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Dissolved organic carbon and apparent oxygen utilization in the Atlantic Ocean

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ABSTRACT

Dissolved organic carbon (DOC) distributions along two Atlantic Meridional Transects conducted in 2005 in the region between 47°N and 34°S showed clear latitudinal patterns. The DOC concentrations in the epipelagic zone (0–100 m) were the highest (70–90 μM) in tropical and subtropical waters with stable mixed layers, and lowest (50–55 μM) at the poleward extremities of the transects due to deep convective mixing supplying low DOC waters to the surface. A decrease in DOC occurred with depth, and lowest DOC concentrations (41–45 μM) in the 100–300 m depth range were observed in the equatorial region due to upwelling of low DOC waters. A strong relationship between DOC and AOU was observed in the σ–t 26–26.5 isopycnal layer which underlies the euphotic zone and outcrops at the poleward extremities of the North and South Atlantic Subtropical Gyres (NASG and SASG) in the region ventilating the thermocline waters. Our observations reveal significant north–south variability in the DOC–AOU relationship. The gradient of the relationship suggests that 52% of the AOU in the σ–t 26–26.5 density range was driven by DOC degradation in the NASG and 36% in the SASG, with the remainder due to the remineralisation of sinking particulate material. We assess possible causes for the greater contribution of DOC remineralisation in the NASG compared to the SASG.

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1. Introduction

The biological carbon pump (BCP) forms an important component of the global carbon cycle (e.g., Thingstad, 1993; Ducklow et al., 2001; Hansell and Carlson, 2001a; Omta et al., 2006). Following the synthesis of CO_2 into organic material during photosynthesis, creating a surface water dissolved inorganic carbon (DIC) deficit (Tsurushima et al., 2002), subsequent processes remove some of this organic matter into the oceans′ interior where it is remineralised, causing a deficit in dissolved oxygen (Doval and Hansell, 2000; Hansell and Carlson, 2001a; Garcia et al., 2005). On a global scale, the upper ocean DIC deficit is balanced by a transfer of CO_2 from the atmosphere to the upper ocean, hence the BCP represents a sink for atmospheric CO_2 (Hansell and Carlson, 2001a). Two mechanisms cause the downward transfer of organic matter: (1) passive sinking of particulate organic carbon (POC), and (2) transfer to depth by overturning circulation at high latitudes or subduction in subtropical gyres of dissolved organic carbon (DOC) that has accumulated in the surface ocean (Hansell, 2002). The spatial variability of the relative contributions of POC and DOC to carbon sequestration is however largely unclear, which is caused by a paucity of high quality DOC data. Recent DOC observations on US Climate Variability (CLIVAR) cruises in the North Atlantic, Pacific and Southern Ocean have started to redress this issue (Hansell, 2002; Carlson et al., 2010; Hansell et al., 2012). In this paper we present observations of DOC concentrations in the tropical and subtropical North and South Atlantic Ocean and use them to estimate the relative contributions of the remineralisation of DOC and POC to apparent oxygen utilization (AOU).

DOC is a continuum of labile, semi-labile, and refractory pools, which are increasingly resistant to photochemical and/or microbial breakdown (Kirchman et al., 1993; Hansell et al., 2012). In the open ocean, DOC originates from in situ biological processes, including plankton exudation/excretion (Collos et al., 1992), grazing (Søndergaard et al., 2000), and cell lysis (Nagata, 2000). However, the ultimate DOC source is primary production (Carlson et al., 1998), at a reported rate of DOC production equivalent to 4–41% of total integrated primary production, with the highest observed values in oligotrophic waters and lowest in upwelling regions (Teira et al., 2001). The remineralisation of DOC

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by heterotrophic prokaryotes is the major removal mechanism (Azam, 1998), although direct assimilation by some marine eukaryotes (Azam and Hodson, 1977; Sherr and Sherr, 1988) may also be important. Accumulation of DOC in surface waters is therefore dependent on a decoupling of microbial consumption from primary production (Carlson et al., 1998). In addition, DOC accumulation is dependent on water column stability, with strongly stratified subtropical oligotrophic waters showing the highest potential for accumulation (Carlson et al., 2010).

The relationship between DOC and AOU, the latter integrating all respiratory processes within a water body since its isolation from the atmosphere, has been intensively studied. Thomas et al. (1995) found a weak relationship in the Equatorial Atlantic (<700 m), while Hansell et al. (1993) observed no covariation in the Southern California Bight (<1000 m). However, Abell et al. (2000) found a strong correlation between total organic carbon (TOC=DOC+POC) and AOU in the North Pacific Subtropical Gyre at water depths <350 m. In recent work, Carlson et al. (2010) reported a good correlation between DOC and AOU in the meso- and bathypelagic North Atlantic, and Santinelli et al. (2010) made similar observations for this part of the water column of the Mediterranean Sea.

The reported contribution of DOC degradation to AOU varies considerably from site to site. Thomas et al. (1995) reported that 10–20% of AOU was derived from DOC remineralisation in the upper 700 m of the Equatorial Atlantic. Doval and Hansell (2000) showed that the degradation of TOC contributed to 35–50% and 30–45% of AOU in the South Pacific and the central Indian Oceans, respectively, at depths from 50 to 300 m. Abell et al. (2000) found that 35–80% of AOU can be explained by TOC remineralisation in the upper 350 m in the North Pacific Subtropical Gyre. Hansell and Carlson (2001b) suggested that TOC decomposition accounted for 15–40% of AOU based on a 5-year time series of observations in the 100–400 m depth range at the Bermuda Atlantic Time Series (BATS) site in the Sargasso Sea. Carlson et al. (2010) reported that between 7% and 28% of AOU could be assigned to DOC oxidation in waters below 100 m in the North Atlantic, and Santinelli et al. (2010) reported that 38% of AOU was due to DOC oxidation in the Levantine Intermediate Water of the Mediterranean Sea.

