Deep-Sea Research I 85 (2014) 47–55

Contents lists available at ScienceDirect

Deep-Sea Research I

journal homepage: www.elsevier.com/locate/dsri

# A role for nitrite in the production of nitrous oxide in the lower euphotic zone of the oligotrophic North Pacific Ocean

Samuel T. Wilson [a,b,*], Daniela A. del Valle [a,b], Mariona Segura-Noguera [a,b], David M. Karl [a,b]

[a] Department of Oceanography, School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI 96822, United States
[b] Center for Microbial Oceanography: Research and Education, University of Hawaii, 1950 East-West Road, Honolulu, HI 96822, United States

ARTICLE INFO

*Article history:*
Received 23 July 2013
Received in revised form
19 November 2013
Accepted 29 November 2013
Available online 13 December 2013

*Keywords:*
Nitrous oxide
Nitrite
Ammonium
Nitrifier-denitrification
Oligotrophic
Euphotic-zone

ABSTRACT

Understanding the role of the oceans in the Earth's changing climate requires comprehension of the relevant metabolic pathways which produce climatically important trace gases. The global ocean represents one of the largest natural sources of nitrous oxide ($N_2O$) that is produced by selected archaea and/or bacteria during nitrogen (N) metabolism. In this study, the role of nitrite ($NO_2^-$) in the production of $N_2O$ in the upper water column of the oligotrophic North Pacific Subtropical Gyre was investigated, focusing primarily on the lower euphotic zone where $NO_2^-$ concentrations at the primary $NO_2^-$ maximum reached 195 nmol $L^{-1}$. Free-drifting sediment trap arrays were deployed to measure N cycle processes in sinking particulate material and the addition of selected N substrates to unpreserved sediment traps provided an experimental framework to test hypotheses regarding $N_2O$ production pathways and controls. Sinking particles collected using $NO_2^-$-amended, unpreserved sediment traps exhibited significant production of $N_2O$ at depths between 100 and 200 m. Subsequent stable isotope tracer measurements conducted on sediment trap material amended with $^{15}NO_2^-$ yielded elevated $\delta^{15}N$ values of $N_2O$, supporting $N_2O$ production via a $NO_2^-$ metabolism pathway. Experiments on seawater collected from 150 m showed $N_2O$ production via $NO_2^-$ metabolism also occurs in the water-column and indicated that the concentration of $NO_2^-$ relative to $NH_4^+$ availability may be an important control. These findings provide evidence for the production of $N_2O$ via nitrifer-denitrification in the lower euphotic zone of the open ocean, whereby $NO_2^-$ is reduced to $N_2O$ by ammonia-oxidizing microorganisms.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Nitrous oxide ($N_2O$) is a potent greenhouse gas influencing Earth's climate by absorbing infrared radiation and acting as a precursor to stratospheric ozone depleting radicals (Ravishankara et al., 2009). In the open ocean, concentrations of dissolved $N_2O$ in the upper 100 m of the water column typically range from 7 to 9 nmol $L^{-1}$ and are therefore typically slightly supersaturated (104–130%) with respect to atmospheric equilibrium (*e.g.* Dore and Karl, 1996a; Forster et al., 2009; Bange et al., 2010). This results in an ocean-atmosphere flux of $N_2O$ that has been estimated to contribute approximately 20% of the total $N_2O$ in the atmosphere (Denman et al., 2007).

$N_2O$ is produced as a by-product of nitrogen (N) metabolism and inoxygenated seawater is typically ascribed to nitrification whereby ammonia ($NH_3$) is oxidized via hydroxylamine to nitrite ($NO_2^-$) (Fig. 1). The strong correlation between $N_2O$ and apparent oxygen utilization (AOU) is considered supporting evidence for $N_2O$ production derived from nitrification (Dore et al., 1998; Nevison et al., 2003). In recent years, our understanding of $N_2O$ in the ocean has improved with the application of molecular (*e.g.* Rotthauwe et al., 1997; Mincer et al., 2007) and stable isotope (*e.g.* Ostrom et al., 2000; Sutka et al., 2006; Santoro et al., 2011) technologies to identify the microorganisms and metabolic pathways responsible for $N_2O$ production. A major discovery was that archaea significantly contribute to the production of $N_2O$ production in the marine environment (Francis et al., 2005; Santoro et al., 2010, 2011; Löscher et al., 2012).

