

Use of the first and second chlorophyll absorption bands for marine biogeochemical patch recognition

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Received 23 February 2004, revised 21 June 2005

Water-leaving spectral signatures were used in the spectral regions where chlorophyll has its first and second absorption bands in order to recognize biogeochemical provinces in the pelagic and coastal ocean. The analysis of spectra collected in eutrophic coastal waters identified a very narrow spectral bandwidth in which the highest correlation between chlorophyll and the first derivative is apparent. A ratio technique using the defined envelope showed that a good relationship exists between the ratio of the reflectance R667/R678 and surface chlorophyll concentrations. The global data set for MODIS 3 used in this study data has a 4.89-km pixel resolution that is mapped on a cylindrical equidistant map projection. The data presented are based on an interpretation of the ratios R443/R551 and R678/R667 that use the spectral region of the two absorption bands of chlorophyll, the fluorescence of chlorophyll at 678 nm and the hinge point at 551 nm. The two selected ratios indicate the response of provinces according to the depth location of absorbing pigments as well as the overall response to integrated concentrations of pigments in the euphotic zone. The results show that biogeochemical provinces can be identified by the ratio technique and upwelling regions, current systems and river discharge can be spectrally separated.

[Key words: Remote sensing, biogeochemical provinces, chlorophyll, current systems, image processing, MODIS.]

Introduction

Global information on marine ecosystems has been acquired with ocean-color satellite monitoring systems that are based on reflectance measurements of water leaving radiances in specific spectral regions where photosynthetic pigments absorb. Basically, three statistically significant components can be derived from such measurements, namely total concentrations of particulate material, chlorophyll containing biomass and detrital material¹. 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 phycobiliproteins. Related to these pigments are degradation products such as chlorophyllides, phaeophorbides and phaeophytins. As chlorophyll concentrations are highly related to oceanic primary production, attempts have also been made to derive production estimates from satellite-derived pigment concentrations².

Seasonality of the strength in primary productivity is determined by several parameters and can be recognized in four primary domains of the pelagic ecosystem: polar, westerlies, trade wind and coastal regions. Biogeochemical provinces in those domains

are characterized by their variety in biogeochemical activity, both physical and chemical³. All domains can be further subdivided into secondary biogeochemical provinces and can be identified either by conventional methods or by remote-sensing techniques. Primary forces used for the characterization of 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, biogeochemical domains and provinces can be recognized based on seasonal cycles of plankton development, the optical field, current systems and the associated mixing rate.

In the open ocean (Case I water), color can be converted to total pigment concentrations, whereas shortcomings are experienced 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 with the changing composition of the main contributors to the water-leaving radiance. The contribution of inelastic sources to water-leaving radiance has been subjected to

modeling efforts showing the important role of sunlight-stimulated fluorescence and Raman scattering of water⁴. In Case II waters, 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 problem in coastal waters where high pigment concentrations are present due to coastal dynamics and transport of nutrients through river effluent and discharge from waste water treatment facilities. Moreover, the inherent variations of one class of material to another limits the use of regionally developed algorithms for retrieving mass concentrations from optical data⁵.

In this study, water-leaving spectral signatures will be applied with focus on the use of remote sensing for chlorophyll patchiness and the use of the spectral regions where chlorophyll has its first and second absorption bands with the objectives to recognize biogeochemical provinces in the pelagic and coastal ocean.

Material and Methods

The basic measurement from which photosynthetic pigment concentrations can be derived is the remote sensing reflectance $R_{rs}(\lambda)$, which is commonly expressed as the ratio of upwelling radiance, $L_u(\lambda)$ to downwelling irradiance $E_d(\lambda)$. The water leaving radiance $L_w(\lambda)$, is the corrected property for the transmission through the air-sea interface and is the component, after atmospheric corrections have been applied, that is sensed by satellites for pigment retrieval. The inherent optical properties backscattering and absorption coefficients of the water column are related to $R_{rs}(\lambda)$ through:

$$R_{rs}(\lambda) = \frac{L_u(\lambda)}{E_d(\lambda)} \approx \text{const} \frac{b_b(\lambda)}{a(\lambda) + b(\lambda)}$$

where $b_b(\lambda)$ is the backscattering coefficient, $a(\lambda)$ the absorption coefficient and a constant⁶. $a(\lambda)$ is comprised of the absorption coefficient for pure seawater, particulates and dissolved materials and it was demonstrated that in the open ocean with Case 1 waters, the spectral variations of $R_{rs}(\lambda)$ are caused primarily by changes of the absorption coefficient of particulate matter.

