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Characterization of light absorption by chromophoric dissolved organic matter (CDOM) in the upper layer of the Red Sea

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ABSTRACT

The absorption coefficient of chromophoric dissolved organic matter (CDOM) is a major variable used in developing robust bio-optical models and understanding biogeochemical processes. Over the last decade, the optical properties of CDOM in the open sea have been intensely studied. However, their variations in clear water are poorly documented, particularly in the Red Sea, owing to the absence of in situ measurements. We performed several cruises in the Red Sea to investigate the spatial distribution of the absorption coefficient of CDOM. The spectral absorption coefficients were determined from 400 nm to 740 nm using a WETLabs ac-s hyper-spectral spectrophotometer. In general, we found a latitudinal gradient in the CDOM absorption coefficient at 443 nm ($a_{CDOM}(443)$) from south to north that is likely influenced by the exchange of water through the strait of Bab-el-Mandeb and the thermohaline circulation of the Red Sea. However, high $a_{CDOM}(443)$ values were observed in the northern Red Sea due to the existence of a sub-mesoscale feature that may induce an increase in phytoplankton production and lead to CDOM production. The $a_{CDOM}(443)$ covaried with the chlorophyll a concentration ([Chl a],) despite a high scatter. Furthermore, the $a_{CDOM}(443)$ for a given [Chl a] concentration was higher than those predicted by global ocean bio-optical models. This study advances our understanding of CDOM concentration in the Red Sea and may help improve the accuracy of the algorithms used to obtain CDOM absorption from ocean color.

1. Introduction

Historically known as "gelbstoff" (Kalle, 1966) and, in English, as "yellow substances" (Shifrin, 1988) due to its high humic matter content, the chromophoric dissolved organic matter (CDOM) is the colored portion of the dissolved organic matter (DOM) in the ocean (Laane and Koole, 1982; Thurman, 1985; Williams and Druffel, 1988; Laane and Kramer, 1990). Marine dissolved organic carbon (DOC) represents the largest reservoir of reduced carbon in the ocean (Hansell et al., 2002) and plays an essential role in the global carbon cycle (Mopper and Kieber, 2002). CDOM is one of the main factors that affects the transmission of light in seawater (Siegel et al., 2002; Nelson and Siegel, 2013). This is crucial for evaluating underwater light availability in seawater, which is an essential variable for several marine organisms (Siegel et al., 1995; Siegel and Michaels, 1996; Vodacek et al., 1997; Nelson et al., 1998; Blough and Del Vecchio, 2002). CDOM affects structures of the marine food web (Smith et al., 1992; Herndl et al., 1993; Häder et al., 1998) by influencing both primary and microbial production. In coastal waters, the distribution and concentration of CDOM are mainly controlled by terrestrial runoff and riverine inputs (Kalle, 1938; Højerslev, 1982; Carder et al., 1989; Twardowski and Donaghay, 2001; Blough and Del Vecchio, 2002; Del Vecchio and Blough, 2004; D'Sa and DiMarco, 2009), whereas in open waters, CDOM has primarily autochthonous origins (Nelson et al., 1998, 2004; Nelson and Siegel, 2002; Steinberg et al., 2004; Ortega-Retuerta et al., 2009; Shank et al., 2010; Organelli et al., 2014). Many studies have shown that CDOM is produced through diverse biological processes (Nelson et al., 1998, 2004; Nelson and Siegel, 2002; Steinberg et al., 2004; Ortega-Retuerta et al., 2009; Shank et al., 2010). CDOM results from both microbial production and degradation processes (Nelson et al., 1998, 2004; Steinberg et al., 2004; Yamashita and Tanoue, 2004), and it can be degraded by photobleaching in surface waters (Vodacek et al., 1997; Nelson et al., 1998, 2004; Siegel et al., 2002, 2005; Twardowski et al., 2002; Del Vecchio and Blough, 2004). Generally,

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CDOM in the open ocean is controlled by biological processes and photobleaching. The spatial distribution of CDOM is influenced by transport, convection, upwelling and other processes that affect water mass circulation.

