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A multispectral remote sensing study of coastal waters off Vancouver Island

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Abstract. In March 1996, a multispectral aircraft survey of the coastal waters off Vancouver Island was carried out using a Compact Airborne Spectrographic Imager (CASI). This survey was combined with in situ measurements of water properties (phytoplankton composition, phytoplankton pigments, absorption spectra of phytoplankton, and concentration of dissolved organic carbon, or DOC). Comparison of the phytoplankton absorption data from this experiment with similar data from other regions shows that phytoplankton community has a significant impact on the spectral form and magnitude of absorption spectra, when normalized to unit chlorophyll-a. Concurrent measurements of in situ properties and aircraft data were obtained at eight stations. The in situ measurements of phytoplankton absorption and estimates of downwelling irradiance based on a clear-sky atmospheric-transmission model are used as inputs to a model of water-leaving irradiance. The modelled irradiances are compared with the remotely sensed values of water-leaving radiances. The observed differences between model and observation are used to evaluate the potential influence of DOC on water-leaving radiance. Practical difficulties of separating the phytoplankton signal from that of the coloured component of DOC (also known as yellow substance) are examined. Algorithms for estimation of the concentration of chlorophyll-a (the major phytoplankton pigment) can be based on their absorption or fluorescence properties. The distribution of chlorophyll-a in the study area is estimated using both these approaches, and possible causes for the observed discrepancies are discussed.

1. Introduction

Estimating water constituents in shallow coastal and inland waters from remotely sensed data on ocean colour is a complex problem. In open-ocean waters,
it is often possible to assume that phytoplankton (along with a cohort of covarying substances) is the single, major constituent responsible for changes in optical properties. It is common to refer to waters in which this assumption holds as Case 1 waters (Morel 1980, Gordon and Morel 1983, Sathyendranath and Morel 1983). On the other hand, in many coastal and inland water bodies (Case 2 waters), a number of constituents, such as yellow substances (the coloured component of dissolved organic material) and suspended material can be present in large concentrations, and vary independently of phytoplankton concentration. Therefore, algorithms developed for Case 1 waters often break down in Case 2 waters. Because several constituents contribute to changes in ocean colour in Case 2 waters, we anticipate that multispectral algorithms will be required for applications in such waters. In the interest of generality of applications, it would also be desirable to base the algorithms on theoretical considerations, rather than on purely empirical grounds.

In this paper, we present the results of a remote sensing experiment carried out off Vancouver Island in March 1996, in waters which have high and variable loads of yellow substances. Hence, these waters can be classified as belonging to Case 2. An aerial survey of the region was carried out using a Compact Airborne Spectrographic Imager (CASI), while in situ measurements were made from a boat for calibration of the remotely sensed data. In situ measurements of phytoplankton absorption and the concentrations of chlorophyll-a (the main pigment in phytoplankton) are used in a model of ocean colour to estimate the water-leaving irradiances, and the model results are compared with observations. We show that the discrepancies between model and observations are related to changes in the concentrations of dissolved organic carbon (DOC). Finally, we develop algorithms for use in these waters for the retrieval of chlorophyll-a concentration. Two algorithms are examined: one based on phytoplankton absorption, and the other based on fluorescence by chlorophyll-a. The differences between the two algorithms, and their possible causes are then discussed.

2. Materials and methods

2.1. General description of the study area

Saanich Inlet is a fjord-like embayment located near the southern end of Vancouver Island, British Columbia, Canada (figure 1). The inlet is 24 km long with a surface area 65 km$^2$, and is connected with the Strait of Georgia at its northern end. The average depth is around 120 m and the main basin has a maximum depth of 228 m. Direct exchange of deep waters with the water outside is restricted by two sills, each approximately 70 m deep. As a result, the lower part of the water column in the inlet is anoxic.

Chlorophyll concentrations in the top 10 m of the inlet are generally high, ranging from 3 to 22 mg Chl-a m$^{-3}$ during the spring and fall (Takahashi et al. 1977), with values of up to 40 mg Chl-a m$^{-3}$ being recorded during the summer months (Gower 1980). Turbidity is also greatest during the summer months, coinciding with phytoplankton concentration (Herlinveaux 1962). In the nearby Strait of Georgia, Secchi depths ranged from 2.3 to 9 m at various stations over a 2-year period (Stockner et al. 1979). Concentrations of dissolved organic carbon in the surface waters ranged from 0.76 to 1.17 mg C l$^{-1}$ in the present study, with values of 1.7–2.6 mg C l$^{-1}$ being recorded in the spring (Frank Whitney, personal communication).
2.2. Aircraft survey

The aircraft survey of the study area was carried out using a Cessna 206 float plane equipped with CASI, which is capable of collecting information in 288 wavebands, in the spectral domain between 403 and 914 nm. However, in using the instrument a compromise must be found between spectral and spatial coverage. If data are collected at 14 or fewer spectral bands selected from the possible range, then full spatial coverage is possible (a swath width of 512 pixels across the flight track). Higher spectral coverage can be obtained only at the cost of decreasing spatial coverage. In this experiment, we operated the instrument in two modes. In one mode, which we call the spatial mode, the data were collected in 14 spectral bands (see table 1) similar to those of the European MERIS (MEdium Resolution Imaging Spectrometer) ocean-colour sensor, which was launched in 2002 aboard the ENVISAT satellite. In the other mode, which we call the spectral mode, the
data were collected in all 288 wavebands, at a reduced spatial coverage of 39 pixels across swath. The data from the spectral mode were used for testing of models and for general algorithm development, whereas the spatial mode was selected specifically for design of algorithms for use with data from the MERIS ocean-colour sensor. Also, the spectral mode could be used to examine whether the selection of wavebands for MERIS was optimal for the envisaged applications. Data from the spatial mode is also used to generate maps of chlorophyll distribution in the study area.

