Biogeosciences Discuss., 7, 4001–4044, 2010
www.biogeosciences-discuss.net/7/4001/2010/
doi:10.5194/bgd-7-4001-2010

Biogeosciences
Discussions

Organic nutrients as sources of N and P to the upper layers of the North Atlantic subtropical gyre along 24.5° N

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Received: 24 April 2010 – Accepted: 20 May 2010 – Published: 31 May 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

There is a longstanding discussion on how the macronutrient requirement of the export production in the North Atlantic subtropical gyre is sustained. In this study we asses the role of dissolved organic nitrogen (DON) and phosphorous (DOP) as sources of new nutrients into the North Atlantic subtropical gyre at 24.5° N. We define, based on measurements of DON, DOP, phytoplankton community structure, stable nitrogen isotopic signals, surface mixed layer depth and ocean color as viewed from space, four regions characterized by different nutrient supply regimes. Within these regions, two distinct loci of N_2 fixation occur associated with different plankton assemblages and separated by a region in which N_2 fixation occurs at levels insufficient to leave its distinctive isotopic fingerprint on the isotopic composition of PON. Here, the phosphorus supply pathways to the mixed plankton assemblage appear to be different. In the wester oligotrophic gyre (70–46° W), the lateral advection of DOP supplies the missing P that, together with, shallow mixed layer, almost permanent stratification and high water temperatures, stimulate diazotrophic growth, which augment TON local accumulation. In the eastern oligotophic gyre (46–30° W), DOP cannot support the P demand as it is exhausted on its way from productive areas. This is inferred from DOP turnover rates, estimated form enzymatic clevage rates, which are shorter (11 ± 8 months) than transit timescales, estimated from a 3-D circulation model (>4 yr). A stronger seasonal cycle in chlorophyll and mixed layer depth, favour some nutrient injections from below. Here additional N sources come from the advected DON which has a turnover-time of 6.7 ± 3 yr, instead fast remineralization and little DOP export are needed to maintain the P requirements. We conclude from these observations that organic nutrient utilisation patterns drive diverse phytoplankton assemblages and oceanic nitrogen fixation gradients.

1 Introduction

Processes governing growth of algae at the surface and subsequent remineralization of organic matter at depth within the oligotrophic, subtropical gyres are still not comprehensively understood. This might limit our capability of forecasting the global carbon cycle as there is observational evidence that oligotrophic areas are expanding as a consequence of global warming (Polovina et al., 2008). The problem goes back to an apparent inconsistency between local measurements of turbulent nutrient supply (Lewis, 1986) and large-scale geochemical estimates of oxygen consumption at depth (Jenkins and Goldman, 1985) in the eastern subtropical North Atlantic. Although the original mismatch of more than an order of magnitude was narrowed down to a factor of 4 by taking into account physical processes feigning oxygen consumption at depth and additional nutrient transport mechanisms as e.g. eddy pumping (McGillicuddy and Robinson, 1997) and double-diffusion (Dietze et al., 2004) this mismatch is still substantial (corresponding to an export production of 35 g C m^{-2} yr^{-1}). Recent research in the oligotrophic gyres has shown that processes like export of organic matter high in C (as e.g. dissolved organic matter) (Kähler and Koeve, 2001) or nitrogen sources other than nitrate, such as N_2 fixation (Gruber and Sarmiento, 1997), atmospheric deposition (Hansell et al., 2007), have the potential to reconcile the above mentioned discrepancy. However, the magnitude and spatial distribution of these alternative N sources remain controversial (Hansell et al., 2004, 2007; Landolfi et al., 2008) and the severe phosphorus depletion in the North Atlantic subtropical gyre (Wu et al., 2000) combined with the lack of external P sources pose the question as to how the P requirements of primary producers and N_2 fixers can be sustained.

An additional source of nutrients to phytoplankton in surface oligotrophic waters may be the pool of 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). The accumulation of DON and DOP is controlled both by biological and physical processes (Bronk, 2002; Karl and Björkman, 2002) the combination of which is not well understood in the North Atlantic gyre. The preconditions for these nutrients to act as a source of new N and P within the subtropical gyre is that they need to be (1) provided externally into the system (allochtonus) and as such, (2) they need sufficiently long remineralization time scales to be advected from nutrient rich areas into the gyre so to become available to the plankton community within the gyre. Allochtonus dissolved organic nutrients may be provided by means of N_2 fixation (Capone et al., 1994; Glibert and Bronk, 1994), which provides DON, and atmospheric deposition, which is a significant source of DON (Cornell et al., 1995) and only of minor importance for DOP (Chen et al., 2007). Instead, physical processes must be invoked to provide both DON and DOP. Field and modelling studies suggest that the wind-driven Ekman and gyre circulation (Williams and Follows, 1998) may quantitatively be important for supplying DON and DOP in the North Atlantic subtropical gyre (NASG) (Charria, 2008; Mahaffey et al., 2004; Roussenov et al., 2006) and North Pacific (Abell et al., 2000) gyre. In these studies, a priori assumptions regarding DON and DOP remineralization timescales and bio-availability have been made.

The bulk of the organic nutrient pool remains mostly uncharacterized at the molecular level (McCarthy et al., 1997; Kolowith et al., 2001). Nevertheless, recent evidence has shown that even refractory components of this pool may act as nutrients sources (Bronk et al., 2007). Semilabile forms of DON and DOP become available to the plankton community through the release of proteolytic enzymes. N bound in DON may be released by aminopeptidases (LAP). LAP are a class of proteolytic enzymes that hydrolyze peptides and proteins liberating smaller peptides and amino acids (Martinez and Azam, 1993; Hoppe, 2003) with a preference for the terminal N of non-polar amino acids (Langheinrich, 1995); LAP may be synthesised by bacteria and phytoplankton (Martinez and Azam, 1993; Hoppe, 2003); The acquisition of P from DOP can be catalyzed by cell surface enzymes such as Alkaline phosphatases (APA) which catalyses the hydrolysis of phospho-monoesters (Karl and Yanagi, 1997) to produce phosphate (PO_4^{3-}). APA has been found to be associated to phytoplankton, bacteria but also dissolved in water (Hoppe, 2003 and references therein). It can be expressed in response to P deficiency and can be repressed by high concentrations of inorganic P (Hoppe, 2003 and references therein). The measurement of the activity of these extracellular enzymes has been used to assess the turnover and bioavailability of the organic nutrient pools (Mather et al., 2008).

Within this study we want to asses (1) the mechanisms that control organic nutrients distribution across 24.5° N (2) investigate the role of the allochthonous supply of dissolved organic nutrients as potential drivers of new production (3) asses the longitudinal variability of the relative contribution of the different nutrient sources to phytoplankton. Based on observations of the surface mixed layer depth, isotopic composition of particulate organic nitrogen combined with estimates of phytoplankton community structure established from HPLC data and dissolved organic nutrient distribution we assess the surface nutrient supply mechanisms identifying biogeochemical signatures of diazotrophy, atmospheric deposition and inorganic and organic nutrient utilization patterns. From the in situ activities of APA and LAP we infer estimates of DON and DOP turnover rates. We then asses the role of lateral transfer of organic nutrients by combining the dissolved organic nutrients turnover timescales with transit timescales derived from a 3-D circulation model. We end with an assessment of the potential of DON and DOP to explain the hitherto enigmatic carbon and nitrogen balances in the subtropical North Atlantic.

2 Material and methods

2.1 Fieldwork and sampling

The North Atlantic subtropical gyre was surveyed during cruise D279 along the nominal latitude of 24.5° N in April–May 2004 (Fig. 1). 131 CTD stations were occupied. At each station up to 24 water samples were collected for the analysis of inorganic nutrients. Along the transect, 280 samples were collected for the analysis of organic nutrients. Samples for the assessment of phytoplankton pigments were collected at four depths from the top 200 meters at approximately every 3rd station. Samples for the determination of particulate organic carbon (POC) and nitrogen (PON) and for the isotopic composition of PON were collected from Niskin bottles fired at the surface (10–25 m) at 30 stations. At a further 9 stations, water was collected directly from the surface (0 m) into large neck 25 L high density plastic carboys to carry out experiments for the determination of DOM hydrolysis through enzyme assays and to measure inorganic and organic nutrients, phytoplankton pigments and δ^{15}N-PON.

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 negligible (<10% of the total N and P pool) whereas the risk of contamination or cell breakage during filtration is very high (Abell et al., 2000). TN concentrations were measured following high temperature catalytic oxidation. (HTCO) performed with a Shimadzu 5000A DOC analyser connected in series with an Antek 705E chemiluminescent nitrogen specific 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 using a Skalar San Plus autoanalyser (Kirkwood et al., 1996). TON and

TOP concentrations were calculated by subtracting the inorganic nutrient from the total nutrient concentrations. The standard deviation of TON and TOP measurements was calculated by assuming Gaussian error propagation. In surface waters the mean standard deviation for TON and TOP measurements equalled 2.3% and 7%, respectively. TONxs, a measure of the TON and TOP imbalance relative to the Redfield ratio (16:1) was calculated as TONxs=TON−16×TOP (Landolfi et al., 2008).

