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Global estimates of net carbon production in the nitrate-depleted tropical and subtropical oceans

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[1] Nitrate availability is generally considered to be the limiting factor for oceanic new production and this concept is central in our observational and modeling efforts. However, recent time-series observations off Bermuda and Hawaii indicate a significant removal of total dissolved inorganic carbon (C_T) in the absence of measurable nitrate. Here we estimate net carbon production in nitrate-depleted tropical and subtropical waters with temperatures higher than 20°C from the decrease in the salinity normalized C_T inventory within the surface mixed layer. This method yields a global value of 0.8 ± 0.3 petagrams of carbon per year (Pg C yr^{-1}, Pg = 10^{15} grams), which equates to a significant fraction (20 – 40%) of the recent estimates (2.0–4.2 Pg C yr^{-1}) of total new production in the tropical and subtropical oceans [*Emerson et al.*, 1997; *Lee*, 2001]. The remainder is presumably supported by upward flux of nutrients into the euphotic zone via eddy diffusion and turbulent mixing processes or lateral exchange. Our calculation provides the first global-scale estimate of net carbon production in the absence of measurable nitrate. We hypothesize that it is attributable to dinitrogen (N_2) fixing microorganisms, which can utilize the inexhaustible dissolved N_2 pool and thereby bypass nitrate limitation. *INDEX TERMS:* 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4806 Carbon cycling; 4825 Geochemistry; 4835 Inorganic marine chemistry; 0330 Atmospheric Composition and Structure: Geochemical cycles. **Citation:** Lee, K., D. M. Karl, R. Wanninkhof, and J.-Z. Zhang, Global estimates of net carbon production in the nitrate-depleted tropical and subtropical oceans, *Geophys. Res. Lett.*, *29*(19), 1907, doi:10.1029/2001GL014198, 2002.

1. Introduction

[2] Net carbon production manifests itself though changes in salinity (S) normalized C_T ($NC_T = C_T \times 35/S$) in oligotrophic oceans. The resulting vertical export of particulate inorganic carbon as $CaCO_3$ (E_{PIC}) and organic carbon in both particulate and dissolved forms (E_{POC} and E_{DOC}, respectively) is related to ΔNC_T as follows:

$$\Delta NC_T = E_{PIC} + E_{POC} + E_{DOC} + A_{POC} + A_{DOC} \quad (1)$$

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The ΔNC_T (mol C m^{-2} yr^{-1}) also includes the particulate (A_{POC}) and dissolved (A_{DOC}) organic carbon accumulating in the mixed layer. Lateral and vertical mixing of waters with different levels of NC_T, and net air-sea CO_2 exchange influence NC_T as well [*Lee et al.*, 2000]. Biological production of particulate and dissolved organic carbon either exported from the surface ocean or accumulating in the surface ocean generally dominates the other processes during the seasonal warming period. This net production of organic carbon in both particulate and dissolved forms occurs in tandem with sea surface temperature (SST) increase and can be quantified by time-integration of the NC_T concentration decrease within the surface mixed layer during the summer season.

[3] Multi-year measurements at the Bermuda Atlantic Time-series Study (BATS, 31°50′N, 64°10′W) and the Hawaii Ocean Time-series (HOT, 22°45′N, 158°W) sites suggest that much of the net carbon production may occur in the absence of measurable nutrients [*Michaels et al.*, 1996; *Emerson et al.*, 1997]. Because of lack of observations this phenomenon has been neither confirmed nor quantified in other nitrate-depleted tropical and subtropical oceans. Analysis of recently collected NC_T data throughout the nitrate-depleted tropical and subtropical oceans, however, shows that decrease in surface NC_T concentration is correlated with SST increase (Figures 1a and 1b) [*Lee et al.*, 2000] and can be quantified using empirical NC_T-SST algorithms along with seasonal changes in SST and in mixed layer depth. Here we quantify the mixed layer NC_T decrease in nitrate-depleted tropical and subtropical oceans with SST >20°C. Furthermore we hypothesize that this net carbon production is a previously undocumented form of new production, one supported by N_2 fixing microorganisms. The new production values determined from the mixed layer NC_T drawdown in the nitrate-depleted waters are compared with literature estimates on N_2 fixation.

