

Large, non-Redfieldian drawdown of nutrients and carbon in the extratropical North Atlantic Ocean (46°N): Evidence for dinitrogen fixation?

*Geun-Ha Park and Kitack Lee*¹

School of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang, 790-784, Republic of Korea

Rik Wanninkhof and Jia-Zhong Zhang

Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration, Miami, Florida 33149

Dennis A. Hansell

Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida 33149

Richard A. Feely

Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, Seattle, Washington 98115-6349

Abstract

Considerable drawdown of total dissolved inorganic carbon (C_T) and oversaturation of oxygen (O_2) within a cold ($\sim 15^\circ\text{C}$) oligotrophic eddy in the extratropical North Atlantic Ocean (46°N , 20.5°W) indicate that, despite the absence of nitrate (NO_3^-), the eddy was highly productive. Estimates of net community production using the mass balances of C_T and O_2 were two to five times greater than those obtained using the mass balance of NO_3^- . The remineralization rates obtained using the integrated rates of C_T and NO_3^- accumulation and O_2 utilization for the upper thermocline waters (35–300-m depth) were in agreement with C_T - and O_2 -based net community production over the same period; however, all the estimates exceeded the NO_3^- -based net community production by a factor of two to five, pointing to a considerable accumulation of NO_3^- in the upper thermocline in excess of changes in the mixed-layer NO_3^- inventory. The amount of this excess NO_3^- suggests that a considerable fraction of the net community production was not supported by the mixed-layer NO_3^- inventory and that an external source of NO_3^- must be present. Of the various mechanisms that might explain the inequity between NO_3^- drawdown in the surface layer and NO_3^- accumulation in the upper thermocline, N_2 fixation is the most viable yet surprising mechanism for producing such excess NO_3^- in this oligotrophic eddy. A significant fraction of net community production in oligotrophic extratropical waters could be supported by processes that are not fully explored or to date have been considered to be insignificant.

¹ Corresponding author (ktl@postech.ac.kr).

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The availability of fixed nitrogen (NO_3^- , NO_2^- , and NH_4^+) in the ocean is considered to be the key factor constraining marine new production. Accordingly, this concept has played a central role in previous observational and modeling efforts (Hood et al. 2000). Multiyear monthly records obtained at the sites of the Bermuda Atlantic Time-Series Study ($31^\circ 50'\text{N}$, $64^\circ 10'\text{W}$) and the Hawaii Ocean Time-Series ($22^\circ 45'\text{N}$, 158°W), however, provide compelling evidence of a significant removal of dissolved inorganic carbon ($C_T = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$), despite the

absence of measurable levels of NO_3^- (Michaels et al. 1996; Karl et al. 1997; Hood et al. 2001). Lee et al. (2002) used a diagnostic model to quantify this unique phenomenon in other NO_3^- -depleted tropical and subtropical oceans and hypothesized that the global estimate of this phenomenon is largely attributable to marine N_2 -fixation activity.

Much of the previous research on marine N_2 fixation has focused on the planktonic cyanobacterium *Trichodesmium* in tropical oceans because *Trichodesmium*—considered to be key global marine diazotrophs—are ubiquitous in warm waters deficient in nitrate. More recently, molecular methods have broadened our horizons in studies of marine N_2 fixation, suggesting the presence of more highly diverse and previously undocumented N_2 -fixing cyanobacteria (Zehr et al. 2001; Montoya et al. 2004). Given that the global distribution of reported *Trichodesmium* blooms is well constrained by seawater temperatures above 25°C (Carpenter and Capone 1992; Karl et al. 2002; Davis and McGillicuddy 2006), it is commonly assumed that N_2 fixation activity in waters colder than this temperature is minor or can be ignored entirely.

In the present paper, however, we report considerable net drawdown of C_T (hereafter referred to as net community production) in an oligotrophic eddy in the extratropical North Atlantic Ocean (46°N , 20.5°W); approximately 70% of the total C_T drawdown is not supported by the mixed-layer NO_3^- inventory if a conventional Redfield stoichiometry is assumed. Our evidence of such a substantial, unaccounted net community production is derived from syntheses of data for several chemical tracers collected in a Lagrangian mode over 3 weeks in June 1998 as part of the Gas Exchange Experiment Expedition (GasEx-98). We assess the veracity of C_T - and NO_3^- -based estimates of net community production by comparing them with estimates obtained using the mass balances of O_2 and PO_4^{3-} within the mixed layer and with remineralization obtained using the rates of C_T , NO_3^- , and PO_4^{3-} accumulation and O_2 utilization for the upper thermocline waters of the eddy.

Methods

Biogeochemical data used in estimating net community production— C_T and nutrient (NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , and $\text{Si}[\text{OH}]_4$) data were collected while aboard the National Oceanic and Atmospheric Administration vessel *Ronald H. Brown* during the GasEx-98 expedition that took place between 25 May and 26 June 1998. This expedition was carried out in an anticyclonic eddy during the postbloom period to make use of ~ 8 Pa ($80 \mu\text{atm}$) differences in the partial pressure of CO_2 ($p\text{CO}_2$) between the atmosphere ($p\text{CO}_{2\text{AIR}}$) and the eddy surface ($p\text{CO}_{2\text{SEA}}$) to optimize the measurements of gas fluxes (Hood et al. 2001; Feely et al. 2002). The analytical methods employed in this study are described in Zhang (2000) for nutrients and Feely et al. (2002) for C_T and $p\text{CO}_2$ in air and seawater. GasEx-98 was focused on determination of the rates of gas exchange at the air–sea interface using novel and independent methods. Environmental conditions within the eddy and measurements of gas exchange rates are described in McGillis et al. (2001).

