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# Light absorption by phytoplankton, non-algal particles and dissolved organic matter at the Patagonia shelf-break in spring and summer

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#### ABSTRACT

Satellite image studies and recent in situ sampling have identified conspicuous phytoplankton blooms during spring and summer along the Patagonia shelf-break front. The magnitudes and spectral characteristics of light absorption by total particulate matter (phytoplankton and detritus) and colored dissolved organic matter (CDOM) have been determined by spectrophotometry in that region for spring 2006 and late summer 2007 seasons. In spring, phytoplankton absorption was the dominant optical component of light absorption (60-85%), and CDOM showed variable and important contributions in summer (10-90%). However, there was a lack of correlation between phytoplankton biomass (chlorophyll-a concentration or [chl a]) and the nonalgal compartment in both periods. A statistically significant difference was found between the two periods with respect to the CDOM spectral shape parameter ( $S_{cdom}$ ), with means of 0.015 (spring) and 0.012 nm<sup>-1</sup> (summer). Nonetheless, the mean  $S_{cdm}$ values, which describe the slope of detritus plus CDOM spectra, did not differ between the periods (average of 0.013 nm<sup>-1</sup>). Phytoplankton absorption values in this work showed deviations from mean parameterizations in previous studies, with respect to [chl a], as well as between the two study periods. In spring, despite the microplankton dominance, high specific absorption values and large dispersion were found  $(a^*_{\rm ph}(440) = 0.04 \pm 0.03 \,\mathrm{m}^2 \,\mathrm{mg} \,[\mathrm{chl} \,a]^{-1})$ , which could be attributed to an important influence of photo-protector accessory pigments. In summer, deviations from general trends, with values of  $a^*_{\rm ph}(440)$  even higher  $(0.09 \pm 0.02 \,\mathrm{m}^2 \,\mathrm{mg} \,[\mathrm{chl}\,a]^{-1})$ , were due to the dominance of small cell sizes and also to accessory pigments. These results highlight the difficulty in deriving robust relationships between chlorophyll concentration and phytoplankton absorption coefficients regardless of the season period. The validity of a size parameter  $(S_f)$  derived from the absorption spectra has been demonstrated and was shown to describe the size structure of phytoplankton populations, independently of pigment concentration, with mean values of 0.41 in spring and 0.72 in summer. Our results emphasize the need for specific parameterization for the study region and seasonal sampling approach in order to model the inherent optical properties from water reflectance signatures.

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1. Introduction

It is well known that the upwelling of visible radiation or reflectance (i.e. apparent optical properties (AOPs)) from a natural water body is determined by the inherent optical properties (IOPs, absorption and scattering) of the optically active constituents, i.e., particulate and dissolved material (Gordon et al., 1988). Understanding the processes that cause changes in the optical behavior of these components and quantifying the variability in their IOPs should improve the accuracy of individual parameter retrieval by remote-sensing techniques (IOCCG, 2006). In addition to quantifying these so-called optically active components, IOPs have been used to estimate biogeochemical variables such as organic carbon, chlorophyll-a, dissolved organic material and total suspended matter (e.g. Twardowski et al., 2005), and primary productivity (Marra et al., 2007; Prieto et al., 2008). Remote sensing studies are increasingly focused on the understanding of both the spatial and temporal variability of primary production over large and regional scales (Behrenfeld et al., 2001). In addition, it is also desirable to quantify the role of both phytoplankton and dissolved organic matter (DOM) in the ocean carbon budget (Siegel et al., 2005; Hu et al., 2006).

