1. Introduction

Variations in the optical reflectance of shelf seas are generated by changes in the concentrations of three classes of optically significant constituents (OSCs): phytoplankton cells, suspended mineral particles, and dissolved coloured organic matter (Kirk, 1994). Optical remote sensing has great potential value for mapping water-quality indicators in these waters (Hu et al., 2004), but attempts to devise empirical algorithms that are capable of simultaneously deriving the concentrations of all three constituents have encountered considerable difficulties (Robinson, 2008; Sathyendranath, 2000). Semi-analytical approaches based on neural networks (Doerffer & Schiller, 2007; Schiller & Doerffer, 1999; Tanaka et al., 2004) or spectral matching (Kuchinke et al., 2009a, b; Lee et al., 1999; Maritorena et al., 2002; van der Woerd & Pasterkamp, 2008; Zawada et al., 2007) offer substantially improved performance, but rely heavily on the quality of the spectral libraries which they employ in look-up tables (in the case of spectral matching) or as training data sets (for neural networks). The recovery of suspended mineral concentrations without accurate estimates of the other optically significant constituents would appear to be a simpler problem, and single-band reflectance algorithms operating in the visible region have been proposed for this purpose (Binding et al., 2003, 2010; Nechad et al., 2010; Sipelgas et al., 2009; Tzortziou et al., 2007). It is necessary, however, to draw a distinction between waters whose optical properties are dominated by suspended mineral particles and those where suspended minerals exert a significant influence but are not present in sufficiently high concentrations to mask the contribution of the other components. Methods for quantifying suspended mineral concentrations in the first, highly turbid, category have recently been proposed by Hommersom et al. (2010). To date, however, there have been no systematic studies of the performance of suspended mineral algorithms in moderately turbid waters where the interfering effects of non-mineral seawater constituents are likely to be significant. The moderately turbid category includes a large proportion of the world’s shallow shelf seas (Shi & Wang, 2010). This paper therefore presents a case study of a semi-enclosed sea and
adjacent estuary (the Irish Sea and Bristol Channel) whose waters exhibit marked spatial and seasonal variability in remote sensing reflectance which is largely driven by changes in the concentrations of suspended mineral particles (Binding et al., 2003; Bowers, 2003). The aim is not to propose a definitive algorithm for recovering suspended mineral concentrations, but to investigate how the optical interactions between pure seawater and its constituents constrain the performance of such algorithms in moderately turbid coastal waters.

2. Methods

2.1. Background theory

Morel and Prieur (1977) suggested that, in cases where inelastic scattering can be neglected, irradiance reflectance ($R$) just below the surface can be related to the backscattering coefficient ($b_b$) and absorption coefficient ($a$) by an expression of the general form

$$ R = \frac{E_u(W)}{E_d(W)} = f_{e,n} \frac{b_b}{a} $$

where $E_u(W)$ is the upward planar irradiance, $E_d(W)$ the downward planar irradiance and the factor $f_{e,n}$ is a variable function of the radiance distribution and volume scattering function. Values for $f_{e,n}$ are difficult to derive from first principles, but early studies using Monte Carlo techniques (Kirk, 1981, 1994; Morel & Prieur, 1977) suggested that Eq. (1) could be approximated by

$$ R \approx C(\mu_b) \frac{b_b}{a} $$

where $C(\mu_b)$ is a function of the mean cosine of the photon distribution just below the surface. The value of $C(\mu_b)$ is therefore strongly dependent on the zenith angle of the refracted solar beam, and is also influenced by the volume scattering function. Converting subsurface irradiance reflectance, $R$, to remote sensing reflectance, $R_{rs}$, requires the introduction of additional terms:

$$ R_{rs} = \frac{L_{w}(a)}{E_o(a)} = \frac{\Gamma}{Q} R $$

where $L_{w}(a)$ and $E_o(a)$ are the vertical water-leaving radiance and downward irradiance in air just above the surface, $\Gamma$ is the ratio of up-welling irradiance to radiance just below the surface, and $Q$ represents the optical processes involved in light crossing the air-water interface (Mobley, 1999). Combining Eqs. (2) and (3) gives

$$ R_{rs} \approx \left[ \frac{C(\mu_b)\Gamma}{Q} \right] \frac{b_b}{a} $$

For a sufficiently restricted set of conditions, which includes a fixed solar angle, cloud-free sky, and limited range of IOP values, the terms enclosed in brackets in Eq. (4) are relatively invariant (Kirk, 1994; Mobley, 1999). The notation can then be simplified by aggregating them as a single parameter:

$$ R_{rs} \approx \kappa \frac{b_b}{a} $$

However $\kappa$ is not strictly a constant of proportionality, and the degree to which it can be treated as such varies from case to case and has to be established numerically. The values of the backscattering and absorption coefficients ($b_b$ and $a$) depend on the concentrations of the main optically significant constituents in the water column, and these are commonly quantified by measuring three proxy variables: the concentration of solvent-extracted chlorophyll (a) (CHL) for phytoplankton; the absorption (relative to pure water) of membrane-filtered seawater at 440 nm (CDOM) for coloured dissolved organic matter; and the total dry weight of material retained on a glass fibre filter after combustion (MSST) for suspended minerals. Total inherent optical properties can be calculated by multiplying the concentration of each constituent by the appropriate specific inherent optical property (SIOP), so that for a given wavelength ($\lambda$)

$$ b_b(\lambda) = b_{b,W}(\lambda) + b_{b,MSST}(\lambda) + b_{b,CHL}(\lambda) $$

$$ a(\lambda) = a_{W}(\lambda) + a_{MSST}(\lambda) + a_{CHL}(\lambda) + a_{CDOM}(\lambda) $$

where asterisks indicate SIOPs, and subscripts indicate constituents (with $W$ for pure seawater). Combining Eqs. (5), (6) and (7), and dropping the notation of wavelength dependence for brevity:

$$ R_{rs} \approx \kappa \frac{b_{b,W} + b_{b,MSST} + b_{b,CHL}}{a_{W} + a_{MSST} + a_{CHL} + a_{CDOM}} $$

