Nitrogen dynamics in the Irish Sea and adjacent shelf waters: An exploration of dissolved organic nitrogen

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Grigorios Moschonas [a, *], Richard J. Gowen [b], Brian M. Stewart [b], Keith Davidson [a]

[a] Scottish Association for Marine Science, Scottish Marine Institute, Oban, Argyll, PA37 1QA, UK
[b] Fisheries and Aquatic Ecosystems Branch, Agriculture Food and Environmental Science Division, Agri-Food and Biosciences Institute, Newforge Lane, Belfast, BT9 5PX, UK

ABSTRACT

Relatively little is known about dissolved organic nitrogen (DON) in the marine environment because research has historically focused on dissolved inorganic nitrogen (DIN). In this study we combine measurements of dissolved organic matter (DOM), DIN, particulate organic nitrogen (PON), dissolved inorganic phosphorus (DIP) and silicon (DIS), with temperature and salinity data from the western shelf region of the UK and Ireland, and with inorganic and organic nitrogen (N) data from the western Irish Sea to develop an understanding of N dynamics in the Irish Sea and adjacent shelf waters, and investigate the role of DON in the nitrogen budget of the seasonally stratifying western Irish Sea. In January 2013, the sampling area was divided by density fronts into 4 regions of distinct oceanography and homogeneous chemistry. DON concentrations accounted for $25.3 \pm 1.8\%$ of total dissolved N (TDN) across all regions. DOM concentrations generally decreased from the freshwater influenced water of Liverpool Bay to the oceanic waters of the Celtic Sea and Malin Shelf. Urea and dissolved free amino acids (DFAA) together made up $27.3 \pm 3.1\%$ of DON. Estimated concentrations in the rivers discharging into Liverpool Bay were 8.0 and 2.1 μmol N L^{-1} respectively: at the high end of reported riverine concentrations. Oceanic nutrient inputs to the Irish Sea only have a small influence on N concentrations. Riverine N inputs to the Irish Sea are substantial but are likely removed by natural N cycling processes. In the western Irish Sea, DON and PON concentrations reached maxima and minima in midsummer and early spring respectively. DIN followed the opposite trend. DON accounted for 38% of the yearly internal N cycling and we estimated that as much as 1.4 ± 1.2 μmol N L^{-1} of labile DON was available as an N source at the start of the spring bloom. Our study supports the view that DON plays an important role in N cycling in temperate shelf and coastal seas and should be included more often in biogeochemical measurements if we are to have a complete understanding of N dynamics in a changing world.

1. Introduction

Historically, research on the nitrogen (N) biogeochemistry of coastal and shelf seas (CSS) has focused on inorganic N. Over the past four decades, N has been established as the main limiting nutrient for primary production in the temperate CSS (although other nutrients may be limiting locally and seasonally) based mainly on measurements of nitrate and ammonium (Howarth, 1998; Howarth and Marino, 2006; Ryther and Dunstan, 1971; Vitousek and Howarth, 1991). There is, however, increasing recognition of the importance of dissolved organic N (DON) to marine primary productivity and biogeochemical cycling. DON has been shown to be an important component of the total dissolved N (TDN) pool in aquatic ecosystems, where DON is often found in higher concentration than that of the inorganic species nitrate, nitrite and ammonium together (Berman and Bronk, 2003), which collectively comprise dissolved inorganic nitrogen (DIN). In CSS, compilations of measurements (Antia et al., 1991; Bronk, 2002; Sipler and Bronk, 2015) and individual studies (Davidson et al., 2013) show that DON sometimes accounts for more than 50% of TDN.

Both laboratory (Antia et al., 1991; Flynn and Butler, 1986) and field (Middelburg and Nieuwenhuize, 2000; Mulholland and Lomas, 2008; Solomon et al., 2010) measurements show the

potential importance of DON to marine primary productivity and biogeochemical cycling. Although the DON pool remains largely uncharacterised (Aluwihare and Meador, 2008), up to ~70% is potentially bioavailable (Bronk, 2002). This fraction contains semi-labile and labile low molecular weight compounds such as urea, dissolved free amino acids (DFAA), amino sugars, nucleic acids, creatine and ATP (Antia et al., 1991; Bronk, 2002; Mulholland and Lomas, 2008; Sipler and Bronk, 2015) some of which can be utilised as N sources by both bacteria and phytoplankton (Bronk et al., 2007; Lønborg et al., 2009b; Pete et al., 2010). Urea is of particular interest because it has been linked to the growth (and blooms) of some species of harmful algae (Glibert et al., 2006, 2005). The importance of including DON in marine studies is exemplified by its significant role (Bronk et al., 1994) in the calculation of new and regenerated production (Dugdale and Goering, 1967), and for modelling carbon fluxes to the deep ocean (Eppley and Peterson, 1979).

