

Interpreting the colour of an estuary

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Abstract

This paper explores the possibility of using water colour to quantify the concentration of coloured dissolved organic matter (CDOM), and through it, dissolved organic carbon (DOC) and salinity in a turbid estuary in which suspended sediments also influence water colour. The motivation of the work is that the method could be applied to water colour measurements made remotely from an aircraft (or, in larger estuaries, a satellite) enabling near-synoptic mapping of surface salinity and DOC distributions. The paper describes observations at 29 stations distributed along the salinity gradient of the Conwy estuary in North Wales. At each station, surface water samples were collected and analysed for salinity, concentrations of DOC, chlorophyll and suspended particles and absorption spectra of CDOM, or yellow substance. Profiles were made of both upwelling and downwelling irradiance in four narrow band channels, and these were used to calculate irradiance reflection and attenuation coefficients. Results show that spectrally averaged light absorption in the estuary is caused principally and equally by mineral suspended solids and yellow substance, with water and chlorophyll in third and fourth place. The CDOM is strongly correlated ($R^2 = 0.99$) in a negative sense with salinity, and more weakly correlated with DOC. There is a linear relationship between CDOM and the ratio of reflection coefficients in the red (670 nm) and blue-green (490 nm) parts of the spectrum, which could be applied to remote sensing; the slope and intercept of the relationship are however different to those found in less turbid water bodies. It is shown that the change in slope and intercept are consistent with the presence, in the Conwy estuary, of suspended particles which influence the water colour. A method is described and tested for inverting water colour measurements in a turbid estuary to give estimates of CDOM in the presence of suspended particles. The solution, which has not been adjusted to fit the data, produces profiles of CDOM, DOC and salinity, which behave reasonably but which currently have a limited accuracy. RMS differences between measured and optically derived parameters for the entire data set are 0.27 m^{-1} (CDOM), 4 PSU (salinity) and $67 \mu\text{M}$ (DOC) although better accuracy is obtained on individual surveys. The fact that there is little bias between predicted and observed parameters indicates that much of the scatter is caused by random measurement error and that the approach is fundamentally sound.

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1. Introduction

The colour of the water in an estuary (provided it is turbid and deep enough so that the bottom cannot be seen) depends upon the optical properties of water and of the materials dissolved and suspended in the water column. These include fine mineral and organic particles, including phytoplankton, and coloured dissolved organic matter (CDOM), or yellow substance. In estuaries, yellow substance is of special interest for two reasons. One is that it is usually present in much higher

concentrations than in other marine systems (Kirk, 1994); the second is that most of it is introduced into the estuary by the river. If the CDOM behaves conservatively in the estuary, as it often seems to do, its concentration can vary in proportion to the concentration of fresh water, and hence inversely with the salinity of the estuary (Monahan and Pybus, 1978; McKee et al., 1999; Bowers et al., 2000). If the concentration of CDOM can be determined by optical measurement, it offers the potential for remote sensing of salinity.

CDOM has a strong optical signature. When present in high enough concentrations in the upper reaches of an estuary, its brown staining of the water is apparent to the naked eye. Measurements of the absorption

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spectrum of CDOM show that it absorbs strongly in the blue, the absorption coefficient decreasing exponentially with increasing wavelength to almost zero in the red (Kalle, 1966; Bricaud et al., 1981; Kopelevich, 1982; Carder et al., 1989). The material itself consists of a variety of aliphatic and aromatic polymers derived from the degradation of terrestrial and aquatic plant material (Kirk, 1994). When rivers flow into estuaries they introduce CDOM produced by the decay of terrestrial plants. This adds to the CDOM produced locally in the estuary by aquatic plants. The CDOM forms a part of the total dissolved organic carbon (DOC) content of the water, and at least in some cases there is a proportionality between the CDOM and the DOC (Gallegos et al., 1990; Ferrari et al., 1996; Stedmon et al., 2000).

In some places, such as the upper reaches of an estuary, and also in some shelf sea areas with a large input of fresh water, yellow substance becomes the principal material controlling variations in water colour. In these circumstances, it has been predicted by theory and confirmed by observation that there exists a linear relationship between the ratio of reflection coefficients in the red and blue, or blue-green, parts of the spectrum and CDOM absorption (Bowers et al., 2000). This relationship appears to be remarkably robust and applies to a variety of water bodies in which the condition that CDOM is the main absorber of light in the blue (and water is in the red) is met (Binding and Bowers, 2003). Binding and Bowers have shown how this relationship, together with a known relationship between CDOM and salinity, can be used to map salinity in the Clyde Sea, Scotland, using satellite ocean colour data.

