

Bio-optical provinces in the eastern Atlantic Ocean and their biogeographical relevance

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Abstract. The relationship between phytoplankton assemblages and the associated optical properties of the water body is important for the further development of algorithms for large-scale remote sensing of phytoplankton biomass and the identification of phytoplankton functional types (PFTs), which are often representative for different biogeochemical export scenarios. Optical in-situ measurements aid in the identification of phytoplankton groups with differing pigment compositions and are widely used to validate remote sensing data. In this study we present results from an interdisciplinary cruise aboard the RV *Polarstern* along a north-to-south transect in the eastern Atlantic Ocean in November 2008. Phytoplankton community composition was identified using a broad set of in-situ measurements. Water samples from the surface and the depth of maximum chlorophyll concentration were analyzed by high performance liquid chromatography (HPLC), flow cytometry, spectrophotometry and microscopy. Simultaneously, the above- and underwater light field was measured by a set of high spectral resolution (hyperspectral) radiometers. An unsupervised cluster algorithm applied to the measured parameters allowed us to define bio-optical provinces, which we compared to ecological provinces proposed elsewhere in the literature. As could be expected, picophytoplankton was responsible for most of the variability of PFTs in the eastern Atlantic Ocean. Our bio-optical clusters agreed well with established provinces and thus can be used to classify areas of similar biogeography.

This method has the potential to become an automated approach where satellite data could be used to identify shifting boundaries of established ecological provinces or to track exceptions from the rule to improve our understanding of the biogeochemical cycles in the ocean.

1 Introduction

Marine phytoplankton stands at the base of most marine food webs and contributes significantly to global primary production. Chlorophyll-*a* (Chl-*a*) concentration as a proxy for phytoplankton biomass and primary production can be monitored on a global scale through remote sensing of ocean colour (McClain, 2009; Saba et al., 2011). However, the phytoplankton community is composed of thousands of species which differ significantly in their role in the ecosystem. Given that some pigments are characteristic of certain phytoplankton groups, inventories of these pigments have been used to determine the approximate abundance of these phytoplankton functional groups (PFTs) (e.g. Letelier et al., 1993; Mackey et al., 1996; Vidussi et al., 2001; Bricaud et al., 2004; Jeffrey et al., 2005; Uitz et al., 2006). Although the use of pigments to determine phytoplankton groups can also bear the risk of errors through the gross simplification of assigning one specific pigment to one group of algae, we believe that the results still give a good approximation of the true phytoplankton composition. It is a method which allows for higher analysis frequency than looking at each sample through the microscope. Furthermore it permits the analysis of a broader range of cell-sizes including the large diatoms,



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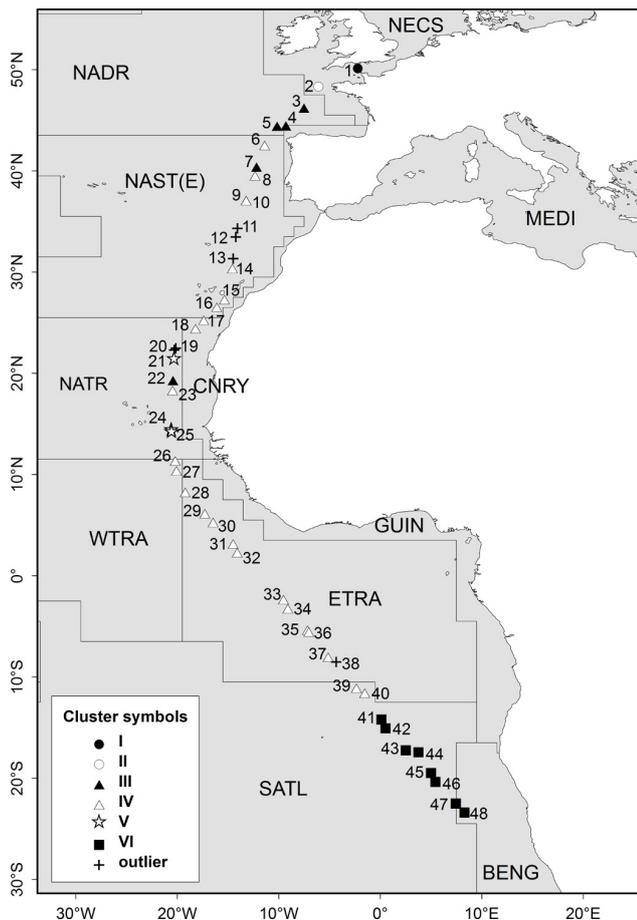


Fig. 1. Map of study area, showing the sample stations during cruise ANT-XXV/1 on RV *Polarstern* in November 2008 overlying the oceanic provinces defined by Longhurst (2006). The symbols represent the pigment-based clusters defined in Fig. 4.

which are too big for flow cytometric analysis as well as the small-celled species such as *Synechococcus* and prochlorophytes which are too small to be identified by microscopy. The importance of pico-prokaryotes and pico-eukaryotes in the marine carbon cycle has been shown frequently in the last three decades for the tropical Atlantic (e.g. Zubkov et al., 2000; Marañón et al., 2001; Barlow et al., 2002; Veldhuis and Kraay, 2004). In this study, pigment composition forms the basis to group the samples by means of an unsupervised clustering analysis, which is subsequently applied to all other bio-optical data sets. We use hyperspectral field data of inherent optical properties (IOPs) such as particulate absorption, and apparent optical properties (AOPs) such as remote sensing reflectance to define ecological units on a north-to-south transect across the eastern Atlantic Ocean. Flow cytometric and microscopic measurements as well as oceanographic data provide additional information to characterize the clusters.

On land, the distinction between different ecosystems such as the edge of a forest or the extent of a desert is generally easier compared to the marine environment. Due to the highly dynamic nature of the oceans and the lack of knowledge about many of those dynamics, these boundaries between ecological units are much harder to observe. They are, however, no less real (Sathyendranath et al., 1995; Platt and Sathyendranath, 1999; Longhurst, 2006). Areas in the world's oceans with similar physical and biological characteristics are generally referred to as ecological or biogeochemical provinces or units (e.g. Platt et al., 2005). Partitioning the ocean into provinces can assist us in understanding complex patterns in the oceans and help us to extrapolate province-specific parameters over large spatial scales for a better estimation of global primary production and carbon budget (Platt et al., 2005; Longhurst, 2006; Barlow et al., 2007). The approximation of ecological parameters (e.g. in modelling or in the interpretation of satellite data) can be more accurate if we know which areas exhibit similar dynamics.

Several studies have used *Chl-a* as one of the descriptors to define marine ecological provinces (e.g. Devred et al., 2007; Hardman-Mountford et al., 2008). The objective of this study was to use pigment composition in conjunction with hyperspectral optical data to establish an ecological geography of the eastern Atlantic Ocean. In light of the recent advances in hyperspectral technology on the remote sensing observing platforms, the possibility of characterizing marine ecological units and phytoplankton communities through hyperspectral measurements becomes increasingly interesting and important. These methods will help to further assess the extension and dynamic of ecological provinces in the ocean on a large spatial and temporal scale. We hypothesize that the bio-optical provinces will largely follow the biochemical provinces previously proposed by Longhurst (2006) although smaller scale spatial deviations are likely given the finer temporal sampling resolution.

2 Methods

2.1 In-situ sample and data collection

2.1.1 Sample collection

Samples were collected at 48 stations, of which 26 were CTD stations, during the ANT-XXV/1 expedition of the RV *Polarstern* in November 2008 along a north-to-south transect through the eastern Atlantic Ocean from Bremerhaven (Germany) to Cape Town (South Africa) (Fig. 1). At the 22 stations without CTD casts only surface waters were sampled through the moonpool of the ship. The CTD stations were performed once a day at noon local time and involved CTD casts with water samplers as well as measurements of remote sensing reflectance. Measurements of surface salinity,

temperature and fluorescence were conducted continuously throughout the cruise and are described in more detail below. Water samples for pigment and absorption analysis were filtered on GF/F filters, shock-frozen in liquid nitrogen and stored at -80°C . Samples for flow cytometry were preserved with 0.1% glutaraldehyde (final concentration), shock-frozen in liquid nitrogen and stored at -80°C (Marie et al., 2005).

2.1.2 CTD profiles and continuous data from onboard ship devices

Temperature, salinity and total Chl-*a* (TChl-*a*) profiles were determined using a Seabird 911 Plus CTD with a Wetlabs ECO FL fluorometer fitted to a rosette system provided with 24×121 Niskin bottles. Density was calculated from salinity and temperature data, and mixed layer depth (Z_m (sigma)) was derived from density profiles using the definition from Levitus (1982), where Z_m is defined as the depth at which a change from the surface density of 0.125 has occurred. Continuous temperature and salinity data were recorded with the onboard thermosalinograph SEABIRD SBE 21 equipped with an external thermometer SBE 38 installed at the bow of the ship (Rohardt, 2009). The data set was processed according to Fahrback et al. (2007).

2.1.3 Radiometric measurements

Underwater optical light fields were measured with hyperspectral radiometers (RAMSES, TriOS GmbH, Germany) measuring profiles of radiance and irradiance. The instruments cover a wavelength range of 320 nm to 950 nm with an optical resolution of 3.3 nm and a spectral accuracy of 0.3 nm. All measurements were collected with sensor-specific automatically adjusted integration times (between 4 ms and 8 s).

A total of 22 radiometric profiles were collected simultaneously with the CTD profiles at noon down to a maximum depth of 190 m, with a radiance sensor measuring upwelling radiance (L_u), and an irradiance sensor measuring downwelling irradiance (E_d). Irradiance at the surface (E_d^+) was measured as a reference with a third sensor placed above-water and allowed normalization of the in-water measurements according to Stramski et al. (2008). One of the in-water sensors was equipped with an inclination and a pressure sensor. To avoid ship shadow, the ship was oriented such that the sun was illuminating the side where the measurements were taking place.

