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Composition of dissolved organic matter along an Atlantic Meridional Transect from fluorescence spectroscopy and Parallel Factor Analysis

Piotr Kowalczuk [a,*], Gavin H. Tilstone [b], Monika Zabłocka [a], Rüdiger Röttgers [c], Rob Thomas [d]

[a] Institute of Oceanology, Polish Academy of Sciences, ul. Powstańców Warszawy 55, PL-81-712 Sopot, Poland
[b] Plymouth Marine Laboratory, Prospect Place, The Hoe, Plymouth PL1 3DH, United Kingdom
[c] Institute for Coastal Research, Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Max-Planck-Str. 1, D-21502 Geesthacht, Germany
[d] British Oceanographic Data Centre, Joseph Proudman Building, 6 Brownlow Street, Liverpool L3 5DA, United Kingdom

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ABSTRACT

Absorption spectra and induced fluorescence excitation emission matrices of colored dissolved organic matter were measured in water samples collected along the Atlantic Meridional Transect in different bio-geographic provinces of the Atlantic Ocean from October to November 2010. The highest values of CDOM absorption coefficient at 305 nm ($a_{CDOM}(305)$), were recorded at the continental margins of the English Channel and Patagonian Shelf. The lowest values of $a_{CDOM}(305)$ were observed in the mixed layer of both North and South Atlantic subtropical oligotrophic gyres. The DOM composition was assessed using fluorescence spectroscopy, Excitation Emission Matrix spectra (EEMs) and the Parallel Factor Analysis (PARAFAC) model in addition to spectral indices calculated from CDOM absorption spectrum and EEMs. Six different components were identified in the EEMs by PARAFAC: Two components were similar to the humic-like fraction of DOM, associated with basin scale microbial mineralization processes. These components represent allochthonous DOM in the biogeographic provinces studied. One component of marine humic-like material of autochthonous origin was associated with DOM production from marine phytoplankton. Three components were associated with protein-like DOM. Two protein-like components had the spectral characteristics of pure tryptophan and tyrosine. There was a significant difference in DOM composition both between bio-geographical provinces and above and below the mixed layer. In the mixed layer in all provinces, except the waters of the Western European Shelf, the DOM was dominated by protein-like components. At the Western European Shelf, it was dominated by humic-like components. Fluorescence intensities of humic-like components were high at the Patagonian Shelf, but were up to 40% lower compared to northern hemisphere shelf waters. Humic-like components made a significant contribution to the DOM composition of the upper mesopelagic layer in all provinces, with the highest values at the Equatorial Upwelling Zone. There was a significant inverse relationship between humic-like components and salinity and temperature and a positive relationship with Apparent Oxygen Utilization. The humification index (HIX) was linearly correlated with the intensity of the humic-like DOM components. These trends suggest that the humic-like components are in dynamic equilibrium between likely microbial production in the deep ocean and photochemical degradation in the mixed layer.

1. Introduction

Dissolved organic matter (DOM), is by far the largest pool of organic matter in the sea. About 97% of all organic carbon in the marine environment is incorporated into DOM with an estimated 665 PgC as dissolved organic carbon (DOC) (Hansell, 2013). The mass of DOC in the sea is comparable with the mass of carbon in the Earth's atmosphere, as CO_2, and the amount of carbon stored in terrestrial ecosystems (Hedges, 2002). The dominant source of organic matter in the world's ocean is autochthonous production, which accounts for more than 95% of the total organic matter. DOM is regarded as a large inert reservoir of carbon in the ocean, which below the mixed layer is isolated from the present carbon cycle. Results of recent studies have changed this paradigm and revealed that DOM is an active and dynamic component in carbon biogeochemical cycles and plays an important role in marine ecosystems (e.g. Jiao et al., 2011). DOM consists of a complex mixture of organic compounds resulting from the breakdown of bacteria, algae and/or higher plants and their continuous transformation through photochemical and microbial processes. Due to their complexity, most DOM in the ocean (>85%) have not been characterized (Benner, 2002). The compounds that have been identified are mainly low or medium molecular weight organic molecules: hydrocarbons, carbohydrates, fatty acids, and amino acids (Benner, 2002). There is insufficient knowledge about the remaining fractions of organic matter, which consist mainly of medium and high molecular weight compounds (e.g. proteins, lipids and their polymers and complexes with

* Corresponding author at: Institute of Oceanology, Polish Academy of Sciences, ul. Powstańców Warszawy 55, PL-81-712 Sopot, Poland.

