Deep-Sea Research Part I 120 (2017) 112–121

Contents lists available at ScienceDirect

Deep–Sea Research I

journal homepage: www.elsevier.com/locate/dsri

# Contrasting patterns of phytoplankton pigments and chemotaxonomic groups along 30°S in the subtropical South Atlantic Ocean

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ARTICLE INFO

*Keywords:*
CLIVAR
Phytoplankton community structure
Biogeochemical provinces
HPLC
CHEMTAX

ABSTRACT

This work describes the spatial distribution of pigments and main taxonomic groups of phytoplankton in the biogeochemical provinces of the subtropical South Atlantic Ocean, along 30°S latitude. Seawater samples (surface to 200 m depth) were collected along 120 oceanographic stations occupied in the early austral spring of 2011, during a CLIVAR Repeat Hydrography cruise. The pigments were identified and quantified by high performance liquid chromatography (HPLC), and CHEMTAX software was used to determine the relative contributions of the main taxonomic groups to total chlorophyll *a* (phytoplankton biomass index). Sampling stations were grouped into three provinces: Africa, Gyre, and Brazil, corresponding to the eastern, central, and western sectors of the transect, respectively. Our results showed that both vertical and horizontal distribution patterns of pigments and taxonomic groups were mainly determined by the availability of light and/or nutrients. Photosynthetic carotenoids (PSCs), associated with small flagellates (mainly haptophytes), dominated the light-limited and nutrient-enhanced deep chlorophyll maximum (DCM) layers of both the Brazil and Gyre provinces, as well as the upwelling influenced surface waters of the Africa province. The latter showed the highest chlorophyll *a* values ( > 1 mg m$^{-3}$) and abundance of dinoflagellates in the coastal region. Photoprotective carotenoids (PPCs) were predominant in the nutrient-poor and well-lit surface layers of the Brazil and Gyre provinces, associated with a low content of chlorophyll *a* (~0.1 mg m$^{-3}$) and dominance of prokaryotes (*Synechoccocus* and *Prochloroccocus*). This study demonstrates that pigment analysis can provide a useful approach to better understand the distribution of phytoplankton communities along physical-chemical gradients in a still undersampled region of the South Atlantic Ocean.

## 1. Introduction

Phytoplankton composition largely determines the trophic organization of pelagic ecosystems and, thus, the efficiency with which organic matter produced by photosynthesis is transferred towards upper trophic levels or exported to the deep ocean (Finkel et al., 2010). These primary producers are responsible for most of the biologically-mediated carbon dioxide transfer from the atmosphere to the oceans and, consequently, play a fundamental role in the biogeochemical cycling of the planet, with different phytoplankton communities having specific biogeochemical roles (Schloss et al., 2007; Nair et al., 2008). To anticipate the effects of $CO_2$ increases on climate, the main recent earth system models are becoming increasingly complex and sophisticated in ocean ecology and biogeochemistry, incorporating complex modules of functional phytoplankton groups that drive marine biogeochemical cycles (e.g., Marinov et al., 2010). Thus, the study of phytoplankton communities provides a fundamental tool in environmental assessment and monitoring, as well as in studies of trophic relationships and ecosystems modeling.

The distribution of phytoplankton in the oceans is governed primarily by the adaptation of communities to characteristic regional conditions such as turbulence, temperature, light, and nutrients (Cullen et al., 2002). Longhurst et al. (1995) proposed a well-reasoned system for dividing the global ocean into biologically meaningful regions, evaluating patterns of productivity using ocean color data. These biogeochemical provinces are useful for comparing and contrasting biogeochemical processes and biodiversity between ocean regions (Oliver and Irwin, 2008). Nevertheless, the boundaries of these provinces are not fixed in time and space; rather, they are dynamic and move according to seasonal and interannual changes in physical forcing (Longhurst, 2006). More recently, complementing this concept, Hooker et al. (2000) explored a vertical partitioning of the ocean into

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http://dx.doi.org/10.1016/j.dsr.2016.12.004
Received 8 October 2015; Received in revised form 5 October 2016; Accepted 5 December 2016
Available online 22 December 2016

a near-surface mixed layer and a deep stratified layer. The two-layer approach is a consequence of the importance of water column stability, which has a relevant effect on ocean biological production (Hooker et al., 2000). Horizontal partitioning of the oceans, which addresses the structure of phytoplankton communities, has been extensively used in several studies, but few of them have taken into account its vertical distribution.

Within this context, the South Atlantic Ocean (SAO) is one of the least investigated regions of the global ocean and, thus, remains relatively poorly understood (Longhurst, 2006). The South Atlantic is particularly important as a region where oceanic properties are exchanged, mixed, and redistributed between different ocean basins. Moreover, it is the only major ocean basin that transports heat from the poles towards the equator (Talley, 2003). The SAO comprises an important part of the meridional overturning circulation (MOC), a worldwide wind- and buoyancy-driven transport that connects all basins and balances the global ocean energy flux (Garzoli et al., 2013). Additionally, the SAO is an important region where anthropogenic $CO_2$ penetrates into deep waters of the global oceans (Murata et al., 2008). The Atlantic Meridional Transect (AMT) Programme has greatly contributed to knowledge on biological processes in this ocean region (Aiken et al., 2000; Robinson et al., 2006). The AMT dataset includes a large set of observations on the structure of phytoplankton communities (e.g., Gibb et al., 2000; Barlow et al., 2002, 2004; Poulton et al., 2006; Aiken et al., 2009). However, zonal east-west transects along the South Atlantic are very scarce. To fill this knowledge gap, the CLIVAR Repeat Hydrography Program aims to sample a set of hydrographic transects over the global ocean for obtaining high-quality measurements with a high resolution on spatial and vertical scales. A suite of physical and chemical parameters is determined throughout the water column to understand the dynamics, interaction, and predictability of the coupled ocean-atmosphere system. The CLIVAR A10 section crosses the SAO at ~30°S through the following biogeochemical provinces (as proposed by Longhurst et al., 1995): Benguela Current Coastal Province, South Atlantic Gyral Province, and Brazil Current Coastal Province. Previous studies have already focused on phytoplankton community composition along this section; however, only surface data were investigated (Bouman et al., 2006, 2011; Barlow et al., 2007).

Accurate *in situ* measurements of phytoplankton composition are vital for advancing our understanding of the marine biogeochemistry, for instance, through development and validation of size-based phytoplankton biogeochemical models and remote-sensing algorithms (Brewin et al., 2014). Studies of phytoplankton community composition have been classically conducted using light microscope analysis, which is very time-consuming and requires a high level of taxonomic skill. An alternative way is through chemotaxonomic methods based on High Performance Liquid Chromatography (HPLC) pigment analysis (Mendes et al., 2015). These methods rely on the relative concentration of pigments that are characteristic of distinct algal taxonomic groups (Wright and Jeffrey, 2006; Higgins et al., 2011). A common approach involves using the software CHEMTAX (CHEMical TAXonomy) on HPLC pigment ratios signatures (Mackey et al., 1996) to determine the relative contribution of phytoplankton groups to total biomass. The HPLC-CHEMTAX approach has been successfully used in many worldwide investigations (e.g., Wright et al., 2010; Schlüter et al., 2011; Mendes et al., 2011, 2012, 2015) and provides valuable information about the whole phytoplankton community including small-size groups, which are normally difficult to identify by light microscopy. In the SAO, however, such studies have mainly been performed in coastal environments (Carreto et al., 2003, 2008; Gonçalves-Araujo et al., 2012; Rodrigues et al., 2014; Barlow et al., 2016) and, consequently, the open ocean remains poorly explored with regard to phytoplankton communities.

