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Longitudinal variability of organic nutrients in the North Atlantic subtropical gyre

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ABSTRACT

We combine modelled timescales of ocean circulation with satellite-retrieved and *in situ* biogeochemical observations collected in spring along 24.5°N in the subtropical North Atlantic. Longitudinal gradients in the distribution of dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) and in other biogeochemical parameters are associated with the longitudinal variability in physical forcing and in the eastward increase of the timescale of advective transport. The western (West of 70°W) and eastern (East of 30°W) margins of the subtropical gyre appear influenced by the productive regions of the Gulf Stream and upwelling zones off Africa, respectively. Within the oligotrophic zone between 70 and 31°W, at approximately 46°W there is a change in the nutrient-controlling factors from the western ultra-oligotrophic with barely any seasonal cycle to an eastern oligotrophic environment with a more intense mixed layer dynamics. The allochthonous supply of semilabile-DOP may be important in the western sector of the oligotrophic gyre (approx. 70–46°W) where, together with the combination of shallow mixed layers, almost permanent stratification and high water temperatures create a niche for the growth of diazotrophs, which we detect from space. Turnover estimates exceeding 3 yr suggest that even reactive fractions of DON are unlikely to be a significant N source. In the eastern sector of the oligotrophic gyre (46–31°W), transit timescales longer than 3 years suggest that the allochthonous supply of the semilabile DOP is negligible due to its exhaustion. Here, an intense mixed layer dynamics favours nutrient supply from below the mixed layer. We speculate that longitudinal variability in physical forcing and gradients in the timescale of advection, combined with distinct turnover timescales of reactive fractions of DON and DOP, drive diverse phytoplankton assemblages and surface nitrogen fixation gradients across our region of investigation.

1. Introduction

There is a longstanding discussion on the source of macronutrients required to support the export of organic matter in the North Atlantic subtropical gyre (NASG). The apparent mismatch between local measurements of turbulent nutrient supply (Lewis et al., 1986) and large-scale geochemical estimates of oxygen consumption at depth (Jenkins and Goldman, 1985) has been reduced by taking into account physical processes, e.g. eddy pumping (McGillicuddy and Robinson, 1997) and double-diffusion (Dietze et al., 2004). However, additional sources of nutrients are still required to account for measured export production (Mouriño Carballido et al., 2011). The pre-condition for nutrients to fuel export production is that they need to be "new", i.e. they need to be provided externally into the system (allochthonous). Allochthonous nitrogen sources from N_2 fixation and atmospheric deposition (Hansell et al., 2004), are thought to be significant (e.g. Mouriño Carballido et al., 2011; Kähler et al., 2010). However, the magnitude and controls of these N sources are still not well constrained (Hansell et al., 2004, 2007; Landolfi et al., 2008; Salihoglu et al., 2008) and the severe phosphorus depletion (Wu et al., 2000) combined with the lack of external P sources pose the question as to how the P requirements of N_2 fixers can be sustained in the NASG.

Dissolved organic nitrogen (DON) and phosphorus (DOP), that account for the major share of the total dissolved N and P pools in surface oligotrophic waters (Jackson and Williams, 1985), have been proposed as sources of new nutrients to the gyre (Williams and Follows, 1998). DON and DOP are mainly produced (e.g. bacterial and phytoplankton exudation, sloppy feeding, viral lysis, and particle dissolution) and consumed by biological activity (uptake

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and remineralisation). Net DON and DOP accumulation (production exceeding consumption) occurs mostly in regions of elevated productivity (Hansell and Carlson, 2001; Bronk, 2002).

The advection of semilabile DON and DOP fractions from productive regions into subtropical gyres is suggested to fuel new production in oligotrophic waters (Williams and Follows, 1998; Mahaffey et al., 2004). Modelling studies suggest that this mechanism may support a significant fraction (>50%) of export production in the NASG (Roussenov et al., 2006; Charria et al., 2008; Torres-Valdés et al., 2009). However, the distributions of modelled organic nutrients are very sensitive to the model assumptions of bio-availabilities and remineralisation timescale (Charria et al., 2008), and the effectiveness of this advection mechanism awaits further testing. To be a significant allochthonous nutrient source DON and DOP need sufficiently long remineralisation time scales to be advected from productive regions to the interior of the gyre where they could fuel growth of the plankton community. DON and DOP pools are not well characterised at molecular level (Aluwihare et al., 2005; Young and Ingall, 2010). They constitute a mixture of compounds turning over on different timescales from hours (labile), months and years (semilabile) to millennia (refractory) (Carlson and Ducklow, 1995). Semilabile components of DON and DOP can be made available to the plankton community by the release of extracellular enzymes synthesised both by bacteria and phytoplankton (Bronk et al., 2007; Arnosti, 2011). The hydrolysis of proteins and peptides into smaller peptides and amino acids can be initiated by aminopeptidases (LAP). Although the products of this hydrolysis may undergo further enzymatic processing, LAP activity reflects an initial step of semilabile DON breakdown (Martinez and Azam, 1993; Hoppe, 2003). DOP is largely (80–85%) composed of phosphate esters (Young and Ingall, 2010). Alkaline phosphatase (AP) has the potential to hydrolyse a broad spectrum of DOP compounds with a preference for phosphomonoesters (e.g. Young and Ingall, 2010). Rates of hydrolysis of specific substrates are widely used to derive information on the potential activities of these extracellular enzymes (e.g. Martinez and Azam, 1993; Hoppe, 2003; Mather et al., 2008; Arnosti, 2011). As the added substrates are only proxies of the naturally occurring fractions hydrolysable by the respective enzyme, these measurements have been used as a metric of the potential utilisation of the reactive, enzyme hydrolysable, DON and DOP fractions.