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phenols and metals). There are two major fractions of humic substances present in aquatic environments: humic and fulvic acids, that differ from each other by molecular weight, chemical composition, chemical properties, aromaticity and optical properties (Harvey et al., 1983; Carder et al., 1989).

The optically active fraction of DOM, especially humic substances, called chromophoric dissolved organic matter (CDOM), is one of the major determinants of the optical properties of natural waters, directly affecting both availability and spectral quality of light in the water column (Jerlov, 1976; Blough and Del Vecchio, 2002). In the pelagic ocean absolute concentrations of CDOM, expressed as the magnitude of the CDOM absorption coefficient $a_{CDOM}(\lambda)$, are extremely low (Nelson and Siegel, 2002). In relative terms, however, the contribution of CDOM to the total absorption of oceanic waters is very high and may reach, in the clearest oceanic waters, more than 90% in the ultraviolet range of electromagnetic spectrum (Morel et al., 2007; Bricaud et al., 2010; Tedetti et al., 2010). CDOM also causes significant attenuation of ultraviolet light in the ocean (Smyth, 2011). Through this process, CDOM is transformed photochemically into inorganic carbon, low-molecular-weight organic compounds, trace gases, and phosphorus- and nitrogen-rich compounds (e.g. Vähätalo and Zepp, 2005; Stedmon et al., 2007). CDOM has the ability to become complexed with trace metals, which can be released through the remineralization of DOM. It is therefore fundamental for better understanding of biogeochemical cycles in the oceans, to differentiate and quantify sources of CDOM and analyze the underlying factors that lead to its variability.

A proportion of the CDOM has an inherent ability to fluoresce. This characteristic is well known (Duursma, 1974) and has been used to estimate CDOM in a range of natural waters (Hoge et al., 1993; Vodacek et al., 1997; Ferrari and Dowell, 1998; Ferrari, 2000). One application of the fluorescence spectroscopy technique is to measure the Excitation Emission Matrix (EEM) (Coble, 1996) through detecting the emission spectra at a series of successively increasing excitation wavelengths. Multivariate statistics can then be used to interpret the resulting EEM spectra (Stedmon et al., 2003), which enables discrimination of different classes of fluorophores based on their excitation/emission maxima. This approach is advantageous when used to interpret the multidimensional nature of EEM data sets, to study variability of DOM in coastal areas (Stedmon and Markager, 2005a). The technique has undoubtedly, improved our understanding of production and degradation processes of DOM fluorescence in the marine environment (Stedmon and Markager, 2005b), and has become a useful tool for tracing anthropogenic pollutants or terrestrial inputs to the oceanic DOM pool (Murphy et al., 2006, 2008).

The distribution of CDOM optical properties along the Atlantic Meridional Transect and its role in photochemical production of carbon monoxide has been studied during previous AMT cruises (Kitidis et al., 2006; Stubbins et al., 2006). The detailed compositional structure of the DOM remains to be quantified. The main objectives of this study were to: i) use the fluorescence spectroscopy technique and PARAFAC, optical properties of CDOM absorption and their spectral indices to assess the composition of the DOM and their spatial variability in both the epipelagic and top of the mesopelagic layers in a range of Atlantic Ocean provinces, ii) from these, to identify regions of enhanced degradation and localized production of fluorescent DOM fractions, iii) to discriminate allochtonous fractions of DOM produced outside of the Atlantic biogeographic provinces by different bacterial, viral or phytoplankton communities over different spatial and temporal scales, and iv) and to discriminate the autochthonous fraction of DOM produced within the biogeographic provinces by bacterial, viral or phytoplankton communities over much shorter time scale.

