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Production and degradation of fluorescent dissolved organic matter in surface waters of the eastern north Atlantic ocean

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ABSTRACT

The distribution and fate of coloured dissolved organic matter (CDOM) in the epipelagic Eastern North Atlantic was investigated during a cruise in the summer 2009 by combining field observations and culture experiments. Dissolved organic carbon (DOC) and nitrogen (DON), the absorption spectra of CDOM and the fluorescence intensity of proteins (Ex/Em 280/320 nm; *F*(280/320)) and marine humic-like substances (*F*(320/410)) were measured in the upper 200 m. DOC and DON showed higher concentrations in the top 20 m than below, and DOC increased southwards, while DON decreased. *F*(280/320) and *F*(320/410) showed maxima near the deep chlorophyll maximum (at about 50 m), suggesting that these fluorophores were linked to phytoplankton production and the metabolism of the associated microbial community. The coloured and fluorescent fractions of DOM showed low levels south of the Azores Front, at about 35 °N, likely due to the accumulated photobleaching of the waters transported eastwards by the Azores current into the study area (at 20°W). Twelve culture experiments were also conducted with surface water (5 m) to assess the impact of microbial degradation processes on the bulk, coloured and fluorescent fractions of DOM. After 72 h of incubation in the darkness, 14 ± 9% (average ± SD) of the initial DON was consumed at an average rate of 0.24 ± 0.14 μmol l^{-1} d^{-1} and the protein-like fluorescence decayed by 29 ± 9% at a net rate of 0.06 ± 0.03 QSU d^{-1}. These rates were significantly lower south of the Azores front, suggesting that DOM in this region was of a more recalcitrant nature. Conversely, the marine humic-like fluorescence increased at a net rate of 0.013 ± 0.003 QSU d^{-1}. The close linear relationship of DON uptake with *F*(280/320) consumption (R^2 = 0.91, p < 0.0001, n = 12) and *F*(320/410) production (R^2 = 0.52, p < 0.008, n = 12) that we found during these incubation experiments suggest that the protein-like fluorescence can be used as a proxy for the dynamics of the labile DON pool and that marine humic-like materials can be produced as a by-product of microbial DOM degradation.

1. Introduction

The largest pool of reactive nitrogen in the open ocean is contained in dissolved organic matter (DOM), which originates mainly from phytoplankton and heterotrophic bacteria exudation, viral cell lysis, protozoan grazing and zooplankton sloppy feeding (Bronk, 2002; Nagata, 2000). Although a variable fraction of the DOM pool can be utilized by marine microbes in hours to days, most of it is recalcitrant to microbial degradation over time-scales of years to millennia (Hansell, 2013). In the coastal ocean, 22 ± 12% (average ± SD of an extensive global data base) of the dissolved organic carbon (DOC) and 35 ± 13% of the dissolved organic nitrogen (DON) is bioavailable with half-life times of ten and six days, respectively (Lønborg and Álvarez-Salgado, 2012). Information about the bioavailability and degradation rates of DOM in open ocean waters is noticeably rarer, particularly in the case of DON, but see the studies by Kirchman et al. (1991) and Lestcher et al. (2013) for the few existing estimates (data range < 3 to 48%).

A fraction of the DOM pool absorbs light strongly in the UV and blue range of the spectrum, with a part of this energy being re-emitted as fluorescence (Coble, 2007; Stedmon and Álvarez-Salgado, 2011). This coloured DOM (CDOM) is a major factor determining the underwater light field and attenuation of UV radiation in the ocean

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(Nelson and Siegel, 2013). The fluorescence emission of CDOM (FDOM) in natural waters is mainly due to protein- and humic-like compounds (Coble, 1996). The protein-like fluorescence is related to the aromatic amino acids (tyrosine, tryptophan and phenylalanine) and has been suggested as a suitable tracer for bio-labile DOM (Yamashita and Tanoue, 2003; Lønborg et al., 2010). Conversely, the resistance to microbial degradation of humic materials has led to consider the humic-like fluorescence as an indicator for recalcitrant DOM, which is either of terrestrial origin or generated as a by-product of the microbial degradation of biogenic organic matter (Nieto-Cid et al., 2006; Yamashita and Tanoue, 2008; Lønborg et al., 2010; Jørgensen et al., 2011, Kowalczuk et al., 2013). Andrew et al. (2013) has also suggested that chemical or microbial modification of terrestrial organic material could also be an alternative source of humic-like FDOM. Although numerous studies have used the fluorescence intensity of protein- and humic-like compounds to trace changes in the composition, production and degradation of DOM (e.g. Coble et al., 1990; Guillemette and del Giorgio (2012)), quantitative relationships between DOM and FDOM properties are still lacking.

In this study we determined the distribution and fate of CDOM during a summer cruise in the Eastern North Atlantic (ENA) Ocean from 42° to 27°N by combining field observations and culture experiments. This study is complementing the work by Lønborg and Álvarez-Salgado (2014), who studied the variability of DOM and CDOM in the dark ENA Ocean and Benavides et al. (2013) who studied the role of N_2 fixation and the uptake and regeneration of DON in the upper water column during the same cruise. In this article we aimed at 1) describing the spatial variability of bulk, coloured and fluorescent DOM components in epipelagic waters (0–200 m); 2) determining the short-term changes in CDOM optical properties during seawater culture experiments; and 3) establishing quantitative relationships between changes in FDOM and DOM bioavailability in the epipelagic ENA Ocean.

