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## Characterization of phytoplankton variability in the Cariaco Basin using spectral absorption, taxonomic and pigment data

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## ABSTRACT

The spectral absorption coefficient of marine phytoplankton provides information on phytoplankton community structure, biomass, and general physiological conditions. These variables are necessary for understanding and predicting ocean productivity, carbon fluxes, underwater light propagation, water quality, and for assessing marine photochemical processes. The Cariaco Basin, located on the continental shelf of Venezuela in the south-eastern Caribbean Sea, is the site of the CARIACO Ocean Time-Series project. Since 1995, CARIACO has collected bio-optical (hyperspectral inherent and apparent optical properties – IOPs and AOPs, respectively), biogeochemical and ecological observations to characterize local ecosystem variations in response to regional and global changes in climate. We examine phytoplankton taxonomic and pigment time series data collected by this program between 2006 and 2012 to understand how seasonal changes in these parameters relate to bio-optical data (i.e., absorption spectra). TChla and accessory pigments varied seasonally in response to changes in the phytoplankton community composition, with higher concentrations of microphytoplankton ( $>20\ \mu\text{m}$ ; 45%) during upwelling (December–April) than during the rainy season (16%; May/June–October/November). Picophytoplankton ( $<2\ \mu\text{m}$ ) dominated during the rainy season (66%). The absorption properties also exhibited seasonal variations. Diagnostic pigments could not be identified in a quantitative way using derivative analysis of phytoplankton absorption, likely because of overlapping of absorption spectra among the pigments present. The POC:TChla ratio at CARIACO was variable and dependent on bulk carbon (not necessarily related to phytoplankton) and the functional groups present at any given time, underscoring the fact that using a fixed ratio of POC:Chla in biogeochemical models can lead to large uncertainties in carbon budgets from coastal zones. Low POC:TChla was associated with microphytoplankton size class (diatoms), while picophytoplankton (cyanobacteria) exhibited higher ratios. These results contribute to furthering our understanding of coastal phytoplankton dynamics and how they relate to optical signatures.

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### 1. Introduction

Advances in bio-optical methods to study phytoplankton focus on the retrieval of products such as pigment concentration, phytoplankton size classes, and functional types from bio-optical data (see IOCCG, 2014 for a complete review). Resolving shifts in phytoplanktonic communities is important to understand the impacts of both natural and anthropogenic changes on marine systems (Le Quere et al., 2005; Muller-Karger et al., 2014). There is a need to acquire more information on phytoplankton community structure, pigment distribution and bio-optical properties in order to further the development of algorithms required for a true global characterization of phytoplankton biodiversity from remote sensing (Devred, Sathyendranath, Stuart, & Platt, 2011; Devred et al., 2013).

The biogeochemistry and optical properties of continental margin waters vary widely because of high biological productivity, inputs of land-derived material, and resuspension of benthic material (D'Sa, Miller, & Del Castillo, 2006; Hoepffner & Sathyendranath, 1992). Additionally, these regions are particularly sensitive to environmental shifts, and their hydrographic and biogeochemical conditions can change within short timescales; resolving shifts in phytoplanktonic populations in these ecosystems is therefore important to better determine the impacts of climate change on coastal marine systems (e.g., Le Quere et al., 2005).

Features of the spectral phytoplankton absorption coefficient have been used to infer phytoplankton size and taxonomic information (Bricaud & Stramski, 1990; Bricaud, Claustre, Ras, & Oubelkheir, 2004; Ciotti, Lewis, & Cullen, 2002; Vijayan & Somayajula, 2014). These techniques are not as sensitive as direct pigment analyses, especially in optically-complex waters with high spatial and temporal variability in both phytoplankton and detritus concentration and composition (Bricaud & Stramski, 1990; Bricaud et al., 2004; Ciotti et al., 2002).

