

SPECTRAL RECOGNITION OF MARINE BIO-GEOCHEMICAL PROVINCES WITH MODIS

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ABSTRACT

Biogeochemical provinces vary due to physical and chemical changes in the marine environment. Water-leaving radiance has been used to investigate naturally occurring pigments in phytoplankton communities. Whereas in the open, ocean colour can easily be converted to total pigment concentrations, there are shortcomings in determining photosynthetic pigments in eutrophied coastal regimes. This is based on the fact that water-leaving radiance in coastal regions varies in relation to the changing composition of the main contributor to the water-leaving radiance.

In order to observe the spectral response of water over a wide range of chlorophyll and accessory pigments, a test site was selected that supports high plankton blooming through nutrient transport from a waste water treatment facility to the marine ecosystem. Several carotenoids were found to correlate with the spectral region where chlorophyll is shown in the second absorption band. As the same pigments are also correlated with each other, this correlation can be regarded as an artifact

The first derivative of reflectance in the near 690 nm region was investigated in this study. The results showed that measurements of spectral reflectance ratios for water-leaving radiance in the spectral region of the second absorption band of chlorophyll could be effective for empirically derived semi-quantitative relationships for concentrations of chlorophyll and related pigments. Measurements with MODIS demonstrate that the ratio 667/678 may be useful as an indicator for high chlorophyll concentrations close to the surface and can be used to describe the upper layer of the euphotic zone. The ratio technique was applied for separating bio-geochemical provinces when compared with chlorophyll measurements based on the first absorption band of chlorophyll. Preliminary results are presented for several oceanic regions using a clustering approach to relate chlorophyll data and the ratio technique.

Keywords: Marine provinces, MODIS, pigments, ocean spectra, currents

INTRODUCTION

Bio-geochemical provinces are characterized by their variety in bio-geochemical activity due to physical and chemical changes in the marine environment. Primary forces in the biogeochemical provinces include vertical mixing rates, stratification of the euphotic zone, nutrient supply and irradiance at the sea surface. Major modifications of these forcing factors result from changes in surface circulation that defines the location and boundaries of provinces with varying primary productivity. Therefore, partitioning the oceans into bio-geochemical domains and provinces can be derived from seasonal cycles of plankton development, the optical field, current systems and the associated mixing rate. Seasonality of the strength in primary productivity is determined by several parameters and Longhurst et al. (1) recognized in their study on bio-geochemical provinces four primary domains of the pelagic ecosystem, namely polar, westerlies, trade winds and coastal regions. All domains can be further subdivided into secondary biogeochemical provinces and can be measured either by conventional methods or by remote sensing techniques.

Water-leaving radiance has been widely used to estimate naturally occurring pigments in phytoplankton communities. Calibration and validation of ocean colour imaging was summarized in (2). Phytoplankton utilizes chlorophyll *a* as light-harvesting pigment whereas other pigments act as accessory pigments of which the most abundant ones are chlorophyll *b* and *c*, carotenoids and

phycobiliprotein. Related to these pigments are degradation products such as chlorophyllides, phaeophorbides and phaeophytins. The ratio between these various photosynthetic products can be used to identify major phytoplankton groups and to establish chemotaxonomic inventories based on analysis with, for instance, high performance liquid chromatography (HPLC).

The structural and optical properties of several pigments related to photosynthesis are very similar and consequently can be seen in the spectra of water-leaving radiance. As plankton is able to extend its optical window through the use of various pigments aside from chlorophylls, it would be of interest to investigate spectral properties of water-leaving radiance with the aim to improving the remote sensing techniques used.

Whereas in the open ocean (Case I water), colour can be converted to total pigment concentrations (see for instance (3)), there are shortcomings in determining photosynthetic pigments in coastal regimes with Case II water. This is due to the fact that the water-leaving radiance in those regions varies in connection with the changing composition of the main contributor to the water-leaving radiance. The contribution of inelastic sources to water-leaving radiance has been subjected to modelling efforts, for instance (4) showing the important role of sunlight-stimulated fluorescence and Raman scattering of water (5). In Case II water, chromophoric dissolved organic compounds (CDOM), inorganic particulate matter, organic debris and phytoplankton vary in their relative compositions, and consequently, do not necessarily co-vary with the water-leaving radiance and pigment concentrations. This decoupling between spectral radiance and pigments is particularly a shortcoming in coastal waters where high pigment concentrations are present due to coastal dynamics and transport of nutrients through river effluent and discharge from wastewater treatment facilities (WWTF). Furthermore, the inherent variations of one class of material to another limits the use of regionally developed algorithms for retrieving mass concentrations from optical data (6).

The photosynthetically active radiation (PAR) covers the spectral region where algae absorb maximal between 400 and 700 nm and where chlorophylls and carotenoids in their isolated form show specific absorption characteristics. The fact that specific accessory pigments are characteristic for taxonomic groups of algae demonstrates the importance in identifying the specific pigments in plankton species as well as in quantifying the ratio of their composition to each other. About 100 algal pigments have been identified (7) that can be grouped into chlorophylls, carotenoids and phycobiliproteins. Carotenoids are widely distributed throughout algal groups and absorb high energy in the spectral region below 500 nm.

Absorption, reflectance and fluorescence spectra need to be examined, with a view to defining the contributions of pigments to water-leaving radiance. Of particular interest is the sun-induced fluorescence of phytoplankton close to the spectral region where the second chlorophyll absorption band is located. High correlation was found between chlorophyll concentration and the water-leaving radiance in this very same spectral region where sun-induced fluorescence of chlorophyll is also present ((8,9,10,11,12). Solar-induced chlorophyll fluorescence was used by Hoge and Swift (13) to study the ocean colour spectral variability whereas Gitelson (14) analysed the peak near 700 nm on radiance spectra and found a good relationship with chlorophyll concentrations.

To further elaborate on the interpretation of water-leaving spectral signatures, for categorizing biogeochemical provinces, the following will focus on the continuing use of remote sensing for chlorophyll estimates, using the spectral region where chlorophyll has its second absorption band and in order to recognise biogeochemical provinces in the pelagic ocean with MODIS data. The experimental work related to the interpretation of MODIS data is described in the following as well.

EXPERIMENTAL BACKGROUND: SAMPLING STRATEGY AND DATA COLLECTION

Description of Test Site

A wide range of chlorophyll and accessory pigments can be expected in regions where eutrophication is encountered. Therefore, a test site was selected that supports high plankton blooming through nutrient transport from a wastewater treatment facility to the marine ecosystem. The en-

hanced primary productivity allows measurements along a well-defined concentration gradient in phytoplankton. The area chosen is the Peconic Bay as shown in Figure 1. The Peconic Bay is separated from Long Island Sound on the North by an elongated and narrow landmass from where it is possible to investigate different environments and ecosystems over a very wide range of salinity. The Bay has its major surface source of freshwater from the Peconic River which flushes through the Peconic Bay Estuary.