Concurrent aircraft and in situ data were collected on 5 and 13 March 1996. On each occasion, the CASI was flown in spectral and spatial modes. The data obtained by the sensor had to be corrected for the atmospheric contribution to the signal reaching the sensor at the aircraft altitude. This atmospheric correction was done empirically. A small segment of the study area was overflown at four altitudes: 500, 1500, 6000 and 8000 ft (152, 457, 1829 and 2438 m). The multi-altitude data were used to establish empirical linear atmospheric correction factors for all sensor look angles. These factors were then used to retrieve the water-leaving radiance from the data collected during the surveys, which were carried out at an altitude of 8000 ft. No effort was made to correct the data for surface-reflected sky radiance (see Hu and Carder 2002, Gould and Arnone 2002).

2.3. In situ measurements

Supporting data were collected from a boat on 5, 13 and 14 March at a total of 12 stations (see figure 1). At each station, the vertical structure of the water column from surface to 150 m was first studied using a CTD (conductivity–temperature–depth) profiler which also carried a sensor for measuring fluorescence by the phytoplankton pigment, chlorophyll-a. Typically, the waters were stratified at these stations, and the vertical structure was characterized by a sub-surface chlorophyll maximum. Water samples were collected at three depths: the surface, the depth of the sub-surface chlorophyll maximum and at one depth immediately below the chlorophyll maximum. The subsurface maximum in chlorophyll-a fluorescence was usually around 5–10 m, and the maximum depth from which water samples were collected did not exceed 15 m.

<table>
<thead>
<tr>
<th>Band number</th>
<th>Lower limit (nm)</th>
<th>Centre (nm)</th>
<th>Upper limit (nm)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>403.5</td>
<td>409.5</td>
<td>415.6</td>
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<tr>
<td>2</td>
<td>436.5</td>
<td>441.7</td>
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<td>483.7</td>
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<td>4</td>
<td>504.8</td>
<td>510.0</td>
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<td>5</td>
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<td>6</td>
<td>555.9</td>
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<td>614.5</td>
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<td>8</td>
<td>659.0</td>
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<tr>
<td>14</td>
<td>859.9</td>
<td>864.4</td>
<td>868.9</td>
</tr>
</tbody>
</table>
After collection, the water samples were kept in the dark, and at the end of each sampling day, they were brought back to the laboratory, and subsamples were used to estimate the concentration of chlorophyll-a using Turner fluorometry (Yentsch and Menzel 1963). Subsamples were also filtered immediately on to GF/F filters and stored in liquid nitrogen for subsequent analyses. The frozen filters were used for analyses of phytoplankton pigments using the High-Performance Liquid Chromatography (HPLC) technique, following the protocol outlined by Head and Horne (1993). The filters were also used for estimating the absorption coefficients of phytoplankton pigments and other material retained by the filter (Sathyendranath et al. 1996, Stuart et al. 1998). Filtered water samples were refrigerated and used subsequently to estimate the concentration of dissolved organic carbon (DOC) by high-temperature combustion (Kepkay et al. 1997), and fluorescent dissolved organic material (DOM) by fluorometry (Chen and Bada 1992). Fluorescent DOM has been related to marine and terrestrial humic substances as well as pteridines and flavins (Chen and Bada 1992).

All the samples from all the depths were used to establish the relationship between phytoplankton absorption and phytoplankton pigments. But only samples collected within 2 h of the aircraft overflight were used for comparisons between model and remote observations and for establishing local algorithms for interpretation of aircraft data.

3. Model of upwelling irradiance

In the approach followed here, we first compute the reflectance $R$ at the sea surface, which is defined as the ratio of upwelling irradiance to the downwelling irradiance at the surface. The modelled reflectance is then used, along with a clear-sky light-transmission model, to estimate the upwelling irradiance, also at the sea surface. We then compare the model with the observations, and examine the possible causes for discrepancies.

The model attempts to simulate reflectance only in the absence of inelastic processes. In the coastal waters under consideration, with high absorption by yellow substances and phytoplankton, we have assumed that the influence of Raman scattering would be negligible. On the other hand, the phytoplankton fluorescence signal in the red part of the spectrum is expected to be significant, because of the high chlorophyll concentrations. But we have not attempted to simulate chlorophyll-a fluorescence in the model. We rely instead on the empirical approach of Gower (1980) to evaluate the usefulness of the fluorescence signal to map pigment concentrations. Therefore, it is important to bear in mind that all comparisons between model and observations should exclude the spectral window extending roughly from 660 to 700 nm which may be influenced by chlorophyll-a fluorescence.

3.1. Reflectance model

Ocean colour, which is determined by spectral variations in reflectance ($R$) at the sea surface, is modelled here as a function of the absorption coefficient, $a$, and the backscattering coefficient, $b_b$, which are both inherent optical properties (Preisendorfer 1976). First, $R$ just below the water at wavelength $\lambda$ is expressed as:

$$R(\lambda) = r(\lambda) \frac{b_b(\lambda)}{a(\lambda)}$$

(1)
where $r$ is a proportionality factor. This is a common model structure, which has been derived by a number of authors (Morel and Prieur 1977, Kirk 1981, 1984, Aas 1987, Sathyendranath and Platt 1997), and is similar in form and performance to yet other models (e.g. Gordon et al. 1975). Although the proportionality factor often takes a value of 0.33 (Morel and Prieur 1977, Sathyendranath et al. 1989), several studies have shown that it can vary by a factor of 2 or more (e.g. Kirk 1984, Morel and Gentili 1991, Sathyendranath and Platt 1997). According to these models, the variability in $r$ is likely to be greater in turbid coastal waters than in clear, open-ocean waters. Therefore, the possibility exists that the value of $r$ in the waters off Vancouver Island may, in fact, be considerably higher than the typical value of 0.33 which has been used successfully in open-ocean waters in the past. Nevertheless, in the absence of any data on $r$ that would be appropriate for the study area, we used a value of 0.33.

The implementation of the model requires that we compute $a$ and $b$, as functions of wavelength. We proceeded as follows.

