

OPTICAL PROPERTIES OF MARINE WATERS AND THE DEVELOPMENT OF BIO-OPTICAL ALGORITHMS

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Introduction

Photosynthesis by phytoplankton in the ocean requires light, water, carbon dioxide and nutrients in the form of nitrates and nitrite. The process of photosynthesis by phytoplankton known as primary production is the major contributor to the global carbon flux in the ocean averaging about 5×10 grams of carbon per annum (Platt and Sathyendranath 1988).

Without any prior knowledge but knowing that light plays a crucial role in the photosynthetic reaction, we can conclude intuitively that studies on the optical properties of the ocean may provide important clues to gaining further insights on primary production and phytoplankton. The need to measure primary production per unit area of the sea surface must be seen in the context of two major long term goals of oceanographic science namely:

- 1) To understand on a global scale, the processes (biological, physical and chemical) that control the spatial and time varying carbon fluxes and associated biogenic elements in the ocean.
- 2) To develop predictive capability of oceanic biogeochemical processes to climate change.

In these lecture notes, we shall begin by introducing the primary optical variables used in the measurement of the optical properties of marine waters. How can in-situ measurements be used in the optical recognition of coastal and open ocean waters. We then look at bio-optical models and algorithms that link optical properties to the concentration of chlorophyll - a biological variable. Finally we bridge the gap between optical properties and the remote sensing of chlorophyll and associated constituents in seawater.

2. Optical Properties of the Ocean

Solar radiation falling on the ocean surface experiences reflection and transmission at the surface. The transmitted component is selectively absorbed and scattered by phytoplankton and their detrital products, and also by other non-biogenous particles. A portion of the transmitted photon flux is converted into chemical energy via photosynthesis in phytoplankton, and the remainder into heat energy by various absorption processes in molecular water. Apart from these effects, the spectral and angular properties of the light field changes with depth, and the intensity of the downwelling photon flux shows an approximate exponential decrease with increasing depth in the ocean. The forward and backscatter events of the downward moving flux results in the establishment of an upward moving flux whose spectral signature contains important information on the constituents of the water medium. The upward flux, otherwise known as the water leaving radiance in remote sensing terminology wends its way to the water-air interface after scattering and absorption events similar to that experienced by the downward flux. We shall discuss the upward flux in the section on bio-optical algorithms of these notes.

In discussing the optical properties of light in the ocean, it is convenient to distinguish between INHERENT and APPARENT optical properties.

Inherent Optical properties (IOP): These properties belong to substances that comprise the aquatic medium only (Preisendorfer 1961). They are spectral in nature, vary with depth, and are independent of the geometry of the light field, or to any external perturbations such as waves, winds, clouds or sun altitude that are nearly always present in the marine environment. The inherent properties of interest are "a", the absorption coefficient, "b", the scattering coefficient, and the volume scattering function.

Apparent Optical properties (AOP): In complete contrast to the IOP's, the apparent optical properties are as Kirk(1983) puts it "properties of the light field that are established within the water body as a result of the incident solar radiation on the ocean surface". The AOP's have spectral characteristics, and are affected by a changing sky state, waves, winds and sun altitude. They vary with depth in the ocean, with latitude and longitude, and time of day. The AOP's of interest are the Radiance L, the upwelling and downwelling irradiances E_u and E_d , the scalar irradiance E_o , the vertical attenuation coefficients K_u , K_d and K_o , and the irradiance reflectance R.

We shall confine our discussion to those properties (AOP and IOP) that are measured experimentally, and from which most of our understanding of ocean waters is known. It is understood that the properties are wavelength dependent, and in most cases shows a depth dependence.

Downward irradiance E_d ($W/m^2/nm$) at a point on the upper hemisphere is the radiant flux per unit area. This is a weighted integral of the radiance L (θ, ϕ) and is expressed as:

$$E_d = \int_{2\pi} L(\theta, \phi) \cos \theta . d\omega \quad (1)$$

Upward Irradiance E_u ($W/m^2/nm$) has a similar definition to E_d , but is referenced to flux over the lower hemisphere, and expressed as:

$$E_u = \int_{-2\pi} L(\theta, \phi) \cos \theta \cdot d\omega \quad (2)$$

Irradiance Reflectance R is the ratio of upward to downward irradiance. It has important implications in remote satellite sensing of ocean colour

$$R = E_u / E_d \quad (3)$$

Radiance L (θ, ϕ) in $W/m^2/nm$) which appears above is the radiant flux in a given direction per unit solid angle per unit projected area. As in the case of irradiance, we can define upward radiance L_u or downward radiance L_d . the former is more frequently measured due to its importance in remote sensing studies.

