Net Community Production, Dissolved Organic Carbon Accumulation, and Vertical Export in the Western North Atlantic

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INTRODUCTION

Phytoplankton blooms spanning the subtropical to the polar latitudes of the North Atlantic occur annually and are central to biogeochemical cycling in the global ocean (Duursma, 1963; Lochte et al., 1993; Sieracki et al., 1993; Carlson et al., 1998; Falkowski, 1998; Behrenfeld, 2010). These blooms are net autotrophic events initiated by an imbalance between phytoplankton division and loss rates, created by favorable abiotic conditions for incident sunlight and subsurface attenuation, surface mixing layer dynamics, nutrients, and temperature (Behrenfeld and Boss, 2018).

When photoautotrophy exceeds net heterotrophic processes within the surface layer, the seasonal net community production (NCP, moles C per unit volume or area per time) can be
estimated from the biological production of oxygen (Plant et al., 2016) or the net drawdown of total carbon dioxide or nitrate as it is fixed to organic matter (Codispoti et al., 1986; Hansell et al., 1993; Hansell and Carlson, 1998). Organic matter resulting from NCP has three main fates: (1) accumulation as particulate organic carbon (POC) in the surface layer followed by export via the passive sinking flux (McCave, 1975), (2) export from the surface layer via vertical migrating zooplankton (Steinberg et al., 2000), and (3) accumulation as suspended organic matter [i.e., dissolved organic carbon (DOC) and suspended POC (POC)] in the surface layer followed by export via physical transport (Carlson et al., 1994; Hansell and Carlson, 1998; Sweeney et al., 2000; Dall’Olmo et al., 2016). The present study examines the third fate, focusing on the accumulation and subsequent vertical export of DOC. We refer to the seasonal accumulation rate of surplus surface layer DOC as ΔDOC (vertically integrated moles C m$^{-2}$ time period$^{-1}$ or moles C L$^{-1}$ time period$^{-1}$).

ΔDOC has been reported to represent a significant fraction of NCP in a variety of environments and ecological states (Carlson et al., 1998; Hansell and Carlson, 1998; Romera-Castillo et al., 2016; Bif and Hansell, 2019). For example, Hansell and Carlson (1998) reported that as much as 59–70% of NCP was partitioned as ΔDOC shortly following a spring bloom in the Sargasso Sea. More recently, Romera-Castillo et al. (2016) analyzed data from seven US Repeat Hydrography cruises (currently called GO-SHIP) and three Spanish cruises (OVIDE, Good Hope, CAIBOX) and found that ΔDOC:NCP largely ranged between 0.10 and 0.40 throughout the Atlantic basin, with an average ΔDOC:NCP of 0.17 for the basin. The ratio was then applied to climatological nitrate data to model ΔDOC throughout the region. While extensive hydrographic data were used in this analysis, there was a paucity of data from the temperate and subpolar western North Atlantic. Furthermore, the data used did not permit the authors to diagnose seasonal variability in ΔDOC:NCP. Seasonal measures of NCP and ΔDOC for the western North Atlantic may help to constrain estimates of NCP partitioning and consequently, outputs from models seeking to predict changes in ΔDOC. Constraining estimates of ΔDOC is necessary to improve evaluations of vertical DOC export in the western North Atlantic.

A variety of food web processes can lead to the production of DOC, including passive and active dissolved organic matter (DOM) release by phytoplankton, grazer-mediated release and excretion, viral cell lysis, and particle solubilization (see review by Carlson and Hansell, 2015). Controlling factors that result in ΔDOC in the surface layer remain unknown but have been linked to nutrient limitation (Cotner et al., 1997; Thingstad et al., 1997), the direct production of recalcitrant compounds by phytoplankton (Aluwihare et al., 1997; Wear et al., 2015b), the alteration of labile DOM by heterotrophic microbes or photo- or phototransformation to recalcitrant compounds (Kieber et al., 1997; Benner and Biddanda, 1998; Ogawa, 2001; Gruber et al., 2006; Jiao et al., 2010), and the composition and metabolic potential of the extant microbial community (Carlson et al., 2004; Morris et al., 2005; DeLong, 2006).

In addition, because different phytoplankton species release different quantities and qualities of DOM, the identity of the dominant phytoplankton in a community may regulate the magnitude of ΔDOC (Conan et al., 2007; Wear et al., 2015b). For example, the dominance of large eukaryotic phytoplankton has been linked to the production of bioavailable DOC that can lead to limited variability in the bulk DOC pool (Carlson et al., 1998; Wear et al., 2015a,b), while the dominance of picophytoplankton in tropical and subtropical systems has been linked to elevated ΔDOC (Hansell and Carlson, 1998; Hansell et al., 2009). Blooms of large eukaryotic phytoplankton relative to picophytoplankton may reflect conditions that favor the production of more bioavailable DOC that has a low potential to accumulate as ΔDOC (Carlson et al., 1998). If distinct phytoplankton species or group can be linked to ΔDOC or ΔDOC:NCP, they may be useful indicators for the conditions that control DOC production and accumulation. Absolute cell abundance data or sequencing data can be used to reveal phytoplankton community structure at the time of sampling; inorganic nutrient drawdown ratios provide information that integrates a previous community’s activity and how that community affects nutrient pools. In the Ross Sea, Sweeney et al. (2000) used ΔSiO$_4$:ΔNO$_3$ ratios to distinguish phytoplankton populations dominated by diatoms from those dominated by non-siliceous species, with greater ratios indicative of a greater relative importance of diatoms. These metrics of phytoplankton community structure can all be used to explore whether distinct species or groups can be used as indicators for the conditions controlling ΔDOC and ΔDOC:NCP. In the North Atlantic where massive spring blooms have been associated with diatoms and the depletion of silicate relative to nitrate (Sieracki et al., 1993), one might expect diatoms to disproportionately contribute to NCP but also produce DOC with high bioavailability, leading to low ΔDOC. Understanding the role of diatoms in the partitioning of NCP may be important in elucidating the mechanisms and conditions that regulate ΔDOC and ΔDOC:NCP.

Regardless of the controls on DOC production and accumulation, ΔDOC in the surface layer has been observed throughout the global ocean (Duursma, 1963; Eberlein et al., 1985; Carlson et al., 1994; Børsheim and Myklestad, 1997; Hansell and Carlson, 1998; Halewood et al., 2012). ΔDOC resisting or escaping rapid microbial degradation is available for horizontal or vertical export via physical processes (Hansell et al., 1997). Seasonal deep convective overturn mixes ΔDOC into the ocean’s interior, where it can support net heterotrophic processes (Carlson et al., 1994, 2004). It is estimated that approximately 0.081 Pg C of DOM are exported out of the upper 100 m of the water column annually in the North Atlantic basin, making this region a quantitatively important location for vertical DOC export (Carlson et al., 2010). However, refining estimates of local ΔDOC and vertical DOC export in the western North Atlantic remains difficult because of limited DOC observations under deep mixed conditions and the necessary assumptions to approximate those conditions (Hansell and Carlson, 1998; Romera-Castillo et al., 2016).