3.2. Absorption model

We assumed that the total absorption coefficient could be parameterized as a function of three components: pure water, phytoplankton pigments, and yellow substances. In Case 2 waters, it is customary to include yet another component, which may represent detritus or other non-pigmented particles such as suspended sediments (Prieur and Sathyendranath 1981). However, in our samples, the absorption by non-pigmented material collected on the filters had a spectral form very like that of yellow substances. Many earlier works (e.g. Roesler et al. 1989, Bricaud and Stramski 1990, Hoepffner and Sathyendranath 1993) have reported similar results. It is possible that at least some of the so-called ‘detrital absorption’ on the filters arises from yellow substances that adsorb on the filters. Therefore, in this analysis, we have combined the yellow substances and detrital material into a common pool, that we shall refer to for convenience, as yellow substances.

It is well known (Bricaud et al. 1981) that the absorption by yellow substances ($a_y$) has an exponential form, which can be expressed as:

$$a_y(\lambda) = a_y(\lambda_0) \exp(-q(\lambda - \lambda_0))$$

where $\lambda_0$ is a reference wavelength, which is taken to be 440 nm here, as is customary, and $q$ (dimensionless) defines the slope of the exponential curve. Bricaud et al. (1981) showed that $q$ takes a mean value of 0.014, but we have set $q$ to 0.011, which is the mean value for $q$ determined for our detrital absorption spectra from the study area. Since we had no measurements of absorption by yellow substances, we assumed, initially, that it varied proportionately with phytoplankton absorption, as in Case 1 waters. That is to say, we assumed $a_y(440) = 0.3 \ a_p(440)$ (after Sathyendranath et al. 2001), where $a_p(440)$ is the absorption by phytoplankton pigments at 440 nm. Absorption by pure water ($a_w$) is modelled here according to Pope and Fry (1997).

The absorption by phytoplankton varies with pigment concentration. In the following discussion we have treated the concentration of chlorophyll-a as the measure of $P$, the pigment concentration. In these experiments, we had two estimates of chlorophyll-a concentration for each sample: one estimate by HPLC, and the other by Turner fluorometry. The correlation between the two measurements is excellent ($r^2 = 0.99$; see figure 2(a)). However, there are some
systematic differences between the two estimates, and the linear fit to the data suggest that the HPLC pigment concentrations were typically lower than the Turner estimates by approximately 5%.

The phytoplankton populations at the sampled stations were dominated by diatoms (Stuart et al. 1998). Phytoplankton absorption at these stations was characterized by relatively low efficiencies for absorption (low values of specific absorption coefficient), compared with what might be expected from some

Figure 2. (a) Comparison of chlorophyll-a concentration (mg m^{-3}) estimated using the HPLC technique and Turner fluorometry. The straight-line regression equation shows excellent correlation, but note that the slope deviates from the one-to-one line by approximately 5%. \( Y = 0.36 + 1.05*X, \ r^2 = 0.99. \) (b) Phytoplankton absorption at 440 nm plotted as a function of chlorophyll-a concentration. The results are presented for both HPLC (open circles, dashed line) and Turner fluorometric techniques (solid triangles, solid line). The two curves plotted represent the rectangular hyperbolae, fitted using the two independent sets of pigment data. In the inset, we have enlarged the portion corresponding to low (<2 mg m^{-3}) pigment concentrations.
measurements in open-ocean waters. This is best illustrated by looking at the relationship between $a_p(440)$ and the chlorophyll-a concentration. In figure 2(b), we have plotted $a_p(440)$ as a function of chlorophyll-a for all the samples collected during the Vancouver experiment. The relationship is non-linear, with the maximum rate of change in absorption with pigment concentration occurring near the origin. A rectangular hyperbola fitted to the data yielded the relationship:

$$a_p(440) = \frac{2.10 \times 0.0411P}{2.10 + 0.0411P}$$

where $P$ stands for pigment (chlorophyll-a) concentration determined by Turner fluorometry. Note that, according to this equation, the rate of change in absorption coefficient per unit pigment concentration, or the specific absorption coefficient, is maximum near the origin, and takes a value of 0.0411 (m$^2$ (mg Chl)$^{-1}$). The second parameter in the fitted equation, 2.10 (m$^{-1}$), represents a saturating value for absorption at very high pigment concentrations. The slope of 0.0477 (m$^2$ (mg Chl)$^{-1}$) is somewhat higher for $P$ estimated from HPLC measurements, as might be anticipated from the relationship seen in figure 2(a). On the other hand, the saturation value of 1.78 (m$^{-1}$) for HPLC pigments is somewhat lower. Note that these initial slopes are much lower than the values that one might observe in some open-ocean waters, for example, the Arabian Sea (Stuart et al. 1998).

All the absorption spectra normalized at 440 nm were averaged to obtain a mean, normalized absorption spectrum for phytoplankton. This average spectrum was used to calculate the phytoplankton absorption at all other wavelengths, once the value of $a_p$ at 440 nm was calculated for each station using equation (3), given the value of $P$ at the surface at that station: if we use the notation $a'_p(\lambda)$ to designate the value of the mean, normalized (dimensionless), spectrum of phytoplankton absorption coefficient at wavelength $\lambda$, then $a_p(\lambda) = a'_p(\lambda)a_p(440)$. The mean shape of the absorption spectrum is relatively flat when compared with similar measurements from the Arabian Sea (see Stuart et al. 1998). These regional differences in the absorption characteristics of phytoplankton are consistent with differences in the pigment composition and community structure of phytoplankton (Stuart et al. 1998), and underscore the need to use local optical characteristics in devising ocean-colour models, whenever possible.