Eq. (8) emphasises the point that the relationship between $R_{rs}$ and the OSM concentrations depends on the ratio of the total backscattering and absorption coefficients, not the backscattering to absorption ratios of the individual constituents, and illustrates the importance of the SIOPs in formulating this relationship. Unfortunately, very few complete sets of the relevant SIOPS exist and none have been published for European shelf seas.

2.2. Study location

Measurements of constituent concentrations and inherent optical properties were carried out at 173 stations, occupied between 2000 and 2006, at the positions plotted in Fig. 1a. Since chlorophyll concentrations above 4 mg m$^{-3}$ were rarely encountered in the Irish Sea and Bristol Channel during this survey, data from adjacent Scottish west coast waters (Fig. 1b.) were included to obtain adequate estimates of phytoplankton optical properties. Radiometer casts for validating the results obtained by radiative transfer modelling were made at a subset of the stations occupied, and these stations are indicated by filled symbols in Fig. 1.

2.3. In situ measurements

Temperature and salinity profiles were measured using a SeaBird SBE 19 CTD. Non-water absorption and beam attenuation coefficients ($\alpha_{nw}$ and $c_{nw}$) were measured in nine wavebands (412, 440, 488, 510, 532, 555, 650, 676 and 715 nm) using WET Labs ac-9 or ac-9 plus instruments which were calibrated using Milli-Q ultra pure water. The ac-9 data were corrected for differences in temperature and salinity between the seawater samples and the pure water used for calibration according to the procedures described in the in ac-9 protocol manual (WET Labs) using coefficients from Sullivan et al., 2006 and CTD profiles obtained at the same time as the ac-9 deployments. Absorption measurements were subsequently corrected for the incomplete collection of scattered light using the ‘proportional’ method of Zaneveld et al., 1994, and non-water scattering coefficients ($b_{nw}$) were derived by subtracting $\alpha_{nw}$ from $c_{nw}$. The Zaneveld correction method sets $\alpha_{nw}$ to zero at 715 nm, and assumes that absorption by suspended particles and dissolved substances can be neglected in the near infra-red waveband. Whilst some early studies supported this assumption (Babin & Stramks, 2002, 2004; Stramks & Wozniak, 2004), its validity is increasingly being questioned (Leymarie et al., 2010; Tassan & Ferrari, 2003; Tzortziou et al., 2006). Monte Carlo modelling of the effect of significant infra-red absorption by mineral particles on ac-9 correction procedures (Leymarie et al., 2010) suggested that $\alpha_{nw}$ could be underestimated by up to 5% at 412 nm and 50% at 676 nm in waters whose optics were dominated by these particles. However this analysis was based on the assumption...
that the absorption coefficient of non-algal particles at 750 nm was 25% of its value at 440 nm, which is at the upper end of the range reported by Tassan and Ferrari (2003) for marine sediments and considerably higher than the 5% suggested by Tzortziou et al. (2006). It is clear that errors in $a_{\text{bbp}}$ arising from the Zaneveld ac-9 correction procedure are most pronounced in the red and near infra-red wavebands, but there is continuing uncertainty regarding their magnitude. The impact of these errors on calculations of remote sensing reflectance is mitigated by the dominant role played by water absorption in this spectral region (see Section 3.3).

Backscattering coefficients ($b_{\text{bbp}}$) in two wavebands centred on 470 nm and 676 nm were measured using a HOBI Labs HS-2 backscattering meter. Compensation for absorption and scattering was applied using the ‘sigma correction method’ recommended by the manufacturer with coefficients calculated from the $a_{\text{bbp}}$ and $b_{\text{bbp}}$ values recorded by the ac-9 during each deployment. Particulate backscattering coefficients ($b_{\text{bbp}}$) were obtained by subtracting the water contribution, which was taken to be half the total scattering values measured by Smith and Baker (1981). Since the HS-2 measured backscattering in only two wavebands, it was necessary to extrapolate between them to obtain values for radiative transfer modelling. Deployment of the HS-2 alongside a Wet Labs ECO BB9 instrument is subsequent cruises confirmed that linear extrapolation between the HS-2 channels at 470 nm and 676 nm gave values within $+/-20\%$ of those measured by the BB9 within this wavelength range.