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}. Note that this method allows 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 flaggelates+cryptophytes) and picoplankton (cyanobacteria+procholorphytes+green flaggelates) were quantified based on measurements of selected biomarker pigments following (Barlow et al., 1997). As chlorophyllide-*a* was not resolved, in this study, total-chlorophyll-*a* (T-chl-*a*) includes mono-vinyl-chlorophyll-*a* and divinyl-chlorophyll-*a* (Div-chl-*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 frozen thereafter. POC, PON and stable nitrogen isotopes analysis was performed on a continuous flow isotope ratio mass spectrometer (IRMS) using a EuroVector 3028 – Ht elemental analyser (EA, EuroVector, Milan, Italy) connected to a Iso-Prime mass spectrometer (GV Instruments, Manchester, UK). Results are reported using the standard notation where the sample ^{15}N/^{14}N ratio is standardized to atmospheric N_2 (Mariotti et al., 1981) as:

$$\delta^{15}\mathrm{N} = \left[\frac{\left(^{15}\mathrm{N}/^{14}\mathrm{N}\right)_{\mathrm{sample}}}{\left(^{15}\mathrm{N}/^{14}\mathrm{N}\right)_{\mathrm{N_2}}} - 1 \right] \times 1000.$$

2.5 Enzyme experiments

At each location, 3 replicate incubations with the fluorigenic substrates, 4-methylumbelliferyl phosphate (4-MUF-P; Sigma) and L-leucine-7-amido-4-methylcoumarin hydrochloride (L-AMC; Sigma) were carried out to assess the activities of APA and LAP respectively as described in (Hoppe, 1983). The substrates were added to a final concentration of $100\,\mu\mathrm{mol\,L^{-1}}$ (Martinez and Azam, 1993). The incubation occurred in the dark at in situ temperature for ∼2 h. APA and LAP activities were determined by measuring the increase in fluorescence over time. Conversion of fluorescence values to nmoles of substrate released per volume of seawater and time ($\mathrm{L^{-1}\,h^{-1}}$) was based on a calibration against 4-MUF and AMC standard solutions. As APA and LAP assays were performed with saturating levels of substrate ($100\,\mu\mathrm{mol\,L^{-1}}$) the reported activities represent potential maximum cleavage rates. This potential activity can be approximated to the maximum rate of substrate turnover (V_{max}) and is related to the total enzyme present in the sample (E_0) and the hydrolysis rate constant (k) though the equation: $V_{\mathrm{sat}} = kE_0 \approx V_{\mathrm{max}}$ (Christian and Karl, 1995). Unless specifically stated here we report the potential activities, V_{max}, in accordance with the bulk of the literature on enzyme activities (Hoppe, 2003). The activites ($V_{\mathrm{in\ situ}}$) based on the ambient substrate concentrations may be derived from the Michaelis-Menten equation:

$$V_{\mathrm{in\ situ}} = \frac{V_{\mathrm{max}} \times S}{K_m + S} \qquad (1)$$

Where ($V_{\text{in situ}}$) is the in situ. uptake rate (µM h^{-1}) of the substrate S, $V_{\max}$ is the maximum velocity of uptake and K_m is the half saturation constant. Using the ambient DON and DOP concentrations as substrate concentrations and assuming that these pools are accessible to the enzymes, Eq. 1 has been used to estimate the in situ enzyme activities, $V_{\text{in situ}}$, which are reported in Sect. 3.7 and also used for computing turnover times as:

$$t = \frac{\text{DOM}}{V_{\text{in situ}}} \tag{2}$$

Where DOM is the ambient DON and DOP pool concentrations and $V_{\text{in situ}}$ is the activity based on the natural concentration of the substrate (i.e. not at saturating level) derived from Eq. (1). As we performed single substrate additions, we estimated the half saturation constants, K_m, from the relationship observed between K_{DOP} and K_{DON}, and corresponding maximum activities measured at saturating substrate levels (r^2=0.86, n=4 and r^2=0.97, n=5, respectively; data not shown) during Michaelis-Menten additions experiments performed during a cruise, AMT16, in spring in the North Atlantic subtropical gyre. The turnover rates derived from Eq. (2) are comparable with the ones derived from equation $T=K_m/V_{\max}$ (Li, 1983) as reported by (Mather et al., 2008).

Note on normalization: the interpretation of enzyme experiment data ($V_{\max}$) is often guided by normalization to some surrogate of biomass. Enzyme activities like APA, AKA are affected by the biomass of the enzyme producers (both autrophic and heterotrophic) and hence biomass normalised data (Specific activities) provide insight into the strength of the related N, P stress (limitation). Normalising to chlorophyll might well result in overestimating the autotrophic component. A more reasonable approach is to normalise the activities relative to total C biomass. However this approach has its problems too as it assumes that all the cells express the same amount of enzyme and this is not the case given the species specific variability expressed in the Sargasso Sea (Lomas et al., 2004). Specific activities give an indication of the physiological status of the cell. From a biogeochemical perspective, however, it is important to address the rate of DOM catalysis. Here we aim to examine the extent to which DON and DOP reservoirs are utilized by the biological community and do not seek to address cell specific N and P stress. Given these difficulties and to allow for comparisons with published data, we present both specific, normalised to POC, and bulk enzyme activities.

2.6 Artifical age tracer: connection time scales diagnosed from a circulation model

The concept of allochthonous supply of dissolved organic nutrients implies that water at a given location hosted, in the past, net production of dissolved organic matter (DOM) elsewhere. Allochthonous supply of dissolved organic matter can only be of relevance if the transport from the production site does not take much longer than the decay time scale of DOM. Otherwise, most of the DOM would have been decomposed on the way already. Hence, to assess the relevance of allochthonous supply of dissolved organic nutrients a measure of the connection time scale to more fertile regions, where net production of dissolved organic matter is likely to occur, is needed. We deduce such a timescale from a state-of-the-art global ocean circulation model. The assumptions are: (1) Advective and diffusive processes, as modeled, are realistic. (2) Significant net production of dissolved organic nutrients occurs only during times (and in regions) where chlorophyll concentrations, as viewed from space, exceed 0.1 mg chl-*a* m^{-3}. More specifically we embedded (online) an artificial clock, counting the time elapsed since surface water parcels (in the uppermost grid-box) hosted chlorophyll concentrations exceeding 0.1 mg chl-*a* m^{-3} into a global configuration of the Modular Ocean Model Version 4p0d (MOM4) from the Geophysical Fluid Dynamics Laboratory (GFDL) in Princeton, New Jersey. The clock is reset locally in the uppermost grid-box whenever monthly climatological chlorophyll as derived from SeaWiFS level 3 mapped 8-day composites (obtained from http://seadas.gsfc.nasa.gov/ftp.html) exceed the threshold. The circulation model was driven by climatological forcing following the Coordinated Ocean Reference Experiments (CORE) (based on Large and Yeager, 2004). Ocean and ice model configurations correspond to those used by GFDL in their coupled climate model CM2.1 (Gnanadesikan et al., 2006; Griffies and Rosati, 2005). The longitudinal resolution is 1 deg and the latitudinal resolution varies between 1 deg in the midlatitudes and 1/3 deg in the Tropics. There are 50 vertical levels with 22 uniformly spaced over the top 220 m. The model was initialized with annual mean temperature and salinity from the World Ocean Atlas 2001 (Boyer and Garcia, 2002; Stephens and Garcia, 2002). A 20 yr spinup preceded the 10 yr integration with the embedded artificial clock.

3 Results and discussion

3.1 Hydrographic setting, inorganic and organic nutrients distributions

Across 24.5° N temperatures gradually decreased and the mixed layer depth (MLD) deepened moving eastwards (Fig. 2). In the centre of the gyre nitrate and phosphate in the upper 100 m were close to the limit of analytical detection (Fig. 3a,b). Both nitrate and phosphate concentrations increased between $\sigma_{\theta g}$ 26 kg m^{-3} and $\sigma_{g\theta}$=26.5 kg m^{-3} where nutrient isolines followed the slopes of isopycnal surfaces.