Once the individual components of absorption were calculated, the total absorption coefficient at any wavelength was obtained by simple addition:

$$a(\lambda) = a_w(\lambda) + a_p(\lambda) + a_s(\lambda)$$

3.3. Backscattering model

The backscattering model was kept relatively simple, and had two components: pure water and particles. Scattering by pure water ($b_w$) was calculated according to Morel (1974), and the ratio of backscattering to total scattering for pure water, $\frac{b_w}{b}$, is known to be 0.5. Following Loisel and Morel (1998), scattering by particles was calculated as a function of chlorophyll-a concentration:

$$b_p(660) = 0.407 P^{0.795}$$

The wavelength dependence of particle scattering was assumed to vary with $P$, the chlorophyll-a concentration, as in Sathyendranath et al. (2001), by setting $b_p(\lambda) = b_p(660)^n$, and $n = \log_{10}(P)$. The particle backscattering ratio, $\frac{b_p}{b}$, which defines the ratio of backscattering by particles to total particle scattering, was
computed according to Ulloa et al. (1994):

\[ \delta_b = 0.01 (0.78 - 0.42 \log_{10}(P)) \]  

(6)

Thus, the backscattering coefficient at wavelength \( \lambda \) was computed as:

\[ b_b(\lambda) = 0.5b_w(\lambda) + \delta_b(\lambda) \]  

(7)

3.4. Estimating upwelling irradiance just below the sea surface

Once the absorption and scattering coefficients were determined, reflectance \( R(\lambda) \) was calculated using equation (1). By definition, \( R \) at any depth is also the ratio of upwelling to downwelling irradiance at that depth, so that we have:

\[ R(\lambda, z) = \frac{E_u(\lambda, z)}{E_d(\lambda, z)} \]  

(8)

An estimate for the downwelling irradiance at the sea surface can be obtained using clear-sky atmospheric-transmittance models. We used the model of Bird (1984), as implemented in Sathyendranath and Platt (1988) to obtain \( E_d(\lambda) \) at the sea surface. This value of \( E_d(\lambda) \) is then used to obtain the upwelling irradiance just below the sea surface:

\[ E_u(\lambda, 0) = E_d(\lambda, 0) \times R(\lambda, 0) \]  

(9)

3.5. Relationship between water-leaving radiance, and upwelling irradiance just below the sea surface

The aircraft measures radiance (flux per unit area per steradian), and not irradiance (flux per unit area), just above the sea surface. Therefore, the modelled irradiance just below the sea surface has to be transformed further to make it directly comparable with the quantity estimated from remote measurements. This involves two steps.

The first step is to establish a relationship linking \( E_u(\lambda, 0) \) to radiance \( L_u(\lambda, 0, \theta, \phi) \) at depth \( z=0 \), where \( \theta \) and \( \phi \) are zenith and azimuth angles respectively, in water. By definition:

\[ E_u(\lambda, 0) = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi/2} \cos \theta L_u(\lambda, 0, \theta, \phi) \sin \theta \, d\theta \, d\phi \]  

(10)

If we could assume the water to be a perfect Lambertian diffuser, then it would follow that \( L_u \) would be a constant for all viewing angles, and the equation would reduce to \( E_u(\lambda, 0) = \pi L_u(\lambda, 0) \). However, it is known that \( L_u \) can vary with the viewing angle, with the type of water under consideration, and with wavelength (Austin 1980, Morel and Gentili 1993). So it is customary to represent the relationship between \( E_u \) and \( L_u \) through a conversion factor \( Q \), such that:

\[ L_u(\lambda, 0, \theta, \phi) = \frac{E_u(\lambda, 0)}{Q(\lambda, 0, \phi)} \]  

(11)

According to Morel and Gentili (1993), \( Q \) could take a value anywhere between 0.3 and 6.5.

The second step is to relate radiance \( L_u \) just below the surface to \( L_w \), the
radiance just above the water, and the necessary equation is:
\[
L_w(\lambda, 0, \theta', \phi) = L_u(\lambda, 0, \theta, \phi)[1 - \rho(\theta)]/m^2
\]  
(12)
where \(\rho(\theta, \phi)\) is the Fresnel reflectivity for rays incident on the sea–air interface at zenith angle \(\theta\). The zenith angle in air \(\theta'\), is related to \(\theta\), the zenith angle in water, through Snell’s principle of refraction: \(m \sin(\theta') = \sin(\theta)\), where \(m\) is the refractive index of sea water. We have set \(m = 1.33\).

Combining equations (11) and (12), we have:
\[
L_w(\lambda, 0, \theta', \phi) = \frac{E_u(\lambda, 0, \theta, \phi)}{Q(\lambda, \theta, \phi)}[1 - \rho(\theta)]/m^2
\]  
(13)

In our field survey, the aircraft flights were directly overhead of the research vessel in the water, such that, when comparing aircraft measurements with modelled values for the stations, we can set \(\theta' = \theta = 0\). For zenith viewing angles, Fresnel reflectance \(\rho \approx 0.02\). The major difficulty in estimating \(L_w\) from \(E_u\) in our case arises from uncertainty in the magnitude and spectral variability of \(Q\). Therefore, we decided to compare directly the modelled \(E_u\) values with the remotely sensed \(L_w\) values to deduce some information about the values of \(Q\) that might be applicable locally.

But we have to recognize that there is another, important, potential source of difference between modelled \(E_u\) values and measured \(L_w\) values: in the model, we have assumed that absorption by yellow substances covaries with phytoplankton absorption. Even though such an assumption would often be valid in open-ocean waters, we recognize that it need not hold in the waters around Vancouver Island. In fact, the main Vancouver Island, and the neighbouring smaller islands, with their rich vegetation, are an excellent source of humic substances, and the waters off Vancouver Island are known to be rich in yellow substances (Gower 1980). Therefore, before proceeding to a comparison of observations and model, we examine through a sensitivity analysis the effect of varying concentrations of yellow substances on reflectance at the sea surface.

4. Influence of yellow substances on ocean colour

To assess the sensitivity of reflectance spectra to changes in the concentration of yellow substances, we simulated a series of reflectance spectra at the sea surface, with a constant pigment concentration (which was assumed, arbitrarily, to be the same as that at Station 8), and a variable absorption by yellow substances (figure 3(a)). In these curves, absorption by yellow substances at 440 nm, relative to that of phytoplankton, varied from 5% to 200%. We see that the reflectance in the blue part of the spectra decreases significantly with increasing absorption by yellow substances, whereas there is no apparent influence of yellow substances in the red part of the spectra.

When these spectra are compared with a simulated spectrum in which the absorption by yellow substances is set to 30% of phytoplankton absorption at 440 nm (as was done in all our routine simulations of the reflectance spectra at our stations), what can we expect to see? To understand the consequences of variable absorption by yellow substances on the comparisons between modelled and observed spectra, we treated the spectrum simulated with 30% absorption by yellow substances as the standard case, and divided the standard reflectance spectrum by each of the simulated reflectance spectra shown in figure 3(a). The results are shown...
in figure 3(b). Clearly, when the denominator and the numerator are the same, as in the middle curve, the ratio of the two reflectances is flat. When the absorption by yellow substances is greater than the simulated standard case, the ratio of reflectances increases in the blue, and conversely, it decreases when the standard case is less than the simulated case. The main feature in these spectra of ratios is the change in the slope of the curves with change in absorption by yellow substances, for wavelengths shorter than around 650 nm.

