Application of Spectral Signatures and Colour Ratios to Estimate Chlorophyll in Singapore’s Coastal Waters

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In this paper, a study of the spectral signatures of coastal surface waters in the Johor and Singapore Straits and the application of colour ratios to estimate chlorophyll is presented. In general, the spectral signatures of coastal waters in Singapore could be represented by two profiles. The first was characterized by a high major reflectance peak at 577 nm which decreased toward the blue and near infra-red (NIR) bands. Such a profile was obtained when chlorophyll levels were low (less than 5 µg l\textsuperscript{-1}). The second profile, which was obtained during periods of high chlorophyll (greater than 10 µg l\textsuperscript{-1}), was characterized by an overall lower reflectance over the visible spectrum, with a distinct absorption trough at 672 nm and reflectance peak at 695 nm. In general, suspended solids (ranging from about 4 to 100 mg l\textsuperscript{-1}) increased reflectance in the green wavebands relative to the red/NIR region. The effect of dissolved organic carbon on the reflectance spectra was generally considered small due to its low concentration (<3 mg l\textsuperscript{-1}). Blue-Green and Red-Near Infrared colour ratios were correlated with chlorophyll \(a\), with the latter generally producing better correlations (\(R^2=0.63\)).

\textbf{Keywords:} spectroscopy; chlorophyll; remote sensing; water quality; suspended matter; coastal

\section*{Introduction}

Traditionally, monitoring of coastal eutrophication is carried out through ship-board water sampling and laboratory analysis for phytoplankton, chlorophyll and nutrient concentration. Such methods are not only labour-intensive, but sampling is also discrete in time and space and so there are limits when bloom areas are very large or inaccessible. Remote sensing offers an alternative method for monitoring water bodies on a large scale and is especially useful for providing synoptic views of algal distributions.

The coastal waters of Singapore are significantly influenced by anthropogenic inputs from both land-based and ship-based sources. As urban development continues, one concern is the potential for eutrophication and the incidence of harmful algal blooms. In order to use remote sensing for assessing the extent of eutrophication, an understanding of the composition of the reflected irradiance signature together with ground-truth measurements of water quality are needed. While remote sensing has been used extensively for both marine and coastal waters in temperate zones (Doerffer, 1992; Gitelson, 1993; Gitelson et al., 1993; Kirk, 1994; Arenz et al., 1996; Han & Rundquist, 1997; Thiemann & Kaufmann, 2000), the applications to coastal waters in South East Asia have been less frequent (Nichol, 1993). Furthermore, the analysis of tropical coastal waters is made more difficult by the complicated effects of varying amounts of photosynthetic pigments, dissolved organic matter (mainly fulvic and humic acids) and suspended sediments (Meybeck, 1988). Large quantities of suspended matter generated from storm runoff and construction activity can cause significant backscattering of light (Milliman & Syvitski, 1992; Nittouer et al., 1995; Loneragan & Bunn, 1999), while dissolved organic matter strongly absorbs radiation, mainly in the blue part of the spectrum (Mobley, 1994; Jorgenson, 1999). These effects are
superimposed on the reflectance spectra of phytoplankton, complicating the derivation of algorithms to estimate the level of algal biomass using remotely sensed data.

In this study, the spectral signatures of water reflectance were measured using a portable spectroradiometer, together with ground-truth measurements of chlorophyll and suspended matter, for selected locations in the Johor and Singapore Straits. Correlations between chlorophyll and spectral colour ratios (i.e. Blue-Green and Red-NIR) were derived from the field data. This was to facilitate a characterization of coastal waters, typical of the tropics, to assist in the interpretation of water quality parameters from remote sensing images.