Since the spectral contribution of chromophoric dissolved organic matter decreases monotonically

with increasing wavelength, CDOM should influence reflectance values only at shorter wavelengths. As a consequence, Case I waters are spectrally regulated mainly by absorption of phytoplankton. Another factor to be considered is that z_{90} the downwelling flux is reduced to 10% of the incident radiation at the surface, and that only 10% of the contribution to $R_{rs}(\lambda)$ comes from below this depth. Excluding the specular reflectance, for remote sensing purposes, z_{90} is defined as the depth above which 90% of the diffuse reflected irradiance originates. Consequently, $R_{rs}(\lambda)$ at wavelengths close to the first absorption band of chlorophyll will respond to a deeper water column than at wavelengths close to the second chlorophyll absorption band in the red.

It was estimated that the depth of sunlight penetration in the sea at z_{90} for clear water is about 55 m near 473 nm while coastal water⁶ shows z_{90} about 1.5 m at 600 nm. In fact, for all water types, the variation of z_{90} in the spectral region of the second absorption band of chlorophyll at around 667 nm, ranges from about 1 m in coastal waters to about 2 m in the clearest water.

With the common algorithms which exploit the absorption properties of phytoplankton at 443 nm relative to 550 nm, the signal is not vertically resolved even though it is heavily weighted towards the surface. High correlation has been found between chlorophyll concentration and the water-leaving radiance in the red part of the spectrum where sun-induced fluorescence of chlorophyll is present⁷⁻¹⁰. Solar-induced chlorophyll fluorescence was used to study the ocean-color spectral variability¹¹ and the peak near 700 nm on radiance spectra and provides a good relationship with chlorophyll concentrations¹².

The identification of the most suitable wavelength for chlorophyll detection using high resolution spectra presented in this study is based on data collected during several cruises undertaken at a test site where high eutrophication occurs in an estuarine zone¹³. Examples from a repeat cruise to regions with varying chlorophyll concentrations of zero-order spectra with their first corresponding derivatives are given in Figs.1-3.

The interpretation of the spectra for coastal eutrophic water shows the major absorption band of chlorophylls at around 420 nm and accessory pigments at around 470 nm and 530 nm to 570 nm can be recognized. The spectral region between 400 nm and 500 nm is characterized by strong absorptions of CDOM, carotenoids and the various chlorophylls.

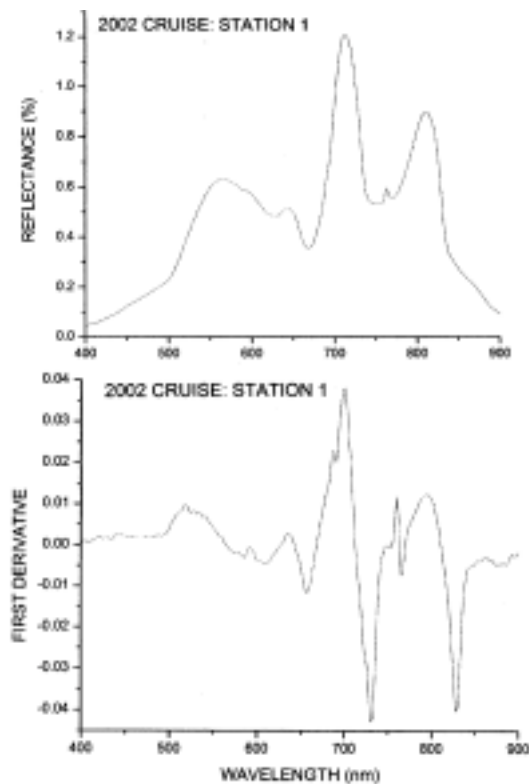


Fig.1—Spectral reflectance (upper graph) and first derivative (lower graph) of coastal water with chlorophyll concentration of 2.4 mg m^{-3} .

Those constituents are responsible for the low sensitivity of reflectance at shorter wavelengths to phytoplankton pigments. Consequently, this wavelength region is not ideal for identifying chlorophyll or related pigments at high chlorophyll concentrations. Minimum absorption of all phytoplankton pigments was observed in the range of 550 nm to 570 nm and results in a peak of reflectance mainly due to scattering by organic and inorganic particles including phytoplankton cells.

Phycobilins (phycocyanin, phycoerytherine and allophycocyanin) show diagnostic absorption bands between 550 nm and 650 nm. Phycocyanin was observed to have pronounced absorption¹⁴ at around 620 nm. The distinctive second chlorophyll absorption band is located at 670 nm but its absorption intensity at concentrations $> 20 \text{ mg m}^{-3}$ was partly offset by scattering by phytoplankton cells. Sun-induced fluorescence is diagnostic at 685 nm but can be significantly altered by reabsorption at chlorophyll concentrations $> 15\text{--}20 \text{ mg m}^{-3}$. Chlorophyll still has a significant absorption at wavelengths 690 nm to 715 nm although it is partially offset by scattering that may result in a shift of the peak position towards longer wavelengths.