Only a few published studies spread over several decades have focused on, or even included, measurements of DON in CSS waters surrounding the British Isles. Most of these have concentrated on the North Sea (Johnson et al., 2012; Riegman and Noordeloos, 1998; Suratman et al., 2008) and the English Channel (Butler et al., 1979; Flynn and Butler, 1986) where the increase in DON after the spring bloom could act as an N source for the microbial community during the nitrate deficient summer months. Two studies were conducted in estuaries discharging to the North Sea, the Thames (Middelburg and Nieuwenhuize, 2000) and Colne (Agedah et al., 2009); one in estuaries discharging to the English Channel (Badr et al., 2008); and a few studies described aspects of dissolved organic matter (DOM) dynamics in Loch Creran and Loch Etive (Lønborg et al., 2009a, 2009b; Solórzano and Ehrlich, 1979, 1977), two fjordic sea-lochs on the west coast of Scotland.

The shelf region to the west of Britain is a potentially important carbon sink (Muller-Karger et al., 2005), and is a location that experiences a range of harmful algal blooms (Davidson et al., 2009; Davidson and Bresnan, 2009; Raine et al., 2010). Considerable research effort has been put into studying the physical (Ellett, 1979; Hill and Simpson, 1989; Pingree et al., 1976, 1999; Simpson and Hunter, 1974), chemical (Gowen et al., 2002; Hydes et al., 2004; Slinn, 1974; Trimmer et al., 1999) and plankton dynamics (Gowen et al., 1998, 1995; Gowen and Bloomfield, 1996; Raine and McMahon, 1998; Williamson, 1956, 1952) of the region. Yet, DON in this region is highly understudied, with only spatially and temporally localised measurements of DON (Davidson et al., 2013; Shammon and Hartnoll, 2002) and amino acids (Poulet et al., 1991; Riley and Segar, 1970; Williams and Poulet, 1986). Here we report the results of a cruise through regions of the Malin Shelf, Irish Sea and Celtic Sea conducted in January 2013 (when nutrient concentrations approach their winter maxima) during which we determined concentrations of both inorganic and organic N, dissolved inorganic phosphorus (DIP) and dissolved inorganic silicon (DIS) and DOC, together with the physical characteristics of the water masses. These data are interpreted in conjunction with measurements of inorganic and organic N concentrations from a 5 year study in the western Irish Sea. Collectively these data provide a baseline against which to evaluate DON concentrations, its spatial and seasonal variability in relation to the physical characteristics of the water column and its contribution to the total N budget of the region.