2. Material and methods

2.1. Field data

Surface water samples (0–200 m) were collected during the CAIBOX cruise on board the R/V *Sarmiento de Gamboa* from 25 July to 14 August 2009 (Fig. 1). Salinity, temperature, chlorophyll *a* (Chl *a*), and inorganic nutrient (Nitrate-NO_3^-, Phosphate- HPO_4^{2-} and Silicate- SiO_4H_4) profiles were obtained at 71 stations (white dots in Fig. 1). Salinity, temperature and fluorescence of Chl *a* (F-Chl *a*) were recorded with a CTD SeaBird 911 and a Sea-Tech fluorometer mounted on a General Oceanics rosette sampler equipped with 24 Niskin bottles of 12 l. Bottle samples were typically collected at 3–4 depths ranging between 5 and 200 m. The CTD salinities were calibrated with bottle samples analysed on board with a Guildline 8410- A Portasal. The F-Chl *a* records were calibrated by filtration of 250 ml of sample water through a Whatman GF/F filter, extraction in acetone (90% v/v), and fluorimetric determination with a Turner Designs 10000 R fluorometer standardised with pure Chl *a* (Sigma) (Yentsch and Menzel, 1963). Water samples for the analysis of inorganic nutrients were collected in 50 ml acid washed polyethylene bottles and preserved in the dark at 4 °C until analysed on board within a few hours.

The squared Brunt-Väisälä frequency (N^2) is commonly used to quantify the stratification of the water column. Following Millard et al. (1990), N^2 can be calculated as:

$$N^2 = -\frac{g}{\rho}\cdot\frac{\partial\rho}{\partial z} = -g\cdot\frac{\partial \ln(\rho)}{\partial z} \quad (1)$$

Where g is the gravity acceleration constant (9.8 m s^{-2}), z is the water depth, and ρ is the water density at depth z. Integration of Eq. 1 between two depth levels (1 and 2), $\overline{N}^2 = -g\cdot \ln(\rho_2/\rho_1)/(z_2-z_1)$, provides a measure of the average stability of the water column between z_1 and z_2. Here we will report values of $\overline{N}$, that is, the square root of $\overline{N}^2$, in min^{-1}. The higher the $\overline{N}$, the larger the stratification.

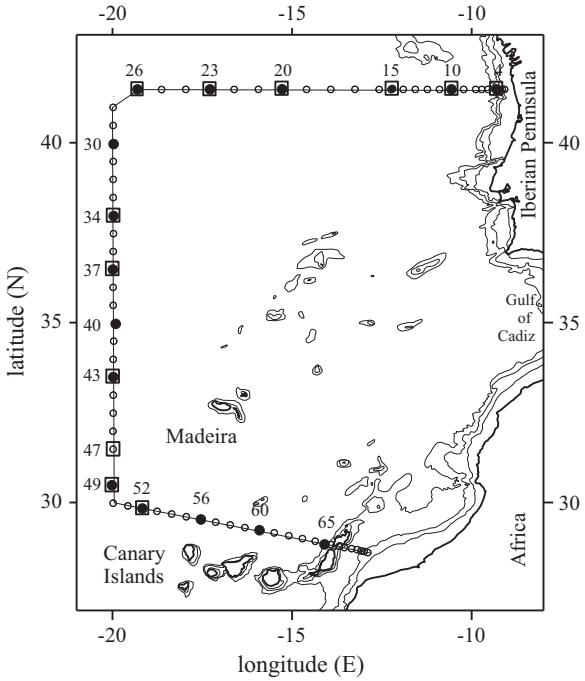

Fig. 1. Map showing the cruise track on board R/V *Sarmiento de Gamboa* over the period 25 July to 14 August 2009. The white dots (○) show the 71 hydrographic stations occupied and the black dots (•) the 16 stations where dissolved organic carbon (DOC) and nitrogen (DON), coloured dissolved organic matter (CDOM) absorption and fluorescence measurements were performed. The framed stations are those where water for the incubation experiments was collected.

Profiles of dissolved organic carbon (DOC) and nitrogen (DON), absorption spectra of coloured DOM (CDOM) and fluorescence intensities of protein- and humic-like substances were obtained at 16 stations (black dots in Fig. 1).

2.2. Incubation experiments

Additional water was collected at 5 m at the first 12 of the 16 stations where DOM variables were measured (framed stations in Fig. 1). This water was used to conduct incubation experiments to measure changes in bulk concentrations and optical properties of DOM over a period of 72 h. Filtration of the water started within 20 min of collection; one part was filtered through a dual-stage (0.8 μm and 0.2 μm) filter cartridge (Pall-Acropak supor Membrane) which had been pre-washed with 10 l of Milli-Q water; the second part was filtered through pre-combusted (450 °C for 4 h) Whatman GF/C filters to establish a microbial inoculum. After filtration, the water was transferred into a 20 l carboy and the microbial inoculum was added to the 0.2 μm filtrate corresponding to 10% of the total volume. Thereafter, the water was transferred into 20 glass bottles of 500 ml (headspace ~100 ml), with four replicate bottles being sacrificed for analyses at times 0, 12, 24, 36 and 72 h. The incubators were kept in the dark at 15 °C, this temperature was chosen as it represents the yearly average water temperature in the top 200 m in our study area. Unfiltered water from these bottles was used at time 0 and 72 h to follow changes in bacterial production (BP). Samples for the analysis of dissolved inorganic nitrogen (NH_4^+ and $NO_3^-+NO_2^-$) and phosphate (HPO_4^{2-}), DOC, total dissolved nitrogen (TDN) and CDOM absorption were collected in four replicates at 0 and 72 h. DOM fluorescence (FDOM) was measured at all time points. The samples for the