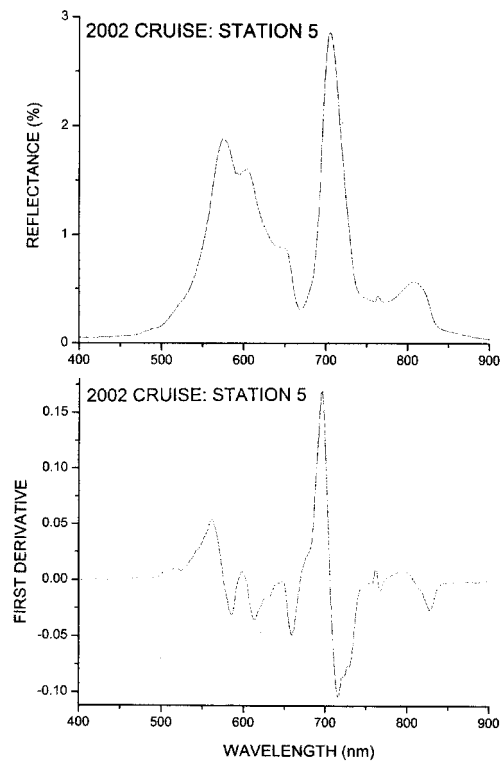


Fig.2—Spectral reflectance (upper graph) and first derivative (lower graph) of coastal water with chlorophyll concentration of 106 mg m^{-3} .

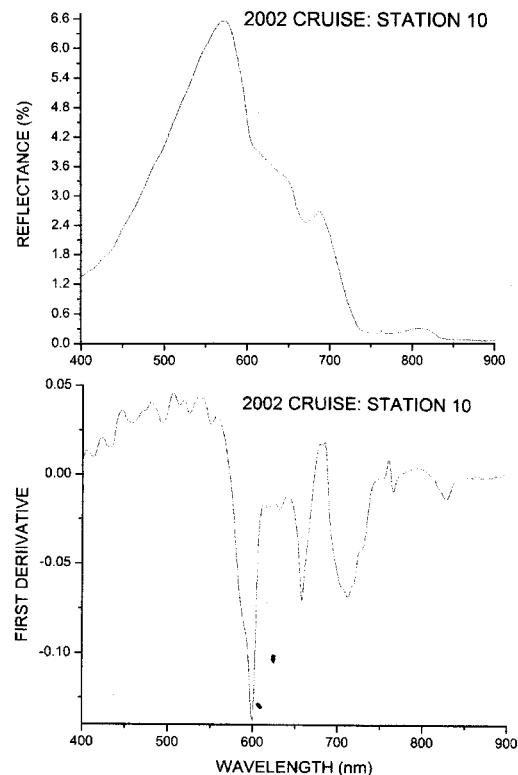


Fig.3—Spectral reflectance (upper graph) and first derivative (lower graph) of coastal water with chlorophyll concentration of 4.5 mg m^{-3} .

The analysis of spectra collected in coastal waters identified a very narrow spectral bandwidth in which the highest correlation between chlorophyll and the first derivative is apparent. A ratio technique using the defined envelope showed that a good relationship exists between the ratio of the reflectance R680/R670 and chlorophyll concentrations. These findings have to be viewed against the results that show that suspended matter seemed to have little or no effect on the position of the red part of the chlorophyll absorption band¹⁵.

With respect to the use of data from the Moderate Resolution Spectroradiometer (MODIS) in this study, only results from the first derivative will be considered to interpret the spectra presented in Figs. 1-3. The first-order spectra showed that at high concentrations of chlorophyll, the spectral region where chlorophyll absorbs strongly in the blue region has less significance than the spectral region of the second absorption band. This is in agreement with numerical differentiation of spectral data that showed that the effects of water can be reduced by a first order derivative, and effects of suspended sediment can be removed by a second-order transformation¹⁶.

MODIS is a passive imaging spectroradiometer which views the Earth and space by means of a continuously rotating scan mirror. MODIS collects data through four focal plane assemblies containing 36 bands spread over the spectral region 412 nm to 14,235 nm. The instrument has a ground nadir resolution of 1000 m and orbits at 705 km. The optical arrangement and scan mirror coverage of $\pm 55^\circ$ from nadir result in a cross track swath of 2330 km and an along track swath of 10 km at nadir. MODIS channels selected for this study are shown in Table 1. The global data set for MODIS 3 used in this study data has a 4.89-km pixel resolution that is mapped on a cylindrical equidistant map projection and is based on the yearly average of the areas investigated.

