

# **Global Biogeochemical Cycles**

# **RESEARCH ARTICLE**

#### **Kev Points:**

- We estimated net community production (NCP) by summing the mixed layer reduction in dissolved inorganic carbon in N-depleted ocean gyres
- The mixed layer C<sub>T</sub> reduction was calculated from an annual C<sub>T</sub> cycle, deduced from global records of surface pCO<sub>2</sub> and total alkalinity
- Our study suggests that N<sub>2</sub> fixation by microorganisms is a major driver for this NCP in the vast areas of ocean gyres

### **Supporting Information:**

- Supporting Information S1
- Data Set S1
- Data Set S2

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# **Carbon-Based Estimate of Nitrogen Fixation-Derived Net Community Production in N-Depleted Ocean Gyres**

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Abstract Accurate estimation of net community production (NCP) in the ocean is important for determining the future trend for carbon dioxide concentrations in the atmosphere and thus for understanding the global carbon cycle and climate change. Most methods for measuring NCP rely on analysis of dissolved fixed inorganic nitrogen species (N), which are believed to be limiting factors for NCP. However, in the vast areas of the ocean gyres only low levels of N are available for phytoplankton during much of the year. In this study the NCP was estimated by summing the seasonal reduction in the concentration of dissolved inorganic carbon ( $C_T$ ) in the surface mixed layer, corrected for changes associated with salinity variation, net air-sea CO<sub>2</sub> flux, horizontal C advection, non-Redfield diffusive C and N fluxes (deviations from the C:N ratio of 7), and anthropogenic nitrogen deposition. The mixed layer reduction in C<sub>T</sub> was calculated from an annual  $C_T$  cycle, deduced from comprehensive records of surface pCO<sub>2</sub> and total alkalinity, using an established thermodynamic model. This method yielded a value of  $0.6 \pm 0.2$  Pg of C, which represents the NCP that occurred during the warming period (approximately 8 months) in the nitrate-depleted  $(< 0.2 \,\mu$ mol/kg) ocean. Our estimate is broadly consistent with the global N<sub>2</sub> fixation rate estimated using the  $^{15}$ N-based method and suggests that N<sub>2</sub> fixation by microorganisms is a major driver for this NCP.

# 1. Introduction

Dissolved forms of fixed inorganic nitrogen (nitrate, NO<sub>3</sub><sup>-</sup>; nitrite; and ammonium: hereafter referred to as N) are indispensable nutrients for marine life and largely determine the phytoplankton biomass throughout much of the global ocean. However, the concentrations of N are low in subtropical ocean gyres, as the sunlit upper layers are permanently stratified and vertical transport (via diffusion and advection) of N from deep waters to the sunlit layers is limited. As a result of low concentrations of N in surface waters of the ocean gyres, new photosynthetic production depends on external (as opposed to recycled) supply of nutrients. In the oligotrophic ocean, N limitation is ameliorated by a diverse assemblage of diazotrophs, which reduce strongly bonded N<sub>2</sub> to ammonia and dissolved organic nitrogen (DON) via an energy intensive process of N<sub>2</sub> fixation (Capone et al., 1997; Karl et al., 2002). This process is known to be a major source of N to the oligotrophic ocean, accounting for approximately 50% of the total external source of N (Galloway et al., 2004; Gruber & Galloway, 2008; Raes et al., 2015).

Despite the potential importance of  $N_2$  fixation in regulating phytoplankton biomass and net community production (NCP) in the oligotrophic ocean, the global rate of N<sub>2</sub> fixation has remained poorly constrained. This is because shipboard measurements based on the acetylene reduction assay or the  ${}^{15}N_2$  assimilation have not been able to resolve the temporal and spatial dynamics of N<sub>2</sub> fixation. Another impediment to obtaining accurate estimates is that these two methods yield different rates of N<sub>2</sub> assimilation into the biomass. This large difference in rate is inevitable because the acetylene method provides an indirect estimate of gross N<sub>2</sub> fixation whereas the <sup>15</sup>N tracer method measures the net rate of <sup>15</sup>N assimilation (Böttjer et al., 2017; Mulholland, 2007; Wilson et al., 2012). Approximately 60% of the measured rates reported to date have been based on the <sup>15</sup>N<sub>2</sub> assimilation method (Luo et al., 2012). Moreover, the <sup>15</sup>N-based rates reported earlier are a factor of 2 or more lower than recent measurements, because the earlier measurements were subject to the problem of incomplete equilibrium of  ${}^{15}N_2$  gas with the seawater sample (Böttjer et al., 2017; Großkopf et al., 2012). Assessment of <sup>15</sup>N isotope abundance in sinking organic matter is an alternative to <sup>15</sup>N-

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labeled incubation methods for estimating the relative contributions of N sources supporting new production. However, data obtained using this method are not sufficient to provide a global estimate. More importantly, the accuracy of this method relies on several key assumptions, including a steady state condition, a low level of export of DON, and an accurate estimate of the <sup>15</sup>N content of the nitrate transported to the upper ocean, all of which need to be confirmed (Böttjer et al., 2017; Gruber, 2016).

