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Revisiting N_2 fixation in the North Atlantic Ocean: Significance of deviations from the Redfield Ratio, atmospheric deposition and climate variability

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ABSTRACT

The average oceanic nitrate-to-phosphate molar ratio (NO_3^-:PO_4^{3-}≈16:1, referred to as the Redfield Ratio) in subsurface waters, which is similar to the average ratio of particulate nitrogen (N)-to-phosphorus (P) in phytoplankton, is the cornerstone in calculating geochemical estimates of N_2 fixation and denitrification rates. Any deviations from this canonical Redfield Ratio in intermediate ocean waters, expressed as N^* (a measure of NO_3^- in excess or deficit of $16 \times PO_4^{3-}$), provides an integrated estimate of net N fluxes into and out of the ocean. In well-oxygenated ocean basins such as the North Atlantic Ocean, N^* estimates are usually positive and can be used to infer that rates of N_2 fixation exceed rates of denitrification. We use this approach to estimate N_2 fixation over the last two decades (1988–2009) based on data collected at the Bermuda Atlantic Time-series Study (BATS) site in the North Atlantic Ocean near Bermuda. Our results indicate that interpretation of the N^* tracer as an estimate of N_2 fixation should be undertaken with caution, as N_2 fixation is not the only process that results in a positive N^* estimate. The impacts of a locally variable nitrogen-to-phosphorus ratio, relative to the fixed Redfield Ratio, in the suspended particulate matter as well as in the subsurface water nutrients and atmospheric N deposition on N^* variability were examined. Furthermore, we explored the role of climate modes (i.e., North Atlantic Oscillation and Arctic Oscillation) on N^* variability. We found that N^* in the subsurface waters was significantly affected by these factors and hence previous estimates of N_2 fixation using this technique might have been substantially overestimated. Our revised estimate of N_2 fixation in the North Atlantic Ocean (0°N–50°N, 20°W–80°W) is $12.2 \pm 0.9 \times 10^{11}$ mol N yr^{-1}, and based on long-term BATS data provides better constraints than both earlier indirect and direct estimates N_2 fixation.

1. Introduction

In one of the earliest oceanographic paradigms, Redfield identified the similarity between the N:P molar ratio of phytoplankton living in the surface ocean and that of dissolved nitrate (NO_3^-) to phosphate (PO_4^{3-}) in the ocean interior, and hypothesised that these deep ocean nutrient concentrations were controlled by the elemental requirements of these surface plankton populations (Redfield, 1934). This ratio was observed to be 16:1. This concept remains a central tenet for our understanding of ocean biogeochemistry, including serving as a 'constant' from which geochemical rate measurements can be derived, and providing context for better understanding of the biogeochemical processes influencing the nutrient cycles of the global ocean. As such, geochemists have estimated N_2 fixation rates based upon deviations from the canonical Redfield Ratio using the N^* tracer, $N^* = ([NO_3^-] - 16 \times [PO_4^{3-}] + 2.90) \times 0.87$, where concentration is measured in molar units (Michaels et al., 1996; Gruber and Sarmiento, 1997). The quasi-conservative N^* tracer, calculates the difference between measured NO_3^- concentrations and expected NO_3^- concentrations, scaled from measured PO_4^{3-} concentrations and the Redfield Ratio of molar N:P (16:1) (Gruber and Sarmiento, 1997). The constant 2.90 and the multiplier 0.87 in the N^* equation were used to force a globally averaged N^* of zero. Thus, the N^* tracer would increase with addition of N through N_2 fixation, and decrease with removal of N through denitrification or anammox, and therefore provides a measure of the net flux of N within the global ocean system.