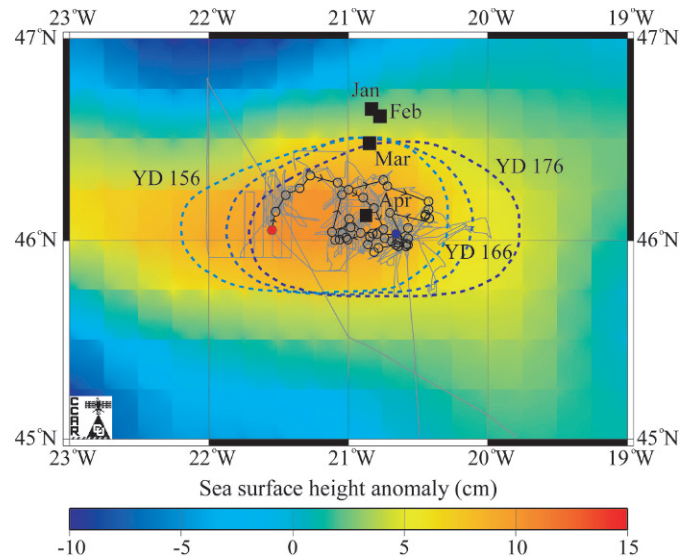


Fig. 1. Locations of C_T , O_2 , NO_3^- , and PO_4^{3-} profile measurements (open circles) overlaid on sea surface height anomaly (cm) of TOPEX/ERS-2 data (Colorado Center for Astrodynamic Research, University of Colorado) on 25 May (the first day of the experiment, day of the year [YD] 146). The red and blue circles represent the locations of the first and last sampling stations, respectively, whereas the open circles indicate other sampling locations. Gray lines represent all the cruise tracks during GasEx-98. Dotted lines are contours of the sea surface height anomaly of 8 cm at YD 156, YD 166, and YD 176. Filled squares denote the approximate movement of the eddy center from January to April 1998 based on the maximum surface height anomaly.

Results

Physical and biogeochemical properties of the oligotrophic eddy—During GasEx-98, the oligotrophic eddy chosen as a study site maintained a distinct body of water with physical and biogeochemical properties that differed from those of the surrounding water (Hood et al. 2001; McGillis et al. 2001; Feely et al. 2002). This eddy had remained approximately stationary for at least 4 months prior to GasEx-98 (see Fig. 1). Photosynthesis during the preceding spring bloom resulted in low $p\text{CO}_2$, nutrient depletion, and large O_2 supersaturation in surface waters within the eddy when the GasEx-98 expedition began. Vertically integrated chlorophyll *a* (Chl *a*) inventories were 30–40% of Chl *a* typically found near the study area during the spring bloom (Bury et al. 2001), indicating that biological productivity in the eddy was unexpectedly high given the low concentrations of nutrients found (Fig. 2C).

The study period was divided into three time segments according to wind conditions: prestorm (Period I, 8 d), storm (Period II, 12 d), and poststorm (Period III, 3 d). During the first 8 d of the study period (Period I), surface waters within the eddy showed the characteristics of oligotrophic condition. Concentrations of NO_3^- , PO_4^{3-} , and $\text{Si}(\text{OH})_4$ remained below 0.06, 0.08, and $0.15 \mu\text{mol kg}^{-1}$, respectively (Fig. 2), with the N:P ratio being less than 1.5. In contrast, the mixed-layer salinity (*S*)–normalized C_T concentration ($\text{NC}_T = \text{C}_T \times 35.67/\text{S}$, where

