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A model for remote estimation of ultraviolet absorption by chromophoric dissolved organic matter based on the global distribution of spectral slope

Chantal M. Swan [a,*], Norman B. Nelson [a], David A. Siegel [a,b], Erik A. Fields [a]

[a] Earth Research Institute, University of California, Santa Barbara, CA 93106, USA
[b] Department of Geography, University of California, Santa Barbara, CA 93106, USA

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ABSTRACT

Absorption of ultraviolet radiation (UV, 280–400 nm) by chromophoric dissolved organic matter (CDOM) precedes a host of light-sensitized surface ocean processes relevant to global climate. These include photo- and biogeochemical cycling of organic material, release of sulfur and carbon-containing gases to the atmosphere, and the photoprotection of marine microorganisms. Synoptic CDOM absorption data in the UV is highly desired yet difficult to estimate by satellite methods as the atmosphere interferes with direct detection of water-leaving UV radiance. The absorption spectrum of CDOM is typically modeled as an exponential function in which a spectral slope parameter, S, describes the rate of decrease in absorption with increase in wavelength. Significant functional relationships are observed in aquatic environments between S and the CDOM absorption coefficient at 443 nm, $a_{CDOM}(443)$. In this paper, we use a large, systematic dataset of spectroscopic CDOM measurements from the U.S. CO_2/CLIVAR Repeat Hydrography Survey to examine the relationship between S and $a_{CDOM}(443)$ as a means to model $a_{CDOM}(\lambda)$ in the UV from ocean color. Our resultant model predicts $a_{CDOM}(\lambda)$ at wavelengths from 325 to 412 nm from the absorption coefficient of colored dissolved and detrital materials (CDM) at 443 nm, $a_{CDM}(443)$, retrieved by an existing semi-analytical ocean color algorithm. Expected agreement (near 1:1) with the training dataset was achieved ($r^2 = 0.71$–0.85, $p = 0$, $n = 127$). Considering inherent satellite data uncertainties as well as the model's limitations in regions with potential terrestrial influence, good correspondence between modeled and *in situ* values was observed during independent validation with open ocean CDOM data, such as from BIOSOPE ($r^2 = 0.77$–0.85, $p < 0.05$, $n = 29$). The model has immediate application in global scale assessments of photochemical rate processes and CDOM cycling in the open ocean due to its simplicity and optimization using a large base of field data (>7500 samples) from diverse Case I waters.

1. Introduction

Chromophoric dissolved organic matter (CDOM) plays a crucial role in marine systems *via* its absorption of ultraviolet radiation (UV, 280–400 nm). Over broad areas of the upper ocean, CDOM can account for as much as 90% of total non-water UV absorption (Johannessen et al., 2003; Nelson et al., 1998; Zepp et al., 2007). UV absorption by CDOM sensitizes a suite of photochemical reactions at the sea surface including dimethylsulfide photolysis (Kieber et al., 1996; Toole et al., 2006); CO_2, CO, and COS release (Mopper & Kieber, 2002; Stubbins et al., 2006; Zafiriou et al., 2008); and transformation of microbial bioavailability of organic matter (Benner & Biddanda, 1998). The quantity of UV absorbed by oceanic CDOM is thus an essential factor in the study of such reactions and their level of impact on biogeochemical cycles and climate (Reader & Miller, 2011; Whitehead & de Mora, 2000; Zepp et al., 2007).

To make global-scale assessments of photochemical processes, synoptic data are essential and primarily acquired through remote sensing. Ocean color algorithms (Carder et al., 1999; Lee et al., 2002; Mannino et al., 2008; Maritorena et al., 2002, 2010; Morel & Gentili, 2009) have proven to be critical for determining visible light absorption by CDOM and its impact on the accuracy of chlorophyll estimates from space (Carder et al., 1989; Nelson & Siegel, 2013; Siegel et al., 2002, 2005a, 2005b, 2013). Recently published empirical models have made use of remotely sensed visible reflectance ratios (or multiple linear regression thereof) to predict the irradiance attenuation coefficient, $k_d(\lambda)$, in the UV, which when combined with knowledge of the relation between $k_d(\lambda)$ and the CDOM absorption coefficient, $a_{CDOM}(\lambda)$, can be used to extrapolate $a_{CDOM}(\lambda)$ in the UV assuming a single spectral slope value (Fichot et al., 2008; Johannessen et al., 2003). The training datasets used to develop even the most sophisticated working algorithms of this sort (*SeaUV* and *SeaUV*$_C$ algorithms, Fichot & Miller, 2010; Fichot

* Corresponding author at: Institute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, Switzerland. Tel.: +41 44 632 09 72.
E-mail address: chantal.swan@usys.ethz.ch (C.M. Swan).

