Nitrification and nitrous oxide dynamics in the Southern California Bight

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Abstract

The amount of primary production fueled by upwelled 'new' nitrate can be used to estimate the amount of organic carbon available for export to the deep ocean. Nitrate production in the euphotic zone from the microbial process of nitrification affects these estimates, yet the controls on nitrification in the upper ocean are debated. This study examines how seasonal cycles in primary production influence rates of nitrification fueled both by ammonia and urea-derived nitrogen (N), and how these processes relate to the distribution of the greenhouse gas nitrous oxide (N_2O) using monthly rate measurements from the San Pedro Ocean Time-series (SPOT) station. Nitrification rates were highest at the onset of upwelling and were correlated with depth-integrated primary production in the lower euphotic zone. Similar ammonia and urea-derived N oxidation rates suggest urea is a significant N source fueling nitrification, particularly below the euphotic zone. Nitrification supplied a large proportion of phytoplankton N demand in the lower euphotic zone, implying significant regenerated production. The Southern California Bight was always a source of N_2O to the atmosphere, which likely was advected into the system from the eastern tropical North Pacific, rather than produced locally from nitrification, and ventilated to the atmosphere during upwelling. Together, the results suggest the coupling of N remineralization and primary production in the upper ocean have important implications for the amount of organic carbon available for export out of the surface ocean, but that transport may dominate over local production in explaining local N_2O dynamics.

Introduction

Coastal upwelling regions are the most biologically productive oceanic ecosystems (Chavez and Messié 2009), accounting for a large fraction of carbon export to the deep ocean

(Buesseler 1998). Primary production–CO_2 fixation by phytoplankton–is fueled by a combination of new (supplied from outside the euphotic zone) and regenerated (remineralized within the euphotic zone) nutrients (Dugdale and Goering 1967). The amount of primary production available for export out of the euphotic zone is largely controlled by rates of organic matter remineralization in the surface ocean (Le Moigne et al. 2016). Nitrification, the oxidation of ammonia (NH_3) to nitrite (NO_2^-) and nitrate (NO_3^-) by ammonia- and nitrite-oxidizing microbes, regulates the form of nitrogen (N) available to fuel primary production, and influences N-based estimates of the fraction of carbon available for export to the deep ocean (Eppley and Peterson 1979).

Organic matter export efficiency--the fraction of primary production leaving the euphotic zone--is controlled by the balance between autotrophic and heterotrophic growth (Falkowski et al. 2003). In much of the open ocean, export efficiencies are low, suggesting a tight coupling between primary production and organic matter remineralization in the upper ocean (Buesseler and Boyd 2009). High export efficiencies are often observed when productivity and remineralization are decoupled, for example in response to episodic pulses of upwelled nutrients and at the start of spring phytoplankton blooms (Buesseler 1998; Henson et al. 2019). During periods of low export efficiency, when the coupling between organic matter remineralization and primary production is strongest (Henson et al. 2019), nitrification in the euphotic zone likely supports a larger fraction of the phytoplankton N demand compared to periods of high export efficiency.

Many studies report measurable rates of marine nitrification in the euphotic zone (Ward 2005; Clark et al. 2007; Peng et al. 2018), and nitrification is increasingly considered an important source of nitrate fueling primary production in the surface ocean (Yool et al. 2007;

Stephens et al. 2019). Nitrification is often thought to be inhibited by light and to only occur in waters below the euphotic zone (Merbt et al. 2012). However, it has also been hypothesized that nitrification is controlled by competition with phytoplankton in the surface ocean for ammonium (NH_4^+; Smith et al. 2014; Wan et al. 2018) and micronutrients (Shiozaki et al. 2016; Shafiee et al. 2019) or by top-down factors such as grazing and viral lysis (Zakem et al. 2018). Despite the important implications for understanding the controls on carbon export, the circumstances under which nitrification is important to the euphotic zone N budget remain unclear.

Generally, nitrification rates are low in the upper euphotic zone, peak just below the euphotic zone, and decrease exponentially thereafter (Newell et al. 2013). This pattern suggests organic matter flux, which also declines exponentially with depth (Martin et al. 1987), controls nitrification rates, though few studies have directly examined this relationship with contemporaneous measurements of both processes (Santoro et al. 2017). The connection between organic matter flux and nitrification rates is mediated through NH_4^+, excreted by both bacteria and zooplankton during the degradation of organic matter (Cho and Azam 1999; Saba et al. 2009). However, recent studies indicate dissolved organic N compounds, such as urea, are additional substrates for ammonia-oxidizing archaea (Bayer et al. 2016; Carini et al. 2018) and widely used in marine environments (Santoro et al. 2017; Carini et al. 2018; Kitzinger et al. 2019). Together, these findings suggest the availability of dissolved organic N compounds provides an additional regulation on nitrification; however, it is unclear what proportion of nitrification is fueled by urea relative to NH_3.

Besides controlling N availability for primary production, the activity of ammonia-oxidizing microorganisms also contributes to the production of the greenhouse gas nitrous oxide (N_2O; Santoro et al. 2011; Kozlowski et al. 2016). N_2O yields from nitrification are

elevated under low oxygen (O_2) conditions (Qin et al. 2017), often observed in the mesopelagic of highly productive upwelling systems, a result of elevated organic matter remineralization rates and sluggish circulation (Diaz and Rosenberg 2008). Combined with the physical ventilation of deep N_2O-enriched water during upwelling (Lueker et al. 2003), upwelling systems are considered 'hotspots' of N_2O emissions to the atmosphere (Nevison et al. 2004; Farías et al. 2015). Yet, until recently (Yang et al. 2020), N_2O emission estimates from coastal upwelling regions were poorly constrained in global N_2O budgets (Buitenhuis et al. 2017), partly due to the high temporal and spatial heterogeneity in N_2O production.