The present work uses the HPLC-CHEMTAX approach to evaluate pigment data collected during the A10 section of the CLIVAR Repeat Hydrography Program. The study aims to increase our understanding of the physical-chemical interactions that affect phytoplankton communities (through pigment composition) at distinct provinces in the subtropical South Atlantic. The phytoplankton distribution patterns have been examined on both horizontal (along ~30°S) and vertical (between the surface and 200 m depth) scales. Within this context, the following specific questions have been posed: (1) How do light and nutrient gradients affect the spatial distribution and composition of phytoplankton biomass? and (2) How does phytoplankton community structure changes with depth?

## 2. Material and methods

### 2.1. Sampling and physical/chemical data

The CLIVAR A10 section in the SAO was conducted aboard the NOAA Ship *Ronald H. Brown* during early austral spring of 2011 (September 26 to October 31). This cruise was part of a decadal series of repeat hydrography sections jointly funded by the NOAA-Climate Observations Division and NSF-OCE within the U.S. CLIVAR/CO2/hydrography/tracer program. The A10 section was nominally along 30°S from approximately 15°E to 50°W. A total of 120 full water column CTD/$O_2$/rosette (Seabird) casts were completed along the section, with a nominal spacing between stations of ~30 nautical mile (nm) but at higher spatial resolution in the eastern and western boundaries (Fig. 1).

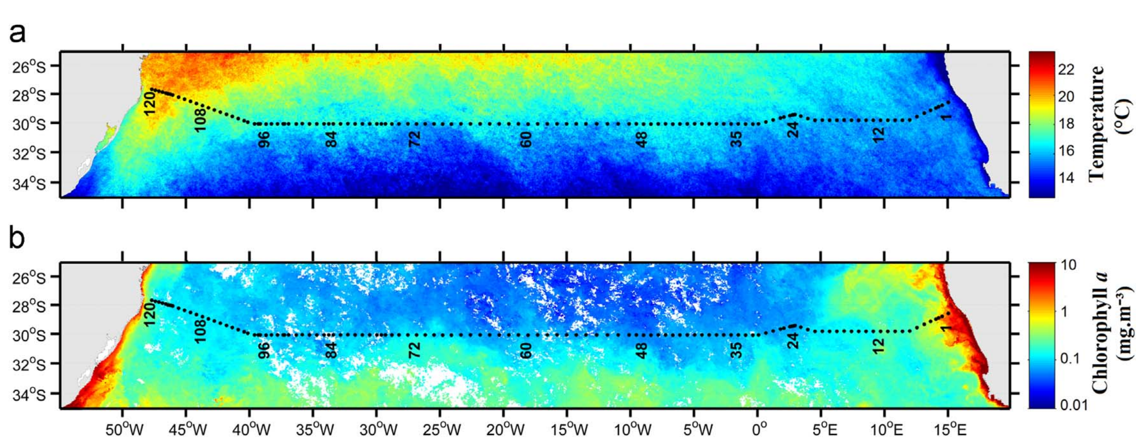


**Fig. 1.** : Satellite composite images of (a) Sea Surface Temperature and (b) Chlorophyll *a* for the cruise period (September 26 to October 31, 2011) in the South Atlantic Ocean. Black dots indicate the stations' locations. Labelled stations indicate locations where high-resolution vertical pigments' profiles are available. Composite images were assembled from daily 4 km resolution MODIS-Aqua satellite images.

**Table 1**
Symbols, names, formulae, concentrations (in ng. $L^{-1}$) of pigments and pigment sums, and values of pigment indices identified in this study (mean ± standard deviation for each province at surface and DCM layer). Tchl *a*=total chlorophyll *a*, PPC=photoprotective carotenoids, PSC=photosynthetic carotenoids, AP=accessory pigments, TP=total pigments.

