



## Research papers

## Water masses, mixing, and the flow of dissolved organic carbon through the Irish Sea

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## ABSTRACT

Observations of coloured dissolved organic matter (CDOM) and salinity have been used to identify water types and mixing in the Irish Sea. Three principal water types are identified: (1) Celtic Sea water, of high salinity and low CDOM which enters the Irish Sea from the south; (2) English coastal water, of low salinity and intermediate CDOM which is introduced into the eastern Irish Sea through rivers and (3) Irish Coastal water, with intermediate salinity and high CDOM. A mixing triangle is used to determine the geographical distribution of these three water types. This shows that the Celtic Sea water flowing northwards mixes initially with Irish water and later with English coastal water so that the mixture leaving the Irish Sea through the North Channel comprises 66% Celtic Sea water, 14% Irish water and 20% English water. We estimate the lateral mixing coefficient to be  $67 \text{ m}^2 \text{ s}^{-1}$ . The CDOM absorption coefficient at 440 nm in the water leaving the Irish Sea is  $0.17 \text{ m}^{-1}$ . Converting this to an estimate of the dissolved organic carbon concentration and multiplying by the volume transport in the North Channel, the net flux of dissolved organic carbon leaving the Irish Sea through the North Channel is calculated to be between 1 and 2 Tg C year<sup>-1</sup>.

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## 1. Introduction

Mixing diagrams, in which one water property is plotted against another, are a useful tool for identifying water types and mixing in the ocean. The classic example is the temperature–salinity (or  $T$ – $S$ ) diagram which enabled the principal water masses of the world's oceans to be identified (Pickard and Emery, 1990; Tomczak, 1999 and references therein). Away from the ocean surface, temperature and salinity can be considered as 'conservative' properties, changed only by mixing between two or more water masses. Observations of the change in temperature and salinity of a core of water as it moves away from its source can then be used to estimate mixing rates (Tomczak, 1981).

Shelf seas are too shallow for temperature to behave conservatively: the temperature of a parcel of shelf water will change with the heat flux through the sea surface, as well as by mixing with adjacent water. It has been suggested that coloured (or chromophoric) dissolved organic matter (CDOM) can be used as an alternative tracer to temperature in shallow water bodies (Hojerslev et al., 1996; Stedmon et al., 2010). CDOM, also known as yellow substance or gelbstoff, is a mixture of compounds

produced by the decay of plant material in the sea and on land. It flows from land into the sea through rivers and is often present in concentrations which can be measured relatively easily in samples of seawater. It has a strong optical signature, absorbing blue light most, giving CDOM-coloured water a yellow or brown appearance when present in high concentration. The colour of CDOM is used in measuring its concentration, which can be expressed as the absorption coefficient of the CDOM at a selected wavelength in the blue or ultra-violet part of the spectrum. CDOM and salinity together have been used successfully to study water types and mixing in the transition zone between the Baltic and North Sea (Malmberg, 1964; Aarup et al., 1996; Hojerslev et al., 1996; Stedmon et al., 2010). In this south-east corner of the North Sea, three water types have been identified: Baltic outflow, German bight and Central North Sea water. Using CDOM–salinity mixing diagrams, Stedmon et al. (2010) were able to map the proportions of the three water types in the region. These maps show the paths taken by the water masses after they leave their source and therefore reveal the slow residual circulation which is difficult to measure in other ways.

To be an effective material for a mixing diagram, CDOM should behave conservatively: that is it should be neither created nor destroyed in the marine environment. In fact, CDOM is created in seawater by the decay of marine algae and destroyed by solar bleaching and microbial activity. Stedmon et al. (2010) tested the

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conservative behaviour of CDOM in the southern North Sea using the slope of the absorption spectrum as an independent variable. They found that the changes in the slope parameter were consistent with the changes in absorption expected if CDOM is behaving conservatively. In their study area, therefore, non-conservative processes are slow compared to the residence time of CDOM.

A desirable condition when using mixing diagrams is that concentrations of tracer in the chosen water types should be constant in time. Ideally, a water type will have fixed values of salinity and CDOM absorption and appears as a single point on a CDOM–salinity mixing diagram. In practice, however, CDOM produced on land may vary in concentration, for example with a seasonal cycle. A water type will then appear as a line parallel to the CDOM axis, rather than as a point, on the mixing diagram. The effect of this variability on the interpretation of the CDOM–salinity mixing diagram in an estuary has been analysed by Bowers and Brett (2008).

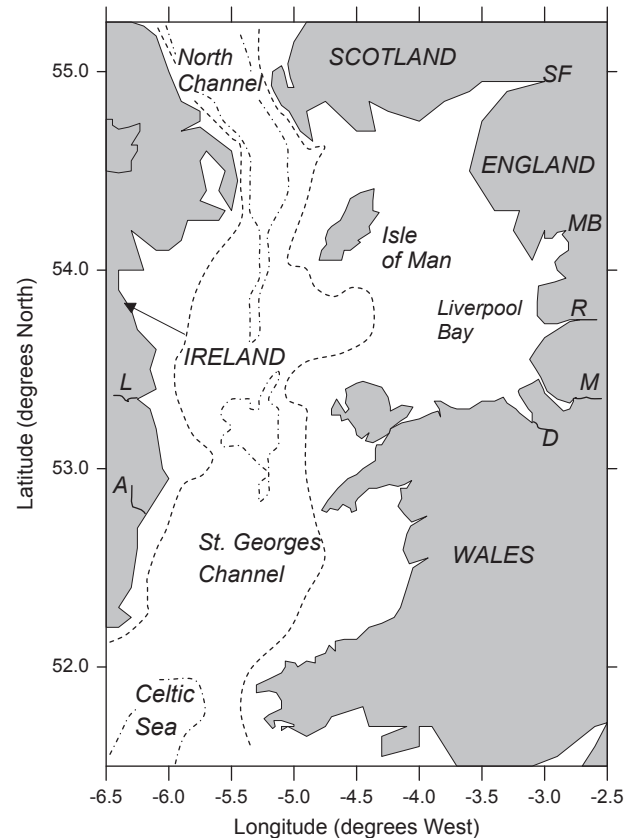
CDOM is part of the pool of dissolved organic carbon (DOC) in seawater. DOC flows into shelf seas from the land and is exported to the deep ocean. The fluxes of DOC are important quantities in the carbon cycle (Worral and Burt, 2007) and there is evidence that the flux of DOC from land to sea is increasing (Evans et al., 2007). Observations of CDOM and DOC concentration, together with estimates of volume transport rates of water in and out of shelf seas can be used to quantify this flux of carbon.