In many turbid estuaries, however, CDOM will compete for its dominance of water colour with suspended particles. Our aim in this paper is to determine to what extent the theoretical linear relationship described above can be applied to an estuary in which suspended particles as well as yellow substance influence water colour, and to consider ways of unravelling the colour signal in such an estuary to derive CDOM and salinity.

2. Study site and methods

The study was carried out in the Conwy estuary, North Wales, and in the waters of Conwy Bay, immediately outside the mouth of the estuary (see Fig. 1). The Conwy is not a large estuary by any standard, but it is in many ways ideal for our purposes. It is not long: the complete gradient of salinity can be sampled quickly by a speedboat (and hence the results are not likely to be affected by changes, during the survey, in the source concentration of yellow substance). In addition, as we shall see, the colour is influenced to almost equal extent by suspended particles and CDOM.

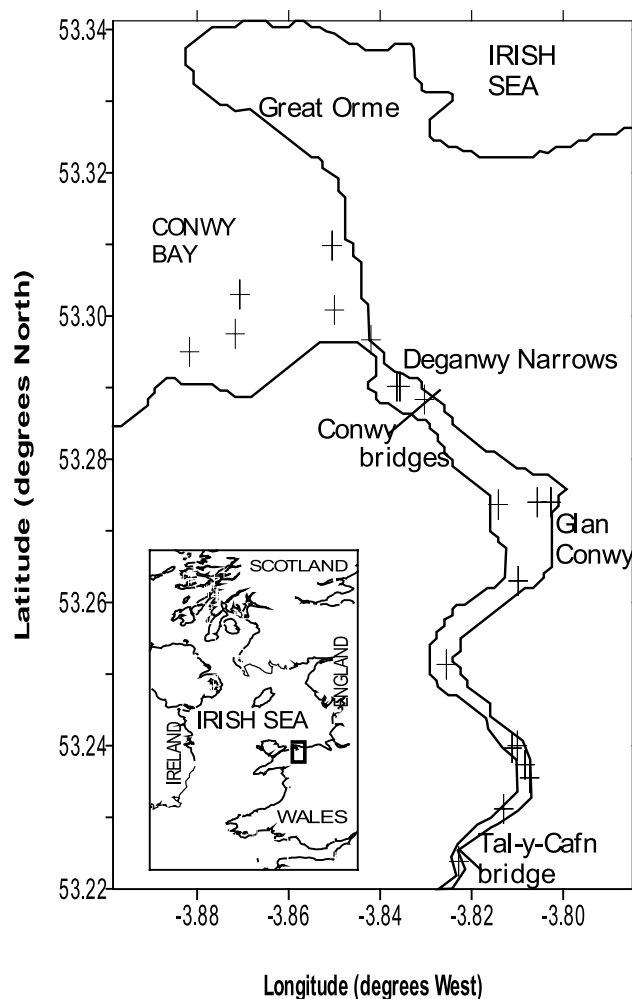


Fig. 1. Map of the Conwy estuary showing place names and locations of sampling stations (+symbols). Tick marks on the vertical axis are at intervals of 1/100th of a degree of latitude: approximately 1.1 km. The inset map shows the position of the estuary in relation to the Irish Sea.

The estuary stretches 22 km from the mouth at Deganwy Narrows to the tidal limit at Llanrwst, some 11 km inland from Tal-y-Cafn. The catchment area for freshwater input to the estuary amounts to 344 km² of mountainous terrain (Nunes and Simpson, 1984). Freshwater discharge has a mean value of about 20 m³ s⁻¹ but this varies widely over the range 0.5–500 m³ s⁻¹ (Simpson et al., 2001). There is a large tidal range at the mouth (6 m at spring tides) and the strong tidal currents that this generates ensure that most of the estuary is vertically well mixed for most of the time.

Stations were occupied outside the mouth of the estuary by the R.V. Prince Madog on 30th March 2002 and on 26th and 27th May 2002. In addition, a rigid inflatable boat (RIB) was used to conduct axial surveys of the estuary at high water (HW) on 26th May (10.42–12.10 BST) and 27th May (12.10–13.09 BST) and at low water (LW) in the evening (19.10–19.50 BST) of 26th May. It is these axial surveys that we concentrate on here.

At each station, surface water samples were taken and analysed for suspended sediments, yellow substance, salinity, DOC and chlorophyll, as well as other determinants which we do not report on here. Suspended sediments were measured by gravimetric analysis using pre-weighed GF/F filters. The filters were rinsed in distilled water to remove salt, left to dry, re-weighed and then baked at 500 °C for 3 h. After cooling, the filters were weighed for a final time to give the mineral suspended solids (MSS) concentration.