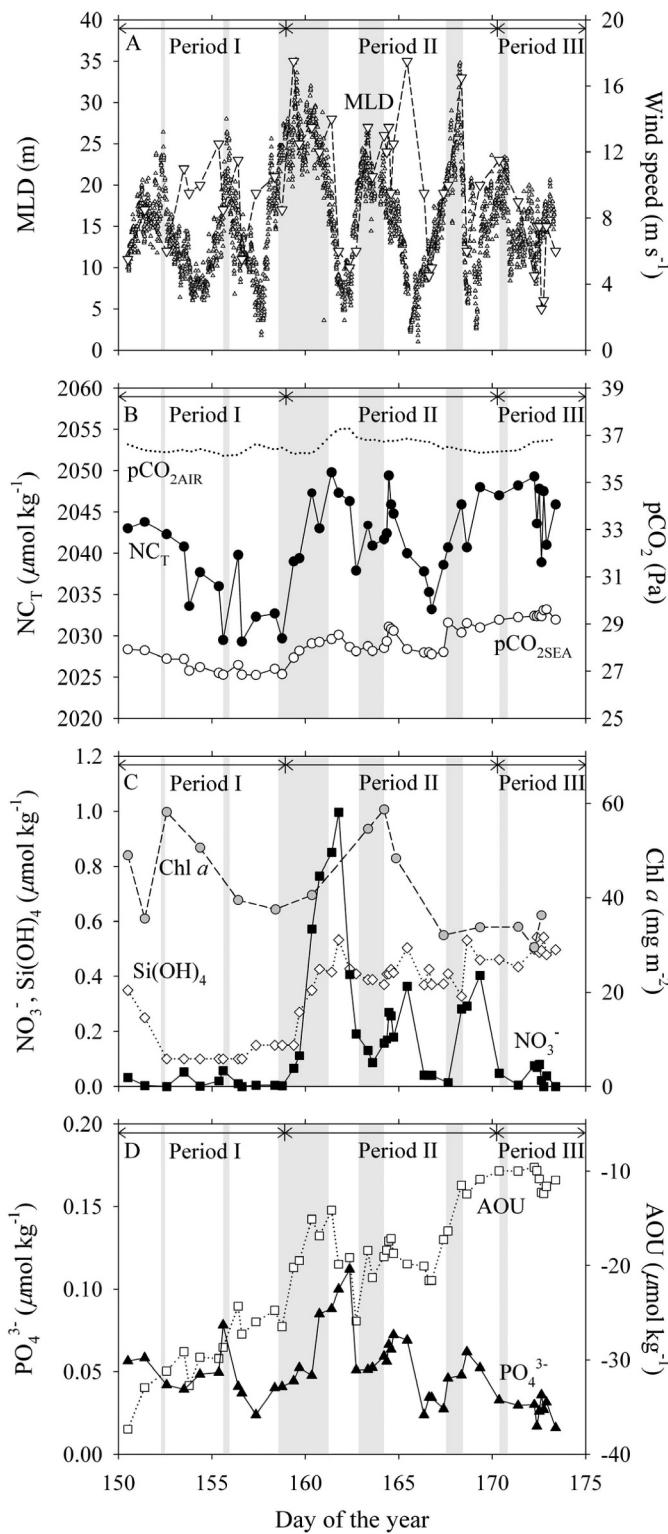


Fig. 2. (A) Wind speeds (small open triangles) and mixed-layer depth (MLD, large open inverted triangles); (B) surface water NC_T (filled circles) and pCO_2 (pCO_{2SEA} , open circles) and pCO_2 values in the atmosphere (pCO_{2AIR}) (dotted line); (C) surface water NO_3^- (filled squares), $Si(OH)_4$ (open diamonds), and vertically integrated chlorophyll a contents (gray circles); and (D) surface water PO_4^{3-} (filled triangles) and apparent oxygen utilization (AOU = saturated O_2 – measured O_2 , open squares)

$S = 35.67 \pm 0.01$ is the mean S within the eddy for the study period) decreased by $13 \mu\text{mol kg}^{-1}$, from $2043 \mu\text{mol kg}^{-1}$ on day of the year (YD) 150 to $2030 \mu\text{mol kg}^{-1}$ on YD 158.

During Period II, three storms passed through the region with large wind speed variations ranging from 3 m s^{-1} to 16 m s^{-1} (Fig. 2A). The C_T , NO_3^- , and PO_4^{3-} concentrations within the surface mixed layer were strongly correlated with the intensity of storm events, although the recorded increases in concentrations lagged behind the timing of initiation of storm events by a few days (shaded bars in Fig. 2). The increases in measured C_T and NO_3^- concentrations following the storm events arise from the net effect of the following processes: supply via entrainment and consumption by phytoplankton and, in the case of C_T , increases due to air–sea gas exchange; however, consumption by phytoplankton was probably less important during the storm periods, when deepening of the mixed layer would constrain the accumulation of phytoplankton and low light availability would reduce photosynthetic activity. In contrast, shallowing of the mixed layer following the storms enabled phytoplankton to accumulate rapidly (gray circles in Fig. 2C), with NO_3^- concentrations dropping to levels $< 0.1 \mu\text{mol kg}^{-1}$ within a day of storm events (filled squares in Fig. 2C). Such high rates of C_T and NO_3^- net uptake (Table 1) came as a surprise. Furthermore, the upward input of NO_3^- and C_T into the mixed layer and subsequent uptake by phytoplankton appear to be decoupled in time (Zhang et al. 2001); the input process occurred primarily during storm periods, whereas the consumption process was rather dominant during poststorm periods.

During Period III, nutrients in the surface waters of the eddy returned to very low concentrations, with the exception of $Si(OH)_4$, which remained at $\sim 0.5 \mu\text{mol kg}^{-1}$. This value was higher than those observed during the prestorm period (Period I), indicating the incomplete utilization of $Si(OH)_4$ by diatoms during Periods II and III.

Estimation of net community production—For each of three time periods (Periods I, II, and III), we determined the rates of net community production (NP_C : expressed in $\text{mmol C m}^{-2} \text{ d}^{-1}$) in the eddy based on changes in NC_T inventory in the mixed layer corrected for carbon fluxes from the atmosphere and via vertical eddy diffusion from the upper thermocline, as described in the following equation (Lee 2001; Table 1):

$$NP_C|_{\Delta D} = H^D + 1 \left([NC_T]^D - [NC_T]^{D+1} \right) + (F_{\text{air-sea}})_{D+1} + K_V(dC_T/dz) \quad (1)$$

←

within the oligotrophic eddy during the GasEx-98 expedition. Shaded bars denote the time windows during which wind speeds were higher than 10 m s^{-1} . The study period was divided into three time segments: prestorm (Period I, 8 d), storm (Period II, 12 d), and poststorm (Period III, 3 d).