| | | Africa Province | | Gyre Province | | Brazil Province | |
|---|---|---|---|---|---|---|---|
| **Symbol** | **Description** | **Surface** | **DCM** | **Surface** | **DCM** | **Surface** | **DCM** |
| Chl *a* | Chlorophyll *a* | 382.3 ± 405.9 | 457.8 ± 390.2 | 58.5 ± 23.3 | 194.1 ± 77.2 | 93.7 ± 45.4 | 268.3 ± 119.7 |
| DV Chl *a* | Divinyl chlorophyll *a* | 21.1 ± 15.1 | 46.6 ± 43.9 | 33.8 ± 15.8 | 90.4 ± 42.1 | 42.7 ± 10.1 | 125.5 ± 55.1 |
| Tchl *b* | Chlorophyll *b*+Divinyl chlorophyll *b* | 48 ± 42.8 | 77.5 ± 41 | 8.2 ± 6.5 | 90 ± 50.4 | 8.5 ± 4.4 | 108 ± 65 |
| Chl $c_2$ | Chlorophyll $c_2$ | 45.9 ± 57.9 | 63.9 ± 54.4 | 5 ± 2.8 | 25.1 ± 12.4 | 7.4 ± 4.5 | 27.5 ± 12.9 |
| Chl $c_3$ | Chlorophyll $c_3$ | 35 ± 26.4 | 58.2 ± 23.1 | 5.1 ± 3.2 | 42.2 ± 17.7 | 6.1 ± 3.5 | 47.3 ± 23.3 |
| Fuco | Fucoxanthin | 40.6 ± 45.1 | 58.7 ± 54.2 | 4.5 ± 3.9 | 16.3 ± 20.7 | 13.4 ± 10.5 | 15.5 ± 8.2 |
| But | 19'-butanoyloxyfucoxanthin | 39 ± 20.2 | 65.3 ± 18.9 | 6.4 ± 3.2 | 50.6 ± 18.7 | 6.1 ± 2.6 | 53.1 ± 27.8 |
| Hex | 19'-hexanoyloxyfucoxanthin | 104.3 ± 57.9 | 128.3 ± 65.7 | 14.9 ± 6.2 | 66.4 ± 25.8 | 16.3 ± 7.8 | 71.8 ± 28.9 |
| Diad | Diadinoxanthin | 38.5 ± 37.5 | 25.4 ± 38.4 | 4.1 ± 2.1 | 5.4 ± 2.4 | 6.2 ± 2.5 | 7.2 ± 2.5 |
| Lut | Lutein | 3.3 ± 1.9 | 3.2 ± 1.5 | 0.2 ± 0.4 | 1.4 ± 1.1 | 0.1 ± 0.2 | 1.8 ± 0.8 |
| Pras | Prasinoxanthin | 4.2 ± 6.4 | 5.4 ± 6.7 | 0.1 ± 0.4 | 2.3 ± 2 | 0.4 ± 0.7 | 6.5 ± 4.8 |
| Allo | Alloxanthin | 2.9 ± 5.3 | 3 ± 5 | 0 ± 0.2 | 0.8 ± 1.5 | 0.1 ± 0.2 | 2.7 ± 1.9 |
| Diato | Diatoxanthin | 3 ± 2.3 | 1.6 ± 1.6 | 0.3 ± 0.4 | 0.2 ± 0.3 | 0.7 ± 0.6 | 0 ± 0.1 |
| Zea | Zeaxanthin | 59.7 ± 36.2 | 67 ± 39.3 | 45.3 ± 11.2 | 43.8 ± 23.9 | 67.9 ± 10.3 | 62.7 ± 37.3 |
| Car | βε-carotene + ββ-carotene | 10.3 ± 9.8 | 14.4 ± 13.1 | 5.2 ± 2.5 | 16.4 ± 8.9 | 8.4 ± 3.9 | 25.2 ± 11.5 |
| Peri | Peridinin | 53.3 ± 166.4 | 56.4 ± 165.7 | 2.1 ± 4 | 3.7 ± 3.1 | 2.4 ± 0.7 | 4.9 ± 2.1 |
| Viola | Violaxanthin | 4.4 ± 3.6 | 4.4 ± 3.4 | 0.6 ± 0.4 | 1.3 ± 0.7 | 0.8 ± 0.4 | 1.4 ± 0.8 |
| Pheide *a* | Pheophorbide *a* | 7.1 ± 9.3 | 10.8 ± 8.6 | 1.4 ± 1.7 | 8.2 ± 4.7 | 1.9 ± 1.2 | 11.6 ± 6 |
| Phe *a* | Pheophytin *a* | 5.7 ± 6 | 8 ± 5.7 | 1.9 ± 1 | 6.8 ± 4.5 | 2.4 ± 1 | 8.3 ± 3.2 |
| Chlide *a* | Cholophyllide *a* | 3.5 ± 3.9 | 3.3 ± 3.9 | 0.1 ± 0.3 | 0.4 ± 0.9 | 0.5 ± 0.8 | 0.3 ± 0.3 |
| **Pigment sum** | | | | | | | |
| Tchl *a* | Chl *a*+DVChl *a*+Chlide *a* | 406.9 ± 402.2 | 507.7 ± 377.8 | 92.4 ± 35.1 | 284.9 ± 105.1 | 137 ± 45.6 | 394 ± 153.5 |
| PPC | Viola+Diad+Allo+Diato+Zea+Car+Lut | 122.2 ± 86.8 | 119 ± 86.9 | 55.7 ± 13.8 | 69.3 ± 32.1 | 84.3 ± 14.1 | 100.9 ± 48.6 |
| PSC | But+Fuco+Hex+Peri+Pras | 241.5 ± 272.6 | 314.1 ± 257.7 | 28 ± 13.4 | 139.3 ± 57.5 | 38.6 ± 20.7 | 151.7 ± 66.4 |
| AP | PPC+PSC+Tchl *b*+Chl $c_2$+Chl $c_3$ | 492.5 ± 475.1 | 632.7 ± 437.8 | 102 ± 34.1 | 365.9 ± 143.4 | 144.9 ± 42.7 | 435.4 ± 183.5 |
| TP | Tchl *a*+AP | 899.5 ± 877 | 1140.3 ± 815.4 | 194.3 ± 68.8 | 650.8 ± 245.3 | 281.9 ± 87.9 | 829.4 ± 333.6 |
| **Photo-pigment index** | | | | | | | |
| $PPC_{TP}$ | PPC/TP | 0.15 ± 0.03 | 0.1 ± 0.03 | 0.3 ± 0.04 | 0.11 ± 0.04 | 0.31 ± 0.05 | 0.12 ± 0.05 |
| $PSC_{TP}$ | PSC/TP | 0.26 ± 0.03 | 0.27 ± 0.03 | 0.14 ± 0.03 | 0.21 ± 0.03 | 0.13 ± 0.03 | 0.19 ± 0.04 |
| $Tchla_{TP}$ | Tchl *a*/TP | 0.45 ± 0.02 | 0.44 ± 0.01 | 0.47 ± 0.02 | 0.44 ± 0.03 | 0.48 ± 0.02 | 0.47 ± 0.04 |

The study area was partitioned into three biogeochemical provinces, as proposed by Longhurst et al. (1995) and here denoted as Brazil, Gyre, and Africa provinces. The provinces' boundaries were determined by a cluster analysis (see Supplementary Material) using sea surface values of four selected environmental variables: temperature, salinity, dissolved oxygen, and total chlorophyll *a* (phytoplankton biomass index).

Physical and chemical data (temperature, salinity, oxygen, nutrients) were obtained from the online CLIVAR database (http://cchdo.ucsd.edu/cruise/33RO20110926). Nutrient analysis (nitrate, silicate, phosphate) was performed using the standard analysis protocol for the WOCE hydrographic program (Gordon et al., 1993). The upper depth of the nitracline was determined from vertical profiles of nitrate concentration as the mean depth where nitrate concentrations turn to a sharp gradient; this was generally observed as the depth below which nitrate concentrations exceeded 1 µmol $kg^{-1}$. Seawater density ($kg.m^{-3}$) was determined from temperature, salinity, and pressure data to evaluate the stratification of the water column. Upper mixed layer (UML) depth was determined as the depth at which potential density values were greater than 0.03 kg $m^{-3}$ from a near-surface value at 10 m depth (de Boyer Montégut et al., 2004). Water column stability (E) was estimated using vertical density variations, as a function of the buoyancy or Brunt-Väisälä frequency ($N^2$), which is defined by $N^2=-(g/\rho).(\partial\rho/\partial z)$ ($rad^2.s^{-2}$), leading to $E=N^2/g$ ($10^{-8}$ $rad^2.m^{-1}$), where g is gravity and $\rho$ is the potential seawater density. Mean E values (between 0 and 100 m) were used in this study.

Photosynthetically active radiation (PAR; λ=400–700 nm) in the upper 30 m layer was measured with a radiometric profiler (HyperPro, Satlantic) during 42 daytime sampling stations. The euphotic layer depth (Zeu), defined as the depth at which the downwelling irradiance of PAR falls to 1% of that just below the surface (Kirk, 2010), was estimated by using an exponential equation that describes the vertical attenuation of PAR: $I_z=I_0.\exp(-k.z)$, leading to Zeu=4.6/k, where I is PAR (µmol.$m^2.s^{-1}$) and k is the attenuation coefficient ($m^{-1}$).

Seawater samples for phytoplankton pigment analysis were collected using Niskin bottles at three depths: surface (10 m), deep chlorophyll maximum (DCM), and below-DCM (where fluorescence levels stabilized at low values). The depths were selected according to the fluorescence profiles determined by an *in situ* fluorometer (ECO FL, WetLabs) coupled to the CTD system. Additionally, at some stations (numbered stations in Fig. 1), water samples were taken from several depths (between the surface and 200 m) to better characterize the vertical distribution of phytoplankton communities. A varying volume of seawater (1.5–3 L) was filtered in dim light onto Whatman GF/F filters (nominal pore size of 0.7 µm and 25 mm diameter) using a vacuum pump (pressure < 5 in Hg) and immediately stored in liquid nitrogen for later HPLC pigment analysis.