All radiometric data were collected during clear sky or nearly clear sky conditions. The pitch and roll data measured by the ship did not exceed values larger than 5° . For the in-water data, the inclination in either dimension was smaller than 14° (Matsuoka et al., 2007). The profile data were averaged in discrete intervals of 2 m down to a depth of 48 m, 4 m for depths between 48 and 80 m and 10 m for

the measurements below 80 m. As surface waves strongly affect measurements in the upper few meters, deeper measurements that are more reliable had to be used and extrapolated to the sea surface (Mueller et al., 2003). Similar to Stramski et al. (2008) a depth interval was defined ($z' = 7$ to 21 m) to calculate the vertical attenuation coefficients for downwelling irradiance and upwelling radiance, (i.e. $K_d(\lambda, z')$ and $K_u(\lambda, z')$, respectively). With $K_d(\lambda, z')$ and $K_u(\lambda, z')$, the subsurface irradiance $E_d^-(\lambda, 0\text{ m})$ and radiance $L_u^-(\lambda, 0\text{ m})$ were extrapolated from the profiles of $E_d(\lambda, z)$ and $L_u(\lambda, z)$. For the calculation of the remote sensing reflectance ($R_{rs}(\lambda)$), the subsurface $L_u^-(\lambda, 0\text{ m})$ was propagated through the water-air interface by applying a transfer coefficient of 0.5425 determined by Stramski et al. (2008) for the same geographical area. $R_{rs}(\lambda)$ was therefore calculated using the above-water reference downwelling irradiance $E_d^+(\lambda)$:

$$R_{rs}(\lambda) = (0.5425 \cdot L_u^-(\lambda, 0\text{ m})) / E_d^+(\lambda)$$

$E_d(\text{PAR}, z)$ profiles were calculated as the integral of $E_d(\lambda, z)$ for all wavelengths from 400 nm to 700 nm for each depth interval. To determine the euphotic depth, Z_{eu} , the natural logarithm of $E_d(\text{PAR}, z)$ was fitted linearly with z :

$$E_d'(\text{PAR}, z') = \exp(m \cdot z' + n) \text{ (with fit parameters } m \text{ and } n)$$

z' varied in steps of 1 cm from 0 m to 200 m depth. The euphotic depth was then calculated from

$$0.01 = E_d'(\text{PAR}, Z_{eu}) / E_d'(\text{PAR}, 0\text{ m})$$

2.1.4 Continuous fluorescence measurements by Fast Repetition Rate fluorimetry (FRRf)

Variable fluorescence was measured continuously with a FastTracka I fluorimeter (Chelsea, West Molesey, UK) in the ship's moonpool at 11 m depth using water pumped through the dark chamber of the instrument by a peristaltic pump. The minimum fluorescence (F0) measurements were used as an indicator for TChl-*a*, as F0 is correlated to the amount of available TChl-*a* pigments (Kolber et al., 1998).

For further analysis, the FRRf measurements were averaged to 10 min intervals. The F0 data taken during daylight were corrected for photochemical quenching by the method developed by Strass (1990). As this method was developed with a standard fluorimeter setup which measures F0, we also used the F0 data instead of the more commonly used Fm data. We tested the analysis with Fm data and the differences were marginal. The surface F0 daytime measurements were corrected for the quench due to light in the surface waters by comparing them to the global radiation data measured by the ship's system. Generally, it can be seen – if values are not too low – that F0 values decrease during daylight due to non-photochemical quenching. The mean of the light measurements during one day was subtracted from the mean of

Table 1. Solvent gradient used for HPLC measurements. Solvent A: 30 % 1 mol l⁻¹ ammonium acetate, 70 % methanol. Solvent B: 100 % methanol.

Gradient [min]	Flow [ml min ⁻¹]	% Solvent A	% Solvent B	Curve
0	1	65	35	
1	1	40	60	6
7	1	15	85	6
13	1	0	100	10
19	1	0	100	6
20	1	65	35	6

the dark measurements of the corresponding day. The resulting offset was added to the day time measurements. In general, day time quenching was low except for areas with Chl-*a* concentration above 0.5 mg m⁻³ where the effect was more pronounced.

Based on the pigment-based clusters identified by the statistical analysis described below, the F0 data for each cluster were calibrated with the TChl-*a* concentrations derived from the HPLC analysis (see Sect. 2.3). In particular, different TChl-*a* conversion factors were calculated for each cluster by comparing the collocated F0 data to the HPLC TChl-*a* value. Using the conversion factor specific for each cluster, the continuous surface TChl-*a* concentrations were calculated from the F0 data. The uncertainties of the TChl-*a* measurements by FRRf in the different clusters were 53 %, 18 %, 20 %, 28 % and 4 % with the number of collocations 4, 12, 3, 7, 8, and 4 for clusters III, IVa, IVb, V, VI, respectively.

2.2 Sample analysis

2.2.1 Pigment analysis

Pigment composition was analysed by High Performance Liquid Chromatography (HPLC) following a method described in Hoffmann et al. (2006) adjusted to our instruments. In short, samples were measured using a Waters 600 controller combined with a photodiode array detector (PDA, Waters 2998) and an auto sampler (Waters 717plus). For solvents and solvent gradient see Table 1. As an internal standard, 100 µl canthaxanthin (Roth) was added to each sample. Identification and quantification of the different pigments were carried out using the program EMPOWER by Waters. A list of the pigments used for this study, their abbreviations and their associated phytoplankton groups can be found in Table 2. The pigment data were quality controlled according to Aiken et al. (2009).

2.2.2 Absorption measurements

Measurements of the particulate absorption were carried out on a dual-beam UV/VIS spectrophotometer (Cary 4000, Varian Inc.) equipped with a 150 mm integrating sphere (external DRA-900, Varian, Inc. and Labsphere Inc., made from Spectralon (TM)) using a quantitative filterpad technique modified as follows (see e.g. Simis et al., 2005). The filters were placed in the center of the integrating sphere using a center-mount filter holder perpendicular to the light beam. A wavelength scan from 300 to 850 nm with a resolution of 1 nm (slit width 2 nm, scan rate 150 nm min⁻¹) was performed, when the reflectance ports were covered with Spectralon(TM) reflectance standards. The baseline was recorded beforehand with a clean, dry filter, and a filter which was soaked for more than 30 min in purified water served as a reference. The absorption coefficient was calculated from optical density (OD) measurements using a path length amplification factor of 4.5 ($\beta = 1/4.5$, Röttgers, personal communication) as $a [m^{-1}] = -\ln(T \cdot A \cdot \beta / V)$, where the transmittance $T = \exp(-OD)$, V is the filtrated sample volume in m³ and A the filter clearance area in m². Results from the original filter gave particulate absorption, a_p . To determine the absorption by non-algal particles (a_{NAP}), the algal pigments were bleached with NaOCl as described in Tassan and Ferrari (1995) and Ferrari and Tassan (1999). The bleached filters were measured as described above. To obtain the particulate absorption of phytoplankton ($a_{ph}(\lambda)$) a_{NAP} was subtracted from a_p .

2.2.3 Flow cytometry

Phytoplankton cells were enumerated from preserved and frozen, unstained samples by using their specific Chl-*a* and phycoerythrin autofluorescence according to Marie et al. (2005). Both Chl-*a* and phycoerythrin are excited with the common 488-nm excitation line and fluoresce at 690 nm (red) and 570 nm (orange), respectively. Flow cytometry was performed on a FACScalibur with an excitation beam of 488 nm, two light scatter detectors at 180° (forward scatter) and at 90° (side scatter) and several photomultipliers detecting at 530 nm (beads), 585 nm (orange fluorescence) and 670 nm (red fluorescence). Phytoplankton groups were separated according to their red and orange fluorescence and scattering characteristics. Yellow-green Fluoresbrite® Microspheres with a diameter of 1 µm (Polysciences) were used as an internal standard. The data were analysed with the instrument software "CellQuest".

2.2.4 Microscopy

Samples were fixated with 2 % buffered formaldehyde (end concentration) and stored in brown glass bottles in a dark, cool and dry place. For analysis, the samples were introduced into a settling chamber and the phytoplankton was

Table 2. List of pigments analysed in this study, their abbreviations used in the text and associated phytoplankton groups, if the pigment is used as a marker pigment in literature. Pigments which have no associated phytoplankton group in this table are not specific for one group.

Pigment	Abbreviation	Diagnostic pigment for	Key references
Alloxanthin	Allo	Cryptophyceae	3, 4
Astaxanthin	Asta		
<i>Monovinyl</i> -Chlorophyll- <i>a</i>	Chl- <i>a</i>		
<i>Divinyl</i> -Chlorophyll- <i>a</i>	DVa	Prochlorophyceae	1, 5, 6, 7
<i>Monovinyl</i> -Chlorophyll- <i>b</i>	Chl- <i>b</i>	Green algae	4
<i>Divinyl</i> -Chlorophyll- <i>b</i>	DVb	Prochlorophyceae	1, 5, 6, 7
Chlorophyll- <i>c</i> _{1/2}	Chl- <i>c</i> _{1/2}		
Chlorophyll- <i>c</i> ₃	Chl- <i>c</i> ₃		
α -carotene	α -car		
β -carotene	β -car		
Diadinoxanthin	Diadino		
Diatoxanthin	Diato		
Fucoxanthin	Fuco	Bacillariophyceae	2, 5, 8
19'-hexanoyloxyfucoxanthin	19HF	Haptophytes	2, 4, 5
19'-butanoyloxyfucoxanthin	19BF	Chrysophyceae	2, 4, 5
Neoxanthin	Neo		
Lutein	Lut		
Peridinin	Peri	Dinophyceae	2, 5
Phaeophytin- <i>a</i>	Phyt- <i>a</i>		
Phaeophytin- <i>b</i>	Phyt- <i>b</i>		
Prasinolaxanthin	Prasino	Prasinophyceae	2, 5
Violaxanthin	Viola		
Zeaxanthin	Zea	Cyanophyceae	1, 4, 7, 8

References: 1: Goericke and Repeta (1992); 2: Letelier et al. (1993); 3: Pennington et al. (1985); 4: Jeffrey et al. (2005); 5: Bjørnland and Lliaaen-Jensen (1989); 6: Partensky et al. (1993); 7: Morel et al. (1993); 8: Gieskes et al. (1988)

allowed to settle for 48 h. Phytoplankton cells were then identified and counted by the Utermöhl method (Utermöhl, 1958; Edler, 1979) using a Zeiss IM35 inverted microscope equipped with phase contrast and 400 \times magnification.

2.3 Data analysis

2.3.1 Interpretation of pigment data

Some pigments have been used in the past as marker pigments for one specific phytoplankton group. Table 2 lists the pigments analysed in this study, their abbreviations, which will be used in the text and the phytoplankton groups to which some diagnostic pigments have been assigned in the past (see references in the table). Two methods were applied to interpret the pigment data. Firstly, phytoplankton size classes were calculated by a procedure proposed by Vidussi et al. (2001), which was subsequently refined by Uitz et al. (2006) and most recently by Hirata et al. (2011). The relative proportions of microphytoplankton (20–200 μ m), nanophytoplankton (2–20 μ m) and picophytoplankton (<2 μ m) were estimated from the concentrations of 7 diagnostic pigments.