Table 1. C_T (NP_C)-based, O_2 (NP_O)-based, NO_3^- (NP_N)-based, and PO_4^{3-} (NP_P)-based estimates of net community production ($mmol\ C\ m^{-2}\ d^{-1}$) for Periods I, II, and III.

Period	NP_C				NP_O^*				NP_N^*			NP_P^*		
	ΔNC_T	$F_{air-sea}$	K_V	NP_C	ΔO_2	$F_{air-sea}$	K_V	NP_O	ΔNO_3^-	K_V	NP_N	ΔPO_4^{3-}	K_V	NP_P
I	31.2	7.5	7.9	46.6 ± 15.4	-19.0	65.8	2.4	49.2 ± 18.5	2.5	5.7	8.2 ± 3.9	19.9	5.2	25.1 ± 4.7
II†	37.1	2.1	2.0	41.2 ± 7.5	14.1	16.6	0.5	31.2 ± 4.8	16.3	1.7	18.0 ± 1.2	25.0	1.8	26.8 ± 2.3
III	8.8	7.2	6.9	22.9 ± 19.6	3.6	18.7	0.8	23.1 ± 6.1	2.9	6.0	8.9 ± 4.2	9.5	5.3	14.8 ± 6.6

* For an absolute comparison, O_2 -based ($mmol\ O_2\ m^{-2}\ d^{-1}$), NO_3^- -based ($mmol\ N\ m^{-2}\ d^{-1}$), and PO_4^{3-} -based ($mmol\ P\ m^{-2}\ d^{-1}$) estimates of net community production (NP_O , NP_N , and NP_P , respectively) were converted to C_T -equivalent-based ($mmol\ C\ m^{-2}\ d^{-1}$) estimates using the elemental ratios of Anderson and Sarmiento (1994).

† For Period II, NP_C , NP_O , NP_N , and NP_P values were calculated for half the period during which C_T , NO_3^- , and PO_4^{3-} concentrations within the mixed layer decreased concomitantly, and the resulting values were divided by 12 days to obtain daily mean rates ($mmol\ C\ m^{-2}\ d^{-1}$).

where D denotes day (the time step); $[NC_T]^D - [NC_T]^{D+1}$ is the difference in NC_T concentration within the mixed layer, H , between subsequent days; F ($mmol\ m^{-2}\ d^{-1}$) is the CO_2 flux from the atmosphere; K_V is the vertical eddy diffusivity across the bottom of the mixed layer; and dC_T/dz ($mmol\ m^{-4}$) is the vertical gradient in C_T concentration between the mixed layer and the upper thermocline. In estimating the vertical diffusive flux of C_T into the mixed layer, we used measured values of dC_T/dz (the mean dC_T/dz is $2.65\ mmol\ C\ m^{-4}$) in conjunction with a K_V value of $0.3\ cm^2\ s^{-1}$ determined using the 1-D Fickian diffusion model constrained with SF_6 data collected during GasEx-98 (Kim et al. 2005). The flux of CO_2 from the atmosphere, $(F_{air-sea})_{D+1}$, was calculated from measured pCO_2 differences between the atmosphere and the eddy surface in conjunction with CO_2 exchange rates. The gas exchange rates used in our calculation were estimated from wind speeds and the gas exchange rate–wind speed parameterization (Wanninkhof and McGillis 1999), which in turn was derived from covariance flux data collected during GasEx-98 (McGillis et al. 2001). Similarly, the rates of net community production using O_2 mass balance constraints (NP_O) were performed following the expression in Eq. 1 (see Table 1).

We also determined the rates of net community production (NP_N) from changes in NO_3^- inventory within the mixed layer, corrected only for diffusive NO_3^- flux from the upper thermocline (Table 1):

$$NP_N|_{\Delta D} = H^{D+1} \left([NO_3^-]^D - [NO_3^-]^{D+1} \right) + K_V (dNO_3^-/dz) \quad (2)$$

where dNO_3^-/dz is the vertical gradient in NO_3^- concentration between the mixed layer and the upper thermocline. The rates of net community production were also estimated using PO_4^{3-} data (NP_P) using the same expression as Eq. 2 after substitution of PO_4^{3-} for NO_3^- (Table 1). During GasEx-98, Zhang et al. (2001) determined the rate of net community production using NO_3^- results obtained from a single diurnal study centered at YD 172 when surface NO_3^- concentrations were at trace levels. The authors used a K_V value of $1.0\ cm^2\ s^{-1}$ to estimate the vertical diffusive flux of NO_3^- into the mixed layer because the increase of $80\ nmol\ kg^{-1}\ NO_3^-$ during the night of the

diurnal study was assumed to be entirely due to vertical eddy diffusion; however, the nighttime cooling of the surface water is likely to have caused the entrainment of NO_3^- from the upper thermocline to the surface via convective mixing. The value of $K_V = 1.0\ cm^2\ s^{-1}$ is therefore likely to represent an overestimation (Kim et al. 2005). NH_4^+ concentrations remained constant ($0.05 \pm 0.02\ \mu mol\ kg^{-1}$) during the study period, suggesting that the production and consumption of NH_4^+ were largely balanced within the mixed layer. Therefore, we did not include NH_4^+ when estimating the net community production based on NO_3^- .