A ratio technique was applied for wavelength regions where chlorophyll has its first and second absorption bands at 443 nm and 667 nm. The ratio 443/551 exemplifies the basic approach for chlorophyll retrieval through satellite remote sensing while the ratio 678/667 is based on the absorption, reflectance and fluorescence properties of chlorophyll. The two chlorophyll absorption bands, on which the ratio technique is based, are spectrally separated by 225 nm. Therefore, 2D scatter plots are expected to be highly uncorrelated and clusters can be analyzed for regions of interest. For analysis of

MODIS data, the software Research Systems' ENVI 3.5 was used. 2D scatter plots were established for identifying clustering of the data through which regions of interest were identified for a qualitative identification of water masses. This procedure allows the comparison of the two ratios simultaneously and permits a 2-band classification of the data.

Taking into account the spectral response of MODIS bands covering 678 nm and 667 nm respectively, it can be demonstrated that both channels are appropriate in applying the ratio R678/R667 as an estimator for chlorophyll concentrations in surface waters. An example of one data set collected during a cruise in near-coastal waters and comparing the chlorophyll concentration with this ratio corresponding to the MODIS channels is shown in Fig. 4.

Results and Discussion

Global observations

The surface distribution of the ratio corresponds to the wind-driven circulation and associated

Table 1 — Band characteristics of the moderate resolution spectroradiometer (MODIS) as applied in the present study

Band	Center Wavelength (nm)	Bandwidth (nm)
8	412	15
9	443	10
10	488	10
11	531	10
12	551	10
13	667	10
14	678	10

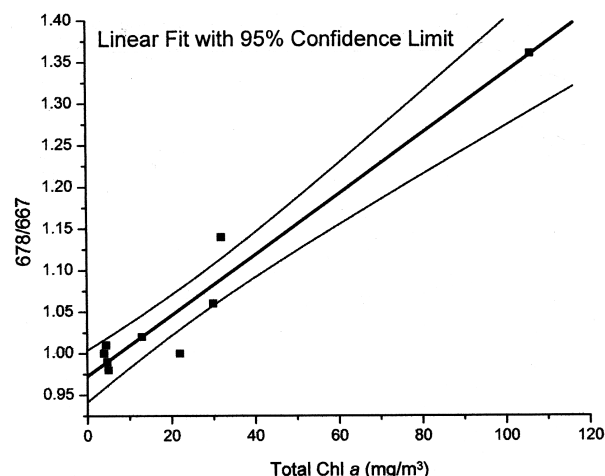


Fig. 4—Relationship between the ratio of MODIS channels 13 and 14 and chlorophyll concentrations.

processes that are responsible for enhancing primary productivity in the oceans. The circulation pattern of the large gyres in the Atlantic Ocean, the Pacific and the Indian Ocean are well characterized by the low ratios as displayed in dark blue in Fig.5. The large vortices in the oceans with their pole-ward circulation are characterized by their narrow and fast flow along the western side of the oceans due to the continental barriers. The western boundary currents such as the Gulf Stream, the Brazil/ Falkland Current in the South Atlantic, the Kuroshio Current and the Somali Current are recognizable with the ratio technique.

Equatorial currents are well characterized by the ratio technique especially in the equatorial Pacific as displayed in yellow/green. Upwelling regimes apparent as red, along the west South American coast, along the west coast of the United States, North West coast of Africa, the Benguela upwelling and the Somali coast are well pronounced. The northern latitudes have high ratios (red) that are in agreement with the high productivity and standing stock in those regions. Part of the Antarctic Circumpolar Current is covered in this analysis and shows high ratio values whereas the Caribbean and the Mediterranean Sea are characterized by low ratio values and are shown in blue and magenta.