In situ radiometric data were collected using a Satlantic SPMR profiling radiometer which measured downwards planar irradiance ($E_d$) and upward irradiance ($I_u$) in 10 nm wavebands centred on 412, 443, 490, 510, 554, 665 and 700 nm. SPMR casts were carried out at least 20 m from the ship to avoid shadow effects, and two casts were averaged for each station. It was not possible to make all the measurements under conditions suitable for satellite remote sensing, and stations with significant cloud cover and occasionally low solar angles were included in the data set. Values for water-leaving radiance and above-surface downward irradiance, which are required for calculations of remote sensing reflectance, were derived by extrapolating SPMR profiles through the air-sea interface using the expressions quoted in the Satlantic ProSoft manual. However since the available version of this code (ProSoft 7.7) contained an error in handling near-surface data, profiles were processed using Matlab scripts written for the purpose.

2.4. Concentrations of optically significant constituents

For CHL determinations, which were carried out in triplicate, water samples were filtered through 25 mm GF/F filters and immediately frozen. Phytoplankton pigments were extracted by soaking the filters for 24 h in neutralised acetone at 4 °C, followed by centrifugation and measurement of the absorbance spectrum of the supernatant relative to an acetone blank in 1 cm path length cuvettes. The measurement was repeated after acidification with dilute hydrochloric acid. Chlorophyll a concentrations were then calculated using the trichromatic equations of Jeffrey and Humphrey (1975). Suspended particles were collected by filtering 5 l of seawater through pre-weighed 90 mm GF/F filters and rinsing with 500 ml of distilled water. The filters were stored frozen until returned to the laboratory, where they were dried to a constant weight in an oven at 100 °C and reweighed to obtain the concentration of total suspended solids (TSS). Values of total mineral suspended solids (MSS$_T$) were obtained by reweighing the filters after they had been placed in a furnace at 500 °C for 3 h, at which point it was assumed that all organic materials had been combusted. For determinations of CDOM, seawater samples were filtered through 0.2 μm membrane filters, with the filtrate being collected in acid-rinsed glass bottles and stored under refrigeration. Absorption by CDOM was measured in a spectrophotometer using 10 cm cuvettes with UV treated ultrapure water as a reference, with care being taken to allow the sample and reference to reach the same temperature before the measurements were carried out.

2.5. Specific scattering and backscattering coefficients

There is currently no available method for physically separating the contributions of different types of particles to the overall scattering coefficients of natural hydrosols. However by plotting MSS$_T$ against CHL for all stations (Fig. 2), it was possible to identify groups of points characterised by relatively high CHL and low MSS$_T$ (Group 1)
and by low CHL accompanied by high MSS\textsubscript{T} (Group 2). Stations falling into these groups were selected by setting thresholds of CHL >4 mg m\textsuperscript{-3} for Group 1 and MSS\textsubscript{T} >4 g m\textsuperscript{-3} for Group 2. Group 1 stations were located mainly in deep Scottish sea lochs, which generally have low concentrations of suspended sediment, whilst those in Group 2 were from relatively shallow, coastal areas of the Irish Sea and Bristol Channel with high suspended sediment concentrations. It was assumed therefore that the scattering properties of Group 1 were primarily determined by phytoplankton cells (measured as CHL) and those of Group 2 by mineral particles of terrigenous origin ([MSS\textsubscript{ter}]). Specific scattering coefficients, *b*\textsuperscript{CHL}(\(\lambda\)) and *b*\textsuperscript{CHL}(\(\lambda\)) for these two classes of material were estimated from the ratio of IOPs to OSCs for the stations in the two groups.

The remaining stations (Group 3) were not classifiable as being dominated by phytoplankton or suspended sediment in Fig. 2. However a plot of *b*\textsuperscript{bbp}(676 nm) against MSS\textsubscript{ter} (Fig. 3.) showed that most of these Group 3 stations were located in a distinct cluster with very low *b*\textsuperscript{bbp} values. These stations were located in areas of the Irish Sea with depths over 30 m and their distinctive optical characteristics included relatively low backscattering ratios, suggesting the presence of larger particles (Fig. 4a.), and absorption coefficients which were higher at 676 nm than at 650 nm, indicating the presence of a significant chlorophyll absorption peak (Fig. 4b.). Examination of samples from 23 of these stations by optical microscopy, carried out by colleagues at the University of Wales Bangor, showed the presence of a high proportion of colonial diatoms: mainly *Leptocylindrus* spp. and *Rhizosolenia* spp. in August 2001 and *Bacillaria paxillifer*, *Paralia sulcata* and *Melosira* spp. in April 2002. Cell concentrations were generally in the range 1 \times 10^4 cells l\textsuperscript{-1} to 5 \times 10^4 cells l\textsuperscript{-1}. We conclude that a significant fraction of the MSS\textsubscript{ter} measured at these stations consists of biogenic minerals in the form of diatom frustules ([MSS\textsubscript{dia}]), and that the contribution of this material to scattering and absorption should logically be included in the phytoplankton-related CHL component.