The spectral light absorption is a major factor contributing to the variation in optical properties of seawater. It can be quantified by the absorption coefficient, which, in turn, consists of absorption by pure seawater, phytoplankton, non-algal particles and colored dissolved organic matter (CDOM). Variability in the absorption coefficient in oceanic (so-called "Case I") waters has been thoroughly documented over the past decades (e.g. Morel, 1988; Bricaud et al., 1998; Reynolds et al., 2001; Morel and Maritorena, 2001). In such waters, phytoplankton and their derivative products are optically dominant, and all other components, except seawater, are often assumed to co-vary with chlorophyll-a concentration ([chl a]). However, parameterization of the absorption coefficient can show significant variability in space and time, mainly where dissolved material or nonalgal particles are not proportional to phytoplankton absorption, and it must consider each of them separately ('Case 2 waters'). Specifically for phytoplankton, pigment packaging (Duyens, 1956) or pigment composition generally can be an important cause of optical variability, even for a given [chl a] (Bricaud et al., 1995, 2004). Thus, particular phytoplankton communities can show a given absorption signature, which may be characteristic of a given region or time. At least in regions where phytoplankton absorption is significant, these variations may affect the reflectance spectra (Carder et al., 1999; Maritorena et al., 2002; Carder et al., 2004). Most semianalytical algorithm approaches relate reflectance to absorption by phytoplankton and dissolved organic matter (e.g. Maritorena et al., 2002). Therefore, there is a need for regional in situ measurements of light absorption, in order to assess or to develop satellite ocean color algorithms.

The performance of semi-analytical models in describing relationships of ocean color to chlorophyll (Carder et al., 2004; Sathyendranath et al., 2001) has been shown to be sensitive to variations in the chlorophyll-specific absorption coefficient (i.e. absorption coefficient normalized to chlorophyll-a unit) due to changes in phytoplankton cell size and pigment composition. Ciotti et al. (2002) and Bricaud et al. (2004) have verified

that the dominant cell size of the algal community, and consequent changes in pigment packaging, could largely explain the natural variability observed in the spectral shape of phytoplankton absorption. Models have been proposed to retrieve information on cell size from spectral absorption measurements (Ciotti et al., 2002) and from values of the specific absorption coefficients (Devred et al., 2005). However, those studies have not separated the relative contributions of pigment packaging and accessory pigment effects but have relied on the co-variation between cell size and accessory pigmentation (Ciotti et al., 1999, 2002; Trees et al., 2000).

Deviations in the relationship between optical properties and [chl a] can be particularly important in high-chlorophyll Case I waters (O'Reilly et al., 1998), such as offshore phytoplankton blooms. Morel et al. (2006) analyzed bio-optical relationships in an upwelling area with no influence from continental runoff, comparing their natural variability with that previously observed in less productive waters. They concluded that the main source of variability is the looseness of the co-variations between the detrital (dissolved and particulate) component and the algal stock.

In the present work, a frontal region (Patagonia shelf-break front) relatively far from the coast, where extensive phytoplankton blooms develop in spring-summer, has been selected for the study of optical properties of both dissolved and particulate material, including phytoplankton. The data provided in the study contribute to documentation of absorption properties in relatively clear and high-chlorophyll waters.

The shelf-break front formed between Argentinean shelf waters and the Malvinas Current (39-51°S) in the South Atlantic has been shown to be associated with a conspicuous band of high chlorophyll throughout spring and summer, detected by ocean color sensors (Acha et al., 2004; Rivas et al., 2006; Romero et al., 2006). In situ studies have found high surface [chl a] (between 1.8 and  $19.9 \,\mathrm{mg}\,\mathrm{m}^{-3}$ ) and primary production rates (between 2.0 and  $7.8 \,\mathrm{g} \,\mathrm{C} \,\mathrm{m}^{-2} \,\mathrm{d}^{-1}$ ) in spring that are comparable to maximal seasonal values at eastern boundary currents (Garcia et al., 2008). The region presents a potentially significant biological control of gases such as O2 and CO2 in surface layers, as suggested by data in Bianchi et al. (2005, 2009) and Garcia et al. (2008). Despite the ecological and biogeochemical relevance of the Patagonia shelf-break front, there are no records of IOP measurements in the study area.

In summary, the main objective of the present work is to study the seasonal variation in magnitude and spectral shape of the absorption coefficients of phytoplankton, detritus and CDOM in the Patagonian shelf-break front. The focus is on the absorption budget during two cruises, carried out in spring 2006 and summer 2007, as part of the PATagonian EXperiment (PATEX) project, conducted within the Brazilian Antarctic Program. Thus, the study seeks to contribute to a better understanding of the phytoplankton absorption properties in oceanic waters with high-chlorophyll content.

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