The objectives of this study were to investigate the seasonal coupling of primary production and nitrification in an upwelling system, and to determine how these processes relate to N_2O production and emissions. This work was carried out over two seasonal upwelling cycles at the San Pedro Ocean Time-series (SPOT) station in the Southern California Bight (SCB; Fig. 1). We measured ammonia and urea-derived N oxidation rates using ^{15}N tracer additions in relation to primary production and measured N_2O concentrations using gas chromatography monthly for two years. Typical of many upwelling systems, the SCB exhibits seasonality in primary production (Henson and Thomas 2007), and previous studies report seasonal trends in export efficiency (Munro et al. 2013; Haskell et al. 2017).

Methods

Study site and sample collection

SPOT is located in the Pacific Ocean 16 km off the coast of California, USA in San Pedro Basin between Los Angeles and Santa Catalina Island (Fig. 1). In San Pedro Basin, the upper ~250 m of the water column is characterized by the southward flow of northern sourced

waters in the California Current (CC) and the poleward flow of the Southern California Countercurrent (SCC) sourced from the tropics (Dong et al. 2009). Below 250 m, the California Under Current (CUC), originating in the eastern tropical North Pacific (ETNP), flows poleward with maximum influence from 100 m to deeper than 400 m (Bograd et al. 2019). Additionally, water circulation is restricted by a sill in San Pedro Basin at ~740 m.

Samples were collected on monthly cruises between September 2014 and August 2016 aboard the R/V *Yellowfin*. Hydrographic data and water samples were collected during the first year using a 12 x 12 L Niskin bottle rosette equipped with a conductivity, temperature, and depth (CTD) instrument package (SBE 9plus, Sea-Bird Electronics, Bellevue, Washington, USA), including dissolved oxygen (SBE 43) and photosynthetically available radiation (PAR, LI-COR, Biospherical Instruments Inc., San Diego, California, USA) sensors. Due to CTD failure, samples during the second year were collected primarily using manually triggered Go-Flo bottles and depths were chosen using a profiling natural fluorometer (PNF) system and Secchi disk. The PNF was used in year one in tandem with the original PAR sensor ensuring consistency. Nutrient and incubation samples were collected from separate CTD casts than N_2O samples. Upwelling intensity was obtained from the National Oceanic and Atmospheric Administration's (NOAA's) Pacific Fisheries Environmental Laboratory (https://www.pfeg.noaa.gov/).

Water for nutrient samples was collected directly from the rosette and stored on ice then frozen at -20 °C until analysis, with the exception of NH_4^+ samples which were analyzed immediately after collection. Samples for urea concentration were collected in triplicate and filtered using 0.22 μm pore size PES Sterivex filters (MilliporeSigma, Burlington, Massachusetts, USA) prior to freezing. Nitrite plus nitrate (NO_x^-) and phosphate (PO_4^{3-}) samples were analyzed unfiltered in triplicate at the Marine Science Institute Analytical Laboratory at the

University of California, Santa Barbara. Concentrations of urea and NH_4^+ were measured using previously described methods (Price and Harrison 1987; Goeyens et al. 1998; Holmes et al. 1999), with mean detection limits of 36 ± 38 nmol L^{-1} and 14 ± 8 nmol L^{-1} for urea and NH_4^+, respectively, with the detection limit for each run defined as the concentration of the blank plus three times the standard deviation of the lowest standard. Urea and NH_4^+ analyses had per run precisions of 16 ± 13 nmol L^{-1} and 7 ± 8 nmol L^{-1}, respectively, based on the standard deviation of either the 100 or 200 nmol L^{-1} standard. Chlorophyll-a (Chl *a*) was measured in triplicate by filtering whole seawater onto GF/F filters using previously described methods (Holm-Hansen and Riemann 1978).

Primary production was measured by quantifying the rate of CO_2 fixation via $H^{13}CO_3$ uptake. Quadruplicate 2 L samples were collected and amended to a final concentration of ~25 μmol L^{-1} of $H^{13}CO_3$. A single bottle was filtered immediately after isotope addition to establish a T_0 atom% ^{13}C of the particulate carbon for each depth. The remaining triplicate replicate bottles were placed in circulating temperature-controlled incubators at ambient temperature and shaded by different mesh size combinations of aluminet screening to simulate ambient light intensity. Incubations were carried out for ~24 h. All samples were filtered onto precombusted (5 h at 400 ˚C) 25 mm GF/F filters (Whatman, Maidstone, Vermont, USA), dried, and stored until analysis on an IsoPrime continuous flow isotope ratio mass spectrometer. Measurements conducted over a 24 h period are generally considered to represent Net Primary Production (NPP = Gross Primary Production – Respiration; Marra 2002), including previous measurements in the California Current system (Munro et al. 2013).

