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Using a Gaussian decomposition approach to model absorption spectra of chromophoric dissolved organic matter

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ABSTRACT

The chromophoric dissolved organic matter (CDOM) is a significant water constituent influencing inherent and apparent optical properties of natural waters and plays a key role in ecosystem functioning. The spectral slope (S) describing the approximate exponential decline in CDOM absorption with increasing wavelength is widely used for tracing changes in the chemical composition of CDOM. The currently accepted method of characterizing CDOM absorption (i.e., fitting a simple exponential model) can lead to loss of information and large errors. We propose a better method for modeling CDOM absorption spectra based on a Gaussian decomposition approach that removes the errors associated with the choice of the spectral range used to estimate S. Using artificially generated spectra with known parameters ($n = 1000$), we show that our method provides robust estimates of S closely resembling the original values. On average, the error on S estimations was 0.16% for the proposed method compared to 27% and 11% for the traditional modeling approaches fitted over 300–700 nm and 240–700 nm respectively. We further demonstrate the ability of the method to decompose and model chromophores present in complex spectra from oceanic water samples from around the world. The proposed method opens avenues for long-term or cross-site comparison studies of the dynamics of the CDOM pool and constitutes a promising supplement to techniques based on CDOM fluorescence.

1. Introduction

Dissolved organic matter (DOM) is the largest dynamic pool of carbon in both marine (Benner, 2002) and freshwater ecosystems (Cole et al., 2007). DOM influences the functioning of aquatic ecosystems in numerous ways. For example, the optical properties of the DOM pool determine underwater light characteristics (Kirk, 1994), the composition of aquatic microbial communities (Foreman and Covert, 2003; Kritzberg et al., 2006), the carbon cycling on local to global scales (Cole et al., 2007) and the mineralization and transport of nitrogen (Markager et al., 2011; Keller and Hood, 2011; Jørgensen et al., 2014). Chemically, the DOM pool is complex and only a small fraction can easily be characterized with chemical methods (Benner, 2002; Seitzinger et al., 2005). Optical techniques such as absorbance and fluorescence have been developed to characterize the DOM pool in aquatic ecosystems (Coble et al., 1990; McKnight et al., 2001). These techniques have their limitations, as it is difficult to link optical characteristics directly to the chemical composition. Nevertheless, they are useful as they are rapid, and therefore cost effective, relative to chemical analyses.

Chromophoric dissolved organic matter (CDOM) is the optically active fraction of the DOM pool. It is well known that optical characteristics of the CDOM pool relate to its biochemical characteristics such as aromaticity (Weishaar et al., 2003) and molecular size (Sharma and Schulman 1999; Helms et al., 2008). CDOM is responsible for much of the underwater variability in light attenuation (Kirk, 1994) and its optical properties are commonly used as a proxy to trace the origin and the dynamic of the DOM pool over time and space in many aquatic ecosystems (McKnight et al., 2001; Stedmon and Markager, 2001; Baker and Spencer, 2004; Yamashita et al., 2013; Jørgensen et al., 2014). An adequate description of the absorption properties of CDOM is necessary in order to understand photochemical and bio-optical processes such as primary production (Markager et al., 2004; Thrane et al., 2014) and to parametrize dynamic ecosystem models (Massicotte and Frenette, 2013; Maar et al., 2016) and remote sensing applications such as ocean color algorithms (Bélanger et al., 2008).

Given that UV–visible absorption spectra of CDOM decrease approximately exponentially with increasing wavelength, different exponential models have been proposed to extract quantitative information about optical properties of CDOM (reviewed in Twardowski et al. (2004)). Eq. (1) presents the most common approach (Stedmon and Markager, 2001):

$$\mathrm{aCDOM}(\lambda) = \mathrm{aCDOM}(\lambda 0)e^{-S(\lambda-\lambda 0)} + K \quad (1)$$

where aCDOM is the absorption coefficient (m^{-1}), λ is the wavelength (nm), $\lambda 0$ is a reference wavelength (nm), K is a background constant

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(m^{-1}) accounting for scatter in the cuvette and drift of the instrument and S is the spectral slope (nm^{-1}) that describes the approximate exponential rate of decrease absorption with increasing wavelength. Higher slopes indicate a more rapid decrease in absorption with increasing wavelength. The S parameter is frequently used as a proxy for tracing photochemical and microbial-induced changes of CDOM (Moran et al., 2000; Twardowski et al., 2004; Helms et al., 2013) or to determine its origin (Stedmon and Markager, 2001).

