Phytoplankton pigment and absorption characteristics along meridional transects in the Atlantic Ocean

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Abstract

Pigment patterns and associated absorption properties of phytoplankton were investigated in the euphotic zone along two meridional transects in the Atlantic Ocean, between the UK and the Falkland Islands, and between South Africa and the UK. Total chlorophyll a (TChla = MVChla + DVChla + chlorophyllide a) concentrations and the biomarker pigments for diatoms (fucoxanthin), nanoflagellates and cyanobacteria (zeaxanthin) appeared to have similar distribution patterns in the spring and in the autumn in the temperate NE Atlantic and the northern oligotrophic gyre. Divinyl chlorophyll a levels (prochlorophytes) were greater in spring at the deep chlorophyll maximum in the oligotrophic gyre, however. Marked seasonal differences were observed in the NW African upwelling region. TChla concentrations were twice as high in the upper mixed layer in the spring, with the community dominated by diatoms and prymnesiophytes (19'-hexanoyloxyfucoxanthin). A layered structure was prevalent in the autumn where cyanobacteria, diatoms and prymnesiophytes were located in the upper water column and diatoms and mixed nanoflagellates at the sub-surface maximum. In the South Atlantic, the Benguela upwelling ecosystem and the Brazil-Falklands Current Confluence Zone (BFCCZ) were the most productive regions with the TChla levels being twice as high in the Benguela. Diatoms dominated the Benguela system, while nanoflagellates were the most ubiquitous group in the BFCCZ. Pigment concentrations were greater along the eastern boundary of the southern oligotrophic gyre and distributed at shallower depths. Deep chlorophyll maxima were a feature of the western boundary oligotrophic waters, and cyanobacteria tended to dominate the upper water column along both transects with a mixed group of nanoflagellates at the chlorophyll maximum.

Absorption coefficients were estimated from spectra reconstructed from pigment data. Although absorption was greater in the productive areas, the TChla-specific coefficients were higher in oligotrophic regions. In communities that were dominated by diatoms or nanoflagellates, pigment absorption was generally uniform with depth and attenuating irradiance, with TChla being the major absorbing pigment at 440 nm and photosynthetic carotenoids (PSC) at 490 nm. Absorption by chlorophyll c and photoprotective carotenoids (PPC) was much lower. Populations where cyanobacteria were prevalent were characterized by high PPC absorption, particularly at 490 nm, throughout most of the euphotic

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zone. The data suggested that the effect of pigments on the variability of phytoplankton absorption was due primarily to the variations in absorption by PPC. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Spatially extensive investigations have been coordinated within the UK Atlantic Meridional Transect (AMT) programme with the purpose of improving our knowledge of biogeochemical processes, ecosystem dynamics and food webs across basin scales in the Atlantic Ocean (Aiken et al., 2000). One of the goals of the programme has been to examine and characterize the properties of biogeochemical provinces (Longhurst et al., 1995), and an objective method was developed to determine the boundaries of physical provinces (Hooker et al., 2000). Another objective has been to conduct ground-truthing measurements of optical and pigment parameters for the validation and calibration of SeaWiFS ocean colour data (Hooker and McClain, 2000). In this regard, the surface distribution pattern of pigments for transects between the UK and the Falkland Islands was discussed by Gibb et al. (2000), and Barlow et al. (in press) have examined the bio-optical properties of surface pigments in relation to ocean colour data of absorption and back scattering for a transect between South Africa and the UK. Observations of the variability in the vertical distribution of phytoplankton pigments and associated absorption properties across Atlantic basins, however, have not yet been reported.

Total chlorophyll $a$ ($T_{Chla}$), defined as the sum of MVChla, DVChla and chlorophyllide $a$, is used as a surrogate marker for the abundance of phytoplankton in the oceans, but other accessory pigments that can be identified and quantified by liquid chromatography (Jeffrey et al., 1997) provide chemotaxonomic information on the range of phytoplankton groups that make up the community structure in the Atlantic (Barlow et al., 1993, in press; Bidigare et al., 1990a; Gibb et al., 2000). The major role of chlorophyll $a$ is to absorb light for photosynthesis, but there is also a range of pigments, such as, chlorophylls $b$ and $c$ plus a variety of carotenoids, that have a significant function in extending the light-harvesting spectrum in the phytoplankton, thus ensuring optimal absorption efficiencies (Kirk, 1994). Other carotenoids, however, serve to protect microalgal cells against the effects of high irradiances, which may damage the photosynthetic apparatus, and these pigments may be termed photoprotective carotenoids (PPC) (Kirk, 1994).

In this paper, the vertical distribution pattern of phytoplankton pigments and associated reconstructed absorption are presented for two AMT cruises. The objectives were to examine the changes in pigment composition and absorption properties over large spatial scales along the two transects, and to assess their relevance with respect to primary productivity models and remote sensing algorithms. These cruises also offered the opportunity for conducting oceanographic investigations in the South Atlantic, which is a poorly studied region of the world ocean in relation to phytoplankton patterns and primary production. The AMT-3 cruise was undertaken in September–October 1996 between the UK and the Falkland Islands, and AMT-6 in May–June 1998 from South Africa to the UK. The AMT-6 cruise along the eastern boundary of the North and South Atlantic allowed a study to be conducted in the high productivity regions of the Benguela upwelling ecosystem, the NW African upwelling system, and the end of the spring bloom in NE Atlantic temperate waters.