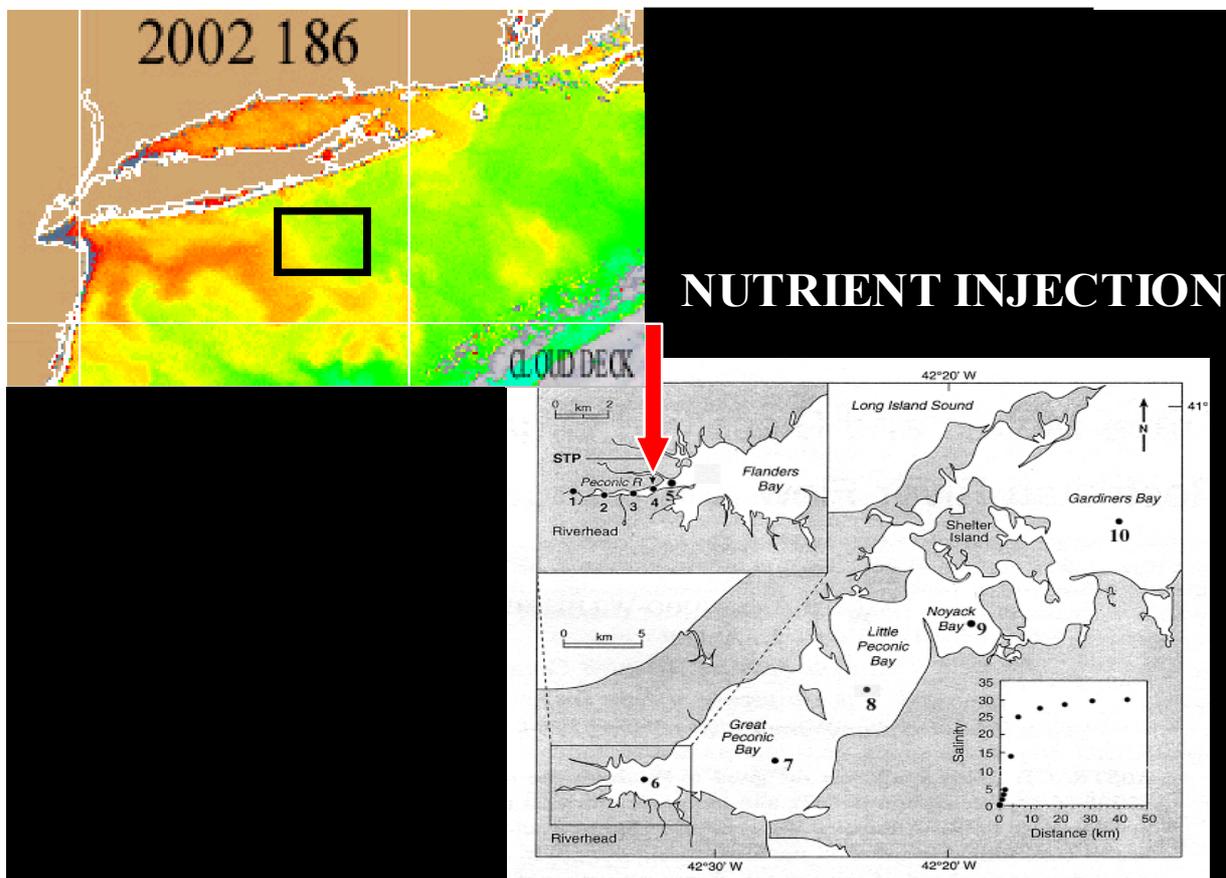


Figure 1: Eutrophication test site in the Peconic Bay. Left: SeaWiFS coverage for Long Island Sound and vicinity with indication of the Hudson River outflow and eutrophication. Lower right: Details of test site.

In identifying the region of maximum eutrophication, real time data acquisition of salinity, temperature and chlorophyll was employed, the latter parameter based on fluorescence measurements and calibration with discrete samples. A representative sample of the eutrophied region is given in Figure 2.

Reflectance measurements

Spectral reflectance measurements were carried out using a GER 1500 spectro-radiometer covering the UV, visible and near infrared. For final analysis, the spectral region between 400 and 850 nm was selected for processing. The spectro-radiometer uses a diffraction grating with a silicon diode array with 512 discrete detectors and has a full width half maximum (FWHM) of 2 nm. The normal mode of the instrument was used, i.e., the integration time was automatically adjusted prior to each scan in response to the light conditions. The results are presented as percent of the incident solar irradiance for the upwelling water column radiance close to the surface radiance.

Pigment analysis

Samples were filtered through 0.7 µm GF/F, 25 mm glass fiber filters and stored in liquid nitrogen. The standard fluorometric method (15) was used to calculate chlorophyll and phaeopigment con-

centrations. The NASA protocol for the fluorometric chlorophyll *a*: Sampling, Laboratory, Methods and Data Analysis (16) was followed.

The HPLC method used was that proposed by Wright et al. (17). Although the absorption peaks for the monovinyl and divinyl chlorophyll *a* co-elute, each compound absorbs differently at 436 nm and 450 nm, and it was therefore possible to correct for the divinyl chlorophyll *a* contamination by monitoring changes in this ratio as a function of changes in the divinyl percentage (18). Accuracy for each pigment compound was based on availability of pigment standards and the selection of pigment specific extinction coefficients. The NASA protocol for HPLC analysis (19) was followed. Concentration of the standards were determined or verified spectrophotometrically using published extinction coefficients (20).

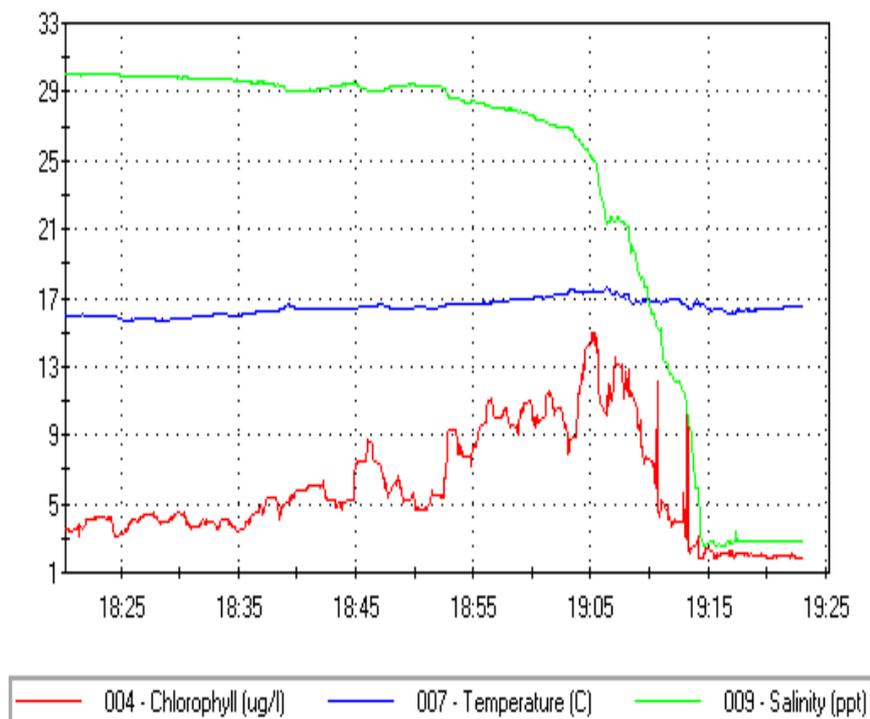


Figure 2: Example of real time data acquisition to determine the location of maximum eutrophication in the Peconic River in 2001. The continuous recordings cover the distance between station 7 (left) and 1 (right), before taking discrete samples on the return trip as shown in Figure 1.

Spectral interpretation

The overall spectral response as a function of salinity of the test site is given in Figure 3. The lower salinity regions are characterized by the strong absorption at shorter wavelengths, a fact that can be attributed to the absorption of high concentrations of CDOM as characterized by dissolved organic carbon concentrations around 550 $\mu\text{M/l}$. Towards the mesohaline region, organic carbon concentrations decrease to 180 to 230 $\mu\text{M/l}$ and eventually reach the Bay, where mixing completes, to 170 to 180 $\mu\text{M/L}$ with corresponding salinities of about 29. Eutrophication is evident at salinities around 15 and is characterized by the strong absorption over the second absorption band of pigments between 600 and 700 nm.