Absorption by CDOM or yellow substance was measured by filtering samples through 0.2 µm Sartorius Minisart filters and measuring the absorption spectrum of the filtrate in a Shimadzu UV-1601 dual beam spectrophotometer. Quartz cells with a path length of 10 cm were used in these measurements, and distilled water was used as a reference. The absorption coefficient was calculated in the way described by Bowers et al. (2000). The absorption coefficient at 440 nm, g_{440} , is reported here. Chlorophyll *a* was measured by filtering at least 500 ml of the sample water through Whatman GF/F filters. The trapped pigments were then extracted overnight, in the dark, at a constant temperature of 5 °C using 90% acetone. The extracted supernatant was compared fluorometrically to known chlorophyll-*a* standards using a Turner designs 10AU fluorometer. Surface salinity was measured using a WTW Cond 315i/Set, a portable salinity temperature and conductivity meter. DOC was determined on filtered (0.2 µm filters) 2 ml samples after acidification with 10 µl of 85% H₃PO₄ and purging with N₂ for 5 min by use of an MQ 1001 TOC analyser (Qian and Mopper, 1996). Glycine and phthalate were used as DOC standards: the instrument was calibrated over the range 50–2000 µM, the calibration intercept being used as the blank. Elaborate precautions were taken to avoid contamination.

Underwater irradiance measurements were made using a four-channel recording irradiance meter (Kratzer et al., 1999). This instrument logs irradiance in four narrow (10 nm) band channels centred on 440, 490, 570 and 670 nm. One profile was made to measure downwelling irradiance, and then the instrument was inverted to measure a profile of upwelling irradiance. Diffuse attenuation coefficients, *K*, were calculated from regressions of the natural logarithm of downwelling irradiance against depth. Irradiance reflection coefficients, *R*, were calculated as the ratio of up- to downwelling irradiance just below the surface.

3. Results

3.1. Variations of properties with distance up the estuary and in relation to each other

Table 1 summarises the range of values found on the axial surveys. An example of the results from one of the

Table 1
Summary of some of the measurements made on axial surveys

	Mean	Minimum	Maximum
Total suspended solids (TSS, mg l ⁻¹)	12.55	4.4	57.0
Mineral suspended solids (MSS, mg l ⁻¹)	9.22	3.2	46.2
Chlorophyll (µg l ⁻¹)	2.89	0.73	9.9
CDOM, g_{440} (m ⁻¹)	1.81	0.26	3.56
DOC (µM)	221	97	333

axial surveys, at high water on 26th May, is shown in Fig. 2. Results from the high water survey on 27th May are very similar to this. The plot shows the along-estuary distributions of salinity, MSS, chlorophyll and yellow substance, or CDOM. The feature to note here is that, as we move up the estuary from the narrows both the MSS concentration and CDOM absorption increase as the salinity falls. The estuary therefore becomes more turbid with distance inland.

The trend of increasing turbidity with distance inland is also apparent in the radiometer measurements. Diffuse attenuation at all wavelengths increases with distance inland. On the 26th, values for the attenuation coefficient at 490 nm increased from 0.2 m⁻¹ at the mouth of the estuary to 4.24 m⁻¹ at Tal-y-Cafn, a 20-fold increase in a distance of only 12 km. The change in turbidity is associated with a change in water colour: near the mouth, reflectance in the blue-green part of the spectrum (490 nm) is greater than that in the red (670 nm), and the water had a green appearance; at the inland end of the survey, reflectance in the red is greater than that in the blue-green and the water looked distinctly brown.

CDOM is strongly correlated with salinity. Fig. 3 shows a plot of CDOM absorption at 440 nm against salinity confirming the distinctive negative relation between these quantities. The yellow substance absorption spectrum had a characteristic exponential decay with wavelength. The shape of this spectrum did not change significantly along the length of the estuary. The mean value of the exponential decay constant (*S* in Table 2) for these data was 0.014 nm⁻¹. Because we are interested in deriving salinity from colour measurements through CDOM, we have determined the relationship between salinity and CDOM absorption by regression. The result for all three RIB surveys (29 stations) is:

$$S = 35.5 - 10.0g_{440} \quad (1)$$

with $R^2 = 0.98$ and standard error of slope = 0.24 and intercept = 0.53. Compared to the river, light absorption by CDOM in the sea is very small, and the slope of this relationship is effectively set by the value of g_{440} in the river just upstream from the saline intrusion. This will vary with time, and in consequence, the slope in Eq. (1) will not be fixed. An equation like (1) will be needed to convert colour measurements into salinity. However,