2. Methods

Seawater was collected from various depths within the upper 200 m with a CTD rosette system on station (450 km spacing for AMT-3; 350 km for AMT-6) and filtered through 25 mm GFF filters to harvest the phytoplankton. The filters were stored
frozen in liquid nitrogen or in a −60°C freezer. Pigments were extracted in acetone with the aid of ultrasonication and clarified by centrifugation. Analysis of pigments was conducted ashore (AMT-3) and on board (AMT-6), following the reverse phase HPLC procedure outlined by Barlow et al. (1997). Pigments were separated with a 3 μm Hypersil MOS2 C8 column on a Shimadzu HPLC system (AMT-3) or on a Thermo Separations Products HPLC (AMT-6). Pigments were detected by absorbance at 440 and 665 nm and identified by retention time and on-line diode array spectroscopy. The monovinyl chlorophyll a standard was obtained from Sigma Chemical Co. and divinyl chlorophylls a and b from R. Bidigare and M. Ondrusék (University of Hawaii) and L. Van Heukelem (University of Maryland). Other pigment standards were purchased from the DHI Institute for Water and Environment, Denmark.

Temperature and salinity were recorded routinely by the CTD, and nutrient samples were drawn concurrently with pigment samples for onboard analysis with an auto-analyser. Photosynthetically active radiation (PAR) was determined from surface and in situ spectroradiometric measurements with Satlantic Inc. radiometers mounted in an Optical Profiling System (SeaOPS) and a Free-Falling System (SeaFALLS) as described by Hooker and McClain (2000).

Absorption spectra of phytoplankton \(a_{\text{ph}}(\lambda)\) were computed from pigment concentrations \(C_i\), mg m\(^{-3}\) and in vivo, weight-specific, absorption coefficients \(a_i^*(\lambda)\), m\(^2\) mg\(^{-1}\) for chlorophylls \(a, b, c\), photosynthetic carotenoids (PSC) and PPC by a reconstruction technique (Bidigare et al., 1990b; Marra et al., 2000):

\[
a_{\text{ph}}(\lambda) = \sum a_i^*(\lambda)C_i.
\]

Peridinin, fucoxanthin, 19′-hexanoyloxyfucoxanthin and 19′-butanoyloxyfucoxanthin constituted the PSC, and violaxanthin, diadinoxanthin, alloxanthin, zeaxanthin and \(\beta\)-carotene the PPC.

3. Results

The cruise tracks for AMT-3 and AMT-6, superimposed on a composite SeaWiFS image of chlorophyll \(a\) for the Atlantic Ocean are shown in Fig. 1. The satellite image illustrates the considerable range in phytoplankton distribution, with high productivity regions along the NW and SW African coastlines and off SE South America. It appears that the chlorophyll \(a\) levels in oligotrophic waters along the eastern boundary of the South Atlantic are about twice as high as those in the oligotrophic gyre offshore from Brazil. For convenience, the data for each cruise will be presented in the sequence coinciding with the direction of the cruise, i.e., north to south for AMT-3 and south to north for AMT-6.

3.1. Pigment distribution

The TChla pattern for AMT-3 (Fig. 2) showed elevated levels on the European shelf (50–48°N), in the NW African upwelling zone (25–10°N), and in the Brazil-Falklands Current Confluence Zone (BFCCZ) (35–51°S). The bulk of the TChla was located in the upper 20–50 m on the European shelf and Falklands regions, but at the sub-surface maximum at 40–50 m in the upwelling area. Very low surface TChla concentrations were recorded in the northern and southern oligotrophic gyres and the chlorophyll maxima were located at depths from 70 m to deeper than 100 m (Fig. 2). The distribution of accessory pigments provided information concerning the components of the phytoplankton community. Fucoxanthin concentrations (diatoms) were most prominent on the European shelf, the NW African upwelling zone and in the Falklands region, while peridinin (dinoflagellates) was only significant at 45–50°N. A summation of 19′-hexanoyloxyfucoxanthin, 19′-butanoyloxyfucoxanthin, alloxanthin and chlorophyll \(b\) was a useful combined signature for nanoflagellates, and Fig. 2 shows that these organisms were ubiquitous throughout the transect, generally matching the distribution pattern for TChla. Zeaxanthin is a biomarker for cyanobacteria and is found in both Synechococcus and Prochlorococcus, whereas divinyl chlorophyll \(a\) is exclusive to Prochlorococcus. Zeaxanthin was widely detected, indicating the ubiquity of cyanobacteria, with Synechococcus appearing to be more important, particularly in the surface layers,
because divinyl chlorophyll \( a \) (prochlorophytes) was more prominent at depth in the tropical and subtropical regions from 40°N to 35°S (Fig. 2). The highest divinyl chlorophyll \( a \) concentrations were observed in the equatorial region at the chlorophyll maxima located at 70–80 m.