For Periods I and III, the C_T - and O_2 -based rates of net community production were calculated from the mean rates of changes in NC_T and O_2 concentrations within the mixed layer, whereas the NO_3^- - and PO_4^{3-} -based rates were calculated only when concentrations of these two species decreased within the mixed layer. For Period II, the C_T -, O_2 -, NO_3^- -, and PO_4^{3-} -based rates were determined only for periods of time (approximately 6 d) during which NC_T , NO_3^- , and PO_4^{3-} concentrations decreased concurrently. All estimates were daily mean rates averaged over the three time periods. In calculating rates of net community production, we ignored the advective flux of C_T , O_2 , NO_3^- , and PO_4^{3-} between the mixed layer and the top of the thermocline. Consequently, the resulting rates of net community production are likely to represent underestimations. In addition, the coherent water properties (e.g., salinity and temperature) of the eddy over the study period suggest the minimal intrusion of C_T , NO_3^- , and PO_4^{3-} into the eddy by lateral diffusion. Therefore, the mass balances of C_T , O_2 , NO_3^- , and PO_4^{3-} within the mixed layer of the eddy were assumed to be reasonable measures of NP.

The C_T -based estimates of net community production are in good agreement with O_2 -based estimates; however, both are two to five times higher than the values yielded by the mass balance of mixed-layer NO_3^- (Table 1). We used a C:N ratio of 7.3 and a C:O ratio of 0.7 (Anderson and Sarmiento 1994) to convert individual estimates to C_T -equivalent-based estimates. The differences between the C_T - and O_2 -based and NO_3^- -based estimates were greatest for Period I, thereafter decreasing for Periods II and III (Table 1). In the following section, we evaluate the accuracy of this marked disparity by comparing C_T -, O_2 -, and NO_3^- -based estimates of net community production