Eq. (1) assumes that absorption spectra follow a continuous exponential decrease as wavelength increases. If this assumption was true the spectral range (or the wavelength interval) used to fit the data should not influence the value of S. However, it is common to observe deviations, shoulders or peaks in absorption spectra (Fig. 1A, B). In these situations, the usefulness of S for characterizing DOM is limited by the spectral range over which it is calculated (Helms et al., 2008). Different spectral ranges, e.g., 300–700 nm, 275–295 nm, 350–400 nm, 280–650 nm, have been proposed to estimate S (Twardowski et al., 2004; Helms et al., 2008; Osburn et al., 2009). Using a narrow wavelength range often provides a different result from that obtained with a broader range (Twardowski et al., 2004) but even broad and quite similar spectral ranges (ex: 240–700 nm vs 300–700 nm) can produce important differences in the estimation of S (Fig. 1A, B). Therefore, the dependence of S on the spectral range over which it is calculated severely limits our ability to compare results from the literature and hamper our understanding on how S varies in different aquatic ecosystems on the global scale. This is a serious issue since about three-quarters of the variability in S from the literature can be explained by the different spectral ranges used in each study (Twardowski et al., 2004). Another shortcoming of the current modeling approaches is that although high determination coefficients are often observed ($R^2 > 0.99$, Fig. 1), residuals from the models often show patterns that clearly violate the homoscedasticity assumption for regression models of uncorrelated and normally distributed residuals (Fig. 1C, D). This suggests that current modeling approaches are not fully capturing or exploiting all the information provided in CDOM spectra.

In this study, we propose a new method to model CDOM absorption spectra. The first objective is to obtain robust estimates of S that are independent of the spectral range used and therefore more reliable and comparable among studies. The second objective is to develop a method that can identify absorption peaks from specific chromophores in spectra. Such peaks can potentially provide additional information about the CDOM pool and dynamics of specific chromophores. The underlying hypothesis in our approach is that specific compounds, or structures in larger molecules, in significant amounts will show up as peaks or shoulders in absorption spectra causing deviations from the expected exponential decay curve (Fig. 1). The proposed method is based on a Gaussian decomposition approach that identifies and models spectral regions where peaks are occurring. Simulated artificial spectra with known characteristics have been used to evaluate the capability of the method to retrieve the true properties of complex spectra. We also tested the method on 290 measured CDOM spectra from the third Danish Galathea expedition that circumnavigated the world in 2006–2007.

2. Methods

2.1. Modeling framework

The new modeling framework is based on two components. The first component models the general exponential decrease in CDOM absorption with increasing wavelength (Eq. (1)). The second component identifies and models regions deviating from the continuous exponential decay curve. A Gaussian decomposition approach is used to model the

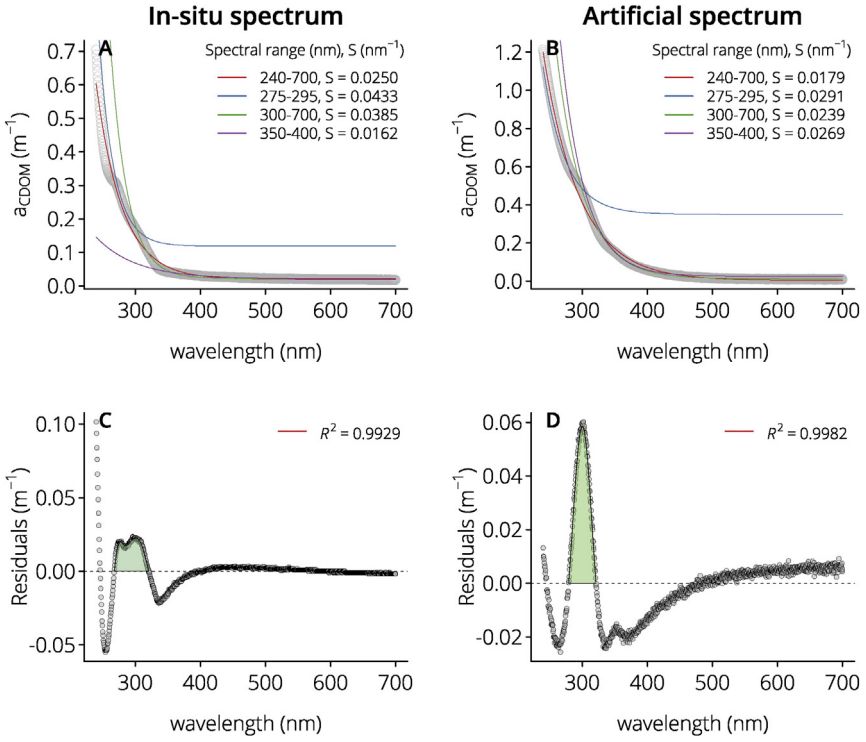

Fig. 1. Absorption spectra (gray dots) and models (lines) fitted using Eq. (1) on (A) in situ and (B) simulated data (parameters used: $a0 = 0.4$, $S = 0.02$, $K = 0.01$; $\lambda 0 = 295$). Fits were obtained using the most common spectral ranges used in the literature (see legend). Residual plots for the model using the complete spectral range (240–700 nm) on (C) in situ and (D) simulated data. Green shaded polygons represent possible deviations not accounted for by the model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)