The latitudinal coverage for AMT-6 was more restricted (34°S–50°N), but TChla concentrations were considerably greater than for AMT-3, especially in the Benguela upwelling system (34–15°S), where high chlorophyll levels were recorded at depths down to 110 m (Fig. 3). In the NW African upwelling system and NE Atlantic temperate waters, TChla was distributed between the surface and 50 m. Fucoxanthin was a major accessory pigment in the Benguela region, indicating the importance of diatoms, as well as being important off NW Africa and on the European shelf. Peridinin was only detected in significant concentrations in the Benguela region. The

![Fig. 1. Cruise tracks for AMT-3 (UK to Falkland Islands) and AMT-6 (South Africa to UK), superimposed on a composite SeaWiFS image of chlorophyll \( a \) distribution.](image-url)
nanoflagellates (Hex + But + All + Chlb) were found throughout the transect, with elevated concentrations in the Benguela, NW Africa and European shelf (Fig. 3). Zeaxanthin (cyanobacteria) was detected throughout the tropical and subtropical regions and also in the Benguela system, but since no divinyl chlorophyll A was detected in the Benguela it appears that only *Synechococcus* was present in the upper 20m in this region (Fig. 3). The highest divinyl chlorophyll A concentrations (prochlorophytes) were recorded in the vicinity of 10°N at depths of 20–30m, and significant levels were also observed at 70–110m in the northern oligotrophic gyre (22–40°N).
The SeaWiFS image (Fig. 1) and the pigment patterns in Figs. 2 and 3 indicate that there were five major regions on each transect reflecting the phytoplankton distribution. Three regions in the northern hemisphere included the temperate NE Atlantic-European shelf (42–50°N), the oligotrophic gyre (22–42°N), and the NW African upwelling system (10–22°N). In the southern hemisphere, the oligotrophic gyre region covered a long section of the AMT-3 track (10°N–35°S) and the fifth region was the BFCCZ (35–51°S). For AMT-6, the Benguela upwelling ecosystem formed one region (15–34°S) and the southern oligotrophic zone (15°S–10°N) another. For each transect, one station was selected for each region as representative of the pigment pattern for that
region, except for the Benguela and Falklands regions, where two stations were selected because of the increased mesoscale activity (and, thus, higher productivity and variance) relative to the other regions.

The pigment, temperature, nitrate, and PAR profiles for the six stations for AMT-3 are presented in Figs. 4 and 5. At 49.68°N there was an adequate nutrient supply, most of the chlorophyll was located in the upper 30 m, no divinyl chlorophyll \( a \) was detected, and there was a rapid attenuation of PAR with the 0.1% light depth at 41 m. The phytoplankton community was mixed: prymesiophytes (Hex) were the main group, but diatoms (Fuc), dinoflagellates (Per), and green flagellates (Chlb) were important constituents,
with cryptophytes (All), pelagophytes (But) and cyanobacteria (Zea) being minor components. In contrast, the 29.49°N oligotrophic site had extremely low nitrate in the upper 100 m, a chlorophyll maximum at 100 m, and the 0.1% light depth at 150 m. The dominant accessory pigments in the upper 60 m were Zea and Hex, and this pattern changed to Hex and Chlb dominance at 100 m and below (Fig. 4). No nitrate was measured in the upper 30 m at 20.08°N, and the chlorophyll maximum and 0.1% light depth were observed at 40 and 80 m, respectively. Zea, Fuc, and Hex were the major accessory pigments in the upper 30 m, Fuc and Hex at the chlorophyll maximum; Chlb gave the highest concentrations from 60–150 m.

Fig. 3. (Continued).
Fig. 4. Vertical profiles of pigments at selected localities in the North Atlantic for AMT-3. TChla—total chlorophyll a (monovinyl + divinyl); DvChla—divinyl chlorophyll a; Fuc—fucoxanthin; Hex—19'-hexanoyloxyfucoxanthin; But—19'-butanoyloxyfucoxanthin; Chlb—chlorophyll b; Zea—zeaxanthin; Per—peridinin; All—alloxanthin.; NO₃—nitrate; Temp—temperature; PAR—photosynthetically active radiation; 0.1%—depth of the 0.1% light level relative to the surface intensity.
The deepest chlorophyll maximum was recorded at 160 m in the southern oligotrophic gyre at 14.89°S, where nitrate was extremely low down to 140 m. Unfortunately, the PAR measurements for this station were very low and inaccurate and are, therefore, not reported. Unusually high Chlb concentrations (relative to the other accessory pigments) were measured in the upper 100 m.
(Fig. 5), although Zea was found in significant levels down to 120 m, and Hex and But were then dominant below 120 m. Station 32.80°S was located at the northern end of the BFCCZ, where eddy formation was occurring. The consequent mixing processes resulted in an increase in nutrients in the upper mixed layer, and the bulk of the chlorophyll was detected in the upper 60 m. Hex was the major accessory pigment in the 60 m layer, together with significant amounts of Zea and But plus minor amounts of other biomarkers (Fig. 5). Chlb was the only pigment to increase substantially below 60 m. The upper 40 m contained most of the pigments at 43.58°S in the BFCCZ, where nutrients were plentiful and the 0.1% light penetrated to 80 m. Hex and Fuc dominated the 40 m layer, but Chlb was the most prominent pigment from 60 to 150 m (Fig. 5).