Up to now, the only application of coastal water type analysis using CDOM–salinity diagrams has been in the same geographical area—the North–Baltic Sea transition zone. The aim of this work is to apply the technique to a different area (the Irish Sea) for the first time. Our objectives are to identify the principal water types (in terms of CDOM and salinity) in the Irish Sea, to calculate mixing rates between these water types and to estimate the flux of dissolved organic carbon from the Irish Sea.

## 2. Study area

The Irish Sea (Fig. 1) is a semi-enclosed shelf sea surrounded by Ireland, Scotland, England and Wales. The sea is in near quarter-wavelength resonance with the semi-diurnal tide and as a result the tidal streams in the area are fast. Mean spring tidal streams exceed  $0.6 \text{ m s}^{-1}$  in amplitude on over 3/4 of the sea bed. The area to the south-west of the Isle of Man has the lowest tidal stream amplitudes and this region becomes thermally stratified in summer (Simpson and Hunter, 1974; Hill et al., 1997). The rest of the Irish Sea remains vertically mixed all year except for the eastern coastal areas such as Liverpool Bay which are regions of freshwater influence (ROFIs; Simpson, 1997) where intermittent freshwater-induced stratification is observed.

Freshwater from land is introduced unevenly around the Irish Sea. The majority of the freshwater runoff (80%) flows into Liverpool Bay through the English rivers: the Mersey, Ribble and those flowing into Morecambe Bay (Bowden, 1955). The residual flow in the Irish Sea is, on average over timescales of a year or more, northwards but it is weak and variable on short timescales. Volume transports have been estimated in a number of ways, including salt budgets (Bowden, 1955), radioactive tracers (Simpson and Rippeth, 1998), recording current meters (Brown and Gmitrowicz, 1995), HF radar Knight and Howarth (1999) and numerical models (Dabrowski et al., 2010). The results of these measurements give volume transports in a northward direction lying in the range  $0.02\text{--}0.14 \text{ Sv}$  ( $1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$ ). For a representative cross-sectional area of  $7 \text{ km}^2$ , this volume flow converts to a residual flow speed northwards of order  $1 \text{ cm s}^{-1}$ . The flow may reverse at times and flow southwards, however (Dabrowski et al., 2010) and it is not spatially uniform. A persistent southward flow on the western side of the



**Fig. 1.** The Irish Sea, showing place names mentioned in the text. The dashed line shows the 50 m isobath and the dot-dash line the 100 m isobath. The main sources of freshwater input are marked and labelled as follows: Dee (D), Mersey (M), Ribble (R), Morecambe Bay (into which flows the River Lune) (MB), Solway Firth (into which flows the river Eden) (SF), Avoca (A), and Liffey (L). The majority of the freshwater input (approximately 80%) flows into the eastern Irish Sea.

North Channel is observed (Brown and Gmitrowicz, 1995) and may be part of a general clockwise circulation around Ireland.

## 3. Distribution of salinity and flushing of the Irish Sea

Observations of salinity in the Irish Sea over many years have been collected and summarised by the UK's Centre for Environment, Fisheries and Aquaculture Science (CEFAS) and are shown in their atlas as distributions in winter and summer (MAFF, 1981). In Fig. 2 we show the surface distribution of annual mean salinity (calculated as the arithmetic mean of the winter and summer values). There is a gradient of decreasing salinity from south to north. Given that there is, on average, a slow, northerly flow, this gradient is consistent with fresh water from land runoff and rainfall at sea being added to the flow as it moves north. If the volume flow rate at the southern entrance to the Irish Sea is  $Q_{IN} \text{ m}^3 \text{ s}^{-1}$  and that at the northern end is  $Q_{OUT} \text{ m}^3 \text{ s}^{-1}$ , the difference between these two is equal to the net rate at which fresh water flows into the sea, that is

$$Q_{OUT} - Q_{IN} = R \quad (1)$$

where  $R$  is the net rate (input–evaporation) of freshwater input to the sea. Bowden (1955) carried out a careful inventory of freshwater inputs; he calculated total riverine inputs to be  $983 \text{ m}^3 \text{ s}^{-1}$  on average of which  $790 \text{ m}^3 \text{ s}^{-1}$  (80%) is introduced via Liverpool Bay. A further  $336 \text{ m}^3 \text{ s}^{-1}$  is added by rainfall on the Irish Sea. These figures give a mean value of  $R$ , neglecting evaporation,

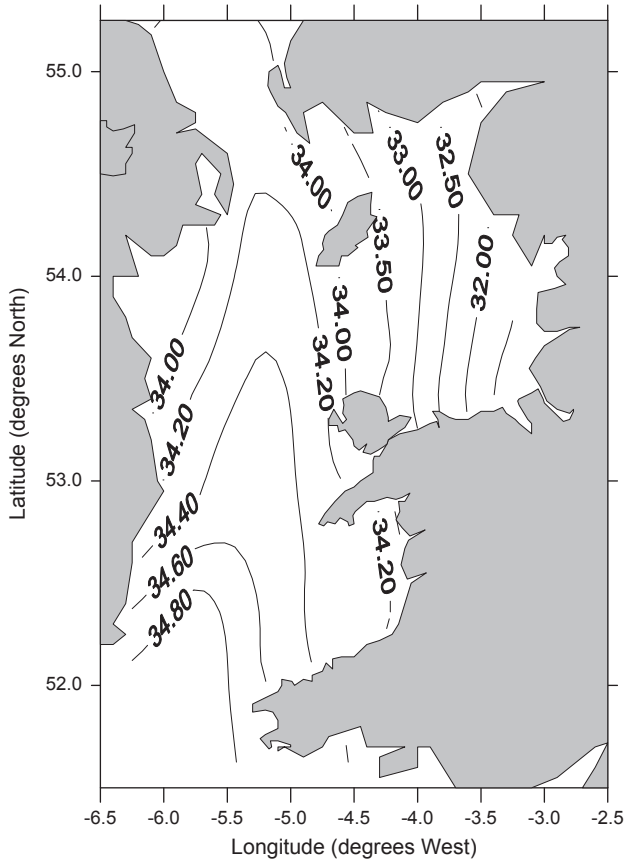


Fig. 2. Distribution of surface salinity, averaged over the year, drawn from data from MAFF (1981).