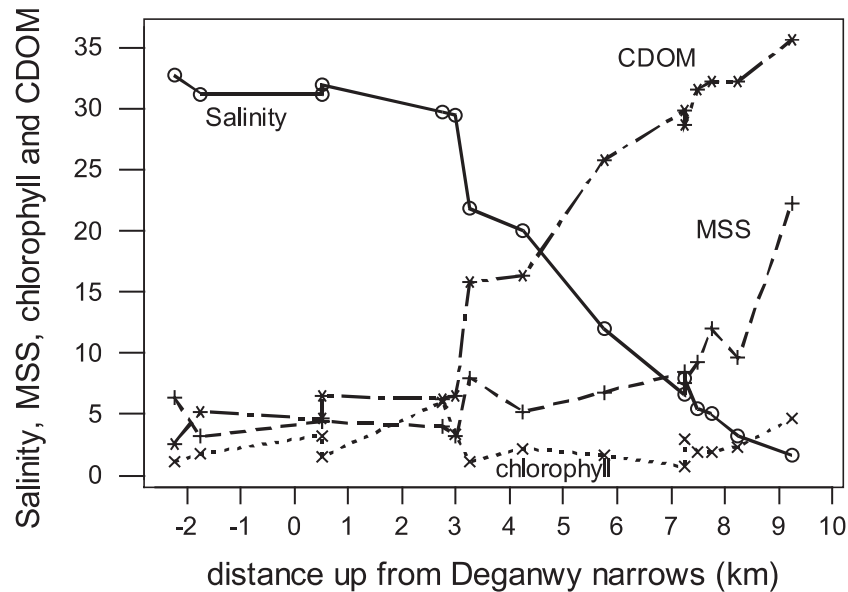


Fig. 2. Longitudinal profiles, for the HW survey of 26/5/02, of salinity (PSU), mineral suspended solids (MSS, mg l^{-1}), chlorophyll ($\mu\text{g l}^{-1}$) and CDOM (expressed as absorption coefficient of filtered water samples at 440 nm, $g_{440} \text{ m}^{-1}$). Values of g_{440} have been multiplied by 10 so that the variation can be seen more clearly.

if the equation is not available from measurement, then it can be constructed (as long as the concentration of CDOM in the sea remains negligibly small compared to the river) by a single measurement of g_{440} in the freshwater source. This, in turn, can be based upon a colour measurement.

In contrast to the yellow substance, the MSS has a relatively weak relationship with salinity ($R^2 = 0.20$). Chlorophyll exhibits no discernible relationship with salinity.

The CDOM or yellow substance forms part of the total pool of DOC in the estuary. In principle, therefore, we would expect a relationship between CDOM and DOC. For all the data, this relationship is relatively

weak ($R^2 = 0.68$). This is because the points from the three different surveys lie on different lines. The reasons for this are not clear to us, but possibly suggest a (fairly rapid) variation in the ratio of CDOM to DOC in the source waters. The results of regression analysis for individual surveys are:

$$\text{HW 26th May DOC} = 184 + 37.3g_{440} \quad R^2 = 0.86$$

$$\text{LW 26th May DOC} = 175 + 28.0g_{440} \quad R^2 = 0.76$$

$$\text{HW 27th May DOC} = 80 + 59.3g_{440} \quad R^2 = 0.98$$

In each case, DOC is given in $\mu\text{mol l}^{-1}$ and g_{440} in m^{-1} .

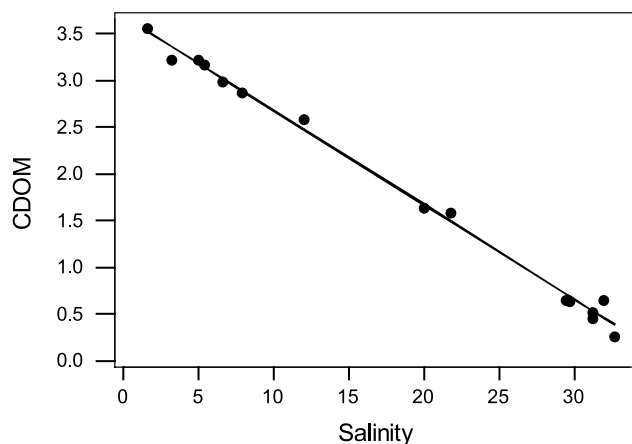


Fig. 3. Variation of CDOM with salinity during the HW survey of 26th May. CDOM is represented by absorption coefficient of filtered sea water samples at 440 nm, g_{440} .