**Materials and methods**

**Study area**

The main sampling survey was carried out in the eutrophic waters of the East Johor Strait at Paku (Station 1, depth 20 m), Sajahat (Station 2, depth 15 m) and Squance (Site 3, depth 12 m) from June, 1997, to December, 1998 (Figure 1). Sampling at these stations was conducted on a fortnightly basis during neap tide. In addition to the routine sampling surveys in the East Johor Strait, selected field surveys were conducted in the West Johor Strait in September, 1999 (seven Stations: W1–W7); East Johor Strait in November, 1999 (seven stations: E1–E7) and Singapore Strait in August, 1999 (nine stations: S1–S9) (Figure 1). This was to provide additional data for comparison with the main sampling survey in the East Johor Strait.

**Field sampling and laboratory analysis**

A hand-held field spectroradiometer (GER 1500, 350 nm to 1050 nm) was used to measure the radiance reflected by the seawater. The % absorption or reflection of sunlight by the water body and magnitude of incident light were measured by taking readings off a teflon diffusing screen (Labsphere Spectralon Reflective Target), which was specially designed and calibrated to reflect white light with minimum absorption. In addition, auxiliary water quality parameters (i.e. temperature, salinity, pH and dissolved oxygen) were measured *in situ* at each station. Surface water samples were also collected and stored in 2·5 l dark polyethylene bottles. These were stored in ice during transport and subsequently filtered for chlorophyll *a* and total suspended solids (TSS) i.e. within 4 h. Samples for dissolved organic carbon were collected in 30 ml glass test tubes, fixed with phosphoric acid and then wrapped in foil.

Chlorophyll *a* was measured according to the method of Strickland and Parsons (1968). Seawater samples (500 ml) (in triplicate) were filtered through 0·45 μm membrane filters, which were then wrapped
in foil and stored in a freezer at \(-20^\circ\text{C}\) before extraction. Acetone (90\%) was used to dissolve the filters together with the algae residue (Parsons et al., 1984). Chlorophyll extracts were then sonicated for 3 min to disrupt phytoplankton cells, refrigerated at 4 \(^\circ\text{C}\) for 24 h, concentrated in a centrifuge (4000 rpm, 16 min) and then analysed with a spectrophotometer (Shimadzu UV160a). Chlorophyll concentration was calculated using the equations developed by Jeffrey and Humphrey (1973).

In the analysis of total suspended solid concentration (TSS), 250 ml seawater samples were filtered in triplicate through pre-weighed 0·7 \(\mu\text{m}\) GF/F filters, within 4 h of collection. The filtered samples were then placed in aluminum weighing dishes and dried at 105 \(^\circ\text{C}\) for 2 h in an oven (Parsons et al., 1984). After heating, the weighing dishes were placed in a dessicator overnight prior to weighing on an analytical balance. This process was repeated until constant mass readings were achieved. Inorganic sediments were obtained in a similar manner after combustion in a furnace at 550 \(^\circ\text{C}\). Samples for dissolved organic carbon (DOC) were filtered through 0·7 \(\mu\text{m}\) GF/F filters and analysed with a TOC Analyser.

### Colour ratio

The basic principle of colour ratios involves two wavebands which show characteristic optical trends of chlorophyll: one corresponding to high absorption and the other, low absorption. In ocean colour remote sensing, the four characteristic bands related to chlorophyll are the blue, green, red and near infra-red (NIR) bands (Dekker et al., 1991; Mittenzwey, 1992; Han et al., 1994; Han & Rundquist, 1997). In this study, three sets of Blue-Green ratios (443/520, 443/550 and 440/577) and a Red-NIR ratio (672/695) were tested.

### Results

#### Water quality in the coastal waters of Singapore

In the context of remote sensing, the three main water quality parameters contributing to surface irradiance are chlorophyll pigments, suspended sediments and dissolved organic substances (yellow substances). However, as the concentrations of dissolved organic substances were relatively small (mean=2·89 mg l\(^{-1}\) in the Johor Strait and 1·37 mg l\(^{-1}\) in the Singapore Strait), the main emphasis of this paper is on chlorophyll and suspended sediments. The supporting measurements of temperature, salinity and nutrients are shown in Table 1.