2.6. Specific absorption coefficients

Suspended particles were collected by filtering 500 ml of seawater through 25 mm diameter Whatman GF/F filters, which were stored frozen until their optical density could be measured. The measurements were made using a custom-built spectrophotometer with a highly collimated single beam in which the filters were placed immediately adjacent to a PTFE diffuser backed by a photomultiplier detector. The filters were moistened with filtered seawater and mounted on a glass slide so that the particle-loaded side of the filter was the first surface encountered by the illuminating beam. A clean filter, similarly wetted and mounted, was used as a blank. Optical density spectra were measured before and after the extraction of pigments in acetone, and subtraction of the two spectra allowed the contributions of phytoplankton pigments and non-algal particles to be determined. For consistency with the treatment of ac-9 data, optical densities were set to zero at 715 nm. The relationship between filter optical

![Fig. 2. Total suspended mineral concentrations (MSS\textsubscript{ter}) plotted against chlorophyll concentrations (CHL) for all stations in Fig. 1. Data were classified as Cluster 1 (high CHL: low MSS\textsubscript{ter}, indicated by triangles), Cluster 2 (low CHL: high MSS\textsubscript{ter}, indicated by open circles) and Cluster 3 (mixed composition, indicated by filled circles).](image)

![Fig. 3. Particulate backscattering at 676 nm (*b*\textsuperscript{bbp}(676)) plotted against total suspended mineral concentrations (MSS\textsubscript{ter}). Stations with a high proportion of diatoms are indicated by filled symbols and labelled MSS\textsubscript{dia}, others as MSS\textsubscript{ter}.](image)

![Fig. 4. Stacked bar charts showing bimodal distributions for the ratios of the coefficients of particulate backscattering to total particulate scattering at 676 nm (\(b_{bbp676}/b_{676}\)) and of non-water absorption at 650 nm to 676 nm (\(a_{bbp650}/a_{bbp676}\)). Stations with high diatom numbers, indicated by filled symbols in Fig. 3., are plotted as shaded bars.](image)
density (ODf) and the apparent absorption coefficient (af) for the material on the filter is given by

\[ a_f(\lambda) = \frac{2.303 \times OD_f(\lambda) \times A}{V} \]  

where A is the effective area of the filter and V the volume of sample filtered. The apparent absorption coefficients of particles collected on glass fibre filters is known to be greater than that of an equivalent concentration of particles in suspension (a_nis), the two coefficients being related by a path length amplification factor β

\[ a_{nis}(\lambda) = \frac{a_f(\lambda)}{\beta} \]  

whose numerical value varies with measurement methodology and filter loading (Bricaud & Stramski, 1990; Lohrenz, 2000; Tassan & Ferrari, 1998). The ‘transmittance plus reflectance’ technique proposed by Tassan and Ferrari (1998) can reduce this variability (Tassan et al., 2000) but it does not avoid the requirement for empirically derived coefficients. For the work reported here, we obtained a value for β by plotting the absorption coefficients with no pathlength compensation against the particulate absorption coefficients measured at the same location in situ using an ac-9. Spectrophotometer measurements were averaged over the 10 nm bandwidths covered by the ac-9 for this purpose. The resulting graph was clearly linear (Fig. 5.), with a gradient derived by geometrical mean regression of \( y = 1.73x \) and a coefficient of determination \( r^2 = 0.90 \).

Specific absorption coefficients for phytoplankton and mineral particles, \( a\text{chl}(\lambda) \) and \( a\text{MSSter}(\lambda) \) were calculated by dividing the absorption coefficients obtained from the analysis of samples on filters by the measured OSM concentrations. For CDOM, the spectral dependence of absorption was described by

\[ \frac{a(\lambda)}{a(440)} = e^{-5(\lambda-440)} \]  

(Bricaud et al., 1981) where \( a(440) \) is the absorption coefficient at 440 nm and the exponent 5 serves as the equivalent of an SIOP.

2.7. Radiative transfer modelling

Radiative transfer modelling of \( R_{rs}(\lambda) \) was carried out using EcoLight 5.0 (Mobley, Sequoia Scientific). In order to replicate typical conditions for acceptable satellite data acquisition, the solar zenith angle was set to 45°, the wind speed to 5 m s\(^{-1}\) and cloud cover to zero.

Specific inherent optical properties were taken from Table 1 with linear interpolation to cover the MODIS waveband of 667 nm. Particulate volume scattering functions were estimated by selecting Fournier–Forand phase functions with appropriate \( b_a/b_p \) ratios from the EcoLight library. Raman scattering was included in the calculations, but chlorophyll fluorescence was set to zero. Appropriate ranges of constituent concentrations were derived from field observations in the Irish Sea and Bristol Channel (McKee et al., 2007): these were 0–1.0 m\(^{-1}\) \( a(440) \) for CDOM, 0–10 mg m\(^{-3}\) for CHL and 0–20 g m\(^{-3}\) for MSSter. Values for the total inherent optical properties of a given volume of seawater were then calculated by summing the contributions of the individual constituents.

2.8. Satellite images

MODIS data for the Irish Sea was obtained from Goddard Distributed Active Archive Centre and processed in our laboratory using SeaDAS 6.1, using the default 2-band aerosol model with iterative NIR correction. Level 2 (\( R_{rs} \)) data was mapped to an equidistant cylindrical projection and further processing was carried out in MatLab.