Nitrification rates

During the first year, incubation samples for ammonia and urea-derived N oxidation rate determination were collected at four depths: the surface, 10% surface irradiance depth, 1% surface irradiance depth, and 100 m. Due to analytical issues with samples from the surface and 10% light depth (see below), during the second year rates were measured at the 1% surface irradiance depth, 75 m, 100 m, and 150 m. All incubations were conducted in triplicate with one no addition control in 500-mL or 1-L polycarbonate bottles. Seawater was collected directly from the rosette and spiked with 30 to 50 nmol L^{-1} ^{15}N-labeled NH_4^+ or urea (≥ 98 atom percent ^{15}N, Cambridge Isotope Laboratories, Tewksbury, Massachusetts, USA) and incubated for 24 h at in situ temperature and light at a shore-based laboratory at the University of Southern California. Depths below the euphotic zone were incubated in a temperature-controlled cooler and 1% surface irradiance samples were incubated in temperature-controlled rooftop incubators using natural sunlight mesh to approximate 1% of surface irradiance, as described above. Subsamples were collected at approximately 0, 8, and 24 h, with the exception of incubations from the 10% and 1% light level depths, which were subsampled at approximately 0, 8, 16, and 24 h intervals, and 0.2 μm syringe filtered into 60-mL HDPE bottles and stored at -20 °C until analysis. Nitrification rate experiments were conducted over 24 hours to capture the full light cycle, as nitrification in the surface ocean exhibits diel periodicity (Smith et al. 2014). In addition, in March 2015, a kinetics experiment was conducted at the 1% surface irradiance depth, where triplicate incubations were spiked with 15, 30, 75, 125, and 250 nmol L^{-1} ^{15}N-labeled NH_4^+ or urea.

From the subsamples, $\delta^{15}N_{NOx-}$ was measured from 10 nmol or 20 nmol of NO_x^- using the denitrifier method (McIlvin and Casciotti 2011) using an isotope ratio mass spectrometer at the Marine Science Institute Analytical Laboratory at the University of California, Santa Barbara or

the Central Appalachians Stable Isotope Facility at the University of Maryland Center for Environmental Science. $\delta^{15}N_{NOx-}$ values were calibrated using USGS32, USGS34, and USGS35 isotope references. Ambient NO_{x-} concentrations were too low (< 1 μmol L^{-1}) in surface and 10% surface irradiance depth samples to provide sufficient analyte for analysis (10 nmol). Carrier additions of 10 nmol of unlabeled NO_3^- were added to these samples prior to sample preparation from two different sampling months (a total of 77 individual timepoint samples) in an attempt to determine nitrification rates at these depths, but rates were still below our limits of detection even with carrier addition. Rates of ammonia and urea-derived N oxidation were calculated using previously described methods (Dugdale and Goering 1967; Damashek et al. 2016) using linear least squares fitting to determine the rate of NO_x^- production. Detection limits were quantified for each rate by calculating the rate necessary to increase the initial $\delta^{15}N_{NOx-}$ by twice the instrument precision (0.2 to 2.5 ‰). Ammonia oxidation and urea-derived N detection limits ranged from 0.001 to 0.34 nmol L^{-1} d^{-1} and 0.005 to 2.40 nmol L^{-1} d^{-1}, respectively, with the lowest detection limits at the 1% surface irradiance depth. Here, all urea-derived N oxidation rates are reported in terms of urea-derived N; the method cannot distinguish if the rate of urea-derived N oxidation is from urea degradation and subsequent N oxidation by the same or different organisms.

Depth-integrated nitrification and primary production were calculated for the lower euphotic zone by trapezoidal integration using values from the 10% and 1% surface irradiance depths. While there is uncertainty in integrating between only two points, we believe this to be a reasonable estimate as both points were within the euphotic zone (above where rates are expected to decrease exponentially) and both points were narrowly separated by 8 to 35 m. Oxidation rates at the 10% light level depth were assumed to be the mean detection limit for

ammonia (0.055 nmol L^{-1} d^{-1}) and urea-derived N (0.082 nmol L^{-1} d^{-1}) oxidation at the 1% surface irradiance depth.

Nitrous oxide and atmospheric fluxes

Dissolved N_2O samples were collected directly from the rosette into 160-mL serum vials; single samples were collected with the exception of surface samples where five replicates were collected. Vials were filled using silicone tubing by placing the tubing at the bottom of the vials and allowing water to overflow by approximately five volumes. Samples were preserved with 200 μL of a concentrated mercuric chloride solution and sealed with gray butyl septa (Thermo Scientific, Waltham, Massachusetts, USA, #200-932) and aluminum crimp tops. Samples were stored at room temperature until analysis.

N_2O concentrations were measured using a headspace equilibration method. A 30-mL ultra-high purity N_2 headspace was introduced to each sample using a 30-mL syringe with a second empty 30-mL syringe inserted into the septum to collect displaced sample water. Each headspace was overpressured with 10 mL of ultra-high purity N_2 to minimize atmospheric contamination. Samples were analyzed on an SRI 8610 Greenhouse Gas Monitoring Gas Chromatograph (GC) equipped with an electron capture detector (ECD), dual HayeSep D packed columns, and a 1-mL sample loop (SRI Instruments, Torrance, California, USA). Ultra-high purity N_2 gas was used as the carrier with the sample loop kept at 60 °C and the column oven kept at 100 °C. Two certified standards, 0.1 ppm and 1 ppm N_2O (Matheson Tri-Gas, Irving, Texas, USA) were used for daily calibration using a linear calibration scheme. N_2O concentrations from the original seawater sample were calculated according to Walter et al. (2006).