The general assumptions are

– Fuco and Peri are diagnostic pigments for diatoms and dinoflagellates, respectively, which dominate the microplankton (>20 μ m),

– However, Fuco is also a precursor pigment of 19HF, which is a diagnostic pigment for nanoplankton (see below) and thus can co-occur in this group. The Fuco concentration used to calculate the proportion of microplankton needs to be corrected for this fact (see Hirata et al., 2011, for details)

– Allo, 19BF, 19HF and total Chl-*b* characterize the nanoplankton (2–20 μ m),

– Picoplankton (<2 μ m) is assessed from Zea

The weighted relationships of these diagnostic pigments were calculated by Hirata et al. (2011) by multiple regression analysis as follows:

$$\% \text{ Pico} (< 2 \mu\text{m}) = 100 \cdot (0.86\text{Zea}) / \text{DPw}$$

$$\% \text{ Nano} (2 - 20 \mu\text{m}) = 100 \cdot (1.2719\text{HF} + 1.01\text{Chl-}b + 0.3519\text{BF} + 0.6\text{Allo}) / \text{DPw}$$

$$\% \text{ Micro} (> 20 \mu\text{m}) = 100 \cdot (1.41\text{Fuco} + 1.41\text{Peri}) / \text{DPw}$$

where $DPw = 0.86 Zea + 1.01 TChl-b + 1.27 19HF + 0.35 19BF + 0.6 Allo + 1.41 Fuco + 1.41 Peri$

As a second tentative interpretation of the pigment data we used the programme CHEMTAX (Mackey et al., 1996), initiated with the pigment ratio matrix proposed by Veldhuis and Kraay (2004) for the subtropical Atlantic Ocean. By using this matrix we can distinguish between the following phytoplankton groups: diatoms, *Synechococcus*-type, *Prochlorococcus* HL (high-light adapted) and *Prochlorococcus* LL (low-light adapted), dinoflagellates, haptophytes, pelagophytes, cryptophytes and prasinophytes.

2.3.2 Statistical analysis

A statistical approach was used to automatically classify the selected open water stations into different groups according to its phytoplankton pigment composition. An unsupervised hierarchical cluster analysis (HCA) was applied based on different input data sets of surface water samples, which included the HPLC pigments and hyperspectral optical data obtained from spectral absorption coefficients and remote sensing reflectances. The unsupervised HCA has been proven useful in other studies based on hyperspectral observations of coastal (Lubac and Loisel, 2007) and open ocean environments (Torrecilla et al., 2011b). This algorithm generates a cluster tree to partition an input data set into subsets or clusters with no previous information regarding membership of input data objects to predefined classes. Each cluster tree is obtained based on a selected linkage algorithm that considers a previously calculated similarity distance between all samples included in the input data set. In this study, an angular distance was utilized when the similarity was computed between pairs of spectra because it reflects better the differences in the spectral shape of optical data. This approach is particularly interesting in our case due to the focus on spectral features related to the specific pigment composition.

The feasibility of using hyperspectral optical data for discriminating phytoplankton pigment assemblages was evaluated by using an objective criterion of cluster similarity, the cophenetic index (Torrecilla et al., 2011b). This index, which ranges from 0 to 1, measures how two cluster trees preserve their structure between data objects. In this study, it provided a measure of similarity between the optical-based cluster trees (i.e. a_{ph} - and R_{rs} -based partitions, respectively) and a reference cluster tree obtained from the HPLC pigment information. As discussed below, the cluster partition obtained from the pigment data served us as a reference for partitioning our data set into distinct groups, each characterized by a different phytoplankton pigment composition. To minimize variability in pigment composition associated with changes in phytoplankton biomass, the input to the cluster analysis in this case was represented by the ratio of individual pigment concentrations to the surface TChl-*a*. In addition, an Euclidean distance was utilized to generate the pigment-based cluster partition, instead of the angular distance used for the

analysis of the spectral data. This type of distance pointed out differences in magnitude of ratios of concentrations of individual pigments to TChl-*a* rather than differences in shape.

Multivariate analyses were conducted with the statistical computing software “R” (R Development Core Team, 2008). Two matrices of similarity by station were created, one for the pigment composition and one for the environmental variables. As for the hierarchical cluster analysis, each station’s pigment concentrations were scaled relative to TChl-*a* to account for differences in magnitude and a similarity matrix was created using Euclidean distance. The environmental variables included for the analysis were surface temperature and salinity as well as location (latitude). As recommended by Clarke and Gorley (2001), environmental parameters were normalized to have a mean of zero and a standard deviation of 1 to account for differing units between variables and a similarity matrix between samples was also created using Euclidean distance. The full biological similarity matrix, based on pigment concentrations, was compared to similarity matrices of differing subsets of parameters as defined by Clarke and Ainsworth (1993) in order to identify those parameters best correlated. The first comparison was that of the more typical “BIO-ENV” setup whereas the fixed biological similarity matrix was correlated (Spearman rank) to an environmental similarity matrix with varying combinations of included parameters. The second comparison was between the fixed biological similarity matrix and a variable similarity matrix with differing subsets of included pigments, i.e. “BIO-BIO” (Clarke and Warwick, 1998; Clarke and Gorley, 2001; Clarke and Warwick, 2001). The BIO-BIO setup allowed for the identification of those pigments most responsible for the overall sample similarities. Due to the high search space of 23 pigments ($2^{23} - 108\,388\,607$ possible subset combinations) a stepwise BIO-BIO procedure, “BVSTEP” (Clarke and Warwick, 1998), was used to efficiently search the subset space for the best combination up to a defined maximum correlation ($\rho = 0.99$).

Ordinations of samples by non-metric multi-dimensional scaling (MDS) were plotted to help visualize sample similarities in terms of community pigment composition. Additional vectors were fit to the MDS ordination for the variables identified by the BIO-ENV and BIO-BIO routines above using the “envfit” function of the R package “vegan” (Oksanen et al., 2010).

Within clusters, differences in environmental parameters (TChl-*a*, surface temperature and salinity, depths of the deep chlorophyll maximum (DCM), Z_{eu} and Z_m (sigma)) were tested following an initial Shapiro-Wilk’s *W* test of normality. Normally distributed data were tested with the independent t-test and non-normally distributed data were tested with a Mann-Whitney-U-test. All tests were considered significant when $p < 0.05$.

2.4 Satellite data

Mean values of marine phytoplankton TChl-*a* concentrations for November 2008 in selected areas around the ANT-XXV/1 cruise were calculated within a 6' spatial grid resolution from the merged daily Full Product Set (FPS) of the GlobColour Archive (<http://hermes.acri.fr/>). The GlobColour TChl-*a* product is based on the merging of MERIS, SeaWiFS and MODIS level-2 data with the GSM model and algorithm, developed by Maritorena and Siegel (2005), over the whole globe with the best resolution of 4.6 km. These TChl-*a* data have undergone an extensive validation based on a validation protocol published in Maritorena et al. (2010).

3 Results

3.1 Physical and biological parameters at the sea surface

Sea-surface temperature and salinity data from the on-board thermosalinograph as well as TChl-*a* fluorescence data from the FRRF are shown in Fig. 2. The locations and numbers of the discrete stations are depicted at the top of the graphic. Temperature and salinity values follow the trend that has been frequently reported (e.g. Sarthou et al., 2003). The Chl-*a* data show distinct features encountered during this cruise. These three data sets allowed us to identify some of the oceanographic features typical for the waters crossed by the ship's track. When exiting the English Channel (EC) the vessel crossed a tidal front (T), characterised by a drop in temperature at the eastern edge of the front and a peak in TChl-*a* fluorescence. The ship track then followed the eastern edge of the Northern Subtropical Gyre, the surface water temperature consistently increasing to a maximum of 30 °C at 7.6° N. At ~22° N and ~15° N the ship's track touched the edge two phytoplankton blooms (B1 and B2). Between ~12° N and ~2° N we encountered the Tropical Salinity Minimum Zone (TSM) associated with the heavy precipitation typical for this area, with a salinity minimum of 33.8 at 4.8° N. The TSM Zone was followed by the Equatorial Upwelling (EqU) characterised by lower temperatures and higher salinity as well as a peak in TChl-*a* fluorescence. A steeper decrease in temperature and increase in salinity give an indication that we crossed the Angola/Benguela front (AF) at ~12° S. The Benguela current marks the north-eastern boundary of the Southern Subtropical Gyre and the last section of the expedition followed this boundary towards Cape Town, South Africa.

3.2 Phytoplankton composition

Figure 3 illustrates the results of the two methods employed to interpret the pigment data for surface samples only. The size class method gives a comprehensible result with some clear features (Fig. 3a). The microplankton showed three

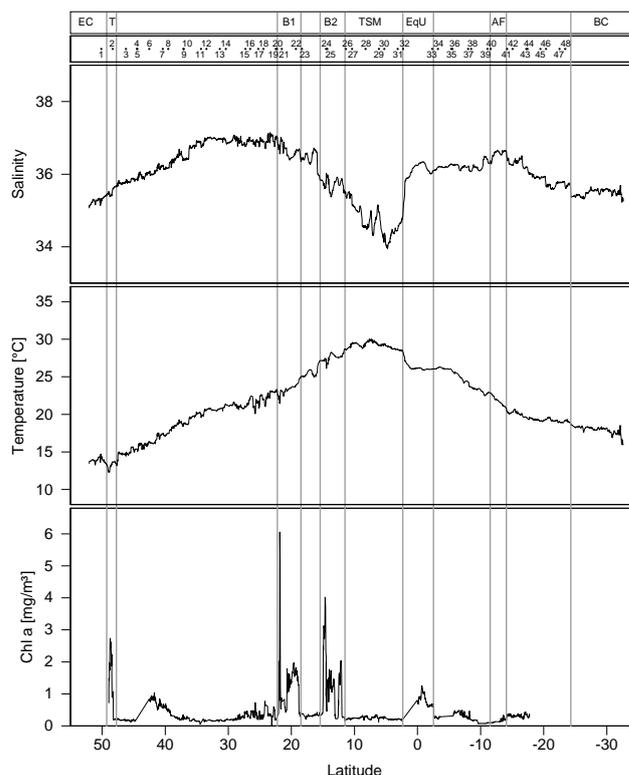


Fig. 2. Major oceanographic features of the transect, dots at the top depict the locations and numbers of the stations where water samples were taken, (EC=English Channel, T=Tidal Front, B1=Bloom No. 1, B2=Bloom No. 2, TSM=Tropical Salinity Minimum Zone, EqU=Equatorial Upwelling, AF=Angola-Benguela Front, BC=Benguela Current), reproduced with own data after Sarthou et al. (2003).

distinct peaks at the stations in the English Channel (EC) and in the blooms (B1 and B2). Picoplankton dominated the community in the tropical and subtropical oligotrophic waters as has been reported before (Gibb et al., 2000; Zubkov et al., 2000; Aiken et al., 2009) whereas nanoplankton and picoplankton were relatively evenly distributed in all other areas of the transect.

Figure 3b shows the results of the CHEMTAX analysis. The colours have been chosen to match Fig. 3a, i.e. phytoplankton groups have been assigned to the respective size classes. Diatoms and dinoflagellates contribute to the microplankton, the cryptophytes, green algae (including chlorophytes and prasinophytes), pelagophytes and haptophytes have been assigned to the nanoplankton and the cyanobacteria are picoplankton. We are aware that this is only a very crude classification as most groups contribute to more than one size class. In this classification we lack the pico-eukaryotes, which also play an important role in the oligotrophic waters (Aiken et al., 2009). However, for an overview of the phytoplankton community, this approach is a helpful tool for the interpretation of pigment data.