3. Results

3.1. SIOPs for radiative transfer modelling

The aim of the radiative transfer modelling was to generate results that were broadly representative of relationships between reflectance and constituent concentrations in coastal waters rather than definitive for a particular station. Frequency distributions were therefore plotted for the SIOPs derived by the methods described above, and typical examples are shown in Figs. 6 and 7. In all cases, the calculated

Table 1

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>( a_{om} )</th>
<th>( b_{om} )</th>
<th>( a^{CHL} )</th>
<th>( a^{MSS} )</th>
<th>( a^{CDOM} )</th>
<th>( b^{CHL} )</th>
<th>( b^{MSS} )</th>
<th>( a^{CHL} )</th>
<th>( a^{MSS} )</th>
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<td>0.06</td>
<td>0.08</td>
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<td>0.12</td>
<td>0.4</td>
<td>0.00165</td>
<td>0.0162</td>
</tr>
<tr>
<td>440</td>
<td>0.0064</td>
<td>0.00490</td>
<td>0.08</td>
<td>0.06</td>
<td>1.0</td>
<td>0.12</td>
<td>0.4</td>
<td>0.00160</td>
<td>0.0160</td>
</tr>
<tr>
<td>488</td>
<td>0.0145</td>
<td>0.00316</td>
<td>0.06</td>
<td>0.04</td>
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<td>0.12</td>
<td>0.4</td>
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<td>0.00260</td>
<td>0.04</td>
<td>0.03</td>
<td>0.43</td>
<td>0.12</td>
<td>0.4</td>
<td>0.00148</td>
<td>0.0154</td>
</tr>
<tr>
<td>532</td>
<td>0.0444</td>
<td>0.00218</td>
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<td>0.02</td>
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<td>0.12</td>
<td>0.4</td>
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<td>0.015</td>
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<td>0.02</td>
<td>0.01</td>
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<td>0.12</td>
<td>0.4</td>
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</table>

SIOPs formed unimodal distributions with well-defined peak values. The most frequently occurring values were selected as representative SIOPs for modelling purposes, and these are listed in Table 1.

The width of these frequency distributions can be attributed to a combination of measurement error and intrinsic variability in specific optical properties between stations, and it is difficult to deconvolute these two factors. However the degree to which the peak values listed in Table 1 captured the variability in the inherent optical properties between stations, and it is difficult to deconvolute these two factors. However the degree to which the peak values listed in Table 1, absorption coefficients of chlorophyll (\(a^*_{\text{CHL}}\)) and terrigenous minerals (\(a^*_{\text{MSS}^*}\)) at 440 nm and for the CDOM absorption exponent (\(S_{\text{CDOM}}^*\)).

\[ a^*_{\text{CHL}} (440): \text{m}^2 \text{g}^{-1} \]

\[ a^*_{\text{MSS}^*} (440): \text{m}^2 \text{g}^{-1} \]

\[ S_{\text{CDOM}}^*: \text{nm}^{-1} \]

Fig. 6. Frequency distributions for the specific absorption coefficients of chlorophyll (\(a^*_{\text{CHL}}\)) and terrigenous minerals (\(a^*_{\text{MSS}^*}\)) at 440 nm and for the CDOM absorption exponent (\(S_{\text{CDOM}}^*\)).

**3.2. Comparisons of SIOPs with other data sets**

Table 1 makes no attempt to represent the spatial and temporal variability in SIOPs observed in more detailed studies (Babin et al., 2003a; Blondeau-Pattisier et al., 2009; Loisel et al., 2010), but the values listed are broadly comparable with those reported elsewhere in the literature. The logarithmic slope for CDOM absorption (0.012 nm\(^{-1}\)) is within the range found by Bricaud et al., 1981 (0.010–0.018 nm\(^{-1}\)) and a little below that reported by Babin et al., 2003a (0.016–0.020 nm\(^{-1}\)) and Tzortziou et al., 2007 (0.014–0.018 nm\(^{-1}\)). The estimate for \(a^*_{\text{CHL}}\) at 440 nm (0.08 m\(^2\) g\(^{-1}\)) is consistent with the measurements of Bricaud et al., 1983 for cultured cells (0.04–0.05 m\(^2\) g\(^{-1}\)) and of Babin et al., 2003a in European coastal waters (0.03 to 0.1 m\(^2\) g\(^{-1}\)). The value of 0.12 m\(^2\) g\(^{-1}\) for \(a^*_{\text{CHL}}\) at 440 nm falls within the range measured by Bricaud et al,1983 (0.07–0.18 m\(^2\) g\(^{-1}\)) and Weidemann & Bannister, 1986 (0.06 to 0.12 m\(^2\) g\(^{-1}\)). The method used to estimate \(b^*_{\text{CHL}}\) included any contribution of other particles which co-varied with chlorophyll, which may explain why the value of 1.6×10\(^{-3}\) m\(^2\) g\(^{-1}\) in Table 1 is rather higher than that measured by Bricaud et al., 1983 in cell cultures (1×10\(^{-3}\) to 2×10\(^{-4}\) m\(^2\) g\(^{-1}\)). However chlorophyll-specific backscattering in phytoplankton cultures exhibits considerable variability (Whitmire et al., 2010), and Vaillancourt et al., 2004 reported a mean value of 8×10\(^{-4}\) m\(^2\) g\(^{-1}\) for 29 species with a range extending over approximately two orders of magnitude. For minerals, the value for \(a^*_{\text{MSS}^*}\) (440) of 0.06 m\(^2\) g\(^{-1}\) is within the range reported by Babin et al., 2003 for non-algal particles (0.033 m\(^2\) g\(^{-1}\) to 0.067 m\(^2\) g\(^{-1}\)) and close to the estimate of Bowers & Binding, 2006 (0.045–0.055 m\(^2\) g\(^{-1}\)) for values of 0.020 nm\(^{-1}\) and 0.018 nm\(^{-1}\) for 29 species with a range extending over approximately two orders of magnitude. For minerals, the value for \(a^*_{\text{MSS}^*}\) (440) of 0.06 m\(^2\) g\(^{-1}\) is within the range reported by Babin et al., 2003 for non-algal particles (0.033 m\(^2\) g\(^{-1}\) to 0.067 m\(^2\) g\(^{-1}\)) and close to the estimate of Bowers & Binding, 2006 (0.045–0.055 m\(^2\) g\(^{-1}\)). The value for \(b^*_{\text{MSS}^*}\) (0.45 m\(^2\) g\(^{-1}\)) is rather higher than the figures given by Bowers & Binding, 2006 (0.25–0.27 m\(^2\) g\(^{-1}\)) but comparable to the results of Stavn & Richter, 2008 (0.35 to 0.65 m\(^2\) g\(^{-1}\)). Our value of 0.036 for the ratio of \(b^*_{\text{MSS}^*}\) to \(b^*_{\text{CHL}}\) at 650 nm is consistent with the observation by Loisel et al., 2007 of a particulate backscattering ratio of 0.0417 in mineral-dominated waters.