Nitrous oxide air-sea fluxes were calculated using gas transfer velocities calculated after Ho et al. (2006) using 16-day prior 10 m wind speeds and were corrected for in situ temperature and salinity after (Wanninkhof 1992). Wind data were obtained from the NOAA's National Data Buoy Center (NDBC) from Station 46025 Santa Monica Basin (33.761 °N 119.049 °W). Wind speed was converted to the wind speed at 10 m using bulk transfer functions (COARE 3.0; Fairall et al. 2003). Equilibrium N_2O concentrations were calculated using the Weiss and Price (1980) solubility equations with an atmospheric mole fraction of 328 ppb (www.esrl.noaa.gov/gmd/hats/).

Data deposition

Nitrous oxide concentration, nutrient concentration, nitrification rate, and primary production data were deposited in the United States National Science Foundation Biological and Chemical Oceanography Data Management Office repository (bco-dmo.org) in association with project number 516643.

Results

Hydrography and nutrients

Sampling at SPOT spanned two annual upwelling cycles, with upwelling initiating in February and peaking in early summer in both years (Fig. 2a; Table 1). Upwelling was evident in sea surface temperatures (SSTs; Table 1) and in the vertical distribution of NO_3^- and PO_4^{3-} (Fig. 2b,c). SSTs varied between 16.3 and 23.1 °C and negatively correlated with surface [Chl *a*] (Pearson, $r = -0.53$, $p < 0.01$, $n = 21$). Depth-integrated primary production in the lower euphotic zone (10% to 1% surface irradiance depths) varied between 1.7 and 27.6 mmol C m^{-2} d^{-1} and the

highest values were observed just prior to the onset of upwelling (Table 1). Several shallow (18 to 23 m) [Chl *a*] maxima were observed reaching 2.6 ± 0.9 μg L^{-1} (mean ± standard deviation) near the onset of upwelling (Fig. 2d). Ammonium concentrations displayed typical vertical distribution patterns, with maxima (0.3 to 0.5 μmol L^{-1}) occurring at the base of the euphotic zone (Fig. 3a). Urea concentrations varied between the detection limit and 0.7 ± 0.3 μmol L^{-1}, with no obvious patterns in depth or time (Fig. 3b).

Nitrification rates

Ammonia oxidation rates ranged from 0.1 ± 0.03 to 35.9 ± 4.2 nmol N L^{-1} d^{-1} and urea-derived N oxidation rates ranged from 0.03 ± 0.00 to 25.3 ± 4.1 nmol N L^{-1} d^{-1} (Fig. 4). The fraction of ammonia oxidation to total N oxidation (NH_4^+ plus urea-derived N oxidation) was greater at the 1% light level depth (0.81 ± 0.11) compared to 100 m (0.52 ± 0.21; paired t-test, $p < 0.001$), and the fraction of urea-derived N oxidation was greater at 100 m (0.48 ± 0.21) than at the 1% light level depth (0.19 ± 0.11; paired t-test, $p < 0.001$). In kinetic experiments, neither ammonia nor urea-derived N oxidation rates at the 1% surface irradiance depth responded to increasing additions of ^{15}N-labeled substrate from 15 to 250 nmol L^{-1} (Fig. 5). Controlling for depth, rates of urea-derived N oxidation correlated with [O_2] (Pearson, $r = -0.58$, $p = 0.003$, $n = 25$) and [urea] (Pearson, $r = 0.46$, $p = 0.003$, $n = 58$), and ammonia oxidation rates weakly negatively correlated with [NH_4^+] (Pearson, $r = -0.29$, $p = 0.03$, $n = 59$). Unlike urea-derived N oxidation, depth-integrated ammonia oxidation correlated with depth-integrated primary production (Pearson, $r = 0.61$, $p = 0.004$, $n = 20$) in the lower euphotic zone.

The proportion of estimated phytoplankton N demand supported by nitrified ammonia in the lower euphotic zone was calculated using depth-integrated oxidation rates and primary

production between the 10% and the 1% surface irradiance depths (Table 1) and a C:N of phytoplankton uptake of 6.6. Nitrified ammonia and urea supplied 0.1 – 47.3% (median 4.9%) and 0.8 – 26.9% (median 0.8%) of N demand (Fig. 6), respectively, with values reaching up to 47.3% for ammonia oxidation and 26.9% for urea-derived N oxidation in October 2015. The fraction of phytoplankton N demand supplied by nitrified ammonia and urea correlated with the 1% surface irradiance depth (Pearson, $r = 0.74$, $p < 0.001$, $n = 20$ and $r = 0.77$, $p < 0.001$, $n = 19$, respectively), with a higher fraction of N demand supplied by newly nitrified NO_3^- as the 1% irradiance depth deepened.