Here we present a seasonal composite of local ΔDOC and NCP based on shipboard and ARGO float data collected in the temperate and subpolar western North Atlantic as a part of the ARGO and NASA North Atlantic Aerosols and
Marine Ecosystems Study (NAAMES) programs. The repeated meridional ship transects and the extensive spatiotemporal coverage of the deployed floats provide a unique opportunity to examine DOC dynamics in the context of the annual plankton cycle. We (1) consider the relationship between seasonal NCP and the partitioning of the resulting organic matter into the dissolved pool in the context of both space and time, (2) estimate vertical DOC export, and (3) examine the ∆DOC:NCP as it relates to variability in environmental conditions and phytoplankton community composition.

MATERIALS AND METHODS

Study Region

The NAAMES program, detailed in Behrenfeld et al. (2019), was designed to resolve the annual dynamics and drivers of the North Atlantic phytoplankton bloom and its subsequent impact on the atmosphere. It was comprised of four field campaigns from 2015 to 2018, each involving coordinated ship, aircraft, remote sensing, and autonomous in situ sensing (ARGO and Biogeochemical-ARGO floats) measurements during transects between 39°N and 56°N latitude and −38 to −47°W longitude (Figure 1). Here, we focus on two NAAMES campaigns at extreme ends of the seasonal cycle, NAAMES 3 in September 2017 (early autumn) and NAAMES 4 in April 2018 (early spring), respectively. The stations occupied during these campaigns were classified into subregions defined by Della Penna and Gaube (2019). The present study represents an ancillary companion project seeking to resolve temporal and spatial DOC dynamics in the western North Atlantic Ocean.

Environmental Data

NAAMES field campaign data are available through NASA's Ocean Biology Distributed Active Archive Center (OB.DAAC). Conductivity-temperature-depth (CTD), discrete inorganic nutrient, and flow cytometry data used here were retrieved from the SeaWiFS Bio-optical Archive and Storage System (SeaBASS1). All CTD casts and seawater samples were collected on the R/V Atlantis using a Sea-Bird Scientific SBE-911+ CTD outfitted with a Wet Labs ECO-AFL fluorometer and 24 10-L Niskin bottles in a typical rosette mount. Chlorophyll maxima (CMs) were estimated for each profile using downcast data from the CTD fluorometer.

Inorganic nutrient concentrations (µmol N or Si L⁻¹) were determined for 15 depths over the surface 1500 m at each station (nominally 5, 10, 25, 50, 75, 100, 150, 200, 300, 400, 500, 750, 1000, 1250, and 1500 m). Samples were gravity filtered directly from the Niskin bottles through inline 47 mm PC filtration cartridges loaded with 0.8 µm polycarbonate filters into sterile 50 mL conical centrifuge tubes. Resultant samples were then stored at −20°C for later analysis using the Lachat QuickChem QC8500 automated ion analyzer at the University of Rhode Island Graduate School of Oceanography Marine Science Research Facility (GSO-MSRF). Precision for nitrite + nitrate analyses are ~0.3 µmol L⁻¹, while precision for silicate analysis is ~0.1 µmol L⁻¹.

DOC concentrations (µmol C L⁻¹) were determined from replicate samples at the same 15 depths where nutrient samples were collected. Samples were gravity filtered directly from the Niskin bottles into pre-combusted (4 h at 450°C) 40 mL EPA borosilicate glass vials. Filtration was performed using 47 mm PC filtration cartridges loaded with pre-combusted (4 h at 450°C) 0.7 µm GF/F filters. Filters were flushed with ~100 mL of sample water before collection. Vials were rinsed three times with sample water before being filled. All DOC samples were acidified to a pH of < 3 by adding 50 µL DOC-free 4 N HCl to 35 mL of sample immediately after collection. Samples were stored at ~14°C in an environmental chamber free of volatile organics until analysis at the University of California, Santa Barbara.

DOC concentrations were measured in batches on Shimadzu TOC-V or TOC-L analyzers using the high-temperature combustion technique (Carlson et al., 2010). Each batch analysis was calibrated using glucose solutions of 25–100 µmol C L⁻¹ in low carbon blank water. Data quality was assessed by measuring surface and deep seawater references (sourced from the Santa Barbara Channel) after every six to eight samples as described in Carlson et al. (2010). Precision for DOC analysis is ~1 µmol L⁻¹ or a CV of ~2%. Local seawater reference waters were calibrated with DOC consensus reference material provided by Hansell (2005). All DOC data for the NAAMES project are available in the SeaBASS (see footnote 1).

Phytoplankton concentrations (cells L⁻¹) were determined for six depths over the surface 100 m at each station (nominally 5, 10, 25, 50, 75, and 100 m) within hours of collection. Samples were analyzed using a BD Influx Flow Cytometer to estimate phytoplankton concentrations for four major groups [Prochlorococcus, Synechococcus, picoeukaryotes (<3 µm), and nanoeukaryotes (3 to ~10 µm) (see methods in Graff and Behrenfeld, 2018)]. The phytoplankton abundance maximum (PAM) for each profile was defined as the depth where the sum concentration of the four major groups was greatest.

Concentrations for nutrients, DOC, and phytoplankton measured at 5 m were assumed to be equivalent to surface concentrations (0 m) as the mixed layer depth was greater than 5 m for all stations and all cruises (Figure 2). All profiles were averaged for each station containing multiple casts (Supplementary Figures S1–S3, S7).

Maximum Mixed Layer Depth Calculations From ARGO Floats

We used temperature, salinity, and pressure data provided by Biogeochemical-ARGO and ARGO (hereafter both referred to as ARGO) profiling floats to determine the maximum annual mixed layer depths in the vicinity of stations sampled during the ship campaigns. To match float profiles with station data, the NAAMES region was subdivided into 1° latitudinal bins. Stations and float profiles were binned to the nearest half degree based on their latitudinal coordinates. For example, a station location of 47.49°N and a float location of 46.50°N were both assigned to the 47°N bin (Figure 1 and Table 1).

1https://seabass.gsfc.nasa.gov/naames
ARGO float data were retrieved from the NAAMES data page. All ARGO floats used were located in the area of study and were either deployed during the NAAMES campaigns or previously by the ARGO or the remOcean programs in support of NAAMES (n = 18). Float data spanned from 5 May 2014 to 2 December 2018, and encompassed 2425 unique profiles.