The vertical attenuation coefficients K_d and K_u (m^{-1}) for downward and upward irradiance respectively are derived properties and are defined below on the assumption that light in the sea obeys an exponential law:

$$K_d = -d(\ln E_d)/dz \quad K_u = -d(\ln E_u)/dz$$

The AOP's defined above (particularly K_d , E_d , E_u , L_u and R) have been measured intensively by a few key workers in this area, as they are easier to measure than the IOP's defined below:

Absorption coefficient 'a' is the absorptance of an infinitesimally thin layer of the medium normal to the beam divided by the thickness of the layer.

Scattering coefficient 'b' is the scatterance of an infinitesimally thin layer of the medium normal to the beam, divided by the thickness of the layer. It can also be defined as the integral over all directions of the volume scattering function. When the limits of the integral are taken from (π) to $(\pi/2)$, the result is the backscattering coefficient b_b .

Attenuation coefficient 'c' is simply $c = a + b$

Relationships between the AOP's and IOP's

There are several relations that link the AOP to IOP, and one of the most useful and simple was first obtained by Prieur and Morel (1975):

$$R = 0.33 (b_b / a) \quad (4)$$

The relation (4) assumes there is no fluorescence emission from the ocean surface (not true in practice for e.g. during planktonic blooms), and is valid for a homogeneous ocean and provided the reflectance $R \ll 1$ (e.g. ~ 0.3)

Kirk (1994) has used Monte Carlo methods to relate K_d , the diffuse attenuation coefficient at the 10% light level to the absorption and scattering coefficients. It is claimed that the relation is valid for extremely turbid waters with $b/a \sim 200$, and for high reflectance $R \sim 0.4$ by:

$$K_d (10\%) = (a^2 + 0.245 ab)^{1/2} \quad (5)$$

Gordon (1989) has shown that a good approximation of the absorption coefficient 'a' close to the sea surface can be obtained by measuring the attenuation K_d , and the average cosine:

$$a = \mu \cdot K_d \quad (6)$$

Relation (6) is a fair approximation if $R \ll 1$, $K_d = K_u$, and $b_b \ll a$. The average cosine μ serves as a correction term for the geometry of the incident light field. These link relations are useful in estimating the harder-to-measure IOP's by the easier-to-measure AOP's. However recent advances by Zaneveld and co-workers (1984) use the reflection tube concept to measure concurrent absorption and scattering coefficients in-situ.

Importance of the absorption coefficient 'a' & the backscattering coefficient b_b

In equ. 4, the reflectance R is an important variable in the development of bio-optical algorithms for satellite remote sensing of ocean colour. R is related to a and b_b , both coefficients being variables that are experimentally difficult to measure in the ocean. However, laboratory studies of a and b_b has yielded useful insight into the optical properties of phytoplankton.

Absorption

The insensitivity of 'a' to environmental perturbations gives it the advantage of being a stable parameter in classifying ocean waters, but this apart, there are further indicators of its importance.

- 1) Lab studies of monospecific phytoplankton cultures (Sathyendranath, Lazarra & Prieur 1987) show that the specific absorption $a^* = a/C$ at 440 nm varies from 0.018 to 0.047 m^{-1} similar to estimated in-situ variations from 0.01 to 0.077 m^{-1} . This variability is influenced by pigment composition and the size distribution of algal cells.
- 2) Different species of phytoplankton can be most clearly identified through the shape of their absorption spectral signatures in the wavelength region 400 nm to 700 nm. Fig.1 shows an example of absorption spectra taken from samples collected in the Western North Atlantic showing variability about a mean basic shape with peaks at 440 nm and 675 nm due to chlorophyll. Note that there is an underlying absorption due to detrital matter which is subtractable from the phytoplankton contribution.

Backscattering

The backscattering coefficient is an IOP, as is the absorption 'a'. It has spectral forms which in general complement absorption peaks. In oligotrophic waters where the dominant contribution is from non-algal cells, the backscatter coefficient is generally 2.2 % (small particles) decreasing to 0.2 % in eutrophic waters with large algal cells (Ahn, Bricaud and Morel 1992). The specific backscatter coefficient also shows high variability with cell size and pigmentation of species, but the magnitude of this variability is generally very low, smaller than the specific backscatter of pure water, and much lower than the specific absorption.