Alternative methods based on biogeochemical models and geochemical tracers (e.g., N\* and P\*) have been used to estimate regional and global rates of N<sub>2</sub> fixation (Deutsch et al., 2007; Gruber & Sarmiento, 1997), but as these are indirect methods so the model predictions need field verification. For example, the N<sub>2</sub> fixation rate estimated from the excess of  $NO_3^-$  in seawater compared with that predicted using measured phosphate (PO<sub>4</sub><sup>3-</sup>; N<sup>\*</sup> = NO<sub>3</sub><sup>-</sup> - 16 × PO<sub>4</sub><sup>3-</sup>) relies on the elemental N:P ratio of organic matter produced by N<sub>2</sub> fixing organisms and those that do not fix N<sub>2</sub>. However, reported N:P ratios of organic matter vary greatly, primarily because elemental stoichiometry depends on taxonomic composition and accumulated detritus; these factors make the estimation of the  $N_2$  fixation rate from  $N^*$  signals unreliable (Martiny et al., 2013). Moreover, the  $N^*$  signal reflects the net effect of  $N_2$  fixation and denitrification and is affected by anthropogenic N that has entered the ocean via atmospheric deposition (Duce et al., 2008; T.-W. Kim et al., 2011; I.-N. Kim et al., 2014). Another indirect method is based on seawater  $P^*$  ( $P^* = PO_4^{3-} - NO_3^{-}/16$ ) or  $P_T^*$  $(P_T^* = [PO_4^{3-} + DOP] - [NO_3^- + DON]/16)$  signals (Deutsch et al., 2007). This method assumes that N<sub>2</sub> fixation activity is more closely associated with sources of elevated P<sup>\*</sup>, probably caused by denitrification in the water column. Therefore, it calculates the difference between surface  $P^*$  values and those predicted from upwelled  $P^*$ , with the difference attributed to N<sub>2</sub> fixation activity. However, it involves the same errors that influence the N<sup>\*</sup>-based method. Therefore, substantial differences in estimates of the N<sub>2</sub> fixation rate based on direct and indirect methods are inevitable.

To overcome the problems inherent in the N<sub>2</sub> fixation measurement methods (direct or indirect) that require conversion of N<sub>2</sub> fixation to NCP, we directly estimated the seasonal reduction of dissolved inorganic carbon  $(C_T = [HCO_3^{-1}] + [CO_3^{2^{-1}}] + [CO_2])$  in the mixed layer during the period of N depletion. A reduction in the concentration of  $C_T$  in the absence of N was first reported at the Bermuda Atlantic Time-series Study (BATS; 31°N, 64°W, http://bats.bios.edu/; Michaels et al., 1994) and the Hawaii Ocean Time-series (HOT; 23°N, 158°W, http:// hahana.soest.hawaii.edu/hot/hot-dogs/) stations (Karl et al., 2003). Subsequently, by applying the empirical algorithms between salinity (S)-normalized  $C_T$  ( $nC_T = C_T \times 35/S$ ) and sea surface temperature (SST) derived from a small  $C_T$  data set ( $n \sim 16,000$ ) to the global ocean. Lee et al. (2002) inferred that this phenomenon could be widespread throughout tropical and subtropical oceans. The major limitation of the study of Lee et al. (2002) was its reliance on a restricted  $C_T$  data set that poorly resolved the seasonal evolution of  $C_T$  in the world ocean.

In the present study, we used large data sets of seawater pCO<sub>2</sub> comprising approximately 6.5 million data, which are 2 orders of magnitude greater than the C<sub>T</sub> data set; this enabled accurate resolution of the seasonal evolution of pCO<sub>2</sub> in much of the world oceans. In particular, the combination of this data set with a surface alkalinity data set (Lee et al., 2006) and the established thermodynamic model for the seawater carbonate system should enable the seasonal evolution of C<sub>T</sub> in the world oceans to be accurately resolved. We describe here a novel method for estimating NCP values in waters containing depleted levels of N, based on the mixed layer nC<sub>T</sub> reduction. The NCP estimate could be attributed only to N<sub>2</sub> fixation (NCP<sub>N2fix</sub>). The values for NCP<sub>N2fix</sub> determined in N-depleted waters were compared with literature values inferred from various estimates of N<sub>2</sub> fixation rates.

# 2. Computation Methods

In the oligotrophic ocean, we estimated the rate of  $NCP_{N2fix}$  from reductions in the  $nC_T$  inventory within the mixed layer and corrected for changes arising from the net air-sea  $CO_2$  flux, horizontal C advection, the diffusive  $C_T$  and  $NO_3^-$  flux, and the atmospheric deposition of pollutant N. To achieve this, we used the following equation:

$$NCP_{N2fix} = \left(AH\left[nC_{T}^{M} - nC_{T}^{M+1}\right]\right) + AF_{AIR-SEA} - Au(dnC_{T}/dx) + AK_{\nu}[dC_{T}/dm - (C/N)dN/dm] - A(C/N)AND$$
(1)

where A (m<sup>2</sup>) is the area of each pixel (4° latitude  $\times$  5° longitude); M is the time step (months);  $[nC_T^M - nC_T^{M + 1}]$  is the decrease in the  $nC_T$  concentration at the mean mixed layer depth