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Nevertheless, hyperspectral particulate absorption coefficient measurements may potentially provide useful information (Bidigare, Morrow, & Kiefer, 1989; Moisan, Moisan, & Linkswiler, 2011; Organelli, Bricaud, Antoine, & Uitz, 2013; Torrecilla, Piera, & Vilaseca, 2009; Torrecilla, Stramski, Reynolds, Millán-Núñez, & Piera, 2011).

Absorption coefficients can also be obtained from remote sensing reflectance through bio-optical models (e.g., Roesler and Perry, 1995; Garver & Siegel, 1997; Lee & Carder, 2004). This can potentially enable the use of satellite data to derive phytoplankton absorption spectra, and provide information on size and composition. Hyperspectral space-based sensors, such as the upcoming Hyperspectral Infrared Imager (HyspIRI), the Pre-Aerosol, Cloud, and ocean Ecosystem Mission (PACE), and the GEOstationary Coastal and Air Pollution Events (GEOCAPE), planned by the National Aeronautics and Space Administration (NASA), will be able to provide remote sensing data – and derivable absorption coefficients, to study phytoplankton dynamics in coastal environments, at regional to global spatial scales, of unparalleled spectral and spatial-temporal resolution. More specifically, the goals of a HyspIRI-class mission include providing observations needed to address some key science questions identified in the National Research Council Decadal Survey (NRC, 2007) and refined by the HyspIRI Science Study Groups and research community (<http://hyspiri.jpl.nasa.gov/science>). Such a mission would help address questions requiring a combination of VSWIR and TIR data. This includes focusing on local and landscape-scale changes in inland, coastal, and open ocean aquatic ecosystems.

Understanding changes in carbon cycling is also fundamental to build accurate biogeochemical budgets for the ocean. More pressing is the need to accurately quantify phytoplankton carbon remotely, and understand how it changes through time. Phytoplankton pigment concentration is typically used as an index of phytoplankton biomass. In particular, total chlorophyll *a* (TChl<sub>a</sub>) has been used as a proxy for phytoplankton carbon (C) biomass. However, the relationship between C and TChl<sub>a</sub> is variable. It depends on a variety of factors such as nutrient availability, light, temperature and taxonomic groups (Behrenfeld, Boss, Siegel, & Shea, 2005; Longhurst & Harrison, 1989; Montagnes, Berges, Harrison, & Taylor, 1994). In order to develop reliable methods for estimating carbon-based biomass and primary production from satellite remote sensing observations, it is essential to accurately parameterize C–TChl<sub>a</sub> relationships.

We examined the relationship between phytoplankton taxonomic, pigment concentration, and bio-optical data collected monthly by the CARIACO Ocean Time-Series Project between 2006 and 2012 in the Cariaco Basin, located in the southeastern Caribbean Sea. We explored phytoplankton taxonomic and pigment time series data to understand how seasonal changes in biological parameters relate to bio-optical data, specifically absorption coefficients. We also assessed the relationship between carbon, chlorophyll *a*, and phytoplankton size classes with the aim of understanding the potential retrieval of these by remote sensing measurements.

## 2. Methods

### 2.1. Study area

The Cariaco Basin is a small tectonic basin located off eastern Venezuela (Fig. 1). It contains two sub-basins, each approximately 1400 m deep and divided by a saddle of ~900 m (Schubert, 1982). The Cariaco Basin is open to the north to the Caribbean Sea in the upper ~140 m, and to the south it features a wide, shallow platform. Most of the sediment that enters the basin comes from the small local rivers that drain directly onto the Unare Platform. The hydrology and hydrography of the region are influenced by the position of the Inter-tropical Convergence Zone (ITCZ). During boreal winter (December–April), strong Trade Winds (>6 m s<sup>-1</sup>) induce wind-driven upwelling in the southern Caribbean Sea. This stimulates high primary production and associated vertical and horizontal organic matter export

(Muller-Karger et al., 2004; Müller-Karger et al., 2010). During boreal summer (May/June–October/November), when the ITCZ has a more northward position, wind-driven upwelling becomes weaker and precipitation increases (Astor, Meri, & Muller Karger, 1998; Lorenzoni et al., 2009). A short (<1 month) secondary upwelling event occurs regularly between June and July, linked to variations in the wind curl (Rueda-Roa, 2012).