Nitrous oxide seasonality

Nitrous oxide concentrations varied from 9.4 to 67.2 nmol L^{-1} (93 - 553% saturated; Fig. 7). Generally, N_2O concentrations were low at the surface, increased to maxima around 500 - 750 m, and decreased again towards the seafloor. Maximum N_2O concentrations coincided with O_2 concentrations between ~8 and 30 μmol O_2 L^{-1} (Fig. 8a) and were associated with a low temperature (< 10 °C) and high salinity (> 34) water mass (Fig. 8b). This water mass was associated with low N anomalies (*N**; $N^* = [NO_3^-] + [NO_2^-] - 16 \times [PO_4^{-3}]$; Altabet et al., 2012) with a minima of -20.2 (Fig. 8c). Surface waters were always oversaturated with N_2O (111 to 215%) and atmospheric fluxes ranged between 1.8 ± 0.9 and 9.1 ± 5.3 μmol m^{-2} d^{-1} (Table 1).

Discussion

Nitrification is a source of nitrogen for phytoplankton during weak upwelling

The aims of this study were to understand how seasonal patterns in primary production influence rates of nitrification, and how these processes relate to N_2O dynamics in an upwelling

system. Nitrification rates measured here (Fig. 4) are consistent with rates previously measured in the SCB (Beman et al. 2011), elsewhere in the CC system (Smith et al. 2014), and are comparable to rates measured in the open and coastal ocean (Newell et al. 2013; Santoro et al. 2017; Tolar et al. 2017; Damashek et al. 2019). Ammonia and urea-derived N oxidation rates were highest at 75 m, which was always deeper than the 1% surface irradiance depth, and rates decreased with depth thereafter (Fig. 4), in line with previous observations of nitrification rates exhibiting a power law distribution with maximum rates at the base of the euphotic zone (Newell et al. 2011; Santoro et al. 2017)

Depth-integrated nitrification correlated with depth-integrated primary production in the lower euphotic zone, demonstrating a potential relationship between biomass and N remineralization in the upper ocean. This is consistent with previous studies observing positive correlations between nitrification and primary production (Shiozaki et al. 2016) and depth-integrated Chl *a* (Santoro et al. 2017). It is logical to assume nitrification is controlled by the supply of NH_4^+ from the degradation of organic matter as they are tightly coupled, but in this study, nitrification rates did not increase with additions of NH_4^+ or urea, likely because nitrifiers were already NH_4^+ saturated (Fig. 5). A previous study reported a similar lack of response to NH_4^+ additions (Shiozaki et al. 2016), while other investigations of ammonia oxidation kinetics report increased rates of ammonia oxidation in response to added NH_4^+ (Newell et al. 2013; Horak et al. 2013). These differences in kinetic responses could be explained by an overestimation of in situ ammonia oxidation rates, different ammonia oxidizing populations, or potentially by differences in rates of NH_4^+ production at different sites, which would have the effect of diluting the added ^{15}N-labeled NH_4^+ to differing degrees. Our data suggest that, at the time of sampling, the ammonia-oxidizing population was not NH_4^+ limited.

Maximum nitrification rates in the upper mesopelagic (Fig. 4) coincided with the onset of upwelling, when carbon export efficiencies are expected to be highest in response to pulses of upwelled nutrients (Buesseler 1998; Haskell et al. 2017). Previously at SPOT, the lowest export efficiencies were observed in fall, with efficiencies increasing through winter and peaking in late February/early March at the onset of upwelling (Haskell et al. 2017). Consistent with these findings, in this study, nitrification supplied the highest proportion of phytoplankton N demand, up to 47%, in fall (Fig. 6). This was calculated using trapezoidal integration of two values in the lower euphotic zone, potentially introducing error into the estimates; however, this error is likely minimal as values were integrated over a narrow depth range and nitrification decreases exponentially with depth below the euphotic zone. Estimates of the contribution of nitrification to phytoplankton N demand in this study are consistent with values previously reported for the California Current system (6 to 36%; Wankel et al. 2007; Stephens et al. 2019). The higher contribution of nitrification to the euphotic zone nitrate reservoir in fall suggests regenerated production is of greater importance during weak upwelling when both primary production and new production are expected to be at a minimum, consistent with a meta-analysis of nitrification and primary production rates that found an inverse relationship between primary production and the fraction of phytoplankton N demand supplied by nitrification (Peng et al. 2018). Primary production off southern California is controlled by NO_3^- input into the euphotic zone and is inversely related to the depth of the nitracline (Eppley et al. 1979). During strong upwelling the nitracline shoals, increasing the fraction of new production to total production; conversely, during weak upwelling, the nitracline deepens increasing the fraction of regenerated production (Eppley et al. 1979). In agreement, the fraction of phytoplankton N demand supplied by nitrification in this study correlated with the 1% irradiance depth, suggesting newly nitrified

NO_3^- is a more significant source of N fueling primary production during oligotrophic conditions when the depth of the euphotic zone increases.

In contrast to 2015, in 2016, the proportion of N supplied by nitrification increased through the beginning of spring upwelling (Fig. 6). Data from 2016 are consistent with the hypothesis proposed by Haskell et al. (2017), who suggested the proportion of regenerated N relative to new N fueling primary production increases through spring as respiration in the euphotic zone increases and export efficiencies decrease. At the onset of upwelling, autotrophic and heterotrophic growth are likely not balanced, with heterotrophy lagging newly fueled autotrophic production. As upwelling proceeds, heterotrophic growth balances autotrophic growth, increasing the proportion of regenerated production and decreasing export efficiency. The lack of congruity from year to year could be attributed to a warm SST anomaly (known as the Blob), which persisted from early 2014 through 2015 (Zaba and Rudnick 2016). This period was associated with weakened advection of colder waters from north to south, and was marked by increased stratification, deepening of the nutricline, and lower Chl *a* concentrations (Zaba and Rudnick 2016). Our data suggest nitrification usually supports less than 5% of primary production in the euphotic zone at SPOT, but can occasionally support up to 47% of primary production when there is weak upwelling.