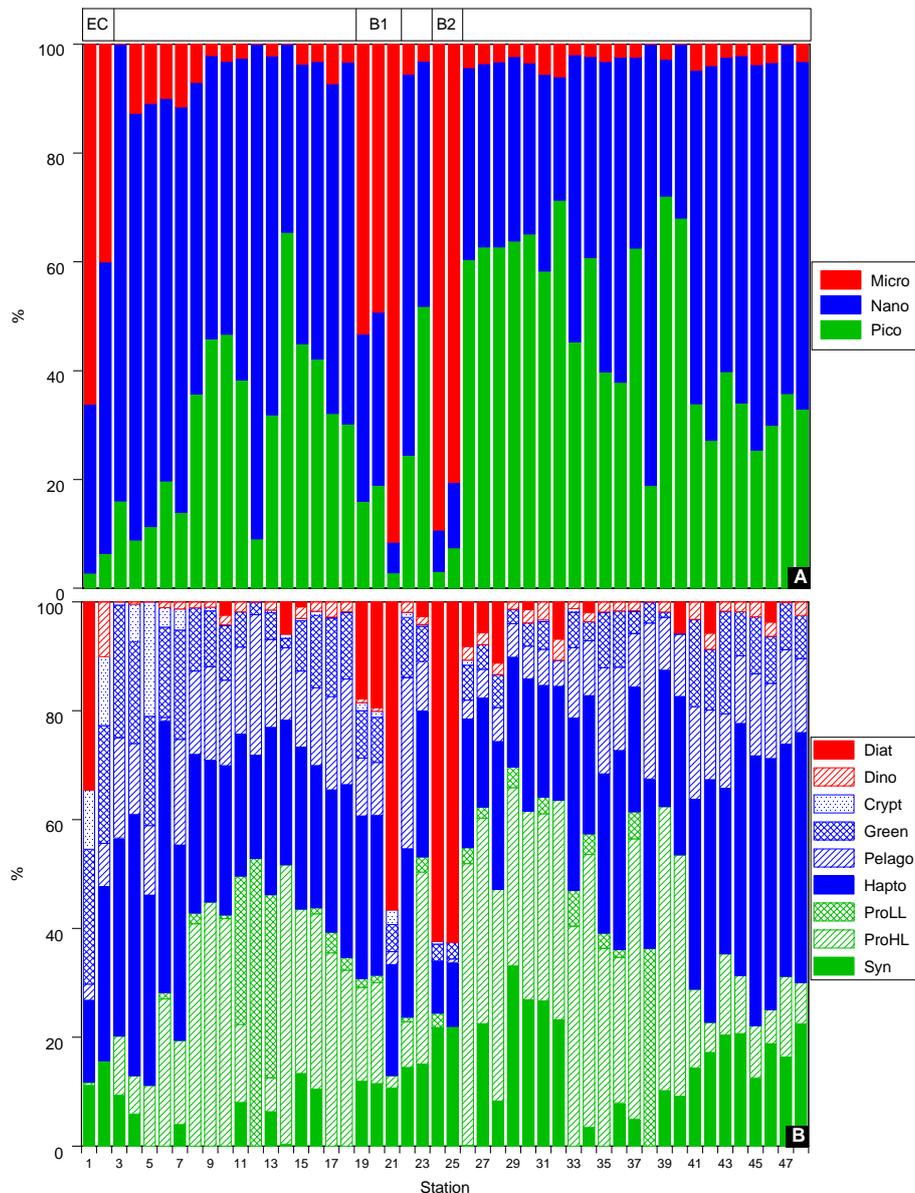


Fig. 3. Phytoplankton composition calculated from pigment composition (A) size classes approach (micro = microplankton, nano = nanoplankton, pico = picoplankton) (B) CHEMTAX approach (Diat = Diatoms, Dino = Dinoflagellates, Crypt = Cryptophytes, Green = Green algae, Pelago = Pelagophyceae, Hapto = Haptophytes, ProLL = *Prochlorococcus* low-light adapted, ProHL = *Prochlorococcus* high-light adapted, Syn = *Synechococcus*-type cyanobacteria, EC = English Channel, B1 = Bloom No. 1, B2 = Bloom No. 2).

Both approaches generalise from pigment composition either directly onto size classes or in the case of the CHEMTAX method from pigment ratios to phytoplankton groups, which have been consecutively grouped into size classes. Although different calculations stand behind the results, the outcome of both methods is quite similar. The microplankton is generally lower in the CHEMTAX calculation, although both approaches account for the fact that Fuco is also a precursor for 19HF and 19BT and is therefore also partially attributed to the nanoplankton. The differences can be mainly detected at stations with high pigment concentrations, such

as station 1 and 2 in the English Channel and station 21, 24 and 25 in the blooms. The microscopic counts only tell us that some microplankton is present at all stations for which this data was available, but it cannot shed light on the distribution of the groups as it discriminates against the picoplankton which is often too small to be counted under the microscope.

Flow cytometric and microscopic data were not available for all stations. The results will be used for clarification of specific stations or clusters in the discussion, but are not shown here in detail.

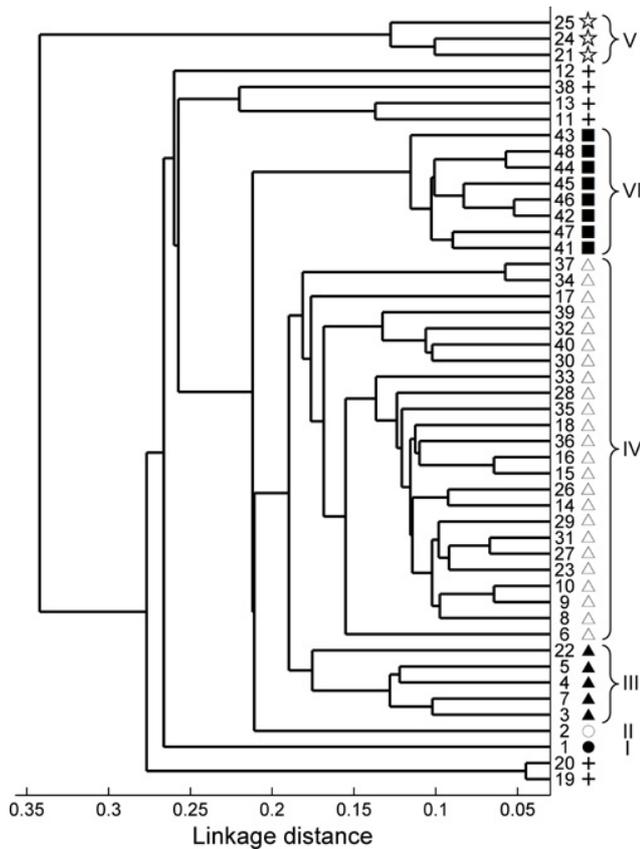


Fig. 4. Cluster tree of stations based on hierarchical cluster analysis of pigment data. Each cluster (assigned at a linkage distance of 0.18) has been assigned a different symbol and roman number.

3.3 Cluster analysis and multivariate statistics

The cluster analysis based on the pigment data resulted in six major clusters (Fig. 4). Each of the six clusters has been assigned a roman number and a different symbol, which will be also reproduced in the other cluster trees based on hyperspectral information. A clear north-to-south structure could be distinguished when stations corresponding to each cluster were plotted on a map (Fig. 1). Due to different pigment composition, stations 11, 12, 13, 19, 20 and 38 clustered away from their geographical neighbours (“outliers”). The clusters and “outliers” will be described in further detail below.

The BIO-ENV and BIO-BIO identified the pigments and environmental factors which best correlate with the sample similarities (Fig. 5, Table 3). Figure 5 shows the stations plotted according to the MDS analysis, which clearly separated the clusters identified by HCA. Vectors show the directions of maximum correlation between the samples and associated variables. The analysis of the environmental variables (surface temperature, salinity and latitude) revealed the combination of latitude and temperature to be best correlated with

Table 3. Best correlated pigments to pigment composition identified by the BIO-BIO routine.

<i>N</i>	Factors	ρ
1	DVa	0.734
2	DVa + Zea	0.847
3	DVa + Zea + Fuco	0.919
4	DVa + Zea + Fuco + DVb	0.958
5	DVa + Zea + Fuco + DVb + Chl- <i>a</i>	0.984

N = number of factors; ρ = Spearman rank correlation coefficient

pigment similarities ($\rho = 0.27$; Fig. 5a). In terms of pigments the analysis between the full matrix with 23 pigments and varying subsets of this pigment matrix identified the combination of DVa, Zea, Fuco, DVb, and Chl-*a* to be mainly responsible for the calculated similarities between samples ($\rho = 0.98$; Fig. 5b).

The cluster analysis was also performed based on $a_{ph}(\lambda)$ -spectra for all 48 stations. Figure 6 depicts the corresponding hierarchical cluster tree and the symbols of the pigment-based clustering for each station. The partition provided by the cluster analysis based on the $a_{ph}(\lambda)$ -data is quite similar to the partition obtained using pigment information, which is reflected in the large value of the cophenetic index of 0.703 (Table 4). In order to optimize our performance, a sensitivity test of the cluster analysis regarding the choice of the spectral range was necessary. This issue is discussed and examined in greater detail in Torrecilla et al. (2011a). In accordance with other studies, the best degree of similarity between these two cluster trees (i.e. the highest cophenetic index) was obtained when the $a_{ph}(\lambda)$ -spectrum was analyzed over the spectral range from 435 to 520 nm, where the most relevant pigments show their main absorption characteristics. Considering this optimal spectral range, cluster I, II, V and VI were exactly reproduced by the $a_{ph}(\lambda)$ -data, whereas clusters III and IV showed a few differences. In particular, stations 6 and 8 (which belong to cluster IV in the pigment-tree) classify with cluster III in the $a_{ph}(\lambda)$ -tree. This may be attributable to a difference in the spectral shape of the $a_{ph}(\lambda)$ -spectra of these two stations at around 470 nm (Fig. S1). The “outliers” of the pigment-based cluster tree 11, 12, 13 and 38 group with the cluster IV stations in the $a_{ph}(\lambda)$ -tree. The main difference, which singles them out in the pigment-tree, is the presence of a considerable amount of DVb, which has its main absorption peak at 479 nm (Fig. S2). Zea and 19HF, which are the dominant pigments in cluster IV, also absorb strongly at that wavelength, which may explain why the a_{ph} -spectra are similar even if the pigment composition differs. Stations 19 and 20 were also considered “outliers” in the pigment-tree due to the dominance of Fuco in the samples. These stations were located just on the outer rim of a diatom bloom off the coast of Western Sahara and Mauritania (see below) which also

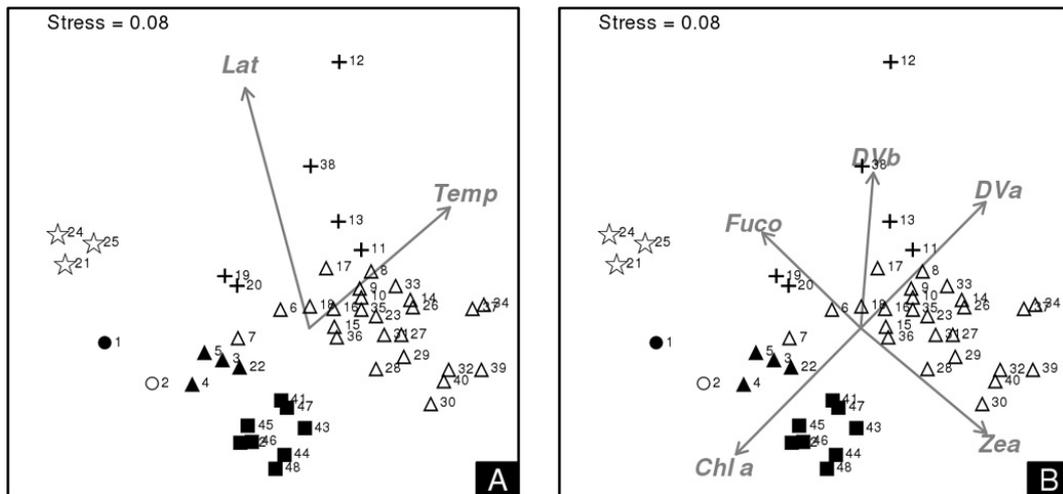


Fig. 5. Multi-dimensional scaling (MDS) plots visualizing sample similarities in terms of pigment composition. Symbols represent pigment-based clusters defined in Fig. 4. Additional vectors were fit to the MDS ordination for the environmental factors (A) and pigments (B) identified by the BIO-ENV and BIO-BIO routines. The fitted vectors have maximum correlation with the corresponding variables.

