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Constraints on nitrogen cycling at the subtropical North Pacific Station ALOHA from isotopic measurements of nitrate and particulate nitrogen

K.L. Casciotti [a,*], T.W. Trull [b,c], D.M. Glover [a], D. Davies [b,c]

[a] Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
[b] Antarctic Climate and Ecosystems Cooperative Research Center, University of Tasmania, Australia
[c] Commonwealth Scientific and Industrial Research Organization, Marine and Atmospheric Research, Hobart, Australia

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ABSTRACT

Nitrogen supply to surface waters can play an important role in the productivity and ecology of subtropical ecosystems. As part of the Vertical Transport in the Global Ocean (VERTIGO) program, we examined the fluxes of nitrogen into and out of the euphotic zone at station ALOHA in the North Pacific Subtropical Gyre using natural abundance stable isotopic measurements of nitrate ($\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$), as well as sinking and suspended particulate nitrogen ($\delta^{15}N_{PN}$). Paralleling the steep gradient in nitrate concentration in the upper thermocline at ALOHA, we observed a steep gradient in $\delta^{15}N_{NO_3}$, decreasing from a maximum of +7.1‰ at 500 meters (m) to +1.5–2.4‰ at 150 m. $\delta^{18}O_{NO_3}$ values also decreased from +3.0‰ at 300 m to +0.7–0.9‰ at 150 m. The decreases in both $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ require inputs of isotopically "light" nitrate to balance the upward flux of nitrate with high $\delta^{15}N_{NO_3}$ (and $\delta^{18}O_{NO_3}$). We conclude that both nitrogen fixation and diagenetic alteration of the sinking flux contribute to the decrease in $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ in the upper thermocline at station ALOHA. While nitrogen fixation is required to explain the nitrogen isotope patterns, the rates of nitrogen fixation may be lower than previously estimated. By including high-resolution nitrate isotope measurements in the nitrogen isotope budget for the euphotic zone at ALOHA, we estimate that approximately 25%, rather than 50%, of export production was fueled by N_2 fixation during our study. On the other hand, this input of N_2-derived production accumulates in the upper thermocline over time, playing a significant role in subtropical nutrient cycling through maintenance of the subsurface nitrate pool. An increase in sinking $\delta^{15}N_{PN}$ between 150 and 300 m, also suggests that fractionation during remineralization contributed to the low $\delta^{15}N_{NO_3}$ values observed in this depth range by introducing a subsurface nitrate source that is 0.5‰ lower in $\delta^{15}N$ than the particle flux exported from the euphotic zone. While the time scale of these observations are currently limited, they highlight the need for inclusion of $\delta^{15}N_{NO_3}$ measurements in a time series program to allow a broader assessment of the variations in subsurface $\delta^{15}N_{NO_3}$ values and the links between subsurface nitrate and export flux at station ALOHA.

1. Introduction

1.1. Station ALOHA nitrogen cycling and export

Station ALOHA is home to one of the longest running oceanographic time series observational programs and much is known about the seasonal dynamics and interannual variability of physical and biogeochemical processes at this site, as well as the long-term trends in physical, chemical, and biological properties (Dore et al., 2002; Karl, 1999; Karl et al., 2001a; Karl et al., 1995). As a representative of one of the earth's largest biomes (Karl et al., in press), it is important to understand what limits primary production and export in this oligotrophic environment. The nitracline at ALOHA is positioned at 110 ± 10 m (Dore and Karl, 1996). These depths are within the euphotic zone, but at or below the limit of maximum winter mixed layer depths (Dore et al., 2002; Fennel et al., 2002). It has been argued, therefore, that nitrate supply to the mixed layer is limited to mesoscale eddy activity and infrequent event-driven pulses or vertical migration of phytoplankton (Karl, 1999; Letelier et al., 2000; Sakamoto et al., 2004; Vaillancourt et al., 2003; Villareal et al., 1993, 1996). This part of the oligotrophic North Pacific Subtropical Gyre also relies on nitrogen fixation as a source of nitrogen for primary production, particularly in the mixed layer or upper euphotic zone (Dore et al., 2002; Karl et al., 1997; Mahaffey et al., 2005). However, productivity in the lower euphotic zone may be largely nitrate-driven (Fennel et al., 2002; Letelier et al., 2004). Of the average 0.8–1 mol C m^{-2} yr^{-1} exported from the euphotic zone at

* Corresponding author.
E-mail address: kcasciotti@whoi.edu (K.L. Casciotti).