Organic nutrients (Fig. 4a,b) constituted the major component of the total N (93 ± 16%) and P (81 ± 23%) pools of the surface layer. The upper 100 m mean TON concentration was of 4.3 ± 1.1 mmol m^{-3} (n=57) consistent with the average concentrations measured further north at the seasonally stratified BATS station (4.2 ± 0.5 mmol m^{-3}). However, our TON measurements exhibited a larger range from 3.1 to 7.2 mmol m^{-3} as compared to the seasonal variability observed at the BATS site (3.4–5.9 mmol m^{-3}) where air-sea exchange of freshwater and heat drive a seasonal cycle of surface mixed layer deepening with an amplitude as high as 300 m. Within the mixed layer, TON concentrations are higher in the west (4.7 ± 1.3 mmol m^{-3}, n=27) relative to the eastern part of the gyre (4.0 ± 0.2 mmol m^{-3}, n=7) (T-Test, alpha=0.05, P=0.056). Below 50 m, only small vertical gradients occurred (Fig. 4a). The mean TON concentrations below 100 m were 3.0 ± 1.2 mmol m^{-3} (n=47). In the central gyre, TOP concentrations were generally low in the surface layer (0.06 ± 0.04 mmol m^{-3}, n=13) and increased below 50 m (0.1 ± 0.06 mmol m^{-3}, n=15) (Fig. 4b) consistent with low TOP surface measurements of 0.074 ± 0.042 mmol m^{-3} previously reported for the Sargasso Sea (Wu et al., 2000). These concentrations are lower then TOP measurements reported for other oceanic gyres (e.g. N. Pacific gyre TOP>0.1 µM, Abell et al., 2000). High surface TOP concentrations (0.22 ± 0.06 mmol m^{-3}, n=2) observed close to NW Africa are consisted with previous measurements in the same region (∼ 0.2 mmol m^{-3} (Vidal et al., 1999); these are also associated with relatively high TON concentrations 4.4 ± 0.47 mmol m^{-3}, n=2 resulting from the vicinity to the upwelling region.

3.2 Phytoplankton community distribution

T-chl-*a* concentrations (Fig. 5) show a minimum between 70° W to 30° W coinciding with Seawifs chlorophyll images (Fig. 6). In this area the deepening of the deep chlorophyll maximum occurred (∼120 m, from calibrated CTD fluorescence, data not shown) was observed. The phytoplankton community was mainly dominated by picoplankton generally representing >50% of the total phytoplankton in the upper 50 m and up to ∼80% (Fig. 7a). The nanoplankton community complemented the picoplankton distribution being ∼30% at the surface and up to ∼50% at depth (Fig. 7b). Microplankton was only a minor component (<15%) of the autotrophic community, with its major contribution found between 50° W and 70° W (10%) (Fig. 7c). In the eastern portion of the gyre procholorophytes became more important relative to the other picoplankton groups (Fig. 8).

3.3 Surface PON isotopic variability

The nitrogen isotopic composition of suspended particulate material has been used to provide information on the possible nitrogen supply mechanisms to the surface ocean. To a first approximation the δ^{15}N of upper ocean organic matter reflects the dominant N source. These include (1) diazotroph-fixed atmospheric N_2 of −2‰ to 0‰ (Minagawa and Wada, 1986), (2) deep NO_3^- of +4.7 to +6‰ (Knapp et al., 2005), (3) atmospheric deposition of nitrate of −2.1 to −5.9‰ (Hastings et al., 2003), and (4) marine DON of +4.1‰ (Knapp et al., 2005). However, the interpretation of the isotopic signal is complicated as it reflects also any isotopic fractionation that has occurred during its assimilation (Wu et al., 1997). Fractionation can occur under nutrient replete conditions as phytoplankton preferentially incorporate the lighter isotope, ^{14}N, causing an increase in the δ^{15}N of the residual nutrient (nitrate) pool and ^{15}N depleted phytoplankton biomass (Wu et al., 1997). In oligotrophic environments, where surface inorganic nutrients are exhausted, this isotopic fractionation does not occur. Secondary producers become enriched in ^{15}N (~3‰) relative to their diet, excrete ^{15}N depleted ammonia, and produce enriched ^{15}N faecal pellets (Checkley and Miller, 1989). A depleted isotopic signal may thus reflect the occurrence of regenerated production inversely, an enriched isotopic signal may indicate the inclusion of higher trophic levels within the sample. The potential inclusion of higher trophic levels in our samples has been checked by evaluating the relationship between δ^{15}N of PON and PON/chl-*a* for subsurface and surface samples, as a positive relationship would be expected if the secondary producers were included in our samples (Waser et al., 2000). Given the lack of relationships found (r^2=0.03, n=24, p<0.05 and r^2= 0.4, n=8, p<0.05, respectively) we infer that the isotopic PON signal is predominantly of autotrophic origin (Mahaffey et al., 2004; Reynolds et al., 2007; Waser et al., 2000).

On the basis of the isotopic δPO^{15}N variability four domains were distinguished. Off the Bahaman coast up to ~70° W, elevated values of δPO^{15}N were observed (Fig. 9) indicating the presence of inorganic nutrients. An extensive region of light δPO^{15}N (average −0.30 ± 0.56‰, excluding the lowest δPO^{15}N of the data set: −4.47‰) was found between ~70° W–46° W. Here, processes such as N_2 fixation and/or atmospheric deposition of N and/or recycled production appeared to be the main N sources. An abrupt change of the isotopic PON signatures occured in the eastern oligotrophic region from 46–30° W where the average δPO^{15}N was 2.71 ± 2.14‰. Here, the lack of measurable nitrate possibly implies the utilization of other ^{15}N enriched N sources such as DON (Knapp et al., 2005) and only a minor contribution of N source from N_2 fixation and/or atmospheric deposition. East of 30° W the isotopic variability (1.08 ± 1.77‰) (large standard deviations) reflected variable conditions resulting from the outcrop of isopycnals and possible lateral advection of DOM from the east following the gyre scale circulation.

3.3.1 Quantification of the relative importance of N_2 fixation

The maximum potential relative contribution of N_2 fixation is now estimated assuming that the depleted signal is mainly of diazotrophic origin. Following previous studies (Capone et al., 2005; Mahaffey et al., 2003; Mino et al., 2002; Montoya et al., 2002), the contrast between the isotopic signal of deep water nitrate (2.65–5‰) and N_2 fixers biomass (–2‰) was used to provide quantitative information on the relative importance of these two different N sources following a two end member isotope mixing model (Montoya et al., 2002). To be conservative, the end members chosen for the analysis were –2‰, to match the lowest δ^{15}N diazotroph biomass signature measured in the North Atlantic (Montoya et al., 2002), and the nitrate values of 2.65 and 4‰ to match the range observed at the base of the euphotic zone in the North Atlantic (Knapp et al., 2005). Here we assume that the isotopic composition of PON is in equilibrium with N sources and that isotopic fractionation in nutrient-depleted surface waters is negligible.

$$\mathrm{N_{fix}}(\%) = \frac{\delta^{15}\mathrm{N_{PON}} - \delta^{15}\mathrm{N_{NO_3^-}}}{\delta^{15}\mathrm{N_{fix}} - \delta^{15}\mathrm{N_{NO_3^-}}} \qquad (3)$$

From this model, using the two nitrate end members, we estimated that N_2 fixation could supply a minimum of 60 to a maximum of 69% of the N in the region 75–46° W. In the narrow region from 46–30° W, 8 to 30% of the fixed N could have been provided by N_2 fixation. East of 30° W N_2 fixation is estimated to supply from a minimum of 34 to a maximum of 49% of the N to phytoplankton. If the role of atmospheric deposition is proved to be trivial then a robust N_2 fixation signal can be inferred on the western part of the subtropical gyre. A gap of the N_2 fixation signal is observed in the

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eastern subtropical gyre. Moving towards the eastern flank N_2 fixation might still play a significant role but other N sources, such as nitrate and DON, appear important as well.

3.4 Surface enzyme experiments

Alkaline phosphatase (APA) maximum activities (V_{max}, Fig. 10a) ranged from 6.5 ± 0.2 nmol 4-MUF L^{-1} h^{-1} in the centre of the gyre to very high values of 62.8 ± 0.4 nmol 4-MUF L^{-1} h^{-1} at approximately 30° W, with an average of 24 ± 19 nmol 4-MUF L^{-1} h^{-1} (Fig. 10a). This variability is within the range of the total APA values reported for the Atlantic Ocean (4–50 nmol 4-MUF L^{-1} h^{-1}; Vidal et al., 2003) with the mean values being consistent with the ones reported in the eastern North Atlantic (∼30° W; 10–30 nmol 4-MUF L^{-1} h^{-1}; Vidal et al., 2003). The low activities reported in the gyre centre agree with previous measurements of APA at the BATS time series (1–10 nmol 4-MUF L^{-1} h^{-1}) and recent particulate APA measurements carried out in the western portion of the north Atlantic subtropical gyre, (20° N, 60–45° W), which reported average values of 4.1 nmol 4-MUF L^{-1} h^{-1} (Wisniewski-Jakuba et al., 2008). Specific Alkaline phosphatase activities (sAPA) ranged from 0.51 to 4.26 nmol 4-MUF L^{-1} h^{-1} mg C^{-1} (mean 1.84 ± 1.36 nmol 4-MUF L^{-1} h^{-1} mg C^{-1}) consistent with observations made at the same latitudes further east (Mather et al., 2008). The lowest values occurred in the centre of the gyre. The peak at ∼30° W remained visible also when APA was normalised to biomass. APA activity did not correlate with any specific phytoplankton group (not shown) indicating that the exploitation of organic P was spread among phytoplankton, as reported elsewhere (Hoppe, 2003). Contrary to expectations no statistically significant inverse correlation was observed between APA and TOP as reported in Mather et al. (2008).