3.2. The photon budget

The absorption coefficient, a , at wavelength, λ , can be expanded as:

$$a(\lambda) = aw(\lambda) + a_p^*(\lambda)[\text{chl}] + a_m^*(\lambda)[\text{MSS}] + a_y^*(\lambda)g_{440} \quad (2)$$

Table 2
Values used in calculating the photon budget

Parameter	Notes
aw	Morel and Prieur (1977, table 1)
a_p^*	Gallegos et al. (1990, table 4)
a_m^*	$0.021 + 0.038 \exp(-0.0055(\lambda - 440))$ based on measurements in the Irish Sea (Bowers et al., 1998)
a_y^*	$\exp(-S(\lambda - 440))$ ($S = 0.018 \text{ nm}^{-1}$, Bowers et al. (2000))

The four terms on the right-hand side of this equation represent, in turn, absorption due to water, chlorophyll, MSS and yellow substance. In the case of chlorophyll and mineral suspended particles, absorption is expressed as a concentration-specific absorption (the * quantity) multiplied by a concentration (in square brackets). In the case of CDOM or yellow substance, absorption is represented by measured absorption at 440 nm, g_{440} , multiplied by a shape function, $a_y(\lambda)$, to give absorption at other wavelengths. The principal term missing from the right-hand side of Eq. (2) is absorption by organic detritus (that is, non-living organic particulate material). The reason for the omission is that at present it is difficult to separate this material from living organic matter. It may be expected however that in an estuary, organic detritus could make a contribution to light absorption.

For these calculations, values of the concentration-specific absorption coefficients (and the shape function for yellow substance) were taken from the literature and are shown in Table 2. With these data, Eq. (2) has been used to calculate the proportion of total light absorbed that is accounted for by the different materials, using the mean concentrations from Table 1. The results will also be sensitive to the data in Table 2 and so will change if the specific absorption characteristics of the Conwy are different to the literature values we have used. The broad picture, however, is likely to remain the same.

The results are shown in Fig. 4. Looking at this figure, we can see that CDOM dominates absorption at the blue end of the spectrum, with MSS in second place. Water and MSS are the important absorbers at the red end of the spectrum. Only a small percentage of light in the estuary is absorbed by phytoplankton. The spectrally averaged percentages for each material are: water,

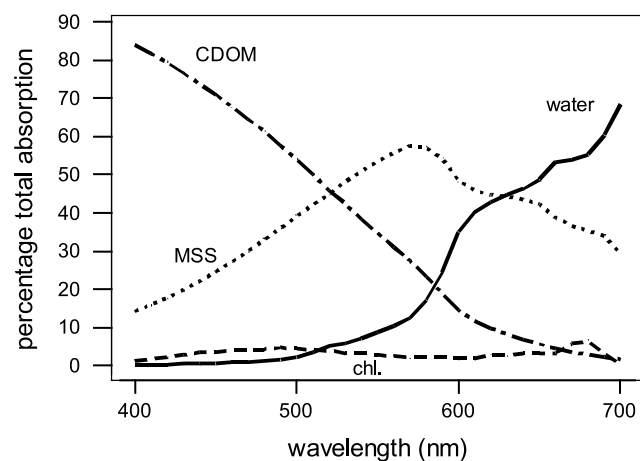


Fig. 4. Estimated spectral variation of light absorption by different materials in the estuary. Lines are drawn for mean observed concentrations using the concentration-specific absorption coefficients (or shape function in the case of CDOM) of Table 2.

22%; chlorophyll, 3%; MSS, 38%; and CDOM, 37%. Between them, therefore, MSS and CDOM account for 3/4 of the light absorbed in the estuary, and each contributes equally to this figure.

Unlike the Clyde Sea, where the relationship between the colour signal and yellow substance has previously been examined (Bowers et al., 2000) we cannot ignore the effects of particle absorption in the red in the Conwy. (In the Clyde 80% of absorption at 670 nm was accounted for by water. In the Conwy the corresponding figure is less than 60%.) We shall see that this fact influences the relationship between water colour and CDOM absorption.