Measuring the CDOM light absorption spectrum, $a_{CDOM}(\lambda)$, to study its distribution and abundance in the open ocean has been a widely used approach over the past decade (Babin et al., 2003; Siegel et al., 2002; Nelson and Siegel, 2013; Organelli et al., 2014). The slope of CDOM absorption from 400 to 500 nm, S_{CDOM}, can be used to indicate changes in the CDOM composition by incorporating ratios of humic to fulvic acids (Carder et al., 1989; Blough and Green, 1995; Vodacek et al., 1997; Moran et al., 2000; Helms et al., 2008). Changes in S_{CDOM} are detected when CDOM is produced by bacteria (Ortega-Retuerta et al., 2009; Yamashita et al., 2013) compared to CDOM generated by others pelagic organisms. Furthermore, numerous field studies (Vodacek et al., 1997; Nelson et al., 1998; Del Vecchio and Blough, 2002, 2004; Twardowski et al., 2002; Swan et al., 2009; Bricaud et al., 2012) have shown an increase in S_{CDOM} associated with a decrease in $a_{CDOM}(\lambda)$ in response to the solar bleaching of CDOM in surface waters. Because CDOM mostly absorbs solar radiation in the UV and blue regions of the spectrum (Carder et al., 1989; Kirk, 1976, 1999; Visser, 1984), CDOM absorption and the resulting remote sensing reflectance may result in inaccuracies when determining the chlorophyll a concentration from satellite imagery analysis, particularly when using both empirical and semi-analytical algorithms (Morel, 1980; Carder et al., 1991; Siegel et al., 2005; Morel and Gentili, 2009a). This generally results in an overestimation of the chlorophyll a concentration in seawater when the CDOM concentrations are high. For example, from both ocean color and in situ data, Morel and Gentili (2009b) noticed that the CDOM concentration in the Mediterranean Sea was twice as high as those measured at the same latitude and chlorophyll a concentration in the Atlantic Ocean. Southeast of the Mediterranean Sea, the Red Sea is a marginal, semi-enclosed oligotrophic basin. Brewin et al. (2015) suggested that a refractory component of CDOM that is resistant to photobleaching might accumulate over time.

The Red Sea is one of the saltiest and warmest deep seas in the world (Belkin, 2009; Longhurst, 2007; Raitsos et al., 2011, 2013). Its typical seawater temperature varies from 21 °C to 28 °C in the north and from 26 °C to 32 °C in the south (Nandkeolyar et al., 2013). The Red Sea is characterized by little precipitation, small riverine discharge (Patzert, 1974) and strong evaporation rates (Sofianos and Johns, 2003). In addition, the Red Sea is represented by horizontal circulation that is mainly dominated by eddies (Yao et al., 2014a, 2014b). The southern part of the Red Sea is connected to the Arabian Sea (Northern Indian Ocean) via the strait of Bab-el-Mandeb. In the north, the Red Sea connects to the Mediterranean Sea via the Suez Canal, although the exchange with the Mediterranean Sea is much less than that with the Gulf of Aden. The Red Sea is considered a large marine ecosystem (Belkin, 2009), and it supports coral reefs, mangroves and seagrass beds that provide crucial habitats for a large variety of marine organisms (Berumen et al., 2013; Almahasheer et al., 2016). The Red Sea is distinguished by strong latitudinal gradients of temperature, salinity and inorganic nutrient concentrations from south to north, primarily dependent on the exchange of water through the strait of Bab-el-Mandeb and the thermohaline circulation of the Red Sea. During the Arabian Sea southwest monsoon season (June to September), the monsoon-driven wind reversal modifies the circulation dynamics of the Bab-el-Mandeb strait, leading to an influx of cool, less salty, and nutrient-rich Gulf of Aden Intermediate Water (GAIW) from the Indian Ocean into the southern Red Sea, increasing phytoplankton biomass and primary production (Neumann and McGill, 1962; Sofianos and Johns, 2007; Raitsos et al., 2013, 2015; Churchill et al., 2014; Dreano et al., 2016; Wafar et al., 2016; Gittings et al., 2017). During the winter monsoon (October to April), the reversal of the wind direction induces a northward advection of cooler, fresher, nutrient-rich surface waters into the Red Sea from the Gulf of Aden.