2. Materials and methods

2.1. The study area

The Atlantic Meridional Transect (AMT) program is a long time data series that started in 1995. The research is conducted on Natural Environment Research Council (NERC) —UK ships between the UK and the Southern Ocean and has currently been under taken on 23 cruises. AMT20 was aboard the RRS "James Cook" between 13 October and 21 November 2010 from Southampton, UK, to Punta Arenas, Chile. Sampling was conducted in six biogeochemical provinces: North Atlantic Drift (NADR), North Atlantic Subtropical Gyre (NAST), North Atlantic Tropical Gyre (NATR), Western Tropical Atlantic (WTRA), South Atlantic Subtropical Gyre (SATL), and South Subtropical Convergence (SSTC) (Longhurst, 1995), to characterize the variability in CDOM over a range of oligotrophic, eutrophic and mesotrophic environments in the Atlantic Ocean. The stations sampled during AMT20 were principally in the North and South Atlantic Gyres, but the productive waters of the Celtic Sea, Patagonian Shelf and the Equatorial Upwelling Zone were also sampled. Data collected in the tropical zone in the NATR and WTRA were pooled together to achieve a larger sample size for statistical analyses (see Table 1). The data from the subtropical Southern Atlantic zone were also pooled for the same reason, except for the three last sampling stations which were located close to the Patagonian Shelf. These latter stations bordered the subtropical front where there was an austral spring Coccolithophore bloom. The following regions were therefore defined to analyze salient trends in DOM: European Continental Shelf Waters (WES), North Atlantic Subtropical Gyre (NAST-E), Equatorial Upwelling (EQU), South Atlantic Subtropical Gyre (SATL), and Patagonian Shelf (PAS).

2.2. Sample collection and processing and spectroscopic measurements

Water samples were collected from mid-morning (1100–1200 h local time) deployments of a Sea-Bird water sampling rosette equipped with a Sea-Bird SBE 911 plus CTD unit, fitted with a Chlorophyll-*a* fluorometer (Chelsea Technologies Group Aquatracka MKIII) and a dissolved oxygen concentration sensor (Sea-Bird SBE43). CTD conductivity data were converted to absolute salinity [g kg^{-1}] using the algorithm developed by McDougall et al. (2012). The following depths were sampled at all stations: 300, 200, 100 and 0 m. In addition, if not co-incident with these depths, samples from the Deep Chlorophyll-*a* Maximum (DCM), bottom of the mixed layer and middle of the mixed layer were also taken. A total number of 214 water samples were collected from 35 stations (Fig. 1). The samples were measured immediately onboard the ship for determination of CDOM absorption and fluorescence EEM, and processed using a two-step filtration: firstly through acid-washed Whatman glass fiber filters (GF/F, nominal pore size 0.7 μm), secondly through acid-washed Sartorius 0.2 μm pore size cellulose membrane filters to remove finer particles. The samples were allowed to warm to room temperature prior to spectroscopic and spectrofluorometric scans.

The CDOM absorption coefficient was measured using a liquid waveguide capillary cell system (LWCC-2100, WPI Inc., USA) with a nominal optical pathlength of 1.094 m, according to the methods described by D'Sa et al. (1999) and Miller et al. (2002). Light is axially introduced into the waveguide via an optical fiber and is transmitted and constrained within the capillary cell by total internal reflection. The light source was a UV/VIS lamp (DH-2000-S, Ocean Optics, USA) equipped with an electronic shutter. At the opposite end of the waveguide, a detection fiber conducts the light that is not absorbed by the aqueous medium to a fiber-optic-based spectrometer that uses a diffraction grating to disperse the transmitted light into a CCD detector array (USB-4000, Ocean Optics, USA). There is an inlet or outlet connection at each end of the waveguide for injecting filtered seawater samples or any other aqueous solution. The injected volume of sample was usually less than 4–5 ml. Before and after injection of the sample volume the capillary waveguide cells were flushed and filled with purified water for blanking. Measurements of absorbance (250–800 nm) were performed using the SpectraSuite software (Ocean Optics, USA). Each sample has been measured with the LWCC system in triplicate to ensure repeatability, after the dark current of the detector