Mixed layer depths ($Z_{\text{MLD}}$) were determined for each float profile using a threshold of the Brunt-Väisälä buoyancy frequency, $N^2$, which was calculated using the function $swN2()$ from the package oce (v 1.0.1) in R. Following Mojica and Gaube (unpublished), $Z_{\text{MLD}}$ was defined as the depth below 5 m at which $N^2$ was greater than its standard deviation:

$$Z_{\text{MLD}} = Z_{N^2 > |\sigma(N^2)|} \quad (1)$$

The deepest $Z_{\text{MLD}}$, including its corresponding month and year, recorded for each 1° latitudinal bin throughout the float sampling period was reported as that bin’s annual maximum mixed layer depth, $Z_{\text{Max MLD}}$ (Figure 1 and Table 1).

**Seasonal Nitrate Drawdown and NCP Calculations**

Estimates of surface layer-integrated NO$_3$ drawdown (ΔNO$_3$, mol N m$^{-2}$ t$^{-1}$) between deep mixed and bloom or post-bloom stratified conditions have been used to determine seasonal NCP for a variety of ecosystems (Codispoti et al., 1986; Takahashi et al., 1993; Yager et al., 1995; Bates et al., 1998; Hansell and Carlson, 1998; Siegel et al., 1999; Sweeney et al., 2000). The challenge with this approach is capturing the surface layer NO$_3$ distribution during deep winter convective mixing when nutrients from depth are redistributed to the surface. In the absence of direct measurements of NO$_3$ during deep convection, we devised an approach to approximate the NO$_3$ profiles at the time of convection ($\text{NO}_3^{\text{Mixed}}$) for each 1° latitudinal bin around each NAAMES station. Specifically, each station’s NO$_3$ profile measured during the post-bloom stratified condition was integrated to the corresponding $Z_{\text{Max MLD}}$ of its latitudinal bin. The integrated NO$_3$ stock was then depth-normalized to the $Z_{\text{Max MLD}}$; thus, providing a volumetric estimate of mixed NO$_3$ concentrations for that station (vertical dashed line in Figure 3A). In cases where latitudinal bins contained stations from both the late spring and early autumn campaigns (44, 48, and 50°N), the NO$_3^{\text{Mixed}}$ profile generated from the early autumn profiles was applied to the late spring campaign. In cases where latitudinal bins only contained stations from the late spring (54

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https://naames.larc.nasa.gov/data2018.html
TABLE 1 | Annual maximum mixed layer depths (Z_{Max MLD}), estimated from ARGO profiles.

| Latitudinal Bin (°N) | ARGO profiles n | November-April Argo Profiles n | Z_{Max MLD} (m) | Latitude of Z_{Max MLD} (°N) | Longitude of Z_{Max MLD} (°W) | Time of Z_{Max MLD} (Month-Year) |
|----------------------|-----------------|-------------------------------|----------------|-----------------------------|-----------------------------|---------------------------------|
| 39                   | 52              | 52                            | 294            | 39.2                        | −40.3                       | April-2018                      |
| 40                   | 17              | 17                            | 484            | 39.9                        | −42.1                       | March-2018                      |
| 41                   | 49              | 26                            | 478            | 41.2                        | −41.5                       | March-2018                      |
| 42                   | 114             | 61                            | 418            | 41.6                        | −41.1                       | February-2018                   |
| 42                   | 114             | 61                            | 418            | 42.2                        | −42.2                       | April-2018                      |
| 43                   | 66              | 51                            | 416            | 42.9                        | −43.9                       | April-2018                      |
| 44                   | 173             | 89                            | 368            | 44.4                        | −43.7                       | February-2018                   |
| 45                   | 113             | 49                            | 404            | 45.1                        | −43.0                       | February-2018                   |
| 46                   | 78              | 37                            | 416            | 45.9                        | −38.8                       | February-2016                   |
| 47                   | 132             | 9                             | 336            | 47.2                        | −39.1                       | March-2018                      |
| 48                   | 90              | 27                            | 508            | 48.0                        | −38.8                       | March-2018                      |
| 49                   | 92              | 46                            | 448            | 48.8                        | −41.7                       | February-2017                   |
| 50                   | 181             | 159                           | 406            | 50.4                        | −40.9                       | March-2017                      |
| 51                   | 177             | 165                           | 386            | 50.9                        | −40.5                       | February-2018                   |
| 52                   | 348             | 274                           | 330            | 51.6                        | −44.0                       | February-2018                   |
| 53                   | 375             | 223                           | 231            | 53.4                        | −41.0                       | December-2015                  |
| 54                   | 219             | 158                           | 223            | 54.1                        | −44.1                       | December-2015                  |
| 55                   | 39              | 32                            | 241            | 54.8                        | −45.9                       | January-2016                   |
| 56                   | 54              | 11                            | 110            | 55.6                        | −44.3                       | November-2015                  |
| 57                   | 56              | 5                             | 284            | 56.7                        | −46.7                       | February-2018                   |

and 56°N), NO₃_{Mixed} profiles were generated from the late spring profiles. Depth-integrated NO₃ drawdown (ΔNO₃_{100 m}, mol N m⁻² t⁻¹) over the surface 100 m (Figure 3A) from the time of deep convection to the time of observation (t) were calculated for each profile as:

\[ \Delta \text{NO}_3_{100 \text{ m}} = \int_0^{100} (\text{NO}_3_{\text{Mixed}}) dz - \int_0^{100} (\text{NO}_3_{\text{Observed}}) dz \]  

(2)

The drawdown was then converted to seasonal NCP (NCP₃₁₀₀ m, mol C m⁻² t⁻¹) by employing the C:N ratio from Redfield (1958) as done by previous studies (Hansell et al., 1993; Yager et al., 1995; Romera-Castillo et al., 2016; Bif and Hansell, 2019).

\[ \text{NCP}_{100 \text{ m}} = \Delta \text{NO}_3 \times 6.6 \]  

(3)

Seasonal depth-integrated NCP was also calculated for the depth horizons of the CM and the PAM to examine how it changed over various depths within the surface layer.

**ΔDOC and Export Calculations**

Seasonal depth-integrated ΔDOC (ΔDOC₃₁₀₀ m, mol C m⁻² t⁻¹) over the surface 100 m from the time of deep convection to the time of observation (t), shown in Figure 3B, was calculated for each profile, as follows:

\[ \Delta \text{DOC}_{100 \text{ m}} = \int_0^{100} (\text{DOC}_{\text{Observed}}) dz - \int_0^{100} (\text{DOC}_{\text{Mixed}}) dz \]  

(4)

ΔDOC₃₁₀₀ m at each station from the time of deep convection to early autumn stratified period provides an approximation of the magnitude of annual DOC export potential from the surface layer (Carlson et al., 1994; Hansell and Carlson, 2001). Demarcating the surface layer at 100 m is consistent with previous studies that have used the same depth horizon to define DOC export from the surface layer into the mesopelagic (Sweeney et al., 2000; Carlson et al., 2002; Hansell and Carlson, 2001).
et al., 2010; Hansell et al., 2012). Thus, annual DOC export out of the surface 100 m ($\text{DOC}_{\text{Export}}$ 100 m, mol C m$^{-2}$ t$^{-1}$) was calculated as the difference in the integrated DOC stocks (100 m to the maximum MLD for each station) between the mixed and the early autumn stratified condition (Figure 3B), as follows:

$$\text{DOC}_{\text{Export}} 100 m = \int_{100}^{\text{ZMax MLD}} \frac{\text{DOC}_{\text{Observed}}}{t} dz - \int_{100}^{\text{ZMax MLD}} \frac{\text{DOC}_{\text{Mixed}}}{t} dz$$

(5)

We acknowledge that $\Delta$DOC is subject to surface circulation and can be advected to a location with enhanced, dampened, or negligible vertical mixing. Because we do not have an explicit means to constrain lateral advection with the available data, the DOC export values reported here assume a static view of the system and represent local vertical export.