Significant urea utilization by nitrifiers in the upper mesopelagic

The importance of organic N substrates, particularly urea, in fueling nitrification both directly and indirectly is increasingly acknowledged (Santoro et al. 2017; Tolar et al. 2017; Damashek et al. 2019; Kitzinger et al. 2019). There is uncertainty in the measurements we present here, as we cannot distinguish between the direct utilization of urea by ammonia

oxidizers and utilization of urea-derived N by ammonia oxidizers following extracellular hydrolysis or heterotrophic remineralization. Previous studies designed to specifically evaluate this possibility by conducting incubations with an unlabeled pool of $^{14}NH_4^+$ have reached differing conclusions. In coastal Georgia, there was little evidence of hydrolyzed urea entering the NH_4^+ pool (Tolar et al. 2017), while in the Gulf of Mexico, urea-derived nitrification rates decreased by as much as 92% in the presence of unlabeled ammonium, suggesting extracellular hydrolysis prior to oxidation (Kitzinger et al. 2019). With this caveat, our data suggest the proportion of ammonia and urea-derived N oxidation to total nitrification varies with depth, implying differential substrate utilization during nitrification in and below the euphotic zone. At the 1% irradiance depth, NH_4^+ fueled a larger fraction of total N oxidation, whereas at 100 m, there was no significant difference. Our results indicate NO_3^- nitrified from NH_4^+ may contribute more to primary production than NO_3^- derived from urea within the euphotic zone, while urea-derived NO_3^- likely only impacts primary production once vertically advected into the euphotic zone during upwelling.

Though the importance of urea to the marine N cycle has been recognized for some time (reviewed by Solomon et al. 2010), the relative importance of different source(s) of urea in the mesopelagic are still poorly understood. NH_4^+ is the primary excretion product of both zooplankton and heterotrophic microbial organic matter remineralization, but uric acid and urea may also be excreted as the breakdown product of purine and pyrimidine catabolism (Solomon et al. 2010). It has been hypothesized that the oxidation of urea-derived N is of greater importance in oligotrophic waters (Damashek et al. 2019), suggesting urea utilization may be more significant under low substrate concentrations. Here, rates of urea-derived N oxidation were similar to ammonia oxidation in the upper mesopelagic, where NH_4^+ is at or near detection limits,

suggesting ammonia-oxidizers are able to use urea despite additional energetic costs. Indeed, urease genes are found in the genomes of ammonia-oxidizing archaea throughout the meso- and bathypelagic (Santoro et al. 2017; Qin et al. 2020). The use of urea by ammonia-oxidizers has both ecological and biogeochemical implications. In an ecological context, the utilization of urea may provide an advantage to some ammonia oxidizers under certain environmental conditions, impacting competition with other organisms for N, including phytoplankton, heterotrophs, and other ammonia-oxidizers. In a biogeochemical context, it is estimated that 50% of sinking particulate N is converted to urea (Cho and Azam 1999), making understanding the fate of urea in the mesopelagic important for modeling the marine N cycle. More data from a variety of systems will be required to develop a predictive understanding of when and where urea utilization by nitrifiers is favored.

Physical processes control the distribution of N_2O in San Pedro Basin

Nitrification in the upper ocean is considered the primary source of marine N_2O emissions to the atmosphere (Zamora and Oschlies 2014), with microbial denitrification supplying the balance (Bianchi et al. 2012). Here, maximum N_2O concentrations were observed well below the euphotic zone (Fig. 7), at depths where nitrification is expected to be minimal (Newell et al. 2013). Depth profiles of N_2O are consistent with previous observations in Santa Monica Basin (Townsend-Small et al. 2014), and the atmospheric fluxes calculated here (1.8 to 9.1 μmol m^{-2} d^{-1}; Table 1) are similar to those previously observed in the CC system (2.9 to 4.6 μmol m^{-2} d^{-1} ; Townsend-Small et al. 2014) and in the oligotrophic Pacific (0.3 to 4.8 μmol m^{-2} d^{-1}; Popp et al. 2002). N_2O fluxes from San Pedro Basin were lower than fluxes from other

upwelling regions, including the Peruvian-Chilean upwelling system (up to 260 μmol m^{-2} d^{-1}; Farías et al. 2015) and the Arabian Sea (40 to 268 μmol m^{-2} d^{-1}; Naqvi et al. 2000).

Emission of subsurface-produced N_2O to the atmosphere requires a mechanism for water to mix towards the surface; upwelling provides a mechanism where N_2O produced below the mixed layer is ventilated to the atmosphere (Lueker et al. 2003; Nevison et al. 2004). In San Pedro Basin, sea-air N_2O fluxes (Table 1) did not correlate with upwelling intensity; however, surface N_2O concentrations negatively correlated with SST (Pearson, r = -0.51, p = 0.01, n = 21), suggesting N_2O is transported into the mixed layer during upwelling. This is in agreement with a previous study, which reported increased surface N_2O oversaturation with decreasing SSTs in response to upwelling (Nevison et al. 2004). Here, piston velocity did not correlate with upwelling intensity or SST, as calculations only consider wind magnitude and not direction. This likely explains why N_2O fluxes did not directly correlate with upwelling intensity. Previous studies report a link between elevated N_2O production and primary production (*e.g.* Farías et al. 2015), but this was not the case in San Pedro Basin where atmospheric fluxes did not correlate with primary production or Chl *a* concentration. The monthly sampling frequency may have missed higher frequency temporal fluctuations in primary production and N_2O production likely lags pulses in primary production. Alternatively, local N_2O production at SPOT is minimal and much of the N_2O is advected into San Pedro Basin from outside the system.