### 2.2. HPLC pigment analysis

The filters were placed in a screw-cap centrifuge tube with 3 mL of 95% cold-buffered methanol (2% ammonium acetate) containing 0.05 mg $L^{-1}$ trans-β-apo-8'-carotenal (Fluka) as an internal standard. Samples were sonicated for 5 min in an ice-water bath, placed at −20 °C for 1 h, and centrifuged at 1100 rpm for 5 min at 3 °C. The supernatants were filtered through Fluoropore PTFE membrane filters (0.2 µm pore size) to rid the extract from the remains of filter and cell debris. Immediately prior to injection, 1000 µL of sample was mixed with 400 µL of Milli-Q water in 2.0 mL glass sample vials, and these were placed in the HPLC cooling rack (4 °C). Methodological procedures for HPLC analysis (using a monomeric C8 column with a pyridine-containing mobile phase) are fully described in Zapata et al.

(2000). The detection limit and quantification procedure of this method were conducted according to Mendes et al. (2007). Pigments were identified from both absorbance spectra and retention times from the signals in the photodiode array detector (SPD-M20A; 190–800 nm; 1 nm wavelength accuracy) or fluorescence detector (RF-10AXL; Ex. 430 nm/Em. 670 nm). Pigments were quantified from peak integration using LC-Solution software (Shimadzu), but all peak integrations were checked manually and corrected where necessary. The HPLC system was previously calibrated with pigment standards from DHI (Institute for Water and Environment, Denmark). The concentrations of pigments were normalized to the internal standard to correct for losses and volume changes. Table 1 lists all pigments detected above the quantification limit and, therefore, analyzed in this study along with their respective abbreviations. The HPLC method presently used allowed for a separation of all pigments, except for chlorophyll *b* and divinyl-chlorophyll *b*, which exhibited the same retention time (co-elution) and, consequently, were presented together as Tchl *b*.

Pigment data were quality controlled according to Aiken et al. (2009). This quality control filter uses a linear relationship between accessory pigments (AP; all carotenoids plus chlorophylls *b* and *c*) and total chlorophyll *a* (Tchl *a*; the sum of monovinyl chlorophyll *a*, divinyl chlorophyll *a,* and chlorophyllide *a*) to either accept or eliminate specific samples. The rules for the quality control of the pigment data were: (1) The difference between Tchl *a* and AP should be less than 30% of the total pigment concentration (TP); (2) Regression analysis between Tchl *a* and AP should have a slope within the range of 0.7–1.4 and must explain more than 90% of the total variance ($r^2 > 0.9$). Our data showed the difference between Tchl *a* and AP always less than 30% of TP and a regression between Tchl *a* and AP with a slope of 1.2 and $r^2$ =0.98.

### 2.3. Photo-pigment indices

As phytoplankton may alter their pigment concentrations and composition in response to variations in irradiance intensity (Higgins et al., 2011), photo-pigment indices were derived according to Barlow et al. (2007) to assess the variation in the contribution of Tchl *a* and carotenoids to the total pigment (TP) pool. Carotenoids were separated as photosynthetic (PSC) and photoprotective (PPC) (see Table 1 for pigments in each category). Accordingly, three photo-pigment indices were symbolized as $\text{Tchl}a_{\text{TP}}$, $\text{PSC}_{\text{TP}}$, and $\text{PPC}_{\text{TP}}$ and defined as given in Table 1. These indices were used to investigate the phytoplankton pigment adaptations in response to light environment regimes across the provinces and throughout the water column.

### 2.4. CHEMTAX analysis of pigment data

The relative contribution of microalgal groups to the overall biomass was calculated using CHEMTAX v1.95 chemical taxonomy software (Mackey et al., 1996) from the class-specific accessory pigments and total chlorophyll *a*. CHEMTAX uses a factor analysis and steepest-descent algorithm to best fit the data onto an initial matrix of pigment ratios (ratio between respective accessory pigments and Tchl *a*). Procedures and calculations are fully described in Mackey et al. (1996).

The initial pigment ratios of major algal classes used here were compiled from Higgins et al. (2011) (see Supplementary Material), with chemotaxonomic groups being identified according to Jeffrey et al. (2011) (see Table 2). The same initial pigment ratio matrix was used on data from the three provinces (Brazil, Gyre, and Africa); however, data from each region were run separately to minimize potential variations in the CHEMTAX optimization procedures. Additionally, to account for variation of pigment ratios with irradiance and/or nutrient availability, these three datasets were further divided into three depth sets: 0–50 m samples, 50–100 m samples, > 100 m samples (see Supplementary Material). Chl *a* was used for calculating the biomass of all groups, except *Prochlorococcus,* for which DV Chl *a* was used. A series of 60 pigment ratio matrices were generated by multiplying each ratio from the initial matrix by a random function to optimize the matrix, and 10% (n=6) of the generated ratios with lowest root-mean-square residual were averaged [see Wright et al. (2009) for further procedure details].

**Table 2**
Chemotaxonomic groups and respective pigments used in CHEMTAX procedures. Pigments in bold correspond to the primary biomarkers (major pigments) of each chemotaxonomic group considered in this study. For further details see Jeffrey et al. (2011). For abbreviations of pigment names, see Table 1.

| Chemotaxonomic group | Pigments used in CHEMTAX |
|---|---|
| Prasinophytes | Chl *a*, **Tchl*b***, Viola, **Pras**, Lut, Zea |
| Chlorophytes | Chl *a*, **Tchl*b***, Viola, **Lut**, Zea |
| Cryptophytes | Chl *a*, **Allo** |
| Diatoms | Chl *a*, **Fuco** |
| Pelagophytes | Chl *a*, **Fuco**, **But**, Chl $c_3$ |
| Dinoflagellates | Chl *a*, **Peri** |
| Haptophytes | Chl *a*, Fuco, **Chlc$_3$**, **Hex**, But |
| *Synechococcus* | Chl *a*, **Zea** |
| *Prochlorococcus* | **DV Chl*a***, **Tchl*b***, Zea |

## 3. Results

### 3.1. Phytoplankton biomass and environmental conditions

The surface longitudinal variations in temperature, salinity, oxygen, and Tchl *a* clearly showed a strong gradient along the A10 section in the SAO, reflecting differences between the identified provinces in this study (Fig. 2). In the Africa province, a less saline (~35.5), oxygen-rich ( > 240 μmol kg$^{-1}$), and cold ( < 18 °C) surface water was observed, associated with relatively high Tchl *a* values (0.5-2 mg m$^{-3}$). Contrarily, the Brazil province was characterized by warmer ( > 20 °C), oxygen-poor ( < 230 μmol kg$^{-1}$), and more saline ( > 36.5) water, associated with low Tchl *a* levels (0.1–0.2 mg m$^{-3}$). The Gyre province presented intermediate values of temperature, salinity, and oxygen (18-20 °C, 35.5-36.5, 230–240 μmol kg$^{-1}$, respectively), whereas Tchl *a* values were similar to that found in the Brazil province (~0.1 mg m$^{-3}$). Mean values of the physical-chemical properties at the surface for each province are shown in Table 3. Despite low mean nutrient concentrations at surface in all provinces, the Africa region presented the highest values across the entire sampled region (Table 3). The mean N:P ratio was also very low at all stations. In the Africa province, the mean DCM depth was approximately coincident with the base of the UML and nitracline depths (~40 m), but shallower than the mean Zeu depth (~70 m). In the Brazil province, the upper layer