Over the period of study, chlorophyll levels fluctuated widely in the East Johor Strait, ranging from 0·5 \(\mu\text{g l}^{-1}\) to 139·4 \(\mu\text{g l}^{-1}\,\text{gl}^{-1}\) with an average value of 10·4 \(\mu\text{g l}^{-1}\). Squance generally showed higher chlorophyll concentrations (average=18·1 \(\mu\text{g l}^{-1}\)) compared to Paku (7·1 \(\mu\text{g l}^{-1}\) and Sajahat (5·9 \(\mu\text{g l}^{-1}\)), partly due to its closer proximity to caged fish farms and its shallow water depth, making it more prone to eutrophication.

The total suspended solids concentration in the East Johor Strait was also highly variable over the period of study. TSS ranged from 2·9 mg l\(^{-1}\) to 28·8 mg l\(^{-1}\) (annual mean=13·6 mg l\(^{-1}\)) in 1997 and from 7·0 mg l\(^{-1}\) to 72·6 mg l\(^{-1}\) (annual mean=26·5 mg l\(^{-1}\)) in 1998. Inorganic sediments varied from a low of 2·9 mg l\(^{-1}\) (Squance) to 45·5 mg l\(^{-1}\) (Sajahat), partly due to its closer proximity to caged fish farms and its shallow water depth, making it more prone to eutrophication.

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**Table 1. Summary of temperature (T), salinity (S), pH, dissolved oxygen (DO) and nutrient measurements (total nitrogen: TN, total phosphorus: TP) in the Singapore and Johor Straits**

<table>
<thead>
<tr>
<th></th>
<th>T ((^\circ\text{C}))</th>
<th>S (ppt)</th>
<th>pH</th>
<th>DO (mg l(^{-1}))</th>
<th>TN (mg l(^{-1}))</th>
<th>TP (mg l(^{-1}))</th>
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<td>38</td>
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<tr>
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<td>Average</td>
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<td>28·2</td>
<td>7·9</td>
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<tr>
<td></td>
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the other stations, consistent with its higher chlorophyll concentration. Dissolved organic carbon (DOC) ranged from 1.13 to 4.54 mg l\(^{-1}\) in 1997 (annual mean = 2.89 mg l\(^{-1}\)) and remained relatively unchanged in the following year, 1998 (1.50 mg l\(^{-1}\) to 3.03 mg l\(^{-1}\)).

The chlorophyll levels in the Singapore Strait are generally lower than that of the Johor Strait, averaging about 1.7 µg l\(^{-1}\), consistent with its lower nutrient content. During the field sampling of the Singapore Strait in August, 1999, chlorophyll levels ranged from 0.5 to 2.4 µg l\(^{-1}\) while TSS ranged from 93.7 to 125.7 mg l\(^{-1}\) (inorganic content >90%). The exceptionally high levels of TSS for this particular survey are likely due to reclamation activities carried out in the nearby islands of Pulau Semakau and Jurong Island. In general, the DOC concentration (mean = 1.37 mg l\(^{-1}\)) in the Singapore Strait was about half that in the Johor Strait. This is mainly due to the higher levels of primary production and organic detritus in the Johor Strait arising from higher nutrient loading (Gin et al., 2000).

Spectral reflectance profiles

The spectral data collected from Paku, Sajahat and Squance can be classified into two general groups, depending primarily on chlorophyll concentration, with suspended solids playing a less important role (Figure 2). Waters with low chlorophyll concentration (<5 µg l\(^{-1}\)) can be characterized by spectra with high reflectance peaks at 577 nm, smaller absorption troughs at 672 nm and smaller reflectance peaks at 695 nm. Conversely, when chlorophyll levels are high (greater than 10 µg l\(^{-1}\)), the reflectance spectra are flatter, with differences between the peaks at 577 nm and 695 nm being much smaller. In addition, a small peak at 719 nm was also observed, which was not as apparent when chlorophyll levels were below 5 µg l\(^{-1}\). For both groups of spectra, random peaks and troughs (due to noise) were observed beyond 900 nm.