Hence the proportion of AOU derived from DOC remineralisation appears to have a large range, from $<20\%$ in equatorial regions to $\sim 80\%$ in subtropical gyres. The fraction of AOU attributable to DOC degradation is an index of the relative importance of DOC transfer to depth through overturning circulation and subduction versus particle export. Therefore one would expect regional variability in the importance of particle sinking versus DOC export to the BCP. We analyzed DOC and AOU observations from two Atlantic Meridional Transects. Firstly we report the spatial distribution of DOC concentrations. We then investigate the bulk relationship between DOC and AOU in water masses isolated from the atmosphere. Finally we derive separate DOC:AOU relationships for the two gyres to examine spatial variability in the relative importance of the factors which cause oxygen utilization and hence carbon sequestration in subsurface waters.

2. Methodology

2.1. Sampling

We sampled during Atlantic Meridional Transect (AMT) cruises 16 (19 May–29 June 2005) and 17 (15 October–28 November 2005) onboard the RRS *Discovery* between South Africa and the UK (Fig. 1). Water samples for the determination of DOC, oxygen, nitrate plus nitrite and chlorophyll concentrations were collected from 10 to 12 depths in the upper 300 m during daily pre-dawn

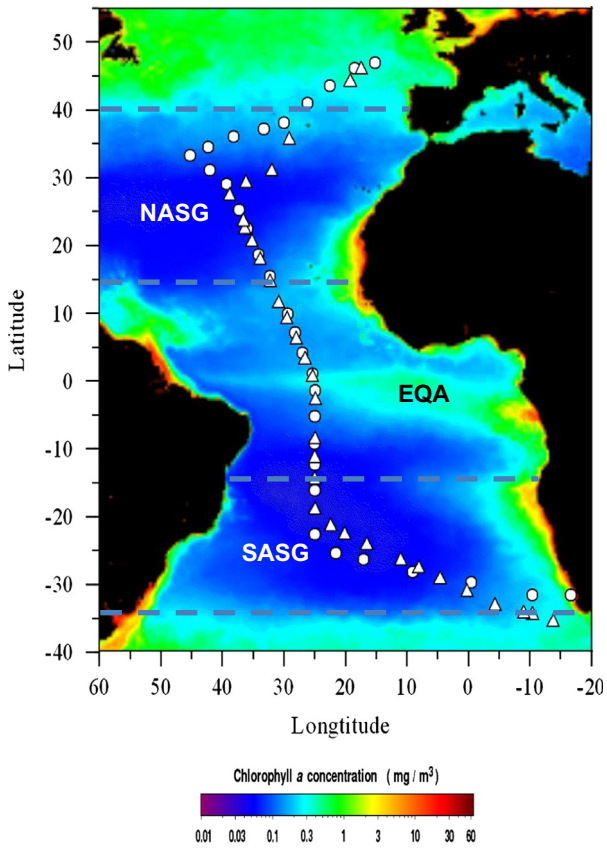

Fig. 1. Cruise track and locations of sampling stations for Atlantic Meridional Transect (AMT)-16 (19 May–29 June 2005) and -17 (15 October–28 November 2005). Circles indicate stations sampled on AMT-16, while triangles indicate stations sampled on AMT-17. The composite satellite image of chlorophyll a distribution was obtained from SeaWiFS (for year 2000; NASA, USA).

deployments of a rosette sampler equipped with 24×20 l OTE (Ocean Test Equipment) bottles and a Sea-Bird 911 CTD equipped with a Seabird oxygen sensor. On every third day during AMT-16 we collected samples from a deeper cast down to ~ 1000 m.

2.2. Dissolved organic carbon

Samples (250 ml) for DOC were filtered immediately through pre-ashed (450 °C, 6 h) Whatman GF/F (0.7 μm pore size) filters using an acid-cleaned glass filtration unit under moderate vacuum (<15 kPa). The filtrate was collected in 20 mL pre-combusted (450 °C, 6 h) glass ampoules, acidified to pH 2 using hydrochloric acid (Fisher, Aristar Grade), flame sealed, and dark-stored in a fridge (4 °C) for subsequent analysis in our shore-based laboratory. Dissolved organic carbon concentrations were determined using a high-temperature catalytic combustion technique with a Shimadzu TOC-5000A analyzer following Pan et al. (2005). Acidified deep Sargasso Sea water, preserved in glass ampoules and provided by D. Hansell (University of Miami), served as a certified reference material. Our daily analysis of the reference material yielded a mean concentration of 45.2 ± 1.2 μM ($n=96$), which was in good agreement with the certified value of 44–46 μM (Hansell and Carlson, 2001a). Our analytical precision, based on the coefficient of variation (standard deviation/mean) of consecutive injections (typically 3–5 injections) of a single sample, was typically $<1\%$.

2.3. Dissolved oxygen

Water samples were drawn from 4 to 6 OTE bottles into 125 mL calibrated borosilicate glass bottles and fixed immediately using

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