 $(H = [H^{M} + H^{M+1}]/2)$  over consecutive months; F (mol·m<sup>-2</sup>·month<sup>-1</sup>) is the net air-sea CO<sub>2</sub> flux; u is the mean horizontal advective velocity (m/s), and dnC<sub>T</sub>/dx is the mean horizontal gradient of nC<sub>T</sub>;  $K_V$  (m<sup>2</sup>/month) is the eddy diffusivity across the bottom of the mixed layer; and dC<sub>T</sub>/dm and dN/dm (mol m<sup>-4</sup>) are the vertical gradients of C<sub>T</sub> and NO<sub>3</sub><sup>-</sup> concentrations in the upper thermocline, respectively. AND is the atmospheric deposition of pollutant N (mol·m<sup>-2</sup>·month<sup>-1</sup>). Equation (1) was applied only when the mixed layer nC<sub>T</sub> concentration decreased over several months of the year (approximately consistent with the period of warming) and only for pixels in which the mean NO<sub>3</sub><sup>-</sup> concentration remained <0.2 µmol/kg. This cutoff point for the NO<sub>3</sub><sup>-</sup> concentration was used because marine cyanobacteria of the genus *Trichodesmium*, which is a cosmopolitan N<sub>2</sub> fixing microorganism, mostly occur in waters where the NO<sub>3</sub><sup>-</sup> concentration is <0.2 µmol/kg (Hood et al., 2004, 2000).

For each pixel, the annual cycle of the mixed layer  $C_T$  concentration was calculated from monthly mean pCO<sub>2</sub> and A<sub>T</sub> data using the carbonic acid dissociation constants of Mehrbach et al. (1973; with the functional forms refitted by Dickson & Millero, 1987), other auxiliary thermodynamic constants (including the solubility of CO<sub>2</sub>; Weiss, 1974; and the dissociation constants for boric acid; Dickson, 1990, and phosphoric acid; Yao & Millero, 1995), and the total boron concentration estimated by Lee et al. (2010). This set of thermodynamic constants was consistent with both laboratory and field data (Lee et al., 1996, 2000). Seawater pCO<sub>2</sub> data collected over a 55-year time span (1957–2012) were normalized to each month of the reference year of 2005 by accounting for oceanic uptake of anthropogenic CO<sub>2</sub> (Takahashi et al., 2014). The estimated monthly mean pCO<sub>2</sub> values for the year 2005 are available at https://www.nodc.noaa.gov/ocads/oceans/ndp\_094/ndp094.html. Monthly mean values of  $A_T$  were estimated from the  $A_T$ -SSS-SST algorithms (Lee et al., 2006) and monthly records of SSS and SST. Monthly mean SSS and SST data are obtained from the World Ocean Atlas 2009 (Antonov et al., 2010; http://www.nodc.noaa.gov/OC5/WOA09/woa09data.html) and National Centers for Environmental Prediction Reanalysis data (https://www.esrl.noaa.gov/psd/data/reanalysis/reanalysis.shtml), respectively. We removed variations in  $C_T$  associated with salinity variations (due to evaporation/precipitation) by normalizing C<sub>T</sub> values to a mean salinity ( $\overline{S}$ ) representing the warming period using nC<sub>T</sub> = C<sub>T</sub> ×  $\overline{S}/S$ , where S is the monthly mean salinity. To calculate the mixed layer reduction in  $nC_{T_r}$  a linear regression was applied to  $nC_T$  data obtained for the selected warming periods. To minimize biases caused by questionable data, we used a traditional mean and standard deviation method to remove those data points. Thus, during fitting of the data we excluded all  $nC_T$  values having residuals (measured values minus those predicted) that exceeded 2 standard deviations from the mean residual value.

To integrate the mixed layer  $nC_T$  reduction during the warming period, we used records of monthly mean mixed layer depth derived using the -0.2 °C vertical temperature gradient (de Boyer Montégut et al., 2004; http://www.ifremer.fr/cerweb/deboyer/mld/Surface \_Mixed\_Layer\_Depth.php). Climatological (time-independent) monthly mean surface  $NO_3^-$  data from the World Ocean Atlas 2013 Version 2 (Garcia et al., 2014; https://www.nodc.noaa.gov/OC5/woa13/) were used to evaluate whether a given pixel had a  $NO_3^-$  concentration < 0.2 µmol/kg. These climatological  $NO_3^-$  data are heavily skewed to the earlier periods (1980s–1990s), whereas the pCO<sub>2</sub> climatological data are skewed to more recent periods (2000s onward). This apparent mismatch could lead to underestimation of the areal extent of N-depleted ocean (for which we had estimated  $NCP_{N2fix}$  values), if the N-depleted subtropical gyres have increased over time between these two periods during which most  $NO_3^-$  and pCO<sub>2</sub> data are available (1980s–1990s for  $NO_3^-$  vs, 2000s onward for pCO<sub>2</sub>). However, the observation of no significant trend of change in the  $NO_3^-$  concentrations found in the HOT and BATS stations (Kavanaugh et al., 2018; Lomas et al., 2013) and in the extended study area (e.g., North Pacific Ocean; Yasunaka et al., 2016) suggests that this climatological  $NO_3^-$  field is representative of the period from 2000 onward.

Following the procedure described by Takahashi et al. (2009), monthly mean net air-sea  $CO_2$  fluxes were estimated using the climatological seawater p $CO_2$  field (Takahashi et al., 2014), atmospheric p $CO_2$  data for 2005, the air-sea gas transfer rate, and the solubility of  $CO_2$  in seawater (Weiss, 1974; see supporting information).