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the Hawaii Ocean Time Series station ALOHA approximately 48%, or 0.4–0.5 mol C m^{-2} yr^{-1}, has been attributed to nitrogen fixation (Karl et al., 1997).

Independent lines of evidence at station ALOHA have highlighted the quantitative importance of N fixation as a mode of new production in the North Pacific Subtropical Gyre. High abundance (Church et al., 2005a; Letelier and Karl, 1996) and diversity (Falcon et al., 2004; Zehr et al., 1998, 2001) of diazotrophic cyanobacteria, as well as tight physical associations between nitrogen fixing cyanobacteria and eukaryotic phytoplankton (Karl et al., 1997; Scharek et al., 1999), illustrate the capacity for nitrogen fixation. In addition, the activity of diazotrophic phytoplankton has been measured through short-term incubation experiments (Dore et al., 2002; Montoya et al., 2004; Zehr et al., 2001) and expression of genes coding for nitrogenase (Zehr et al., 2001; Church et al., 2005b). In addition to instantaneous measurements, the contribution of nitrogen fixation to seasonal and annual export production has been inferred through nitrogen stable isotopic budgets (Dore et al., 2002; Karl et al., 1997) and geochemical modeling of gas ratios and nutrient stoichiometry (Karl et al., 1997; Fennel et al., 2002; Deutsch et al., 2007; Emerson et al., 1995). The results of these studies highlight the potential importance of N fixation as a mode of new production in the North Pacific Subtropical Gyre.

If the euphotic zone is neither gaining nor losing nitrogen, the export of particulate nitrogen (PN) from the surface ocean should be balanced by supplies of new nitrogen through nitrate input, nitrogen fixation, and atmospheric deposition. Moreover, if steady state can be assumed on an annual timescale, then the nitrogen isotopic content of the incoming and outgoing nitrogen fluxes should also balance. While long-term changes in the nutrient inventories have been observed at ALOHA (Karl et al., 1997, 2001a, b), the time scale for this change is long relative to the fluxes through the system. A nitrogen isotope balance approach has been taken by Karl et al. (1997) and Dore et al. (2002) to estimate that the fraction of annual export production supported by nitrogen fixation at ALOHA averages about 48%, with a seasonal pattern that indicates a higher fraction of export supported by N_2 fixation in the summer when waters are strongly stratified, and a lower fraction of export supported by N_2 fixation in the winter when mixed layers extend down to 100 m.

The construction of isotope budgets to infer annual rates of N_2 fixation at ALOHA relied on sparse measurements of nitrate $\delta^{15}N$ $\delta^{15}N_{NO_3}‰ = [((^{15}N/^{14}N)_{NO_3}/(^{15}N/^{14}N)_{AIR}) - 1] * 1000)$ in the North Pacific (Liu et al., 1996; Voss et al., 2001), but none at or near station ALOHA. Based on these measurements, the supply of nitrate to the surface water at ALOHA has been assumed to possess a $\delta^{15}N$ value of +6.5‰ (Dore et al., 2002). As noted by Mahaffey et al. (2005) if the $\delta^{15}N$ of nitrate sources to the euphotic zone at ALOHA are less than 6.5‰, the N input from N_2 fixation may be less than currently estimated from long-term measurements of sinking $\delta^{15}N_{PN}$ values. Since that time, a few $\delta^{15}N_{NO_3}$ measurements have been reported from station ALOHA (Mahaffey et al., in press; Sutka et al., 2004), but these data were not used to confirm or refute this assumed isotopic value for nitrate entering the euphotic zone at station ALOHA. Indeed, because of the strong gradients in the water column, high spatial resolution nitrate isotopic data are required for this assessment, and to determine the accuracy of isotope-based fluxes of new and export production and the integrated contribution of nitrogen fixation to subsurface nitrate at this site. These fluxes have important implications for understanding the mechanisms of carbon export from the North Pacific Subtropical Gyre and the physical and ecological constraints on new production in the oligotrophic ocean.