The Red Sea is deemed oligotrophic mainly due to the depletion of nutrients in the upper layer. This nutrient depletion becomes especially important in the central and northern Red Sea in response to northward advection. The northern Red Sea is marked by significant physical variability, with deep mixed layers occurring in the winter and strong stratification in the summer. These dynamics drive the seasonal changes in trophic levels from oligotrophy in summer to bloom conditions in winter-spring (Raitsos et al., 2013). Based on remotely sensed data, the maximum chlorophyll a concentrations in the north-central Red Sea rise during winter but remain the lowest throughout the Red Sea during this time. Raitsos et al. (2013) suggested that anti-cyclonic eddies may be a potential mesoscale feature responsible for the higher productivity observed in the region (particularly during summer). The eddies occupying the central Red Sea are bounded by coastal coral reef structures and could influence the Red Sea ecosystem via the exchange of nutrients, chlorophyll a, and other organic matter between the open sea and coastal reefs.

The interaction of wind and thermohaline processes facilitate an intrusion of cold, low-salinity and nutrient-rich waters into the upper layers of the Southern Red Sea from the Gulf of Aden, which makes this part of the Red Sea a more productive region than the northern and central parts. The seasonal cycle of phytoplankton biomass in the Red Sea appears to be controlled by physical processes (winter mixing, mesoscale eddies, horizontal advection and the influx of water from Bab-el-Mandeb) that determine the availability of nutrients to the euphotic layer. However, dust deposition and nutrient input from coral reefs may also contribute to the productivity of the Red Sea. Essential information about the seasonal cycle of the phytoplankton biomass in the Red Sea is provided in the recent publications of Raitsos et al., (2013, 2015), Triantafyllou et al. (2014) and Racault et al. (2015).

Bricaud et al. (2010) and Morel and Gentili (2009a) proposed empirical global bio-optical relationships between the inherent optical properties (IOPs) and some biogeochemical parameters, such as the chlorophyll a concentration, in oligotrophic waters. These relationships can then provide the ability to assess the variability of biogeochemical parameters from in situ measurements or ocean color.

Although robust statistical relationships (Bricaud et al., 2010; Morel and Gentili, 2009a) were established between the CDOM absorption coefficients and chlorophyll a, representative of the open ocean, no direct measurements of CDOM absorption have been collected in the Red Sea until now. The Red Sea waters and the regional empirical bio-optical relationships can be more affected by little precipitation, small riverine discharge and desert dust events than other regions are. The recent study of Brewin et al. (2015) assessed the bio-optical characteristics of the Red Sea, and the authors hypothesized that the Red Sea has a higher CDOM concentration per unit of chlorophyll a than do other regions. They suggested that the overestimation of the chlorophyll a concentration in the Red Sea, as retrieved from the standard bio-optical algorithms used to process ocean color remote sensing measurements, could have been due to an excess of CDOM absorption per unit of chlorophyll a. However, this hypothesis has never been tested.

The aim of this study was to examine if an excess of CDOM exists in Red Sea waters per unit of chlorophyll a. Particular attention was given to the CDOM absorption coefficients because these coefficients have not been measured in previous studies. Using in situ measurements of CDOM absorption collected during different cruises performed in the Red Sea (from October 2014 to April 2015), we investigated the spatial variations in CDOM concentration, as derived from measurements of spectral light absorption coefficients and the CDOM spectral slope values from the surface down to 200 m depth. In addition to documenting CDOM distribution and its relationship with chlorophyll a, this study aims to advance the state of the art regarding CDOM light absorption coefficients and provide key information to develop regional algorithms such that the chlorophyll a and CDOM absorption coefficients can be retrieved accurately.

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