Aminopeptidase maximum activities (V_{max}), LAP, (Fig. 9) were highest at the western end of the transect (32.9 nmol AMC L^{-1} h^{-1}), and decreased rapidly until ∼50° W (9.4 ± 0.2 nmol AMC L^{-1} h^{-1}). Values increased again towards the eastern side of the gyre where they reached 20.61 ± 2.9 nmol AMC L^{-1} h^{-1} (Fig. 8). These values are comparable to LAP rates expressed in natural populations of *Synechococuss* (27–98 nmol AMC L^{-1} h^{-1}) (Martinez and Azam, 1993). The pattern of specific aminopeptidase activity normalised to POC (sLAP) was similar to LAP. sLAP ranged from 0.65–2.24 nmol 4 AMC L^{-1} h^{-1} mg C^{-1} with a mean of 1.62 ± 0.5 nmol AMC L^{-1} h^{-1} mg C^{-1}. LAP activities were weakly anti-correlated with TON concentrations (r^2= 0.51, n=8, p<0.2). The increase in LAP activity towards the eastern margin of the subtropical gyre may be associated with the increase in divinyl-chl-*a*, a biomarker for Prochloropytes (r^2=0.40, n=8, p<0.5). This is consistent with their ability to utilise organic molecules which has been demonstrated in both physiological (Zubkov and Sleigh, 2005) and genetic (Moore et al., 2002) studies.

3.5 What controls DON and DOP distribution?

The distribution of organic nutrients is determined by the combined effects of advection, diffusion (physical control) and production and removal processes. As these effects might well oppose one another locally it is not straightforward to draw conclusions regarding where (and via which process) organic nutrients are produced or decomposed. Coupled biogeochemical ocean circulation models (as e.g. used by Torres-Valdés et al., 2009) are tools well suited for that purpose but underlying assumptions are not transparent to all readers. Here, for the sake of simplicity, in order to disentangle the single contribution of these processes, we use simple thought experiments in combination with an artificial tracer that counts the time elapsed since a water parcel's chl-*a* exceeded 0.1 mg m^{-3} (released in a circulation model, explained in Sect. 2.6). We start with an idealized scenario and then add single processes and see how our thought experiment distribution approaches reality. We refer to "new" or "old" waters to indicate the time elapsed since a water parcel's chl-*a* exceeded 0.1 mg m^{-3} (Fig. 11). We assume that DON and DOP production occurs in waters exceeding 0.1 mg m^{-3} chl-*a*.

3.5.1 Physical control

In this idealized scenario we assume that only physical processes control organic nutrients' distribution. Our assumptions are that (1) active/direct (coming from living biota) sources and (2) sinks of DON and DOP within the gyre are negligible. Please note that the indirect DON and DOP source coming from the remineralization of POM occurring along the circulation pattern remains active. Following the 3-D gyre circulation, the DOM derived from POM below the euphotic layer is entrained back into the surface layer following the so-called nutrient spiral (Jenkins and Doney, 2003). Under these conditions we expect older waters, in the region from 49–34° W (Fig. 11), to be associated with higher DOM concentrations, a homogenous surface layer with no vertical gradients and, as an effect of the Ekman pumping, a deepening of the dissolved organic matter isolines towards the gyre centre. This scenario is consistent with the small TON ($3.0 \pm 1.2\,\mathrm{mmol\,m^{-3}}$ (n=47) and TOP ($0.1 \pm 0.06\,\mathrm{mmol\,m^{-3}}$, n=15) vertical gradients below 100 m and with the increasing depth of the isolines towards the gyre centre. But clearly physical transport alone cannot explain the zonal and vertical gradients of these species observed in the upper 100 m.

3.5.2 Physical transport and Biological consumption

If we allow organic nutrients to be taken up by biology in oligotrophic waters while keeping direct production processes negligible, then we expect younger waters to be associated with higher TON and TOP concentrations and high biological consumption to be associated with low TON and TOP concentrations as reported in Mather et al. (2008). Consistently we find high TON and TOP concentrations close to the African continent (Fig. 4) (4.4 ± 0.4 and $0.22 \pm 0.06\,\mathrm{mmol\,m^{-3}}$, respectively) indicative of young-fresh material produced within the upwelling zones off Africa. Further, in the upper 100 m we find that the zonal TOP distribution follows the gradient of the artifical age tracer with lowest TOP concentrations occurring within water masses that have left productive regions for more then 3 to 5 yr earlier. This is consistent with the concept that

TOP is produced in more productive areas (where chl-*a* exceeds 0.1 mg m^{-3}) and that it is transported into the gyre while it is depleted by biological consumption. However, no clear pattern emerges from the enzyme activity variability and organic nutrients distribution. For example the inverse relationship between TOP and APA reported by Mather et al. (2008) was not observed in this study. Instead, the lowest APA activities (Fig. 9) measured in the central part of the gyre were associated with the oldest waters as diagnosed by our artificial age tracer and low TOP concentrations (0.06 ± 0.04 mmol m^{-3}, n=13). A reason for this discrepancy might be the station locations sampled during the survey carried out by Mather et al. (2008). They are concentrated in regions predominantly characterized by waters which had left productive regions in less then one year earlier. In fact, the peak of both APA and sAPA (4.26 nmol 4-MUF L^{-1} h^{-1}) measured at ∼32° W coincides with a region of low DOP concentration (0.07 mmol m^{-3}) similar to the what was measured further North during AMT16 and reported by Mather et al. (2008). This location coincides with a boundary region where old and new waters meet. Hence, inputs of fresh DOP possibly stimulated high APA and fast DOP cycling. These results imply the existence of complicated relationships between enzyme activity, organic nutrients availability and distribution and water mass age, which are not well understood.

Unlike TOP, TON gradients don't follow the trend of transit time estimates (compare Figs. 4a and 11). However a weak anti-correlation of LAP activities with TON concentrations (r^2=0.51, p<0.2, n=8) is observed (not shown). The increase in LAP activity towards the eastern margin of the subtropical gyre may be associated with the increase in divinyl-chl-*a*, a biomarker for Prochloropytes (r^2=0.51, n=8, p<0.2), consistent with their ability to utilise organic molecules (Zubkov and Sleigh, 2005; Moore et al., 2002). The large accumulation of TON in ∼2 yr "old waters" corresponding with the lowest LAP activity indicates either the presence of refractory material or that additional N sources were present. Hence, the zonal TON variability in the upper mixed layer cannot be explained simply by a combination of the gyre scale circulation and organic nutrient consumption, other local processes appear to be occurring.

3.5.3 Physical transport, biological consumption and local sources

Let us now allow DON and DOP production to occur. In productive regions of the ocean biotic processes such as cell growth, death, exudation, viral lysis and grazing are the main sources of DON and DOP (Bronk, 2002; Karl and Björkman, 2002). Within oligotrophic regions however, N_2 fixation and atmospheric deposition must be invoked to locally supply, and/or enhance the production of TON. Sources of TOP are not known. Atmospheric nutrient inputs occur at very high N:P ratios (Baker et al., 2003), therefore this allochthonous nutrient source appears to be significant solely for nitrogen supply and not for P. The accumulation of TON in the upper 50 m of the region 70–46° W where a depleted isotopic PON signal is observed, together with a large TONxs signal (Landolfi et al., 2008), give a strong indication that atmospheric deposition and/or N_2 fixation are modulating TON distribution locally.

3.6 Is the lateral advection efficient in supplying organic N and P into the gyre?

TON and TOP remineralization timescales: TON and TOP turnover rates have been calculated using equation 2 after having estimated the Michaelis-Menten constant K_m and $V_{\text{in situ}}$ as described in Sect. 2.5. As a certain degree of uncertainty is contained within the K_m values, which are only estimates and not actually measured, we decided to investigate the sensitivity of our results to changes in the K_m values. To do so we calculated the $V_{\text{in situ}}$ using the minimum, the maximum and the average of the estimated K_m 's. This allowed us to obtain the largest range of possible $V_{\text{in situ}}$. From the so calculated $V_{\text{in situ}}$ we calculated the turnover rates which, thus represent the largest range of possible turnovers given the range of estimated K_m's. The estimated LAP K_m values ranged from 2175 to 314 (average 1103 ± 574) µM. Given the large sensitivity of $V_{\text{in situ}}$ to K_m values, surface TON turnover rates range from a minimum of 2.2 ± 0.9 yr up to 15.0 ± 6.8 yr with an average of 7.6 ± 3.4 yr. These turnover times appear short as compared to the TON turnover times estimated in the N. Pacific gyre (18 yr) from vertical TON gradients (Abell et al., 2000). Similary APA K_m estimates, which ranged from 31 to 297 µM with an average of 114 ± 91 µM, yielded a an average surface TOP turnover rate of 10.9 ± 7.7 months with a minimum of 3.0 ± 2.1 to a maximum of 28.4 ± 20.2 months. These turnover times are grater then, but of the same order of magnitude, of the average ones reported for the NASG (5.5 ± 2.3 months) by Mather et al. (2008); but are shorter than the ones estimated in the N. Pacific gyre (Abell et al., 2000) which, are in the order of 4 yr, reflecting the extreme phosphorous deficiency of the area (Wu et al., 2000).