Colour ratios

Calculation of the Red-NIR (672/695) ratio using the combined data from the East and West Johor Straits showed a reasonably good power correlation (R\(^2\) = 0.68, n=102) (Figure 6), in contrast to the
Blue-Green ratios (i.e. 443/520, 443/550 and 440/577) (average $R^2 = 0.27, 0.15$ and $0.05$ respectively, $n = 102$). When the data was analysed according to location, spectra from the West Johor Strait gave good correlations with chlorophyll for both the Blue-Green and Red-NIR ratios ($R^2 = 0.90, 0.89, 0.81$ and $0.84$ for the ratios 443/520, 443/550, 440/577 and 672/695 respectively) (Figure 7). In the November survey of the East Johor Strait, a relatively good negative correlation was obtained between the Red-NIR ratio (672/695) and chlorophyll ($R^2 = 0.79$) while the Blue-Green ratio 443/520 produced a positively sloped power curve, with an $R^2$ of $0.66$. However, no correlation was obtained between any colour ratio and chlorophyll for data from the Singapore Strait ($R^2 = 0.05$, $n = 49$). This was partly due to the small range in chlorophyll measured for these waters (i.e. between 1 and $2.4 \mu g l^{-1}$). No significant correlation was also observed when both data sets from the Johor and Singapore Straits were combined.

**Discussion and conclusions**

In turbid, productive coastal waters, the varying compositions of suspended matter, DOC and phytoplankton make it difficult to apply universal remote sensing models for predicting water quality compared to open ocean waters. For this reason, many site-specific models have been developed using ground-truth data from a variety of environments (Hinton, 1991; Aguirre-Gomez, 2000; Kratzer et al., 2000; Millie et al., 1995), including studies of chlorophyll in a number of temperate coastal waters e.g. North Wales (Kratzer et al., 2000), the Irish Sea (Bowers & Mitchelson-Jacob, 1996), Chesapeake Bay (Harding et al., 1992) and Nantucket Shoals (Campbell & Esaías, 1985). In this study, we examine the reflectance spectra from the tropical, coastal waters of Singapore, in combination with ground-truth data. Unfortunately, the results could not be extrapolated to remote sensing data as significant cloud cover was present at the time of sampling. Nevertheless, the salient features of the captured spectra act as a preliminary step towards the development of algorithms for remote sensing applications of this region in the future.

**Characteristics of the reflectance spectra from coastal waters of Singapore**

All spectral profiles measured showed high absorption in the UV and blue bands. High absorption in the UV bands has been attributed to water itself (Quikenden & Irvin, 1980), particularly in the presence of dissolved oxygen (Kirk, 1994), while absorption in the blue wavelengths is due primarily to chlorophyll and dissolved organic carbon (DOC) (Mobley, 1994).
Chlorophyll pigments play a particularly important role in the absorption of blue light, generally leading to low reflectance between 400 and 500 nm (Vertucci, 1989; Dekker et al., 1991; Gitelson, 1993; Arenz et al., 1996). Phytoplankton carotenoids (accessory pigments) can also strongly influence absorption at wavelengths near 440 nm (Kirk, 1994). In addition, DOC absorb predominantly at the blue and UV wavelengths (Mobley, 1994; Jorgenson, 1999). However, DOC also absorbs light across other wave-
lengths of the spectrum that might otherwise have been backscattered, thus reducing the potential for reflectance (Witte et al., 1982; Dekker, 1993). A water body with DOC as its primary component (e.g. 55 mg l\(^{-1}\)) reflects very little light and the reflectance is relatively uniform across the spectrum (Arenz et al., 1996). Witte et al. (1982) showed that higher DOC concentrations lead to a considerable decrease in reflectance at 550 nm and 650 nm and a slight decrease at 750 nm. However, in the present study, such trends were not observed as the DOC levels of water in the Johor and Singapore Straits were typically lower than 5 mg l\(^{-1}\).