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et al., 2008) tend to favor the U.S. coastal water bodies and North Atlantic Ocean. The authors themselves note the need for datasets inclusive of a greater variety of optical domains to improve parameterizations, especially due to assumptions inherent when using empirical relationships between optical properties (Fichot et al., 2008). Larger field datasets and additional approaches for estimating UV absorption by CDOM that are optimized to handle both productive pelagic regimes as well as the vast oligotrophic deserts of the open ocean, the subtropical gyres, are thus desirable. The general need to incorporate field data from diverse oceanographic provinces in bio-optical model development serves as motivation for the present study. Here we employ a large, systematic set of global field observations of CDOM in a novel yet simple approach toward predicting $a_{CDOM}(\lambda)$ in the UV from the remotely sensed absorption coefficient of colored dissolved and detrital materials (CDM) at 443 nm, $a_{CDM}(443)$, which is the quantity retrieved by existing ocean color algorithms.

Spectral light absorption by CDOM in the ocean, which can be measured either by *in situ* instruments or from discrete water samples *via* absorption spectroscopy, is frequently modeled as an exponential function over a short wavelength interval (Eq. (1)) (Bricaud et al., 1981):

$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_o)\exp^{-S(\lambda-\lambda o)} \quad (1)$$

where λ and λ_o are a desired known wavelength and reference wavelength, respectively, and S is a spectral slope parameter modeled through either a linear fit to the log-transformed spectrum, or a nonlinear fit to the curve of the spectrum over the spectral range considered (Stedmon et al., 2000; Twardowski et al., 2004).

The selection of wavelength interval as well as the fitting routine used in computing S can greatly affect the interpretation of data, which has often complicated comparison of results across CDOM studies (Del Vecchio & Blough, 2004; Stedmon et al., 2000; Twardowski & Donaghay, 2002; Twardowski et al., 2004). On the other hand, the option of wavelength interval selection for computing S has resulted in a variety of investigations into CDOM composition and dynamics using the spectral slope parameter. Several permutations, including ratios of S determined for progressive wavelength intervals, as well as the functional relationship of S to the magnitude of CDOM absorption, have been proposed as investigative tools for understanding both source and diagenetic state of CDOM in aquatic environments (Del Castillo & Coble, 2000; Helms et al., 2008; Kitidis et al., 2006; Loiselle et al., 2009a, 2009b; Nelson et al., 2007, 2010; Stedmon & Markager, 2003; Weishaar et al., 2003; Zhang et al., 2007). An inverse relationship between S and $a_{CDOM}(\lambda)$ at a given wavelength has been documented within a number of studies (Bricaud et al., 2010; Del Castillo & Coble, 2000; Rochelle-Newall et al., 2004; Stedmon & Markager, 2001, 2003; Stedmon et al., 2000; Vodacek et al., 1997; Yacobi et al., 2003). This relationship has been used to diagnose the relative contributions of terrestrial *versus* marine organic matter, as well as the effect of end-member mixing on the optical properties of coastal waters (Del Vecchio & Blough, 2004; Stedmon & Markager, 2001, 2003).