Depth profiles for the selected AMT-6 stations (Figs. 6 and 7) indicated the high nutrient levels in the Benguela region at stations 28.93°S and 24.75°S with the consequent elevated TChla concentrations and shallow euphotic zones. The phytoplankton at 28.93°S were a mixed community that was dominated by diatoms (Fuc) and dinoflagellates (Per), and contained nanoflagellates (Hex, But, Chlb, All) and cyanobacteria (Zea) as minor components. Station 24.75°S was dominated entirely by diatoms, and the high levels of fucoxanthin and chlorophyll a at 100 m indicated that diatom cells were sedimenting out of the euphotic zone. Onboard microscopic analysis revealed these organisms to be large Coscinodiscus sp. cells. Nitrate was depleted in the upper 35 m at the southern oligotrophic station, 5.87°S, where the chlorophyll maximum was located at 40 m and the 0.1% light depth at 85 m (Fig. 6). Of the accessory pigments, Zea and divinyl chlorophyll a dominated the upper 20 m, and Hex dominated at the deeper depths to 120 m. Zea concentrations declined below 20 m, but all the other accessory pigments increased at the chlorophyll maximum, including significant levels of divinyl chlorophyll b.

During AMT-6, the TChla and nitrate levels in the NW African upwelling region (station 20.41°N) were much greater than those observed during AMT-3, and the community largely comprised prymnesiophytes (Hex) and diatoms (Fuc), with cyanobacteria (Zea) as a minor group (Fig. 7). The northern oligotrophic station, 28.68°N, had a deep chlorophyll maximum at 145 m, extremely low nutrients down to this depth, and a deep euphotic zone where the 0.1% light penetrated to 165 m. Hex and Zea were the major accessory pigments to 100 m, and although Hex and But were significant at the chlorophyll maximum, divinyl chlorophyll b increased substantially at 145 m (Fig. 7). At 48.45°N, TChla concentrations of 2 mg m⁻³ were recorded down to 30 m, nitrate was low (but measurable), and the 0.1% light depth was located at 40 m. Hex was the dominant accessory pigment, but significant concentrations of Fuc were also observed; microscopic analysis suggested that Phaeocystis sp. was associated with these biomarker pigments.

3.2. Pigment absorption

Direct measurements of phytoplankton absorption were unavailable. A reconstruction technique was used to generate appropriate spectra, but this technique has certain limitations. The first is that the in vivo spectra are reconstructed from in vitro spectra in organic solvents, with absorption maxima shifted to match the corresponding in vivo peaks (Bidigare et al., 1990b); thus the packaging effect for pigments bound into pigment–protein complexes in the photosynthetic membranes is not taken into account. Secondly, the weight-specific absorption coefficients are available only for two of the major carotenoids, namely fucoxanthin and β-carotene, and these were used to represent the coefficients for the PSCs and the PPCs, respectively. These assumptions introduce certain errors, because the absorption properties of the PSC’s and PPC’s are not identical (Jeffrey et al., 1997). They do have similarities, however, and the specific extinction coefficients for peridinin, 19-hexanoyloxyfucoxanthin and 19-butanoyloxyfucoxanthin in ethanol are within 11–14% of the coefficient for fucoxanthin (Jeffrey et al., 1997). Similarly, the extinction coefficients for violaxanthin, diadinoxanthin, alloxanthin, and zeaxanthin are within 2–8% of the β-carotene coefficient (Jeffrey et al., 1997). Despite the limitations of the reconstruction technique, the
method does provide an estimate of "unpackaged" coefficients that are useful for comparing the absorption characteristics of contrasting phytoplankton communities.

Examples of uncorrected absorption spectra for two AMT-6 stations are presented in Fig. 8 to illustrate the difference in pigment absorption between two contrasting phytoplankton communities.
communities. The 24.75S sample from the Benguela upwelling system was dominated by diatoms (Fuc, Fig. 6) and monovinyl chlorophyll a, chlorophyll c and PSC were the main absorbing pigments in the blue–green region of the spectrum, and monovinyl chlorophyll a in the red. A mixed
community of small cells, cyanobacteria (Zea) and prymnesiophytes (Hex), was prevalent at the surface at 5.87S (Fig. 6). PPC was the dominant absorbing group at blue–green wavelengths, with secondary absorption by divinyl plus monovinyl chlorophyll a at both blue and red wavelengths. The reconstructed whole-cell absorption coefficients ($a_{\text{ph}}$) at 24.75S were considerably higher than at 5.87S, because of the greater mass of pigments in the phytoplankton community. The blue absorption for $a_{\text{ph}}$ at 24.75S peaked at 440 nm because of strong monovinyl chlorophyll a absorption; $a_{\text{ph}}$ at 470 and 490 nm for the 5.87S sample was dominated by PPC absorption (Fig. 8).

