Characterization of dissolved organic matter fluorescence in the South Atlantic Bight with use of PARAFAC model: Relationships between fluorescence and its components, absorption coefficients and organic carbon concentrations

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ABSTRACT

In this study, the CDOM absorption coefficient at 350 nm [$a_{CDOM}(350)$] and CDOM excitation emission matrix (EEM) fluorescence were used to estimate annual fluxes of dissolved organic carbon (DOC) from the Cape Fear River to Long Bay in the South Atlantic Bight. Water samples were collected during a 3.5 year period, from October 2001 through March 2005, in the vicinity of the Cape Fear River (CFR) outlet and adjacent Onslow Bay (OB). Parallel factor analysis (PARAFAC) of CDOM EEM spectra identified six components: three terrestrial humic-like, one marine humic-like and two protein-like. Empirical relationships were derived from the PARAFAC model between DOC concentration and $a_{CDOM}(350)$, total fluorescence intensity and the intensities of respective EEM components. DOC concentration and CDOM optical parameters were very well correlated and R^2 values ranged from 0.77 to 0.90. Regression analyses revealed that the non-absorbing DOC fraction, in DOC concentration estimated from CDOM optical parameters, varied with the qualitative composition of the CDOM. DOC concentration and intensity of the humic-like CDOM components characterized by excitation maxima at longer wavelengths have significantly higher estimated non-absorbing DOC compared to the analogous relationships between DOC and intensity of the humic-like CDOM components characterized by excitation maxima at shorter wavelengths. The relationships between DOC concentration and intensity of one of the protein-like components resulted in significantly reduced non-absorbing DOC fraction in DOC concentration estimation. Results of regression analyses between fluorescence intensities of specific EEM components and CDOM-specific absorption coefficients suggest that the relative proportion of humic-like CDOM components (characterized by excitation maximum at longer wavelengths) and the main protein-like component have the most impact on the values of $a^*_{CDOM}(350)$. Based on the relationships between $a_{CDOM}(350)$, Cape Fear River flow, and DOC concentrations, DOC fluxes were estimated for 2002, 2003 and 2004. DOC fluxes varied from 1.5 to 6.2×10^{10} g C yr^{-1}, depending on river flow.

1. Introduction

Oceans play a major role in controlling the world's climate through regulation of atmospheric CO_2 levels by ocean–atmosphere exchange processes (source and sink of CO_2). A large reservoir of carbon is stored mainly in the form of dissolved organic matter (DOM). For this reason, systematic studies of the distribution and cycling of carbon have been conducted since 1980 mainly in the framework of the Joint Global Ocean Flux Studies (JGOFS) program. JGOFS primarily addressed the central oligotrophic gyres of the Atlantic and Pacific Oceans, and both marine Arctic and Antarctic polar regions. Dissolved organic matter is by far the largest pool of organic matter in the sea. About 97% of all organic carbon in the ocean is bound in DOM (Hansell and Carlson, 1998). The estimated carbon mass of DOC is 685 Gt (Hansell and Carlson, 2001). The mass of DOC in the sea is comparable to the mass of carbon in the Earth's atmosphere as CO_2 and the amount of carbon in terrestrial ecosystems. An understanding of the mechanisms and processes regulating the amount of DOM in the sea is critical in order to understand the global carbon cycle. Therefore, research on marine DOM has intensified over last 30 years (Hedges, 2002). The main result of JGOFS was elucidation of the spatial and temporal variability of DOC in oceanic systems and its sources and

sinks on various temporal scales. The dominant source of organic matter in the world's oceans is autochthonous production, which accounts for more than 95% of total organic matter. The input of terrestrial DOM represents only 2–3% of the total oceanic DOM pool, although it may be a dominant source of DOM in coastal zones (Opsahl and Benner, 1997). In the past, DOM has been regarded as a large inert reservoir of carbon in the ocean, which below the oceans' mixed layer is excluded from the current carbon cycle. Numerous studies have revealed that DOM is an active and dynamic component in carbon biogeochemical cycles and plays important roles in marine ecosystems (e.g., Mopper et al., 1991; Hansell and Carlson, 2002; Gonsior et al., 2009). Previous DOC studies were accomplished mainly through field studies and collection of water samples for laboratory analysis (Hansell and Carlson, 2001, 2002). To better assess DOC dynamics in various areas of the world oceans, there is a critical need to apply new techniques for DOC observations, including satellite imagery, that offer greater spatial and temporal resolution.

The components of DOM that absorb light, mainly humic substances, cause water to appear yellowish. For that reason, this colored fraction of DOM was previously named 'Gelbstoff', or yellow substances (Kalle, 1966), but is now commonly referred to as CDOM (chromophoric dissolved organic matter). CDOM absorption is highest in the UV wavelengths and decreases exponentially with increased wavelength (Jerlov, 1976; Kirk, 1994). CDOM is one of the major determinants of the optical properties of natural waters and it directly affects both the quantity and spectral quality of light in the water column (Jerlov, 1976; Blough and Del Vecchio, 2002; Hargreaves, 2003). Through its effects on solar radiation in the water column, CDOM may stimulate or hinder primary production and temperature stratification (e.g., Mopper and Kieber, 2002). Photochemical reactions of CDOM produce 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 can produce complexes with trace metals that are later released into the marine environment during DOM remineralization. Therefore, the ability to differentiate and quantify sources of CDOM and the factors underlying its variability is fundamentally important for understanding biogeochemical cycles in the oceans.