3.3. The water colour signal and CDOM

Following earlier studies (Bowers et al., 2000; Binding and Bowers, 2003), we have plotted in Fig. 5 CDOM absorption at 440 nm, g_{440} , against the ratio of reflection coefficients in the red (670 nm) and blue-green (490 nm) parts of the spectrum. A straight line fit to the data in Fig. 5 has the equation

$$g_{440} = 1.45[R(670)/R(490)] - 0.478 \quad (3)$$

with $R^2 = 0.94$ and standard error of intercept and slope being 0.066 and 0.032, respectively. There is, therefore, a good relationship between CDOM absorption and this colour ratio which could, on the face of it, be used for remote sensing of CDOM (and hence salinity) in this estuary. The slope and intercept are, however, different from the earlier studies. In a variety of water bodies where suspended sediment levels were low, values for slope and intercept (using combined data from Bowers et al. (2000) and Binding and Bowers (2003)) were

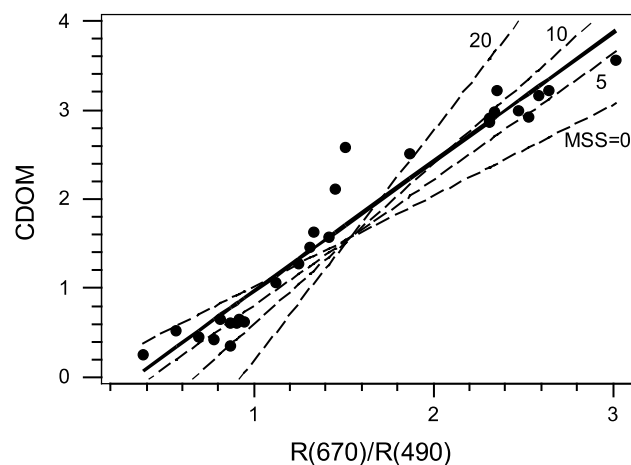


Fig. 5. Relationship between CDOM and the reflectance ratio $R(670)/R(490)$ for all stations. CDOM is represented by its absorption coefficient at 440 nm, g_{440} . The solid line shows the results of a least squares fit to the data points and the dashed lines are the theoretical relationships (Eq. (4)) for the values of MSS indicated (in mg l^{-1}).

approximately 0.8 and -0.07 , respectively. In the next section we show that the change in slope and intercept is consistent with the higher values of MSS in the Conwy estuary and the fact, in particular, that MSS makes a significant contribution to light absorption in the red. If this interpretation is correct, it means that the relationship shown in Fig. 5 is sensitive to MSS concentration and hence will change with time. What is needed, therefore, is an inversion method for obtaining CDOM from colour measurements which allows for the effects of particle absorption.

4. Theoretical considerations and inversion

Bowers et al. (2000) showed how the relationship between CDOM absorption and a ratio of reflection coefficients in the red and one other wavelength can be derived from first principles. This relationship is:

$$g_{440} = ((a_{wR} + a_{pR}) / (a_{y2}^* \gamma)) R_R / R_2 - (a_{w2} + a_{p2}) / a_{y2}^* \quad (4)$$

Here, subscripts R and 2 refer to the red and another part of the spectrum. a_w is absorption by water and a_p is absorption by particles. a_{y2}^* is the value of the shape function for CDOM at the second chosen wavelength (see Table 2). The factor γ allows for variation of the backscattering coefficient with wavelength ($\gamma = 1$ corresponds to wavelength independent backscattering). From this equation we can see that, provided particle absorption is constant, we may expect a linear relationship between g_{440} and R_R / R_2 .

In the calculations below, wavelength 2 is taken as 490 nm, which corresponds to one of the SeaWiFS wave bands. For zero particle absorption, using data from Table 2 and $\gamma = 1$, we would expect a value for the slope in Eq. (4) of about 1, and an intercept of about 0. As particle absorption increases, the slope will increase and the intercept will become increasingly negative. This explains qualitatively the results in the Conwy estuary, where a slope greater than 1 and an intercept less than zero are observed. Quantitatively the agreement is not at present exact. Some theoretical lines for different particle loading, drawn from Eq. (4) and Table 2 are shown in Fig. 5 (dashed lines) (we can see that for a continuous gradient of MSS along the estuary we might expect a curved relationship between g_{440} and this colour ratio; surprisingly there is no evidence for curvature in the right sense in the data). For a mean MSS concentration of 10 mg l^{-1} , the theory predicts a slope of 1.80 and an intercept of -1.2 , compared to observed values of 1.45 and -0.478 . In making these calculations, we have assumed that particle absorption is entirely by mineral particles and that the coefficients in Table 2 apply. There are therefore good reasons why

there is a quantitative difference between observations and theory, one of which is that we have ignored absorption by organic detritus, which will contribute to both a_{p2} and a_{pR} . Closer agreement could be achieved by allowing for this and by tuning the parameters in Table 2 (still within values reported in the literature). Here, however, we are not interested in tuning the theory to fit the observations, but rather in exploring practical methods of inversion.