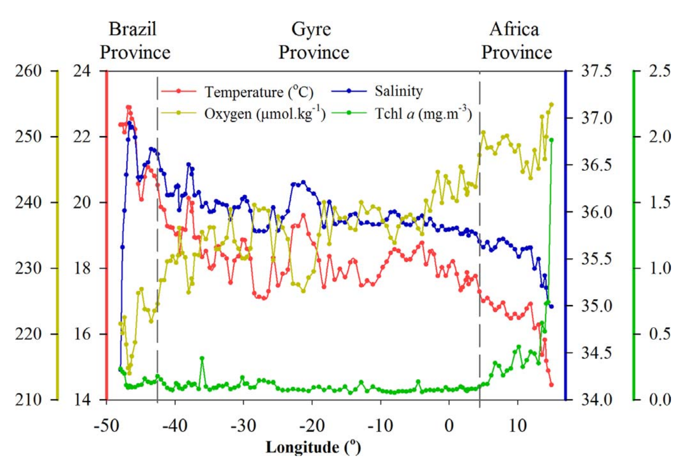


**Fig. 2.** : Surface longitudinal variation of selected variables (temperature, salinity, oxygen and total chlorophyll *a*), used in the cluster analysis to define the three provinces in this study: Brazil, Gyre and Africa provinces. Dashed lines indicate provinces' limits.

**Table 3**
Mean ± standard deviation of environmental variables at surface (or water column for Zeu, DCM, UML, Nitracline and E) for each province, in the study area.

| | Africa Province | Gyre Province | Brazil Province |
|---|---|---|---|
| Temperature (°C) | 16.35 ± 0.77 | 18.34 ± 0.7 | 21.7 ± 0.97 |
| Salinity | 35.5 ± 0.22 | 36 ± 0.19 | 36.4 ± 0.65 |
| Oxygen (μmol.kg$^{-1}$) | 248.62 ± 2.84 | 235.8 ± 4.71 | 220.76 ± 4.07 |
| Nitrate (μmol.kg$^{-1}$) | 1.36 ± 1.68 | 0.02 ± 0.04 | 0.01 ± 0.03 |
| Silicate (μmol.kg$^{-1}$) | 3.09 ± 1.93 | 1.13 ± 0.3 | 1.09 ± 0.86 |
| Phosphate (μmol.kg$^{-1}$) | 0.28 ± 0.17 | 0.11 ± 0.05 | 0.07 ± 0.04 |
| N:P | 3.38 ± 2.84 | 0.17 ± 0.47 | 0.11 ± 0.43 |
| Zeu depth (m) | 70.8 ± 10.7 | 93.3 ± 9.9 | 88.1 ± 10.5 |
| DCM depth (m) | 43.8 ± 18.1 | 99.6 ± 22.5 | 82.2 ± 26.3 |
| UML depth (m) | 40.5 ± 19 | 52.8 ± 32.2 | 27.6 ± 14 |
| Nitracline depth (m) | 38.4 ± 29.3 | 128.9 ± 30.3 | 119.2 ± 55.4 |
| E ($10^{-8}$ rad$^2$.m$^{-1}$) | 142.4 ± 84.3 | 92.9 ± 72.2 | 400.5 ± 511.9 |

showed the highest mean stability value (~400×10$^{-8}$.rad$^2$.m$^{-1}$) and the shallowest mean UML depth (~25 m). The mean DCM in this province was similar to Zeu depth (~85 m), but both shallower than the nitracline (~120 m). The Gyre province was characterized by the lowest mean stability value (~90×10$^{-8}$.rad$^2$.m$^{-1}$), an UML depth of about 50 m, and the deepest mean Zeu (~90 m) and nitracline (~130 m) depths.

In terms of vertical distribution of phytoplankton biomass (Fig. 3), the highest Tchl *a* concentrations (mostly > 1 mg m$^{-3}$) were found at the surface in the Africa province. In the Brazil province, Tchl *a* concentration at the surface was low (0.1–0.2 mg m$^{-3}$), reaching a maximum of 0.5 mg m$^{-3}$ at around 50–100 m. The Gyre province was characterized by low surface Tchl *a* concentrations (< 0.1 mg m$^{-3}$), with an evident DCM (0.2–0.4 mg m$^{-3}$) around 100 m depth closely associated with the base of the euphotic layer and strongly coupled to the nitracline.

### 3.2. Phytoplankton pigments concentrations

A total of 22 phytoplankton pigments was identified in this study, and their concentrations at both surface and DCM layers reflect the distinct ocean regimes between the provinces (see Table 1). Highest mean pigment concentrations were found in the Africa province, with no significant differences between the surface and DCM depths. The lowest mean pigment values were registered in the Gyre province. On the other hand, both the Gyre and Brazil provinces showed marked differences in pigment concentrations between the surface and DCM depths. In the Africa province, Hex (haptophytes marker) was the main accessory pigment, with a mean concentration exceeding 100 ng L$^{-1}$ and a significant contribution (~50 ng L$^{-1}$) of Peri (dinoflagellates marker). The Brazil and Gyre provinces presented similar pigment composition patterns: DV Chl *a* (*Prochlorococcus* marker) was the main pigment at the surface with a significant contribution of other accessory pigments (Chl *b,* But and Hex), a typical pigment profile of the nanoflagellate-dominated plankton community, at DCM. A consistency of Zea (prokariotes marker) concentrations was observed along all provinces, both at the surface and DCM layer, with values ~45–68 ng L$^{-1}$.

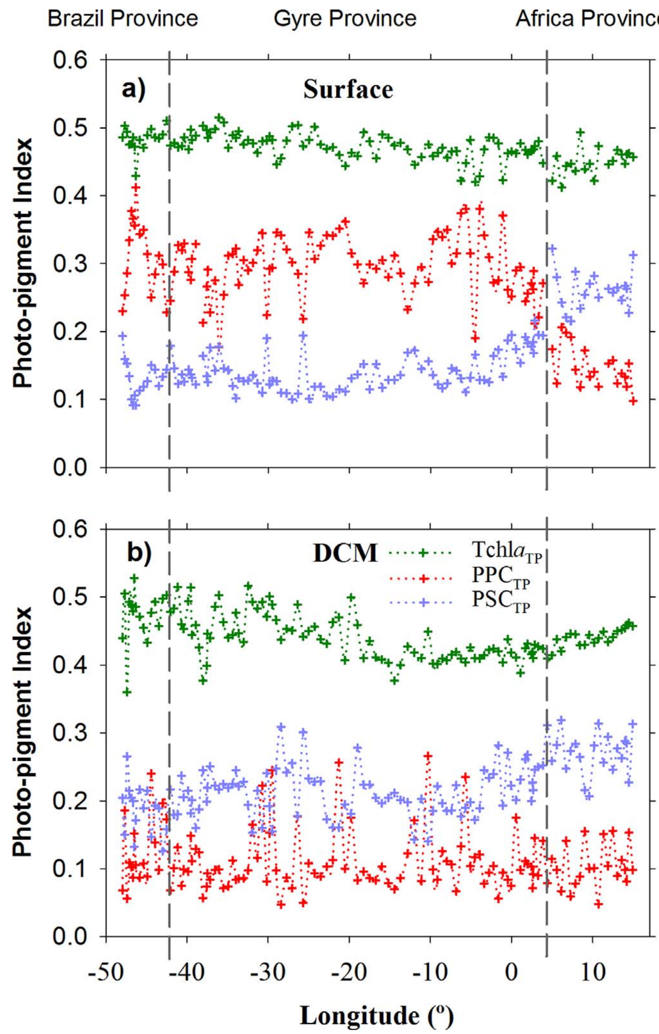


**Fig. 4. :** Longitudinal variations of Photo-pigment indices at (a) surface and (b) DCM depth in the study area. Tchl$a_{TP}$=total chlorophyll *a* to total pigments, PPC$_{TP}$=photoprotective carotenoids to total pigments, PSC$_{TP}$=photosynthetic carotenoids to total pigments. Dashed lines indicate the provinces' limits.