The “unpackaged” TChla specific absorption coefficients ($a_{\text{ph}}/C_3$) were greater at 440 nm, compared to 490 nm, and varied between 0.044 and 0.092 mg m$^{-1}$ and from 0.023 to 0.078 mg m$^{-1}$, respectively (Fig. 9). For AMT-3, there was a uniformity or a decrease in $a^*_{\text{ph}}$ with decreasing irradiance, expressed as percentage of surface PAR, except for station 32.80S, where $a^*_{\text{ph}}$ increased. Similar observations were made for the AMT-6 stations, although there was more variability in $a^*_{\text{ph}}$ with changing irradiance compared to AMT-3 (Fig. 9). Specific coefficients were low at stations with elevated TChla concentrations (49.68°N, 43.58°S, AMT-3; 28.93°S, 24.75°S, AMT-6) and highest at localities in oligotrophic waters (29.49°N, 14.89°S, AMT-3; 28.68°N, AMT-6) where TChla levels were low.

The pigment composition of phytoplankton characterizes the absorption properties of a community, and three contrasting stations were selected to assess the role of each pigment group in phytoplankton absorption (Fig. 10). TChla accounted for approximately 50% of absorption at 440 nm, and PSC for 60% at 490 nm, in a mixed, temperate population of nanoflagellates, diatoms and dinoflagellates at 49.68°N (Fig. 4; AMT-3). For a diatom-dominated community at 24.75S (AMT-6) in the Benguela ecosystem (Fig. 6), the TChla absorption was 60% at 440 nm, and 80% of the absorption at 490 nm was attributable to PSC (Fig. 10). In oligotrophic waters at 5.87S (AMT-6), cyanobacteria were dominant in the upper 20 m, and the deeper sub-surface chlorophyll maximum population consisted mostly of nanoflagellates and prochlorophytes (Fig. 6). TChla absorption accounted for 40–50% at 440 nm, together with prominent PPC absorption (40%) in the upper euphotic zone (Fig. 10). At 490 nm, PPC absorption was the highest (70%) in the upper euphotic zone, and then declined below the 10% light depth, where PSC absorption increased substantially (Fig. 10). Absorption by chlorophylls $b$ and $c$ was low in these three communities, contributing <20%.

4. Discussion

4.1. Phytoplankton communities

The AMT cruises were essentially confined to investigating only the autumn and spring seasons in the Atlantic because of the logistical programme of the research vessel (Aiken et al., 2000). During AMT-3 (September–October 1996), it was autumn in the North Atlantic and spring in the south; for AMT-6 (May–June 1998), it was autumn in the South Atlantic and spring in the north. Thus, for the NE Atlantic, the two seasons can be compared because the cruise tracks were similar (Fig. 1). The cruise tracks in the southern hemisphere were on opposite sides of the South Atlantic basin, and therefore, the communities along the eastern and western boundaries could be compared, even though the observations were made in different seasons.

The phytoplankton in the temperate NE Atlantic and the northern oligotrophic gyre appeared to have similar characteristics for both the autumn and spring seasons. TChla levels were similar (Figs. 2 and 3) as well as the distribution pattern for diatoms (Fuc) and nanoflagellates (Hex + Butt + All + Chlb). Dinoflagellates (Per) were detected only in the upper water column on the European shelf during autumn (Fig. 2), but were virtually undetectable in the spring (Fig. 3). The cyanobacterial pattern (Zea) also appeared to be similar for both seasons, although the concentrations of divinyl chlorophyll a (prochlorophytes) were greater in the spring (AMT-6) at the deep chlorophyll maxima in the oligotrophic gyre (Figs. 2 and 3). The selected vertical profiles
confirmed the observations of the contoured data, but provided more detail on subtle differences. The profiles for 49.68°N and 48.45°N indicated a more diverse nanoflagellate community in the temperate NE Atlantic during autumn (AMT-3) compared to the spring (AMT-6), with chlorophyll b being significant in autumn but not in the spring (Figs. 4 and 7). At 29.49°N and 28.68°N, both communities displayed a layered structure, typical of oligotrophic communities, where cyanobacteria (Zea) and prymnesiophytes (Hex) dominated the upper 80–100 m, and a group of mixed flagellates were abundant at the chlorophyll maximum and below (Figs. 4 and 7). Chlorophyll b was most prominent at the deep maximum during both seasons, and this was due to the increased synthesis of divinyl chlorophyll b in prochlorophyte cells at depth to maximize their absorption of low intensity blue light (Fig. 7, 28.68°N).

These observations are consistent with other studies in the North Atlantic. Bidigare et al. (1990a) and Barlow et al. (1993) reported diatom