The approach we try in this paper is to use a second colour ratio to create two simultaneous equations which we solve for both g_{440} and particle absorption. Eq. (4) can be written for the red and a *third* wavelength as:

$$g_{440} = ((a_{wR} + a_{pR}) / (a_{y3}^* / \gamma')) R_R / R_3 - (a_{w3} + a_{p3}) / a_{y3}^* \quad (5)$$

γ' is the ratio of backscattering coefficients at wavelengths R and 3. Assuming particle absorption is by mineral particles (MSS) only, then particle absorption at one wavelength can be related to particle absorption at other wavelengths through the formulation in Table 2. If we further take $\gamma = \gamma' = 1$, then Eqs. (4) and (5) form a pair of simultaneous equations with two unknowns: g_{440} and a single particle absorption.

Taking wavelength 2 as 490 nm and wavelength 3 as 570 nm, the ratio of particle absorption at these wavelengths to that in the red is:

$$\begin{aligned} a_{p3} / a_{pR} &= 0.039 / 0.032 = 1.22 \\ a_{p2} / a_{pR} &= 0.049 / 0.032 = 1.53 \end{aligned} \quad (6)$$

With these definitions, Eqs. (4) and (5) can be solved for particle absorption in the red, and CDOM concentration.

The RMS difference between values g_{440} computed in this way and those observed is 0.27 m^{-1} . In considering this result, it should be borne in mind that the predictions are not reliant on the observations made here to any extent. The predictions are made from theory-based Eqs. (4) and (5), and values of parameters from the literature. The parameters needed are:

- (1) absorption of water at 670 nm
- (2) values of the shape function of yellow substance at 490 and 570 nm
- (3) the ratios of specific absorption by particles at 490 and 570 nm to that at 670 nm.

The solution to the simultaneous equations also provides an estimate of light absorption by suspended particles, and hence information relevant to suspended particle concentration. Regression of computed particle absorption coefficients in the red against concentration of mineral suspended sediments (MSS) gives $R^2 = 0.58$ for the relationship

$$a_{pR} = 0.038[\text{MSS}] - 0.07 \quad (7)$$

with standard error of slope and intercept being 0.006 and 0.05, respectively. The intercept is therefore not significantly different from zero. The slope is approximately the mass specific absorption of MSS in the estuary at this wavelength (670 nm), and is a locally determined value for the Conwy. It is close to the value of $0.032 \text{ m}^2 \text{ g}^{-1}$ for $\lambda = 670 \text{ nm}$ measured in the Irish Sea (Table 2). It is encouraging to find that the closure of the equations yields a solution which is consistent with the data we have fed in.

Fig. 6 shows longitudinal profiles of (a) salinity and (b) DOC for the high water survey on 26th May. Both observed values and values predicted from the colour are shown in these diagrams. The predicted DOC and salinity both behave in a reasonable way: salinity decreases and DOC increases up the estuary, but the

