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# CONTINENTAL SHELF RESEARCH

# 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 m<sup>2</sup> s<sup>-1</sup>. The CDOM absorption coefficient at 440 nm in the water leaving the Irish Sea is 0.17 m<sup>-1</sup>. 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

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0278-4343/\$ - see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.csr.2013.02.007 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



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 quarterwavelength 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 m s<sup>-1</sup> 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 freshwaterinduced 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 0.02–0.14 Sv (1 Sv= $10^6$  m<sup>3</sup> s<sup>-1</sup>). For a representative cross-sectional area of  $7 \text{ km}^2$ , this volume flow converts to a residual flow speed northwards of order 1 cm s<sup>-1</sup>. 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  $Q_{IN}$  m<sup>3</sup> s<sup>-1</sup> and that at the northern end is  $Q_{OUT}$  m<sup>3</sup> s<sup>-1</sup>, the difference between these two is equal to the net rate at which fresh water flows into the sea, that is

$$Q_{OUT} - Q_{IN} = R \tag{1}$$

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 m<sup>3</sup> s<sup>-1</sup> on average of which 790 m<sup>3</sup> s<sup>-1</sup> (80%) is introduced via Liverpool Bay. A further 336 m<sup>3</sup> s<sup>-1</sup> is added by rainfall on the Irish Sea. These figures give a mean value of *R*, neglecting evaporation,

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