However the specific details underlying $N_2O$ production via nitrification in the open ocean remain unclear. In this study, the role of $NO_2^-$ in the production of $N_2O$ at the base of the euphotic zone is investigated. $NO_2^-$ is not an immediately obvious candidate for stimulating $N_2O$ production in aerobic habitats. The redox state of $NO_2^-$ limits its direct involvement in $N_2O$ cycling in the upper ocean as oxidation to $NO_3^-$ is not known to yield $N_2O$ and denitrification is not considered significant in well-oxygenated seawater, except possibly in the interior of large particles (Karl et al., 1984). Furthermore, $NO_2^-$ concentrations are generally low ($<20$ nmol $L^{-1}$) in the open ocean, with the exception of the distinct peak at the base of the euphotic zone referred to as the primary $NO_2^-$ maximum (PNM) (Lomas and Lipschultz, 2006). It

* Corresponding author at: Department of Oceanography, School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI 96822, United States. Tel.: +1 808 956 0573.
*E-mail address:* stwilson@hawaii.edu (S.T. Wilson).

0967-0637/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.dsr.2013.11.008

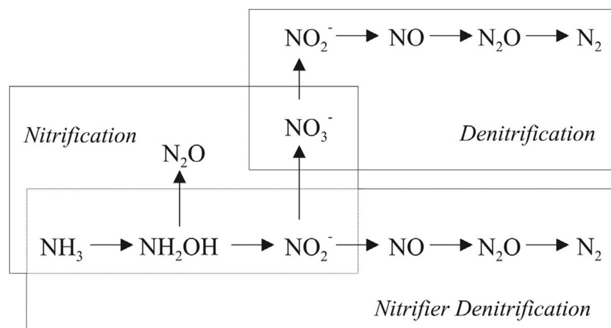


**Fig. 1.** Schematic diagram of the nitrification, denitrification, and nitrifier-denitrification pathways (redrawn from Wrage et al., 2001). The production of $N_2O$ (and also NO and $N_2$) via nitrifier-denitrification is not well understood at present.

has been proposed that the PNM results from ammonia-oxidizing microorganisms that oxidize $NH_3$ to $NO_2^-$ (Olson, 1981). However other studies indicate that the PNM most likely reflects an imbalance in phytoplankton N exudation, due to incomplete assimilation of $NO_3^-$ (Kiefer et al., 1976; Lomas and Lipschultz, 2006). In the North Pacific Subtropical Gyre (NPSG), both processes appear to contribute to the PNM although there may be a subtle vertical segregation leading to distinct upper and lower PNM processes (Dore and Karl, 1996b).

Nonetheless there are several lines of evidence that $NO_2^-$ plays an active role in the production of $N_2O$. The release of $N_2O$ via $NO_2^-$ metabolism is currently referred to as the 'nitrifier-denitrification' pathway whereby $NO_2^-$ is reduced to NO and then to $N_2O$ analogous to the classic denitrification pathway (Fig. 1). The nitrifier-denitrification pathway has been identified in laboratory-maintained cultures of ammonia-oxidizing bacteria (Shaw et al., 2006; Frame and Casciotti, 2010) and ammonia-oxidizing archaea (Santoro et al., 2011).

In this study, we evaluate N cycling in the surface ocean from a series of water column measurements, on-deck incubations, and amendment experiments conducted using free-drifting sediment trap arrays in the oligotrophic North Pacific Subtropical Gyre. Our findings indicate that $NO_2^-$ metabolism represents a possible microbial metabolic pathway for $N_2O$ production in both sedimenting particles and those suspended in the water column. We discuss how nitrifier-denitrification can be accommodated into our current understanding of $N_2O$ dynamics and the wider N cycle in the marine environment.

## 2. Methods

### 2.1. Oceanographic fieldwork

The fieldwork was conducted onboard the R/V *Kilo Moana* during three oceanographic cruises in the NPSG. The water column profiles and sediment trap experiments were conducted at 24° 45′N, 157° 45′W, approximately 100 nautical miles to the north of Station (Stn) ALOHA (Karl and Lukas, 1996) in September 2011 during the BioLINCS cruise. Additional experiments were conducted at Stn ALOHA (22° 45′N, 158°W) in February and June 2013 during HOT cruise 249 and 253, respectively.