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Fig. 8. Examples of reconstructed phytoplankton ($a_{ph}$) and pigment ($a_{pig}$) absorption spectra for two surface samples from AMT-6; $a_{Chla}$ — monovinyl chlorophyll a; $a_{TChla}$ — divinyl plus monovinyl chlorophyll a.
Fig. 9. Profiles of chlorophyll \( a \) specific absorption coefficients \( (a_{ph}^*, \text{m}^2\text{mg}^{-1}) \) at 440 and 490 nm, plotted as a function of the percentage of surface PAR, or depth, at selected localities for AMT-3 and AMT-6.
Fig. 10. Proportional contribution of chlorophyll $a$ (Chla-abs), chlorophyll $b$ (Chlb-abs), chlorophyll $c$ (Chlc-abs), photosynthetic carotenoids (PSC-abs) and photoprotective carotenoids (PPC-abs) to absorption at 440 and 490 nm at selected localities for AMT-3 and AMT-6.
dominance during spring bloom investigations that were conducted early in the season, followed by a succession to nanoflagellates when key nutrients declined. The temperate NE Atlantic in June 1998 corresponded to the end of bloom conditions, so nanoflagellates were the dominant organisms. The phytoplankton pattern in the northern oligotrophic region appears to be consistent during all seasons, because a similar layering structure of pigments has been demonstrated in North Atlantic oligotrophic waters by Claustre and Marty (1995), Babin et al. (1996), Lazzara et al. (1996) and Goericke (1998). Barlow et al. (in press) and Gibb et al. (2000) estimated the contribution of divinyl chlorophyll \( a \) to TChla in the northern gyre can be up to 50% in surface waters, indicating the importance of prochlorophytes. Divinyl chlorophyll \( a \) concentrations in this study were greater at the subsurface maximum than at the surface, but accounted for similar proportions at 37–53% for AMT-3 and 31–50% for AMT-6.

Seasonal differences in upwelling are a well-known feature of the NW African region, with upwelling being driven by changes in the trade winds (Mittelstaedt, 1983). Upwelling occurs throughout most of the year but is strongest in May–June, particularly at 20–25°N (Wooster et al., 1976). The AMT-3 and AMT-6 data reflected these seasonal changes (Figs. 2–7) and, during the spring, the phytoplankton biomass extending for a distance of some 350 km offshore (Barlow et al., in press). Consequently, high TChla concentrations were recorded in the upper mixed layer, and the community was dominated by diatoms (Fuc) and prymnesiophytes (Hex) with cyanobacteria (Zea) being of secondary importance. In the autumn, the effects of upwelling were weaker, TChla levels were much lower and subsurface maxima had developed. Consequently, the phytoplankton community was distributed in layers: (a) cyanobacteria, diatoms and prymnesiophytes in the upper water column; (b) diatoms and nanoflagellates at the subsurface maximum; and (c) green flagellates increasing below the maximum layer.

In contrast to the North Atlantic, the South Atlantic is a vastly understudied area with respect to phytoplankton, and the only comprehensive investigations of primary production and picoplankton for the western boundary appear to be those from the AMT programme as discussed by Zubkov et al. (1998, 2000), Maranon and Holligan (1999) and Maranon et al. (2000). Primary production estimates for the Benguela ecosystem along the southeastern boundary have been reported by Brown et al. (1991). Very few pigment investigations have been undertaken, however, and this report, and those of Barlow et al. (in press) and Gibb et al. (2000), appear to be the only studies in the South Atlantic.

Two high productivity regions are evident in the South Atlantic in Fig. 1. These are BFCCZ off the coast of Argentina and the Benguela upwelling region along the SW African coast. The southern oligotrophic waters that were encountered during AMT-3 extended from 10°N to 30°S and from 10°N to 15°S for AMT-6. TChla levels were twice as high in the Benguela region compared to the BFCCZ (Figs. 2 and 3), and high fucoxanthin concentrations down to 100 m in the Benguela indicated the importance of diatoms in this upwelling ecosystem (Fig. 6). Fucoxanthin was measured in the BFCCZ, but at much lower levels, and, while peridinin (dinoflagellates) was very low, this pigment was elevated in the surface layers in the southern Benguela. Nanoflagellates were the most ubiquitous phytoplankton group in the BFCCZ (Figs. 2 and 5), and although the biomarker pigment concentrations for this group were greater in the surface layers in the southern Benguela, the organisms were generally only of secondary importance because of the dominance of diatoms (Fig. 6). No prochlorophytes were found in either of these regions, but the detection of zeaxanthin indicated the presence of cyanobacteria, most likely \textit{Synechococcus}, in the upper mixed layer in both the Benguela and the BFCCZ.

The southern oligotrophic waters for both AMT-3 and AMT-6 were dominated by cyanobacteria and nanoflagellates, but the pigment concentrations were greater along the eastern boundary and tended to be distributed at shallower depths (Figs. 2 and 3). In the equatorial zone, the maxima for divinyl chlorophyll \( a \) and zeaxanthin were located at 70–80 m on AMT-3 and centred at the equator, whereas for AMT-6,
their maxima were at 30 m and centred at 10°N. These observations suggested that the western South Atlantic was more oligotrophic than in the east, and this is confirmed by the satellite image in Fig. 1. Deep chlorophyll maxima were a feature of the western transect, and a maximum at 160 m was observed at 14.89°S during AMT-3 (Fig. 5). The layered structure of pigments in oligotrophic waters can be noted at 14.89°S and at 5.87°S (AMT-6), where cyanobacteria tended to dominate the upper water column and mixed flagellates the chlorophyll maximum (Figs. 5 and 6). An interesting feature along the western cruise track was the elevated chlorophyll levels that were recorded at a number of stations in the upper 100 m, as is illustrated in Fig 5 at 14.89°S. The chlorophyll b profiles did not match the divinyl chlorophyll a profiles, suggesting that green flagellates are more abundant than prochlorophytes along the western boundary of the South Atlantic. The chlorophyll b profiles for stations 32.80°S and 43.58°S also indicated that green flagellates were significant in the BFCCZ, but here they increased at depths below 60 m (Fig. 5).