of  $1319 \text{ m}^3 \text{ s}^{-1}$ . Conservation of salt within the Irish Sea requires that

$$Q_{OUT}S_N = Q_{IN}S_S \quad (2)$$

where  $S_N$  and  $S_S$  are the salinities of the outflow and inflow respectively. Taking  $S_N = 34$  and  $S_S = 34.8$  from Fig. 2 and solving Eqs. (1) and (2) gives  $Q_{OUT} = 57,000 \text{ m}^3 \text{ s}^{-1}$  (or  $0.06 \text{ Sv}$ ), which lies in the middle of the range of measured values. Dividing the volume of the Irish sea by  $Q_{OUT}$  gives the flushing time as approximately 1 year.

#### 4. Surface distribution of CDOM

On a number of cruises over the years 2003–2009, surface water samples (collected with a bucket at a depth of 0.5 m) were taken in the Irish Sea and analysed for CDOM absorption. The samples were filtered through Millipore filters (pore size  $0.2 \mu\text{m}$ ) and stored in a refrigerator (at  $-2^\circ \text{C}$ ) on board ship. On return to the laboratory (as soon as possible after the end of the cruise, samples were allowed to warm to room temperature and the absorbance spectrum of the filtrate measured in a 10 cm path-length cell using a Shimadzu UV-1601 dual beam spectrophotometer with a distilled water reference blank. The absorption of the filtrate at 440 nm ( $g_{440}$ ; Kirk, 1994) was calculated as

$$g_{440} = \frac{2.303}{L} (A(440) - A(750)) \quad (3)$$

where  $L$  is the pathlength of the cell and  $A(\lambda)$  is the absorbance at wavelength  $\lambda$ . Absorbance at 750 nm is subtracted to remove the effects of residual scattering. The total number of observations of  $g_{440}$  available to us within the borders of the Irish Sea is 355.

In addition to the CDOM absorption measurements, a further 146 fluorometric measurements of CDOM were made on cruises in the early 1980s. In this data set, filtered seawater samples were placed in a Turner benchtop fluorometer, illuminated at 365 nm and CDOM fluorescence at 460 nm was measured. These results were expressed in millifluorescence (mfl) units (Agnew, 1983). To compare these two sets of data, observations of both absorption and fluorescence were averaged into grid elements measuring  $1/4$  degree latitude by  $1/2$  degree longitude (approximately 28 km square). In grid elements for which both types of measurements were made, the average value of CDOM absorption was regressed against the average value of fluorescence. This produced the following relationship between CDOM fluorescence and absorption in the Irish Sea:

$$g_{440} = 0.1 + 0.015F \quad (4)$$

where  $F$  is the CDOM fluorescence expressed in millifluorescence.  $R^2$  for this regression is 0.7 and the standard error of the slope and intercept are 0.025 and 0.003 respectively.

Eq. (4) was applied to the fluorescence measurements to convert them to  $g_{440}$ , which extended the number of grid elements in which estimates of CDOM absorption were available. The resulting number of observations of CDOM concentration in each grid element is shown in Fig. 3. The distribution is uneven, with good coverage in a zonal band across the centre of the Irish Sea but with a scarcity of observations in the North Channel and on the Welsh side of St. George's channel.

Fig. 4(a) shows the distribution of CDOM in surface water. The highest values of  $g_{440}$  are found in Liverpool Bay with a second maximum on the Irish coast. The Liverpool Bay maximum is

