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# Bio-optical characterization of the northern Antarctic Peninsula waters: Absorption budget and insights on particulate backscattering

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## ABSTRACT

We utilize a comprehensive set of bio-optical properties collected in the northern Antarctic Peninsula to contribute to the poor documentation of in situ bio-optical measurements in the Southern Ocean. The relative contributions of phytoplankton, colored dissolved organic matter (cdom) and detritus to light absorption highlight the importance of phytoplankton, but cdom contribution is often important in the blue range of the spectra despite its roughly constant values at 443 nm along the three orders of magnitude of total chlorophyll-a concentration, [TChl a], (0.019-2.91 mg m<sup>-3</sup>) observed in the upper 100 m. The particulate backscattering coefficient,  $b_{\rm bn}(\lambda)$ , was remarkably low if compared to other oceanic waters, but agrees with previous studies in the Southern Ocean. Even with very low absorption, detritus was the component better correlated with particulate backscattering in the Antarctic Peninsula, while phytoplankton cells (dominant in the particles pool) mostly covaried with particulate scattering. Particulate backscattering ratios ( $b_{bp}(\lambda)$ ) divided by the particulate scattering coefficient,  $b_{\rm p}(\lambda)$ ) were also below values observed in other oceanic waters. The spectral diffuse attenuation coefficient,  $K_d(\lambda)$ , was highly correlated to [TChl a] ( $R^2 = 0.90$  at 443 nm) and showed no dependence on  $b_{bp}(\lambda)$ . Indeed,  $K_d(443)$  and non-water absorption coefficients at 443 nm were related by a 1 to 1 dependence. The shape of the spectral remote sensing reflectance varied little responding mainly to variability in [TChl a], while [TChl a] vs. maximum band ratios dependence deviated from global trends in a very similar fashion as in other studies of the Southern Ocean, likely due to very low  $b_{\rm bp}(\lambda)$ .

## 1. Introduction

The optical properties of seawater can be reconstructed from the additive contributions of water molecules, phytoplankton, nonalgal particles (mainly detritus) and colored dissolved organic matter (*cdom*), called bio-optical components. The magnitude and spectral shape of light absorption and scattering, inherent properties (Preisendorfer, 1961) are altered by changes in concentrations and compositions of these components (e.g., IOCCG, 2006). The characterizations of optical properties in different portions of the ocean are necessary steps for using optical measurements, performed by *in situ* and remote platforms as tools for biogeochemical studies (e.g., Johnson et al., 2009).

In case 1 waters, where phytoplankton and its co-varying particulate and dissolved materials govern the optical signal (Gordon and Morel, 1983; Morel and Prieur, 1977; Prieur and Sathyendranath, 1981), parameterizations of bio-optical properties as functions of chlorophyll-*a* concentration have been useful for biogeochemical modeling (e.g., Morel, 1988). Chlorophyll-*a* concentrations are used to predict optical coefficients such as the particulate (e.g. Bricaud et al., 1998) and phytoplankton (e.g., Bricaud et al., 2004; Bricaud et al., 1995) absorption, the particulate beam attenuation (e.g., Behrenfeld and Boss, 2006; Loisel and Morel, 1998), the particulate scattering (e.g. Gordon and Morel, 1983; Huot et al., 2008) and the particulate back-scattering (Antoine et al., 2011; Dall'Olmo et al., 2009; Huot et al., 2008).

While variations in the phytoplankton absorption coefficient are well documented, spectral absorption of *cdom* (e.g., Babin et al., 2003; Bricaud et al., 1981) and detritus (e.g., Babin et al., 2003; Bricaud et al., 1995) have been less systematically investigated, and because of that, frequently disregarded or simple assumed to covary with chlorophyll-*a* concentration (Carder et al., 1991; but see Ciotti et al., 1999). *In situ* measurements of the beam attenuation coefficients have long been carried out routinely as an index for particles (see Bartz et al., 1978), in contrast to the backscattering coefficient that only recently became systematically measured (e.g., Antoine et al., 2011; Slade and Boss, 2015; Huot et al., 2008; Reynolds et al.,

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Fig. 1. Geographic locations of the sampling stations in the Gerlache Strait (GS, triangles), Bransfield Strait (BS, stars), northwestern Weddell Sea (NWW, circles). NWW<sub>HT</sub> denotes "high transparency" for two stations sampled in 2014 (asterisks). In GS, BS and NWW, most of the stations of 2013 were sampled in 2014 and are indicated with the edge markers in black.

2016; Twardowski et al., 2007). Backscattering measurements may provide information on particulate organic matter (Stramski et al., 2008), phytoplankton carbon concentration (Graff et al., 2015, 2016), chlorophyll-*a* to autotrophic carbon ratios (Cetinić et al., 2015) and particle size distributions (Kostadinov et al., 2009; Loisel et al., 2006; Slade and Boss, 2015).