The main source of N_2O is likely advection into the system from the oxygen deficient zone in the ETNP, where water column denitrification is a potentially large source of N_2O (Babbin et al. 2015). ETNP-sourced waters are evidenced by a low O_2, low N^*, low temperature, and high salinity water mass enriched in N_2O (Fig. 8). The transition between northern sourced surface waters (CC and SCC) and southern sourced bottom waters (CUC) in the SCB typically

occurs along the σ_θ = 26.5 kg m^{-3} isopycnal (Bograd et al. 2019), consistent with the mixing of low- and high-N_2O containing water masses in this study (Fig. 8b). Maximum N_2O concentrations were observed at 500 m, slightly deeper than waters predicted to have maximum CUC influence, but at depths where water is ultimately sourced from the ETNP (Bograd et al. 2019). However, the lack of sampling resolution in this study between 250 and 500 m makes it possible that the true N_2O maximum of the CUC was missed. Previous studies demonstrate the transport of denitrification influenced water from the ETNP through the CC system (Castro et al. 2001; Townsend-Small et al. 2014), with *N** values showing maximum NO_3^- deficits in the CUC between 400 - 1000 m (Castro et al. 2001). Alternatively, the accumulation of N_2O could be from local advection into San Pedro Basin or local production at depth, a result of long bottom water residence times (Berelson 1991). Local N_2O production from nitrification was estimated using the nitrification N_2O yield parameterization of Ji et al. 2018, with the nitrification rate measured each month at the deepest depth (100 or 150 m) and the O_2 concentration at the depth of the N_2O maximum. Local production from nitrification is an unlikely source of the high N_2O concentrations measured here, as it would take between 9 and 122 years to produce the maximum N_2O concentrations measured, significantly longer than residence times (140 days at 300 m and 500 days at 700 m; Jackson, 1986) at depth in the Southern California Bight. Local water column and sediment N_2O production in San Pedro Basin via denitrification is likely minimal, as O_2 concentrations at 500 m were too high (~12 to 32 μmol L^{-1}), and previously measured benthic N_2O fluxes (-0.2 and -1.2 μmol m^{-2} d^{-1}) in the SCB indicate sediments are a sink for N_2O (Townsend-Small et al. 2014). Transport of N_2O from the ETNP, rather than local production, is likely the source of the midwater column N_2O maxima observed in San Pedro Basin. Natural abundance stable isotope measurements that can potentially resolve the relative

contributions of nitrification and denitrification to N_2O in the SCB (Bourbonnais et al. 2017) would help to further constrain these conclusions.

Conclusions

Overall, a decoupling between primary production and organic matter remineralization in the upper ocean is thought to drive high organic carbon export efficiencies (Buesseler 1998; Henson et al. 2019). Our data lend support to this hypothesis, showing nitrification supplied a lower proportion of phytoplankton N demand at the initiation of upwelling, when primary production and organic matter remineralization are most likely to decouple in response to nutrient pulses. When primary production and organic matter remineralization are likely coupled, as upwelling progresses and during periods of weak upwelling, nitrification supplied a higher proportion of phytoplankton N demand. The relationship between primary production, nitrification, and N_2O production is less clear; however, it is apparent physical forcing controls N_2O dynamics in San Pedro Basin. Nitrification is not the major source of N_2O in San Pedro Basin, but the bulk of the N_2O emitted to the atmosphere is likely advected into the system from the ETNP and ventilated to the surface during upwelling. With the predicted expansion and shoaling of oxygen deficient zones (Naqvi et al. 2010), the CC system may become an increasing seasonal source of N_2O to the atmosphere as more N_2O is advected into the system. To increase our understanding of carbon export to the deep ocean and its impact on N_2O production, simultaneous time series measurements of primary production, export efficiency, and nitrification are needed.

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Table 1. Summary of hydrographic parameters at San Pedro Ocean Time-series (SPOT) between September 2014 and August 2016. Depth-integrated values are integrated between the 10% and 1% surface irradiance depths.