Horizontal advective transports impact the seasonal  $nC_T$  cycle (and therefore the magnitude of  $nC_T$  reduction). The rate of horizontal  $nC_T$  transport between the analysis pixels was estimated using the horizontal  $nC_T$  gradient and the current velocity during the warming period. The zonal and meridional gradients in  $nC_T$  were estimated from the  $nC_T$  field, calculated from climatological  $pCO_2$  and  $A_T$  data. Zonal and meridional flows were estimated from the monthly climatological current field computed for the period 1993–2017

using the Geostropic and Ekman Current Observatory product (Sudre et al., 2013), in which geostrophic and Ekman velocities were estimated from the combination of satellite altimetry and scatterometer wind stress data.

The flux of  $C_T$  and  $NO_3^-$  from the upper thermocline into the mixed layer via eddy diffusion could either increase or decrease the mixed layer reduction in nC<sub>T</sub> resulting from NCP<sub>N2fix</sub> depending on whether the ratio of the fluxes of  $C_T$  and  $NO_3^-$  from the upper thermocline was less than or greater than 7, respectively. Specifically, if the flux ratio of  $C_T$  and  $NO_3^-$  into the mixed layer is greater than 7 (indicating that the flux of  $C_T$  is in excess relative to that of  $NO_3^-$ ), the excess  $C_T$  would offset the  $nC_T$  reduction. The monthly fluxes of  $C_{T}$  and  $NO_{3}^{-}$  into each pixel via eddy diffusion were calculated using a basin-scale vertical gradient (Table S1 in the supporting information) of  $C_T$  and  $NO_3^-$  representing the given pixel and eddy diffusivity,  $K_V$  of 0.2– 0.3 cm<sup>2</sup>/s representing the upper thermocline of a subtropical ocean (Kim et al., 2005; Ledwell et al., 1998). Vertical  $C_T$  and  $NO_3^-$  data were obtained from the Global Ocean Data Analysis Project Version 2 (Olsen et al., 2016; https://www.nodc.noaa.gov/ocads/oceans/GLODAPv2/). The mixed layer reduction in nCT was then corrected for the  $C_T$  difference in the ratio of  $C_T$  flux and that calculated using the concurrent flux of NO<sub>3</sub><sup>-</sup> multiplied by a C:N ratio of 7 (Table S1). During the warming period, the mixed layer generally shoals but intermittent entrainment (e.g., caused by eddies and storms) also occurs due to short periods of windinduced mixed layer deepening (McGillicuddy et al., 2007; Zhang et al., 2001). The effect of the entrainment process on the mixed layer nC<sub>T</sub> budget would be similar to that of the diffusive flux. However, its influence is probably insignificant, given that the evolution of mixed layer temperature can be accurately predicted without accounting for entrainment (Gruber et al., 1998).

The NCP contributed by AND was estimated by multiplying the rate of atmospheric N deposition by a C:N ratio of 7. The rate of AND was obtained from multimodel global data sets of atmospheric N deposition, simulated particularly for the year 2000 (Lamarque et al., 2013; http://data.ceda.ac.uk/badc/accmip/data/GISS/).

# 3. Results and Error Analysis

In the widespread areas of the tropical and subtropical oceans the surface  $nC_T$  concentration decreased during the period of N depletion, which started in early spring and extended to late fall. The rate of  $nC_T$  decrease differed spatially, but the general trend among the oceans examined indicated a strong inverse correlation between  $nC_T$  and SST during the warming period (Figure 1). The accuracies of the estimated  $nC_T$  reductions were assessed by comparing the  $nC_T$  reductions measured for periods spanning 24–26 years at the BATS and the HOT stations against the estimates for those pixels encompassing these time-series stations. The NCP<sub>N2fix</sub> values (0.9 ± 0.2 mol C/m<sup>2</sup> per 8 months at HOT and 1.7 ± 0.3 mol C/m<sup>2</sup> per 8 months at BATS) estimated using time-series data were consistent with values based on pCO<sub>2SW</sub> and A<sub>T</sub> data (1.0 ± 0.2 mol C/m<sup>2</sup> per 8 months and 1.5 ± 0.2 mol C/m<sup>2</sup> per 8 months, respectively), which were determined from pixels that include the HOT and BATS stations (Figure 2). This is a strong indication that the proposed method can accurately reproduce the seasonal evolution of surface C<sub>T</sub> and its total reduction. Note that the AND contributions to the seasonal  $nC_T$  reductions at the BATS and HOT stations were relatively small (<10% at BATS and <5% at HOT).

When individual estimates (Data Set S1) for all pixels in which the mixed layer nC<sub>T</sub> reduction occurred in the absence of N were integrated globally, the results yielded NCP<sub>N2fix</sub> of 0.6  $\pm$  0.2 Pg C per 8 months (Pg = petagrams = 10<sup>15</sup> grams; Figure 3) after corrections were made for changes arising from net air-sea CO<sub>2</sub> flux (0.03 Pg C per 8 months), horizontal C<sub>T</sub> flux (0.15 Pg C per 8 months), diffusive C<sub>T</sub> (0.09 Pg C per 8 months) and NO<sub>3</sub><sup>-</sup> (0.09 Pg C per 8 months) fluxes, and atmospheric N deposition (0.05 Pg C per 8 months; Tables S1 and S2).