Table 4. Cophenetic indices between pigment-based and optical-based cluster trees obtained using different spectral ranges of $a_{ph}(\lambda)$ and $R_{rs}(\lambda)$. In the case of the remote sensing reflectance data, the 2nd derivative was used to obtain a better cophenetic index.

	Cophenetic index
Phytoplankton absorption data – $a_{ph}(\lambda)$	
Hyperspectral (1 nm resolution), range 350–750 nm	0.454
Hyperspectral (1 nm resolution), range 435–520 nm	0.703
Remote-sensing reflectance data – $R_{rs}(\lambda)$	
Hyperspectral (1 nm resolution), range 350–750 nm	0.330
Hyperspectral (1 nm resolution), range 435–580 nm	0.498
Hyperspectral 2nd derivative, range 435–580 nm	0.625
Optimal derivative parameters: BS = 9, WS = 9	

characterized station 21. Station 21 clusters with station 24 and 25 in the pigment-tree as it was dominated by Fuco, but stations 19 and 20 had a smaller percentage of Fuco (compared to total pigment) and were also characterized by the presence of DVa which delineated the stations before and after the bloom. Due to such differences in pigment composition it could be expected that these stations also partition separately with the absorption spectra. However, only station 19 clustered alone in the $a_{ph}(\lambda)$ -tree; station 20 was associated with the cluster IV stations.

To explore the potential of remote sensing information in distinguishing different bio-optical provinces, the partition of the stations was also carried out based on 22 $R_{rs}(\lambda)$ -spectra (Fig. 7). This cluster analysis also yielded satisfactory results with a cophenetic index of 0.624 (Table 4). As reported in past studies in which the aim was also the identification of phytoplankton pigment assemblages from

$R_{rs}(\lambda)$ -spectra (Torrecilla et al., 2011b), a good performance was only achieved when considering the second derivative of $R_{rs}(\lambda)$ -spectra over the spectral range of 435 to 580 nm. Our ability to discriminate phytoplankton pigment assemblages from the derivative of $R_{rs}(\lambda)$ -spectra was optimized by selecting the most suitable parameters used in the spectral derivative computations. In particular, we determined that the optimal values for the smoothing filter window and band separation were 9 nm for remote-sensing reflectance. Due to time constraints at the start of the cruise, no $R_{rs}(\lambda)$ measurements were collected at the stations corresponding to clusters I and II. Whereas clusters III, V and VI were well reproduced, cluster IV showed some discrepancies, similar to the analysis based on $a_{ph}(\lambda)$ -data. The same outlier stations 12, 20 and 38 which clustered separately in the pigment-based tree due to the high concentration of DVb, were associated with the cluster IV stations in the optical data (Fig. S3).

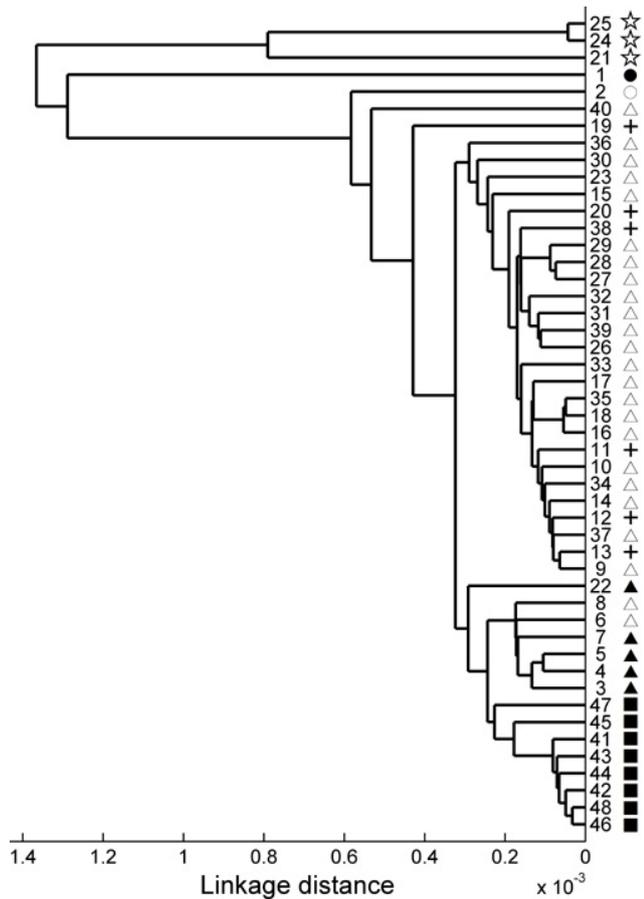


Fig. 6. Cluster tree of stations based on phytoplankton absorption ($a_{ph}(\lambda)$). Symbols correspond to pigment-based clusters (Fig. 4).

Station 6 (cluster IV in the pigment-tree) was singled out in the $R_{rs}(\lambda)$ -tree.

3.4 Cluster characterization

Table 5 summarizes the main characteristics of the pigment-based clusters which are discussed in further detail below.

Cluster I comprised only station 1, which was located in the English Channel. It was clearly different from all other stations. The pigment composition was dominated by Chl- a , Fuco and Chl- b , the CHEMTAX interpretation suggested that diatoms and green algae were the main contributors to the phytoplankton assemblage. Pigment composition and flow cytometry data confirmed that prochlorophytes were absent at this station as could be expected from a coastal area and temperate latitudes. The clustering of the absorption data also separated this station from the rest.

Cluster II was again composed of a single station (station 2) with a unique pigment signature. The local phytoplankton bloom and the strong stratification at this station observed in the temperature and density profiles suggested that we crossed a tidal front. Figure 8 shows a satel-

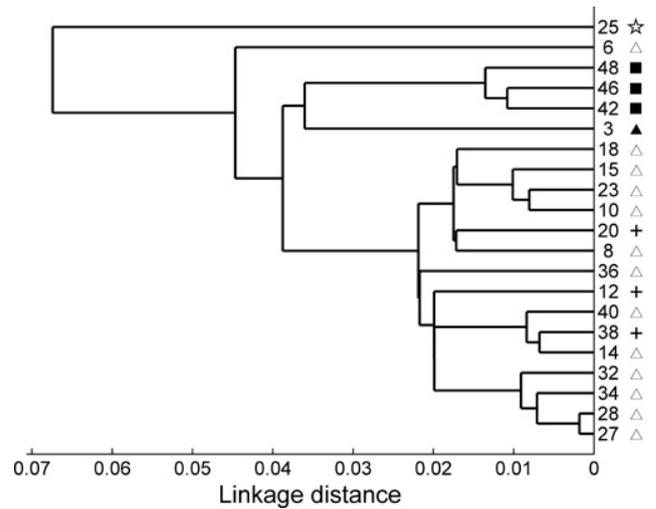


Fig. 7. Cluster tree of stations based on remote sensing reflectance ($R_{rs}(\lambda)$). Symbols correspond to pigment-based clusters (Fig. 4).

lite image of surface TChl- a with the in-situ data plotted as coloured circles. Pigment, microscopic and flow cytometric analysis imply that the bloom was mainly composed of haptophytes, green algae, dinoflagellates and phycobilin-containing cyanobacteria (*Synechococcus*). The pigments that made this station unique in terms of pigment data were a high concentration of Peri (up to 100 times more concentrated than at any other station) and the lack of DVa. The cluster analysis of absorption spectra also singled this station out.

Cluster III was geographically rather patchy, although 3 of the 5 stations that made out the cluster (Stations 3–5) were located to the South of cluster II, west of the Bay of Biscay. The two other stations (station 7 and 22) were geographically scattered among clusters IV and V. The dominant pigments were Chl- a and 19HF and the main phytoplankton groups at these stations were haptophytes, green algae and pelagophytes. Absorption spectra of those stations did also not differ significantly.

Cluster IV was the biggest cluster and united all stations with DVa, Zea and 19HF as dominant pigments. As can be expected from this pigment composition the flow cytometry analysis revealed high cell number of prochlorophytes and a smaller number of phycoerythrin-containing cyanobacteria at most of the stations joined in this cluster. CHEMTAX calculations confirmed the dominance of *Prochlorococcus* (HL), followed by haptophytes, pelagophytes and *Synechococcus*-type cyanobacteria. The size class calculation also corroborated a dominance of picophytoplankton with over 50% at most stations. The absorption spectra were very similar for these stations, so that – with the exception of stations 6, 8, 19 and 20 – the clustering based on absorption data formed the same cluster.