4.2. Absorption properties

The variations in community structure along the two transects highlighted the adaptability of the phytoplankton to changing environmental conditions. Productive regions usually have a high rate of supply of nutrients, and mesotrophic and oligotrophic areas have low or depleted levels of key nutrients. In surface waters, light is not a limiting environmental parameter, but it is attenuated with depth, so phytoplankton must adapt to variations in both the availability of light and nutrients in the euphotic zone. Absorption of irradiance drives the process of photosynthesis, and the phytoplankton communities synthesize appropriate chlorophylls and carotenoids to optimize their light-harvesting capabilities (Kirk, 1994). The pigment composition of the various communities strongly influences the pattern of absorption in phytoplankton cells, and these properties have been examined for the various regions.

Estimates for $a^\text{ph}_{(440)}$ and $a^\text{ph}_{(490)}$ were within the global range of 0.01–0.18 m$^2$/mg Chl$^{-1}$ for absorption coefficients in the blue part of the spectrum (Bricaud et al., 1995), but tended to lie in the lower part of this range (Fig. 9). This may be due to errors associated with the spectral reconstruction technique, but also related to other chromophores that absorb in the blue region of the absorption spectrum. These include phycocerythins, cytochromes, and other non-chlorophyll and carotenoids pigments that occur naturally in phytoplankton. In high productivity waters, the coefficients tended to remain uniform with decreasing irradiance, except at site 20.41°N (AMT-6) in the upwelling zone, where $a^\text{ph}$ decreased with depth. Coefficients at other sites were variable; at oligotrophic stations, 29.49°N and 14.89°S, $a^\text{ph}$ decreased with attenuation in irradiance, but at 28.68°N, 32.80°S and 5.87°S, $a^\text{ph}$ increased with depth. Generally, though, there was a tendency for $a^\text{ph}$ to decrease with depth and attenuated light, as has been observed in the Californian Current (Sosik and Mitchell, 1995), the tropical North Atlantic (Lazzara et al., 1996) and the equatorial Pacific (Lindley et al., 1995; Dupouy et al., 1997).

There were significant differences in the pattern of absorption by the various pigments groups. In diatom-dominated communities, most of the absorption was due to chlorophylls a and c plus the photosynthetic carotenoids, whereas photoprotective carotenoids accounted for a large proportion of absorption in nano- and picoplanktonic populations (Fig. 8). In the higher productivity regions of the temperate NE Atlantic, the Benguela ecosystem, and the BFCCZ, absorption by the pigment groups were generally uniform with decreasing irradiance with chlorophyll a being the main absorbing group at 440 nm and PSC at 490 nm. Examples of this pattern are illustrated in Fig.10 for a mixed community (49.68°N) and a diatom population (24.75°S), with chlorophyll c and PPC being secondary absorbers, and chlorophyll b absorption being very low. Oligotrophic waters were characterized by high PPC absorption in the upper layers of the euphotic zone, particularly at 490 nm, as is shown in Fig. 10 for 5.87S. This pattern is attributable mainly to the
photoprotecting role of zeaxanthin in cyanobacteria near the surface. In the lower euphotic zone, where the community changed to nanoflagellates, PPC absorption declined, and PSC and chlorophyll c absorption increased.

In order to determine the effects of environmental variables on absorption, the relationships between $a^*_\text{ph}$ and nitrate concentration, as well as irradiance and temperature were examined (Fig. 11). The regressions were weak, but $a^*_\text{ph}$ showed a tendency to increase with decreasing nitrate concentrations, and to increase with an increase in irradiance and temperature. Specific absorption at both 440 and 490 nm increased significantly at nitrate concentrations below 0.1 mmole m$^{-3}$ (Fig. 11a and b). No significant regressions were obtained when chlorophylls $a + b + c$ and PSC specific absorption were plotted against the environmental variables, but there were some weak relationships for PPC (Fig. 12). There was a general tendency for $a^*_\text{ppc}$ to increase with an increase in PAR and temperature with a stronger regression relationship for temperature than irradiance (Fig. 12c–f). A constant low value of $a^*_\text{ppc}$ was displayed over a large range of nitrate concentrations, but $a^*_\text{ppc}$ increased substantially at levels below 0.1 mmole m$^{-3}$ (Fig. 12a and b).

The data show that the effect of pigments on the variability of $a^*_\text{ph}$ was due primarily to variations in absorption by PPC. Where absorption was mainly by the photosynthetic chlorophylls and carotenoids, $a^*_\text{ph}$ was uniform with attenuating irradiance down the water column. PPC levels increased in cyanobacterial-nanoflagellate communities where TChla concentrations were low; however, PPC absorption and $a^*_\text{ppc}$ increased substantially at levels below 0.1 mmole m$^{-3}$ (Fig. 12a and b). As PPC levels and absorption declined with depth, there was a concomitant decrease in $a^*_\text{ph}$. These effects of PPC on $a^*_\text{ph}$ appear to be universal. Using absorption and fluorescence techniques, Sosik and Mitchell (1995) showed that the PSC absorption was less variable than $a^*_\text{ph}$ in the Californian Current, and they attributed $a^*_\text{ph}$ variability to changes in PPC absorption. Investigations in the tropical Pacific showed results similar to the observations reported here and led to the conclusion that $a^*_\text{ph}$ variations were primarily, but not exclusively, caused by changes in the concentration and absorption of photoprotective pigments (Lindley et al., 1995; Allali et al., 1997; Dupouy et al., 1997). An analysis of absorption and pigment data from the Arabian Sea and around Vancouver Island by Stuart et al. (1998) showed 58% of the variability in absorption at 440 nm was due to the package effect, but at 490 nm, a greater part of the variation (up to 68%) could be explained by changes in the relative proportions of the three major carotenoids, fucoxanthin, 19′-hexanoylfucoxanthin and zeaxanthin.