The CARIACO Ocean Time-Series Project has been collecting oceanographic observations at the CARIACO station (10°30' N, 64°40' W), within the Cariaco Basin, since 1995. These data have helped characterize the seasonality of biogeochemical processes in the basin (Astor et al., 1998; Muller-Karger et al., 2004; Müller-Karger et al., 2010; Thunell, Benitez-Nelson, Varela, Astor, & Müller-Karger, 2007). Between about 1995 and 1999, observations show regular cycles of strong upwelling. During the 2000s, and particularly during 2004–2005, intensity of the Trade Wind over the southern Caribbean decreased during the boreal winter, resulting in a reduction in upwelling intensity. This led to lower annual primary productivity and ecosystem shifts in the Cariaco Basin (Taylor et al., 2012) with respect to average conditions during previous years.

### 2.2. Measurements and data analysis

A total of 68 monthly cruises to the CARIACO Ocean Time-Series station were conducted between July 2006 and August 2012 using the *R/V Hermano Ginés* of the Fundación la Salle de Ciencias Naturales (FLASA). Only surface (1 m) data were used in this study. Salinity and temperature data were collected with a Seabird SBE25 CTD mounted on a 12 8-L bottle rosette. For phytoplankton taxonomic identification, 500 ml of water were collected into HDPE bottles and fixed with a 4% formalin solution neutralized with sodium tetraborate. For high performance liquid chromatography (HPLC) analyses, between 0.5 and 2 L of water (depending on the biomass concentration present) were vacuum-filtered through a 47 mm glass fiber filter (Whatman GF/F, 0.7 μm pore size). Filters were stored folded in aluminum foil at –20 °C at sea. Once on land, the HPLC samples were moved to a –40 °C freezer until analyzed. Particulate organic carbon (POC) was sampled by vacuum-filtering 2 L of water through a 47 mm glass fiber filter (Whatman GF/F, 0.7 μm pore size); filters were refrigerated and subsequently oven-dried at 60 °C. POC concentrations were obtained by running the filters through a Perkin Elmer 2400 elemental analyzer.

Phytoplankton taxonomy was analyzed at the Universidad de Oriente (Boca de Río), Venezuela, using the Utermöhl technique (Hasle, 1978) with 100 mL sedimentation chambers and a settling period of 48 h. Taxonomic identification was done through an inverted microscope (Axiovert Carl Zeiss). HPLC analyses were conducted at Horn Point Laboratory, Maryland (HPL; from July 2006 to July 2010), and at the NASA Goddard Space Flight Center, Maryland (GSFC; From August 2010 to August 2012) following the method described in Van Heukelem and Thomas (2001) and Hooker et al. (2005). All data are openly available online (CARIACO Home Page: <http://imars.marine.usf.edu/cariaco/cariaco-ocean-time-series-program>; BCO-DMO; <http://www.bco-dmo.org/project/2047>). The major HPLC pigments used in this manuscript are shown in Table 1. Seven major diagnostic pigments (DP) were used to calculate the proportions of micro-, nano-, and picophytoplankton present at any given time, following Uitz, Claustre, Morel, and Hooker (2006). Specifically, the fraction of each pigment-based size class was calculated as:

$$\begin{aligned} \text{Microphytoplankton (>20 } \mu\text{m)} &= (1.41[\text{Fuco}] + 1.41[\text{Peri}]) / \text{DP} \\ \text{Nanophytoplankton (2 to 20 } \mu\text{m)} &= (0.60[\text{Allo}] + 0.35[19\text{BF}] \\ &\quad + 1.27[19\text{HF}]) / \text{DP} \\ \text{Picophytoplankton (<2 } \mu\text{m)} &= (0.86[\text{Zea}] + 1.01[\text{TChlb}]) / \text{DP} \end{aligned}$$

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