi-

mental incubations with variability in CH<sub>4</sub> 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 CH<sub>4</sub> production, and an ~3 year lag time was observed between peak phosphate concentrations and the period when CH<sub>4</sub> concentrations reached values equivalent to equilibrium with the atmosphere. For context, a cessation in CH<sub>4</sub> production with a standing stock of 2.3 nmol kg<sup>-1</sup> and a sea-air flux of 1.5 μmol m<sup>-2</sup> d<sup>-1</sup> (Table 1) would cause CH<sub>4</sub> 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 CH<sub>4</sub> 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)  $\text{N}_2\text{O}$  concentrations (solid line) compared with the predicted  $\text{N}_2\text{O}$  values when the ocean is in equilibrium with the atmosphere (dashed line). (b) Monthly aggregated values of  $\text{N}_2\text{O}$  saturation with the mean (green line and symbols) and the individual data points. (c) Vertical profiles (5–175 m) of  $\text{N}_2\text{O}$  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  $\text{CH}_4$  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  $\text{CH}_4$ , loss processes including microbial oxidation and sea-air fluxes also determine the net concentration of  $\text{CH}_4$ . Due to the effect of temperature on microbial  $\text{CH}_4$  oxidation (Bussman et al., 2015), an increase in the rate of  $\text{CH}_4$  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  $\text{CH}_4$  concentrations (Figure 1). Furthermore, the rates of oxidation reported to date are much lower compared to the loss of  $\text{CH}_4$  to the overlying atmosphere (Ward et al., 1987).

### 3.2. Nitrous Oxide

The temporal trends of dissolved  $\text{N}_2\text{O}$  concentrations are very different from those described for  $\text{CH}_4$ . During 2008–2016, near-surface (5 and 25 m averaged) concentrations of  $\text{N}_2\text{O}$  ranged from 5.9–7.4  $\text{nmol kg}^{-1}$  with an overall mean concentration of  $6.5 \pm 0.3$  (SD)  $\text{nmol kg}^{-1}$ , which is equivalent to a saturation value of  $102 \pm 3\%$  (Figure 3a). The mean saturation state for  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  is approximately 20 times more soluble than  $\text{CH}_4$ , dissolved  $\text{N}_2\text{O}$  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  $\text{nmol kg}^{-1}$  in predicted  $\text{N}_2\text{O}$  concentrations based on atmospheric equilibrium. The time series measurements at Station ALOHA reflected this predicted variability with the lowest concentrations of  $\text{N}_2\text{O}$  (5.9  $\text{nmol kg}^{-1}$ ) 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  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  supersaturation during May–September is the warming of the surface seawater if it occurs at a more rapid rate than the ventilation of  $\text{N}_2\text{O}$  to the atmosphere. Such conditions are facilitated during summer by the calm conditions and stratified water column. Moreover, the steady increase of  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  production in the surface waters at Station ALOHA (Dore et al., 1998; Dore & Karl, 1996). An estimate of  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  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  $1.5 \text{ nmol kg}^{-1}$  occurring gradually across a 150 m depth horizon. The shallow vertical gradient in  $\text{N}_2\text{O}$  concentrations throughout the euphotic zone results in an upward flux to the near-surface waters which can be calculated using the  $\text{N}_2\text{O}$  concentration gradient across the base of the mixed layer as defined by an offset of 0.125 in potential density anomaly ( $\sigma_\theta$ ) 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  $0.15 \pm 0.17$  (SD)  $\text{nmol N}_2\text{O m}^{-2} \text{ d}^{-1}$  into the mixed layer is exceeded by loss of  $\text{N}_2\text{O}$  to the atmosphere via sea-air gas exchange which is calculated at  $0.5 \pm 0.9$  (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  $\text{N}_2\text{O}$  in the surface waters results from in situ production assuming steady state conditions and no horizontal advection.

#### Acknowledgments

The data set presented here resulted from the dedicated sample collection by members of the HOT program and additional individuals including D. A. Viviani, D. Böttjer, and G. Terlouw. We are particularly grateful to S. Curless and the leadership of M. Church during 2009–2016. We thank N. Maximenko and J. Hafner for assistance with the surface current data and the two anonymous reviewers who provided helpful comments on the manuscript. The dissolved gas data used in this study can be found in the supporting information. The atmospheric concentrations of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  measured at the NOAA Mauna Loa Observatory are available online at: <https://www.esrl.noaa.gov/gmd/dv/data/>. The wind data from the WHOTS mooring are available online at <http://uop.whoi.edu/projects/WHOTS/whots-data.htm> and are funded in part by the Ocean Observing and Monitoring Division, Climate Program Office (100007298), the National Oceanic and Atmospheric Administration under grant NA14OAR4320158 to the Woods Hole Oceanographic Institution, and by NSF grants OCE-0327513 and OCE-752606. This work was supported by grant 3794 from the Gordon and Betty Moore Foundation (D. M. K.). In addition, we acknowledge NSF for support of the HOT program (including the most recent OCE1260164 to M. J. C. and D. M. K.), the Center for Microbial Oceanography: Research and Education (C-MORE; EF0424599 to D. M. K.), the Simons Collaboration on Ocean Processes and Ecology (SCOPE; 329108 to D. M. K.), and the International Balzan Foundation (to D. M. K.). Partial salary support for S. T. W. was provided by the Global Research Laboratory Program (2013K1A1A2A02078278) through the National Research Foundation of Korea (NRF). This work is a contribution of C-MORE and SCOPE.

#### 4. Conclusions

In summary, near-monthly measurements of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  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  $\text{CH}_4$  concentrations in the surface ocean have declined since 2013 and are now at atmospheric equilibrium, indicating decreased in situ net  $\text{CH}_4$  production. The decline in  $\text{CH}_4$  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  $\text{CH}_4$  inventories was triggered by the elevated phosphate that occurred during 2012–2013. It is now imperative to determine how far the decline in  $\text{CH}_4$  extends across the NPSG and to continue the long-term observations to document further changes in the water column  $\text{CH}_4$  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  $\text{CH}_4$  fluxes in the NPSG. In contrast to  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  is evident during the months of May–September. The comparability of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  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  $\text{CH}_4$  and  $\text{N}_2\text{O}$  across the global oceans and thereby help to determine the hydrographic and biogeochemical factors that influence their ambient concentrations.

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