Selected individual spectra for various salinity domains are shown in Figure 4. They demonstrate that in addition to the well pronounced *in vivo* chlorophyll absorption, other accessory pigments are associated with the spectra. Before discussing the spectral response curves for eutrophied regions, the open ocean water spectrum with low concentrations of pigments should be reviewed as given in Figure 5. Basically, the major absorption of chlorophylls at around 420 nm and around 670 nm can be recognized.

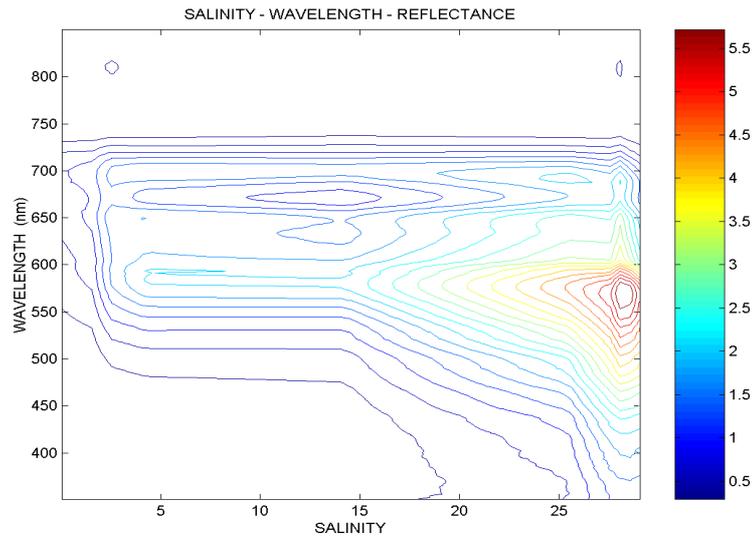


Figure 3: Spectral response in the test site as a function of salinity and reflectance based on the stations shown in Figure 1. The colour bar represents the code for isolines of reflectance $R(O)$ in percent. Data were collected on a cruise in 2001.

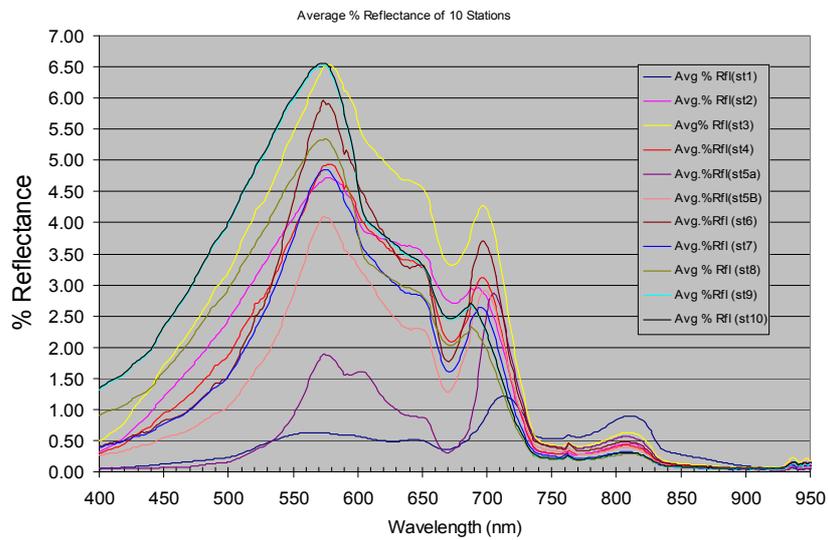


Figure 4: Averaged subsurface irradiance reflectance $[(R(O))]$ spectra through the salinity gradient based on data collected on a cruise in 2002.

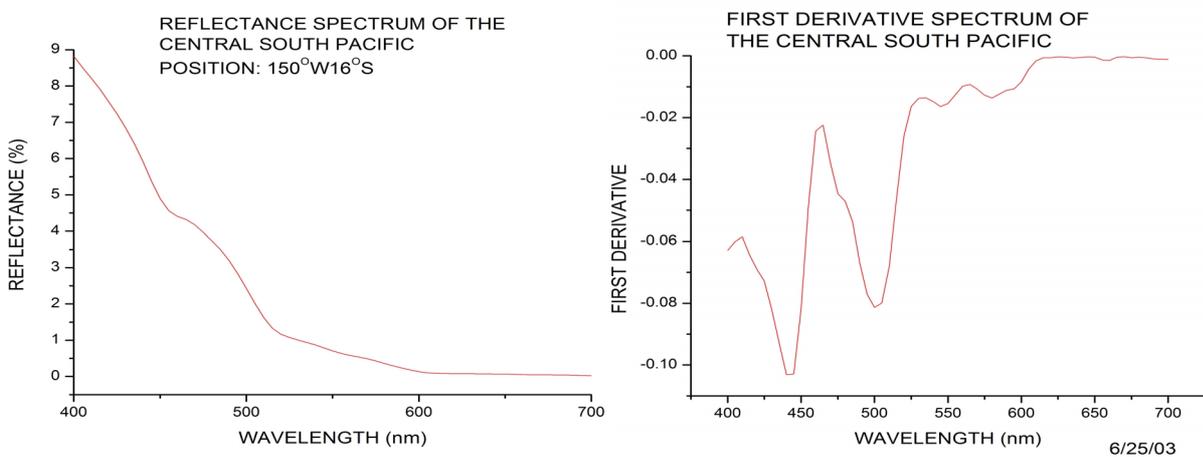
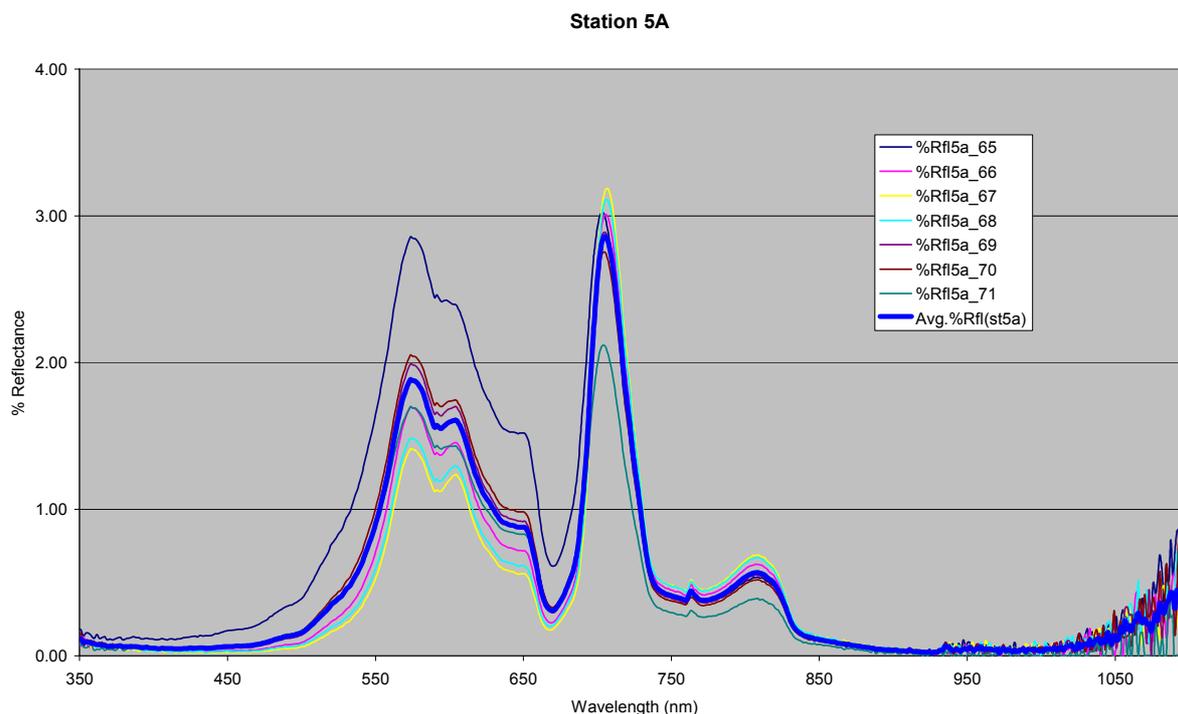


Figure 5: Reflectance $[(R(O))]$ spectrum of clear ocean water (left) and first derivative (right). The raw data were provided by Dr. S. Maritorea, University of California.