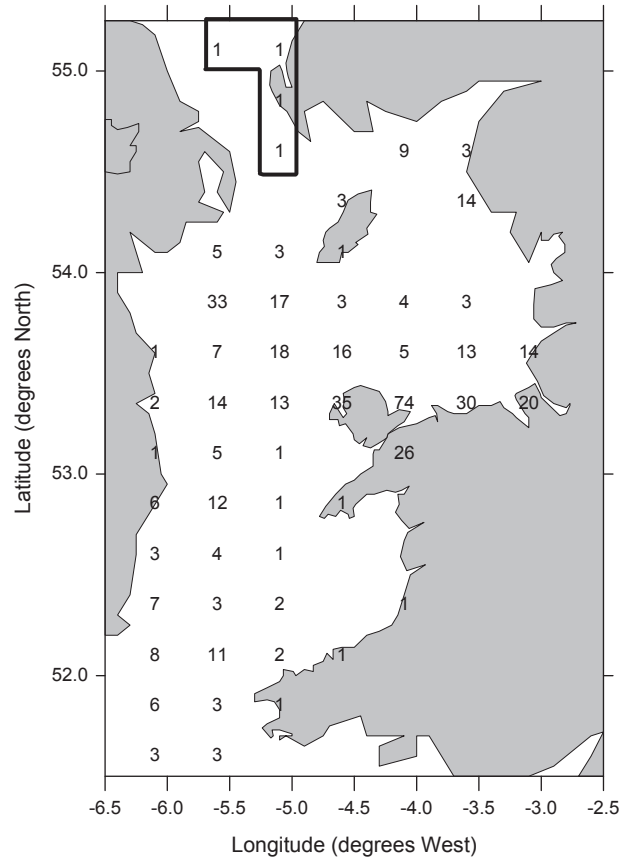
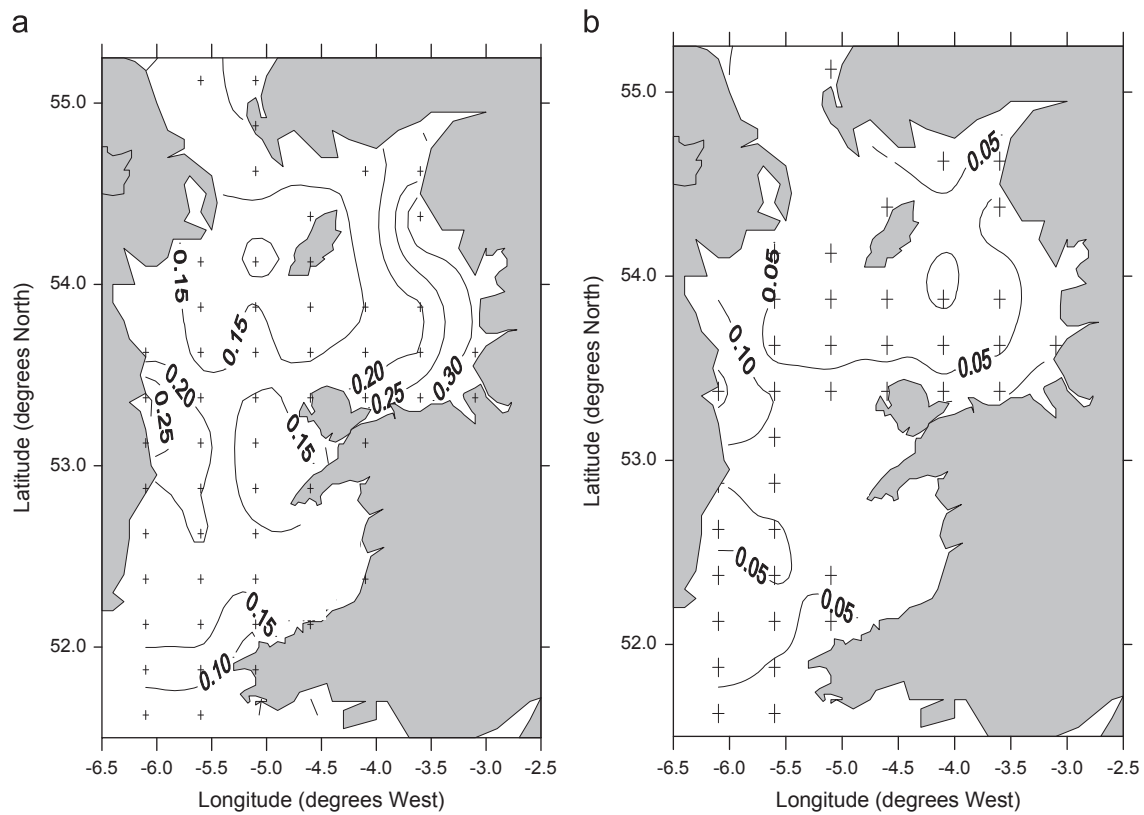


Fig. 3. The number of observations of surface CDOM concentration in grid elements of  $1/4$  degree of latitude by  $1/2$  degree of longitude. The four observations in the polygon marked at the top of this figure were averaged to provide a CDOM absorption coefficient in the North Channel.



**Fig. 4.** (a) Distribution of CDOM 'concentration' in the surface waters of the Irish Sea. Concentration is expressed as the absorption coefficient of filtered seawater at 440 nm, in units of per metre. Contour interval is  $0.05 \text{ m}^{-1}$ . The plus symbols indicate grid elements in which data is available. (b) Standard deviation of CDOM absorption coefficients about the mean value in each grid element. Units are  $\text{m}^{-1}$ . Plus symbols show location of grid elements for which a standard deviation can be calculated.

produced by the freshwater runoff through the English rivers. Irish rivers, although not contributing as high a volume of fresh water as their English counterparts, are a rich source of coloured organic material, at least in the region at about  $53^\circ\text{N}$  shown in Fig. 4(a) where the Avoca river flows into the Irish Sea (White et al., 2005). A similar finding about the distribution of CDOM was reported by Bowers et al. (2002) using a smaller sub-set of the observations reported here. There is a suggestion in Fig. 4(a) that the CDOM-stained water introduced into the Irish Sea from the Irish coast moves southwards. This would be consistent with the postulated density-driven clockwise circulation around Ireland. We have some (unpublished) ADCP measurements in this region which show a residual flow southwards close to the Irish coast. There is also a pool of low CDOM absorption to the west of the Isle of Man. The average CDOM absorption at the southern entrance to the Irish Sea is less than  $0.1 \text{ m}^{-1}$ .

Observations in the North Channel are sparse but taking an average of the absorption measurements in the four grid elements encompassed by the box in Fig. 3 gives a value of  $g_{440} = 0.17 \text{ m}^{-1}$  with a standard deviation of  $0.02 \text{ m}^{-1}$  ( $N=4$ ). The geographical distribution of the standard deviation of  $g_{440}$  about the mean value in each grid element is shown in Fig. 4(b). The variability of CDOM absorption tends to be greatest near the coast, in particular near the sources of CDOM in Liverpool Bay and on the Irish coast.

Coverage in the southern entrance to the Irish Sea is relatively good (Fig. 3) but the values of  $g_{440}$  are relatively low there (less than  $0.1 \text{ m}^{-1}$ ; Fig. 4(a) and Table 1). This is perhaps surprising considering the proximity of the Severn estuary to the southern entrance of the Irish Sea. The Severn has a large catchment and could be expected to have a high concentrations of CDOM in its outflow. The concentration and fate of CDOM in the Severn outflow would be a fruitful area of study in the future.