The importance of marine N_2 fixation as a source of new nitrogen in the ocean has been recognised for decades (e.g., Dugdale and Goering, 1967; Lipschultz et al., 2002; Gruber and Sarmiento, 1997). Incubation-based 'biological' measurements of N_2 fixation rates are commonly made but by their nature are short-term measurements and result in large errors/uncertainties when propagated to longer temporal and extrapolated to larger spatial scale rate estimates. For this reason, geochemical rate estimates are attractive as they integrate

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N_2 fixation signals over longer temporal periods and larger spatial scales and thus have reduced uncertainty relative to direct biological measurements. However, there are several distinct scenarios that can alter dissolved NO_3^-:PO_4^{3-} ratios independent of denitrification and N_2 fixation with implications for the interpretation of calculated N^* rate measurements. First, the ocean receives significant nutrient inputs from aerosols (e.g., Duce et al., 2008), which generally have very high N:P ratios (Baker et al., 2010). Second, some phytoplankton groups that contribute to the downward flux of particulate organic matter have particulate matter ratios much different from the canonical Redfield Ratio even under balanced exponential growth. For example, both unicellular cyanobacteria taxa *Prochlorococcus* and *Synechococcus* (Bertilsson et al., 2003; Heldal et al., 2003; Martiny et al., 2013) and the colonial cyanobacterium *Trichodesmium* (Letelier and Karl, 1996; Mahaffey et al., 2005) have N:P ratios from ~24–45, while diatoms have N:P ratios of ~11:1 (Quigg et al., 2003). As a corollary to this, the cellular particulate matter N:P ratios depend in part on in situ growth rates (i.e., the growth rate hypothesis). Rapid growth results in lower N:P ratios, but not always less than the canonical Redfield Ratio, while slower growth results in higher N:P ratios (Klausmeier et al., 2004). Earlier N_2 fixation rates may have been incorrectly estimated when non-Redfield uptake stoichiometries for different phytoplankton groups were not considered (e.g., Mills and Arrigo, 2010).

With the above caveats in mind, we have extended the analysis of the Bermuda Atlantic Time-series Study (BATS) nutrient time-series record to provide a revised estimate of N_2 fixation from earlier estimates (Bates and Hansell, 2004; Hansell et al., 2004). We have used BATS data to estimate N^* in the Subtropical Mode Water (STMW); a wedge of water with uniform density (σ_θ=26.4–26.6, also known as 18 °C water) located in the subsurface between ~100 and 500 m depth (Palter et al., 2005). We have also estimated N^* in the water mass below the STMW, referred to here as Labrador-Mediterranean Water (LMW). This paper not only extends N^* analyses of BATS data by a decade compared to previous studies, but also takes into account a new time series dataset on particulate organic nitrogen and phosphorus (PON and POP, respectively) concentrations and their fluxes at various depths in the ocean at BATS, and their respective impacts on N^* as it related to interpretation of N_2 fixation rates.

2. Materials and methods

2.1. Sampling site and measurement techniques

The Bermuda Atlantic Time-series Study (BATS) site (31° 40′N, 64° 10′W) located in the western North Atlantic Ocean (Fig. 1) provides a unique opportunity to study N_2 fixation with its long time-series of dissolved and particulate nutrients. For this analysis, monthly dissolved nutrient (NO_3^-, PO_4^{3-}) concentrations from October 1988 to February 2009 were used. Routine quality control and assurance techniques have been performed to identify individual data that fall outside a 95% confidence interval derived from the entire dataset (e.g., Bates and Hansell, 1999). NO_3^- and PO_4^{3-} have an imprecision of ~0.12 μmol kg^{-1} and 0.02 μmol kg^{-1}, respectively, that results in an overall N^* error of ~5–15% (e.g., Knap et al., 1993; Bates and Hansell, 2004). Suspended particulate organic nitrogen (PON) and phosphorus (POP) concentrations from November 2003 to December 2009, and particulate fluxes of PON and POP from October 2005–December 2010, using surface-tethered particle interceptor traps at 150, 200, and 300 m, were used in this analysis. All phosphorus chemical analyses were determined as described in Lomas et al. (2010).