To assess the relevance of allochtonus supply of dissolved organic nutrients within the gyre, we now compare the timescales of advection diagnosed by our artificial age tracer with the estimated time scales of DON and DOP decay. From this tracer we can infer a zonal gradient in DOM advection timescales ranging from 1 to >4 yr (Figs. 11, 12). Given that the remineralization timescales of DON are longer (6.7 ± 3 yr) then the timescale of water exchange between the DON productions sites and the gyre interior, the lateral transfer of dissolved organic nitrogen appears to be an active mechanism for providing N into the gyre. Instead, the estimated TOP residence time of the order of 11 ± 8 months (longest potential residence time <4 yr), implies that the relevance of allochtonous DOP lateral transport is higher in the west as transit times become longer then 2 yr in the east. This is consistent with DOP being degraded on its way from the productive regions and implies that DOP is unlikely to be a significant P source as it becomes exhausted east of ∼49° W. This finding is in contrast with what has previously been observed in the N. Atlantic (Mahaffey et al., 2004) and N. Pacific gyres (Abell et al., 2000) and what has been diagnosed from modelling studies by Roussenov et al. (2006) and Torres-Valdés et al. (2009). In all these studies DOP has been found to contribute up to 70% of the modelled particulate phosphorus export. This discrepancy, relative to the work of Mahaffey et al. (2004), could result form their survey being concentrated on the eastern margin of the subtropical gyre where DOP concentrations are higher relative to the gyre interior (this study); Differences relative to the modelling studies of Roussenov et al. (2006) and Torres-Valdés et al. (2009), arise from TOP degradation rates used in their models. A sensitivity study has shown that modelled dissolved organic nitrogen distribution results appear very sensitive to parameter values of dissolved organic matter remineralization (Charria et al., 2008). In the N Pacific the finding of Abell et al. (2000) of a TOP resistant to rapid decay as compared to the this study can account for these contrasting results. The lack of "new" P sources into the eastern section of the oligotrophic gyre poses the question on how new production coming from N sources such as N_2 fixation, atmospheric deposition and allocthonus DON can be maintained?

3.7 Dissolved organic nutrients contribution to new production

We now estimate the upper limit of the contribution of organic nutrients to supporting export production assuming that the hydrolysis of DON and DOP only contribute to export production. To do so we use the range of the in situ hydrolysis rates ($V_{\text{in situ}}$) calculated from Eq. (1) using the ambient TON and TOP concentrations and the range of estimated K_m's. The so derived range of in situ LAP and APA rates suggest that DON and DOP hydrolysis could potentially supply from 0.03 to 0.19 mol N m^{-2} yr^{-1} (0.5 ± 0.01 mol N m^{-2} yr^{-1}) of N and from 0.01 to 0.06 mol P m^{-2} yr^{-1} of P (average 0.02 ± 0.02 mol P m^{-2} yr^{-1}) into the gyre. The historical geochemical estimates of export production in the Sargasso Sea require 0.5 mol N m^{-2} yr^{-1} of nitrogen and and 0.034 mol P m^{-2} yr^{-1} of phosphorus (Jenkins and Goldman, 1985). If we assume that this estimate is representative of export production also in our region, it would imply that DON could provide a minimum of 5% to a maximum of 37% (average 11%) of N and DOP a minimum of 18% to $\gg$100% (average 48%) of the P requirements. The importance of DON as a new N-source is limited compared to the role of DOP, due to the difficulty in providing P from mechanisms analogous to N_2 fixation and atmospheric deposition. However, from the turnover times analysis the input of "new" P from DOP advection appears to be negligible in the eastern portion of the subtropical gyre; Hence, for the maintenance of the above mentioned rates of export production both fast DOP remineralization and small DOP export are needed i.e. most of the P channelled from DOP into the living stock needs to be remineralised into the upper euphotic layer implicitly calling for P poor organic material export.

3.8 Longitudinal variability of the nutrients supply mechanisms

With the suite of information gathered in the previous sections we now construct a picture of the functioning of the NATS at 24.5° N. Inorganic nutrient rich surface waters and T-chl-*a* concentrations higher than 0.1 mg m^{-3} West of 70° W and East of 30° W mirror the influence of the gulf stream and the upwelling off Africa, respectively which bound the oligotrophic gyre to the west and east, respectively. Within the oligotrophic gyre, zonal gradients in the temperatures fields and the mixed layer depth (MLD) (Fig. 2) highlight a distinct difference between the West and East. Higher water temperatures (23.9 ± 0.8 °C) were measured west of 46° W, as compared to the temperatures measured on the eastern side of 46° W (20.8 ± 1.4 °C). The average depth of the mixed layer in the region from ~70° W to ~46° W was 26 ± 14 m. East of 46° W the MLD deepened (105 ± 30 m). The ML zonal gradient appears to be a stable feature as can be diagnosed from the MLD climatology (Fig. 13). This spatial variability appears to be driven by the amplitude of the seasonal cycle of the surface layer that is higher in the east than in the west, a feature clearly correlated with the annual cycle of surface chlorophyll concentrations as viewed from space (Fig. 6). The variability of the physical structures implies very different nutrient supply mechanisms that are reflected in all our biogeochemical observations.

The domains distinguished on the basis of the variability of the isotopic δPO^{15}N signal (Fig. 9) coincide with the separations based on the MLD (Fig. 13) and seasonal variability (Fig. 6). The region between ~70° W–46° W where shallow MLD and light δPO^{15}N are observed (0.29 ± 0.98‰; excluding the lowest δPO^{15}N of the data set: −4.47‰), indicates that N is being provided by N$_2$ fixation and/or atmospheric deposition of N and/or recycled production. Here cyanobacteria dominate the picoplankton community and TON and TOP exhibit two opposing trends. In the surface layer TON accumulates relative to TOP inducing high surface TONxs elevated values of TON (Landolfi et al., 2008). These features are a diagnostic for processes that selectively introduce a source of N but not P, implying major roles of N_2 fixation and atmospheric deposition. A possible source of TON, without any significant addition of TOP, can result from diazotroph activity, which are known to release a substantial part of their fixed nitrogen into the DON pool (Glibert and Bronk, 1994; Mulholland et al., 2004), that appears to be rapidly consumed (Knapp et al., 2005; Meador et al., 2007) and thus channeled into the TON pool (Landolfi et al.,2008). The increase of TON and possible utilization of surface TOP will amplify the contrasting TON and TOP trends. In this western region of the gyre high fixation rates by *Trichodesmium* are well documented (Capone et al., 2005; Carpenter et al., 2004). The temperature control of the growth of the genus *Trichodesmium* (Breitbarth et al., 2007) and the utilization of organic P species by these diazotrophic organisms is well known (Sohm and Capone, 2006). Hence, these large N_2 fixers may have been favoured in this portion of the gyre by the shallow ML, higher water temperatures ($23.9 \pm 0.8\,^\circ$C) and the presence of advected DOP which appears to be a significant source of P before it gets exhausted on its way to the eastern portion of the gyre. However, the very low (–4.47‰) $\delta PO^{15}N$ observed at one station (65° W) might hint towards a non-negligible atmospheric N source as North America's anthropogenic N sources are characterized by low isoptopic (–7‰) signals (Hastings et al., 2003). However, the atmospheric deposition of N rich organic material alone, could not explain the surface TOP depletion as compared to the subsurface values (<30 m) (Fig. 4).

In the eastern sector of the oligotrophic gyre (46–30° W), a higher seasonal amplitude of the surface mixed layer induces a deeper MLD which intercepts the depth of the nutricline, allowing the possible injection of nitrate from deep layers. Here the role of advected DOP as a P source appears to be minimal due to its near complete exhaustion (age tracer >4 yr). These phenomena fit well with a decrease in TON and TOP concentrations and an enriched isotopic signal (2.20 ± 0.45‰) recorded in PON, which points to little N_2 fixation but instead the utilization of ^{15}N enriched N sources such as nitrate and advected DON (Knapp et al., 2005). In this region the picoplankton community shifts to a procholorophytes dominated community as suggested by the increase of

Div-chl-*a* (Fig. 8). These organisms are characteristic of oligotrophic regions and have the potential to utilise organic forms of N (Moore et al., 2002). Some strains, adapted to high light conditions, lack the genes required for nitrate utilisation (NO_3^- permease and NO_3^- reductase) so that the utilisation of organic forms of nitrogen is very probable (Zubkov et al., 2003).

East of 32° W the isotopic variability 1.08 ± 1.77‰ (large standard deviations) reflects variable conditions (mirrored also in the MLD) resulting from the outcrop of isopycnals with densities $>26\,\mathrm{kg\,m^{-3}}$ allowing higher inorganic nutrient concentrations at the surface. Here, as diagnosed by our age tracer, production and advection of freshly formed DOM from the neighbouring upwelling region, provide allochthonous N and P which, together with N_2 fixation and/or atmospheric deposition all act as new N sources for the phytoplankton community.