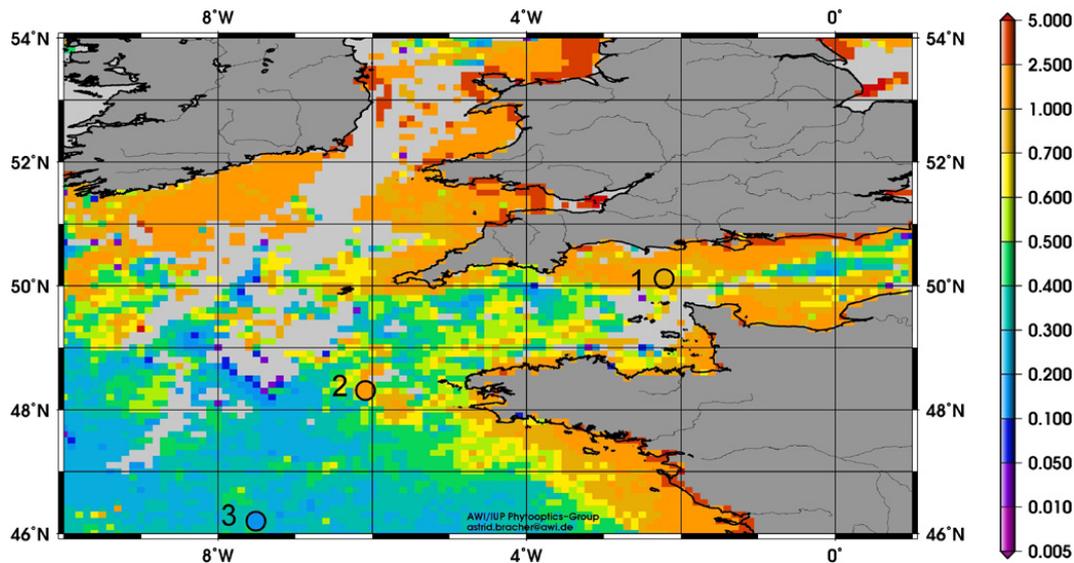


Fig. 8. Satellite image of the English Channel depicting TChl-*a* concentrations [mg m^{-3}] from the merged daily Full Product Set (FPS) of the GlobColour Archive as a monthly average for November 2008 with in-situ data of stations 1, 2 and 3.

Table 5. Summary of cluster properties.

Clus.	Stat.	Dom. Pig.	TChl- <i>a</i> [mg m^{-3}]	Temp. [$^{\circ}\text{C}$]	Salinity	DCM [m]	Z_{eu} [m]	Z_{m} [m]	Longh. Prov.
I	1	Fuco, Chl- <i>b</i>	0.73 ^a	14.18 ^a	35.31 ^a	No DCM	n.d.	mixed	NECS
II	2	Chl- <i>b</i> , 19HF	2.06 ^a	13.32 ^a	35.42 ^a	No DCM	n.d.	56 ^a	NECS (tidal front)
III	3–5, 7, 22	19HF	0.60 ± 0.26	17.39 ± 3.26	35.08 ± 0.29	No DCM	68 ^a	67, 96 (2 profiles)	NADR (and others)
IV-N	6, 8–10, 14–16, 18	Zea, DVa, 19HF	0.34 ± 0.16 ^b	19.71 ± 2.10 ^b	36.62 ± 0.35 ^b	76.8 ± 20.6	88.7 ± 6.6	77.3 ± 11.0 ^b	NAST (E)
IV-S	26–37, 39–40	Zea, DVa, 19HF	0.22 ± 0.06	26.82 ± 2.32	35.56 ± 0.77	59.3 ± 8.8	84.9 ± 15.5	33.6 ± 17.7	ETRA
V	21, 24–25	Fuco, Diad, Chl- <i>c</i> _{1/2}	3.24 ± 1.66	25.27 ± 2.65	36.01 ± 0.39	37 ^a	35 ^a	13 ^a	Blooms (CNRY?)
VI	41–48	Zea, 19HF	0.32 ± 0.09	19.55 ± 0.48	35.99 ± 0.25	39.5 ± 7.3	63.3 ± 8.7	33.3 ± 16.1	SATL
Outliers	11, 13	Zea, DVa, DVb	0.10	20.24	36.91	n.d.	n.d.	n.d.	NAST (E)
			0.16	20.73	36.96				
	12	DVb, DVa, 19HF	0.23	20.66	36.97	n.d.	n.d.	n.d.	NAST (E)
	19, 20	Fuco, DVa, Zea	0.64	22.98	36.90	n.d.	n.d.	n.d.	NATR?
			0.82	23.11	37.00				
	38	DVb, DVa, 19HF	0.19	23.42	36.21	n.d.	n.d.	n.d.	ETRA

Clus. = Clusters; Stat. = Stations; Dom. Pig. = Dominant pigments (in addition to chl-*a*) common to all stations within the cluster; TChl-*a* = chl-*a* + DVa (Mean ± SD); Temp. = Surface temperature (Mean ± SD); Salinity = Surface salinity (Mean ± SD); DCM = Deep Chlorophyll Maximum; Z_{eu} = euphotic depth; Z_{m} = Mixed layer depth (sigma); Longh. Prov. = assigned Longhurst Provinces: NECS = Northeast Atlantic Shelves Province, NADR = North Atlantic Drift Province, NAST (E) = North Atlantic Subtropical Gyral Province (East), ETRA = Eastern Tropical Atlantic Province, CNRY = Canary Current Coastal Province, SATL = South Atlantic Gyral Province; NATR = North Atlantic Tropical Gyral Province; n.d. = no data

^a one data point or one profile only, ^b significantly different from sub-cluster IV-S ($p < 0.05$)

Geographically however, these stations could be divided into a northern (IV-N, comprising stations 6, 8–10 and 14–18) and a southern sub-cluster (IV-S, stations 26–40, with the exception of station 38), which were separated by cluster V. The TChl-*a* concentrations and the oceanographic data also confirmed this division: thermoclines and pycnoclines were significantly deeper in the northern than in the southern

sub-cluster ($p < 0.01$). The DCM was not as clearly defined in the northern cluster as it was in the southern sub-cluster, where we found a pronounced TChl-*a* peak just below 50 m at all stations. Most stations of the northern sub-cluster showed two TChl-*a* maxima, the second one often just below Z_{eu} . The surface TChl-*a*, surface salinity and Z_{m} were significantly lower in IV-S than in its northern counterpart,

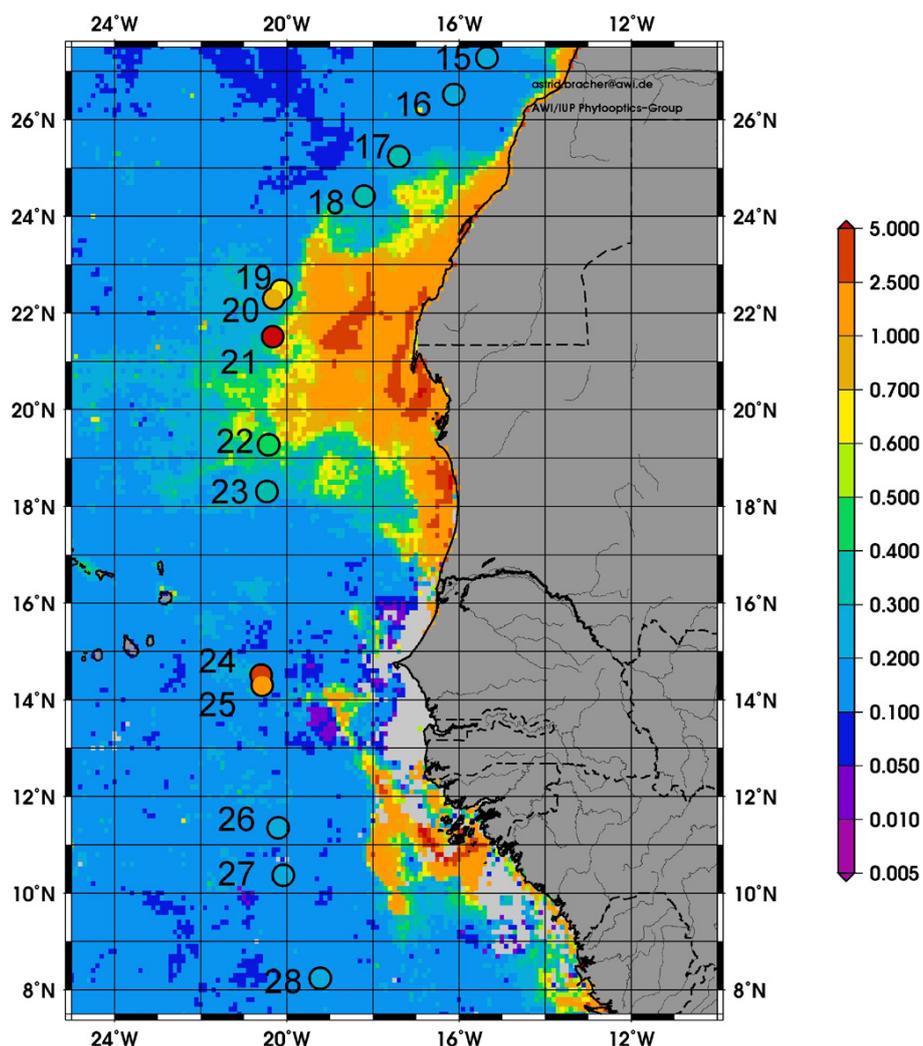


Fig. 9. Satellite image of the east Atlantic Ocean along the coast of North-West Africa depicting TChl-*a* concentrations [mg m^{-3}] from the merged daily Full Product Set (FPS) of the GlobColour Archive as a monthly average for November 2008 with in-situ data of stations 15–28.

whereas SST was significantly higher ($p < 0.05$). The gradient between nutrient-poor waters at the surface and nutrient-rich waters at depth was much stronger in the southern compared to the northern sub-cluster ($< 0.2 \mu\text{M}$ nitrate at the surface in both areas and $5\text{--}10 \mu\text{M}$ nitrate at 200 m in IV-N compared to $> 20 \mu\text{M}$ nitrate at 200 m in IV-S, Koch and Kattner, 2011).

Sub-cluster IV-N, at the eastern edge of the North Atlantic Subtropical Gyre along the Canary Current, bordered onto the south of station 5 (cluster III), but was also not consistent geographically. Several outliers and a station belonging to another cluster (station 7, cluster III) were scattered among the stations of cluster IV-N. Sub-cluster IV-S was separated from IV-N by cluster V and was geographically a very consistent cluster. It extended from approximately 12°N to $12\text{--}13^\circ \text{S}$, encompassing the Equatorial Counter Current and the Southern Equatorial Current.

Cluster V comprised the “bloom stations” with Fuco as the dominant diagnostic pigment and high TChl-*a* concentrations between 1.3 and 5.3 mg m^{-3} . The cruise track crossed two different blooms (Fig. 9) and stations 21, 24 and 25 lay at the edge of these blooms. Note that the satellite picture is a 4 week average, which may explain the difference between the in-situ measurements and the satellite data. At the point in time when we passed the bloom, it probably had slightly different dimensions than on the averaged picture. The blooms mainly consisted of diatoms (approx. 60 % of TChl-*a*), some haptophytes and *Synechococcus*-type cyanobacteria. In the clustering of the $a_{\text{ph}}(\lambda)$ -data station 21 was separated from station 24 and 25. The samples 19 and 20 (outliers) were taken on the edge of the first bloom. Their main diagnostic pigments were Fuco (characteristic for diatoms and for the bloom) and DVa (characteristic for *Prochlorococcus* and the open ocean).