For comparison, Figure 6 shows the spectrum with high chlorophyll concentrations in the test region cited in Figure 1. Aside from the larger variation due to heterogeneity of the plankton distribution, the spectra exhibit two pronounced absorption bands. Furthermore, the inflexion point of the red-edge, due to reemission of photons from chlorophyll *a*, is indicated but strongly masked above 700 nm by the high absorption of water.

The spectral region between 400 nm and 500 nm is characterized by strong absorption of CDOM, carotenoids and the various chlorophylls. Those constituents are responsible for the low sensitivity of reflectance at shorter wavelengths with respect to phytoplankton pigments. Consequently, this specific wavelength region is irrelevant for identifying chlorophyll and/or related pigments in coastal waters. Minimum absorption of all phytoplankton pigments is observed in the range of 550 nm to 570 nm and results in a peak of reflectance mainly due to scattering of organic and inorganic particles as well as due to phytoplankton cell walls.



*Figure 6: Reflectance spectra for the eutrophicated region in the Peconic Bay, based on a cruise in 2002. Total chlorophyll *a* concentrations determined by HPLC for this station is 106.0 mg/m³.*

Phycobilins (phycocyanin, phycoerytherine and allophycocyanin) show diagnostic absorption bands between 550 nm and 650 nm. Phycocyanin was observed to have pronounced absorption at around 620 nm. The distinctive second chlorophyll absorption band is located at 670 nm but its absorption intensity at concentrations $> 20 \text{ mg} \cdot \text{m}^{-3}$ is offset by scattering of cell walls. Sun-induced fluorescence is diagnostic at 685 nm but can be significantly altered by reabsorption at chlorophyll concentrations $> 15\text{-}20 \text{ mg} \cdot \text{m}^{-3}$ (14). Chlorophyll still has a significant absorption at wavelengths 690 nm to 715 nm although it is partially offset by scattering which results in a shift of the peak position towards longer wavelengths (compare Figures 4, 5 and 6).

The first derivative of reflectance in the near 690 nm region was used by Rundquist et al. (20) and was further investigated by Szekiolda et al. (21) documenting new data sets. Based on the position of the second absorption band of chlorophyll, determined by the reflectance spectra and their corresponding first derivative, shown in Figure 7, the spectra were subjected to a correlation coefficient at 670 nm. That approach identified highest correlation at 680 nm as shown in Figure 8. The derivative of the spectra can be compared with the results reported by Goodin et al. (22), demonstrating that the first-order curves of water are practically zero at all wavelengths and that suspended matter in water is a second-order effect.

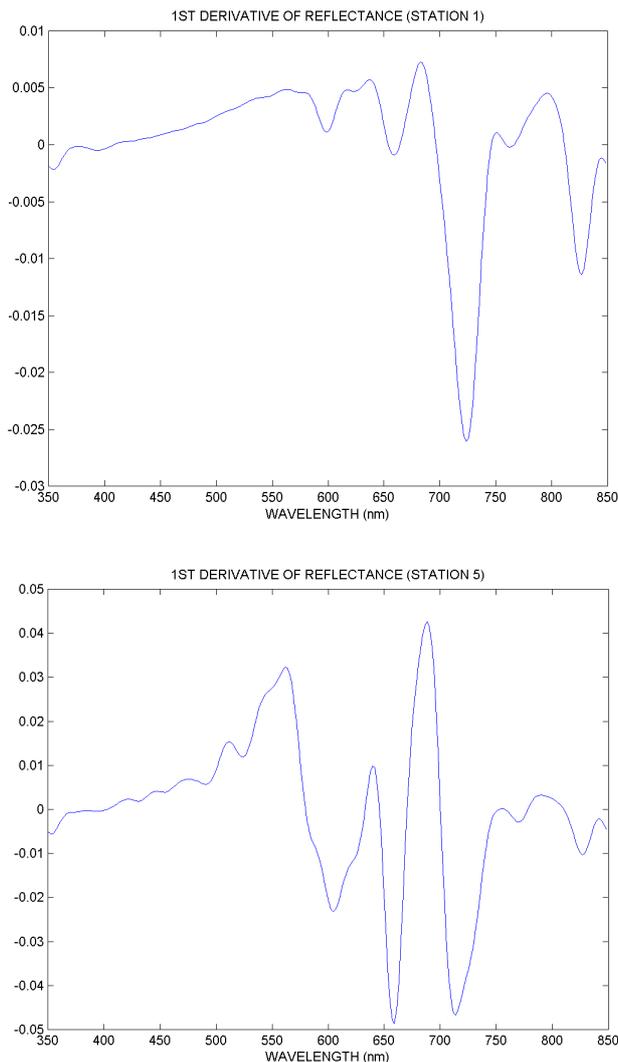


Figure 7: Upper: First derivative spectrum of coastal water with 1.6 mg chlorophyll per cubic meter. Lower: First derivative of coastal water with 27.2 mg chlorophyll per cubic meter.

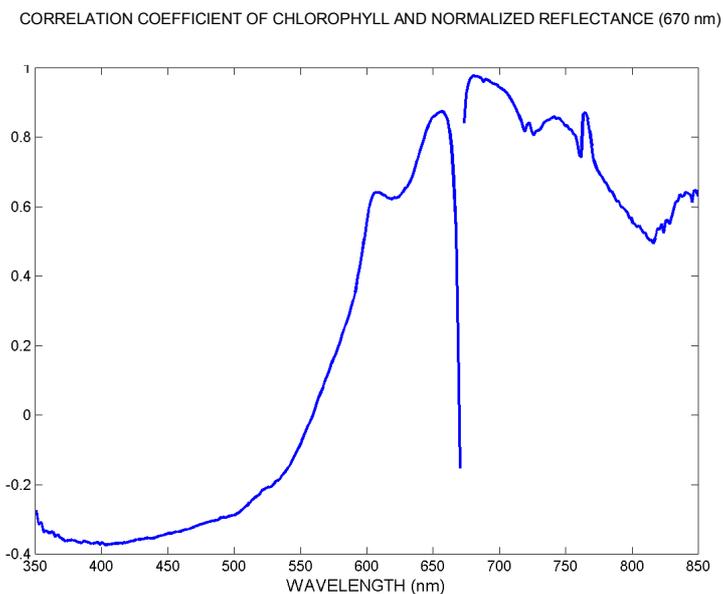


Figure 8: Correlation coefficient for chlorophyll and normalized reflectance at 670 nm from cruise 2001.