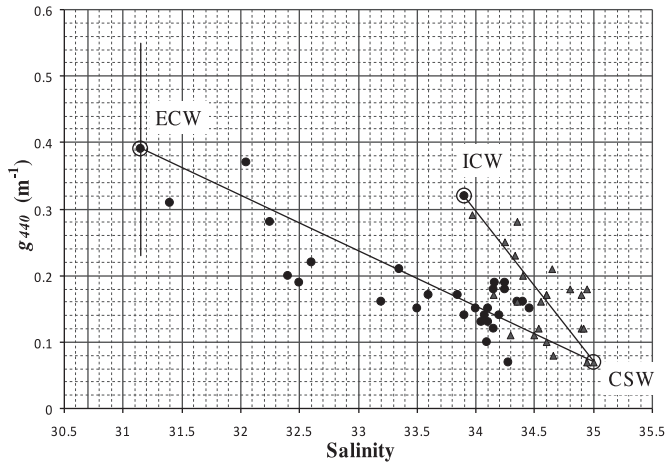
**Table 1**  
Water types.

Type	Salinity	Range	$g_{440} (\text{m}^{-1})$	St. dev.
Celtic Sea	35.0	0.2	0.07	0.01
English coastal	31.15	0.7	0.39	0.16
Irish coastal	33.90	0.0	0.32	0.17

## 5. Mixing diagrams for the Irish Sea

In order to produce a mixing diagram of salinity against CDOM, CEFAS salinity data was averaged into the same grid elements as the CDOM data, namely  $1/4$  degree latitude by  $1/2$  degree longitude. The underlying assumption in analysing the data in this way is that both CDOM and salinity distributions are representative of the long term, climatic mean. The fact that salinity was not measured coincidentally with CDOM is assumed not to be critical. The resulting mixing diagram is shown in Fig. 5. The data points in this figure show considerable scatter but they do, in general, lie along one of two converging lines. The ends of these lines correspond to the water types of the Irish Sea. A putative analysis therefore includes three water types, which can be identified by the mean  $g_{440}$  and salinity values in the grid elements at the ends of these lines. The point of convergence of the lines corresponds to the high salinity, low CDOM water characteristic of the southern entrance to the Irish Sea. We can identify the characteristics of this water type, which we shall call Celtic Sea Water (CSW), with the salinity and  $g_{440}$  values of the most south-westerly grid element in our data, namely  $g_{440} = 0.07 \text{ m}^{-1}$  and  $S = 35.0$  (Table 1). Table 1 also includes the standard deviation of  $g_{440}$  about the mean in the relevant grid element and the difference between summer and



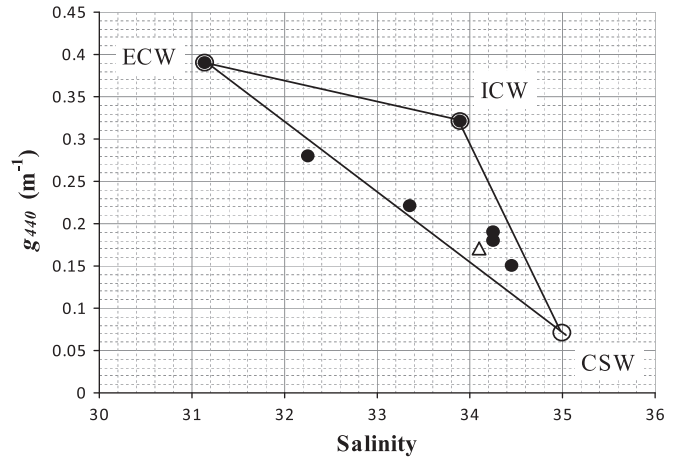


**Fig. 5.** Plot of mean  $g_{440}$  against mean salinity in each grid element. Solid circles show data points as pairs of  $g_{440}$ –salinity values. The data has been divided into two geographical regions: closed circles represent grid elements from the northern half of the Irish Sea (above 53.25°N) and triangles are from grid elements south of this latitude. The larger, open, circles represent the 3 water types (ECW, ICW and CSW) believed to be mixing in the Irish Sea. The lines joining these water types represent perfect mixing lines along which a mixture of any two water types should lie. The vertical line through the ECW point represents the standard deviation of  $g_{440}$  about its mean value for ECW.

winter salinity in the CEFAS data set. The two other principal water masses are the low salinity, high CDOM English Coastal Water (ECW), originating in Liverpool Bay, with  $g_{440}=0.39\text{ m}^{-1}$  and  $S=31.15$  and the relatively high salinity, high CDOM Irish Coastal Water (ICW) with  $g_{440}=0.32\text{ m}^{-1}$  and  $S=33.90$ .

We have coded the points in Fig. 5 according to their geographical location. Triangles represent grid elements south of latitude 53.25°N and circles represent grid elements north of this latitude. The data points are scattered but it can be said with some certainty that in the southern half of the Irish Sea (triangles), mixing is primarily (although not exclusively) between Celtic Sea water entering from the south and Irish coastal water. In the northern half of the Irish Sea (circles) mixing is between the Celtic Sea water, now containing some Irish water, and English coastal water.

The scatter of the points in Fig. 5 about straight lines joining the water types (or end members) is consistent with the variability, with time, of these end members, although it also may indicate non-conservative behaviour of CDOM. When two water types, of constant conservative properties, mix, the mixture lies along a straight line joining the two water types on a mixing diagram. If, now, the properties in one of the end members change with time (but remain conservative), the properties in the mixture will depend on the properties of the end member *at the time the water left its source*. The result is that the points representing the mixture on the mixing diagram will now lie both above and below the line joining (the mean values of) the end members. The scatter of the points about the line will be somewhat less than the variability in the end member. This reduction depends on the flushing time of the water body receiving the mixture (Bowers and Brett, 2008). In Fig. 5 we have marked the standard deviation of  $g_{440}$  in English Coastal water. The scatter in the points about the line joining the mean properties of ECW and CSW is somewhat less than the variations in  $g_{440}$  in the end member, and so is consistent with the above view. Similar reasoning applies to the scatter along the CSW–ICW line. There is a suggestion in the data (not shown here) that the variation of  $g_{440}$  in English Coastal Water is seasonal. It may, therefore, be possible to correct for the varying position of the end members by taking into account the time of year of the



**Fig. 6.** Plot of  $g_{440}$  against salinity for a line of grid elements across the Irish Sea between latitudes 53 1/4 and 53 1/2 degrees north. Solid circles show data points as pairs of  $g_{440}$ –salinity values. Open circles represent the three water types (ECW, ICW and CSW) considered to be mixing in the Irish Sea. The triangle shows the mean  $g_{440}$  and salinity values in the North Channel.

observations, but at present the data set is too small to do anything other than taking annual means in each cell.