### 3.3. Photo-pigment indices

Photo-pigment indices showed that Tchl$a_{TP}$ was relatively constant

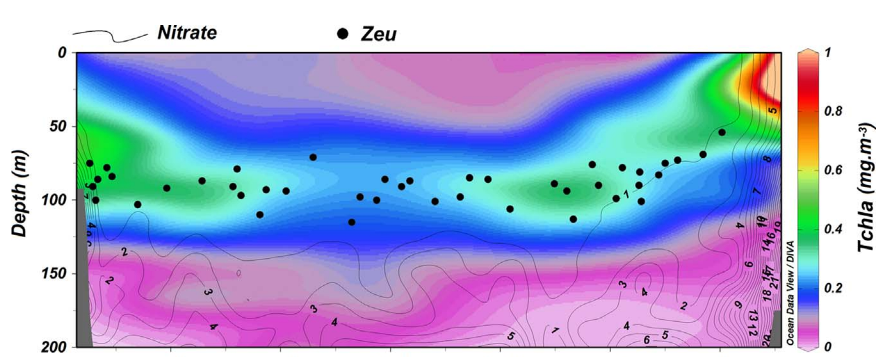


**Fig. 3. :** Vertical distribution of Tchl *a* along the 30°S transect. Contour lines indicate nitrate concentration (μmol.kg$^{-1}$). Black dots indicate the euphotic layer depth (Zeu).

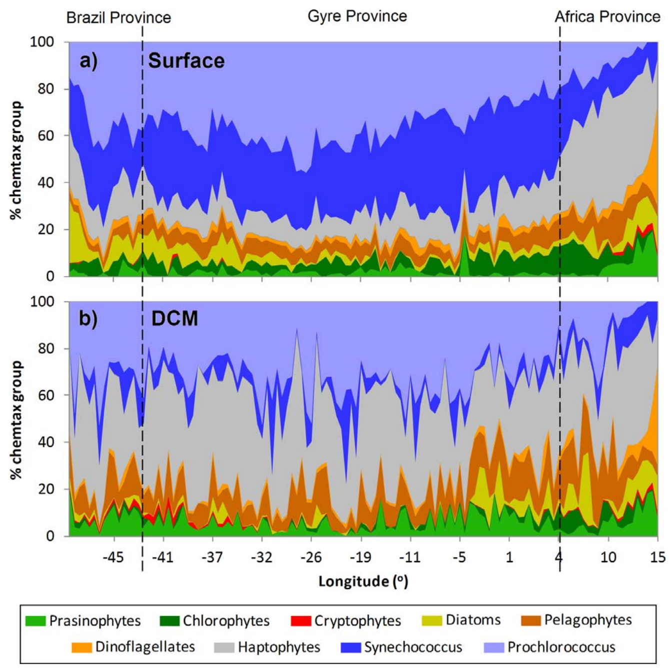


**Fig. 5. :** Longitudinal variations of phytoplankton groups (relative percent contributions to Tchl *a*) derived from CHEMTAX at (a) surface and (b) DCM depth in the study area. Dashed lines indicate the provinces' limits.

along the transect at both the surface and DCM layers, ranging between 0.4 and 0.5 (Fig. 4). $PPC_{TP}$ at the surface was relatively elevated (~0.3) in the Brazil and Gyre provinces, declining to low values (~0.1) in the Africa province. Contrarily, $PSC_{TP}$ at the surface was ~0.3 in the Africa province, declining to ~0.1 in both Brazil and Gyre provinces. At the DCM depth, however, $PPC_{TP}$ was always low (~0.1), while $PSC_{TP}$ ranged between 0.2 and 0.3 along the study area.

### 3.4. Distribution of phytoplankton groups

In the Africa province, the community was dominated by flagellates (mainly Haptophytes) both at surface and DCM layers (Fig. 5). In both Brazil and Gyre provinces, however, the community was dominated by prokaryotes (*Synechococcus and Prochlorococcus*) at surface, and replaced by Haptophytes and *Prochlorococcus* at the DCM depth. Diatoms and dinoflagellates, both at the surface and the DCM depth, made a very small contribution to the phytoplankton community in most stations, except in the Africa province, where Dinoflagellates increased at the coastal zone. It is important to note a low but consistent contribution of Prasinophytes and Pelagophytes along the DCM depth of all provinces.

Vertical distributions of the phytoplankton groups (contribution to Tchl *a*) are shown for two selected and representative stations from each province (Fig. 6). In coastal waters of the Africa province (St. 1), the phytoplankton community was more diverse and abundant and mainly composed of Dinoflagellates (~40%) and Haptophytes (~20%), with the highest biomass values in the 0–40 m upper layer (Fig. 6a). In the oceanic zone of the Africa province (St. 12), phytoplankton diversity and abundance decreased. Dinoflagellates were almost absent, and Haptophytes emerged as the most important group ( > 40%), with a significant contribution of Pelagophytes (~20%), from the surface down to 150 m (Fig. 6b). In the Gyre province (St. 48 and St. 60), the phytoplankton community was mainly represented by *Synechococcus* and *Prochlorococcus* at the surface, while Haptophytes and *Prochlorococcus* appeared as the dominant groups at the DCM depth (Figs. 6c and d). In the Brazil province, a DCM was also evident but at shallower depths than in the Gyre province. The oceanic waters of the Brazil province (St. 108) were dominated by *Synechococcus* and *Prochlorococcus* at the surface, while Haptophytes and *Prochlorococcus* appeared as the dominant groups at the DCM depth (Fig. 6e). In the coastal zone of the Brazil province (St. 120), a great diversity of taxonomic groups was observed, with a significant contribution of Diatoms (~25%) at the surface, while Haptophytes, Prasinophytes and Pelagophytes were observed at the DCM depth (Fig. 6f).

## 4. Discussion

Horizontal distribution of marine phytoplankton communities can be predicted to a certain extent by temperature and nutrients (Acevedo-trejos et al., 2013), while light and nutrient availability, which can be affected by turbulence conditions, determine the phytoplankton distribution over depth (Cullen et al., 2002). The subtropical SAO sampled in this work encompasses biogeochemical provinces with distinct oceanographic regimes (deep ocean *vs.* coastal regions, upwelling zones, oligotrophic gyre), providing an ideal scenario for studying changes/adaptations of phytoplankton communities to distinct environmental conditions.