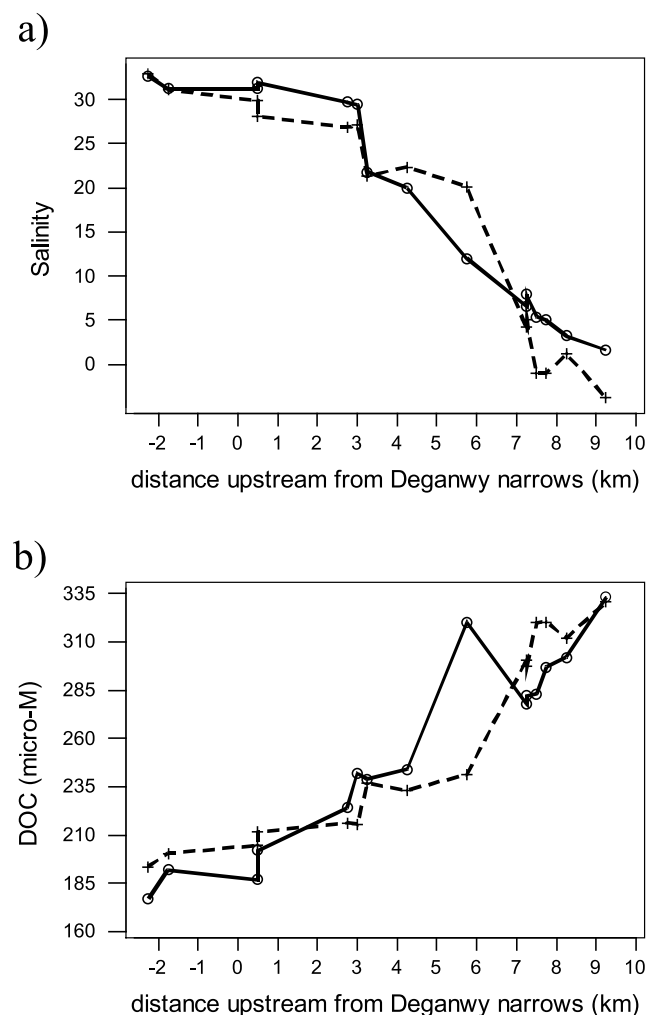


Fig. 6. Longitudinal profiles of observed and predicted (a) salinity and (b) DOC for the HW survey of 26th May. In each case, observations are shown by the open circles joined by solid lines, and the predictions by crosses joined by dashed lines. The predictions are derived from the solution to simultaneous equations involving two colour ratios.

accuracy of the predictions is disappointing. Because some of the predicted CDOM values are higher than those observed in the upper reaches of the estuary, some of the predicted salinities are negative. The RMS difference between observations and predictions in the case of salinity is 3.6 PSU and that in the case of DOC is $27 \mu\text{M}$. For data from all three surveys the RMS differences are 4.0 PSU (salinity) and $67 \mu\text{M}$ (DOC).

5. Discussion

The aim of this paper was to examine the water colour signal in an estuary for evidence that it contained enough information to derive light absorption by yellow substance, or CDOM, and through it the salinity and DOC concentration. This is a tall order, especially in an estuary where suspended sediments also add to the colour signal, but Fig. 6 shows that we are getting close to making this potentially useful method work.

An encouraging aspect of this work is the consistency between theory and observation. We considered a theoretical model, based on fundamental physics, relating water colour to absorption by dissolved and particulate material. Parameters in this model, where needed, have been taken from the literature, and have not been tuned at all to fit the present data set. The model predicts that, as suspended sediment is added to water containing yellow substance, a linear relationship between the red to another colour reflectance ratio and yellow substance absorption will exist but the slope and intercept of this line will change with particle absorption. The observations in the turbid yellow-stained waters of the Conwy provide evidence for this linear relationship, and the slope and intercept differ from those found in water with low particle absorption in a way which is qualitatively consistent with this theory. By using two colour ratios simultaneously it is possible to solve for both yellow substance and particle absorption. The resulting relationship between particle absorption and particle concentration is close to the expected trend (based on literature values in nearby waters). We have therefore used the observations to test the model for self-consistency, and it has passed this test reasonably well.

A disappointing aspect of this work is the accuracy of the predictions of salinity and DOC. An accuracy of 4 PSU in salinity is not good enough for practical purposes. In looking for ways of improving this accuracy, we must consider both the observations we have made and the assumptions in the theory.

It is tempting to blame the theory for the poor agreement between predicted and observed values. After all, we have made bold assumptions that we can neglect light absorption by organic detritus, that backscattering is constant with wavelength, and that general literature-derived values of mass specific absorption coefficients

can be applied. Despite this, the lack of bias between observed and predicted values suggests that these are not serious problems to deriving CDOM absorption from water colour. Certainly there is a problem with the theory because it does not predict exactly the observed slope and intercept of the CDOM absorption versus colour ratio relationship (this can probably be improved by using locally derived mass specific absorption coefficients and other factors we discussed earlier). However, this does not seem to be critical. The problem is more of scatter than of bias.

Turning to the observations, for the whole data set, the RMS variation of salinity about the line relating it to yellow substance is just over 1 PSU. This means that, even if the CDOM could be determined *exactly* from water colour, there would still be an error of 1 PSU in the salinity predictions. Of course, if yellow substance is behaving conservatively, we would expect a perfect relationship between it and salinity: the scatter of order 1 PSU probably indicates the level of uncertainty in the g_{440} measurements. Small differences in temperature between the CDOM sample and the distilled water blank are known to influence spectrophotometric measurements of g_{440} . Some of the remaining part of the error in predictions lies in the experimental determination of the colour ratio. Reflection coefficients cannot be determined exactly. In fact, they are difficult to measure in choppy water from a small boat. An error in reflectance ratio of 10% would produce an error in predicted salinity of nearly 4 PSU. Careful measurements of reflectance are therefore needed for accurate predictions of salinity.

In summary, this paper has demonstrated the potential of a method for deriving CDOM, DOC and salinity from measurements of water colour in an estuary. The accuracy of the method needs to be improved if it is to be of practical use, and this will involve more, and careful, measurements.

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