The stations belonging to cluster VI were clearly defined and separated through their bio-optical traits from the other stations. Geographically they were also located together at the eastern edge of the Southern Subtropical Gyre, adjoining cluster IV-S to the south. The stations in this cluster were dominated by haptophytes (approximately 45 % of total biomass) and *Synechococcus*-type cyanobacteria. Dominant marker pigments were Zea and 19HF, which influence strongly the shape of the absorption spectra (Fig. S2). The $a_{\text{ph}}(\lambda)$ -spectra of the stations of cluster VI also formed one well separated cluster in the $a_{\text{ph}}(\lambda)$ -tree. The microscopic analysis identified the haptophytes as coccolithophores.

4 Discussion

The multivariate analysis identified the combination of temperature and latitude as the main environmental variables responsible for the spread of the data on the basis of pigment composition (Fig. 5b). The Spearman rank correlation coefficient for these two parameters was $\rho = 0.266$; salinity did not improve the correlation ($\rho = 0.213$). In this analysis only temperature, salinity and latitude were incorporated as other possible environmental variables, such as Z_{eu} or Z_{m} were only available for a smaller subset of stations.

Temperature was the most important environmental variable if only one variable was considered ($\rho = 0.235$). It is an important variable in itself and the temperature dependence of phytoplankton has been frequently reported in the literature (e.g. Platt et al., 2005; Li, 2009; Burgmer and Hillebrand, 2011). The effect of temperature can be direct, as many species have a tolerance of a certain temperature range outside of which they cannot survive (e.g. Partensky et al., 1999; Breitbarth et al., 2007), or can be indirect by influencing predators, photosynthesis rates or nutrient availability (Carder et al., 1999; Sathyendranath et al., 2001; Bouman et al., 2003; Platt et al., 2005).

Temperature is a variable which is commonly recorded, easy to measure and can be observed from satellites, which is an important issue in the wake of global observations of ocean dynamics. Moreover, temperature is part of other physico-chemical processes such as stability of the water column (Platt et al., 2005) and thus can be seen as the manifestation of more complex physical structures. Bouman et al. (2003) were able to explain between 43 and 49 % of the variance in the specific absorption coefficients of phytoplankton at certain wavelengths with temperature. They showed that temperature can be a proxy for two main turbulence-nutrient regimes: high temperatures are generally associated with conditions of low turbulence and low nutrients, low temperatures with those of high turbulence and high nutrients. Platt et al. (2005) identified a clear temperature dependence for phytoplankton community structures. Temperature has even been used to estimate concentrations of nitrate

over regional and global scales (Sathyendranath et al., 1991; Switzer et al., 2003).

Including latitude improved the correlation and thus allowed us to explain more of our data variability than with temperature alone. Latitude was used as an environmental factor as it implies several variables which were not available at all or not at the resolution needed for the statistical analysis. The transect covered several contrasting physico-chemical regimes or climatic zones (gyres, upwelling, temperate, subtropical, tropical regions, coastal and open waters) and latitude could be the environmental factor standing for the influence of such complex variables as light availability, cloud cover, mixed or stratified waters, upwelling etc. However, the low Spearman rank correlation factor of 0.266 suggests that many more factors are involved in the complex dynamics behind the pigment/phytoplankton distribution and that latitude alone cannot cover the variability caused by other physical forces. The link between physical forcing and ecosystem structure has been established by Margalef (1978) more than three decades ago and has been corroborated and added on to by several authors (e.g. Agustí and Duarte, 1999; Cullen et al., 2002; Wang et al., 2009). Phytoplankton ecology is described as an expression of the turbulence and nutrient conditions presented by ocean physics, although it should be kept in mind that not all limiting nutrients are supplied from below through mixing and/or upwelling processes. Iron can be introduced through aeolian deposits, as could be seen in the case of the second bloom encountered on our cruise, or nitrogen can be fixed from the atmosphere by diazotroph algae.

The analysis emphasizes that the forces behind phytoplankton community structure (here expressed through the index of pigment distribution) are complex and cannot easily be reduced to one variable. However, in combination with another biological or bio-optical variable such as TChl-*a*, phytoplankton absorption or pigment composition, temperature can be a powerful variable to supplement the measurements and identify boundaries of bio-optical provinces.

4.1 Pigments

Generally, our results coincide with previously published works, especially with data from the Atlantic Meridional Transect (AMT) programme. The AMT cruises also crossed the Atlantic from north to south and specifically AMT cruise 6 had a very similar cruise track to ANT-XXV/1. The phytoplankton pigment data of the AMT cruises between 1995 and 2005 has been summarized in Aiken et al. (2009). The trends are similar with overall low TChl-*a* concentrations and TChl-*a* peaks in the English Channel and at $\sim 20^\circ$ N in the Northwest-African Upwelling. A second bloom at $\sim 14^\circ$ N as was encountered on our cruise was not recorded by the AMT cruises. Aiken et al. (2009) found significant correlations between TChl-*a* and accessory pigments (AP), which could be divided by trophic states and dominating

phytoplankton size groups. The slope of TChl-*a* vs. AP in oligotrophic areas (TChl-*a* < 0.25 $\mu\text{g l}^{-1}$, picoplankton dominating) was > 1.00, indicating that on average the concentration of AP was greater than TChl-*a*, which we could corroborate with our results (data not shown). For the meso- and eutrophic regimes the slope for our data was below 0.9 (i.e. on average more TChl-*a* than AP), whereas Aiken et al. (2009) reported that results were inconclusive for these areas.

Aiken et al. (2008) used the AMT data and other historical data to investigate links between bioenergetic scale and certain bio-optical traits (BOT) that are specific properties of phytoplankton types. They identified the change in the TChl-*a*/AP ratio as “the biggest factors that alter the shape of ocean colour spectra” and showed that the three phytoplankton size classes can be identified and associated to three previously defined basic biomes on the basis of this ratio. The TChl-*a*/AP ratio shows the relative change of blue (Chl-*a*, centered at 443 nm) to green (carotenoids, centered at 490 nm) absorption, which lies within the wavelength range identified by our statistical approach as the optimal spectral range for clustering $a_{\text{ph}}(\lambda)$ - and $R_{\text{rs}}(\lambda)$ -data. With our approach we would like to develop a statistical method to investigate the detailed relationships between pigment distribution (and what it implies in terms of phytoplankton groups) and hyperspectral properties of the ocean surface in the biogeographical context of marine provinces.

The BIO-BIO routine identified the combination of the five pigments DVa, Zea, Fuco, DVb and Chl-*a* to be mainly responsible for the calculated similarity “distances” between samples (Fig. 5b, Table 3). By including these five pigments the Spearman rank correlation coefficient ρ reached a value of 0.98. DVa alone already accounted for $\rho = 0.73$, which rose to $\rho = 0.85$ when Zea was included. Fuco as a representative of larger-celled groups such as diatoms, haptophytes or pelagophytes (in the latter two groups it is present as a precursor for the marker pigments 19HF and 19BT, respectively) was the third important predictor, followed by DVb. With DVb, DVa and Zea three markers specific for cyanobacteria were identified as important pigments correlated to the distribution of phytoplankton groups. Figure 5b demonstrates that these three pigments dominated the formation of cluster IV and of the outliers 11, 12, 13 and 38, which were conspicuous due to their high concentration of DVb. Chl-*a*, which occurs in all phytoplankton groups other than *Prochlorococcus* is the fifth main variable correlated to the pigment distribution of our samples and spreads the samples in the opposite direction than DVa.

DVa and DVb are unique marker pigments for *Prochlorococcus* and do not occur in other species (Chisholm et al., 1992; Goericke and Repeta, 1992). The fact that they were two of the main predictors of the clustering of the pigment matrix emphasizes the importance of this group of cyanobacteria. *Prochlorococcus*, one of the three known genera of the prochlorophytes, was discovered in the late 1980s (Chisholm et al., 1988) and is – with an approxi-

mate mean cell size of 0.6 μm – the smallest known photosynthetic organism (Partensky et al., 1999). It has been estimated to account for 30–60% of the TChl-*a* in subtropical oligotrophic regions and thus plays a key role in global primary production and carbon cycling (Partensky and Garczarek, 2010). *Prochlorococcus* occurs ubiquitously between 40° N and 40° S throughout the euphotic zone and even below. Genetic and physiological diversity make it unique and explain the numerical abundance and broad habitat. Recently developed molecular approaches have revealed different ecotypes which dominate at different depths or latitudes (Zinser et al., 2007; Zwirgmaier et al., 2007). Generally two main groups of ecotypes of *Prochlorococcus* have been distinguished: high-light adapted (HL) and low-light adapted (LL) types. Pigment analysis can differentiate between these two ecotype groups as they differ in their DVb:DVa ratio (Moore and Chisholm, 1999; Veldhuis and Kraay, 2004). DVb is specific for LL ecotypes of *Prochlorococcus* as it absorbs the blue light that penetrates deepest into the water column (Moore and Chisholm, 1999), and explains the spread of the samples 11, 12, 13 and 38 which are different from all other samples due to the high concentration of DVb. The diversity of the LL group is much wider than that of HL group (Partensky and Garczarek, 2010). Some LL ecotypes have been found to co-occur with HL ecotypes at the surface, especially in mixed water columns at higher latitudes (Zwirgmaier et al., 2007) and thus could be a proxy for mixed rather than stratified conditions. Johnson et al. (2006) showed that temperature is significantly correlated with shifts in *Prochlorococcus* ecotype abundance, thus linking our main biological with the major environmental predictor. Temperature explained the spread of the data on the MDS plots in the same direction as DVa.

Zea is a general marker for all cyanobacteria and occurs in both main genera *Synechococcus* and *Prochlorococcus*. DVa and Zea described most of cluster IV, which was dominated by small cells. Fuco is a marker pigment for diatoms, but is also – as pointed out earlier – a precursor for 19HF and 19BT which are specific for haptophytes and pelagophytes (Vesk and Jeffrey, 1987; Wright and Jeffrey, 1987). Clusters I, II, III and V, dominated by nanoplankton and/or microplankton, were mainly described by Fuco and Chl-*a*.

Here, we showed that a few pigments with distinct optical features can describe a clustering based on the matrix of a broad pigment composition of each sample. It became clear, that the picophytoplankton and more specifically *Prochlorococcus* were responsible for most of the variability in the eastern Atlantic Ocean. Dandonneau and Niang (2007) also observed that differences in pigment composition in their samples from the North Atlantic and Tropical Pacific could mainly be explained by their DVa content. Thus we agree with Marañón et al. (2001) that picophytoplankton should not be regarded as a background and relatively invariant component of the community, but rather as a main driver of most of the latitudinal variability in total photoautotrophic

biomass and production in the tropical and subtropical eastern Atlantic Ocean.