Examining equ. 4 and from lab data we can surmise that the variability of the specific absorption a^* will be the main contributor to variations in R. Thus if R can be measured with sufficient radiometric resolution (~ 2nm) and accuracy, we have a means to identify species changes by in-situ measurements of R spectra. During a bloom condition where a single species of phytoplankton dominates optical properties, high resolution R measurements may be invaluable in interpreting concurrent satellite ocean colour data. In non-bloom conditions, the presence of a mix of phytoplankton types will wash out spectral structure making it difficult to identify plankton types. In sediment dominated coastal waters, the remote sensing interpretation will be more difficult. A new approach is required in this case.

Classification of ocean waters

We shall follow the simple classification of Prieur and Sathyendranath (1981) by saying that ocean waters are either CASE 1 or CASE 2. Table 1 summarises the classification.

Case 1 waters have optical properties that are largely determined by the presence of phytoplankton, their detritus (composed of unpigmented parts of algal cells, and breakdown products such as the phaeopigments), and dissolved organic matter (DOM) which is composed of a mixture of humic and fulvic acids.

Case 2 waters may or may not contain the components associated with Case 1 waters, and in addition may have organic matter (DOM), resuspended sediments, terrigenous yellow substances from river run-off, and other non-chlorophyllous particles of clay and sand. Coastal waters are an example of Case 2 waters.

In the remote sensing context, chlorophyll retrieval algorithms for coastal waters are more complex, as the chlorophyll signal from phytoplankton has to be separated from signals due to suspended sediments and other particles. Further complications result if different components have similar spectral signatures: an example of recent measurements by Roessler et al (1989) show that the spectral signature of detrital matter and DOM are very similar (see figs.1 & 2).

Bio-optical Models

Most of the bio-optical models to date, have sought to relate optical variables to C , the chlorophyll a concentration and the phaeopigments. The models are essentially statistical relations obtained by regression analysis on a large dataset of measurements taken in Case 1 waters. Models for case 2 waters are lacking due to the increased complexity of these waters.

Prieur & Sathyendranath (1981) have modelled the absorption coefficient a in terms of C using data collected on cruises to the Central E. Pacific, Sargasso Sea, Gulf of Mexico, the West Coast of Africa and the Indian Antarctic. The data belongs to the period 1970 to 1977. They arrived at the non-linear relation:

$$a(\lambda) = [a_w(\lambda) + A(\lambda).C^{0.65}] \quad (9)$$

The values of $A(\lambda)$ are tabulated at different wavelengths and the relation is valid for $C < 10 \text{ mg.m}^{-3}$. The index 0.65 of C has been attributed to the influence of non linear changes of living algae C to detrital or microbial materials.

Morel(1988) carried out a statistical analysis of data over the period 1969 to 1986 from several French and American cruises in different parts of the world's ocean where the phytoplankton content varied over a large range (3 to 300 mg.m^{-3}) and found that $K_d(\lambda)$ could be expressed by a power law of the form:

$$K_d(\lambda) = K_w(\lambda) + x.C^y \quad (10)$$

Here x and y are tabulated at different wavelengths with the index y slowly varying from 0.668 at 400 nm with peaks at 0.707 at 440 nm and 0.697 at 675 nm.

The scattering coefficient b has also been modelled in terms of C by Gordon and Morel (1983) using in-situ measurements of b at 550 nm during French cruises in the years 1970 to 1979. the regression to this dataset followed :

$$b(\lambda) = b_w + (550/\lambda).0.3 C^{0.62} \quad (11)$$

There have been no in-situ measurements of the backscatter coefficient as a function of C , due to a lack of instrumentation in this area of measurement. Recently, promising work by Maffione et al (1991) has seen the development of a backscatter sensor which measures the optical signal at a weighted angular averaged value at 150 o and a wavelength of 565 nm.

It is worth observing that the bio-optical models are:

- * Valid for case 1 waters only i.e chlorophyll driven
- * Do not account for changes in pigment composition/cell size
- * Do not show an explicit depth dependence being biased by surface data.

Satellite versus in-situ estimates of Primary production (PP)

When it comes to the question of comparing in-situ estimates of PP with satellite sensed estimates, show large discrepancies and errors can occur. Some reasons are:

** In many parts of the ocean, biomass is distributed in the shape of non-uniform profiles having a deep chlorophyll maximum (DCM) frequently located deeper than one attenuation length ($1/K_d$), and changing in structure and season. The satellite senses a weighted estimate of the chlorophyll concentration limited to at most one attenuation length. This means that a large part of the biomass can pass undetected by the satellite sensor. Assuming a generalised Gaussian distribution to represent biomass, Platt & Sathyendranath (1988) show errors can be considerable when the DCM lies near the surface, and modest if the DCM is at the base of photic zone. The error can be corrected if the shape of the biomass profile is known, which is very often nor freely available.