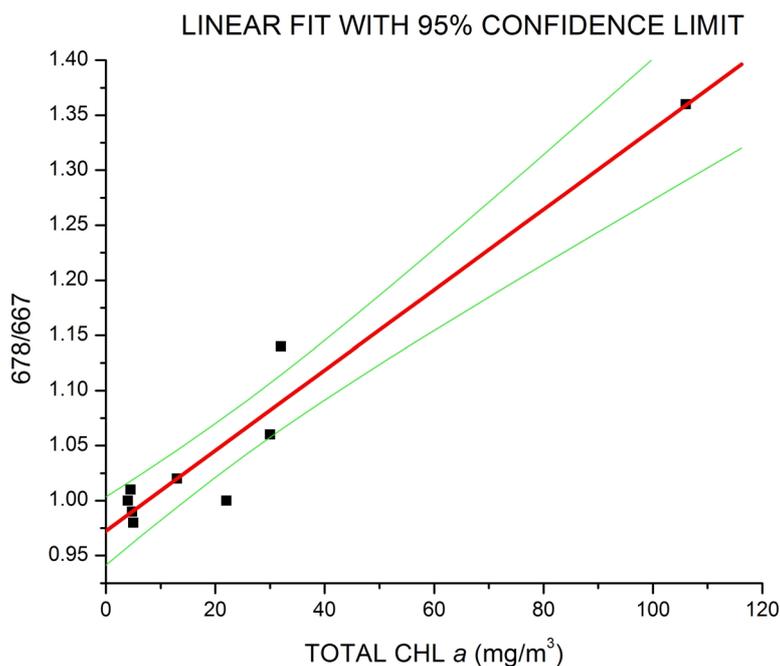


Figure 9: Data from a repeat cruise in 2002 to evaluate the ratio from MODIS bands with chlorophyll concentrations.

A repeat cruise in 2002 demonstrated the reproducibility of the spectral location of highest correlation and the identified wavelengths were used to correlate chlorophyll and the ratio 680/670. The spectral data were also correlated with the spectral channels of MODIS in the bands 667 nm and 678 nm of which the corresponding results are given in Figure 9.

Previously reported results (21) showed that measurements of spectral reflectance ratios for water-leaving radiance in the spectral region of the second absorption band of chlorophyll could be effective in empirically deriving concentrations of chlorophyll and related pigments. However, one has to consider the fact that at the wavelengths considered in this study, the spectral response of phytoplankton corresponds only to the upper layer. Therefore, satellite-derived chlorophyll, using the first absorption band, will show a disparity that is mainly due to the absorption characteristics of water. Otherwise, advantage can be taken of the varying photon penetration depth as a function of wavelength in order to locate the depth of chlorophyll concentration by comparing calibrated radiance data in terms of chlorophyll. Typically, upwelling regimes show the highest chlorophyll concentrations close to the surface whereas tropical and sub-tropical mid-oceanic regions have their pigment maximum at greater depths that is related to the location of the thermocline.

MODIS OCEAN OBSERVATIONS

The following shows an approach in evaluating the application of the 678/667 ratio with derived remote sensing reflectance based on MODIS data for coastal waters. The ratio technique based on field and laboratory measurements demonstrates that it may be useful as an indicator for high chlorophyll concentrations to describe the upper layer of the euphotic zone. Furthermore, it is evident that chlorophyll concentrations derived from algorithms using the spectral response over the first absorption band of chlorophyll, result in an integrated value that is greater than the corresponding photon penetration depth at longer wavelengths. Areas where the MODIS chlorophyll algorithms were compared with the ratio technique included upwelling regimes with their associated eddy fields. The Benguela and the Agulhas current systems with their upwelling regimes are shown in Figure 10 A, B and C.

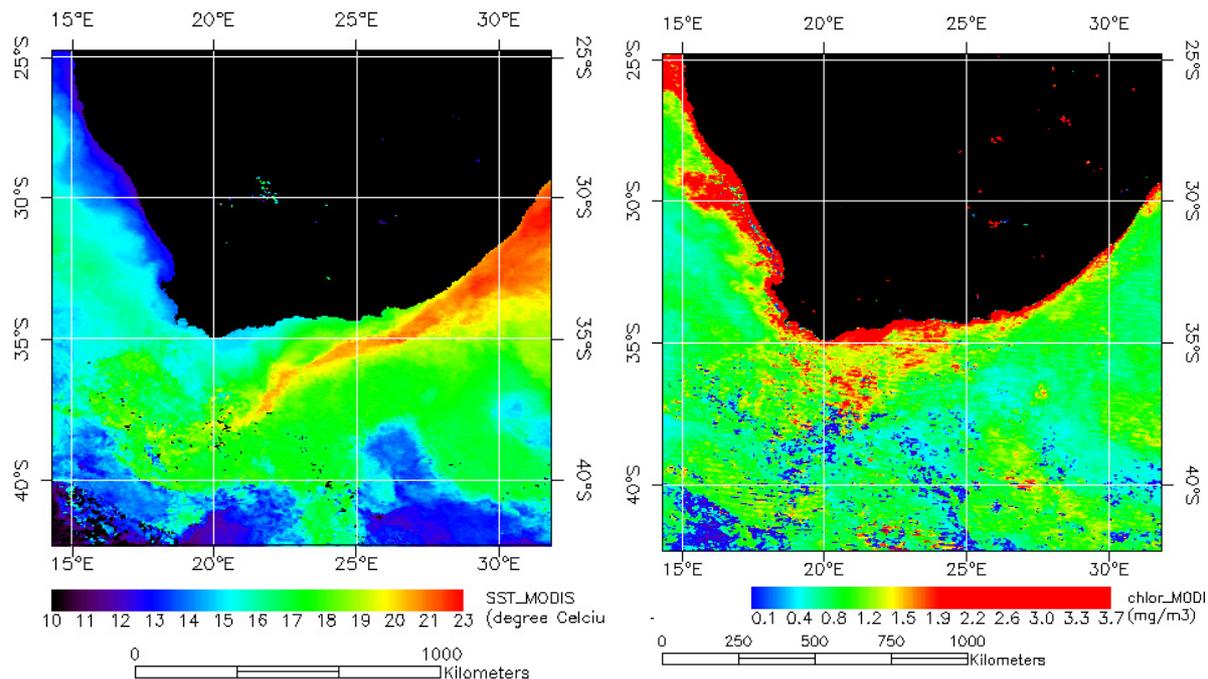


Figure 10 A,B: Comparison between patterns in temperature (left) and MODIS derived chlorophyll (right).