A considerable number of phytoplankton pigments have been detected in this work, and therefore, data reduction was necessary to extract the most relevant information on the biogeochemical characteristics of the environment (Mendes et al., 2015). As expected, chlorophyll *a* was a major pigment in the studied phytoplankton communities, but $Tchla_{TP}$ values were similar among the provinces (see Fig. 4 and Table 1), demonstrating that the ratio of Tchl *a*/total pigments was highly conservative, as suggested by Trees et al. (2000). This implies that accessory pigments play an important role on phytoplankton adaptive strategies to survive in the environment. Consequently, phytoplankton pigments and ratios (indices) can be used to determine changes in phytoplankton community structure and/or physiological responses to environmental settings. For instance, high concentrations of photosynthetic carotenoids (PSCs) normally indicate regions of high productivity and a dominance of large phytoplankton cells, whereas high photoprotective carotenoid (PPCs) proportions suggest oligotrophic conditions associated with small phytoplankton cells (Gibb et al., 2000). On the other hand, it has been shown that phytoplankton communities accumulate more PPCs to mitigate the photo-oxidative damage of cells caused by high irradiance (PAR) levels and/or ultraviolet radiation (Moreno et al., 2012), whereas increases in PSCs are used to compensate light limitation (Rodríguez et al., 2006). In fact, in this study, the highest proportions of PPCs were observed in surface nutrient-depleted waters of both the Brazil and Gyre provinces, with a dominance of prokaryotes, indicating an oligotrophic condition (see Figs. 4 and 5). Inversely, flagellates (specifically dinoflagellates in the coastal zone) were the dominant group in the nutrient-rich upwelling influenced surface waters of the Africa province. This pattern agrees well with previous phytoplankton pigment observations in the SAO (Barlow et al., 2007; Aiken et al., 2009). At the DCM depth, in turn, high proportions of PSC were found, associated with a clear dominance of flagellates (mainly haptophytes) along all provinces (see Figs. 4 and 5).

The DCM reflects a trade-off to phytoplankton communities exposed to two opposing resource gradients: nutrients supplied from below and light supplied from above (Huisman et al., 2006). Within this context, the distance between the nitracline and the base of the mixed layer highly affects vertical fluxes of nitrate in the ocean (Painter et al., 2008). For example, in subtropical gyres there is limited nutrient renewal at the surface due to the nitracline being almost always deeper than the upper mixed layer (Neuer et al., 2007; Painter et al., 2008). This led some investigators to postulate the presence of two distinct layers within the euphotic zone: a well-mixed upper layer where primary production is supported primarily by regenerated forms of nitrogen and a lower layer where production is predominately supported by new nutrients (primarily nitrate) that enter the euphotic zone

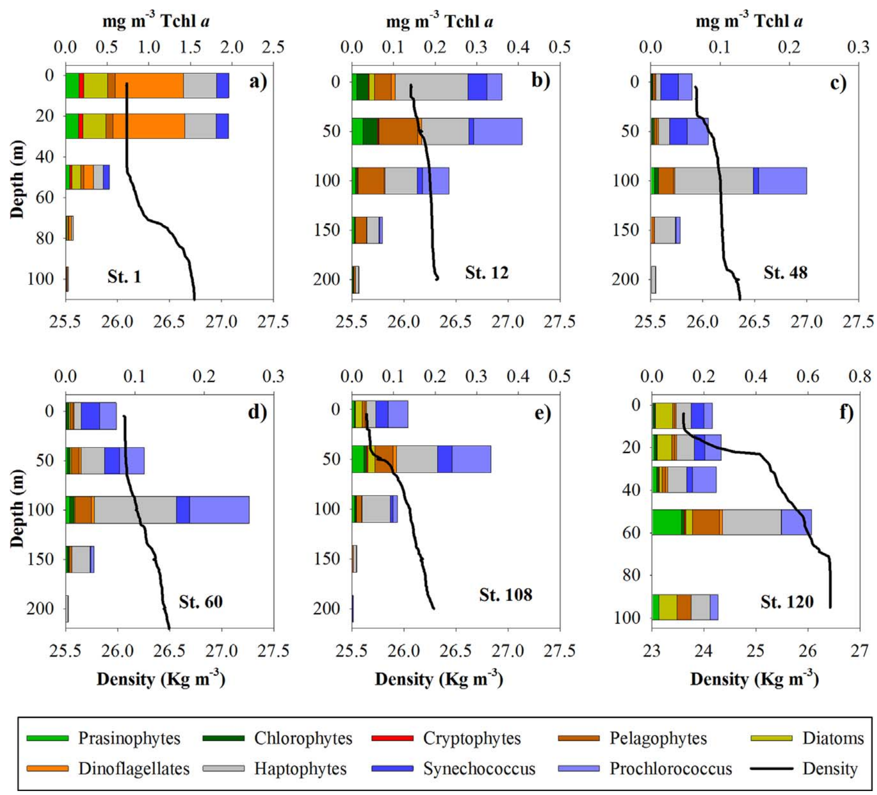


**Fig. 6. :** Vertical distribution of phytoplankton groups' biomass (as Tchl *a* concentration) derived from CHEMTAX at selected stations representative of each province identified in this study, and respective density profiles: (a,b) Africa province; (c,d) Gyre province; (e,f) Brazil province. Note the different scales.

(Painter et al., 2007), enhancing phytoplankton biomass and forming the DCM (Mignot et al., 2014). By controlling the metabolism *vs.* size-scaling relationship, nutrient supply plays a major role in determining community size structure and the energy flow through the pelagic ecosystems (Marañón et al., 2007). Thus nanoflagellate groups, as found mainly at DCM depths in this study (see Fig. 5), are expected to grow and dominate those deep environments. In fact, it has been reported that the nano size fraction of plankton is important in subtropical zones of the Atlantic (Tarran et al., 2006) and that a deep nanoflagellate population can develop close to the nitracline at very low light levels (Claustre and Marty, 1995).

The southern Benguela area (co-located in this study with the Africa province) is a highly dynamic region influenced by local wind patterns that drive upwelling/relaxation cycles on timescales of days (Hutchings et al., 2009). A quasi-meridional front develops between recently cold-upwelled enriched waters at the coast and warmer oligotrophic offshore waters (Belkin et al., 2009). This strong cross-shore temperature gradient, coincident with the ambient nutrient concentrations, strongly influences the phytoplankton assemblages (Resende et al., 2007; Kudela et al., 2010). In general, the coastal upwelling communities are dominated by microplankton, the nearshore area by nanoplankton, and the offshore oceanic waters are mainly composed of prokariotes (picoplankton) (Fishwick et al., 2006; Hirata et al., 2009). Results presented here for the Africa province showed dinoflagellates to be the dominant group near the coast, responding to the upwelling signal and corresponding to the highest values of Chl *a*, while nanoflagellates (mainly haptophytes) appeared at intermediate environments (between nearshore and offshore) (see Fig. 6a,b).