**3.3. Modelled relationships between MSS\(_{\text{ter}}\) and \(R_{\text{rs}}\)**

Fig. 10 shows the fraction of the total absorption and backscattering coefficients contributed by pure water to seawater containing a range of suspended mineral concentrations (with CDOM and CHL set to zero). The calculations employed the specific inherent optical properties for MSS\(_{\text{ter}}\) listed in Table 1, absorption coefficients for pure water from Pope and Fry (1997) and scattering coefficients for pure seawater from Smith and Baker (1981). The backscattering coefficients are strongly influenced by MSS\(_{\text{ter}}\) in all wavebands, but the absorption coefficients are dominated by water at longer wavelengths. Consequently the ratio of the two coefficients becomes increasingly determined by MSS\(_{\text{ter}}\)-related backscattering at the red end of the spectrum. This explains the relative insensitivity of remote sensing reflectance calculations to errors in the determination of particulate absorption. For a mineral concentration of 20 g m\(^{-2}\), for example, an under-estimate of 50% in particulate absorption at 676 nm would result in an error of only 10% in the total absorption coefficient in this waveband. Since remote sensing reflectance can be linked to
the ratio of the backscattering and absorption coefficients \(\frac{b_b}{a}\), the key to effective remote sensing of suspended minerals is to select a waveband where this ratio is sensitive to values of MSS below an extended dynamic range. Fig. 10 shows that this condition is best satisfied at the long wavelength end of the spectrum.

When CHL and CDOM are set to zero, Eq. 8 becomes simply

\[
R_{rs}(\lambda) \approx \frac{b_M(\lambda) + b_{MSS}(\lambda)MSS}{a(\lambda) + a_{MSS}(\lambda)MSS}.
\]

The degree of proportionality in the relationship between \(R_{rs}(\lambda)\) and \(\frac{b_b}{a}\), i.e. the variability of \(\kappa\), was investigated by carrying out a set of Ecolight modelling runs at ac-9 wavelengths incorporating SIOPs from Table 1, zero cloud cover and a solar angle of 45°. For MSS concentrations between 0.1 and 20 g m\(^{-3}\), these calculations generated values of \(\kappa\) ranging from 0.046 to 0.052, with an overall mean of 0.049. Eq. (12) therefore gives useful insights into the relationship between \(R_{rs}\) and MSS in situations where the contributions of other optically significant constituents can be neglected. When MSS\(_{ter}\) = 0, it gives the reflectance of pure seawater. When MSS\(_{ter}\) values are high, the term in brackets tends towards \(b_{MSS}/a_{MSS}\), and the reflectance is determined by the ratio of backscattering to absorption for suspended minerals. The relationship between \(R_{rs}\) and MSS\(_{ter}\) at intermediate values takes the form of a set of saturation curves whose shape is strongly wavelength-dependent. These curves are shown in Fig. 11, where the symbols indicate the results obtained by radiative transfer modelling using Ecolight and the lines show \(R_{rs}\) calculated from Eq. (12), incorporating SIOPs from Table 1 with \(\kappa\) set to 0.049.

This figure shows that the assumption of a single value for \(\kappa\) does not replicate the Ecolight results exactly, but it gives a reasonable approximation for most wavebands. It also indicates that the relationship between \(R_{rs}\) and MSS\(_{ter}\) is always curved, even though the curves are close to linear in the red wavebands for MSS\(_{ter}\) below 20 g m\(^{-3}\). Further calculations indicated that no simple waveband ratio significantly extends the region of near-linearity. Since chlorophyll fluorescence may contribute to the signal detected at 687 nm, and wavebands beyond 700 nm are used in atmospheric correction algorithms (Shi & Wang, 2009), it can be concluded that the SeaWiFS band at 670 nm or the MODIS band at 667 nm are the most suitable in practice for estimating MSS values using single-band algorithms. A similar conclusion was drawn from a more complex analysis of the underlying optics by Nechad et al. (2010), and is supported in the study of the relationship between turbidity and reflectance in tropical coastal waters by Ouillon et al. (2008).