The partitioning of seasonal NCP into $\Delta$DOC was calculated as the ratio between $\Delta$DOC and NCP (Figure 4C and Supplementary Figure S6). To examine how $\Delta$DOC and $\Delta$DOC:NCP changed over various depth horizons within the surface layer, they were estimated within the surface 100 m, the CM, and the PAM.

### Seasonal Silicate Drawdown Calculations

The depth-integrated seasonal drawdown of SiO$_4$ ($\Delta$SiO$_4$ 100 m) relative to $\Delta$NO$_3$ 100 m was used as an index of the relative importance of diatoms in NO$_3$ drawdown, as opposed to other phytoplankton groups. Greater $\Delta$SiO$_4$:$\Delta$NO$_3$ ratios indicate the greater relative importance of diatoms or other siliceous phytoplankton in contributing to NCP$_{100}$ m (Sweeney et al., 2000). $\Delta$SiO$_4$ 100 m was calculated following the same approach described above to determine $\Delta$NO$_3$ 100 m.

### Statistical Analyses

Model I linear regressions were used to assess the comparability of $\Delta$DOC:NCP estimates as well as latitudinal trends in those estimates. Regressions were computed using the function lm() from the package stats (v 3.5.1) in R (v 3.5.1). Model fits with $p$-values $\leq 0.05$ are described herein as "significant," while those with $p$-values $\leq 0.01$ are described as "highly significant." T-tests were used to determine if slopes were different from 0, with $p$-values $\leq 0.05$ indicating significant likelihood. The Breusch–Pagan test against heteroskedasticity was performed on each model using the function bptest() from the package lmtest (v 0.9-37) with the argument studentized set to TRUE in R (v 3.5.1). From this test, $p$-values $\leq 0.05$ suggest heteroskedasticity and indicate that the spread of the residuals is not constant with the fitted values. In this case, the regression model's ability to predict a dependent variable is not consistent across all values of that dependent variable. Standardized (reduced) major axis model II linear regressions were used to explore relationships among deep mixed conditions, NCP, $\Delta$DOC:NCP, $\Delta$DOC, inorganic nutrients, and broad phytoplankton groups. As with the model I linear regressions, model fits with $p$-values $\leq 0.05$ are described as "significant" and those with $p$-values $\leq 0.01$ are described as "highly significant." A Welch two-sample $T$-test was performed to compare $\Delta$DOC:NCP between seasons using the function t.test() from the package stats (v 3.5.1) in R (v 3.5.1).

### RESULTS

#### ARGO Float-Based Maximum Mixed Layer Depth Estimates

A total of 2425 profiles were recorded in the NAAMES study region between 5 May 2014 and 2 December 2018. The minimum and maximum number of profiles for each 1° latitudinal bin within the NAAMES study region were $n = 17$ (40°N) and $n = 375$ (53°N), respectively, with a mean of $n = 127$ and the

![FIGURE 4](https://example.com/figure4.png) Vertical profiles of volumetrically estimated (A) NCP (difference between NO$_3$$_{\text{Mixed}}$ and NO$_3$$_{\text{Observed}}$ at each depth) × 6.6), (B) $\Delta$DOC (difference between NO$_3$$_{\text{Observed}}$ and NO$_3$$_{\text{Mixed}}$ at each depth), and (C) subsequent $\Delta$DOC:NCP. The NO$_3$ and DOC profiles used to make these estimates were taken from station 5 at 51.7°N and −39.5°W. The green dotted line denotes the chlorophyll maximum (CM), and the blue dotted line demarcates the phytoplankton abundance maximum (PAM).
median of \( n = 92 \). Figure 1 illustrates the temporal coverage obtained by combining data from the ARGO floats in the vicinity of each station (within 1° latitudinal bin). The maximum MLD (\( Z_{\text{Max MLD}} \)) determined for each 1° latitudinal bin in the NAAMES region occurred between the months of November and April and ranged from 110 to 508 m. A total of 1491 profiles were recorded during this period, with a minimum, maximum, mean, and median number of profiles for each 1° latitudinal bin at 5 (57°N), 274 (52°N), 78, and 49, respectively (Table 1). The range, mean, and median of \( Z_{\text{Max MLD}} \) was greater than the mixed layer depths recorded for all cruises within the NAAMES campaign, which ranged between 6 and 214 m (Figure 2), indicating that conditions reflecting deep convection were not captured during the NAAMES occupations.

\( Z_{\text{Max MLD}} \) determined for each bin was then used to reconstruct mixed nutrient and DOC profiles required to calculate seasonal NCP and \( \Delta \text{DOC} \).

**NCP, \( \Delta \text{DOC} \), and Vertical DOC Export**

Estimates of seasonal NCP from the mixed condition to the early autumn stratified period ranged between 1.67 and 6.70 mol C m\(^{-2}\), with a median of 4.69 and a mean of 4.29 mol C m\(^{-2}\) (Table 2). \( \Delta \text{DOC}:\text{NCP} \) over the same period ranged from 0.14 to 0.35, with a median and mean of 0.17 and 0.20, respectively (Table 2).

Vertical profiles of volumetrically estimated NCP (difference between \( \text{NO}_3^{\text{Mixed}} \) and \( \text{NO}_3^{\text{Observed}} \) at each depth \( \times 6.6 \)) and \( \Delta \text{DOC} \) (difference between \( \text{DOC}^{\text{Observed}} \) and \( \text{DOC}^{\text{Mixed}} \) at each depth) show that NCP and \( \Delta \text{DOC} \) were both most pronounced within the shallowest depth horizons of the surface layer (Figure 4 and Supplementary Figures S4, S5). \( \Delta \text{DOC}:\text{NCP} \) estimates were similar whether calculated for the upper 100 m, to the depth of the CM, or the depth of the PAM (Supplementary Table S1).