2. Computation Methods

[4] We estimate an annual rate of global new production in the nitrate-depleted oligotrophic waters, E_{NP}, for each 4° latitude × 5° longitude grid cell, from changes in the NC_T inventory within the surface mixed layer corrected for

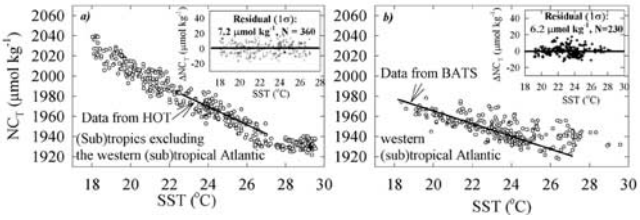


Figure 1. Plots of NC_T versus sea surface temperature in areas between 40°N and 40°S. (a) NC_T data in (sub)tropics excluding the western (sub)tropical Atlantic Ocean. (b) NC_T data in the western (sub)tropical Atlantic Ocean. Data collected for waters with temperatures higher than 20°C and with no measurable amount of nitrate (<0.1 μmol kg^{-1}) are used to generate the fits. The solid lines are the regression results for data collected from the HOT and BATS sites. Insets are residual plots of ΔNC_T (ΔNC_T = measured NC_T - calculated NC_T from the derived algorithms) for BATS and HOT.

changes due to net air-sea CO_2 flux in the following manner:

$$E_{NP}\,|_{\Delta M} = \left(AH^{M+1}\left[NC_T^{M} - NC_T^{M+1}\right]\right) + AF_{AIR-SEA} \qquad (2)$$

Where M denotes month (the time step); A (m^2) is the area of each grid cell; $[NC_T^{M} - NC_T^{M+1}]$ is the NC_T concentration decrease in the mixed layer, H, between subsequent months; and F (mol m^{-2} $month^{-1}$) is the net air-sea CO_2 flux. The upward flux of NC_T via advection and diffusion during the seasonal warming period can counteract the mixed layer NC_T decrease resulting from N_2-supported new production. However, vertical NC_T flux concurrently delivers nitrate from depth to support additional new production and subsequent export of carbon is believed to occur in much the same C:N ratio as it is delivered to the euphotic zone.

[5] Planktonic marine cyanobacteria of the genus Trichodesmium, cosmopolitan marine N_2 fixing microorganisms, occur only in waters where temperatures are warmer than 20°C and nitrate concentrations are lower than 0.1 μmol kg^{-1} [see *Hood et al.*, 2000] therefore, equation (2) is only applied when the mixed layer NC_T concentration decreases with time (seasonal warming period) and only for grid cells in which SST is higher than 20°C and nitrate concentration is less than 0.1 μmol kg^{-1}. Seasonal mean nitrate data used in this study were obtained from the World Ocean Atlas 1998. For each grid cell, the mean annual cycle of surface NC_T concentration is estimated using derived regional NC_T-SST relationships (Figure 1) [*Lee et al.*, 2000], along with monthly mean SST fields for 1990 from the National Center for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) reanalysis. Global records of monthly mean mixed layer depth [http://www.nodc.gov/oc5/mixdoc. html] derived from vertical density gradients are used to integrate the total NC_T decrease within the mixed layer.

3. Results and Error Analysis

[6] An important assumption in our approach and conclusions is that temporal NC_T decrease in the mixed layer can be quantified by using NC_T-SST relationships derived from large-scale spatial NC_T and SST data along with observed temporal SST and mixed layer depth fields. The results of this method are compared favorably with multiyear records of monthly NC_T and SST observations from the BATS and the HOT sites [*Lee et al.*, 2000]. Surface NC_T values observed during the late spring-late summer period at these time-series sites, when nitrate concentrations are less than 0.1 μmol kg^{-1} and SST higher than 20°C, are inversely correlated with mixed layer temperature [*Bates et al.*, 1996; *Winn et al.*, 1998] and resulting relationships are in quantitative agreement with the regional algorithms.

[7] The change in the mixed layer NC_T yields a new production of 0.8 ± 0.3 Pg C yr^{-1} in nitrate-depleted warm tropical and subtropical oceans (Table 1, Figure 2). The effect of net air-sea CO_2 flux is less than 10% of the global total and is accounted for (Table 1). The estimated global value is subject to errors due to uncertainties in the following sources: (1) The empirical NC_T-SST relationships; the average uncertainty in the regional NC_T-SST relationship is 20% [*Lee et al.*, 2000]. To estimate possible uncertainty caused by derived NC_T-SST relationships, the algorithms for all the grid cells are allowed to vary by 20% to obtain annual minimum and maximum new production. The difference between the annual maximum and minimum rate is 0.32 Pg C yr^{-1}, which is used as the error of the estimated global rate. An average of 20% uncertainty in derived relationships is estimated solely from uncertainties of the fits between basin-scale C_T data and SST. It does not include errors associated with seasonal extrapolation of these derived relationships because verification of seasonal extrapolation is not possible except for the BATS and HOT sites where the comparison is robust [*Lee et al.*, 2000]. (2) Climatological mixed layer depth fields; the global total using mixed layer

Table 1. Estimated Rates of Total and N_2-Supported New Production (Pg C yr^{-1}) in Nitrate-Depleted Waters (SST >20°C and nitrate <0.1 μmol kg^{-1}) During the Warming Period