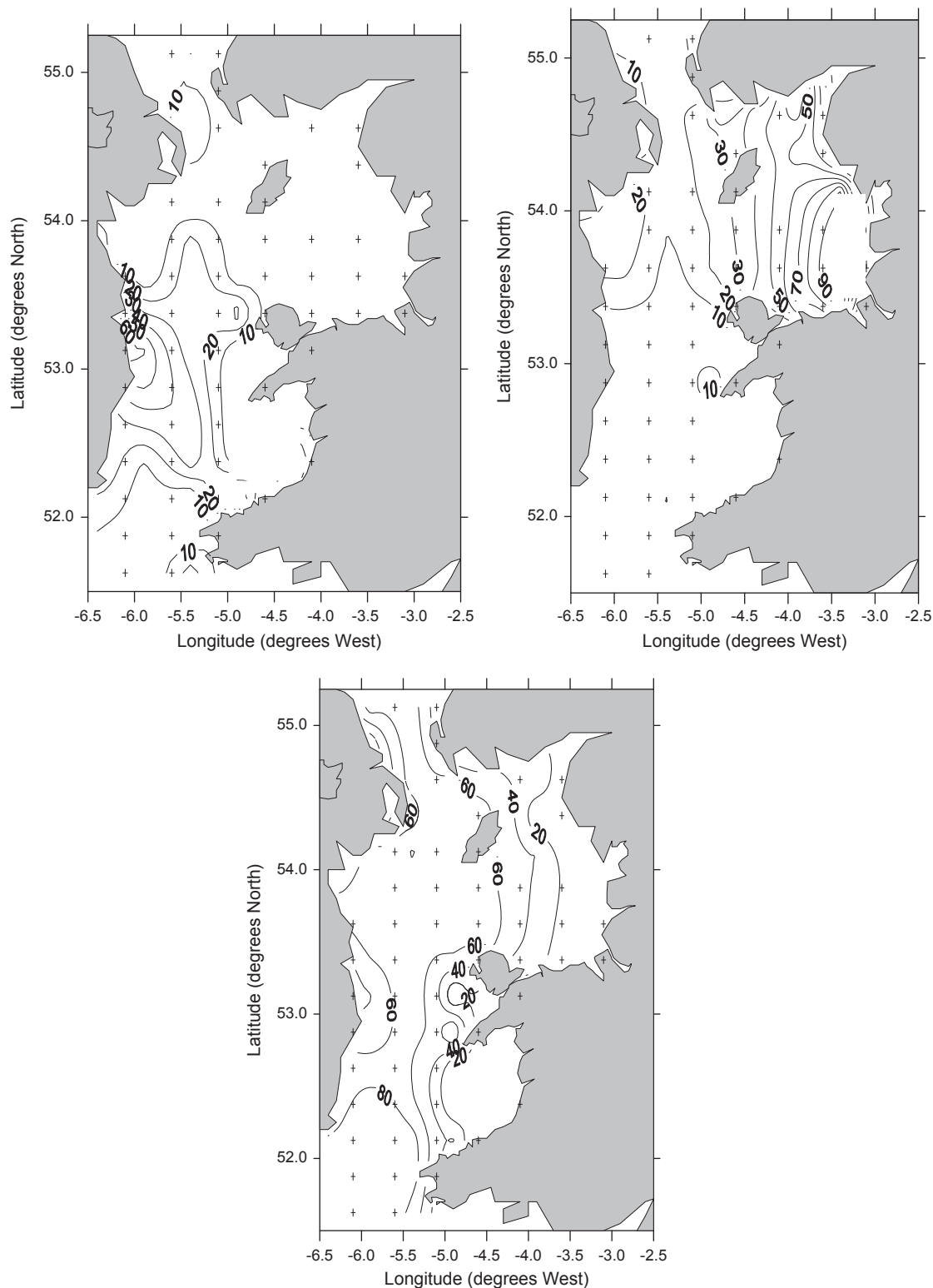
The effect of variability with time can be reduced by considering only a line of cells across the centre of the Irish Sea where most observations are available and hence where seasonal effects will tend to smoothed out. Fig. 6 shows the results of doing this for the 7 cells lying between 53.25°N and 53.5°N. The points lie in V-shape with the apex of the V occupied by the cell containing the highest proportion (the 'core') of Celtic Sea water. In this core the water is composed of approximately 70% CSW, 23% ICW and 7% ECW (the method for calculating these proportions is described in the next section). On its passage northwards between Wales and Ireland, the Celtic sea water has therefore mixed principally with Irish water on its western flank. The triangle symbol in Fig. 6 shows the mean salinity and  $g_{440}$  value averaged over the four grid elements in the North Channel. This point lies on a line joining the core of Celtic water at 53.25–53.5°N with English coastal water. As the flow continues northwards from the middle of the Irish Sea, therefore, the core of Celtic water mixes predominantly with English coastal water on its east flank. The mixture that emerges from the North Channel comprises approximately 66% CSW, 20% ECW and 14% Irish water.