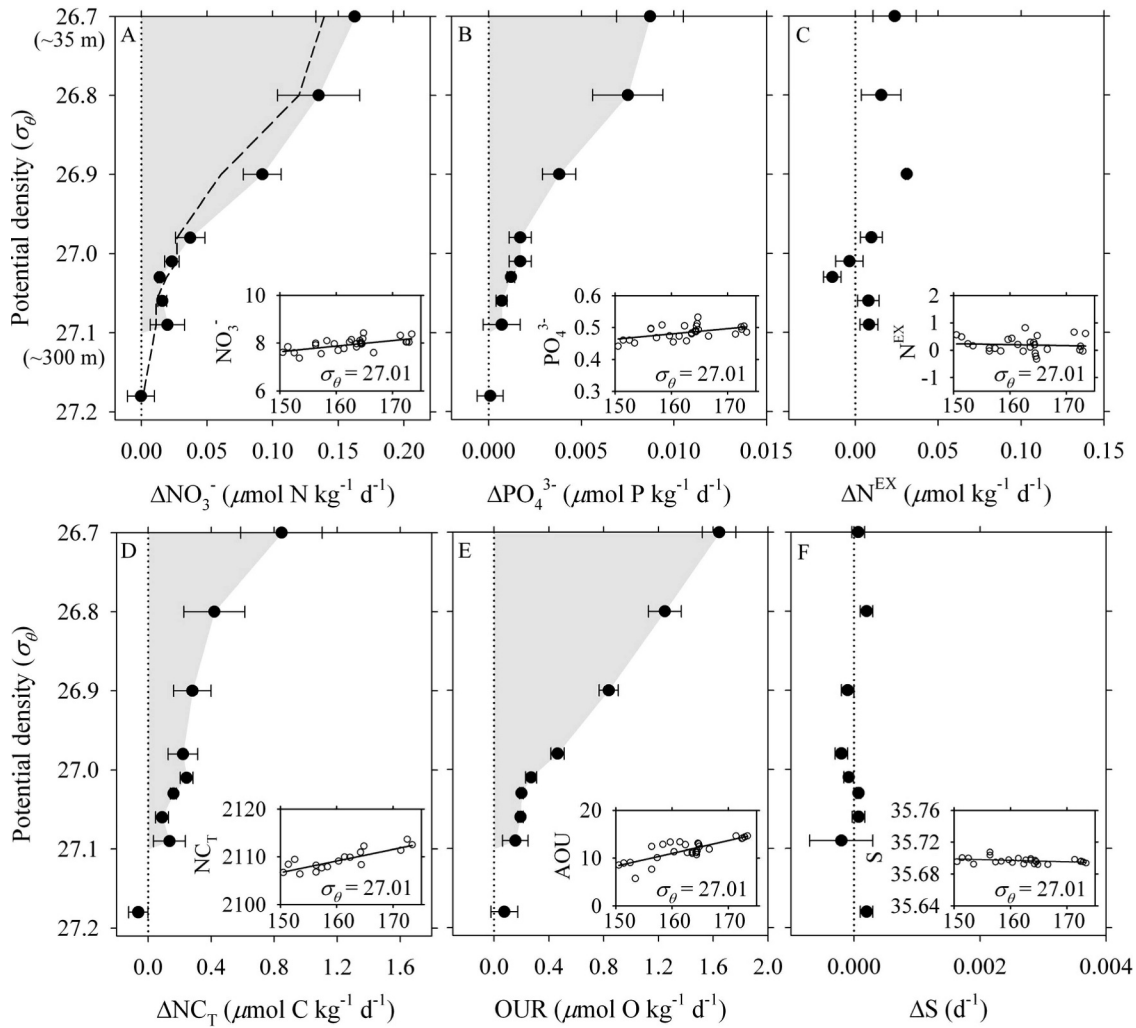


Fig. 3. Rates of increase in (A) NO_3^- (ΔNO_3^-); (B) PO_4^{3-} (ΔPO_4^{3-}); (C) N^{EX} ($\Delta\text{N}^{\text{EX}}$) ($\text{N}^{\text{EX}} = \text{NO}_3^- - 16 \times \text{PO}_4^{3-}$); (D) NC_T (ΔNC_T); (E) oxygen utilization rate (OUR); and (F) salinity (ΔS) during the study period (YD 150–173) as a function of potential density between $\sigma_\theta = 26.70$ and $\sigma_\theta = 27.18$ (equivalent to a range in water depth of 35–440 m). The dashed line in (A) is a smooth fit of ΔNO_3^- values predicted from ΔPO_4^{3-} using a $\text{NO}_3^- : \text{PO}_4^{3-}$ ratio of 16. Calculated $\Delta\text{N}^{\text{EX}}$ value is not shown in (C) for times when either ΔNO_3^- or ΔPO_4^{3-} values are either zero or negative values. Error bars were estimated using $\sigma = \{(\Delta)^2/(n-1)\}^{0.5}$, where σ is the standard deviation, Δ is the difference between fitted values and individual data, and n is the number of data. Insets show data of all parameters used in calculating the rates of remineralization on the isopycnal surface of $\sigma_\theta = 27.01$.

with the remineralization rates obtained from the integrated rates of C_T , NO_3^- , and PO_4^{3-} accumulation and O_2 utilization over the study period for the upper thermocline waters of the eddy.

Estimation of in situ remineralization rates in the upper thermocline—A comparison of the accumulation rates of C_T , NO_3^- , and PO_4^{3-} within the upper thermocline and their removal rates from the eddy surface will provide insight into the factors that possibly cause the large disparity between C_T - and O_2 -based and NO_3^- -based estimates. Over a 3-week period, the accumulation rates (A; $\text{mmol m}^{-2} \text{d}^{-1}$) of C_T (A^C), NO_3^- (A^N), and PO_4^{3-} (A^P) for the upper thermocline associated with the remineralization of organic matter were estimated by integrating the mean profiles ($f-A^C$, $f-A^N$, and $f-A^P$) of accumulation rates (see insets of Fig. 3 as examples of

accumulation on specific isopycnals) for all isopycnal surfaces over the approximate depth range between 35 m, which is maximum mixed-layer depth during the study period, and 300 m, where the accumulation rates of C_T , NO_3^- , and PO_4^{3-} approach zero (see Fig. 3):

$$A^{\text{C,N,P}} = \int_{35}^{300} f - A^{\text{C,N,P}} dz \quad (3)$$

The rate of O_2 utilization associated with the remineralization of organic matter was also estimated by integrating the mean profile of O_2 utilization rates for all isopycnal surfaces over the same depth range. To enable a direct comparison, all estimates were converted to C_T equivalents ($\text{mmol C m}^{-2} \text{d}^{-1}$) using the elemental ratios of Anderson and Sarmiento (1994) (Fig. 4).

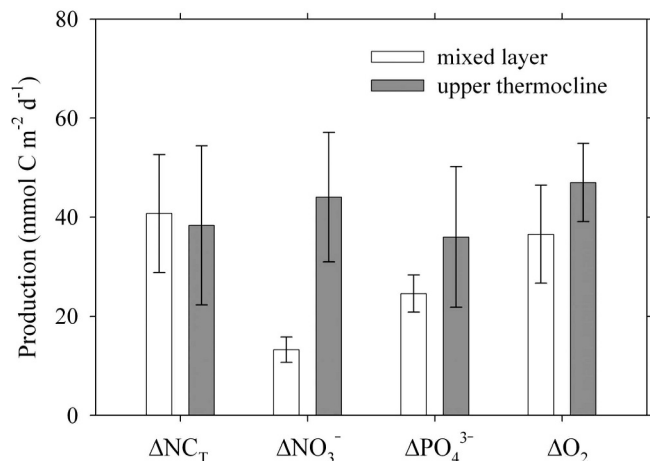


Fig. 4. Comparison of the removal rates (equivalent to rates of net community production, in $\text{mmol C m}^{-2} \text{d}^{-1}$) of C_T , NO_3^- , and PO_4^{3-} and the rate of net O_2 production (open bars) from the mixed layer of the eddy and the accumulation rates of C_T , NO_3^- , and PO_4^{3-} , and O_2 utilization (gray bars; equivalent to rates of remineralization, in $\text{mmol C m}^{-2} \text{d}^{-1}$) integrated over a water depth of 35–300 m in the upper thermocline during the study period (YD 150–173). All estimates were converted to C_T -equivalent-based estimates ($\text{mmol C m}^{-2} \text{d}^{-1}$) using the elemental ratios of Anderson and Sarmiento (1994). Error bars for removal rates were estimated as the sum of errors in each component derived from uncertainties in measured vertical diffusivity, gas exchange rate, and carbon and nutrient parameters. Error bars for remineralization rates were estimated from uncertainties in their rates of increase along isopycnal surfaces.