We see from these simulations that we cannot infer anything about the factor $Q$...
from comparisons of the model and observations, until we account for the influence of variable yellow substances on the modelled reflectance spectra.

5. Comparison of model and observations
The model was able to simulate many of the features seen in the observations. An example is shown in figure 4. The ratio of the modelled irradiance spectrum to the observed radiance spectrum, however, was not flat. Typically, the ratio was high in the blue, and decreased towards the red end of the spectrum. The slope of these curves varied from station to station. As discussed previously, if the simulated absorption by yellow substances was less than the actual values at the station, this

![Figure 4](image)

Figure 4. Comparison of model and observation. Remotely sensed data collected in full-spectral mode is used in the comparison. Example for Station 8. (a) Modelled spectra of upwelling irradiance ($E_u(\lambda, 0)$). (b) Remotely sensed radiance spectra after empirical correction for atmospheric noise ($L_w(\lambda, 0)$). (c) Ratio of model to observation ($E_u(\lambda, 0)/L_w(\lambda, 0)$). The straight line is the linear best fit to the ratio as a function of wavelength, for wavelengths from 400 to 650 nm. $\log(E_u/L_w) = 1.68 + -0.00136*\lambda$, $r^2 = 0.86$. 

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could lead to a non-zero slope of the type seen here, especially in the blue–green–yellow part of the spectrum. The absorption by yellow substances is not expected to influence the red part of the spectrum, except in extreme cases.

Therefore, to test whether spectral variations in the ratio of model to observation were related to variations in yellow substances, we first fitted a linear equation to the spectrum of the (log-transformed) ratio, for the wavelength interval from 400 to 650 nm (see figure 4(c)). The slope and the intercept varied from station to station. We then examined whether the variations in the slope and intercept of the fitted lines were associated with changes in the concentration of dissolved organic carbon (DOC) (figure 5). In fact, variations in DOC concentration, relative to chlorophyll-a concentration, were responsible for more than 80% of the variance in the slope and intercept of the spectrum of ratios. As anticipated from the model simulations, we see that the slope becomes more negative with increasing concentrations of DOC, and the intercept increases with DOC concentration. It has to be pointed out that the yellow substances comprise only a part of the total DOC. In our field data there was a good correlation between measured concentrations of total DOC and fluorescent DOM ($r^2 = 0.66$), which may explain

Figure 5. (a) The intercept and (b) the slope of the straight line fitted to the spectrum of irradiance–radiance ratio (see figure 4 for an example) plotted as a function of the relative concentration of DOC (estimated as the ratio of DOC concentration (measured in $\mu$ mol m$^{-3}$) to chlorophyll-a concentration (measured in mg m$^{-3}$)). Each point corresponds to a station. The number of observations is eight.
why we were able to get good correlations between apparent absorption by yellow substances and concentration of DOC.

It appears from the comparison between model and observations that absorption by yellow substances is important and varies independently of phytoplankton absorption in these waters. Variable absorption by yellow substances emerges as the main agent responsible for the slope in the spectral ratio of model to observation. We can interpret this as indirect evidence that spectral variations in $Q$ are not significant.

To infer something about the magnitude of $Q$ and its variability in the study area from the information available, we need to use a spectral domain within which factors other than $Q$ do not influence the comparison. We have seen that yellow substances had a significant influence on the shape of the remotely sensed signal in the 400–650 nm domain. We also know from previous studies off Vancouver Island (Gower 1980, Gower et al. 1984) that the spectral domain in the 660–700 nm region is influenced by chlorophyll-a fluorescence, though it is not modelled here. This leaves a narrow window of 650–660 nm, which could be used to infer something about the factor $Q$.

We calculated averages in the 650–660 nm spectral window, for measured values of $L_w$ and modelled values of $E_u$, and then computed $Q$ as the ratio of average $E_u$ to average $L_w$, divided by $m^{2/0.98}$ (see equation (13)). The factor $Q$ was quite variable, ranging from about 2 to 8. Interestingly, $Q$ was highly correlated with log-transformed radiance ratios in the red part of the spectrum: $r^2 = 0.88$ for ratio of $L_w(664)$ to $L_w(550)$ (band 8/band 5; see figure 6), and $r^2 = 0.84$ for ratio of

![Figure 6](image-url)

Figure 6. Plot of $Q$ against the log-transformed ratio of water-leaving radiance in band 8 over band 5. Linear regression yielded an $r^2$ value of 0.88. The factor $Q$ was computed as the ratio of $E_u$ to $L_w$ divided by $m^{2/0.98}$. Both $E_u$ and $L_w$ values were averaged over the spectral range 650–660 nm in these computations of $Q$. $Y = -11.90 - 33.65 X$, $r^2 = 0.88$. 
The correlation between $Q$ and the log-transformed band ratios was low ($r^2 < 0.2$) in the spectral region from 442 to 560 nm, where absorptions by phytoplankon and yellow substances have a dominant effect on the reflectance spectra. Intriguingly, $Q$ showed no significant correlation with chlorophyll-a, DOC concentration, or the magnitude of the detrital absorption at 350 nm. Using a model, Sathyendranath et al. (1989) have shown that the reflectance signal in the red part of the spectrum (they used 640 nm) is correlated with particle scattering. Here, we see a correlation between $Q$, which is determined by particle scattering, and the water-leaving radiance in the red part of the spectrum. However, the source of this scattering remains unknown. The possibility exists that the variability in $Q$ is an artefact resulting from the surface-reflected sky radiance, which was not corrected for (see Hu and Carder 2002).