Regional values of NCP<sub>N2fix</sub> differed distinctly among latitudinal bands (Figure 3). Values for the latitude bands of 20–30°N and 20–30°S appeared to be higher than that for the lower latitude band of 20°N–20°S. It is important to note that seasonal nC<sub>T</sub> drawdown in N-rich areas outside of the study area is considerably greater than that observed in the N-depleted region. For example, the NCP integrated for all areas except the N-depleted region was estimated to be 6.6 Pg C per 8 months, which is consistent with the range (5.9–7.2 Pg C per 8 months) reported by Lee (2001), based on the seasonal cycle of nC<sub>T</sub> concentrations derived from monthly mean pCO<sub>2</sub> and A<sub>T</sub> data, and regional nC<sub>T</sub> relationships (Lee et al., 2000).





**Figure 1.** Examples of monthly mean values of  $nC_T$  (filled squares) and SST (open circles) for pixels (4° × 5°) in our analysis. The black solid lines show the linear regression lines for the  $nC_T$  decrease during the warming period. The red dots represent measured  $nC_T$  values at the BATS (b) and the HOT (c) stations, which are normalized to a single reference year (2005) using the linear regression trend of  $1.55 \pm 0.12 \mu mol \cdot kg^{-1} \cdot year^{-1}$  for BATS and  $1.75 \pm 0.13 \mu mol \cdot kg^{-1} \cdot year^{-1}$  for HOT. The black solid lines show the linear regression lines for the measured  $nC_T$  decrease and the red shaded areas represent the estimated uncertainty (1 $\sigma$ ). SST = sea surface temperature; BATS = Bermuda Atlantic Time-series Study; HOT = Hawaii Ocean Time-series.

The effect of horizontal nC<sub>T</sub> transport on estimates of the nC<sub>T</sub> drawdown in each pixel depended on the sign and magnitude of the horizontal C<sub>T</sub> gradient and current velocities (Figure S1). In the subtropical gyres of the North and South Pacific Ocean, the horizontal nC<sub>T</sub> transport increased the seasonal nC<sub>T</sub> drawdown because of the poleward increase in nC<sub>T</sub> and the poleward surface current. However, our NCP<sub>N2fix</sub> values are underestimated for areas between 12°N and 24°N in the Atlantic Ocean, where both the eastward increase in the nC<sub>T</sub> gradient and the westward surface current decreased the seasonal nC<sub>T</sub> drawdown. The net horizontal nC<sub>T</sub> transport in all basins for which NCP<sub>N2fix</sub> values are available was estimated to be in the range -0.04 to 0.13 Pg C per 8 months (Table S2).

 $NCP_{N2fix}$  values are not sensitive to the addition of  $NO_3^-$  via entrainment of subsurface waters and eddy diffusion. In oligotrophic oceans,  $NO_3^-$  transported into the euphotic layer is completely utilized along with  $C_T$  at the Redfield C:N ratio of 7. Therefore, the  $NCP_{N2fix}$  value, which is determined based on changes in  $C_T$  in  $NO_3^-$  depleted waters, would be affected only by the small residual  $C_T$  resulting from deviations in the C:N ratio in upwelled water. The diffusive  $C_T$  flux could have decreased our local and global  $NCP_{N2fix}$  estimates,





**Figure 2.** Estimates of NCP<sub>N2fix</sub> from integration of seasonal nC<sub>T</sub> reductions observed at the (a) HOT and (b) BATS stations. NCP<sub>N2fix</sub> values averaged over 26 and 24 years at the HOT and the BATS stations, respectively, were compared with the estimates for those pixels including the BATS and the HOT stations and with those based on field N<sub>2</sub> fixation-based measurements (Böttjer et al., 2017; Orcutt et al., 2001). The dashed bar for the (b) BATS station indicates the revised rate obtained after correcting for errors associated with incomplete <sup>15</sup>N<sub>2</sub> equilibrium and assessments of the abundance of N<sub>2</sub> fixing organisms. The revised rate is a factor of 8 greater than the reported rate at the BATS station. HOT = Hawaii Ocean Time-series; BATS = Bermuda Atlantic Time-series Study; NCP = net community production.

whereas the diffusive  $NO_3^-$  flux could have increased our  $NCP_{N2fix}$  estimates. However, their combined contributions to the global  $NCP_{N2fix}$  estimate were negligible (<1%), because the C:N ratios of diffusive  $C_T$  and  $NO_3^-$  fluxes from the upper thermocline were close to the Redfield ratio of 7 throughout most of our



**Figure 3.** NCP<sub>N2fix</sub> in N-depleted waters (NO<sub>3</sub><sup>-</sup> concentrations <0.2  $\mu$ mol/kg are indicated as black solid boxes). White pixels within the solid boxes indicate no C<sub>T</sub> drawdown during the warming period. NCP<sub>N2fix</sub> values are expressed as mol C/m<sup>2</sup> for 8-month warming season. The integrated NCP<sub>N2fix</sub> calculated using equation (1) was 0.6 ± 0.2 Pg C per 8 months. The colored circles show gridded synthesis of N<sub>2</sub>-supported NCP calculated from direct measurements of N<sub>2</sub>-fixation rates (data from Luo et al. (2012; https://doi.org/10.1594/PANGAEA.774851). NCP = net community production.

study area (Table S1). The N contribution via episodic N input from depth associated with mesoscale eddies cannot be accurately estimated because of inadequate knowledge of this diffusive flux in terms of location and time (Pidcock et al., 2016). One way of estimating this effect is to perform a sensitivity analysis by varying the  $K_V$  value, because eddies are known to enhance vertical diffusivity (McGillicuddy et al., 1998). The diffusivity-driven NCP ranged from 0.003 to 0.014 mol C per 8 months when the  $K_V$  was varied from 0.1 to 0.5 cm<sup>2</sup>/s; this has only minor impact on our NCP<sub>N2fix</sub> estimates.