Using the local \( Z_{\text{Max MLD}} \) for each station, we estimated annual \( \text{DOC}_{100} \) for each station along the NAAMES meridional transect (42°N–53°N) to range between 0.34 and 1.15 mol C m\(^{-2}\) (Table 2), with a mean of 0.77 mol C m\(^{-2}\). Estimates of \( \text{DOC}_{100} \) are not included in Table 3. This is because it would be inappropriate to calculate DOC export for the late spring, a season far removed from the timing of deep convection. It is the bulk DOC pool during the stratified condition, just before the late autumn/winter, that will be subject to deep convection. Mesopelagic DOC concentrations in the early autumn were observed to be lower than those of the mixed condition (Figure 3 and Supplementary Figure S2), suggesting that after DOC is exported, it is remineralized by the mesopelagic community (Carlson et al., 2004, 2011). \( \Delta \text{DOC}:\text{NCP} \) over a range of NCP magnitudes was observed to be significantly greater in the early autumn (mean 0.20 ± 0.06) than the late spring (mean 0.11 ± 0.06) (Tables 2, 3 and Figures 5, 6A). Vertical DOC export was observed to increase in magnitude with increasing NCP (Figure 6B).

**Partitioning of NCP**

\( \Delta \text{SiO}_4^{\text{N}}:\Delta \text{NO}_3^{\text{N}} \) in the early autumn generally increased with increasing latitude and ranged from 0.36 to 0.70, which would suggest that 36–70% of phytoplankton biomass in the region was represented by diatoms or other siliceous phytoplankton like silicoflagellates. \( \Delta \text{DOC}:\text{NCP} \) displayed a strong and highly significant negative relationship with \( \Delta \text{SiO}_4^{\text{N}}:\Delta \text{NO}_3^{\text{N}} \) (Figure 7). \( \Delta \text{DOC}:\text{NCP} \) also showed significant moderate to strong direct relationships with Prochlorococcus abundance within the depth horizons of the CM and PAM (Figure 8). When compared to flow cytometry cell abundance estimates of other broad phytoplankton groups (Synechococcus, picoeukaryotes, and nanoeukaryotes), the \( \Delta \text{DOC}:\text{NCP} \) ratio only demonstrated a weak negative relationship with picoeukaryotes over the PAM depth horizon (Supplementary Table S2).

**DISCUSSION**

Of the \(~9\) Pg C of global annual carbon export to the ocean interior by the biological carbon pump (DeVries and Weber, 2017), approximately 1.27 Pg C are exported in the North Atlantic alone, indicating that the biological carbon pump in the North Atlantic is an important component of the global carbon cycle (Sanders et al., 2014). The biological carbon pump is driven by a complex set of processes, including a passive sinking flux of organic particles (McCave, 1975), an active transport of organic carbon and \( \text{CO}_2 \) by vertically migrating zooplankton (Steinberg et al., 2000), and the physical transport of dissolved and suspended organic matter by subduction and convective mixing (Carlson et al., 1994; Hansell et al., 2009; Dall’Olmo et al., 2016). To predict changes in the North Atlantic biological carbon pump under different climate scenarios, it is necessary to reduce the uncertainties in the magnitude and contribution of these different pathways (Sanders et al., 2014; Siegel et al., 2016). Although contributions by passive fluxes and vertical migrating organisms to carbon export can be obtained on...
TABLE 2 | Seasonal net community production (NCP) and its partitioning into DOC in the upper 100 m as well as DOC export out of the upper 100 m for the early autumn campaign. CM refers to the chlorophyll maximum and PAM refers to the phytoplankton abundance maximum.

| Station | Latitude (°N) | Longitude (°W) | Bin (°N) | Subregion | Date (yyyy-mm-dd) | CM (m) | PAM (m) | Mixed \( \text{NO}_3 \) (µmol N L\(^{-1}\)) | Mixed DOC (µmol C L\(^{-1}\)) | Mixed SiO\(_4\) (µmol Si L\(^{-1}\)) | \( \Delta \text{NO}_3 \) (µmol N m\(^{-2}\)) | NCP (mol C m\(^{-2}\)) | \( \Delta \text{DOC} \) NCP | DOC Export (mol C m\(^{-2}\)) | \( \Delta \text{SiO}_4 \) | \( \Delta \text{SiO}_4 : \Delta \text{NO}_3 \) |
|---------|--------------|----------------|----------|-----------|-------------------|--------|---------|----------------|----------------|----------------|----------------|---------------|----------------|----------------|----------------|----------------|
| 1A (0)  | 42.25        | −44.72         | 42       | GS/Sargasso | 2017-09-04        | 75     | 50      | 8.5            | 56.1           | 3.7            | 0.80           | 5.25           | 1.15           | 0.22           | 1.15           | 0.29           | 0.36           |
| 1       | 42.39        | −42.95         | 42       | GS/Sargasso | 2017-09-04        | 75     | 50      | 3.8            | 54.7           | 1.7            | 0.25           | 1.67           | 0.58           | 0.35           | 0.58           | 0.10           | 0.38           |
| 2       | 43.71        | −42.90         | 44       | Subtropical | 2017-09-05        | 50     | 40      | 10.1           | 53.6           | 7.3            | 0.71           | 4.69           | 0.96           | 0.21           | 0.96           | 0.39           | 0.55           |
| 1.5     | 44.37        | −43.37         | 44       | Subtropical | 2017-09-06        | 38 ± 13 | 0       | 13.1           | 55.9           | 7.8            | 0.94           | 6.17           | 1.04           | 0.17           | 1.04           | 0.57           | 0.61           |
| 3       | 47.01        | −40.11         | 47       | Subtropical | 2017-09-08        | 34 ± 8 | 16 ± 8  | 4.7            | 54.3           | 2.1            | 0.20           | 1.29           | 0.34           | 0.26           | 0.34           | 0.08           | 0.43           |
| 3.5     | 48.05        | −39.25         | 48       | Subtropical | 2017-09-09        | 25     | 25      | 13.9           | 51.3           | 7.4            | 1.02           | 6.70           | 1.04           | 0.15           | 1.04           | 0.58           | 0.57           |
| 4       | 48.64        | −39.13         | 49       | Subtropical | 2017-09-10        | 39 ± 13 | 16 ± 8  | 13.1           | 51.6           | 8.3            | 0.93           | 6.15           | 0.93           | 0.15           | 0.93           | 0.66           | 0.70           |
| 4.5     | 50.14        | −39.26         | 50       | Temperate   | 2017-09-11        | 25     | o       | 10.7           | 52.4           | 4.7            | 0.61           | 4.05           | 0.76           | 0.19           | 0.76           | 0.29           | 0.48           |
| 5       | 51.68        | −39.51         | 52       | Temperate   | 2017-09-12        | 50     | 10      | 12.4           | 56.0           | 7.5            | 0.85           | 5.70           | 0.83           | 0.15           | 0.83           | 0.54           | 0.63           |
| 5.5     | 52.65        | −39.61         | 53       | Subpolar    | 2017-09-13        | 25     | 10 ± 9  | 13.0           | 54.4           | 7.3            | 0.42           | 2.79           | 0.45           | 0.16           | 0.45           | 0.24           | 0.58           |
| 6       | 53.36        | −39.55         | 53       | Subpolar    | 2017-09-14        | 18 ± 7 | 10 ± 9  | 12.7           | 52.7           | 6.7            | 0.42           | 2.76           | 0.39           | 0.14           | 0.39           | 0.24           | 0.59           |