Subtropical ocean gyres are considered to be the marine analogues of terrestrial deserts because of chronic nutrient depletion and the low standing stocks of organisms (Karl et al., 1995). While biological productivity within these oligotrophic regions may be relatively small, their contribution is significant to the total production due to the great surface dimension of the open oceans (McClain et al., 2004). In the present study, the Gyre province showed an upper mixed layer with almost undetectable nutrient levels and the presence of a DCM in the vicinity of the light-limited nitracline (see Table 3 and Fig. 3). Additionally, two distinct vertical structures of pico-phytoplankton habitats were found for *Synechococcus* and *Prochlorococcus*. The first occupied primarily surface waters, while the second was distributed throughout the water column with a subsurface maxima (see Figs. 5 and 6c,d), as also observed in Zubkov et al. (2000). *Prochlorococcus* can successfully inhabit the entire euphotic zone due to photoacclimation abilities of different ecotypes, physiologically and genetically distinct (Hickman et al., 2010). These ecotypes can be characterized by varying DVChl *b* to DVChl *a* ratios, indicating their adaptation to high-light (low DV Chl *b*/DV Chl *a* ratios) or low-light (high DV Chl *b*/DV Chl *a* ratios) environments (e.g., Carreto et al., 2008). In fact, in the present study, the highest concentrations of Tchl *b* were detected at the DCM of all provinces. Therefore, this pattern seems to be more associated with photoadaptation (and photoacclimation) processes occurring in different *Prochlorococcus* ecotypes than to the biomass of *Prochlorococcus* itself. The relative abundance of these ecotypes in the oceans is also related to changes in other environmental factors, like temperature, nutrients and vertical mixing dynamics (Bouman et al., 2006, 2011; Johnson et al., 2006; Zinser et al., 2007).

Haptophytes (e.g., coccolithophores) was an important group contributing to phytoplankton biomass in the Gyre at DCM depths (see Figs. 5 and 6c,d). Competition for light and nutrients strongly determines where and when Haptophytes will either flourish or fail (Gregg and Casey, 2007). These organisms have a slow growth and a fast sinking rate, but their low nitrate half-saturation constant and low light saturation for growth enable them to both efficiently utilize nutrients at reduced concentrations and effectively use low available irradiance. The key to success of these organisms in the global ocean is to find areas where nutrients and light are low enough to inhibit growth of large groups (e.g., diatoms), but vertical mixing is high enough to prevent sinking losses and provide some nutrients from deep water masses (Gregg and Casey, 2007). Once thought to be homogeneous and static habitats, there is increasing evidence that oligotrophic gyres exhibit substantial physical and biological variability on different time scales (McClain et al., 2004). Seasonal pulse events of new nutrients into the euphotic layer can occur due to deepening of mixed layer down to the nitracline (Cermeño et al., 2008). On the other hand, the relative position of the DCM depth with respect to the nitracline migrates over seasonal timescales as a function of varying irradiances in the water column (Mignot et al., 2014; Letelier et al., 2004). The distinct mechanisms of light adaptation and nutrient tolerance of each phytoplankton group determines their relative dominance in this environment, as in the case of haptophytes found in this work.

In the Brazil province, a prevalence of warm tropical water at the surface sets a strong thermocline, separating deep nutrient-enriched waters from the euphotic zone, leading to a low productivity condition at the surface (Brandini, 2006). In this region, most of biological energy in the surface layer comes from regenerated production from the constant recycling of nutrients by the microbial community, and an occasional rise in new production is fundamentally linked to seasonal processes of enrichment, such as local and small-scale upwelling events or continental river runoff (Metzler et al., 1997). In fact, it has been suggested that this region can be classified as “oligotrophic water with coastal influence” (Gonzalez-Silvera et al., 2004). However, due to a frequent oceanic intrusion of nutrient-rich water mass in the bottom boundary layer on the continental shelf, the DCM is a typical oceanographic feature observed in this region and generally undetectable in remote sensing ocean color images (Brandini, 2006; Brandini et al., 2014). The DCM formation and community composition observed in the present study for this province (see Figs. 3 and 6e,f) agrees with previous studies (Odebrecht and Djurfeldt, 1996). The occurrence of this DCM is essential for the maintenance of pelagic and demersal fish resources in this region (Matsuura, 1996).

Near the Brazilian coast, the relatively low salinity at the surface (see Fig. 2) is commonly observed due to influence of continental river runoff (Möller et al., 2008; Campos et al., 2013). This relatively fresh and warm surface water mixed with bottom water of an incomplete upwelling stage can trigger a high stability and shallow UML (Lima et al., 1996) as observed in this study (see Table 3). However, the influence of this coastal water apparently did not affect the phytoplankton biomass and community composition at the surface. The low-biomass and prokaryote dominance at the surface (see Fig. 6e,f) agrees with previous studies in this region (Brandini, 1990; Odebrecht and Djurfeldt, 1996; Gonzalez-Silvera et al., 2004; Garcia et al., 2005).

## 5. Conclusions

Phytoplankton biomass and community composition in the Subtropical South Atlantic Ocean varied according to distinct provinces along 30°S, and they were associated with distinct nutrient and light conditions. In the Africa province, due to influence of the Benguela upwelling system, highest Tchl *a* concentrations ($> 1$ mg m$^{-3}$) were found at surface, associated with a relatively shallow UML (0–50 m), and no evident DCM. The euphotic layer tended to be shallow, associated with high and homogeneously distributed nitrate concentrations in the entire water column. The community in this province was dominated by flagellates (mainly haptophytes and dinoflagellates in the coastal zone). In the Brazil province, the euphotic layer was relatively deep (75–100 m) with low surface nitrate concentrations ($<$ 1 µmol.kg$^{-1}$), which increased at depths below 50 m. Tchl *a* concentration at the surface was low (0.1–0.2 mg m$^{-3}$), reaching a maximum of 0.5 mg m$^{-3}$ at around 50–100 m. Towards the coast, lower salinity waters were associated with a diverse phytoplankton community, with important contributions of diatoms and various nanoflagellate groups at the surface and the DCM layers. The Gyre province was characterized by low surface Tchl *a* concentrations ($< 0.1$ mg m$^{-3}$), with an evident DCM around 100 m depth closely associated with the base of the euphotic layer and strongly coupled to the nitracline. The community was dominated by prokaryotes, with two distribution patterns: while *Synechoccocus* was majorly found at the surface, *Prochloroccocus* was abundant throughout the water column, sharing dominance with small flagellates (mainly haptophytes) at the DCM depth. At this layer, a significant enhancement in Tchl *b* concentration (also seen in the Brazil province) suggested the occurrence of distinct *Prochloroccocus* ecotypes, adapted to different light regimes (surface *vs* deep layers). The HPLC-CHEMTAX approach proved to be a powerful tool for mapping phytoplankton communities’ distribution along the subtropical South Atlantic Ocean and also provided useful information on their physiological adaptations.

## Acknowledgments

This study is a contribution to the activities of the Brazilian High Latitudes Oceanography Group (GOAL). GOAL has been funded by the Brazilian Antarctic Program (PROANTAR), the Brazilian Ministry of the Environment (MMA), the Brazilian Ministry of Science, Technology and Innovation (MCTI) and the Council for Research and Scientific Development of Brazil (CNPq). We thank captain and crew of the RV *Ronald H. Brown* and the NSF/ NOAA-funded U.S. CLIVAR Repeat Hydrography Program (funding provided by the NOAA Climate Program Office and the NOAA Atlantic Oceanographic and Meteorological Laboratory). We are very grateful to Simon Wright, from the Australian Antarctic Division, for providing CHEMTAX v.1.95, and to Luciano Azevedo for collecting all optical data and seawater samples for pigments analysis. M. L.V. Araujo and C.R.B. Mendes acknowledge financial support from the CAPES Foundation (Coordination for the Improvement of Higher Education Personnel). We are thankful for the constructive criticism of two anonymous reviewers, which helped to improve the manuscript.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.dsr.2016.12.004.

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