Atmospheric N deposition would increase our estimate, but its influence was largely confined to areas north of the N-depleted subtropical and tropical oceans (Lamarque et al., 2013), where our estimate was almost 0. As a result, the contribution of atmospheric N deposition to the estimated NCP<sub>N2fix</sub> for the ocean areas where C<sub>T</sub> removal in the absence of N occurred concurrently was only 0.05 Pg C per 8 months.

Our estimate of NCP<sub>N2fix</sub> may be affected by errors in estimates of the mixed layer nC<sub>T</sub> fields, the mixed layer depth, horizontal C<sub>T</sub> flux and the net air-sea CO<sub>2</sub> flux. The fits between nC<sub>T</sub> and month for all the pixels had a mean uncertainty of ±15%, which led to an uncertainty of ±0.1 Pg C per 8 months in our estimate. The mean difference in the mixed layer depth calculated using two independent criteria (the water depth at which vertical gradients in density and temperature become  $\Delta \sigma_{\theta} = 0.03 \text{ kg/m}^3$  and  $\Delta t = 0.2 \text{ °C}$ , respectively) resulted in a difference of ±0.1 Pg C per 8 months. Uncertainty associated with the horizontal C<sub>T</sub> flux depends on uncertainties about current velocities (assumed to be ±50% error, based on Quay & Stutsman, 2003) and the horizontal nC<sub>T</sub> gradient among pixels (±25%, estimated in this study from the fit between nC<sub>T</sub> and latitude or longitude). In combination, these uncertainties accounted for a difference of ±0.06 Pg C per 8 months in our global NCP<sub>N2fix</sub> estimate.

The uncertainty in estimation of the net air-sea CO<sub>2</sub> flux resulted in a difference of ±0.03 Pg C per 8 months, depending on the choice of parameterizations between the gas exchange rate and the wind speed. In producing the pCO<sub>2</sub> climatology used in our analysis to estimate  $nC_T$ , Takahashi et al. (2009) used a 2-D lateral transport model to account for the effect of the lateral transport of water on pCO<sub>2</sub> interpolation for each pixel. This effect led to a systematic bias of +1.3 µatm of the interpolated pCO<sub>2</sub> and thereby an error of 0.04 Pg C per 8 months in our estimate of net air-sea CO<sub>2</sub> flux, which is equivalent to 5% of our NCP<sub>N2fix</sub> estimates. Our value (0.03 Pg C per 8 months) of net air-sea CO<sub>2</sub> flux includes correction for systematic bias of interpolated pCO<sub>2</sub> value. One outstanding issue in error estimates associated with the net air-sea CO<sub>2</sub> flux is interannual variability in net air-sea CO<sub>2</sub> flux in all pixels for which NCP<sub>N2fix</sub> values were available. We addressed this issue using multiannual pCO<sub>2</sub> climatology provided by Landschützer et al. (2014). For the ocean areas in which  $nC_T$  reduction occurred in the absence of N, interannual variability in the net air-sea CO<sub>2</sub> flux was estimated to be ±0.06 Pg C/year (1 $\sigma$ ) for the period 1998–2011. The magnitude of this flux variability may be an error in our NCP<sub>N2fix</sub> estimates arising from the net air-sea CO<sub>2</sub> flux and is comparable with the pCO<sub>2</sub> interpolation error reported by Takahashi et al. (2009) for the pCO<sub>2</sub> climatology.

In summary, the probable error in the estimated  $NCP_{N2fix}$  because of all sources of error was ±0.2 Pg C per 8 months.

# 4. Discussion

### 4.1. Factors Influencing NCP<sub>N2fix</sub> Occurred During Periods of N Depletion

The NCP<sub>N2fix</sub>, estimated by integrating the reduction in mixed layer C<sub>T</sub> over the 8-month period of N depletion, potentially includes NCP contributed by sources other than N<sub>2</sub> fixation. To exclusively attribute our NCP<sub>N2fix</sub> to N<sub>2</sub> fixation, it is necessary to evaluate other contributions. One of these is utilization of DON by non-N<sub>2</sub> fixing microorganisms during photosynthesis. This possibility is difficult to assess because the comparable DON utilization has yet to be reported (Church et al., 2002; Johnson et al., 2010; Karl et al., 2003), and consequently, we cannot discount this process as an alternative explanation because seawater DON data are not adequate to assess this explanation.