4.2 Bio-optical geography

By applying an unsupervised hierarchical cluster analysis to pigment and hyperspectral data from the eastern Atlantic Ocean, we have demonstrated the potential applicability of pigment composition, absorption coefficients and remote sensing reflectance for identifying different bio-optical units or provinces. To assess our bio-optical approach with an established biogeography, we compared our provinces/clusters to the widely used system defined by Longhurst (2006). Longhurst proposes a global partitioning into 4 biomes or basic vegetation types within the pelagic realm of the oceans: the Polar, Westerlies, Trades and Coastal biome. Within the biomes, 51 provinces are defined on the basis of a global dataset including satellite images of surface chlorophyll fields and regional oceanography data, also considering many previous proposals for partitioning the oceans. Although the boundaries of the provinces are forced into a static grid as a matter of convenience, Longhurst points out that the position of the borders is dynamic and varies on annual, seasonal or even shorter time scales. As our optical data were not continuous, we occasionally included the continuous temperature, salinity and TChl-*a* measurements to identify the boundaries. In Fig. 1 the stations with their assigned cluster symbols are plotted on a map depicting Longhurst provinces (shapefile from VLIZ, 2009).

Cluster I and II belong to the continental shelf of Western Europe, described by Longhurst as the Northeast Atlantic Shelves Province (NECS). The English Channel is strongly dominated by tidal forces, a fact that was corroborated by the density, temperature and TChl-*a* fluorescence profiles of these stations which showed strong mixing of the water column. Our analysis separated the two stations into two clusters which is probably due to the fact that station 2 (cluster II) was situated in a tidal front. The boundary to the next cluster at this point in time, was probably situated just after station 2, at around 47.5° N where a sudden rise in sea surface temperature and salinity occurred after the tidal front (Figs. 2 and 8).

The stations joined in cluster III do not all belong to the same geographical province. Stations 3–5 lay in the southeast corner of Longhurst's North Atlantic Drift province (NADR). In this province wind speed in autumn and winter is greater than anywhere else except in the Southern Ocean which induces anomalous deepening of the mixed layer to more than 500 m along the European continental edge. Stations 3 and 5 showed a pycnocline at ~100 m depth during our cruise at the beginning of November which might deepen as winter progresses. Stations 3–5 also showed no DCM. For stations 7 and 22 we do unfortunately not have CTD profiles for comparison, but we can deduce some information from the data of station 6. Especially the TChl-*a* fluorescence profile data showed a change from station 6 southwards where a

small DCM could be detected and after station 5 pycno- and thermocline moved upwards. Bio-optical traits join these stations together, but oceanographic data and geography show that stations 7 and 22 belong to different oceanic provinces.

The sub-cluster IV-N lay within Longhurst's North Atlantic Subtropical Gyral Province (East) (NAST(E)). However, this area was bio-optically not consistent and many outliers lay alongside the stations of cluster IV-N. These inconsistencies might be explained by typical physical processes in this region such as eddy-driven vertical advection, internal waves or salt fingering (McGillicuddy et al., 2003; Oschlies et al., 2003; Dietze et al., 2004; Dandonneau and Niang, 2007). Particularly the occurrence of DVb in the outliers 11–13 suggested a recent upwelling of LL *Prochlorococcus* ecotypes or a mixed water column (see above). Moreover this region is influenced by Mediterranean water eddies (meddies), which flow out of the Strait of Gibraltar and move southwards once they have detached from the continental slope. Although meddies are usually encountered at several 100 m depth they have been shown to influence surface water characteristics (Richardson et al., 2000; Siedler et al., 2005). Another possible disturbance comes from seamounts, which can also spawn eddies and have influence on the water column above them (Comeau et al., 1995; Christiansen and Wolff, 2009). Station 12 (outlier) for example lay exactly above the Seine seamount at 24° N and 14° W.

The sub-cluster IV-S with stations 26–40 was also geographically a very consistent cluster and lay within Longhurst's Eastern Tropical Atlantic Province (ETRA). It extended from approximately 12° N to 12–13° S, encompassing the Equatorial Counter Current and the Southern Equatorial Current. The boundaries were clearly defined to the North by the bloom (cluster V discussed below) and to the South by the Angola Frontal System (between 12 and 13° S) characterized by a change in PFTs and an abrupt increase in salinity. To the North of the Equator, we encountered the typical Tropical Salinity Minimum Zone, followed by the Equatorial Upwelling identified by a rise in salinity, a drop in temperature and higher TChl-*a* concentrations (Fig. 2). Pérez et al. (2005) describe the typical phytoplankton community or size structure for this region as rather constant with the contribution of picoplankton to total Chl-*a* always exceeding 45 %, a description which is corroborated by our results.

Although the pigment composition joined the “bloom-stations” together (cluster V), it was clear from our continuous TChl-*a* measurements and the satellite picture that the stations belonged to two different blooms (Figs. 2 and 9). In the clustering of the $a_{ph}(\lambda)$ -data station 21 was also separated from stations 24 and 25. The northern bloom (station 21) was due to a major upwelling focus in this area south of Cape Blanc (Western Sahara) off the coast of Mauritania. The outliers 19 and 20 were samples that were taken on the edge of the bloom and represented a transition zone between the oligotrophic waters of the tropical Atlantic and the upwelling area. Their main diagnostic pigments were Fuco

(characteristic for diatoms and for the bloom) and DVa (characteristic for *Prochlorococcus* and oligotrophic areas). There were no profile data from station 21, but station 20 showed a very strong DCM at around 90 m with high TChl-*a* concentrations (1.6 mg m^{-3}) with the same dominant pigments as the surface bloom.

The southern bloom (stations 24 and 25) lay within the African dust veil where a special characteristic of the wind regime is the dust-laden nature of the northeast trades, wherever their back trajectory lies over the Saharan desert. These so-called Harmattan winds carry mineral dust over the ocean from 25° N to 10° S . The $a_{\text{ph}}(\lambda)$ -spectra of these two stations had very different shapes compared to all other samples of this cruise. The high absorption in the spectral region below 400 nm is very unusual and was present in all replicates of these stations. The most probable explanation for the altered spectral shape is dust retained on the filters resulting from the aeolian dust deposits to the ocean, a phenomenon previously described for this region (Croft et al., 2004; Baker et al., 2006; Pohl et al., 2011). Particularly iron is a limiting nutrient which can enhance the primary production in the tropical North Atlantic (Mills et al., 2004). The results from aerosol and iron measurements from the same cruise showed high concentrations of both at the relevant latitudes and thus confirm our hypothesis (Neogi et al., 2011).

Station 25 also showed a strong DCM with high TChl-*a* concentrations (2.2 mg m^{-3}). The DCM here however was much shallower (40 m) and consisted of a different phytoplankton assemblage with 19HF as the dominant marker pigment (haptophytes). Thus the bloom at the surface triggered through aeolian deposits could be partially or fully unconnected to the phytoplankton community at depth. In Longhurst's biogeography both blooms would probably be assigned to the Canary Current Coastal Province (CNRY) which comprises the southerly coastal flow of the eastern boundary current of the North Atlantic from Cape Finisterre in North Portugal to Cape Verde in Senegal. The seaward boundary is defined by Longhurst to be approximately 200–400 km offshore and the cruise track was between 300 and 450 km offshore at these latitudes.

Geographically stations 22 and 23 lay in the same region and could theoretically also belong to CNRY although they have been clustered differently on the account of their pigment composition (cluster III and IV, respectively). These two stations lay between the two blooms and had comparatively low TChl-*a* concentrations ($>0.5 \text{ mg m}^{-3}$). As the cruise track lay on the approximate boundary between CNRY and its western neighbour, the North Atlantic Tropical Gyral Province (NATR), these two stations could also belong to NATR, which is characterized by the lowest TChl-*a* in the North Atlantic.

The stations belonging to cluster VI were clearly defined and separated through their bio-optical traits from the other stations. They differ in pigment composition, $a_{\text{ph}}(\lambda)$ - and $R_{\text{rs}}(\lambda)$ -spectra and were clearly located in Longhurst's South

Atlantic Gyral Province (SATL), which comprises the anticyclonic circulation of the South Atlantic, excluding the coastal boundary currents. According to Marañón et al. (2000) we can expect minimal Chl-*a* values in the central regions of the gyre and higher values around the periphery. This cruise sampled the eastern edge of the Southern Subtropical Gyre and yielded surface TChl-*a* values of $0.32 \pm 0.09 \text{ mg m}^{-3}$, which is approximately the same as in the respective area in the Northern Hemisphere (cluster IV-N, see Table 5). The DCM at 30–50 m was not as sharp as in other areas and had about twice the amount of TChl-*a* than the surface, but very similar pigment composition. However, this does not necessarily mean that the DCM was also the biomass maximum, as it has been shown that the carbon to Chl-*a* ratio can decrease with depth in gyral areas (Marañón et al., 2000). The northern boundary of this province was clearly defined by our bio-optical data between stations 40 and 41, around $12\text{--}13^\circ \text{ S}$. This coincides fairly well with the boundary set by Longhurst for SATL (approximately 10° S). The Angola-Benguela-Front marks this boundary. It corresponds to the convergence zone between the north-moving surface waters of the Benguela and the south-flowing Angola Current, and could be identified with surface temperature and salinity data at exactly the position between the stations which mark the bio-optical boundary. The southern boundary was probably after our last discrete water sample at $\sim 25^\circ \text{ S}$ when we entered the Benguela current.

5 Conclusions

It is clear, by the comparison of our clusters and the Longhurst provinces, that in some areas a more dynamic approach is needed to do the ecosystem justice. Different approaches based on bio-optical data have been proposed, such as the classification by Hardman-Mountford et al. (2008) based on satellite-derived chlorophyll data or the fuzzy c-means clustering algorithm by Moore et al. (2009) where optical water types are classified by the statistical properties of their associated $R_{\text{rs}}(\lambda)$. It becomes clear that the characterization of provinces in the dynamic marine realm cannot hold true for every season and every year, no matter if it is based on an averaged data set over several years or on the data of one specific year. To define marine provinces and their boundaries in space and time, a method has to be used which involves information of the spatial and temporal parameters in question. Thus, we suggest for the future the application of a cluster analysis to hyperspectral datasets from space once they are available with the simultaneous pigment as our validation tool. The proposed method would be similar to the clustering approach by Devred et al. (2007), who used a combination of optical and physical information to define provinces in the northwest Atlantic, but making use of hyperspectral resolution data sets. Hyperspectral sensors mounted on platforms such as buoys, gliders or satellites

could provide the data to identify shifting boundaries of established provinces or to track exceptions from the rule in order to improve our understanding of the biogeochemical cycles in the ocean. Several approaches have already been proposed to detect PFTs from satellite sensors (e.g. Alvain et al., 2008), but only Bracher et al. (2009) used hyperspectral data. However, dominant PFT identification is a slightly different concept than clustering different spatially distributed phytoplankton assemblages. Our method allowed us to define different bio-optical provinces on the basis of phytoplankton community structure and their bio-optical features, instead of a small set of functional groups. In terms of globally significant issues such as carbon export and primary production our hyperspectral and similarity-based approach represents a possibility for a fast and detailed assessment of the state of a temporally and spatially variable environment. However, before this novel approach can be applied at a global scale, it will be necessary to validate it on larger databases consisting of simultaneous pigment and optical information from more diversified waters.

Supplementary material related to this article is available online at:

<http://www.biogeosciences.net/8/3609/2011/bg-8-3609-2011-supplement.pdf>.

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