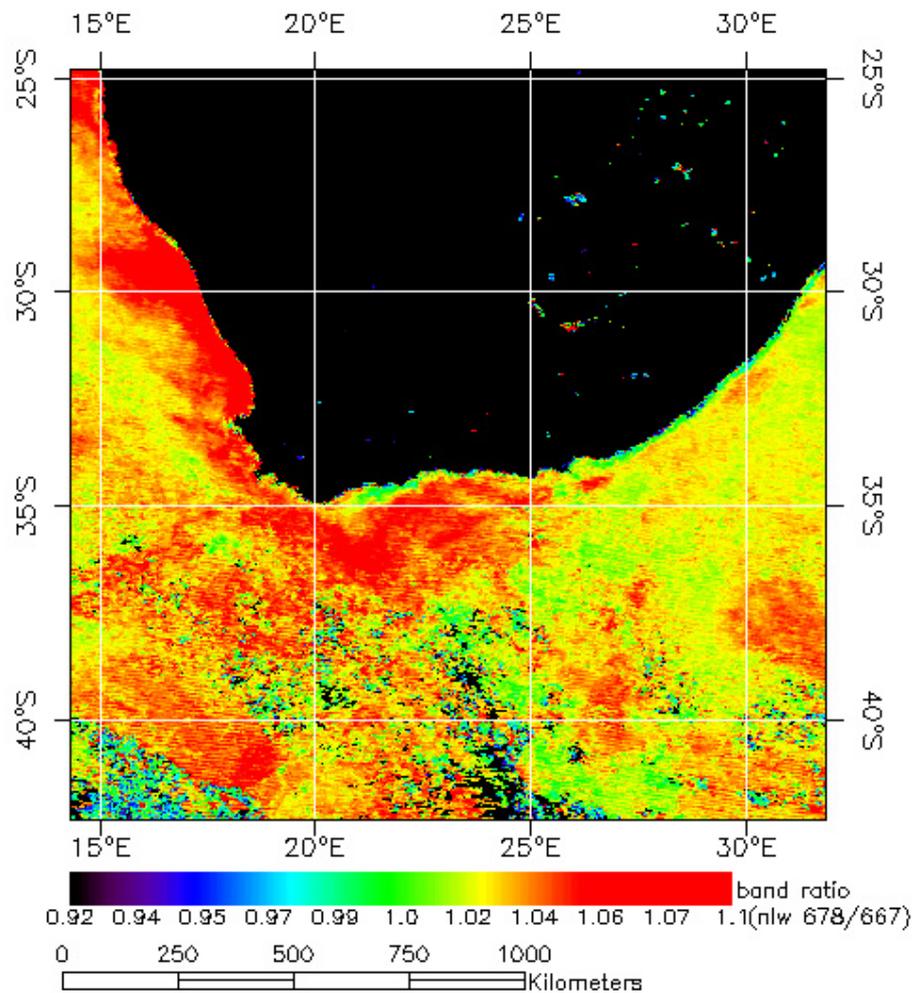


Figure 10 C: MODIS 678/667 ratio for the upwelling regime connected with the Benguela-Agulhas current system in July 2002.

As a comparison, another test site selected for recognizing boundaries of a biogeochemical system is the upwelling regime along the Somali coast where the near coastal current changes its direction in response to the monsoonal fluctuations. The analyzed coverage for the Somali upwelling temperature, band ratio 678/667 and chlorophyll is presented in Figure 11.

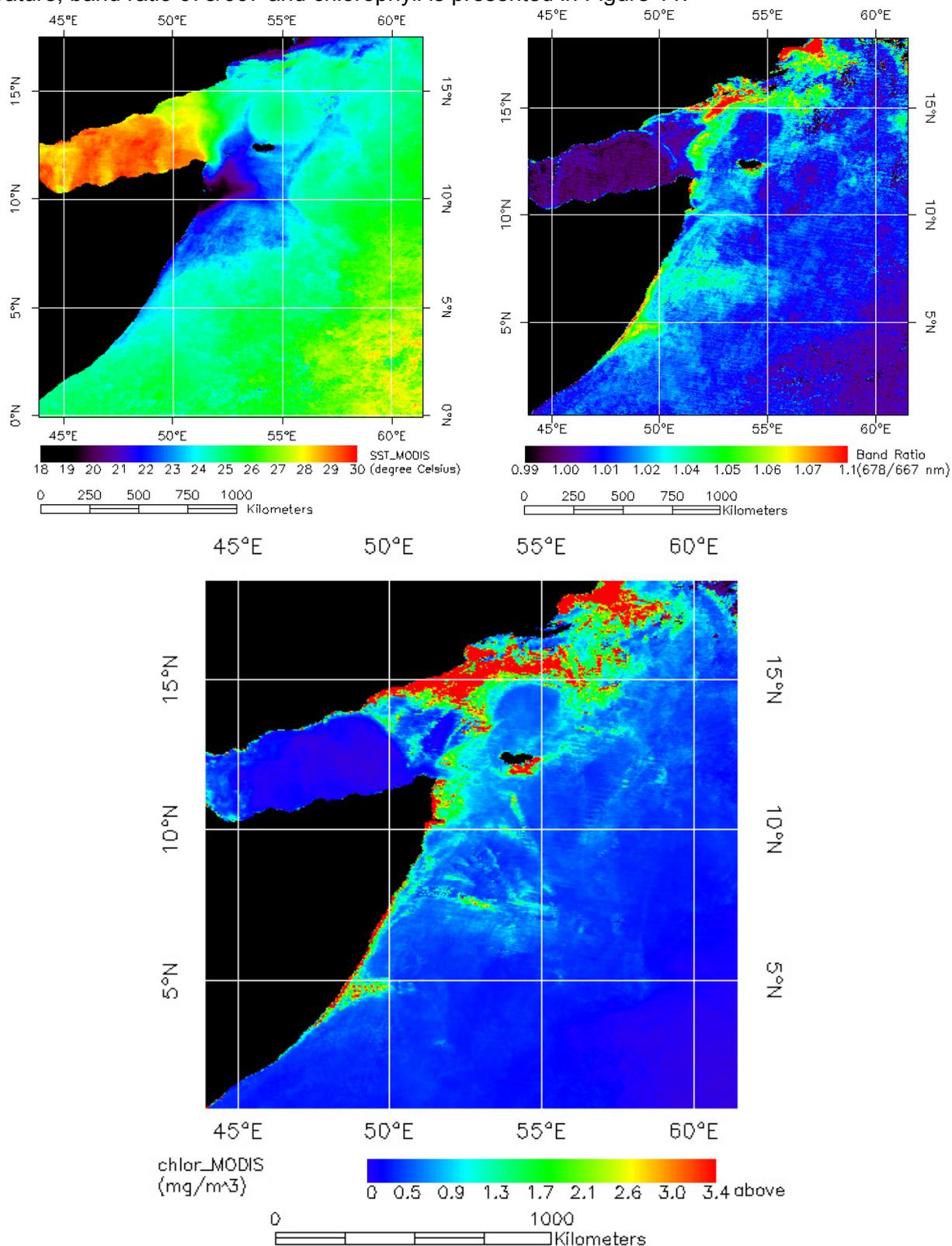


Figure 11: Temperature pattern (upper left) and 667/68 ratio image (upper right) and chlorophyll concentrations for the Somali upwelling region in July 2002, based on MODIS monthly averaged data.

Earlier observations with satellites (23) demonstrated that cold water patches are generated by upwelling in the coastal regime and that they are advected along the outer edge of the anticyclonic eddy. The ratio data also identified the resulting pattern and shows agreement with the patchiness in chlorophyll distribution as observed with the MODIS chlorophyll algorithm.

Scatter diagrams were used in a qualitative attempt to categorize patterns related to the chlorophyll regimes, as identified by the ratio technique and the MODIS chlorophyll algorithm. The principle of interpreting the clusters in the scatter diagrams is shown in Figure 12. Exporting the regions of interest (RIO) to the image allows the identification of provinces as shown in Figure 13.