Lateral transport of N from the N-rich gyre margins added nutrients to the gyres from which much of our  $NCP_{N2fix}$  was derived. As noted in section 2, the flux ratio of  $C_T$  and  $NO_3^-$  to the subtropical gyre is a key measure in determining the impact of lateral N transport on  $NCP_{N2fix}$  in oligotrophic gyres. The C:N ratio in waters intruding from the gyre margins was greater than 7, except in the South Pacific Ocean (Letscher et al., 2016).

The slight elevation of the C:N ratio (relative to the Redfield value) for the intrusion waters indicates that our  $NCP_{N2fix}$  values for all basins other than the South Pacific were only slightly underestimated, because the  $C_T$  remained after the complete consumption of N would have offset our  $NCP_{N2fix}$  estimate. However, such offsets would have been minor.

Another biological process that could affect the NCP<sub>N2fix</sub> occurring in the N-depleted ocean is selective N mining via vertical migration of phytoplankton. The results of a recent study indicate that in the N-limited ocean the diatom *Rhizosolenia* changes buoyancy to descend to the nitracline to acquire NO<sub>3</sub><sup>-</sup> then returns to the surface to carry out photosynthesis. This N mining mechanism could transfer significant amounts of NO<sub>3</sub><sup>-</sup> from depth (1–79.9 mmol N·m<sup>-2</sup>·year<sup>-1</sup>; Villareal et al., 2014). As much as 80 mmol N·m<sup>-2</sup>·year<sup>-1</sup> (equivalent to a total NCP of 0.56 mol C·m<sup>-2</sup>·year<sup>-1</sup>, half of the rate we estimated at the HOT station) could be similarly mined below the HOT station (Johnson et al., 2010). In contrast to all established physical mechanisms that simultaneously bring N and C from depth to the surface, this newly identified process mines only NO<sub>3</sub><sup>-</sup> from the nitracline. The global significance of this process in the N budget of the upper ocean is difficult to assess because of the limited research currently undertaken (Johnson et al., 2010).

The above evaluation shows that it is not possible to unequivocally assign the contributions of alternative processes to our estimate of NCP<sub>N2fix</sub> occurring in oceans where the levels of NO<sub>3</sub><sup>--</sup> are below 0.2  $\mu$ mol/kg.

## 4.2. Comparisons of NCP<sub>N2fix</sub> at the HOT and BATS Stations and the South Pacific Ocean

Of the possible explanations for our estimate of NCP<sub>N2fix</sub>, a major process is considered to be marine N<sub>2</sub> fixation, which generally occurs at a high rate in warm waters lacking N. To compare our estimate with measurements of the N<sub>2</sub> fixation rate, a C:N ratio of 7 was used to convert the rates of N<sub>2</sub> fixation to those of NCP<sub>N2fix</sub>. Based on the <sup>15</sup>N<sub>2</sub> assimilation method, the rate of N<sub>2</sub> fixation at the HOT station, averaged over the period of June 2005–December 2013, was 0.56 mol C·m<sup>-2</sup>·year<sup>-1</sup> (Böttjer et al., 2017), which is only half our rate estimated for a pixel that includes the HOT station (Figure 2a). However, the <sup>15</sup>N<sub>2</sub>-based rates of NCP<sub>N2fix</sub> are comparable with our estimate, given that underestimation is an inherent problem associated with the <sup>15</sup>N-based method, which measures the net N<sub>2</sub> fixation rate rather than the gross rate (Böttjer et al., 2017; Mulholland, 2007; Wilson et al., 2012).

In contrast, the rates measured at the BATS station are only 6% of our estimate and do not fall within the uncertainty bracket of our estimate (Figure 2b). The rates reported at the BATS station were based on the earlier erroneous method (incomplete <sup>15</sup>N<sub>2</sub> equilibrium) and thus may have underestimated the true rate of N<sub>2</sub> fixation by a factor of 2 or more (Großkopf et al., 2012). Another explanation for measurements being considerably lower at the BATS station than our C<sub>T</sub>-based estimate is that the <sup>15</sup>N-based measurements at this station were designed to assess the contribution from *Trichodesmium* only (Orcutt et al., 2001). The difference between the <sup>15</sup>N-based estimates and our estimate may arise from large errors in assessments of the abundance of N<sub>2</sub> fixing organisms, associated with use of a conventional net sampling method. Application of an in situ digital microscope indicated a *Trichodesmium* abundance fourfold greater than that determined using the net sampling method (Davis & McGillicuddy, 2006). If these two sources of error are considered, the revised rate could be as high as 0.8 mol C·m<sup>-2</sup>·year<sup>-1</sup> (an eightfold increase). Moreover, the rates based on field measurements directed solely at *Trichodesmium* could be also underestimated because N<sub>2</sub> fixation is not limited to this cyanobacterium; other unicellular cyanobacteria in the ocean may contribute significantly to the N budget (Moisander et al., 2010; Thompson et al., 2012).