Date	Upwelling intensity (m^3 s^{-1} 100 m coastline^{-1})	SST (°C)	Surface [Chl *a*] (μg L^{-1})	Depth at 1% surface irradiance (m)	[NO_x^-] at 1% surface irradiance (μmol L^{-1})	Depth-integrated [Chl *a*] (mg m^{-2})	Depth-integrated primary production (mmol m^{-2} d^{-1})	Depth-integrated ammonia oxidation rate (μmol m^{-2} d^{-1})	Depth-integrated urea-derived N oxidation rate (μmol m^{-2} d^{-1})	N_2O atmospheric flux (μmol m^{-2} d^{-1})
9/10/2014	143	22.9	0.2	56	4.2	19.6	8.0	77.8	9.2	5.1 ± 2.2
10/1/2014	51	21.5	0.3	62	5.8	33.1	4.0	26.4	NS	6.5 ± 3.4
11/12/2014	20	19.7	0.5	56	2.8	44.0	6.7	95.0	23.9	5.1 ± 3.1
12/8/2014	2	18.6	0.4	53	3.6	29.6	4.7	142.1	46.4	2.6 ± 1.6
1/15/2015	-1	16.8	0.4	56	0.7	56.4	5.0	NS	NS	3.2 ± 2.1
2/18/2015	39	16.4	1.2	36	5.7	47.7	22.2	236.9	102.8	2.4 ± 1.2
3/12/2015	72	17.2	0.4	51	3.8	29.1	4.0	20.8	16.1	2.2 ± 1.2
4/22/2015	168	16.9	0.3	30	0.9	13.4	8.1	NS	NS	9.1 ± 5.3
5/20/2015	212	17.6	0.3	45	11.8	25.7	13.2	48.5	22.0	6.4 ± 3.2
6/17/2015	269	18.9	0.3	35	7.4	12.0	7.0	13.0	1.2	1.8 ± 1.0
7/14/2015	178	20.2	0.2	47	4.0	24.8	3.7	8.1	1.4	2.5 ± 1.2
8/5/2015	229	22.0	0.4	52	1.5	36.4	6.5	7.5	2.7	1.8 ± 0.8
9/9/2015	95	22.4	NS	45	1.0	45.2	9.2	1.4	1.7	1.9 ± 1.0
10/20/2015	74	23.1	0.3	92	8.8	56.4	1.7	118.8	67.6	2.4 ± 1.1
11/18/2015	39	18.9	0.4	NS	NS	NS	NS	NS	NS	3.4 ± 2.2
12/16/2015	76	17.5	1.3	33	0.7	28.5	NS	NS	NS	2.6 ± 1.7
1/16/2016	13	16.3	1.1	31	0.4	48.6	10.9	3.6	1.2	5.6 ± 3.5
2/10/2016	38	16.3	0.3	45	1.7	24.8	27.6	144.5	10.2	2.4 ± 2.4

3/16/2016	163	17.5	1.0	34	3.7	24.4	17.8	202.3	21.2	
4/13/2016	165	17.8	0.5	41	14.5	37.5	3.7	66.4	16.6	5.2 ± 4.2
5/18/2016	218	19.2	0.4	49	15.4	30.6	18.9	156.9	22.6	3.4 ± 1.6
6/15/2016	248	17.4	0.6	53	19.3	71.8	10.0	132.3	45.7	2.9 ± 1.5
7/12/2016	271	21.8	0.3	54	12.1	35.5	9.2	41.9	6.9	1.8 ± 0.9
8/10/2016	253	22.1	0.2	68	17.0	27.1	15.8	275.0	57.7	2.2 ± 0.97

Upwelling intensity was obtained from the National Oceanic and Atmospheric Administration's Pacific Fisheries Environmental Laboratory (https://www.pfeg.noaa.gov/). SST, sea surface temperature; Chl *a*, chlorophyll *a*; NO_x^-, nitrate + nitrite; NS, no sample.

Fig. 1 Map of the location of the San Pedro Ocean Time-series (SPOT) station between Los Angeles and Santa Catalina Island with an inset of California, USA. Lines indicate bathymetry, with 50 m, 200 m, 500 m, and 1000 m contours.

Fig. 2 Upwelling intensity (a), nitrate + nitrite (NO_x^-) (b), phosphate (c), and chlorophyll *a* (d) at SPOT between September 2014 and August 2016. Black circles indicate where discrete samples were collected. Upwelling intensity was obtained from the National Oceanic and Atmospheric Administration's Pacific Fisheries Environmental Laboratory (https://www.pfeg.noaa.gov/).

Fig. 3 Time series of ammonium (a) and urea (b) concentrations at SPOT between September 2014 and August 2016. Black circles indicate where discrete samples were collected.

Fig. 4 Ammonia (red) and urea-derived N (black) oxidation rates at the 1% surface irradiance depth (a), 75 m (b), 100 m (c), 150 m (d) at SPOT between September 2014 and August 2016. Error bars indicate the standard deviation of triplicate samples. Missing values indicate where samples were not collected or where ambient NO_x concentrations were too low to analyze.

Fig. 5 Ammonia (red) and urea-derived N (black) oxidation rates at the 1% surface irradiance depth at SPOT in March 2015. The horizontal axis represents substrate concentration (^{15}N addition + ambient concentration). Error bars indicate the standard deviation of triplicate samples.

Fig. 6 The percent of phytoplankton nitrogen (N) demand supplied by ammonia oxidation (red) and urea-derived N oxidation (black) and upwelling intensity (grey line) at SPOT between September 2014 and August 2016. Upwelling intensity was obtained from the National Oceanic and Atmospheric Administration's Pacific Fisheries Environmental Laboratory (https://www.pfeg.noaa.gov/).

Fig. 7 A time series of nitrous oxide concentration at SPOT between September 2014 and August 2016. Black circles indicate where discrete samples were collected.

Fig. 8 The relationships between nitrous oxide and oxygen concentrations between September 2014 to September 2015 (a) and between potential temperature and salinity colored according to nitrous oxide concentration (b) and nitrogen anomaly (N^*) (c) between September 2014 to August 2016 at SPOT, where σ_θ isopycnals are depicted by the solid grey lines.