Note that the values of $Q$ as computed here are tied to the $r$ value of 0.33 used in equation (1). If there were variations in $r$, then they were subsumed in the computed variations in $Q$, since our measurement protocol was insufficient to separate the variations in $Q$ from those in the parameter $r$ in equation (1). The computed range of $Q$ is in reasonable agreement with the theoretical range proposed by Morel and Gentili (1993). But this is not conclusive proof that the value of $r$ used here is appropriate. Perhaps the poor correlation between estimated $Q$ and the sea-water constituents indicates that $r$ is also variable in these waters. On the other hand, that DOC concentration is able to explain the spectral differences between model and observations suggests that the spectral variations in estimated $Q$ are small. The difficulty with explaining $Q$ unambiguously suggests that one should explore algorithms for these waters that are based on ratios of water-leaving radiances at different wavelengths, rather than on their absolute magnitudes. In the absence of spectral variation in $Q$, taking ratios would eliminate $Q$ from the equations, and hence any potential errors arising from failure to model $Q$ successfully.

One of the difficulties of remote sensing in Case 2 waters is associated with the problem of distinguishing the influence of phytoplankton signal from that of yellow substances. The results presented here indicate clearly that yellow substances are present in sufficient quantity to influence the remotely sensed signal significantly, and that they vary independently of pigment concentrations. Furthermore, we see from an analysis of $Q$ that there is probably a scattering component to the upwelling irradiance that also varies independently of pigments and yellow substances. Under such conditions, how successfully can we retrieve pigment concentrations from remote observations? In the following sections we examine the potential to exploit pigment absorption and pigment fluorescence to quantify phytoplankton distribution in these waters. The approach followed in the next section in developing algorithms is empirical, but the results from the theoretical analyses presented here are used as a guide to choosing approaches that are more likely to succeed.

6. Algorithms for pigment retrieval

Two types of algorithms have been used in the past for retrieval of pigment concentrations from remotely sensed data: those that use variations in ocean colour resulting from pigment absorption, and those that use the chlorophyll fluorescence signal. The former algorithms typically exploit the blue–green part of the spectrum, whereas the latter type exploits the red part of the spectrum. It is understood that these two types of algorithms are not equivalent, but complementary in some
respects (Sathyendranath 1986). In this dataset, we had the necessary information for developing both these types of algorithms, and they are treated next.

In our experiment, we were able to obtain only eight stations of concurrent in situ and aircraft observations. This is a somewhat limited dataset for developing multispectral algorithms with many independent variables as inputs, since we would not have many degrees of freedom for parameter estimations. Furthermore, since all the available data had to be used for establishing the model by multiple regression, we had no independent data available for testing the validity of the algorithm. Therefore, we decided to use additional criteria for establishing the validity of algorithms. One such criterion was to map the phytoplankton distribution in the study area using different algorithms, and examine whether the map showed pigment concentrations that were within the range of all the in situ observations. Though this is not a rigorous test, it turned out, nevertheless, to be a useful one. Since only the spatial mode data had the spatial coverage necessary for this additional test, we confine the algorithm development in this instance to the data collected in spatial mode.

6.1. Absorption-based algorithm

We worked with spectral radiance values normalized to the radiance at 550 nm (band 5) in our development of algorithms that exploit the influence of phytoplankton absorption on ocean colour. This MERIS band is a convenient band for normalization, since phytoplankton absorption is almost a minimum at this waveband such that the signal is likely to be influenced little by variations in phytoplankton concentration. Furthermore, normalizing the spectra to the value obtained at one waveband avoids to a large extent the variations in signal due to variations in incoming solar radiation. This type of normalization has also been used successfully in many algorithms in use today (see O’Reilly et al. 1998, Carder et al. 1999).

We also know from the previous analyses that yellow substances vary independently of phytoplankton in these waters, and so we have to deal with at least two variable components that influence ocean colour in the blue and green parts of the spectrum. Under such circumstances, we need more than a single reflectance ratio to develop useful algorithms; furthermore, our analyses show that absorption by yellow substances is very important in the blue part of the spectrum, and so the classical blue–green ratio may not be ideally suitable for these waters, for retrieval of phytoplankton pigment concentration.

Therefore, we proceeded by best-subset regression models, with the chlorophyll-a concentration as the independent variable, and normalized, MERIS-band signals as the dependent variables, to obtain suitable algorithms for this region. We used log-transformed data, since it is known, from both practical and theoretical points of view, that log-transformation of reflectance ratios and pigments is recommended when establishing algorithms by linear regression techniques (Sathyendranath et al. 1989). Because we had only eight sets of concurrent observations, we could not use more than three dependent variables in these statistically determined algorithms. Typically, we found that algorithms using the blue bands performed poorly when they were used to map the pigment concentrations in the region, in the sense that the mapped concentrations were often several times higher than the local in situ observations. The best results were obtained using band 4 (centred at 510 nm) and band 7 (centred at 620 nm), both normalized to band 5 (centred at 550 nm) (see
The following multiple regression equation was obtained using these band ratios: 
\[
\log_{10} P = -0.1904 - 9.22 \log_{10}(S(4)) - 1.56 \log_{10}(S(7)),
\]
where \( S(4) \) is the signal at band 4 normalized to that at band 5, and \( S(7) \) is the signal at band 7, also normalized to the band 5 signal. The explained variance was high (*)
\( r^2 \approx 0.94 \). Furthermore, in the map produced using this algorithm, the chlorophyll-a concentrations \( P \) were in a range similar to the in situ observations.

The improvement in the multiple regression when adding band 7 to band 4 was small, but statistically significant (*\( r^2 \) without band 7 \( \approx 0.88 \)). It is interesting to note that chlorophyll-a has a small absorption band centred at around 623 nm (Stuart et al. 1998), which might account for the usefulness of band 7 in mapping pigment concentration. Besides, in the type of waters under investigation, the blue part of the spectrum is likely to be strongly corrupted by absorption due to yellow substances, which renders it unsuitable for use in phytoplankton pigment retrieval algorithms. According to Stuart et al. (1998), the relationship between the 620 nm absorption band and chlorophyll-a concentration is much more stable than those at other chlorophyll-a absorption bands, presumably because this small absorption band is little influenced by the flattening effect. This spectral region is also relatively unaffected by other phytoplankton pigments, with the notable exception of phycocyanin, a biliprotein found in some cyanobacteria (Jupp et al. 1994).