As part of the Vertical Transport in the Global Ocean (VERTIGO) program, we occupied station ALOHA for a 3-week period from June 20 to July 11, 2004. This cruise occurred immediately following HOT 160 (June 14–18, 2004) and preceding HOT 161 (July 12–14, 2004). During the VERTIGO cruise many physical, chemical, and biological parameters were measured repeatedly over the 3-week period, including primary productivity, new and regenerated production, and particle export and attenuation through the mesopelagic zone (Buesseler et al., 2008). These measurements were designed to capture the surface properties related to particle flux measured at nominal depths of 150, 300, and 500 m, as well as to examine the mechanisms controlling particle flux attenuation. During this expedition, observations of particle export flux (Buesseler et al., 2007), were similar to the low levels historically observed in July and August at station ALOHA (Christian et al., 1997; Dore et al., 2002; Karl et al., 1996). Although the particle fluxes are low at this oligotrophic site, mesopelagic particle attenuation at ALOHA is very efficient, with 20% or less of the carbon flux at 150 m passing 500 m (Buesseler et al., 2007). If remineralization drives this flux attenuation, or at least keeps pace with it, this could represent a significant flux of nitrogen into the subsurface, accumulating as nitrate.

The current study was undertaken to examine mesopelagic nitrogen remineralization and nitrogen supply to the euphotic zone at station ALOHA using high-resolution $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ measurements in the context of the particle flux dynamics studied by the VERTIGO program. Measurements of nitrate $\delta^{15}N$ and $\delta^{18}O$ ($\delta^{18}O‰ = [((^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{std})-1]*1000$), as well as sinking and suspended particulate nitrogen $\delta^{15}N$, were made through the upper mesopelagic (150–500 m) where the bulk of particulate export is remineralized. We relate the isotopic distributions in nitrate and particulate nitrogen to uptake and remineralization of nitrogen in the upper water column. These results allow us to assess the influence of nitrogen fixation and particle remineralization on the accumulation of nitrate in the upper thermocline.

2. Methods

2.1. Sample collection

All samples reported here were collected within 18 nautical miles of station ALOHA (22°45′N, 158°W) in the North Pacific Subtropical Gyre during June 20–July 11, 2004. Over the 3-week period, samples were collected for $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ measurements from 11 profiles, ranging from depths of 150–3000 m. Samples were collected from 10 L Niskin bottles into 60 mL HDPE Nalgene bottles, rinsed three times with sample before final volumes were collected. Samples were frozen immediately on board, transported frozen, and stored at −20 °C until isotopic analysis.

Suspended particles were graciously provided by J. Bishop from the Multiple Unit Large Volume Filtration System (MULVFS; Bishop et al., 1985) at depths of 30, 54, 79, 104, 153, 202, 326, 474, 572, and 770 m. Particles were collected from 3840 to 12,790 L of seawater (J. Bishop, personal communication), depending on the depth, by filtering in-situ over a four hour period through a 53 μm nylon mesh and then two layers of (pre-combusted) QMA quartz fiber filter (1 μm nominal pore size). The MULVFS QMA filters were subsampled upon retrieval in a HEPA-filtered laminar flow hood by excising 47 mm discs, which were then frozen.

Sinking particles were collected in replicate Neutrally-Buoyant Sediment Traps (NBST's; Buesseler et al., 2000; Valdes and Price, 2000) deployed at nominal depths of 150 m (3 traps), 300 m (2 traps), and 500 m (2 traps). The traps were each deployed for two 3–5-day collections during the cruise. Each trap held five replicate tubes containing 500 mL brine (freeze-condensed