Besides increased absorption by water in the red and NIR bands, two other optical trends characteristic of chlorophyll pigments were observed in these bands. The first was a minor absorption trough at 672 nm, followed by a fluorescence peak at 695 nm. Absorption at 672 nm is due mainly to absorption by chlorophyll \(a\) pigments (Mobley, 1994) and to a lesser extent, absorption by oxygen and water (Gower, 1999). The secondary reflectance peak at 695 nm is due primarily to sun-induced fluorescence of chlorophyll \(a\). Chlorophyll \(a\) has a natural sun-stimulated fluorescence at 684 nm and 690 nm, leading to a peak at approximately 690 nm (Carder & Stewart, 1977; Vertucci, 1989; Babin, 1996). The cause of the prominent reflectance peak in the NIR region has also been explained by anomalous scattering caused by the absorption minima at 675–680 nm (Morel & Smith, 1977) and a minimum in the combined absorption curves of algae and water (Vos et al., 1986). However, the peak at 684 nm was not observed in our data, presumably due to the influence of suspended matter and DOC, which helped to mask the fluorescence emission peak at 684 nm (Vertucci, 1989).

Atmospheric oxygen, with absorption at 687 nm, also increases this masking effect (Gower, 1990). Another reason for the deviation from the expected 684 nm is due to strong absorption by water itself at the end of the red spectrum, near the infra-red zone. Similar results were also published by Kirk (1994) and Morel and Smith (1977).

Unlike typical Case 1 waters (i.e. phytoplankton dominating waters in the open ocean) where the water appears blue in colour, Singapore waters are generally greenish/brown due to the combined effects of chlorophyll, sediments and DOC i.e. reflective of Case 2 waters (Nichol, 1993). Being a semi-enclosed water body with high nutrient inputs from a number of point and non-point sources, the Johor Strait is a eutrophic system with highly fluctuating chlorophyll levels (Gin et al., 2000). In comparison, the waters in the Singapore Strait are more open and subject to strong tidal currents and mixing and thus, have generally lower chlorophyll concentrations than in the Johor Strait. In both cases, a distinct reflectance peak in the green spectrum (maximum at 577 nm) is observed, which is the result of low absorption by chlorophyll, coupled with background scattering due to particulates (Dekker & Peters, 1993). Note that in an earlier study, we examined the effects of suspended marine clay on phytoplankton reflectance spectra under controlled conditions (Gin et al., 2001a) and found that natural clays tended to increase the amount of green reflectance relative to the red/NIR region. This supports the field data results where high suspended solids concentrations were observed in the Singapore Strait (~100 mg l\(^{-1}\)) and Johor Strait (up to about 80 mg l\(^{-1}\)).

As chlorophyll concentration increased, relatively greater reflectance was observed in the NIR region compared to the blue-green waveband, with more prominent peaks at 695 nm and 719 nm. In addition,
the overall reflectance profile is generally flatter for high chlorophyll waters than those from low chlorophyll waters, consistent with higher absorption in the former. These changes are consistent with an earlier study under controlled conditions (Gin et al., 2001a) as well as other studies of inland reservoirs and lakes (Gitelson, 1992; Arenz et al., 1996; Thiemann & Kaufmann, 2000). Roesler and Perry (1995) also showed that the maximal reflectance in estuarine waters with very high chlorophyll concentrations (>25 µg l⁻¹) generally occurred at around 565 nm.