2. Materials and methods

2.1. Quasi-synoptic survey

Sampling was carried out between 3 and 13 of January 2013 on-board the Agri-Food and Biosciences Institute research vessel (RV) *Corystes*. A total of 74 stations were sampled in areas of the Malin Shelf, Irish Sea and Celtic Sea (Fig. 1, Fig. A1) and encompassed oceanic and inner shelf waters and the region of freshwater influence (ROFI) in Liverpool Bay. At each station, a SBE 9 plus CTD (Sea-Bird Electronics) mounted on a SBE 32 Carousel water sampler supporting 12 niskin-type 5 L bottles was deployed to record vertical profiles of temperature and conductivity, and to obtain water samples from depths selected on the basis of the density structure of the water column. Inorganic nutrients and phytoplankton pigments were sampled at all 74 stations, while DON was sampled at 35 of these stations. A shipboard SBE 21 SEACAT thermosalinograph (Sea-Bird Electronics) fitted with an input from the ship's navigational system and receiving water from the ship's seawater supply (depth ~5 m) was used for recording temperature and conductivity
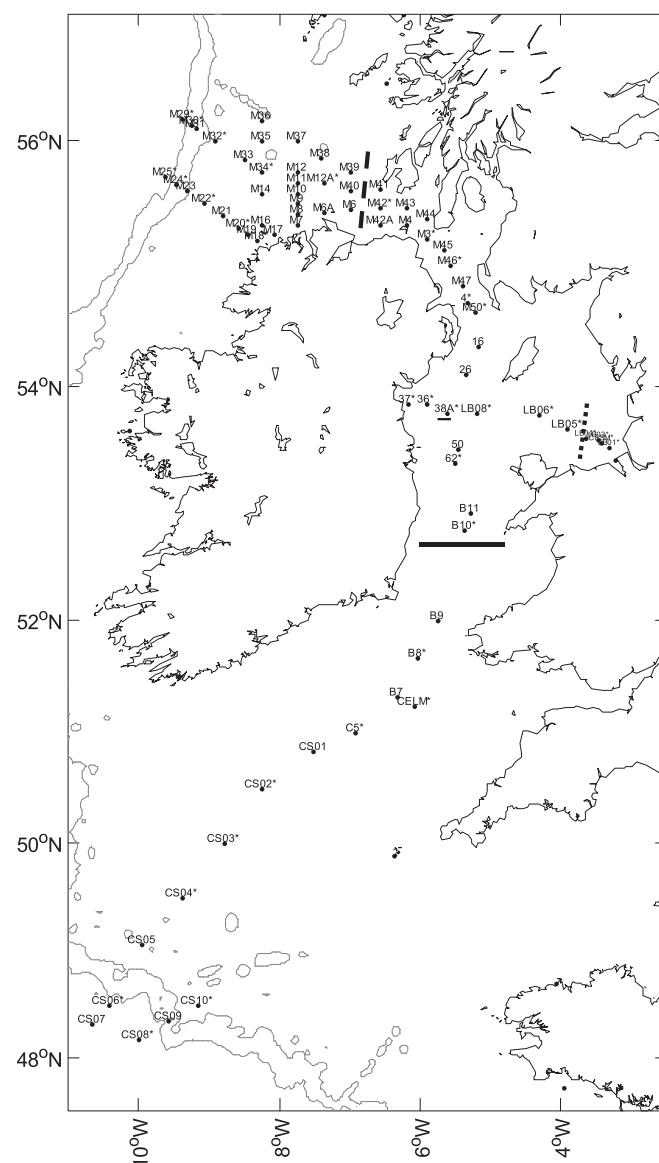

Fig. 1. A map of the western shelf region showing the positions of the stations sampled in January 2013 and the approximate positions of the observed fronts (see text). Superscripted asterisks denote stations where DON was sampled. Station 38A, the location of the seasonal study, is underlined. Contour lines (grey) show the 200 m and 1000 m isobaths at the shelf slope. Fronts: Islay front (dashed), Liverpool Bay front (dotted), St. George's Channel front (solid).

along the ship's track.

The International Thermodynamic Equation of Seawater 2010 in the GSW Oceanographic Toolbox (IOC et al., 2010; McDougall and Barker, 2011) was used to calculate absolute salinity (g kg^{-1}), conservative temperature (°C), and potential density (kg m^{-3}) from practical salinity and in-situ temperature downloaded from the instruments. The salinity variable presented in this study is absolute salinity with units of g kg^{-1}, rather than practical salinity which has no units (McDougall and Barker, 2011). Near surface salinity, temperature and density data are the averages for the first 10 m of the water column. Nutrient concentrations were integrated with and then divided by depth (maximum sample depth of each station) to obtain water column average concentrations for each nutrient. Nutrient concentrations are presented in units of μmol L^{-1} which are equivalent to 10^{-3} mol m^{-3} (SI) or mmol m^{-3} (SI). Both physical and chemical parameters in this paper are presented thus, unless otherwise specified in figure labels.

Samples for the determination of urea, DFAA, and dissolved inorganic nutrient concentrations were filtered through precombusted 10 mm or 25 mm glass fibre filters (0.7–1 μm nominal pore size prior to combustion) using clean plastic syringes, and stored frozen in polyethylene acid-washed sample bottles at −20 °C until analysis. Dissolved inorganic nutrients were analysed on a 5 Channel QuAAtro autoanalyser (Seal Analytical), configured for the simultaneous determination of DIN, DIP, and DIS in sea water (Seal Analytical, 2011a, 2011b, 2011c, 2011d, 2011e).

Urea analysis was performed using the manual diacetyl monoxime method (Mulvenna and Savidge, 1992), adapted for room temperature (Goeyens et al., 1998), use of a single reagent and low sample volumes (Revilla et al., 2005). Samples were thawed overnight, 4 ml of each replicate was transferred to 15 ml polypropylene centrifuge tubes, the reagent was added and the solutions were mixed by vortex before being incubated at 22 °C in the dark for 72–84 h (Goeyens et al., 1998). Then, absorbance was measured by spectrophotometry at 520 nm on an Evolution 300 UV–Vis Spectrophotometer (Thermo Scientific).