The emerging picture is one where the North Atlantic oligotrophic subtropical gyre, biogeochemically different from the gyre flanks, is characterised by a phytoplankton community shift from west to east. The reasons for this shift appears to be related to different N and P supply mechanisms and is ultimately controlled by physical forcing which provide allochtonus TOP particularly enhanced in the west and a temperature and MLD gradients. In the western oligotrophic gyre (~70–46° W) TOP allochthonous supply may provide the missing P to drive N_2 fixation which appears to provide up to 61 ± 17% of the new N. In the eastern subtropical gyre (~46–30° W) TOP becomes exhausted and an increasing importance of DON and nitrate emerges. These findings fit very well with the reports of a zonal shift in the dominance of N_2 fixation with large colonial cyanobacteria of the genus *Trichodesmium* dominating in the west, and major role of the unicellular diazotrophos in the East (Montoya et al., 2007). We speculate that different diazotrophic communities emerge in response to different P limitation patterns across the subtropical gyre.

4 Conclusions

The oligotrophic North Atlantic subtropical gyre at 24.5° N is characterised by an unexpected spatial variability. The reasons for this variability are related to different nutrient supply mechanisms, which are caused by DOM advection, temperature and MLD gradients. Based on our data, chlorophyll as viewed from space, climatological density and an integration of an artificial age tracer embedded in a general circulation model we distinguish four regimes along 24.5° N. The western and eastern flanks of the gyre are influenced by the gulf stream and the wind driven upwelling off the African coast, respectively. Within the oligotrophic stretch between (70–30° W), at approximately 46° W there is a distinct regime shift from ultraoligotrophic with barely any seasonal cycle to an oligotrophic environment. Within these oligotrophic regions the phosphorus and nitrogen supply pathways to the mixed plankton assemblage appear to be different. In the ultraoligotrophic western part we identified a surface mixed layer depth seasonal cycle with a modest amplitude of 20 m which imply weak local processes and almost permanent stratification. Transit times of water parcels stemming from more productive waters (as derived from a circulation model) in the order of 2 yr suggest that allochthonous TOP provides a source of new P before it gets exhausted on its way from the productive source regions into the eastern part of the gyre. Here biogeochemical proxies suggest that N_2 fixation provides the dominant N supply likely enhanced by shallow mixed layer depth, high water temperatures and allochtonus DOP.

In the eastern region (East of 46° W) of the subtropical gyre the presence of a higher seasonal amplitude of the surface mixed layer and the deepening of the MLD allow for inorganic nutrient injections from deep layers. Transit times of water parcels longer then 2 yr imply a potential role of allochthonous TON as a N source whereas TOP appears exhausted. These factors and a lower sea surface temperature as compared to the west, induce a different community structure dominated by picoplankton and with prochlorophytes being the dominant picoplankton group. Here the isotopic analysis leave little place of N_2 fixation but rather phytoplankton's N sources appear to be DON and nitrate. The missing P appears to be provided by a combination of phosphate and fast DOP cycling and little DOP export below the permanent thermocline. We conclude from these observations that oceanic nitrogen fixation occurs in regions with diverse organic nutrient utilisation patterns.

Acknowledgements. We thank S. Reynolds for performing enzyme experiments on AMT 16. Thank you to M. Bolshaw for assisting with isotopic analyses. Thank you to P. Kähler, and L. C. Da Cunha for their valuable comments. We thank the CAU Excellence Cluster "The future ocean" and The Deutsche Forschungsgemeinschaft (SFB 754) who provided financial support.

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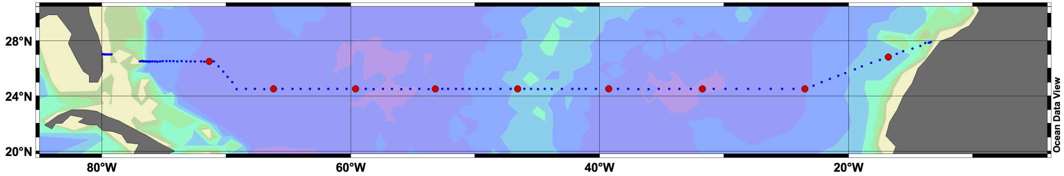

Fig. 1. Sampling stations location across the North Atlantic at a nominal latitude of 24.5° N. Red dots indicate stations where surface incubations to determine enzyme activities have been carried out.

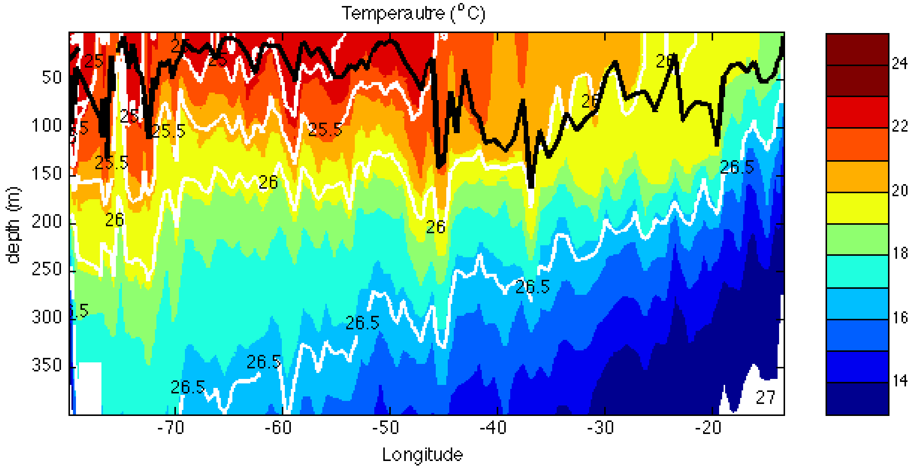

Fig. 2. Longitudinal section of temperature (°C) across the North Atlantic at 24.5° N . White contours represent contours of sigma-theta (kg m^{-3}). The black solid line represents the depth of the mixed layer (MLD) calculated using the sigma-theta criterion of 0.125 kg m^{-3}.

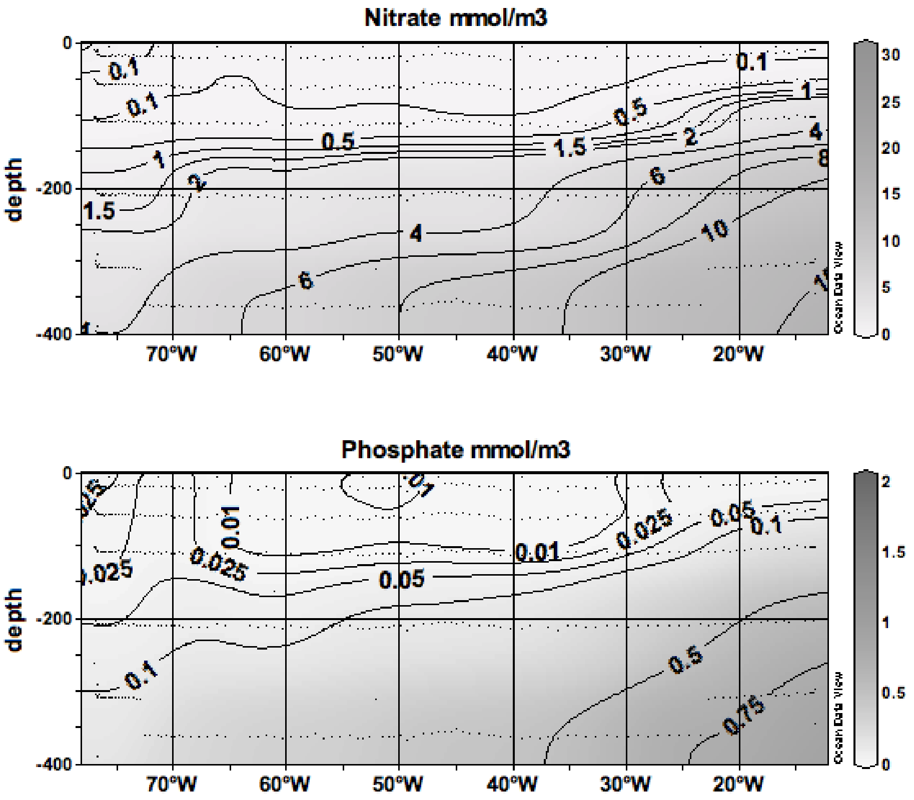

Fig. 3. Longitudinal section of nitrate (mmol m^{-3}) **(a)** and phosphate (mmol m^{-3}) **(b)** in the North Atlantic at 24.5° N.