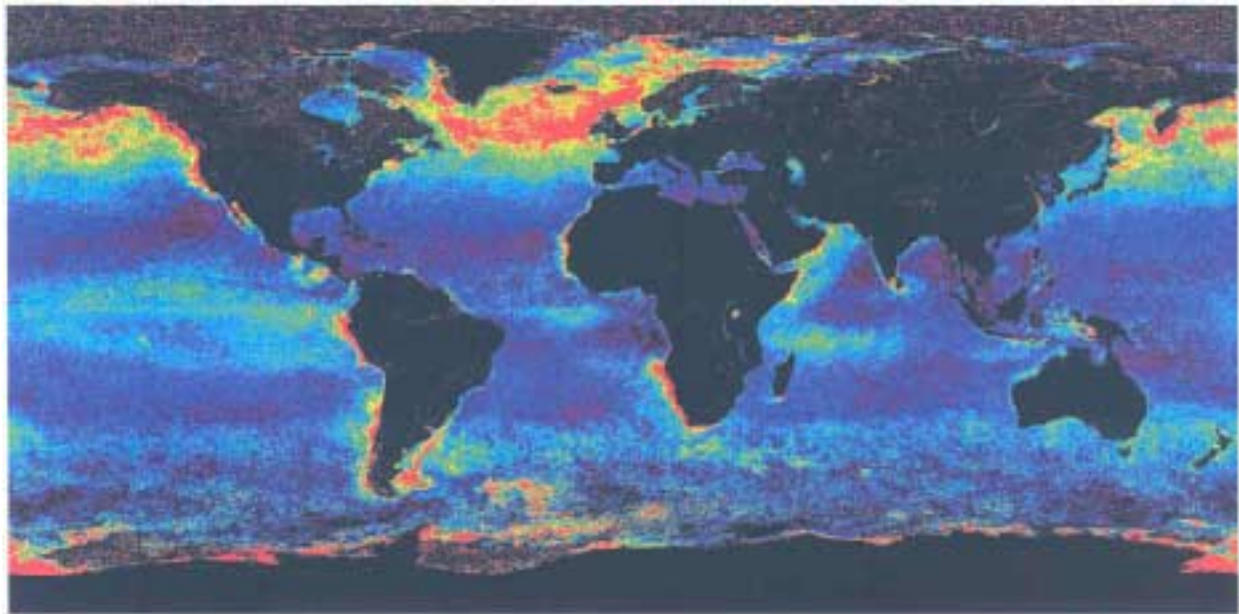


Fig.5—Global presentation of the ratio for the wavelengths 678 nm and 667 nm. Ratios are displayed from low ratios in dark blue to red as the highest value using rainbow color annotation.

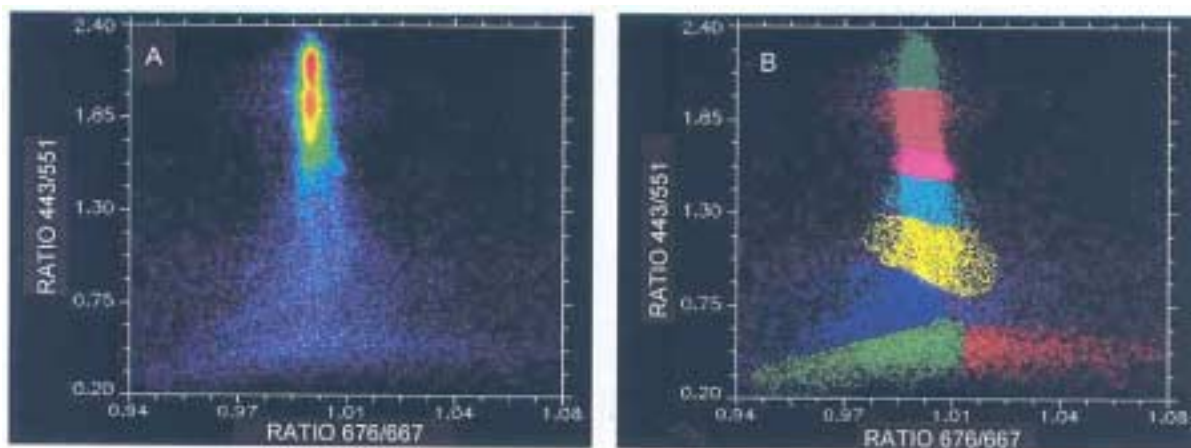


Fig.6—Scatter plots in the discharge region of the Amazon: A) All data in the scatter plot. B) Clusters used to identify region of high sediment load due to river discharge in the near-coastal region.

River Discharge

Amazon

The Amazon has an annual discharge of approximately $175,000 \text{ m}^3 \text{ sec}^{-1}$, which is about 4.6 times that of the Zaire River and about 11 times that of the Mississippi River, and carries high loads of suspended sediments into the coastal discharge region. The scatter diagrams shown in Fig.6 identify one cluster that is related to the river discharge in the near-coastal region. Basically, it shows that the ratio 678/667 stays constant while the data based on the

ratio 443/555 varies. The corresponding region of interest (ROI) was established and resulted in the location of the water near the major effluent, as shown in Fig.7.

Comparing the patterns recognized in the chlorophyll algorithm in Fig. 8, it is evident that the use of the ratio technique and the separation of clusters aids in separating the regime that carries mainly the sediment load from the Amazon effluent. The regions of interest further divide the provinces into sub-categories as shown in Fig. 7.