Other datasets used in this analysis included the following: (i) Global Ocean Data Analysis Project (GLODAP) (Key et al., 2004) data; (ii) World Ocean Atlas (WOA) (World Ocean Atlas, 1998) data, and; (iii) data from RV *Atlantic Explorer* cruise X0705 (Lomas et al., unpublished data), which sampled in the STMW formation region north of Bermuda (Fig. 1). Atmospheric deposition data, both aerosol and rainwater samples were collected at the Prospect sampling site in Bermuda, from January 1989 to December 1999 (Bates and Peters, 2007). NO_3^- concentrations in both aerosol and rain samples were measured by ion chromatography using a Dionex DX100. Analytical precision, determined by 5 replicates during each batch of analyses, had a standard deviation of 5%. The dry deposition flux was calculated by multiplying NO_3^- concentrations and its deposition velocity in aerosol (1.5 cm s^{-1}; Schafer et al., 1993). Wet deposition flux was estimated by multiplying NO_3^- concentrations in rainwater and rainfall amount on the corresponding day.

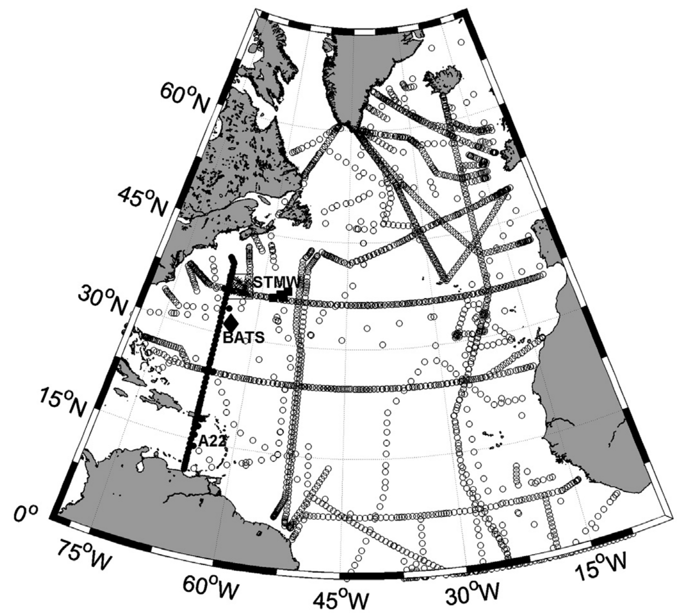

Fig. 1. Map of the North Atlantic Ocean showing the sampling locations of the data used in the present study. BATS site is shown by a filled diamond. Open and filled circles are sample locations from the data of GLODAP project (Key et al., 2004), filled circles are A22 section that is used for section plot in Fig. 2a. Cross symbols in a box are from the WOA data that are used to analyse the climatology at the STMW formation region. Filled squares are from the X0705 cruise that lies on the latitude of the STMW formation region.

Monthly indices of the North Atlantic Oscillation (NAO) and the Arctic Oscillation (AO) were obtained from the Climate Prediction Centre-National Oceanic and Atmospheric Administration (CPC-NOAA) and converted into annual indices by taking the mean of values in a calendar year. Winter season indices were calculated as the mean of values from January to March.

2.2. Geochemical calculations

N^* was calculated using the 'regional scale' parameterisation of the global equation (Deutsch et al., 2001; Eq. (1)). Canonical Redfield Ratio has been used for global geochemical estimates of N_2 fixation, while regional subsurface NO_3^-:PO_4^{3-} ratio was considered for estimating N_2 fixation in the North Atlantic Ocean:

$$N^* = [NO_3^-] - R \times [PO_4^{3-}] \quad (1)$$

where R is the molar NO_3^-:PO_4^{3-} ratio in deep (> 2000 m) water for the region being analysed; in this case 14.63 ± 0.02 (mean ± std error of 2022 samples). The regional N^* parameterisation was used rather than the previously used tracer DIN_{xs} (e.g., "excess DIN"; Hansell et al., 2004; Bates and Hansell, 2004) or the global N^* parameterisation because the DIN_{xs} and global N^* calculations, which both assume a globally constant R value of 16:1 (the Redfield Ratio) rather than the measured local R value, resulted in negative values at depths of