Within this study we first present *in situ* observations of physical properties, inorganic and organic nutrients, phytoplankton pigment concentrations, isotopic composition of particulate organic nitrogen and turnover estimates of enzyme-hydrolysable fractions of DON and DOP derived from enzyme activity measurements. We then combine these observations with satellite-retrieved observations of *Trichodesmium*-like bloom occurrence and of chlorophyll variability. Finally, we put the collected data into the context of the prevailing 3D circulation with a model-based advection time estimate. Our aim is to gather information on the biological and physical factors affecting the distribution of organic nutrients along 24.5°N and gain insight on the potential role of allochthonous supply of reactive DON and DOP fractions in support of new production in our region of study.

2. Material and methods

2.1. Fieldwork and sampling

Along the nominal latitude of 24.5°N, 131 CTD stations were sampled in the North Atlantic subtropical gyre in April–May 2004 during cruise D279 onboard RRS Discovery. Water column samples were collected for the analysis of inorganic and organic nutrients, phytoplankton pigments. Surface samples were collected for particulate organic carbon (POC) and nitrogen (PON) and for the isotopic composition of PON analysis. Additionally, at 9 stations surface water was collected into wide-neck 25 L polyethylene carboys (Nalgene). Subsamples were taken to measure inorganic and organic nutrients, phytoplankton pigments and δ^{15}N-PON, and carry out short (2 h) enzyme assays to determine semilabile DON and DOP potential hydrolysis rates at the time of sampling.

2.2. Inorganic and organic nutrients

Inorganic nutrient (nitrate+nitrite and orthophosphate, hereafter nitrate and phosphate, respectively) concentrations were measured immediately on board using a Skalar San Plus autoanalyser (Skalar Analytical B.V., Breda, Netherlands) according to standard colorimetric techniques (Kirkwood et al., 1996). The analytical precision was 1.1% and 0.9% with detection limits of 0.1 mmol m^{-3} and 0.01 mmol m^{-3} for nitrate and phosphate, respectively. Samples for total nitrogen (TN) and total phosphorus (TP) analysis were drawn directly from Niskin bottles into 60 mL sterile high-density polystyrene bottles, frozen, and returned to the National Oceanography Centre Southampton for subsequent analysis on shore. Samples were not filtered as particulate matter is considered ≤10% of the total N and P pool, and the risk of contamination or cell breakage during filtration is very high (Abell et al., 2000). TN concentrations were measured by high temperature catalytic oxidation (HTCO) with a Shimadzu 5000A DOC analyser in line with an Antek 705E chemiluminescent nitrogen detector (Antek Instruments, Houston, TX, USA) (Alvarez-Salgado and Miller, 1998). The coefficient of variation (CV) of replicate measurements was typically 2%. The accuracy, determined by the use of consensus reference materials (CRM, Dr. Hansell Laboratory, Miami) was within 5% of the CRM concentrations. TP samples were photooxidised according to the method used by Sanders and Jickells (2000) and subsequently analysed for inorganic P according to standard colorimetric techniques. TON and TOP concentrations were calculated by subtracting the respective inorganic nutrient from total nutrient concentration. As in oligotrophic regions particulate matter is ≤10% of total organic matter (Abell et al., 2000; Lomas et al., 2010), here on we refer to TON and TOP as DON and DOP, respectively. The DON and DOP oxidation efficiencies of our samples were greater than 90%. The standard deviation of DON and DOP measurements was calculated by assuming Gaussian error propagation. Coefficient of variation (CV) of DON and DOP measurements equalled to ~5% and ~10%, respectively.

2.3. Photosynthetic pigments

Approximately 5 L of seawater were filtered onto GF/F filters for the analysis of photosynthetic pigments. Following Barlow et al. (2004), pigments were separated and analysed by HPLC (ThermoFinigan HPLC, Thermo Fisher Scientific Inc. USA). The limits of detection were 0.001 mg m^{-3}. This method allows us to separate also mono-vinyl-chlorophyll-*a* and divinyl-chlorophyll-*a* (Div-chl-*a*), zeaxanthin and lutein. Major phytoplankton groups, microplankton (diatoms+dinoflagellates), nanoplankton (golden-brown flagellates+cryptophytes) and picoplankton (cyanobacteria+procholorphytes+green flagellates) were quantified based on measurements of selected biomarker pigments following Barlow et al. (1997). Total chlorophyll-*a* (T-chl-a) was estimated as the sum of chlorophyll-*a* allomers mono-vinyl-chlorophyll-*a* and divinyl-chlorophyll-*a*.

2.4. δ^{15}N of PON

Samples (8 L) were filtered onto precombusted (550 °C for 4 h) GF/F 47 mm filters (Whatman, Ltd. UK). Filters were immediately