Ocean	Region	Area ($\times 10^{12}$ m^2)	Net air-sea CO_2 flux[a] (Pg C yr^{-1})	N_2-supported new production[b]	Annual new production[c]
Atlantic	40°N–40°S	49.1	0.03	0.2	1.09
Indian	North of 40°S	43.3	0.01	0.1	0.79
Pacific	40°N–40°S	119	−0.02	0.5	2.29
Global	40°N–40°S	211.4	0.02	0.8	4.17

[a] The gas-exchange formulation proposed by *Wanninkhof* [1992] for long-term winds is combined with the global climatology of ΔpCO_2 [*Takahashi et al.*, 1997] to estimate the net air-sea CO_2 flux for each grid cell in which the mixed layer NC_T concentration decreases as season progresses.

[b] N_2-supported new production is estimated from integrating decrease of the mixed layer total NC_T during the warming period and values are corrected for changes in net air-sea CO_2 fluxes.

[c] An annual rate of new production is obtained from *Lee* [2001].

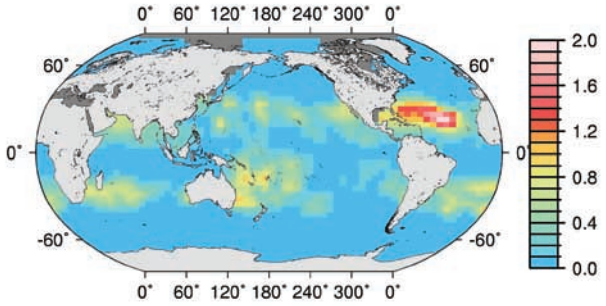


Figure 2. N_2-supported new production in nitrate-depleted warm waters. Values are expressed as mol C m^{-2} yr^{-1}. A globally integrated value using equation (2) is 0.8 ± 0.3 Pg C yr^{-1}.

depth fields derived from vertical density gradients are on average 10% lower than the value using those from vertical temperature gradients, although the magnitude of the error may vary geographically. (3) Net air-sea CO_2 fluxes; the estimated global rate is subject to an error of ±0.03 Pg C yr^{-1} depending on the choice of relationships between gas exchange and wind speed. The probable error of the estimated global rate due to these three sources of error is dominated by (1) and thus is about ±0.3 Pg C yr^{-1}.

4. Discussion

[8] Our estimates of new prodcution in nitrate-depleted waters do not prove that N_2 fixation is the cause. But it is a distinct possibility. Therefore we compare our results with estimates and known regional patterns of N_2 fixation. In the comparison we assume that N_2 fixing microorganisms are exclusively responsible for the mixed layer NC_T drawdown in nitrate-depleted warm waters, and we also assume an elemental C:N ratio of 7 to convert marine N_2 fixation rates to new production.

[9] Several methods to determine N_2 fixation rates at the HOT site show broad agreement. New production rates derived from direct measurements of nitrogenase activity of isolated *Trichodesmium* colonies are in accord with the rate obtained from an indirect method using mass balance of the N:P ratio in upper thermocline waters. However, they are smaller than the rate estimated from the ^{15}N isotopic composition of exported particulate matter [*Karl et al.*, 1997] and our estimate for the grid point including the HOT site (Figure 3a). Rates derived from multi-year direct measurements of N_2 fixation rate with *Trichodesmium* biomass at the BATS site [*Orcutt et al.*, 2001] are significantly smaller than our estimate for the grid point including the BATS site (Figure 3b). Directly measured rates are possibly underestimates because they do not include the potential contributions from other N_2 fixers that are found at these time-series sites [*Zehr et al.*, 2001]. In addition to the well-recognized contributions from *Trichodesmium*, other less well-described N_2 fixation pathways are also possible, including endosymbiotic association of unicellular cyanobacteria and eucaryotic algae (especially diatoms) and free-living autotrophic and heterotrophic prokaryotes. Moreover, the N_2 fixation process is well known to be variable in both time and space, which makes large-scale direct estimation of stochastic bloom phenomena inaccurate if not biased.

[10] Our estimated global new production rate supported by N_2 fixation of 0.8 ± 0.3 Pg C yr^{-1} is approximately 4 times higher than the values derived from extrapolation of the limited direct shipboard measurements of N_2 fixation rates to the global scale using a historical dataset for *Trichodesmium* abundance (Figure 3c) [*Capone and Carpenter*, 1982; *Carpenter and Capone*, 1992]. When a more recent comprehensive representation of global *Trichodesmium* abundance is used, an average N_2 fixation rate that is derived from numerous direct measurements at various sites in the tropical oceans yields a global rate [*Capone and Carpenter*, 1999] which agrees well with our value (Figure 3c). Our global estimate is also similar in magnitude to the values derived from anomalies in the ratio of N:P in the upper thermocline waters of the North Atlantic and North Pacific [*Gruber and Sarmiento*, 1997; *Deutsch et al.*, 2001]. This geochemical method does not quantify gross N_2 fixation but rather net N_2 fixation. Thus, it would not capture N_2 fixation if a certain marine environment simultaneously supports temporally coupled and comparable rates of N_2 fixation and denitrification [*Karl et al.*, 1997]. If nitrogenase activity occurs during the seasonal cooling period and/or a fraction of new production is supported by high abundance of N_2 fixers in coastal regions and in marginal seas [*Capone and Carpenter*, 1999], our inferred new production supported by N_2 fixation would be low.