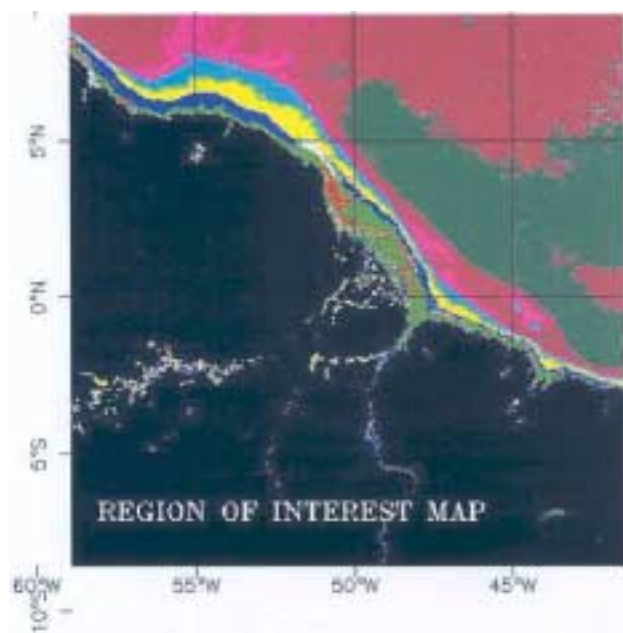


Fig.7—Identification of high suspended sediment load as based on the interpretation of the scatter diagram shown in Fig. 6.

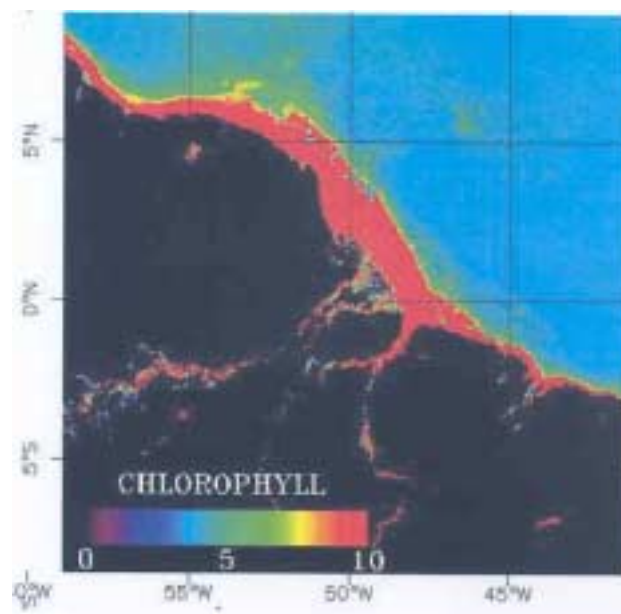


Fig.8—Chlorophyll patchiness in the Amazon regime.

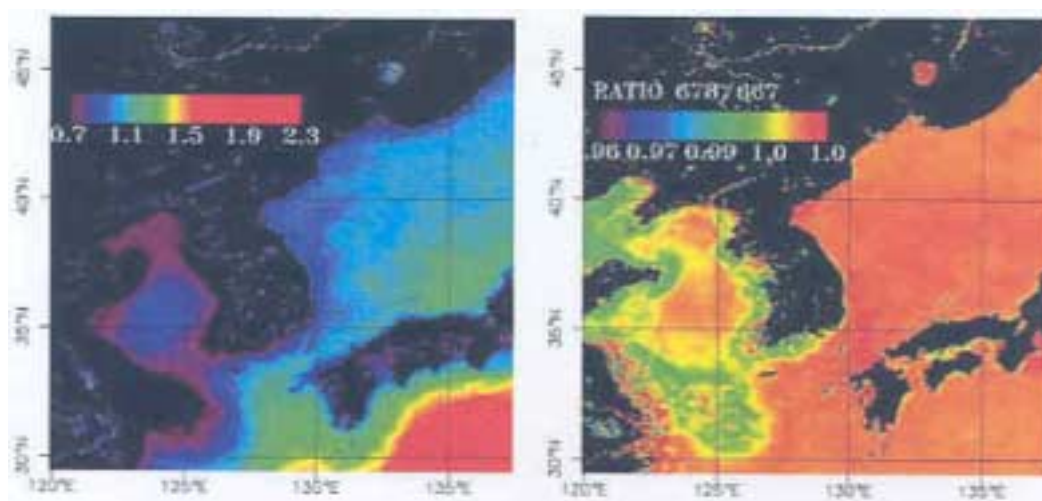


Fig.9—Water-leaving radiance ratios 443/551 (left) and 678/667 (right).