Although the principle optical property of CDOM was established almost 50 years ago, optical properties of CDOM were not a major focus of investigations, even with the JGOFS programs. Ocean color remote sensing has been the primary driver for optical studies of CDOM in the oceans for the last two decades. There are two main aspects responsible for the increased interest in CDOM and its characterization for remote sensing. First, the absorption spectra of chlorophyll *a* and CDOM overlap in the blue region of the electromagnetic spectrum. Application of early remote sensing algorithms, which had not taken into account the presence of CDOM, led to a significant overestimation of chlorophyll *a* concentration, especially in coastal oceans and semi-enclosed seas (IOCCG, 2000). Second, the optical properties of CDOM have allowed ocean color remote sensing studies of organic carbon cycling on global and regional scales. Technological developments in observational techniques, both remote and *in situ*, applied in studies of global biogeochemical cycles, resulted in a better understanding of CDOM distribution in the ocean due to increased sampling resolution in time and space and by linking CDOM with other environmental parameters that control its variability. The number of publications on optical properties of CDOM, its distribution and spatial and temporal variability, and on modification of CDOM optical properties by natural processes has grown considerably during the last two decades. Critical overviews of results have been presented for the numerous studies in coastal environments (Blough and Del Vecchio, 2002, and references therein) and in open oceanic waters (Nelson and Siegel, 2002, and references therein).

Del Castillo (2005) assessed the influence of CDOM on apparent optical properties of sea water and its impact on development of empirical ocean color retrieval algorithms to separate remote sensing reflectance spectra by the contributions of optically active constituents of sea water. In the latest review on CDOM optical properties, Coble (2007) assessed a novel approach to studies on CDOM fluorescence properties and methods leading to a better understanding of cycling of identified CDOM components in aquatic environments. A number of physical, chemical and biological processes all influence the distribution and optical properties of CDOM (see cited reviews and reference therein for detailed descriptions). Among the most important are export of terrestrially-derived CDOM to oceans and its dilution in oceanic waters, photochemical bleaching, bacterial degradation and autochthonous production of CDOM by plankton.

In situ and remote sensing measurements of optical properties of CDOM are easy to conduct and make the use of CDOM absorption or fluorescence as a proxy for DOC concentration very attractive. Although CDOM contributes approximately 20% to the total DOC pool in the open ocean and up to 70% in coastal areas (Coble, 2007), a direct link establishing a global relationship between CDOM and DOC has not been attained. CDOM is a complex mixture of heterogeneous organic compounds, each having individual optical properties. Therefore, the estimation of the universal bulk carbon-specific CDOM absorption coefficient, $a^*_{CDOM}(\lambda)$, defined as the ratio $a_{CDOM}(\lambda)/DOC$, seems almost unfeasible (Woźniak and Dera, 2007). Another aspect that complicates a global DOC–CDOM relationship, is that processes responsible for production, decomposition and distribution of the bulk DOC and CDOM components are decoupled in oceanic systems.

In oligotrophic subtropical gyres and central open ocean areas not in close proximity to terrestrial influence, there is a significant time phase shift between maximum DOC concentration produced by phytoplankton blooms and maximum CDOM absorption (Nelson et al., 1998; Siegel et al., 2002). Additionally, in surface waters, CDOM absorption is quickly diminished by intensive photobleaching (Vodacek et al., 1997; Johannessen et al., 2003). Below the mixing zone, there is usually an increase in CDOM absorption in contrast to the decrease in DOC levels (Nelson et al., 2007). The strong correlation between both $a_{CDOM}(\lambda)$ and DOC exists only in areas where variability of both parameters is controlled by mixing of fresh and oceanic waters. Several studies have reported a good correlation between $a_{CDOM}(\lambda)$ and DOC in coastal areas (Green and Blough, 1994; Vodacek et al., 1995; Ferrari et al., 1996; Vodacek et al., 1997; Ferrari, 2000; Chen et al., 2002; Rochelle-Newall and Fisher, 2002; Del Vecchio and Blough, 2004). These local and highly-variable relationships are valuable for studying carbon cycling in coastal areas because they enable the application of ocean color remote sensing to capture synoptic DOC distribution in fine spatial and temporal resolution (e.g., Del Castillo and Miller, 2008).

We have collected an extensive time series of CDOM optical property data between 2001 and 2005 in the South Atlantic Bight. In this study, fluorescence excitation emission matrix (EEM) spectra were reassessed using a novel technique of statistical modeling, parallel factor analysis, PARAFAC. PARAFAC modeling was applied to identify purely statistical fluorophore components that are responsible for specific regions within EEM spectra (Stedmon et al., 2003). This new approach resulted in the identification of six components (three terrestrial humic-like, one marine humic-like and two protein-like) and established compositional characteristics of CDOM in contrasting waters in the study area as well as revealing temporal variability of derived components (Kowalczuk et al., 2009). Results from PARAFAC modeling and data sets of $a_{CDOM}(350)$ and DOC concentrations were used to achieve the following: i) establish relationships between CDOM fluorescence intensity, absorption coefficient and DOC concentration; ii) assess variability of the carbon-specific CDOM absorption coefficient, $a^*_{CDOM}(350)$ along a salinity gradient; iii) assess the impact of different CDOM components identified by PARAFAC on $a^*_{CDOM}(350)$ and carbon-specific CDOM fluorescence; and iv) apply the derived relationships to estimate DOC export by the Cape Fear River to the coastal ocean under different hydrological regimes.