In the open ocean, increases in S are generally an indication of the process of solar photobleaching, as greater proportional absorption loss relative to initial occurs with increase in wavelength across the UV-visible spectrum (Del Vecchio & Blough, 2004; Swan et al., 2012; Twardowski & Donaghay, 2002; Vähätalo & Wetzel, 2004; Vodacek et al., 1997). Photobleaching regulates the global surface distribution of CDOM as modulated by autochthonous production pathways and vertical mixing of CDOM. Climatology of $a_{CDM}(443)$ in the surface ocean (Fig. 1) from SeaWiFS reveals distinct patterns that support this, reflecting the relative impact of solar bleaching of CDOM with latitude, and vertical input of elevated CDOM from sub-thermocline waters (Nelson & Siegel, 2013; Siegel et al., 2002, 2013). A stark contrast is observed, for example, between the belt of elevated CDOM abundance in the eastern equatorial Pacific upwelling region relative to the CDOM-depleted waters that have longer surface residence times, such as the subtropical gyres of the major ocean basins (Fig. 1). This suggests that throughout most of the open ocean where terrestrial sources of organic material have little influence, photobleaching is the primary control on the relationship between S and $a_{CDOM}(\lambda)$. The univocal nature of the relationship provides a potential means for extrapolating satellite-derived $a_{CDM}(443)$ into the UV, assuming the absence of riverine influence (Stedmon & Markager, 2001).

In this study, we develop a model based on the relation between S and $a_{CDOM}(443)$ from thousands of field measurements of CDOM absorption spectra from a wide range of oceanic biomes, including temperate shelf seas, waters in proximity to the Antarctic ice shelf, the oligotrophic subtropical gyres in both hemispheres, productive subarctic gyres and active upwelling zones at the equator. Model coefficients are then tuned using input of $a_{CDM}(443)$ from the semi-analytical GSM algorithm (Siegel et al., 2002) in order to estimate CDOM absorption over 325–412 nm from ocean color. In the following sections we describe the development, validation and interpretation of the model using archival data from SeaWiFS and MODIS Aqua, and indicate its potential applications.

2. Data and methods

2.1. CLIVAR data

Global field measurements of CDOM absorption used in model development and validation were acquired through spectroscopy of filtered seawater samples collected along selected transects as part of the U.S. CO_2/CLIVAR Repeat Hydrography Survey from 2003 through 2008. The station locations of data from transects used in the present study are superimposed on the surface map of $a_{CDM}(443)$ (Fig. 1) and listed along with dates of collection in Tables 1 and 2. The model development dataset consisted of 8 CLIVAR transects totaling 7611 discrete measurements of CDOM absorption throughout the global ocean in regions with contrasting trophic conditions, and from depths ranging from the surface to 5500 m deep.

The A20 and A22 sections sampled waters of the Sargasso Sea, Gulf Stream, U.S. continental shelf and sections of the Caribbean Sea, as well as the North Atlantic subtropical mode water (relatively low in CDOM) and North Atlantic Deep Water masses (Nelson et al., 2007). The P16S and P16N transects collectively covered the meridional North Pacific along 210° longitude, sampling the productive subarctic gyre and coastal waters near Alaska, the eastern equatorial Pacific upwelling zone characterized by elevated CDOM, the subtropical gyres in both hemispheres that are relatively low in CDOM, and Antarctic circumpolar and bottom waters (Swan et al., 2009). The I8S and I9N transects spanned the meridional Indian Ocean along approximately 90° longitude sampling Southern Ocean waters close to the ice shelf, then northward into the Indian Ocean equatorial regime as influenced by the Indonesian throughflow, and up into the relatively fresh and warm waters of the Bay of Bengal. The I6 transect sampled the polar front of the Indian sector of the Southern Ocean as well as the relatively fresh and highly productive surface waters of the Agulhas current system flowing around South Africa. Finally, the P18 transect further sampled waters of the eastern Pacific, including the hyper-oligotrophic subtropical gyre in that region. The model development dataset derives from a single methodology, comprising the first large systematic dataset of CDOM that captures the range of variability in CDOM spectral signature throughout the world ocean, thus optimizing the potential for global applicability of the model.

A subset of CLIVAR data consisting of 3 transects from the surface ocean spanning both hemispheres (CLIVAR A16N, A16S and P2) was reserved for independent validation of the model. The A16N cruise sampled waters of the North Atlantic, including subarctic freshwater lenses originating from Arctic waters flowing through the Denmark Strait, as well as waters in the vicinity of the North Atlantic Deep