In the case of some of the reflectance spectra from the East Johor Strait, the peaks are spread over a wider range of wavelengths, from about 480–580 nm. In an earlier study, we investigated the effects of suspended marine clay on the reflectance spectra of water under controlled conditions (Gin et al., 2001b). In that study, we found that the presence of organic material in natural marine clays gave a broad peak between 440 to 580 nm, similar to the broad peaks observed in the additional spectra captured from the East Johor Strait (Figure 4). Although the concentration of suspended solids was somewhat lower than that of the Singapore Strait, the organic content of suspended solids in the East Johor Strait (~30%) was slightly higher than the Singapore Strait (<10%). Thus, this could be one factor contributing to the spectral widening in the green band. Another reason could be the result of reabsorption of fluoresced photons by chlorophyll (Collins et al., 1985).

**Colour ratios**

From the results, it appears that as chlorophyll increases, the power correlations of Blue-Green and Red-NIR ratios with chlorophyll approach some constant value. Thus, for very high levels of chlorophyll, the difference in colour ratio may become insignificant and the technique of applying colour ratios to estimate chlorophyll may be less effective. This was also highlighted by Jorgenson (1999) who found that estimating high concentrations of chlorophyll was often difficult due to the loss in sensitivity of the Blue-Green ratio when chlorophyll absorption became more extensive.

In our study, a comparison of the Blue-Green and Red-NIR colour ratios for data from the Johor Strait shows that the Red-NIR ratio consistently produces better correlations with chlorophyll, despite its weaker penetration powers at 672 and 695 nm. Other studies of inland lakes have also shown the Red-NIR ratio to be a more effective predictor of chlorophyll

Figure 7. Correlation between chlorophyll concentration and the (a) Blue-Green ratios 443/520, (b) 443/550, (c) 440/577 and (d) the Red-NIR ratio (672/695) for data collected in the West Johor Strait.
The Blue-Green ratio is less effective because the greater signal noise in the blue and green bands as a result of the greater penetration power of blue and green wavebands, compared to the red and near infra-red bands. Singapore coastal waters are relatively shallow, especially in the Johor Strait where water depths are often less than 15 m during neap/low tide sampling. The deeper the light penetration, the greater the signal noise generated as a result of bottom sampling. Another factor is the presence of DOM. While overall concentrations of DOM in Singapore waters are low, the levels in the Johor Strait are twice that of the Singapore Strait. This could have some influence since DOM, like chlorophyll, preferentially absorbs radiation in the 400–500 nm range (Davis, 1980; Davies-Colley, 1983; Arenz et al., 1996), thus enhancing the dominance of the green peak and hence, the application of the Blue-Green ratio (Jorgenson, 1999).

Thus, the different compositions of suspended sediments and dissolved organic substances in the Johor and Singapore Straits imply that application of a single colour ratio for estimating chlorophyll may be difficult. In extrapolating the spectral results of this study to remote sensing, the difficulty is further exacerbated by the limited spatial and spectral resolution of most space-borne ocean colour sensors (Cracknell, 1999; Doerffer et al., 1999). Without adequate spectral resolution, for example, it will be difficult to discriminate the various optically active parameters, such as phytoplankton pigments, DOC and suspended sediments. These are some of the limitations of existing satellites, such as the Coastal Zone Color Scanner (CZCS) (Barale & Doerffer, 1993). Richardson et al. (1994) also showed the importance of bandwidth in the application of remote sensing for monitoring chlorophyll, as many of the absorption peaks of chlorophyll are very narrow. Furthermore, the reflectance spectra of algae-laden waters consist of the overlapping spectra of individual pigments in a natural population of mixed species (Lillesand & Kiefer, 1994). Nevertheless, the launch of new hyperspectral remote sensors, with better spatial and temporal resolution in the nearby future will help to remedy some of these problems. One promising example is MERIS, which will also be the first satellite to measure the natural, sunlight-stimulated fluorescence of chlorophyll. This method has been shown to work for airborne detection of chlorophyll concentrations in Case 2 waters, where the high concentrations of DOC and suspended matter may pose a problem (Gower, 1999; Doerffer et al., 1999).

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