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Decomposition of in situ particulate absorption spectra

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ABSTRACT

A global dataset of in situ particulate absorption spectra has been decomposed into component functions representing absorption by phytoplankton pigments and non-algal particles. The magnitudes of component Gaussian functions, used to represent absorption by individual or groups of pigments, are well correlated with pigment concentrations determined using High Performance Liquid Chromatography. We are able to predict the presence of chlorophylls *a*, *b*, and *c*, as well as two different groups of summed carotenoid pigments with percent errors between 30% and 57%. Existing methods of analysis of particulate absorption spectra measured in situ provide for only chlorophyll *a*; the method presented here, using high spectral resolution particulate absorption, shows the ability to obtain the concentrations of additional pigments, allowing for more detailed studies of phytoplankton ecology than currently possible with in-situ spectroscopy.

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1. Introduction

The absorption of light in the ocean is routinely used to infer the concentration of the absorbing constituents in seawater. The total particulate absorbing matter is composed of both phytoplankton and non-algal particles such as detritus and minerals. Different phytoplankton groups have evolved unique pigment assemblages for optimizing light absorption, both for photosynthetic and photoprotective purposes. These different pigment assemblages result in variations in phytoplankton absorption spectra, which can be used to characterize phytoplankton populations, for example based on pigment ratios (Mackey et al., 1996) or size classification algorithms (Uitz et al., 2006).

Extracting information about different pigments and phytoplankton groups from particulate absorption spectra is a challenging task that past studies have met with mixed success. Hoepffner and Sathyendranath (1991, 1993) and Lohrenz et al. (2003) used Gaussian functions to represent absorption by different chlorophyll and carotenoid pigments and decompose laboratory-measured phytoplankton absorption spectra. Other approaches include derivative analysis (Bidigare et al., 1989), discriminant analysis (Johnsen et al., 1994), neural networks (Bricaud et al., 2007), similarity algorithms (Millie et al., 1997; Kirkpatrick et al., 2000), and inverse modeling for extraction of pigment-specific absorption spectra (Moisan et al., 2011). However, in all of these past studies, laboratory measurements of phytoplankton absorption spectra have been used, either with phytoplankton cultures or with natural samples collected in situ. In this study, we use a Gaussian decomposition method to extract pigment information from particulate absorption spectra measured in situ; spectra are measured by pumping water through an instrument deployed on board and therefore water samples are not handled. In situ data can be obtained with high temporal and spatial resolution under highly variable environmental conditions, and thus provide a wide range of phytoplankton absorption spectra through both space and time.

2. Data and methods

2.1. Particulate absorption and pigment data

The spectral absorption data used in this work were measured with a WETLabs AC-S instrument, an in situ spectrophotometer that provides hyperspectral absorption and attenuation data in the range 400–750 nm with ~4 nm resolution (Moore et al., 1997; Rhoades et al., 2004). The spectral range and measurement wavelengths vary slightly between sensors and for a specific sensor following factory calibration. Several different AC-S instruments were used during the collection of spectral absorption in this study. The instruments were deployed using an in-line system that allows nearly continuous sampling of surface ocean water; details of the flow-through system are provided in Slade et al. (2010). Total absorption was measured on unfiltered bulk seawater, followed by 0.2 μm-filtered measurements for ten minutes every hour, or five minutes every half-hour in coastal waters. Particulate absorption data is obtained using a series of steps; after one-minute binning, 0.2 μm filtered data are interpolated to the time of the total measurement and are subtracted:

$$a_p(\lambda) = a_{tot}(\lambda) - a_{0.2\ \mu m}(\lambda) \quad (1)$$

where $a_p(\lambda)$ is particulate absorption, $a_{tot}(\lambda)$ is total absorption, and $a_{0.2\ \mu m}(\lambda)$ is the filtered fraction. The resulting $a_p(\lambda)$ spectra are then simultaneously corrected for small temperature differences between total and filtered measurements and for scattering using the proportional scattering correction (Slade et al., 2010). In the rare cases where the c-side lamp of the AC-S burned out mid-leg (~5% of match-up data points used in this study), a flat scattering correction was applied, similar to the correction used with laboratory spectrophotometers (Boss et al., 2013).

Five different AC-S sensors from four different labs (serial numbers 007, 043, 057, 082, 091) were used with the flow-through technique during the Tara Oceans expedition, a 2.5 year-long expedition from fall of 2009 to spring of 2012 along a 57,000 nautical miles oceanic route spanning the Indian, Atlantic and Pacific oceans (Karsenti et al., 2011). The particulate absorption data from Tara Oceans have been binned to one-minute temporal resolution. Data points with coincident HPLC data are selected from this one-minute binned dataset (hereafter "match-up points"); 87 of the 210 match-up