The integrated rates of C_T , NO_3^- , and PO_4^{3-} accumulation and O_2 utilization for the upper thermocline can be biased, albeit not considerably, if mixing between the eddy and the surrounding water is inaccurately accounted for. To explore this possibility, we estimated the rate of salinity change for each isopycnal surface in the depth range of 35–440 m (Fig. 3F). A mixing coefficient for each isopycnal surface was estimated on the basis of two salinity end members representing the same isopycnal surface within the eddy and the surrounding water, respectively, in conjunction with the measured rate of change of salinity obtained from the same isopycnal surface. The resulting mixing coefficients indicate that, over the 3-week study period, the upper thermocline water within the eddy appeared to be mixed with the surrounding water no more than 3% when averaged over all isopycnal surfaces. We then estimated the contribution of mixing to the rates of C_T , NO_3^- , and PO_4^{3-} accumulation and O_2 utilization based on mixing coefficients and the two sets of end-member values of C_T , NO_3^- , PO_4^{3-} and apparent oxygen utilization ($\text{AOU} = \text{saturated } \text{O}_2 - \text{measured } \text{O}_2$) representing the eddy and the surrounding water. The end-member values representing the conditions of the eddy were obtained from the first 3 d of GasEx-98, whereas the values representing the conditions of the surrounding water were obtained from the World Ocean Atlas 2005 (Antonov et al. 2006; Garcia et al. 2006a,b) and the nearest sampling station (46°N , 20°W) occupied during the CLIVAR/ CO_2 repeat hydrography cruise A16N in June 2003 (Feely et al. 2005). Our

calculations indicate that mixing led to slight overestimates of the integrated rates of C_T (4%), NO_3^- (3%), and PO_4^{3-} (3%) accumulation and O_2 (1%) utilization for the upper thermocline. The results shown in Fig. 4 were corrected for these overestimations.

The integrated accumulation rates of C_T , NO_3^- , and PO_4^{3-} are in good agreement: the difference between the two most disparate of the three estimates is statistically insignificant (within the uncertainties of the two estimates) (Fig. 4). The measured rate of O_2 utilization is also in good agreement with the rates predicted from the accumulation rates of C_T , NO_3^- , and PO_4^{3-} (Fig. 4). All four independent chemical tracers yielded a mean remineralization rate of $41.4 \pm 5.1 \text{ mmol C m}^{-2} \text{d}^{-1}$. This rate of remineralization is indistinguishable from the C_T -based and O_2 -based rates of net community production, meaning that almost all the organic matter exported from the eddy surface during the study period was quickly remineralized in the upper thermocline during the same period.

In contrast, the integrated accumulation rate of NO_3^- for the upper thermocline over a 3-week period is approximately three times the removal rate from the overlying mixed layer over the same period. Such a contrasting difference shows unequivocally that NO_3^- accumulated in the upper thermocline in excess of its removal from the mixed layer of the eddy.

Discussion

Causes of temporally variable differences between C_T - and O_2 -based and NO_3^- -based estimates of net community production—Several factors are potentially important in explaining the temporally variable differences in the C_T - and O_2 -based and NO_3^- -based estimates of net community production for cold waters ($\sim 15^\circ\text{C}$) within the oligotrophic eddy in the extratropical North Atlantic.

Results derived from the analysis of water column nutrient data suggest diazotrophy in the surface waters. The measured rates of NO_3^- increase ($\mu\text{mol N kg}^{-1} \text{d}^{-1}$) within the 35–300-m-depth range (equivalent to $\sigma_\theta = 26.70$ – 27.10) were generally higher than those predicted from the measured rates of PO_4^{3-} increase ($\mu\text{mol P kg}^{-1} \text{d}^{-1}$) multiplied by the N:P stoichiometry of 16 (Fig. 3A,B). As a result, the ratios of increases in NO_3^- to those in PO_4^{3-} were generally higher than 16.

We calculated N^{EX} ($\text{N}^{\text{EX}} = \text{NO}_3^- - 16 \times \text{PO}_4^{3-}$) (Bates and Hansell 2004) to quantify the excess concentrations of NO_3^- relative to the PO_4^{3-} quota, assuming Redfield stoichiometry. The rates of increase in N^{EX} within the 35–300-m-depth range indicate that excess NO_3^- was derived mostly from the remineralization of organic matter rich in N, relative to the biological P quota, produced in the overlying eddy surface (Fig. 3C). Furthermore, the fact that the accumulation rate of NO_3^- for the upper thermocline was significantly higher than its removal rate from the mixed layer of the eddy also points to the in situ generation of excess NO_3^- in the upper thermocline (Fig. 4).