### 2.2. Hydrographic and biogeochemical measurements

The hydrographic conditions of the water column were measured using a conductivity, temperature, and depth (CTD) rosette system coupled with chlorophyll fluorescence (Seapoint) and $O_2$ (SeaBird SBE 43) sensors. The fluorescence and $O_2$ sensors were calibrated using discrete fluorometric analysis of chlorophyll *a* (Strickland and Parsons, 1972) and dissolved $O_2$ (Carritt and Carpenter, 1966), respectively. The water column was sampled for a range of biogeochemical parameters using Niskin-like 'Bullister' bottles attached to the CTD-rosette. Of specific interest to this study are the measurements of nitrogenous nutrients, particulate carbon/nitrogen (POC/PON), and $N_2O$. Seawater samples for nutrient analysis ($NH_4^+$, $NO_2^-$, and $NO_3^-$) were collected into acid-washed 125 mL polyethylene bottles, capped, and then stored frozen. $NO_2^-$ and $NH_4^+$ concentrations were quantified onboard with the spectrophotometer method described in Hansen and Koroleff (1999) using a liquid core waveguide with a 2 m path-length for added sensitivity. Nutrient analysis for $NO_2^-$ plus $NO_3^-$ was performed on land using a Bran+Luebbe Autoanalyzer III when $NO_3^-$ concentrations exceeded 0.1 μmol $L^{-1}$ (*i.e.* for samples collected below a depth of 100 m) and using a chemiluminescence technique with its greater detection limit of 1 nmol $L^{-1}$ for the upper water-column (0–100 m) samples (Dore and Karl, 1996b). $NO_3^-$ concentrations were subsequently calculated from both sets of analyses by subtracting $NO_2^-$ values. Seawater samples for PON were collected onto 25 mm diameter combusted (450 °C, 5 h) and acid-washed glass fiber filters (Whatman GF/F). The filters were stored frozen until analysis using a Carlo Erba NC 2500 elemental analyzer with a Finnigan MAT ConFlo II coupler with acetanilide ($C_8H_9NO$) and dried plankton material used as the primary and secondary standards, respectively.

Seawater samples for $N_2O$ analysis were collected in either 76 or 240 mL crimp sealed vials. Sample bottles were filled from the bottom to at least three times overflowing, and poisoned with 200 μL of saturated mercuric chloride ($HgCl_2$) solution. $N_2O$ concentrations were determined using a gas chromatograph (GC) (Agilent 7890A) fitted with an electron capture detector (ECD). A weighed sub-sample was transferred from the sample bottle to a 250 mL purge chamber under positive pressure and sparged using helium at 80 mL $min^{-1}$. The gas stream subsequently passed through a nafion drier (Perma Pure LLC), drierite (VWR), and carbosorb (Europa Scientific) before being cold-trapped on a 1 mL sample loop containing PorapaK Q 80/100 (Sigma-Aldrich) submerged in a small dewar of liquid nitrogen. After purging, the sample loop was heated to 90 °C and injected onto a 30 m × 0.32 mm GS-CarbonPLOT capillary column (J&W Scientific) via a stainless steel 6-port switching valve (Valco). The GC oven temperature was 40 °C and the ECD was maintained at a temperature of 250 °C. The $N_2$ flow rate to the ECD was 60 ml $min^{-1}$ and the carrier gas was helium at 1.6 mL $min^{-1}$. Data acquisition was performed using ChemStation software version B.03.01. The ECD was calibrated for $N_2O$ using a 101 ppmv (±2%) primary standard in nitrogen (Scott-Marrin). Seawater concentrations were calculated with the functions for the Bunsen solubility coefficients provided by Weiss and Price (1980) with temperature and salinity provided by the CTD. Percent saturations were calculated using an atmospheric $N_2O$ mixing ratio of 0.325 ppmv obtained from the Global Monitoring Division (GMD; http://www.esrl.noaa.gov/gmd/) of the National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ERSL).

For a separate set of experiments, seawater samples were amended with $^{15}N$-labeled compounds and the relative $\delta^{15}N$ enrichment of $N_2O$ was measured at the end of the incubation period. To determine the isotopic composition of $N_2O$, dissolved gases were purged from the seawater sample using a sparging set-up similar to that described above for quantifying concentrations. The gas sample was then cryofocused for a second time before injecting onto a Porobond Q (25 m × 0.32 mm) analytical column (J&W Scientific) maintained at 17 °C, using the method of Popp et al. (1995). $N_2O$ was then introduced directly into the ion source of a MAT 252 isotope-ratio-monitoring gas chromatograph/mass spectrometer (irmGC/MS). $N_2O$ concentration and stable-isotope ratios were measured simultaneously by monitoring the ion currents of masses 44, 45, and 46 using the Finnigan ISODAT

Download English Version:

https://daneshyari.com/en/article/4534550

Download Persian Version:

https://daneshyari.com/article/4534550

Daneshyari.com