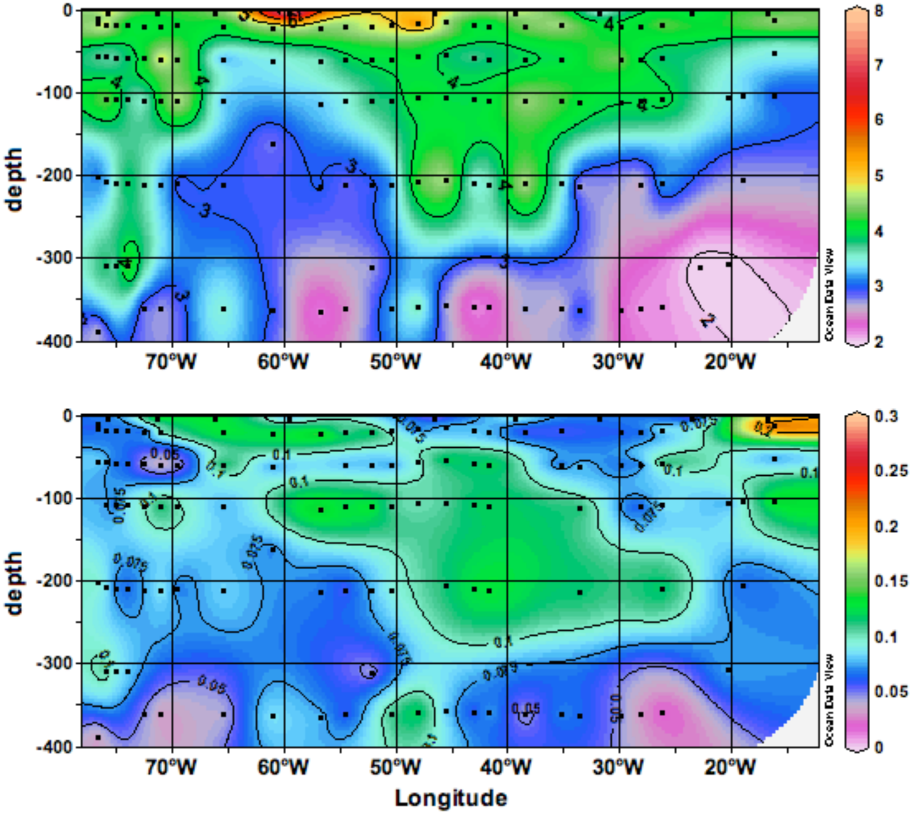

Fig. 4. Longitudinal section of TON (mmol m^{-3}) **(a)** and TOP (mmol m^{-3}) **(b)** in the North Atlantic at 24.5° N.

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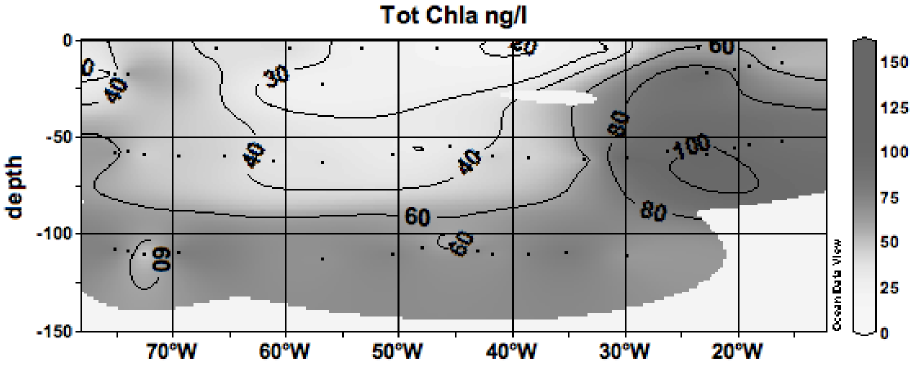

Fig. 5. Longitudinal section of total chlorophyll-*a* (g chl-*a* m^{-3}) in the North Atlantic at 24.5° N.

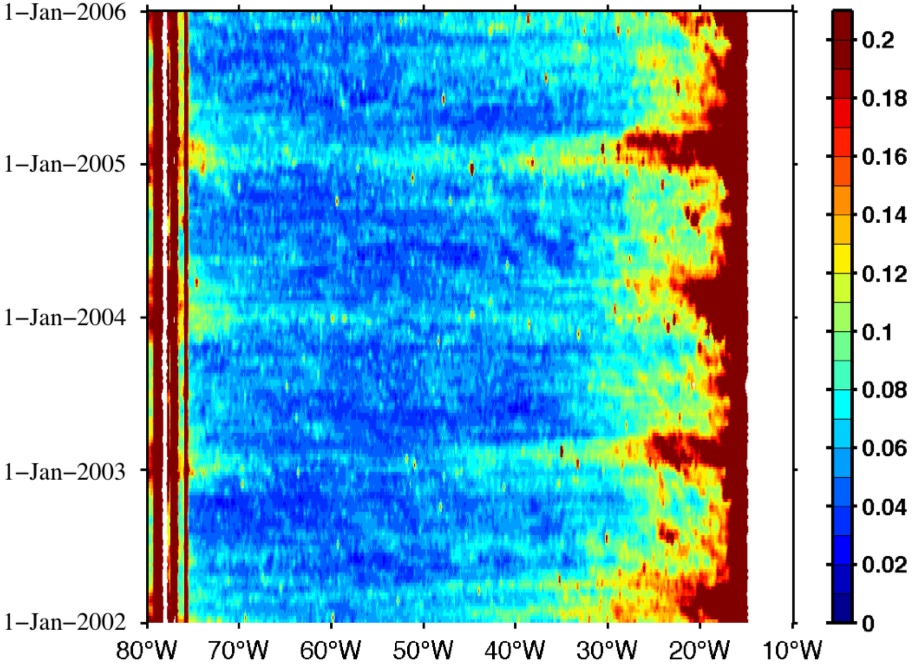

Fig. 6. 6 Hofmoeller Diagram of SeaWifs chlorophyll along 24.5° N.

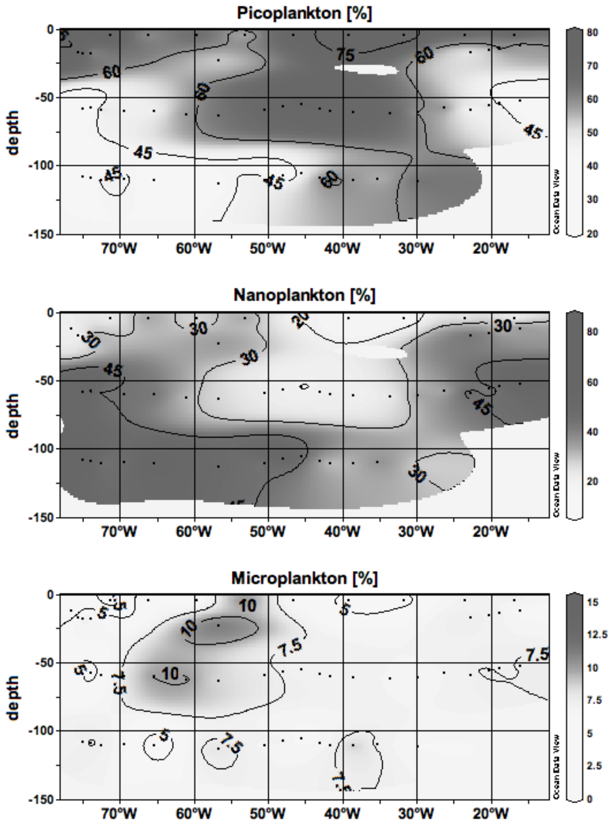

Fig. 7. Longitudinal section of the phytoplankton picoplankton **(a)** nanoplankton **(b)** and microplankton **(c)** percentage % in the North Atlantic at 24.5° N.

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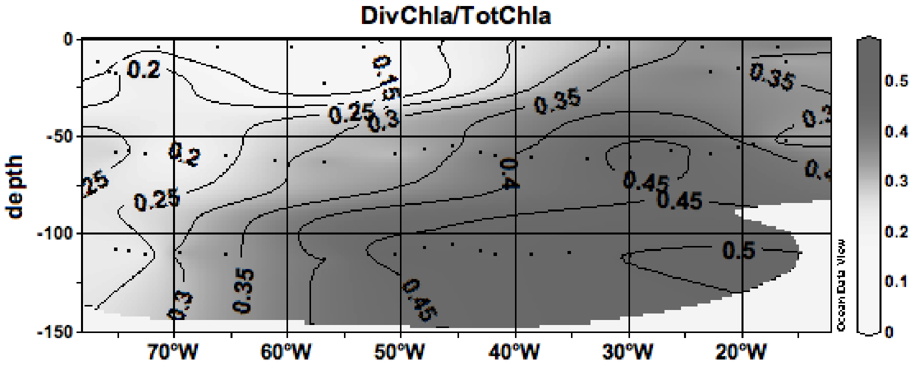

Fig. 8. Longitudinal section of fraction of divinyl chlorophyll-*a*/total chlorophyll-*a* in the North Atlantic at 24.5° N.