We also examined the possibility of other sources of fixed nitrogen that can support part, if not all, of the net

community production at our study site; however, they appear to be less likely candidates. For instance, atmospheric input of fixed nitrogen is estimated to be 2–10 mmol N m⁻² yr⁻¹ (Galloway et al. 1995, 2004), which could sequester carbon at a rate of 0.04–0.20 mmol C m⁻² d⁻¹ from the mixed layer if all the airborne fixed nitrogen were deposited in this study area and made readily available to microorganisms. During the study period, carbon sequestration induced by such levels of airborne fixed nitrogen could account for less than 2% of the net community production estimated using the mass balance of NO₃⁻. A further source of fixed nitrogen is the remineralization of dissolved organic nitrogen (DON), which might also have fueled carbon removal at the study site; however, there was no appreciable DON drawdown for the initial 8 d (Period I) of the study period, during which NO₃⁻ concentrations were close to or below the detection limit. This lack of appreciable DON drawdown indicates that DON did not significantly support biological activity at the study site. However, this source remains a possibility because DON measurements were not performed for Periods II and III.

Fixed nitrogen can also be supplied across the flanks of the eddy from the neighboring surface waters rich in NO₃⁻; however, this flux of NO₃⁻ is likely to be accompanied by a matching flux of PO₄³⁻ in the near Redfield proportion (i.e., N:P = 15.1 ± 0.4), which is an average value of four N:P ratios representing the four grid cells (1° latitude × 1° longitude) of the World Ocean Atlas 2005 (Garcia et al. 2006b) surrounding the study site. The subsequent export of organic matter from the mixed layer and remineralization in the upper thermocline would also occur in much the same C:N:P ratio as that in which it is delivered to the eddy; therefore, this mechanism cannot adequately explain the disparity between the amount of nitrate removed from the eddy surface and the amount of nitrate accumulated in the upper thermocline (Fig. 4). Entrainment of thermocline waters into the mixed layer during storm periods could also contribute to non-Redfieldian behavior within the mixed layer if the C:N:P ratio of such entrained waters differed from the Redfield ratio. However, our analysis indicated that entrainment during three storm periods brought C, N, and P into the mixed layer in near Redfield proportions (C:N:P = 147 ± 27:16.4 ± 0.4:1).

During the study period, the PO₄³⁻ concentrations never became fully depleted (Fig. 2D); however, low PO₄³⁻ concentrations (<0.1 μmol kg⁻¹) in the surface mixed layer are known to be stressful to phytoplankton and diazotrophs. Previous studies indicate that when PO₄³⁻ concentrations become low, phytoplankton and diazotrophs may be able to mine P from the dissolved organic phosphorous (DOP) pool (Dyhrman et al. 2006; Fu et al. 2006). This source of P could potentially account for our finding that PO₄³⁻-based net community production was smaller than the integrated rate of PO₄³⁻ accumulation for the upper thermocline (Fig. 4). However, this remains a conjecture because DOP measurements were not performed during the study period, and, furthermore, the disparity observed between NP_p and PO₄³⁻ accumulation in the upper thermocline is within the uncertainties of the estimations.

Our inability to identify alternative mechanisms causing the large differences in the C_T and O₂-based and NO₃⁻-based estimates of net community production in a cold oligotrophic eddy in the extratropical North Atlantic Ocean leaves N₂ fixation as the most likely, though very surprising, process. However, if the difference between surface N removal and its accumulation in the upper thermocline was due entirely to N₂ fixation, the required production rate of fixed nitrogen would be approximately 4.2 ± 1.8 mmol N m⁻² d⁻¹ (equivalent to 31 mmol C m⁻² d⁻¹; see Fig. 4). This rate is approximately an order of magnitude higher than previously reported values (0.06–0.5 mmol N m⁻² d⁻¹) in tropical and subtropical warm waters (Karl et al. 1997; Zehr et al. 2001; Capone et al. 2005), indicating that it may be unrealistically high. In addition, it is not entirely clear which microorganisms could be responsible for fixing nitrogen at the study site, as the few measurements of biological parameters undertaken during the study period were not targeted toward identifying diazotrophs. Difficult to explain as well is the apparently rapid export and mineralization of the biogenic particles formed during NP. Rapid growth of phytoplankton normally result in a bloom (accumulation of biomass in the surface layer), with a delay in the export particles. But the rapid subsurface accumulation of NP by-products (with NP, export, and mineralization events occurring multiple times over a relatively brief 3 weeks of observations) suggests immediate and rapid export of the particles. Rapid export is inconsistent with expectations for *Trichodesmium* or for diazotrophic picoplankton, both of which would be expected to be exported slowly and both of which are normally found to fix N₂ in warm waters. Diatoms containing diazotrophic symbionts are known to occur in the ocean (Villareal and Carpenter 1988), but the availability and drawdown of silicate was not great, arguing against a role for these organisms.

In future works, well-designed experiments should be conducted to determine whether such non-Redfieldian removal of nitrate and carbon is a widespread phenomenon in oligotrophic extratropical waters. If this phenomenon is indeed found to be widespread, the results of such experiments should facilitate the identification of the mechanisms underlying the production of excess NO₃⁻.

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