However, against these advantages of the 620 nm band, there is also a disadvantage: the chlorophyll-a absorption at 620 nm is very small compared with its absorption in the blue, and so the usefulness of this band for pigment retrieval may be limited to high-chlorophyll, high-yellow-substance waters, like the ones under investigation here.
6.2. Fluoresentce-based algorithm

We followed Gower (1980) in developing a fluorescence algorithm, using bands 8, 9 and 10 to determine a fluorescence line height (FLH). All the bands were normalized to band 5 (centred at 550 nm) in this analysis, as in the case of the absorption-based algorithm. A baseline was established as a straight line linking the radiances at bands 8 and 10, and the height of the signal above the baseline at band 9 was estimated as

\[
F = S(9) - S(8) - \left[ S(10) - S(8) \right] 16.1 / 40.25
\]

where \( F \) is the fluorescence line height, \( S(8), S(9) \) and \( S(10) \) are the signals at bands 8, 9 and 10, respectively (all normalized to band 5), and 16.1 and 40.2 are the differences in wavelengths between the centres of bands 8 and 9, and bands 8 and 10, respectively (see table 1 for the location of the band centres). Note that this calculation estimates the height of the signal at band 9 over a linear baseline drawn between the signals at bands 8 and 10. FLH was then plotted against chlorophyll-a concentration as determined by Turner fluorometry (figure 8) and a linear fit to the data points yielded \( F = 0.00927 \, P \), with \( r^2 = 0.65 \).

6.3. Comparison of the two algorithms

The maps produced using the absorption-based algorithm and the fluorescence-based algorithm are shown in figure 9. These two maps show some similar features, but there are also some striking differences. For example, the contrasts in the pigment distribution are less pronounced, and the maxima and minima less marked, in the FLH-based algorithm than in the absorption-based algorithm. A number of physical or physiological factors may contribute to differences between fluorescence-based and absorption-based algorithms. The common sources of differences

![Figure 8. Fluorescence line height (F) plotted against \( P \), the chlorophyll-a concentration (determined by Turner fluorometry) for the eight stations for which we had concurrent aircraft and in situ data. \( F = 0.00927 \, P \), \( r^2 = 0.65 \).]
Figure 9. Maps showing the distribution of pigments in the study area. The maps were generated using CASI data collected in spatial mode on 13 March 1996 in the Saanich Inlet. The left panel shows the result of applying the algorithm based on bands 4 and 7, both normalized to band 5. The middle panel shows the result of applying the algorithm based on the fluorescence line height (FLH). The right panel shows the colour code used in the two maps.
are enumerated below, and summarized in table 2 (see also IOCCG 1999). We then attempt to evaluate the importance of these factors for our particular dataset, and for the analyses used here.

1. Typically, phytoplankton exert an influence on ocean colour through their absorption, more than through their scattering. Therefore, the relationship between phytoplankton pigments and remotely sensed signal would be non-linear (see equation (1)). On the other hand, one often sees linear relationships between FLH and pigment concentration (e.g. Gower 1980) except at very high concentrations when the signal may show signs of saturation (Kishino et al. 1984).

2. As phytoplankton absorption increases, there is a decrease in reflectance, and hence in the remotely sensed signal. The fluorescence signal, on the other hand, increases with concentration (unless saturation sets in).

3. Because of the reciprocal relationship between pigment absorption and reflectance, the ocean-colour signal in the blue approaches instrument noise levels at high pigment concentrations. Absorption-based algorithms are therefore most sensitive and effective at low pigment concentrations. On the other hand, FLH increases with concentration, and the fluorescence algorithms are expected to function best at high pigment concentrations (unless the fluorescence signal saturates).

4. As we saw earlier in the sensitivity analyses, the blue–green part of the spectrum is prone to influence from yellow substances, whereas one does not anticipate yellow substance absorption to be significant in the red part of the spectrum except perhaps in the most extreme cases. However, increased absorption by yellow substances could lead to a decrease in the light absorbed by phytoplankton cells and therefore, in the phytoplankton fluorescence (Fischer and Kronfeld 1990). Thus, any influence of yellow substances on the fluorescence signal would be indirect rather than direct.
5. Spectrally dependent scattering can influence absorption-based algorithms for pigment retrieval, especially if the scattering occurs independently of pigment concentration, as in some Case 2 waters. Fluorescence algorithms, on the other hand, are likely to be less susceptible to such effects, since the fluorescence line height has a distinct shape, which spans a narrow wavelength range, and its magnitude is measured above a baseline which is designed to correct for any variations in the background signal.

6. The remotely sensed signal arises from a finite depth of the water column, with the percentage of contribution increasing towards the surface. About 90% of the total signal comes from a layer extending from the surface to the so-called ‘penetration depth’, which is a function of the attenuation coefficient for downwelling irradiance, $K$ (Gordon and McCluney 1975). The coefficient $K$ is wavelength dependent. If there is vertical structure in the water column, the wavebands for which the penetration depth is deeper would be more influenced by this structure than those wavebands with a shallow penetration depth. Typically, penetration depth is substantially greater in the blue–green part of the spectrum than in the red (Sathyendranath 1986). Thus, absorption-based algorithms which rely on the blue and green parts of the spectrum are more likely to reflect vertical structure than the fluorescence signal in the red.

7. Atmospheric-correction algorithms in use with satellite sensor data on ocean colour require extrapolation of atmospheric signal from the near infrared towards the blue part of this spectrum. The errors in extrapolation are likely to increase towards the blue part of the spectrum. Thus, absorption-based algorithms which rely on the blue and green parts of the spectrum are likely to be more vulnerable to errors in atmospheric correction than fluorescence algorithms which use the red part of the spectrum.

8. All pigments absorb light, therefore the blue–green algorithms (or, more generally, absorption-based algorithms) are influenced by all the pigments that absorb at the wavebands used in the algorithms. In contrast, only pigments belonging to photosystem II contribute to fluorescence at ambient temperatures.