Mixed \( \text{NO}_3 \), DOC and SiO\(_4\) are estimates of the "mixed" condition reflective of winter / spring deep convection, estimated by redistributing the early autumn observed profiles to the maximum MLD. \( \Delta \text{NO}_3 \), \( \Delta \text{DOC} \), and \( \Delta \text{SiO}_4 \) are depth-integrated \( \text{NO}_3 \) drawdown, DOC accumulation, and SiO\(_4\) drawdown over the surface 100 m from the time of deep convection to the time of observation. DOC Export refers to DOC export out of the surface 100 m, calculated as the difference in the integrated DOC stocks (100 m to the maximum MLD for each station) between the mixed and the early autumn stratified condition.
individual research campaigns, assessing the contribution of the vertical redistribution of $POC_1$ and $DOC$, respectively, to carbon export requires an understanding of the interplay between the seasonal net production of $POC_1$ and $DOC$ and the extent of physical convective mixing at any given location. By combining ARGO float data with satellite estimates of $POC_1$, one study demonstrated that the seasonal accumulation and physical removal of total $POC_1$ in the North Atlantic could account for 23 to >100% of the carbon export flux into the mesopelagic (Dall’Olmo et al., 2016). Applying this approach to estimate the contribution of $DOC$ to vertical carbon export would be difficult without a remote-sensing proxy for the bulk $DOC$ pool in the open ocean. Direct measurements of $DOC$ at regular temporal intervals over numerous annual cycles at time-series study sites is arguably the most powerful approach to resolving the contribution of $DOC$ to vertical carbon export (Copin-Montégut and Avril, 1993; Carlson et al., 1994; Bøsrheim and Myklestad, 1997; Hansell and Carlson, 2001). This approach, however, is only feasible at a limited number of locations.

### Constraints on Post-convection Conditions Challenges Estimations of $\Delta DOC$ and NCP

Studies that make direct $DOC$ measurements at the time of deep convection and during stratified periods (i.e., post-bloom) can provide estimates of seasonal $DOC$ accumulations ($\Delta DOC$). Concomitant measurements of $TCO_2$, inorganic nutrients, or oxygen between those periods permit estimates of NCP (Codispoti et al., 1986; Hansell et al., 1993; Bates et al., 1998; Plant et al., 2016). Combining the corresponding $\Delta DOC$ and NCP estimates provides insight into how much of NCP becomes seasonally accumulated $DOC$ ($\Delta DOC$ : NCP), thereby providing constraints on estimates of vertical $DOC$ export potential (Hansell and Carlson, 1998; Carlson et al., 2000; Sweeney et al., 2000; Hansell and Carlson, 2001). A major
FIGURE 7 | Model regressions comparing the ΔDOC:NCP in the surface 100 m; (A) model regression for the ΔSiO\textsubscript{4}:ΔNO\textsubscript{3} ratio versus latitude and (B) standard major axis model II regression for ΔDOC:NCP versus ΔSiO\textsubscript{4}:ΔNO\textsubscript{3} ratio. Each point represents estimates for a station on the early autumn cruise. Points are filled by the subregional classification of the station as presented in Figure 1.

FIGURE 8 | Standard major axis model II regressions comparing the ΔDOC:NCP ratio with the absolute abundance Prochlorococcus, integrated to the chlorophyll maximum (CM) (A) and the phytoplankton abundance maximum (PAM) (B) for each station. Each point represents estimates for a station on the early autumn cruise. Points are filled by the subregional classification of the station as presented in Figure 1.

challenge to estimating ΔDOC:NCP is being able to capture direct measures of DOC and inorganic nutrients at the time of deep mixing when their respective concentrations are homogenously distributed throughout the deep mixed layer. Measures of DOC and inorganic nutrient profiles during both seasonally vertically stratified and maximally mixed conditions allow for the calculation of net DOC production from NO\textsubscript{3} drawdown (estimates of NCP). However, capturing maximal deep convective mixing events is difficult at best.

In the absence of direct measurements, previous studies have defined criteria to predict pre-bloom nutrient and surface DOC concentrations. In their study of upwelling-driven phytoplankton blooms in the northwestern portion of the Santa Barbara Channel, California, Wear et al. (2015a) used nutrient and salinity fields to characterize recently upwelled water at 5 m and then identified waters meeting those nutrient and salinity conditions as “pre-bloom” source waters, reflective of initial mixed conditions. DOC values in these source waters were used as background concentrations from which ΔDOC values were calculated. In Romera-Castillo et al. (2016), the authors applied a representative ΔDOC:NCP value derived from cruise-based estimates to climatological nitrate data to model ΔDOC
throughout the Atlantic. They calculated $\Delta DOC$ and NCP as the difference in DOC and nitrate concentrations, respectively, between the surface and underlying source waters, which varied with latitude. In the North Atlantic, mixed condition values for DOC and nitrate concentrations were taken from 200 m with the reasoning that winter vertical mixing commonly reaches that depth. Here, we used ARGO float observations to retrieve the maximum MLDs measured in 1° latitudinal bins in the NAAMES study region (Figure 1 and Table 1). We then redistributed early autumn stratified DOC and NO$_3$ profiles over their corresponding local maximum MLD to estimate DOC$_{\text{Mixed}}$ and NO$_3$$_{\text{Mixed}}$ concentrations (Figure 3), allowing estimations of $\Delta DOC$ and NCP at occupied stations.

**Leveraging ARGO Datasets Empower Analysts to Simulate Pre-bloom Conditions**

With a current global fleet of over 3900 autonomous floats, the ARGO program has made great contributions to improving our understanding of physical and biogeochemical variability in the oceans (Riser et al., 2016; Claustre et al., 2020). Probing the rich dataset generated by these floats can provide reasonable estimates of annual maximum MLDs across expansive areas of the ocean at 1° latitudinal resolution (Figure 1 and Table 1). These estimates of annual maximum MLDs can then be used to simulate the redistribution of DOC and nitrate profiles observed during the early autumn stratified periods and allow approximate reconstructions of the mixed profiles for each variable (Figure 3). Combining ARGO data collected in the NAAMES region with profiles collected during the early autumn stratified period, we were able to estimate mixed DOC and nutrient concentrations in the absence of direct measurements.