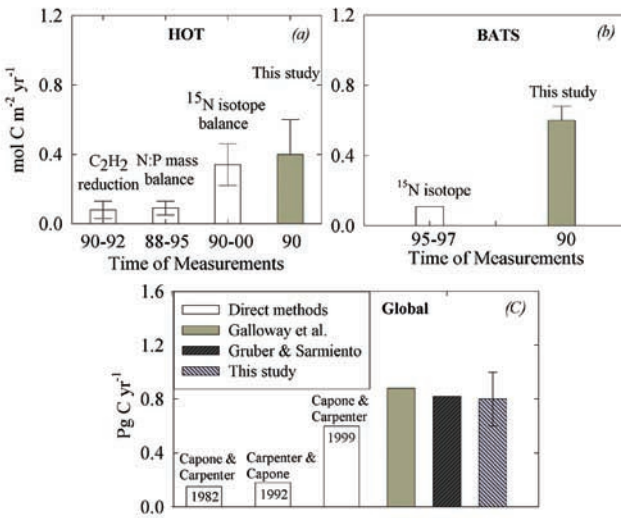


Figure 3. Comparison of our regional rates of N_2-supported new production with direct measurements (a) at the HOT [*Karl et al.*, 1997] and (b) BATS sites [*Orcutt et al.*, 2001]. Direct measurements based on acetylene (C_2H_2) reduction used a 3:1 conversion from C_2H_2 reduced to N_2 fixed. Error bars for our results are standard deviations from average values for 6 grid cells surrounding the HOT and BATS sites. (c) Comparison of our global rate of N_2-supported new production with the annual rates estimated by direct [*Capone and Carpenter*, 1982; 1999; *Carpenter and Capone*, 1999] and other [*Galloway et al.*, 1995; *Gruber and Sarmiento*, 1997; *Deutsch et al.*, 2001] methods. We assume an elemental C:N ratio of 7 to convert marine N_2 fixation rates to new production. The error bar for our global estimate is obtained from uncertainties involved in estimating NC_T and H in equation (2).

[11] There are other sources of nitrogen that can support new production in nitrate-depleted waters but they appear to be less likely candidates. Inputs of fixed nitrogen from the atmosphere into the global oceans are estimated to be about 18 teragrams of nitrogen (Tg N yr^{-1}, Tg = 10^{12} grams) [*Galloway et al.*, 1995], which could sequester a maximum of 0.14 Pg C yr^{-1} if all of the atmospheric nitrogen was bioavailable and was deposited in the oligotrophic waters. Another possibility is that dissolved organic nitrogen (DON) utilization rather than N_2 fixation fuels the NC_T drawdown in nitrate-depleted waters. There is no appreciable DON drawdown during the spring-summer warming period at the HOT site [*Church et al.*, 2002]. However, this remains a possibility due to a lack of DON measurements in the world ocean except for the HOT site.

[12] Comparison of our new production estimate with those inferred for N_2 fixation provided by other studies critically depends on knowledge of the C:N ratio in dissolved and particulate organic matter produced by marine N_2 fixers. However, we do not know enough about all of the complex processes leading to this C:N stoichiometry. The elemental C:N ratio of 7 used in this study for conversion of N_2 fixation rates to new production is much lower than the measured ratios of 20–30 in semi-labile dissolved organic matter produced by phytoplankton [*Church et al.*, 2002]. A large range of the elemental C:N ratio results in a similar magnitude of uncertainty in values of N_2-supported new production derived from direct measurements and indirect geochemical methods.

[13] The distribution of N_2-supported new production shows distinct regional patterns in the global oceans (Figure 3). Significantly higher values are estimated for the tropical North Atlantic Ocean compared to the values for other basins. This is qualitatively consistent with results from other geochemical studies [*Michaels et al.*, 1996; *Gruber and Sarmiento*, 1997]. It has been postulated that the atmospheric iron supply, which is essential for N_2 fixation, plays a role in governing the spatial distribution of N_2 fixation [*Falkowski*, 1997]. Evidence for Fe-limitation is largely circumstantial; direct field assessments are not yet available.

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