9. The blue–green algorithms are strictly a function of the bio-physical structure of the phytoplankton; in particular, these are influenced by the pigment complement in the phytoplankton population and by the manner in which the pigments are packaged into individual cells (the flattening effect). The chlorophyll fluorescence, on the other hand, could be influenced by photosynthesis, since photosynthesis and fluorescence are alternate pathways for a photon that has been absorbed by a phytoplankton cell, as shown by Topliss and Platt (1986).

Items 1 to 3 imply that one or the other algorithm may perform better, depending on the circumstances. According to item 4, the absorption-based algorithm may be in error in waters with high yellow substances, particularly if the algorithm is based on blue–green wavebands. However, we have steered away from the blue wavebands in our absorption-based algorithms to avoid, or at least minimize, the errors due to the influence of yellow substances. By avoiding the blue wavebands, we expect that we have also minimized the errors due to the signals approaching the noise level of the instruments (item 3), since the absorption by phytoplankton and by yellow substances is lower in the green and yellow wavebands used here, relative to that in the blue bands. Since the waters in the study area were stratified vertically, item 5 could indeed be a source of differences between the two algorithms. Item 6 is not applicable in our study, since
atmospheric correction applied in this instance was based on multi-altitude flights, and correction factors developed for each waveband varied independently of the others. It has been shown (Lutz et al. 2000) that in waters with high concentrations of cyanophytes, there could be significant differences between the absorption and fluorescence signals of phytoplankton, since most of the chlorophyll-a in cyanophytes are typically associated with photosystem I rather than with photosystem II. However, we know from cell identifications carried out in the study area that the phytoplankton population was mostly diatoms, and we do not expect that a mismatch between the distribution of pigments in photosystems I and II (item 8) could be a source of difference between the two algorithms in our study area. On the other hand, the possibility exists that the fluorescence yield of phytoplankton in the study area per unit pigment concentration was variable (item 9).

To examine this possibility, we mapped FLH per unit chlorophyll-a (estimated using the absorption-based algorithm) over the study area (figure 10(a)). This map indicates that there is indeed much variability in the fluorescence yield of phytoplankton in the study area. If the errors in the estimated FLH and chlorophyll-a concentration are negligible, the mapped fluorescence yield would be a function of the health of the phytoplankton population. The scatterplot of the data (figure 10(b)) clearly shows a group of data points with a much higher FLH per unit chlorophyll than the major cluster of points. The frequency distribution of the data (figure 10(c)) does not resolve these two clusters into distinct populations. So the possibility exists that the variability in fluorescence yield results from a single phytoplankton population in various stages of growth and decay. This would be consistent with the HPLC analyses and microscopic observations, which did not reveal any major differences in the phytoplankton populations sampled from the study area. The ‘tail’ of the frequency distribution, corresponding to the data points with high FLH:Chl ratios, would imply lower growth rates, since more of the light absorbed by the phytoplankton is re-emitted as fluorescence rather than being used for photosynthesis. It is thus likely that the higher FLH:Chl ratios were associated with the senescent phase of a bloom. Topliss and Platt (1986) showed that the fluorescence line height, when normalized to chlorophyll-a concentration, was in fact inversely related to the initial slope \( \alpha_B \) of the photosynthesis–irradiance curve. Perhaps the differences between the two maps showing the distribution of pigments in the study area (figure 9) reflect, at least partially, differences in the photosynthetic rates of the phytoplankton in the study area. However, in the absence of measurements of photosynthesis during this study, it is not possible to confirm this.

Another way to examine whether there was variability in fluorescence yield of chlorophyll is to plot the measured, in situ fluorescence at the surface against pigment concentration (Turner fluorometry) at the surface, for all the in situ stations (figure 11). Note that there are more points in figure 11 than in figure 8, since in this plot we could use all our in situ stations, rather than just those stations with a concurrent aircraft overflight. When all the stations are considered as an ensemble, it appears once again that the fluorescence per unit pigment concentration was quite variable in the sampling area. In figure 8 with a smaller dataset, Station 20 appears as an outlier. However, the additional points in figure 11 confirm that Station 20 reflects real variability in the fluorescence yield in the field. The in situ fluorescence and the remotely sensed fluorescence are not directly comparable: the former technique measures fluorescence from a small volume of water induced by a small light source within the instrument, whereas the latter
measures sunlight-induced fluorescence from a much larger volume of water. However, the *in situ* data do provide evidence to support the argument that the features seen in figure 10(a) are truly indicative of real variability in fluorescence.

Figure 10. (a) Map showing the distribution of fluorescence line height (FLH) normalized to chlorophyll-a concentration (estimated using bands 4 and 7, see text for details) in the study area. (b) scatter plot of FLH vs chlorophyll-a concentration (estimated from bands 4 and 7) and (c) frequency distribution of the FLH:Chl ratio.
yield, rather than just noise in the algorithms. Thus, it is now becoming possible to realize the potential for the use of remote sensing to map the photo-physiological state of phytoplankton. Satellite sensors such as MERIS would make it possible to apply similar methods at the global scale.

7. Conclusion

In our field surveys, we did not measure absorption by coloured dissolved organic matter for use in the model simulations. However, we did have measurements of DOC concentrations, which could be used for an indirect validation of the model, and to establish the potential influence of yellow substance on reflectance spectra. It should, however, be pointed out that it is not always necessary that DOC be correlated with the coloured component of DOC. It was fortuitous in this case that it was so in the study area, and that it could be used for validation of the model. But our results appear to suggest that, at least in those areas where such a relationship exists, it should be possible to use remotely sensed data to map DOC concentrations in the surface waters.

The study presented here highlighted some important differences between the absorption-based algorithm and fluorescence-line-height based algorithm for mapping pigment distribution. We have \textit{a priori} no reason to doubt the performance of one over the other, and the intriguing and exciting possibility
exists that the differences reflect real differences in fluorescence yield, and that these are indicative of variability in the photosynthetic properties of phytoplankton, as shown by Topliss and Platt (1986) for another area. Thus, these results support the suggestion that absorption-based algorithms and fluorescence-based algorithms be treated as independent methods that bring complementary information (IOCCG 1999), rather than as two techniques that yield the same result.

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