As these estimates were the foundation for calculating approximate $\Delta DOC$, its contribution to NCP, and potential DOC export flux in western North Atlantic (Tables 2, 3 and Figure 3), we sought to compare them to wintertime (January to March) data from two publicly available data products, the Global Ocean Data Analysis Project version 2 2019 (Gv2, 2019) and the World Ocean Atlas 18 (WOA18) (see analyses in Supplementary Material). Unfortunately, these two data products contained limited wintertime data for the NAAMES study region and the available data displayed relatively shallow winter MLDs compared to our maximum MLD estimates. For these reasons, using Gv2, 2019 and WOA18 data to constrain the conditions under deep convection for the NAAMES region was problematic and made comparisons with this study's data equivocal. However, interrogating these publicly available data products did underscore the difficulty in defining the magnitude and conditions of deep mixing for the western North Atlantic, even with extensive, historical datasets. Data from the ARGO program, as used in this study, can help to hone estimates of the maximal extent of deep convective mixing, critical to constraining $\Delta DOC$, its contribution to NCP, and potential DOC export flux. However, this is not an infallible approach either.

Our approach to capturing deep convective mixing over a wide range of latitudes at 1° resolution using ARGO float data can also be limited by sampling resolution (i.e. number of floats, profiling frequency). While the float data for most of the latitudinal bins in the NAAMES region contain mixing estimates deeper than 200 m (Table 1 and Figure 2), it is possible that the ARGO floats missed deeper mixing events at or near our station locations, leading to underestimates of local deep mixing. However, the ARGO-based maximum mixed layer depths presented here are deeper than the winter mixed layer depths from the Gv2 and WOA18 data products, from wintertime ARGO climatological data, as well as those observed on the late autumn NAAMES campaign [i.e., closest campaign to the timing of deep convection (November 2015)] (see analyses in Supplementary Material and Supplementary Figure S13). Regardless, the derived variables (i.e. $\Delta DOC$, NCP, and vertical DOC export) presented here are realistically constrained but should be considered conservative estimates. Other caveats with the approach have been noted in previous studies that have calculated NCP from nutrient deficits and are summarized below.

**Caveats Limit Approximations of NCP From Nitrate Drawdown**

NCP derived from nitrate drawdown is taken as an approximation of new production, that is, the net production utilizing inorganic nitrogen provided from outside sources such as deep mixing and/or upwelling (Dugdale and Goering, 1967). This approximation ignores the contributions of new nitrogen from atmospheric deposition, river inputs, and nitrogen fixation, which may lead to underestimates of NCP. Recent convergent estimates from an inverse biogeochemical and a prognostic ocean model suggest that the input of newly fixed nitrogen from microbial fixation, atmospheric deposition, and river fluxes can account for up to 10% of carbon export in the NAAMES region (Wang et al., 2019). In addition, nitrification within the surface layer can lead to overestimates of new production (Santoro et al., 2010). Though direct measures of nitrification rates are scarce, previous studies have demonstrated that nitrification can be an insignificant source of nitrate in the surface layer of the subarctic North Atlantic and the Sargasso Sea (Fawcett et al., 2015; Peng et al., 2018). The approach used here does not allow us to constrain the contributions of new nitrogen from the processes described above, thus nitrate drawdown was our best approximation of NCP.

Redfield stoichiometry (C:N = 6.6) is commonly used to convert nitrate drawdown to NCP in carbon units (Hansell et al., 1993; Yager et al., 1995; Romera-Castillo et al., 2016; Bif and Hansell, 2019). We recognize that DOM production and accumulation in the surface layer can be C-rich relative to Redfield stoichiometry, having C:N ratios ranging from 12 to 15 in surface waters (Williams, 1995; Hansell and Carlson, 2001; Hopkinson and Vallino, 2005), and that these values may change over the course of a phytoplankton bloom (Sambrotto et al., 1993; Bury et al., 2001; Körzinger et al., 2001). Using Redfield stoichiometry to convert NO$_3$ drawdown to NCP may underestimate true NCP if a significant fraction of organic matter production was C-rich relative to Redfield stoichiometry, ultimately leading to slight overestimates of $\Delta DOC$NCP.
Laws (1991) argues that applying the Redfield ratio to seasonal nitrate drawdown can underestimate NCP by as much as 15–30%, other studies have demonstrated that the seasonal drawdown of $TCO_2$ relative to $NO_3$ drawdown is close to 6.6 in some high latitude systems (Yager et al., 1995; Bates et al., 1998). Thus, employing Redfield stoichiometry is a useful approach when comparing $\Delta DOC:NCP$ with previously published studies.

$\Delta DOC:NCP$ Linked to Ecosystem State

The range of $\Delta DOC:NCP$ reported here is comparable to those previously reported from a variety of locations in the North Atlantic under different ecological states and NCP magnitudes (Hansell and Carlson, 1998; Romera-Castillo et al., 2016 and the references therein). $\Delta DOC:NCP$ increased from late spring to early autumn and vertical DOC export increased as seasonal NCP increased into the early autumn (Tables 2, 3 and Figures 5, 6). This may reflect changes in both ecosystem state (i.e., nutrient availability) and plankton community composition (Hansell and Carlson, 1998; Carlson et al., 2000). Differences in predominant phytoplankton community members might lead to differences in the magnitude of DOM accumulation, perhaps due to differences in the quantity and quality of the DOM produced (Conan et al., 2007). We observed a seasonal progression in the partitioning of NCP into $\Delta DOC$, with $\Delta DOC:NCP$ increasing between the late spring and early autumn (Figure 5). This finding is consistent with previous bloom observations in the Ross Sea (Carlson and Hansell, 2003). Prior studies have shown phytoplankton bloom progression is coincident with increases in DOC production and accumulation, which could be in part due to nutrient limitation (Duursma, 1963; Ittekkot et al., 1981; Eberlein et al., 1985; Billen and Fontigny, 1987; Carlson et al., 1994; Williams, 1995; Wear et al., 2015a), but these relationships are not universal (Carlson et al., 1998). While some studies have demonstrated increases in DOC concentrations with increases in Phaeocystis primary production and biomass (Eberlein et al., 1985; Billen and Fontigny, 1987), Carlson et al. (1998) observed little change in the bulk DOC pool during the early phase of an Antarctic Phaeocystis bloom. The authors reported low total DOC production (0.44 mol C m$^{-2}$) in the Antarctic relative to the oligotrophic Sargasso Sea (1.7 mol C m$^{-2}$). Also, the authors observed that while $\sim$50% of the newly produced DOC in the Sargasso Sea escaped microbial consumption and instead accumulated as $\Delta DOC$, only $\sim$28% accumulated as $\Delta DOC$ in the Antarctic, indicating that newly produced DOC in the Antarctic was largely bioavailable to the extant heterotrophic microbial community and was largely removed prior to deep convective mixing. These observations led to the hypothesis that the low seasonal production of DOC and its high bioavailability in the Ross Sea may have been tied to the size structure and composition of the phytoplankton community there.