## 6. Water mass proportions

The description of the mixing of water types given in the last section can be quantified by calculating the proportion of the three water types in each cell. This can be done by solving the three conservation equations for salt, CDOM and volume (Hojerslev et al., 1996; Stedmon et al., 2010). For example, if the characteristic CDOM and salinity of Irish coastal, English coastal and Celtic sea water are respectively  $g_i, S_i; g_e, S_e$  and  $g_c, S_c$ , then the proportion of Celtic Sea water in a sample which has  $g_{440}=g$  and salinity  $S$  is

$$P_c = \frac{(g-g_i)(S_e-S_i)-(g_e-g_i)(S-S_i)}{(g_e-g_c)(S_i-S_c)-(g_i-g_c)(S_e-S_c)} \quad (5)$$

with similar expressions for the proportions of Irish coastal and English coastal water. If a cell lies outside the triangle formed by the three water types on the  $g_{440}$ –salinity diagram, these equations will return a negative proportion for one of the water masses and a correction is needed. The procedure we adopted in this case was to assume that points lie outside the triangle because of

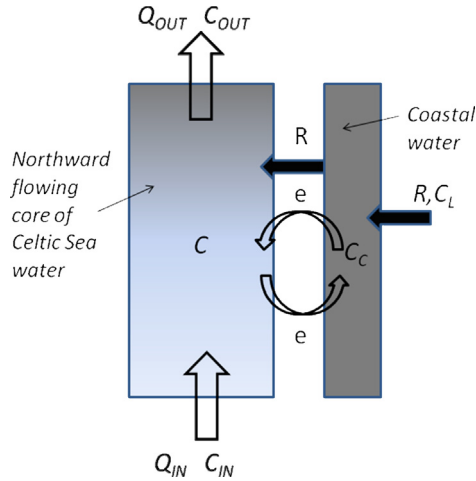


**Fig. 7.** Geographical distributions of the proportions of (a) Irish Coastal water; (b) English Coastal water and (c) Celtic Sea water.

seasonal variations in (mainly) the  $g_{440}$  values of the end member water types. If a negative proportion of one water type was returned, the  $g_{440}$  value of the relevant end member was adjusted to make the proportion of that water type zero and correspondingly to increase the proportions of the two other water types. The values of the end members were changed just for individual points which returned a negative proportion (that is, points that lie outside the mixing triangle). In all cases the adjustments were less

than one standard deviation of the end member values and so are consistent with the variability in the end member discussed above.

Fig. 7 shows the proportions of each water type mapped onto the Irish Sea. Information such as this is of interest to policy makers who wish to identify the impact of land discharges on the sea, for example in identifying causes of eutrophication (Tett et al., 2007). These maps show that Irish coastal water is confined mostly to the western half of St. George's channel. English coastal



**Fig. 8.** Schematic showing the core of Celtic Sea water flowing northwards through the Irish Sea and mixing with coastal water during its passage. The meaning of the concentrations and fluxes is described in the text.

water is spread over a larger area in Liverpool Bay and to the east of the Isle of Man but does not reach southwards into St. George's channel. The core of Celtic Sea water travels northwards through St. George's channel and then to the west of the Isle of Man. The proportion of Celtic Sea water in this core falls from 100% to 65% during its transit of the Irish Sea. This dilution of Celtic Sea water makes it possible to form an estimate of the lateral mixing coefficient.

## 7. Lateral mixing

Fig. 8 shows a schematic of the transport and mixing processes for CDOM in the Irish Sea. For simplicity, we have assumed that there is just one body of coastal water (an average of English and Irish coastal waters). This coastal water body (with CDOM concentration  $C_C$ ) is fed by runoff from the land, which brings CDOM coloured water. The volume flux of water from land is  $R \text{ m}^3 \text{ s}^{-1}$  and it contains a land-derived concentration of CDOM equal to  $C_L$ . During its passage northwards, the core of Celtic Sea water mixes with the coastal water, becoming more coloured with distance to the north. Let this mixing be represented by an exchange coefficient  $e$  equal to the volume of water exchanged per unit time between the core of Celtic Sea water and the coastal water. Let the flow of water in to the southern entrance of the Irish Sea be  $Q_{IN}$ , with CDOM concentration  $C_{IN}$  and the flow out of the north channel be  $Q_{OUT}$  with CDOM concentration  $C_{OUT}$ . In steady state, the fluxes of CDOM in and out of the coastal water must balance and so we can write

$$RC_L + eC = (R + e)C_C \quad (6)$$

where  $C = (C_{IN} + C_{OUT})/2$  is a reasonable assumption for the average CDOM concentration in the core water. Balancing the fluxes of CDOM in the core water gives

$$Q_{IN}C_{IN} + (R + e)C_C = Q_{OUT}C_{OUT} + eC \quad (7)$$

Eq. (7) can be solved for the exchange coefficient  $e$ . Taking  $Q_{OUT} = 57,000$ ,  $Q_{IN} = 55,700$  and  $R = 1300$  (all in cubic metres per second) from Section 3 and  $C_{OUT} = 0.17$ ,  $C_{IN} = 0.07$ ,  $C = 0.12$  and  $C_C = 0.36$  from Section 4 (all these are values of  $g_{440}$  in per metre; the coastal water value is an average of that for the English and Irish water masses) gives  $e = 22,000 \text{ m}^3 \text{ s}^{-1}$  in round figures. This exchange coefficient can be converted to a lateral diffusion

coefficient by multiplying by the width of the core and dividing by the cross-sectional area through which the mixing takes place.

Taking the width of the core as 50 km and the cross-sectional area as the length of the Irish Sea (330 km) times the average depth (50 m) gives a lateral diffusion coefficient equal to  $67 \text{ m}^2 \text{ s}^{-1}$ . This is a reasonable figure for these waters. In the channel between Wales and Ireland, horizontal mixing coefficients have been estimated as  $40 \text{ m}^2 \text{ s}^{-1}$  for diffusion across the direction of tidal streams and  $600 \text{ m}^2 \text{ s}^{-1}$  for diffusion along them (Bowden, 1950; Hunter, 1975). Given the uncertainties in the estimating procedure, we can conclude that the mixing coefficient calculated from the dilution of the northward flow with mainland water is consistent with that estimated from that expected in the tidal flows of the Irish Sea.

Given this value of the exchange coefficient, Eq. (5) can be solved for the 'land' concentration of CDOM, giving  $C_L = 3.6 \text{ m}^{-1}$ . This is our estimate of the average  $g_{440}$  value in the rivers flowing into the Irish Sea.