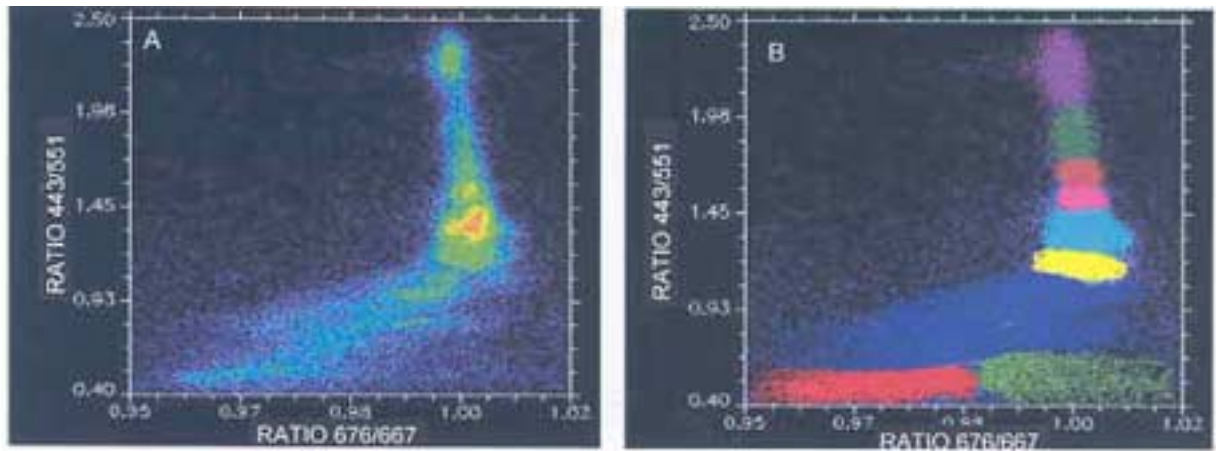


Fig.10—A) Scatter diagram of the Changjiang region. B) Regions of interest in which the clusters for annotation in Fig. 11 have been identified.

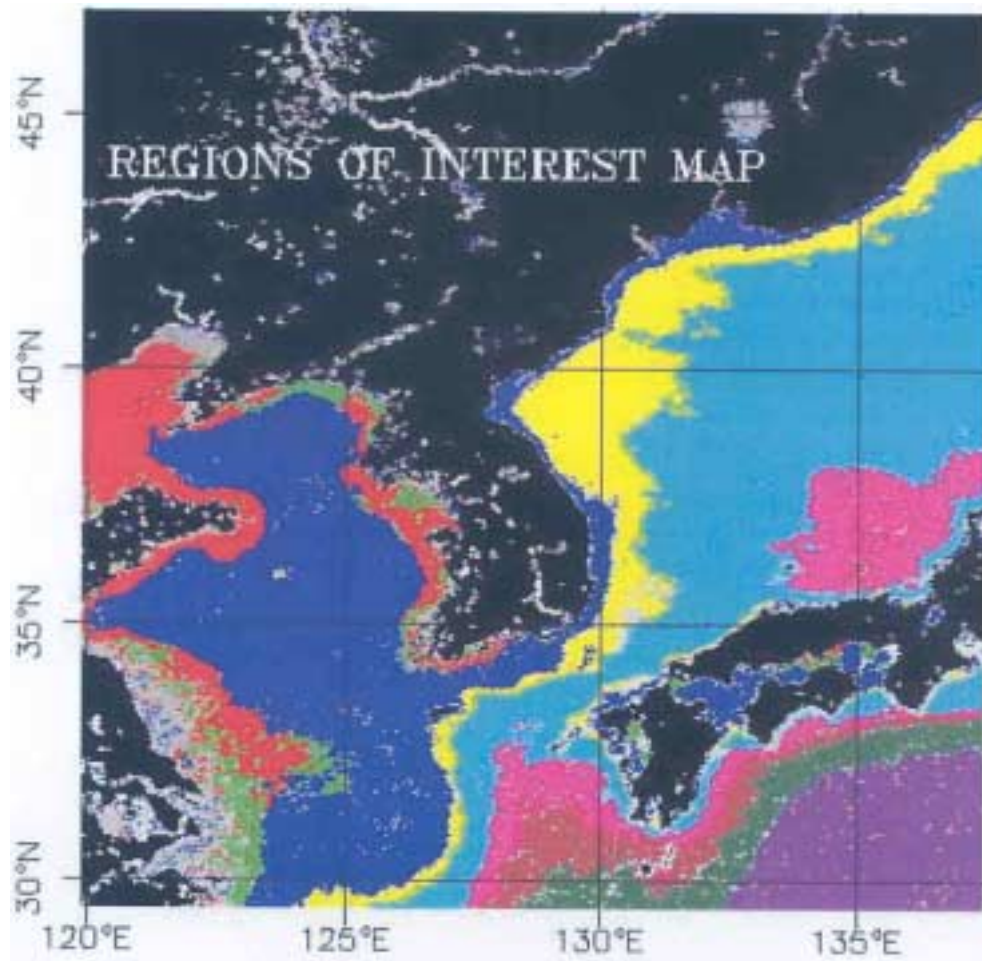


Fig.11—Region of interest map for the region shown in Fig. 9 is based on the scatter diagram and cluster identification given in Fig. 10.