For the area defined by 20–30°S and 100–120°W in the South Pacific, our NCP<sub>N2fix</sub> estimate (0.8 mol C/m<sup>2</sup> per 8 months) was comparable to the value (0.4 mol C/m<sup>2</sup> per 4 months; i.e., 0.8 mol C/m<sup>2</sup> if scaled up for 8 months of the warming period) derived from the winter-summer mixed layer C<sub>T</sub> difference (Bender & Jönsson, 2016). The congruence of estimates based on these two methods supports the accuracy of our method. In contrast, Knapp et al. (2016) reported a low N<sub>2</sub> fixation rate (a maximum of approximately 100  $\mu$ mol N·m<sup>-2</sup>·day<sup>-1</sup>, which is equivalent to 0.25 mol C/m<sup>2</sup> per 8 months) in the same area. One source of error in our NCP<sub>N2fix</sub> estimate may have been lateral intrusion of N-rich water (C:N ratio < 7), which could have resulted in overestimation of the NCP<sub>N2fix</sub>. The difference may also have arisen from errors in direct measurements based on the incomplete equilibrium of <sup>15</sup>N<sub>2</sub> gas, which can result in underestimation of







the N<sub>2</sub> fixation rate by 40–60%. These sources of error may collectively have contributed to differences in the  $NCP_{N2fix}$  estimates for the South Pacific based on our method and the <sup>15</sup>N-based method.

# 4.3. Global Comparisons of NCP<sub>N2fix</sub>

Our NCP<sub>N2fix</sub> value of  $0.6 \pm 0.2$  Pg C per 8 months falls within the range of 0.3-1.0 Pg C/year, which has been derived from extrapolation of shipboard N<sub>2</sub> fixation measurements to the global ocean (Großkopf et al., 2012; Luo et al., 2012, 2014; Figure 4). However, regional- and basin-scale comparisons are not appropriate because most field measurements have been heavily biased toward the Atlantic Ocean.

The  $P^*$  method in conjunction with inverse modeling also yielded a comparable rate of 0.79 Pg C/year for NCP<sub>N2fix</sub> supported by N<sub>2</sub> fixing microorganisms (Deutsch et al., 2007). However, differences are apparent

in regional comparisons. For example, the P<sup>\*</sup> method yielded the highest rate in the eastern Pacific Ocean, where N is abundant because of equatorial upwelling, and the P<sup>\*</sup> values are also highest. In contrast, our method did not calculate the NCP<sub>N2fix</sub> for this area, because in this area the N concentration is high throughout the year. Another area of contrast is the Southern Ocean, where the P<sup>\*</sup> method yielded a considerable level of NCP<sub>N2fix</sub> supported by N<sub>2</sub> fixers, but our method did not indicate any NCP<sub>N2fix</sub>.

Comparison of our NCP<sub>N2fix</sub> values with those obtained in other studies depends on the C:N ratio chosen to represent the value for dissolved and particulate organic matter produced by marine N<sub>2</sub> fixers. The elemental C:N ratio of 7 that we used for conversion of N<sub>2</sub> fixation rates to NCP<sub>N2fix</sub> appears to be consistent with the values directly measured for *Trichodesmium* biomass but is much lower than the ratios (20–30) measured for semilabile dissolved organic matter produced largely by N<sub>2</sub> fixers (Church et al., 2002; Mulholland, 2007). The large variations among reported elemental C:N ratios are another source of uncertainty in estimates of N<sub>2</sub>-supported NCP derived from direct measurements and indirect geochemical methods.

Much of the NCP<sub>N2fix</sub> we calculated occurred in waters where the supply of iron and phosphate, which are limiting elements for N<sub>2</sub> fixation, is sufficient to support diazotrophs (Ward et al., 2013). During the warming period, when C<sub>T</sub> declined in the absence of N, the seasonal reduction in PO<sub>4</sub><sup>3-</sup> was also observed within the mixed layer of the ocean. The total PO<sub>4</sub><sup>3-</sup> reduction yielded a NCP<sub>N2fix</sub> (Data Set S2) of 0.3 Pg C per 8 months (Figure S2) using the C:P ratio of 195:1 representing particulate organic matter collected from the N-depleted ocean (Martiny et al., 2013). The PO<sub>4</sub><sup>3-</sup> -based NCP<sub>N2fix</sub> rate is approximately half of the C<sub>T</sub>-based rate we determined. The difference between these rates may be insignificant given the large uncertainty (a factor of 4 greater than 195) in the C:P ratio of organic matter produced by N<sub>2</sub> fixing organisms.

# 5. Conclusions and Implication

The proposed method provides the global-scale NCP<sub>N2fix</sub> of 0.6  $\pm$  0.2 Pg C per 8 months in the vast areas of the N-depleted ocean, where NCP<sub>N2fix</sub> cannot be accurately estimated using conventional methods for N<sub>2</sub> fixation activity. Our estimate represents NCP<sub>N2fix</sub> that occurred during the warming period (approximately 8 months) and thus is certainly low, as our value does not include N<sub>2</sub>-fixer-derived NCP during the cooling period as well as that which occurred in coastal waters.

The key requirement that NCP<sub>N2fix</sub> can play a direct role in oceanic uptake of anthropogenic CO<sub>2</sub> is if it can change with future climate variations (Falkowski, 1997). A growing number of experiments and modeling studies pointed to the enhancement of the growth of N<sub>2</sub>-fixing diazotrophs under high pCO<sub>2</sub> conditions (Dutkiewicz et al., 2015). This finding further suggests that NCP<sub>N2fix</sub> in the vast areas of the N-depleted ocean gyre could be increased as a result of the enhancement of N<sub>2</sub> fixation activity, thus providing a negative feedback to the ocean carbon cycle. Ultimately, N<sub>2</sub> fixation will be limited by the availability of phosphate, iron, and other trace nutrients.

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