### 3.4. Sensitivity to interfering substances

The analysis of the previous section leaves unanswered the question of how MSS\(_{ter}\) retrieval is affected by the presence of other optically significant constituents. The effects of the separate addition of either CDOM or CHL on the relationship between remote sensing reflectance at 667 nm and MSS are shown in Fig. 12, with the symbols again indicating Ecolight numerical results and the lines solutions of Eq. (12). Since CDOM affects only the total absorption coefficient...
(the denominator of Eq. 8), increasing CDOM always decreases \( R_{rr} \) for a given MSS\(_{rer} \). Adding CHL alters both the total absorption and back-scattering coefficients and affects both the numerator and denominator in Eq. (2), and for the SIOPs in Table 1 increases \( R_{rr}667 \) for MSS\(_{rer} \) values below 2 g m\(^{-3}\) and decreases \( R_{rr} \) above this value. Further calculations, involving around 20,000 Ecological runs, indicate that the envelope enclosed by the maximum and minimum values in Fig. 12 contains all the \( R_{rr}667 \) values which are consistent with a given MSS\(_{rer} \) when both CDOM and CHL are present and allowed to vary independently over the full range in the model (0–1 m\(^{-1}\) for CDOM, 0–10 g m\(^{-3}\) for CHL).

3.5. Predictive capability of a model incorporating regionally representative SIOPs

In regions such as the Irish Sea, frequent cloud cover makes match ups with satellite overpasses rarely possible, and spatial heterogeneity reduces the correspondence between point sampling and pixel-averaged remote sensing observations. For this study, therefore, radiative transfer results were compared with \( R_{rr} \), 667 observations derived from SPMR deployments. As a preliminary step, errors for \( R_{rr} \) and MSS\(_{rer} \) observations were estimated for stations where duplicate sample analyses or casts were carried out. These were taken to be the standard deviation of the residuals obtained from a linear least squares fit to scatterplots of all duplicate observations for the two variables, and were +/−0.7 g m\(^{-3}\) for MSS\(_{rer} \) and +/−0.001 sr\(^{-1}\) for \( R_{rr} \).

Fig. 13 shows \( R_{rr}667 \) derived from in situ radiometric profiles at the stations mapped in Fig. 1 plotted against measurements of MSS\(_{rer} \) for surface water samples taken at the same stations.

Upper and lower boundaries calculated using Ecological with SIOPs from Table 1 are superimposed.

The classification of stations as being dominated by MSS\(_{rer} \) or MSS\(_{dia} \) (Section 2.5) is indicated by filled and open symbols, and error bars are included only for MSS\(_{rer} \) stations to avoid over-congestion of the plot. Three significant conclusions can be drawn from Fig. 13. The first is that the radiative transfer calculations generated \( R_{rr}667 \) values that were largely consistent with SPMR observations. This result indicates a considerable degree of consistency between three sets of independent measurements (OSCs, IOPs and radiometric profiles), and demonstrates that the procedures employed for deriving representative SIOPs in
Table 1 have not introduced any systematic bias. The second is that the spread in the $R_{rs_{667}}$ vs $MSS_{ter}$ relationship observed for this set of data (at least for $MSS_{ter}$ in the range 4 g m$^{-3}$ to 14 g m$^{-3}$) can be accounted for by the degree of variability introduced by unconstrained CDOM and CHL values even when variability on the SIOPs themselves is not included in the analysis. The third is that the presence of biogenic silica with a very low specific backscattering cross section has a significant effect on the direct problem of estimating $R_{rs}$ from MSST but little effect on the inverse problem of estimating $MSS_{ter}$ from $R_{rs}$. The degree of variability shown in Fig. 13 suggests that, in the absence of definite knowledge of CHL and CDOM concentrations, any algorithm recovering $MSS_{ter}$ should report the maximum and minimum concentrations consistent with a specified range of these constituents. For the range considered in this study, the upper ($u$) and lower ($l$) boundaries derived from radiative transfer calculations can be approximately described by second order polynomials of the form:

$$MSS_{ter(u)} = 26014 \times (R_{rs_{667}})^2 + 916 \times (R_{rs_{667}}) - 0.13$$

$$MSS_{ter(l)} = 2508 \times (R_{rs_{667}})^2 + 768 \times (R_{rs_{667}}) - 0.77$$

This approximation allows maximum and minimum $MSS_{ter}$ values to be derived from $R_{rs_{667}}$ observations without incurring a significant computational overhead.

### 3.6. An illustrative example

Fig. 14 shows a contour map of $R_{rs_{667}}$ for the region of interest derived from a MODIS image acquired on May 2nd 2007. The map exhibits spatial patterns previously reported by Bowers (2003), with high reflectances occurring in the major estuaries and in regions with high tidal velocities off Anglesey (NW Wales) and Wicklow Head (on the Irish coast). Transects are drawn on Fig. 14 from the open waters of St Georges Channel (point A) east into the Bristol Channel (point B) and north east into the Irish Sea (point C). The upper and lower limits for $MSS_{ter}$ retrievals along these transects, calculated using Eqs. (13) and (14), are illustrated in Fig. 15. The transects start in waters of low reflectance (and, by implication, low...
MSS<sub>ter</sub> values). Transect A-B shows a steep rise in suspended mineral concentrations starting at 140 km, which is where it enters the turbid Severn Estuary. Transect A-C shows a more gentle rise in MSS<sub>ter</sub> levels at 100 km from the starting point, which is where it crosses the front between the seasonally stratified waters of St Georges Channel and the tidally mixed waters of the central Irish Sea (Simpson & Hunter, 1974).