Total DFAA concentrations were determined by the o-pthaldehyde fluorometric method (Parsons et al., 1984), optimised for the use of 3-mercaptopropionic acid in the reagent which gives better reliability than mercaptoethanol (Aminot and Kérouel, 2006). Samples were thawed overnight, and 5 ml of each replicate transferred to 15 ml polypropylene centrifuge tubes. The reagent was added and each solution was mixed by vortex and allowed to stand for 2 min before its fluorescence was measured on a Trilogy laboratory fluorometer (Turner Designs). The method was calibrated with glycine standards and the DFAA concentrations were expressed as a glycine equivalent (Parsons et al., 1984; Tada et al., 1998). In a preliminary test of the procedure, the method was calibrated with both glycine and serine, as recommended by Aminot and Kérouel (2006), but as no notable difference was found between the two standards, glycine alone was chosen as the standard for the sample analysis.

Samples for the determination of dissolved DOC and DON concentrations were filtered, to remove particles, through precombusted 25 mm glass fibre filters (0.7–1 μm nominal pore size prior to combustion), using acid-washed glass syringes, acidified with 50 μl 85% orthophosphoric acid, and stored in sealed precombusted glass containers at 4 °C in the dark until analysis (Davidson et al., 2007). Analysis of DOC and DON was performed by high temperature catalytic oxidation (Walsh, 1989) with nondispersive infrared and chemiluminescence detections on a Shimadzu TOC-Vcph total organic carbon (TOC) module connected to a Shimadzu TNM-1 total N (TN) module. The measurements were quality checked at each run with an external reference of Florida Strait water at 700 m. DOC concentrations were determined

directly after the acidified samples were sparged with air to remove dissolved inorganic carbon. DON concentrations were calculated indirectly by subtracting DIN from TDN, and the propagated error was calculated by combining errors in quadrature (Taylor, 1997):

$$ERR_{DON} = \sqrt{ERR_{TDN}^2 + ERR_{NH4}^2 + ERR_{TOxN}^2}.$$

Samples for the determination of phytoplankton pigments were collected on 25 mm glass fibre filters (0.7–1 μm nominal pore size) by gentle vacuum filtration, and were stored frozen at −20 °C in 15 ml centrifuge tubes until analysis. Prior to analysis on-board RV *Corystes*, pigments were extracted in 90% neutralised acetone for 24 h. Chlorophyll and phaeopigment concentrations were determined on a 10-AU filter fluorometer (Turner Designs) before and after acidification with 8% HCl acid (Tett, 1987).

Multivariate patterns of chemical variables, including chlorophyll and phaeopigments, across stations were visualised in multivariate space with Principal Component Analysis (PCA) and were tested for no differences across regions with the nonparametric permutation-based analysis of similarities (ANOSIM) test (Clarke, 1993; Clarke and Green, 1988). This approach is similar to the multivariate approach of Fehling et al. (2012) for phytoplankton communities on the west Scottish Shelf.

2.2. Seasonal study

Sampling was carried out at approximately 6 week intervals at station 38A in the Western Irish Sea (Fig. 1) between January 1999 and January 2004. Water samples were obtained with niskin-type bottles from selected depths, filtered through 25 mm Whatman Cyclopore polyester membranes (1 μm nominal pore size), and stored frozen prior to analysis. DIN was analysed on a Bran and Leubbe TRAACS 800 autoanalyser as above. DON was determined over the concentration range 0.06–50.0 μmol N L^{-1}. Samples mixed with hydrogen peroxide were digested by UV photolysis (Armstrong et al., 1966) using a Metrohm 705 UV digester, where DON and DIN in the sample were oxidised to nitrate. TDN was then determined when digested samples were analysed for nitrate. The high temperature catalytic oxidation and UV oxidation method, used to determine TDN concentrations in samples collected during the spatial survey (Section 2.1) and the seasonal study respectively, are broadly comparable (Bronk et al., 2000; Walsh, 1989; Worsfold et al., 2008). DON concentrations and associated errors were calculated as the difference of DIN and TDN and in quadrature respectively as above. Particulate material was collected on precombusted glass fibre filters, dried, and encapsulated in aluminium foil, then analysed for particulate organic N (PON) by flash combustion on a Carlo Erba NA1500 elemental analyser. All values from samples collected during a given month were combined into a monthly average and are presented thus in this paper.