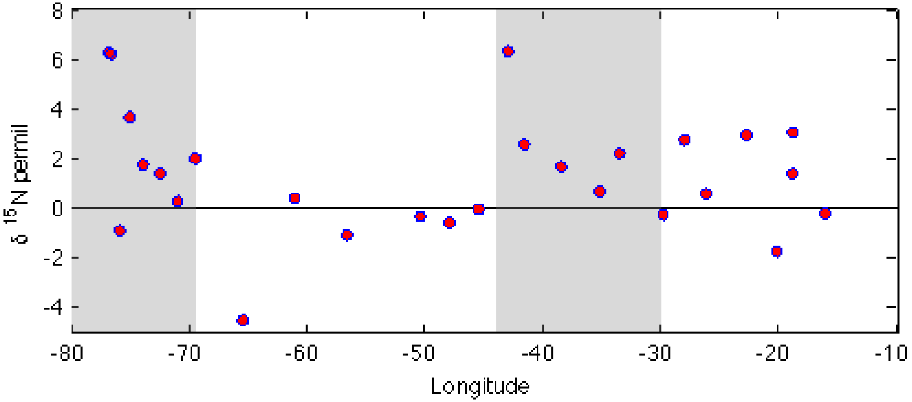

Fig. 9. Longitudinal surface distribution of $\delta PO^{15}N$ in the North Atlantic at 24.5° N. The grey area represents the subdivision of the transect into isotopically homogenous regions. Please note that this subdivision reflects the depth of the MLD.

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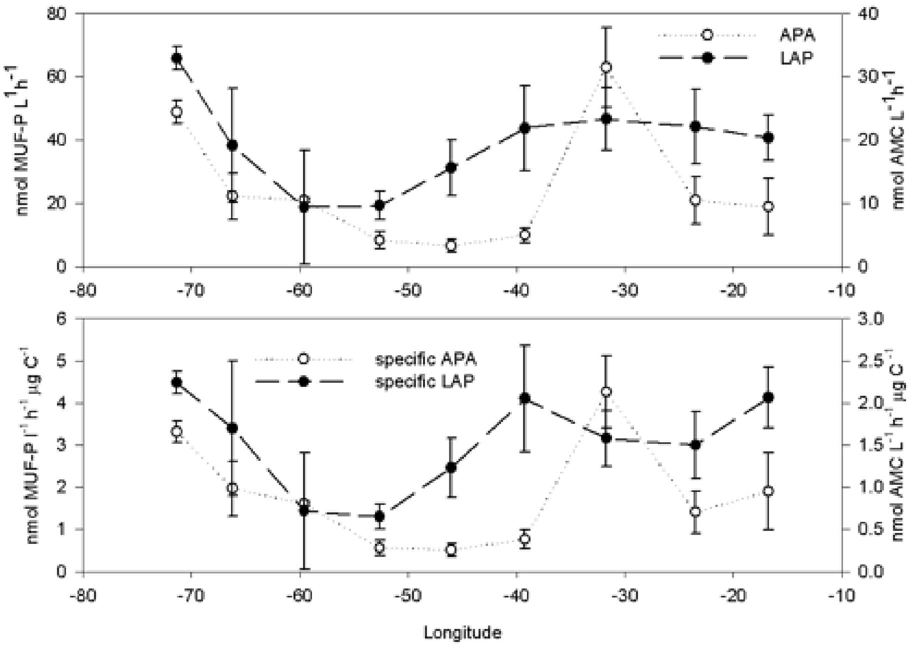

Fig. 10. Longitudinal surface (0 m) distributions of APA (nmol 4-MUF L^{-1} h^{-1}) **(a)** and LAP (nmol AMC L^{-1} h^{-1}) **(b)** and specific activities in the North Atlantic at 24.5° N.

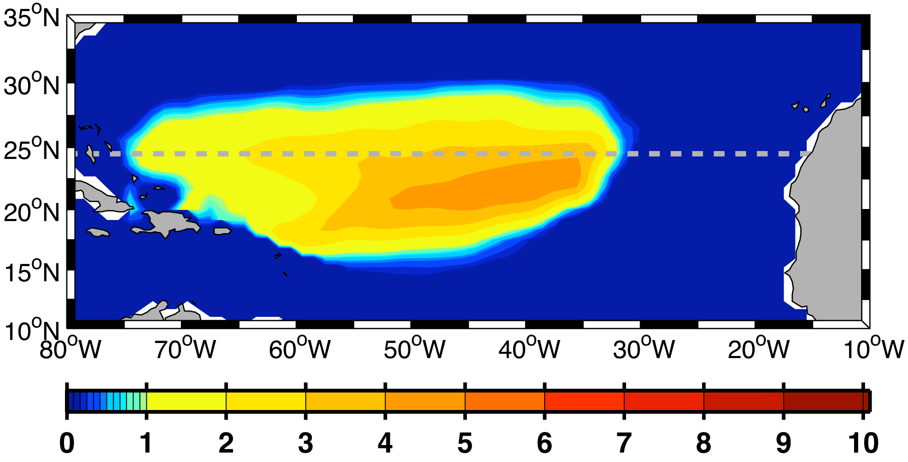

Fig. 11. Model estimate of the time elapsed since surface water parcels hosted chlorophyll-*a* concentrations exceeding 0.1 mg m^{-3}. The unit is years. The dashed grey line is at 24.5° N.

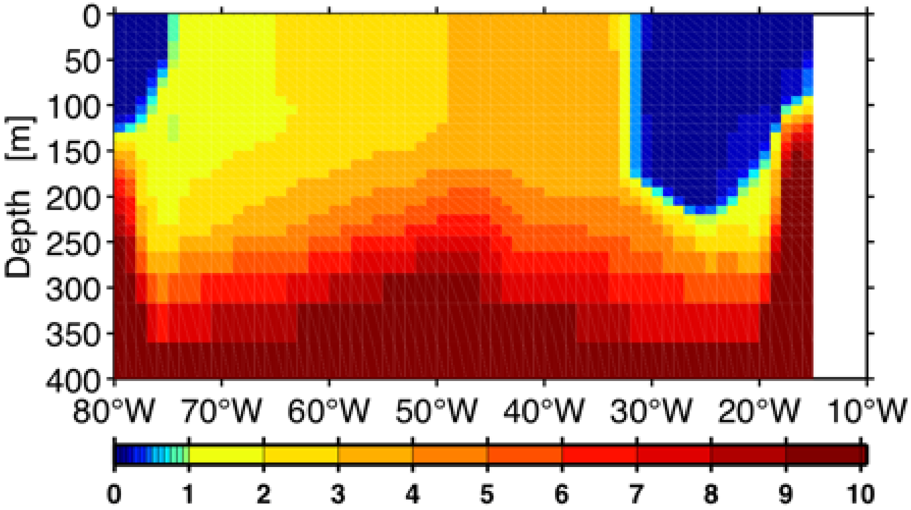

Fig. 12. Zonal section along 24.5° N of the (modeled) time elapsed since surface water parcels hosted chlorophyll-*a* concentrations exceeding 0.1 mg m^{-3}. The unit is years.

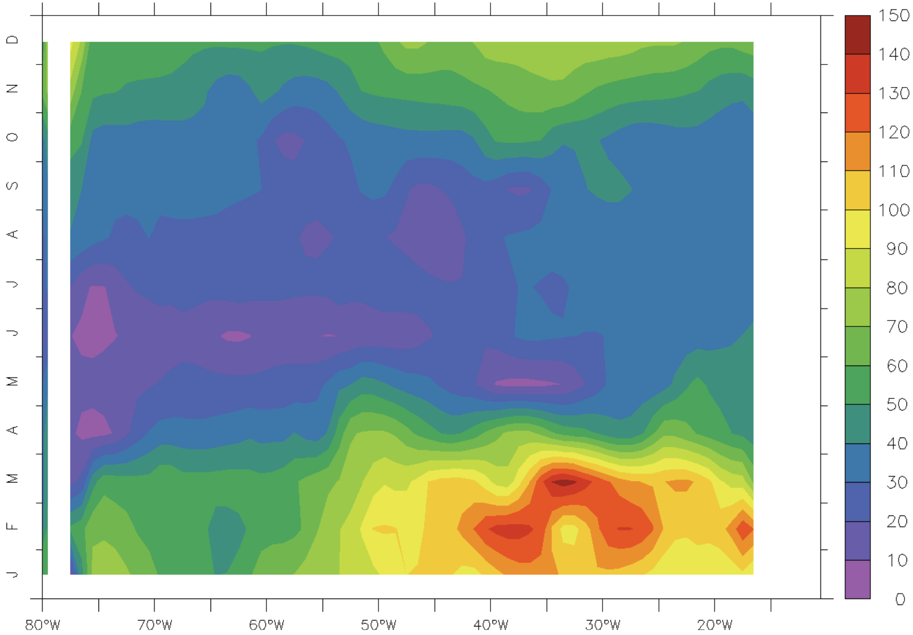

Fig. 13. MLD climatology. Hoffmueller diagram of surface mixed layer depth along 24.5° N based on the WOA01 climatology. The surface mixed layers were calculated as the depth where density sigma$_0$ is 0.125 higher than the density at the surface.