No measurements of the other photosynthetic pigments (the phycobiliproteins) were undertaken during this study, so the role of phycoerythrin and phycocyanin in cyanobacterial and cryptophyte absorption is undetermined. The proportional absorption by these phycobiliproteins was probably very low compared to the key photosynthetic chlorophylls and carotenoids, however. None of the filters had a characteristic pink tinge indicative of significant phycobiliprotein levels, and filters from oligotrophic stations only had a yellowish colour indicative of zeaxanthin. Apparently, the levels of zeaxanthin were considerably higher than the concentrations of phycobiliproteins, particularly in the surface layers, suggesting that the photoprotective role of zeaxanthin was greater than photosynthetic absorption by phycobiliproteins in the upper euphotic zone. Support for the assumptions presented here is provided by the following data: (a) Allali et al. (1997) and Dupouy et al. (1997) for the equatorial Pacific; (b) Sathyendranath et al. (1996, 1999) and Stuart et al. (1998) for the NW Indian Ocean; (c) Hoepffner and Sathyendranath (1992), Lutz et al. (1996) and Stuart et al. (2000) for the NW Atlantic. In these studies, no significant absorption due to phycoerythrin was found at 550 nm, even in regions where cyanobacteria were important components of the phytoplankton community. An exception to these observations was reported by Bricaud et al. (1995), where a significant shoulder was visible at 550 nm on the absorption spectra of samples from the tropical NE Atlantic that apparently contained high abundances of cyanobacteria.

It was estimated that the proportion of absorption by PPC in the upper euphotic zone in
oligotrophic regions can be up to 40–50% at 440 nm and up to 60–75% at 490 nm. This raises the question about the efficiency of photosynthetic activity and the quantum yield of carbon fixation, because only 25–50% of the light absorbed would be available for photosynthesis. This proportion of absorption by the photosynthetic carotenoids and chlorophylls, and phycobiliproteins to a lesser extent, may be considered to be photosynthetically usable radiation (PUR) (Morel, 1991). Effectively, PUR drives photosynthesis and, thus, it is important that PUR be used in primary productivity models rather than PAR. Sosik and Mitchell (1995) and Lindley et al. (1995) have also suggested that only absorption by photosynthetic pigments should be used in such models. Obtaining accurate measurements of PUR is not straightforward, however, but a combination of PAR and phytoplankton absorption measurements, together with pigment reconstructions using more accurate absorption coefficients than are presently available to determine the proportion of PSC and chlorophyll versus PPC absorption, may be one way to estimate PUR.

Current models for determining primary production incorporate chlorophyll concentration as one of the parameters (e.g. Behrenfeld and Falkowski, 1997; Platt et al., 1991) with a view to use the satellite pigment data to estimate productivity on larger scales than has previously been possible. One problem with such models is that chlorophyll is a poor surrogate for primary productivity. Chlorophyll only accounts for about 50% of the total pigment in most marine ecosystems and absorbs light in the blue part of the spectrum between 400 and 470 nm with the
secondary absorption being around 670 nm. Chlorophylls \( b \) and \( c \) plus the carotenoids all absorb light across the blue–green region of the spectrum (400–550 nm), which overlaps the chlorophyll \( a \) absorption. Interpretation of ocean colour data is, therefore, quite complex, because all pigments need to be considered instead of chlorophyll \( a \) alone. The SeaWiFS remote sensing algorithm uses a ratio of reflectances at 490 and 555 nm to estimate chlorophyll concentrations (Maritorena and O’Reilly, 2000), but most of the absorption at 490 nm is due to the carotenoids, so the algorithm is effectively a carotenoid algorithm.

Carotenoids show a ubiquitous relationship with chlorophyll \( a \) on a global scale (Trees et al., 2000), which probably explains the robustness of the algorithm for chlorophyll \( a \). This study has demonstrated, however, that there is considerable variability in the composition of the carotenoids between PSCs and PPCs across a range of oceanic provinces. Because the PPCs account for a significant proportion of pigment absorption, particularly in oligotrophic regions, the chlorophyll–carotenoid relationship needs to be revisited in terms of absorption properties that are meaningful for accurate determinations of primary
production. As a contribution towards this goal, Moore and Aiken (in press) examined the relationship between remotely sensed reflectances and absorption, and developed bio-optical models that relate absorption not only to chlorophyll a but also to the photosynthetic and photoprotective carotenoids. Further research is required in the development of these models so that primary productivity can be derived from these absorption properties and remotely sensed reflectances.

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