The Huanghai Sea and the Changjiang river discharge

The Huanghai Sea was selected as another test site to identify patterns in a region with high river discharge (Figs.9-11). The oceanographic situation in the Huanghai Sea is influenced by conditions in the East China Sea (ECS) and the Bohai Sea as well as by the transport of warm water from the Kuroshio Current coming from the South. The current patterns in the ECS may be approximately divided into two parts by drawing a line from the northernmost point of Taiwan to the Chejudo Island. On the eastern side of this line is one main arm from the Kuroshio that enters the ECS through the passage northeast of Taiwan. Due to the high river discharge by the Changjiang, the Huanghai Sea is of particular interest and was a subject of earlier studies on clustering of multi-channel satellite data^{17,18}. The maximum runoff of the Changjiang over 30 years is about $92,600 \text{ m}^3 \text{ sec}^{-1}$ with an annual discharge of $9.25 \times 10^{11} \text{ m}^3$. About 50% of the sediments carried by the Changjiang are deposited at the mouth. The main patterns recognized are related to the hydrography, bathymetry and river discharge. Figure 9 represents the water leaving radiance for 667 nm and at 678 nm respectively. The comparison between the two wavelengths of water leaving radiance shows the effect of absorption by chlorophyll at 667 nm and the natural fluorescence of phytoplankton at 678 nm. The outflowing water from the Changjiang dominates the coastal region but another significant source is erosion of the northern Jiangsu coastline.

Regions of interest (ROI) were established for the images shown in Fig.9 with the corresponding scatter diagrams shown in Fig.10. The ratio image R_{678}/R_{667} and the display of the ROI are displayed in Fig. 11. It is noticeable that the ratio image and the image with the regions of interest indicate the various provinces. The coastal water, displayed in yellow, identifies the boundary between the water masses from the main arm derived from the Kuroshio that enters the ECS through the passage northeast of Taiwan.

The data presented are based on a qualitative interpretation of the ratios R_{443}/R_{551} and R_{667}/R_{678} that use the spectral region of the two absorption bands of chlorophyll. The MODIS data used in this study are based on climatology set of one year. Consequently, many oceanic features are smoothed. Nevertheless, the selected samples in applying the ratio technique and identification of the regions of interest demonstrate that a new tool can be applied for recognizing and

separating biogeochemical provinces that are related to biophysical processes.

With respect to the interpretation of the recognized patterns, it has to be realized that chlorophyll concentrations derived from water-leaving radiance by satellites represent not only a composite of various pigments, but is also an optically weighted concentration over a portion of the upper water column from which the light is being reflected. The effective penetration depth¹⁹, z_{90} , the depth from which 90% of the upwelling radiance originates, ranges for Case I water at 443 nm from about 40 m at chlorophyll concentration of around 0.04 mg m^{-3} and decreases to $< 1 \text{ m}$ at concentration of around 40 mg m^{-3} . In addition, calculations showed that a perfect reflector placed at various depths responds according to wavelength²⁰. For instance, placed at a depth of 2 m, 86% of the incident energy for the spectral region would return, at 500-600 nm, 55%, for the 600-700 nm spectral region, 11%, for the 700-800 nm spectral region, and 0.2% for the 800-1100 nm spectral region, respectively. This serves as an argument that the application of the two selected ratios indicates the response of provinces according to the depth location of absorbing pigments. The data presented indicate that provinces can be divided by the introduced ratio technique and regions of interest and that water masses in coastal areas with river discharge can be spectrally separated.

Acknowledgement

The satellite data used in this study were acquired as part of NASA's Earth Science Enterprise. The algorithms for sea surface temperature and chlorophyll were developed by the MODIS Science Teams. The data were processed by the MODIS Adaptive Processing System (MODAPS) and Goddard Distributed Active Archive Center (DAAC), and are archived and distributed by the Goddard DAAC. The work on spectra was partly sponsored through a grant from NOAA, Cooperative Agreement, No. NA17AE 1625.

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