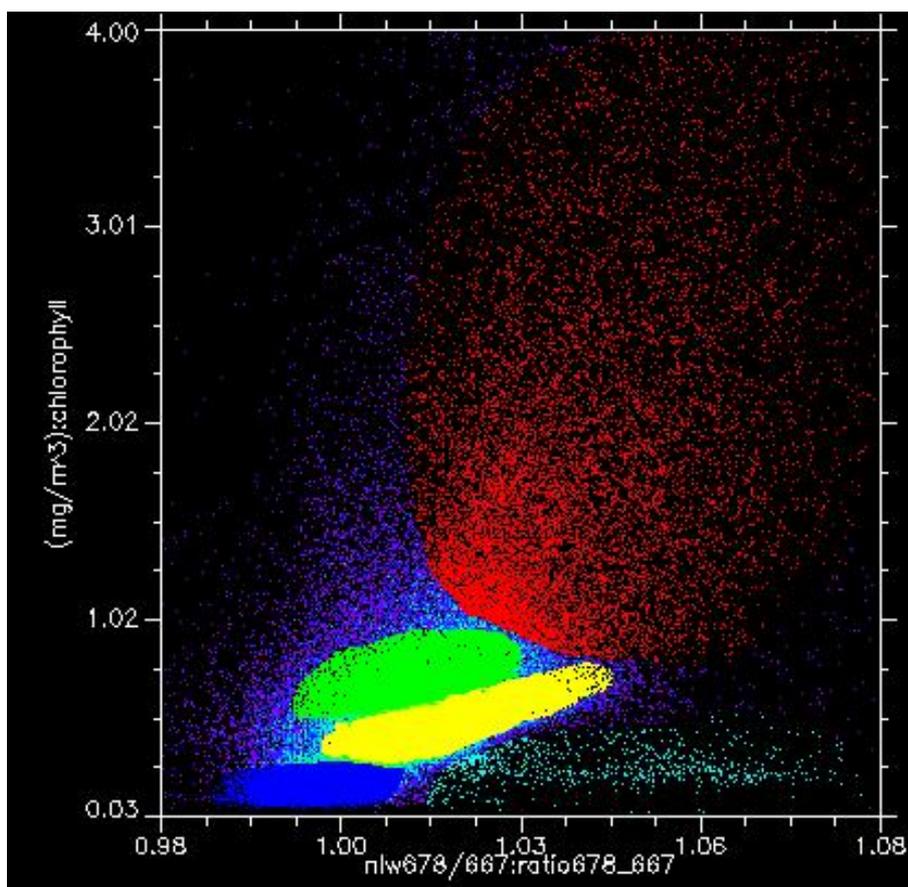


Figure 12: Regions of interest (ROI) based on a scatter diagram for chlorophyll (y-axis) and the ratio 678/667 (x-axis) for the region shown in Figure 11.

The ratio technique was extended to the Central Atlantic using the monthly averaged data derived from MODIS in May 2003 and focused on the Gulf Stream System as shown in Figure 14. The Florida Current can be seen as the section of the system covering the area from the Florida Straits to south of Cape Hatteras. The Gulf Stream is the part of the system extending from Cape Hatteras to the Grand Banks. The Loop Current and the Antilles Current and inflow from the shelf and the Sargasso Sea are part of the mechanisms to feed the Florida Current. The Loop Current is the current that flows through the Yucatan Straits through the Gulf of Mexico. After leaving the Florida Straits, the current decreases its velocity from $140\text{--}180\text{ cm}\cdot\text{s}^{-1}$ but broadens and deepens with an increase in transport. Downstream off Cape Hatteras, the current shift seawards with depth and has a width around 100 km with a maximum velocity at the surface of around $150\text{ cm}\cdot\text{s}^{-1}$.

The region between Cape Hatteras and the southwest border of Georges Bank, the Middle Atlantic Bight (MAB), includes a permanent front at the continental shelf-edge and another forming the northern boundary of the Gulf Stream. The water masses that are separated by these fronts are MAB shelf water, the slope water and Gulf Stream water. Interaction among these water masses includes small-scale interleaving at the shelf-edge front and the entrainment of shelf water by the Gulf Stream near Cape Hatteras.

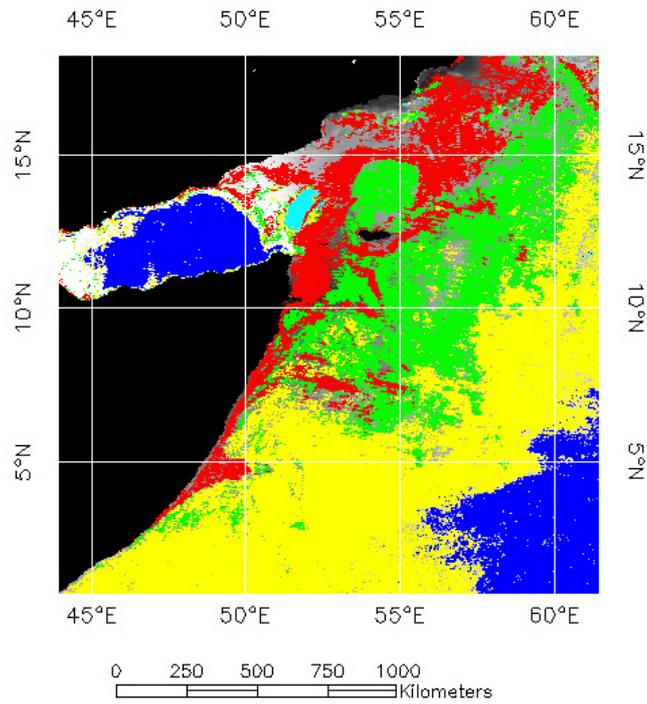


Figure13: Distribution of regions of interest as shown in Figure 12 .

For the area shown in Figure 14, clustering of regions of interest was achieved with the scatter diagram shown in Figure 15. The results of the ratio image and resulting display of the exported regions of interest from Figure 15 are given in Figure 16. Comparing the results with the presentation of enhanced chlorophyll data in Figure 14, it is evident that patch recognition with the ratio technique provides new information that relates to the various provinces connected with the off-shore region of the Gulf Stream system. In particular, plankton blooming in the near-surface water appears to be enhanced and the boundaries for the Loop Current and the Gulf Stream are better delineated.