## 8. Export of dissolved organic carbon

Although measurements in the North Channel are scarce at present, on the basis of the observations available to us in the 4 grid elements in this area (Fig. 3), the mean  $g_{440}$  value is  $0.17 \text{ m}^{-1}$  with a standard deviation of  $0.02 \text{ m}^{-1}$ . Unfortunately, it is not straightforward to convert this to a mass concentration of dissolved organic carbon. CDOM is only a part of the total dissolved organic carbon (DOC) pool and it appears to be a variable part. For example, Bowers et al. (2004) describe three different relationships between DOC and CDOM measured at different time in Conwy Bay and the Conwy estuary in north Wales. Recent data from Finland and elsewhere suggest that there may be a relationship between the mass-specific absorption coefficient of CDOM (the  $g_{440}:\text{DOC}$  ratio) and the spectral slope of the absorption coefficient (Asmala et al., 2012). For this paper, we apply the relationships given in Bowers et al. (2004) as the only ones available for the Irish Sea that we know of. These give DOC concentrations of 90, 180 and  $190 \mu\text{mol l}^{-1}$  for a  $g_{440}$  value of  $0.17 \text{ m}^{-1}$ .

Taking the average flow rate out of the Irish Sea to be  $57,000 \text{ m}^3 \text{ s}^{-1}$  and a DOC concentration in this flow in the range  $90\text{--}190 \mu\text{mol l}^{-1}$ , the dissolved carbon exported through the North Channel will lie between 61 and  $130 \text{ kg s}^{-1}$  or between 2.5 and  $5 \text{ Tg year}^{-1}$ . The net export of dissolved carbon from the Irish Sea will be somewhat less than this because there is an input of carbon from the Celtic Sea through St. George's channel. Hydes et al. (2001) present measurements of DOC in the surface waters of the Celtic Sea in the range  $50\text{--}90 \mu\text{mol l}^{-1}$ , i.e. about half the value in the north Channel. This ratio of 2:1 between DOC concentrations in the north and south is about the same as what we observe in the  $g_{440}$  values. Since the water volume discharge into the southern channel is only a little less than in the north (about  $56,000 \text{ m}^3 \text{ s}^{-1}$  from Eq. (1)) we estimate the net input of dissolved carbon to the Irish Sea from rivers to be about half the output through the North Channel, i.e. in the range  $1\text{--}2 \text{ Tg year}^{-1}$ . The total flow of dissolved organic carbon to the sea from Great Britain has been estimated as  $2 \text{ Tg year}^{-1}$  (Worrall and Burt, 2007). The Irish Sea receives only some west coast British rivers, but also Irish Rivers which we have seen are rich in CDOM and hence, presumably, DOC. Our estimate of the flux of dissolved carbon from the Irish Sea therefore appears to be of the right order of magnitude. Furthermore, the input of DOC from rivers to the Irish Sea is similar to the fluxes from rivers to other coastal water bodies:  $1.2 \text{ Tg year}^{-1}$  into the southern North Sea (Thomas et al., 2005) and  $2 \text{ g year}^{-1}$  net export from the Baltic Osburn and Stedmon (2011).

## 9. Discussion

This paper has presented the first account of using the distributions of both salinity and coloured dissolved organic matter (CDOM) to identify water types and mixing in the Irish Sea. There are a number of assumptions and weaknesses in using this type of analysis. In this paper, we have only considered surface distributions. This is probably not a problem in the areas of the Irish Sea which are vertically mixed all year but our analysis provides no information on processes happening below the thermocline in stratified areas. An implicit assumption in all mixing diagrams is that the tracers used in the analysis are behaving conservatively. We have carried out no test of the conservative behaviour of CDOM in the study area in this work. The minimum in surface CDOM absorption to the west of the Isle of Man (Fig. 4a), an area which stratifies in summer and is known to be biologically productive, may indicate non-conservative behaviour of CDOM in this region. However, this is not certain: variations in the spatial distribution of CDOM absorption may also be caused by temporal variations in CDOM as it leaves the source. The fact that lateral mixing coefficients derived from the CDOM distribution are consistent with coefficients derived in other ways for these waters supports the notion of conservative behaviour.

Finally, in order to make use of all the available CDOM data, we have compared the CDOM data base with a climatological mean salinity field, ignoring inter-annual and seasonal variations. In fact, there are significant variations in the CDOM concentration in the end members which contribute, along with the other uncertainties discussed above, to the scatter in the mixing diagrams presented here.

Despite these weaknesses, a tentative picture of processes in the Irish Sea has emerged which could not have been composed in a quantitative way without using a technique like the one we have employed here. Celtic Sea water entering the southern entrance of the Irish Sea flows northwards mixing first predominantly with Irish coastal water on its western flank, so that by the time it has reached the middle of the Irish Sea, the core comprises 70% of the original Celtic Sea water with the majority of the remainder being water from the Irish coast. As the core continues northwards it mixes with water from Liverpool Bay on its eastern flank reaching the North Channel as a mixture of 66% of the original Celtic Sea water and the remainder now mostly is English water.

Because of the problem of source variability, it is tempting to dismiss CDOM as a useful tracer in the Irish Sea. There are, however, two good reasons for persisting with this material. The first is that it has an optical signature. As well as being relatively easy to measure in samples of collected seawater, CDOM is amenable to remote sensing using visible band satellite imagery. In turbid coastal waters, such as the Irish Sea, the optical signal associated with suspended sediments must be allowed for interpreting the water colour (Bowers et al., 2004; Del Castillo and Miller, 2008; Tiwari and Shanmugan, 2011), but this may be a tractable problem. Given the expense and time involved in collecting the data at sea required to construct even a partially complete map of CDOM distribution in coastal waters, the potential role of satellite remote sensing should not be overlooked. If sufficiently accurate algorithms can be developed, satellite colour data could be used to study both the geographical distribution of CDOM in surface waters and, by using time series of images, its response to temporal variations in the source.

The second advantage of CDOM as a tracer in shelf seas is related to the current importance in studying the export of carbon from the land to the ocean via the continental shelf. CDOM is part of the total dissolved organic carbon (DOC) content of seawater. The CDOM:DOC ratio is variable, but recent studies have suggested that it can be quantified if the slope of the absorption spectrum of CDOM is known (Helms et al., 2008; Spencer et al., 2012; Asmala et al., 2012). In principle, this slope is implicit in ocean colour

measurements. If both the CDOM concentration and spectral slope can be derived from space, this would enable the mapping of DOC concentrations in surface waters.

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