A large dispersion is generally observed in global empirical relationships developed for bio-optical properties or parameter as functions of chlorophyll-a concentration (e.g. Bricaud et al., 1998; O'Reilly et al., 1998) that could be associated with methods, instruments, as well as actual regional differences (Morel and Maritorena, 2001). Indeed, the empirical relationships between reflectance ratios and chlorophyll-a concentration, tools for estimating phytoplankton biomass from remote sensing, are significantly different in samples observed in Antarctica compared to the other oceanic regions (e.g., Dierssen and Smith, 2000; Reynolds et al., 2001), also manifested as errors in the chlorophyll-a retrievals when global algorithms of ocean color are applied (e.g., Garcia et al., 2005; Szeto et al., 2011). These differences have been attributed to unique "packaged" phytoplankton absorption characteristics (Dierssen and Smith, 2000; Mitchell and Holm-Hansen, 1991), but the contribution of distinct particulate backscattering coefficients cannot be overruled (Brown et al., 2008). In fact, in situ particulate backscattering measurements in Antarctica have shown low magnitudes (Dierssen and Smith, 2000; Revnolds et al., 2001), but they remain too scarce to provide conclusive results (see Dierssen, 2010). Retrievals of chlorophyll-a concentration in the Antarctic Peninsula by global ocean color algorithms generally over and underestimate in situ low and high chlorophyll-a, respectively, and this aspect is generally related to a lower water leaving reflectance and a narrower variation in the blue-green band ratio (Zeng et al., 2016) as well as low backscattering coefficients in the green part of the spectrum at high chlorophyll-a (Dierssen and Smith, 2000). However, the mechanisms which control the ocean color variability in the Southern Ocean need to be further understood.

This work describes variations in the bio-optical properties in the northern Antarctic Peninsula observed during late austral summers of 2013 and 2014. To the best of our knowledge, our work is the first to describe concurrent measurements of absorption, scattering, back-scattering, diffuse attenuation coefficients and remote sensing reflectance in the Antarctic Peninsula. The main goal of this study is to report the relative contributions of phytoplankton, *cdom* and detritus to light absorption and to access potential relationships between scattering and backscattering coefficients and chlorophyll-*a* concentration,

comparing to previous relationships found elsewhere. A complementary purpose of this study is to explore the prediction of chlorophyll-*a* concentration and absorption coefficient from the diffuse attenuation coefficient for downward irradiance,  $K_d(\lambda)$ . This is of special interest because  $K_d(\lambda)$  is a relatively simple measurement to obtain in the field and provides absorption (e.g., Loisel and Stramski, 2000), justified by the dominance of absorption in the diffuse attenuation process (Morel et al., 2007), particularly in waters where backscattering is low. Finally, we characterize the variability in the hyperspectral remote sensing reflectance,  $R_{\rm rs}(\lambda)$ , and evaluate the relationships between and  $R_{\rm rs}(\lambda)$  ratios and chlorophyll-*a* concentration.

## 2. Material and methods

#### 2.1. Sampling

Data were collected during two oceanographic cruises in the northern tip of the Antarctic Peninsula in the austral summers of 2013 (14 February–3 March) and 2014 (8–24 February). The study area covered the Gerlache Strait (GS), which separates the Palmer Archipelago from the Peninsula, the Bransfield Strait (BS), between the southern Shetland Islands and the Peninsula, and the northwestern Weddell Sea (NWW). A total of 89 and 70 stations were sampled in 2013 and 2014, respectively (Fig. 1). A detailed description of sampling strategy can be found in Ferreira *et al.* (in press).

Discrete samples for determination of chlorophyll-a concentration and spectral absorption coefficients were collected at 5, 15, 25, 50, 75 and 100 m at night, and only at 5 m during the day. Profiles of inherent optical properties were acquired down to 100 m in all day and night stations. Above water hyperspectral reflectance's were recorded during the day. Radiometric profiles (see 2.5) to obtain the spectral  $K_d(\lambda)$  were performed less often, because of the unfavorable sea conditions commonly found in Antarctic waters. Therefore, the number of data for each dataset and analysis is variable and informed when pertinent. The data of discrete samples from 5 to 100 m were grouped in layers according to vertical variations of light. The first optical depth has implications for remote sensing application, while the others keep consistency with our previous work (Ferreira et al., in press). Briefly,  $L_{> 37\%}$  corresponds to the layer between surface and the first optical depth, at which the downward irradiance 37% of its value just below the surface. The data within  $L_{> 37\%}$  contributes mostly to the ocean color signal that corresponds only to the first portion of the photic zone returning a weighted average value over this layer (Sathyendranath and

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