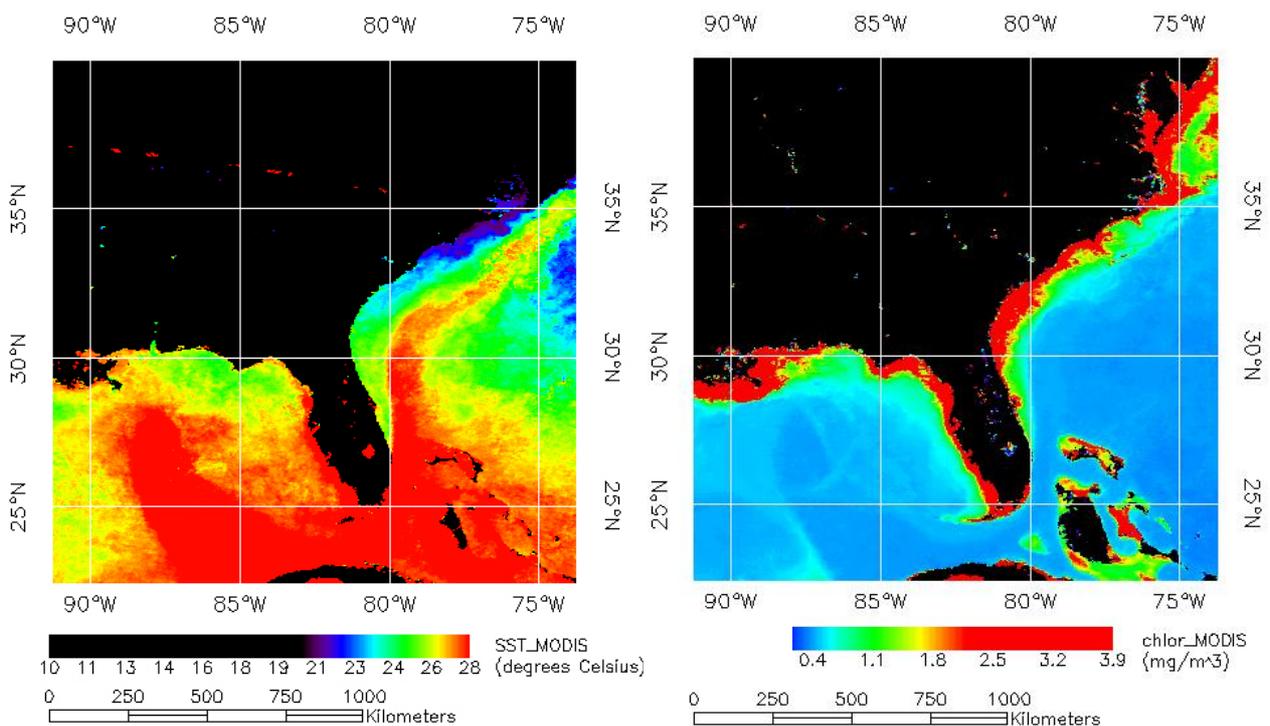


Figure 14: Sea surface temperature (left) and chlorophyll (right) derived from MODIS May 2003 for the Gulf Stream system.

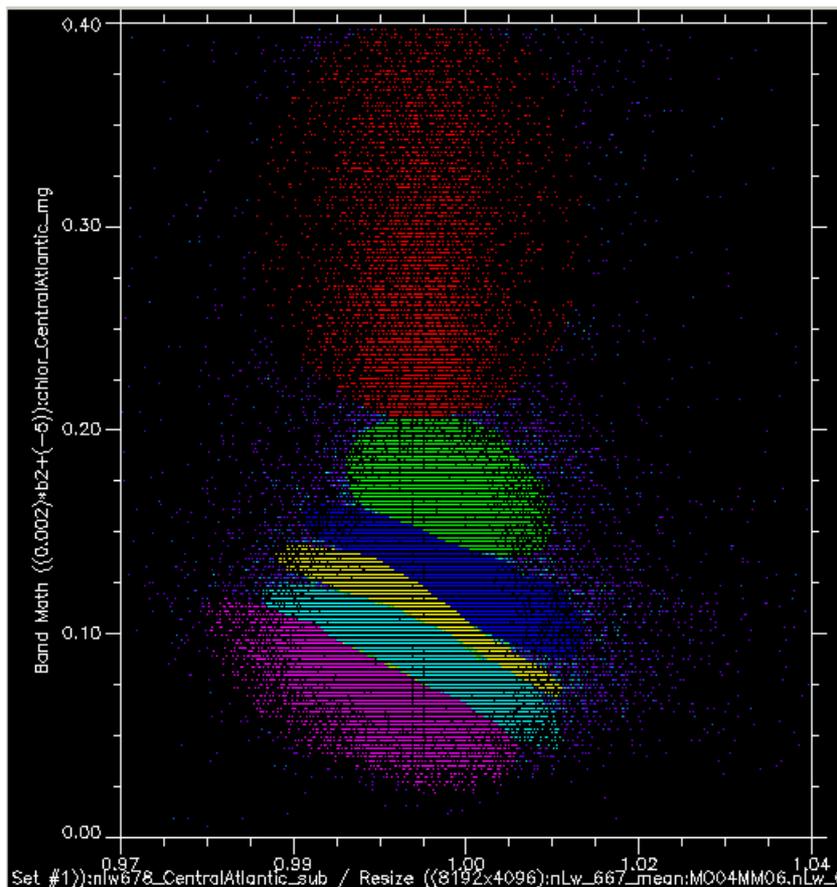


Figure 15: Scatter diagram of the Gulf Stream system shown in Figure 14 that gives the interpreted clustering in the scatter diagram as regions of interest (ROI) for chlorophyll (y-axis) and the ratio 678/667 (x-axis). High concentrations for the coastal regions and the effect of bathymetry of the Bahama Banks were not considered.

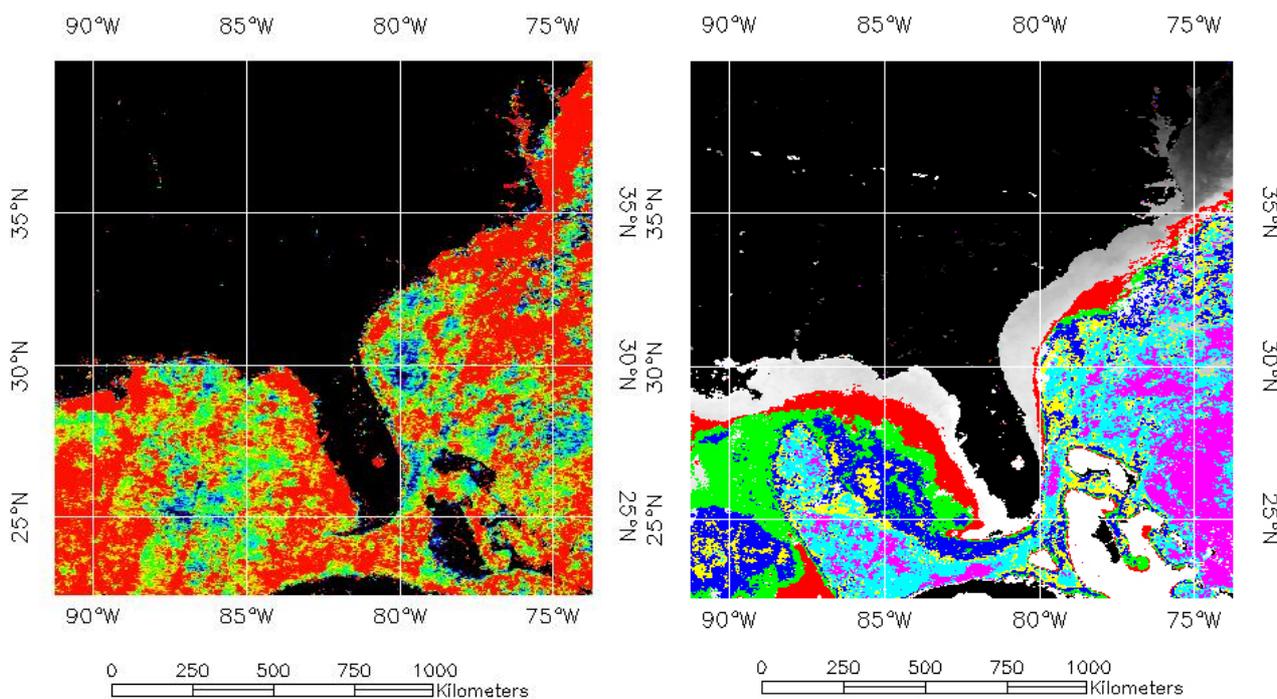


Figure 16: Presentation of the ratio 678/667 (left) and exported regions of interest from Figure 15 (right).

CONCLUSIONS

In conclusion, it can be stated that advantage can be taken of the second absorption band of chlorophyll that is diagnostic for chlorophyll concentrations in the upper part of the euphotic zone. Furthermore, it can be concluded that the ratio technique can be used as an indicator for separating biogeochemical provinces when compared with chlorophyll measurements based on the first absorption band of chlorophyll. The ongoing research incorporates preliminary and qualitative findings for a quantitative approach and for consideration of applications on the global scale.

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