The figure shows that it is possible to locate major features and transitions in mineral particle distributions to within a few kilometres in spite of the calculated uncertainties in absolute values. This capability is potentially important for validating sediment transport models using ocean colour imagery.

4. Discussion

Many practical applications of optical remote sensing involve the mapping of suspended sediment concentrations in regions of moderate turbidity. Examples include monitoring river outflow and plume dispersal (D’Sa & Ko, 2008; Lahet & Stramski, 2010; Warrick et al., 2004, 2007), assessing the environmental footprint of dredging operations (Islam et al., 2007; Siegelas et al., 2006, 2009), and determining the geographical extent of the effects of extreme events such as hurricanes and tsunamis on the coastal zone (Chen et al., 2009; Lohrenz et al., 2008; Yan & Tang, 2009; Zawada et al., 2007). In addition, quantitative estimates of relatively low concentrations of suspended minerals play a key role in predicting light penetration in coastal seas (Tian et al., 2009), modelling underwater visibility (Zaneveld & Pégau, 2003), and tracking the transport of pollutants such as heavy metals and radionuclides (Battle et al., 2008; Charlesworth et al., 2006).

Given the nature of these applications, and their potential economic and legislative implications, it is important that remotely sensed suspended sediment concentrations are accompanied by an explicit assessment of the associated uncertainties. The aim of the present study is to quantify the extent to which these uncertainties originate in the sensitivity of remote sensing reflectance to the presence of non-mineral materials in moderately turbid waters. The radiative transfer calculations employed for this purpose incorporated SIOPs which are broadly characteristic of the Irish Sea and adjacent waters, and generally consistent with values reported for other shelf sea areas. The results confirmed that the relationship between remote sensing reflectance and suspended sediment concentration saturates with increasing concentration in all wavebands (and waveband ratios) in the visible region of the spectrum, and that the range of approximate linearity is greatest for red wavelengths. However since chlorophyll fluorescence can contribute significantly to water-leaving radiance above 670 nm and wavelengths above 700 nm are frequently employed for atmospheric correction, signals in the 660–670 nm band are the obvious choice for visible-band MSS algorithms. Taking the MODIS R<sub>rs,667</sub> signal as an example, it is possible to draw three main conclusions. First, as noted by Bowers et al., 1998; Eleveld et al., 2008; Nechad et al., 2010 and Zhang et al., 2010, the relationship between red-waveband reflectance and MSS<sub>ter</sub> becomes noticeably curved at concentrations above 20 g m<sup>−3</sup>. Second, the effect of CHL and CDOM over most of the MSS<sub>ter</sub> range considered (2.5–20 g m<sup>−3</sup>) is to reduce the R<sub>rs,676</sub> signal, leading to under-estimates of MSS<sub>ter</sub> by single waveband algorithms. Third, since the presence of other optically significant constituents is sufficient to account for the variability in the relationship between R<sub>rs</sub> and MSS<sub>ter</sub> in the Irish Sea reported by Binding et al. (2005), caution is required if this variability is to be interpreted in terms of changes in particle size distributions (van der Lee et al., 2009).

It is interesting to compare the magnitude of the uncertainties in MSS recovery introduced by the presence of unknown concentrations of non-mineral seawater constituents with those due to errors of observation. The target accuracy for the recovery of water-leaving radiances from the SeaWiFS and MODIS Aqua satellite radiometers is +/−5%. Vicarious calibration procedures suggest that this figure is significantly exceeded in practice, especially at the long wavelength end of the visible spectrum (Franz et al., 2007; Gregg et al., 2009). It is possible, however, that vicarious calibration over-estimates errors in the red wavebands because the reference sites are located in oceanic waters where the red reflectance signals are very low. A +−10% error in R<sub>rs</sub> 667, which is a reasonable minimum estimate for coastal waters, would generate uncertainties in a single-waveband linear MSS algorithm of 2 g m<sup>−3</sup> at a concentration of 10 g m<sup>−3</sup>. This is significantly lower than the figure of 7 g m<sup>−3</sup> computed for the modelled range of interfering substances using Eqs. (13) and (14).

One conclusion arising from this study is that the products of MSS algorithms in optically complex waters could usefully be reported in terms of upper and lower possible values, rather than as percentage errors. This procedure has several advantages. It emphasises the fact much of the uncertainty in MSS retrieval arises from the composition of the water body being inadequately known rather than from errors of observation. It reflects the fact that, over most of the relevant range, the effect of interfering substances is not to introduce random errors but to cause remote sensing algorithms to systematically underestimate MSS values. It also allows the range of possible values to be adjusted in response prior knowledge of seasonal or spatial variations in the likely range of constituent concentrations. Further refinement of the model of shelf sea optics developed in this paper requires a clearer understanding of the optical properties of suspended mineral particles. Methodological problems currently prevent the direct determination of the scattering and NIR absorption coefficients of these particles in natural mixtures, and remarkably little information is available on their likely variability (Bowers & Binding, 2006; Snyder et al., 2008). Since remote sensing products are highly sensitive to the SIOPs of mineral particles, particularly the specific backscattering coefficient, this is an area which is in need of further study.

References