** Satellite sensor averages over depth and area. Ship estimates of PP are measurements at discrete points in the ocean.

** Bio-optical models and productivity modelling are chlorophyll dominated. Little or no attention has been paid to the role of accessory pigments e.g. chlorophyll b, and the carotenoids in primary productivity. At deeper depths in the water column, the blue and red wavelengths (435 nm and 675 nm) are quickly attenuated, and chlorophyll is no longer an effective light harvesting pigment (Smith et al 1989). Phytoplankton rely on accessory pigments to absorb blue green light at deeper depths.

Bio-optical Retrieval Algorithms

Satellite remote sensing of the spectral changes in the water leaving radiance L_w is the proper tool for the rapid global space time estimation of chlorophyll a. Other rapid platform methods attempted on a smaller scale has been the continuous flow through fluorometry which offers a picture of the chlorophyll fluorescence field along the ship's track.

It has been customary since Clarke et al (1970) to construct algorithms based on radiance or reflectance ratios using two different wavelengths e.g. 440 nm and 550 nm. This blue-green approach is intuitively satisfying as it is based on a previous knowledge of the shape of the phytoplankton absorption spectrum i.e. chlorophyll and its degradation products absorb maximally at 440 nm and minimally at 550 nm. Ratio algorithms have the advantage of not depending upon absolute radiances to compute chlorophyll. They are inherently sensitive to relative changes in chlorophyll compared to other components in the ocean.

$$\frac{(R_{\lambda_1})}{(R_{\lambda_2})} = \frac{L_w(\lambda_1).Q(\lambda_1).Ed(\lambda_2)}{L_w(\lambda_2).Q(\lambda_2).Ed(\lambda_1)}$$

There is a slight variability of the Q and Ed ratios which can be safely neglected (Sathyendranath 1986). Therefore we have the approximate but useful result that the ratio of water leaving radiance is proportional to the ratio of the reflectances.

The most widely used Case 1 chlorophyll retrieval algorithms takes the form:

$$C = A. [R_{440} / R_{550}]^{-B} \quad (16)$$

Despite the approximations, the algorithm works well for true Case 1 waters. Gordon and Morel (1983) estimate that the pigment concentration C can be retrieved to within a factor of 2 (+ 40%) over the full range $0.02 < C < 20$ mg.m⁻³. Morel (1980) used linear

regression on his data, and found $A = 1.62$, $B = -1.40$, and a correlation coefficient of 0.76. When Case 2 points in the dataset are excluded, $A = 1.92$, $B = -1.80$, with a correlation coefficient of 0.97.

The algorithm described in equation (16) fails to produce correct estimates of C in the following situations:

** In eutrophic waters with very high pigment values $C > 20 \text{ mg/m}^3$.

** In Case 2 coastal waters having high concentrations of CDOM (coloured dissolved organic matter), and suspended sediments. Light scatter from sediments uncorrelated with chlorophyll corrupts ratio algorithms.

** In blooms of blue-green algae such as *Synechococcus* where phycoerythrin has absorption peaks at 551 nm and 545 nm.

For Case 2 waters, results of Sathyendranath et al (1982) indicate that the effect of suspended sediments is to produce a background offset to the water leaving radiance with changes of phytoplankton and yellow substances introducing an alteration in the spectral forms. It appears that whatever chlorophyll is present in yellow substance dominated Case 2 waters may be retrieved by using an additional satellite band at 400 nm in a correction procedure.

Summary

In these notes, some of the basic concepts in ocean optics have been introduced. A study of the optical properties gives us an insight on the role played by phytoplankton, detritus, dissolved organic matter (DOM), and suspended sediments in controlling these properties. These studies have been applied in understanding the marine signal reaching a satellite sensor.

We realise from the literature that a major objective of marine optics is to accurately estimate primary production in all water types. Coupled to this objective is the development of PP models that use in-situ data, local bio-optical models and ocean colour data to estimate chlorophyll from space. Even when this capability is possible, broader problems need to be tackled:

- A) What are the seasonal and inter-annual changes in primary production ?

- B) What is the response of PP to different physical forcing functions e.g wind stress curl, and currents. What is the nature of the coupling between biological and physical processes?. Can we predict the evolution of changes in primary production to climate changes ?.

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