Bloom of large eukaryotic phytoplankton relative to picophytoplankton may reflect conditions that favor the production of more bioavailable DOC that has a low potential to accumulate as $\Delta DOC$ (Carlson et al., 1998). Wear et al. (2015a,b) demonstrated in field and experimental work at a coastal upwelling site that, as diatom dominated blooms transitioned from a nutrient-replete to a Si-stressed state, there were corresponding increases in the fraction of bloom-produced DOC that became bioavailable to heterotrophic bacterioplankton. Comparatively in tropical and subtropical systems, the dominance of picophytoplankton appears to lead to greater DOC accumulation (Carlson et al., 1998; Hansell and Carlson, 1998; Hansell et al., 2009). It is important to emphasize, however, that the relative contribution of a phytoplankton size class does not necessarily dictate the magnitude of $\Delta DOC$ and the fractionation of NCP into $\Delta DOC$. Rather, their relative abundance may be indicative of the environmental conditions that control the net partitioning of NCP as $\Delta DOC$. For instance, higher $\Delta DOC:NCP$ ratios may reflect greater extracellular DOC release from primary production due to differences in cell surface area; volume ratios (Karl et al., 1996). In hydrographically stable conditions, elevated $\Delta DOC:NCP$ ratios may reflect the increased transformation of labile DOM to more recalcitrant compounds due to nutrient limitation of heterotrophic bacterioplankton production, physical separation of bacterioplankton assemblages capable of using recalcitrant DOM, or further transformation by phototransformation (Cotner et al., 1997; Kieber et al., 1997; Benner and Biddanda, 1998; Jiao et al., 2010). Conversely, cell physiological stress in response to physical mixing may also lead to the increased production of DOC, resulting in higher $\Delta DOC:NCP$ ratios (Hansell and Carlson, 1998).

The contribution of larger phytoplankton, like Phaeocystis and diatoms, may also illuminate what conditions drive NCP partitioning. For example, the larger contribution of Phaeocystis relative to picoeukaryotes observed by Carlson et al. (1998) may reflect conditions that favor the production of more bioavailable DOC that has a low potential to accumulate as $\Delta DOC$. In support of this, the authors noted that the increased production of bioavailable DOC in silicate-limited conditions may be an adaptive strategy by diatoms to promote heterotrophic remineralization of dead diatom frustules to dissolved silicate. Thus, in waters where silicate drawdown exceeded nitrate drawdown, we may infer that they were not only occupied by silicifying phytoplankton like diatoms but also that those phytoplankton may have become Si-limited over time, producing bioavailable DOC inconsequential to carbon accumulation and vertical export. Indeed, the ratios of nutrient deficits, particularly $\Delta SiO_4$ and $\Delta NO_3$, and NCP have been used to provide a broad signature of the composition of the community that may have been responsible for NCP and $\Delta DOC$ (Sweeney et al., 2000; Carlson and Hansell, 2003). With knowledge of either or both phytoplankton community composition and signatures of nutrient limitation, we can glean the environmental conditions that control the partitioning of NCP into $\Delta DOC$.

$\Delta DOC:NCP$ and Vertical DOC Export

Reflect Conditions Favoring Non-Siliceous Phytoplankton

To determine whether linkages could be made between the observed partitioning of NCP and distinct ecosystem states, we explored the relationships between $\Delta DOC:NCP$,
highly significant inverse relationship with Synechococcus and the abundance of NCP functional groups other than siliceous phytoplankton (e.g., where the phytoplankton community is dominated by Prochlorococcus, and long-term stability of Prochlorococcus that the abundance of Prochlorococcus was a moderate to strong indicator of DOC:NCP and DOC accumulation within both the depth horizons of the chlorophyll and PAMs (Figure 8). This relationship, in combination with those of the nutrient deficits aforementioned, is intriguing. Together, they suggest that in stratified waters with a higher presence of Prochlorococcus, DOC accumulation and ΔDOC:NCP are elevated.

It is not clear in our study if elevated Prochlorococcus concentrations lead to the direct production of recalcitrant DOC or if the group simply represents an environmental indicator of other physical and/or food web interactions that result in ΔDOC. It has been proposed that Prochlorococcus may disproportionately contribute to the enhanced concentrations and long-term stability of DOC in the oligotrophic ocean (Braakman et al., 2017). The correlations between elevated Prochlorococcus, reduced ΔSiO₄:ΔNO₃, increased DOC accumulation, and increased ΔDOC:NCP reported here is consistent with this hypothesis. The linkages made here may be important to understand the specific mechanisms that drive the partitioning of NCP and the accumulation of DOC and would benefit from future experimental work targeting the role of Prochlorococcus in these processes.

DOC Is an Important Vertical Export Term in Temperate and Subtropical Western North Atlantic

In this study, we have estimated that 20 ± 6% NCP accumulated as ΔDOC by early autumn in the western North Atlantic region occupied by NAAMES (Table 2). Applying this estimate to a climatological model like that of Romera-Castillo et al. (2016) may help constrain estimates of ΔDOC throughout the western North Atlantic at a higher resolution. An annual DOC export of 0.34–1.15 mol C m⁻² (mean 0.77 mol C m⁻²) out of the surface 100 m indicates that physical mixing of DOC is an important component of the biological carbon pump for this portion of the North Atlantic. Because the ARGO floats used here may not have captured the deepest local mixing event at any given station location, our estimates of annual ΔDOC are considered conservative. Similar to previous studies, we calculate ΔDOC in the surface 100 m to be equivalent to vertical DOC export (Hansell and Carlson, 2001; Romera-Castillo et al., 2016; Bif and Hansell, 2019). However, a fraction of ΔDOC could be laterally transported and/or remineralized by heterotrophic bacterioplankton, thus becoming unavailable to downward mixing by convective overturn. We may further constrain our estimates of DOC export by distinguishing horizontal from vertical transport and also accounting for the bioavailable fraction of DOC that is rapidly remineralized by microorganisms (Copin-Montégut and Avril, 1993; Carlson et al., 1994; Börsheim and Myklestad, 1997). DOC bioavailability and its impact on vertical DOC export for the NAAMES study region will be discussed in a subsequent manuscript. Finally, our data suggest that in conditions resulting in low Si-drawdown, Prochlorococcus or the conditions they reflect may play a significant role in the accumulation of annual ΔDOC and the partitioning of NCP, providing a framework for future investigations of the mechanisms driving these processes.

DATA AVAILABILITY STATEMENT

The shipboard data generated for this study are publicly available in the NASA SeaWiFS Bio-optical Archive and Storage System (SeaBASS, https://seabass.gsfc.nasa.gov/naames). The ARGO float data used for this study are available on the NAAMES data page (https://naames.larc.nasa.gov/data2018.html). All processed data, code, and analyses are available on GitHub (https://github.com/nbaetge/naames_export_ms).

AUTHOR CONTRIBUTIONS

This manuscript, containing only original data, has not been published elsewhere. NB and CC conceived of the study, experimental design, and collected the samples. NB analyzed the data. All authors assisted with data reduction and contributed to the revision and editing of the final manuscript. All authors are aware of and accept responsibility for this manuscript and have approved the final submitted manuscript.
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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2020.00227/full#supplementary-material

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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