3. Results & discussion

Our aim was to develop an understanding of N dynamics (with a focus on DON) in the Irish Sea and adjacent shelf, and investigate the role of DON in the nitrogen budget of the Irish Sea, especially the seasonally stratifying western region. To achieve this we combined the results from two initially independent studies: (i) a quasi-synoptic survey of DIN and DON (together with DIP, DIS, and other chemical parameters), measured in relation to the physical oceanography of the western shelf region, with particular emphasis on oceanic and riverine sources of N to the inner shelf; and (ii) a 5 year seasonal study of DIN, PON and DON at Station 38A in the western Irish Sea.

Our analysis approach was to first gain an understanding of the physical oceanography and spatial chemical patterns of the western

shelf region and then use it to quantify the N budget of the western Irish Sea and the role of DON. So, we: (i) looked at the oceanography and divided the sampling area into different hydrodynamic regions based on the position of observed density fronts and the temperature and salinity characteristics of each station (Section 3.1.1); (ii) tested the hypothesis that each hydrodynamic region has distinct multivariate chemistry (Section 3.1.2); (iii) described spatial patterns of individual nutrients (Section 3.2.1), and evaluated N inputs to the Irish Sea (Section 3.2.2); (iv) combined this information with data from the seasonal study of N at Station 38A to quantify the N budget of the western Irish Sea, to evaluate the role of DON, and estimate the potential contribution of DON to spring bloom production (Section 3.2.3).

3.1. Oceanography

3.1.1. Physical boundaries

The physical oceanography of the sampling area was characterised by three density fronts identified by marked near surface gradients in temperature, or salinity, or both (Fig. 2). On the Malin Shelf, a salinity front extended from Malin Head to the west of Islay (Fig. 2a) and separated warm (8.8–10.5 °C), saline (35–35.6 g kg^{-1}) oceanic water to the west from cooler (8.6–10.1 °C) and fresher (33.8–34.9 g kg^{-1}) coastal water to the east in the North Channel and the western Irish Sea. Stations to the west of the front became progressively warmer and more saline with proximity to the 1000 m isobath (Fig. 3).

In the Irish Sea, a density front marked by gradients in temperature and salinity (Fig. 2b) separated the water of the western Irish Sea from the water of the Liverpool Bay. Stations in Liverpool Bay were characterised by low near surface temperature (7.1–8.3 °C) and salinity (29.6–33.4 g kg^{-1}). Further south, a
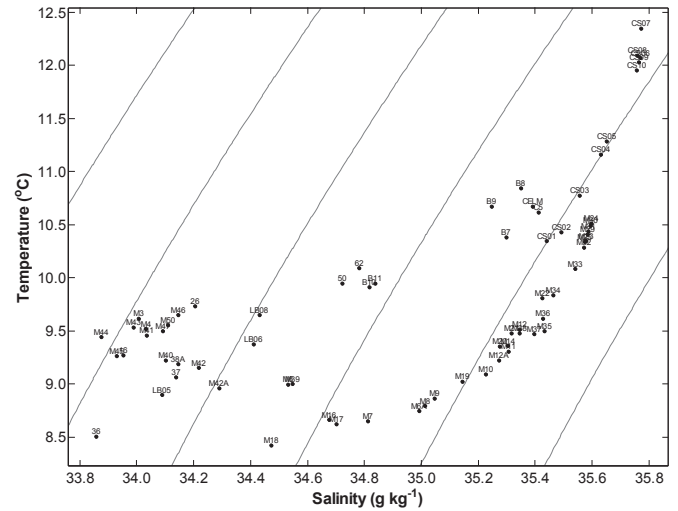
Fig. 3. A temperature and salinity plot of mean near surface temperature and salinity at each station. Low salinity Liverpool Bay stations LB01 to LB04 (salinity range 29.8–33.4 g kg^{-1}) have been omitted for clarity. Contour lines connect points of equal potential density.

density front, also marked by gradients in temperature and salinity (Fig. 2c,d) was present in the vicinity of the northern end of St. George's Channel. Across the Celtic Sea the water became more oceanic in character and stations over the Celtic Sea shelf slope (200–1000 m isobaths) reached higher near surface temperature (10.3–11.9 °C) and salinity (35.2–35.8 g kg^{-1}) than the slope stations on the outer Malin Shelf (Fig. 3).

Previous studies (cited below in this section) have demonstrated that these three density fronts are recurrent winter features. The
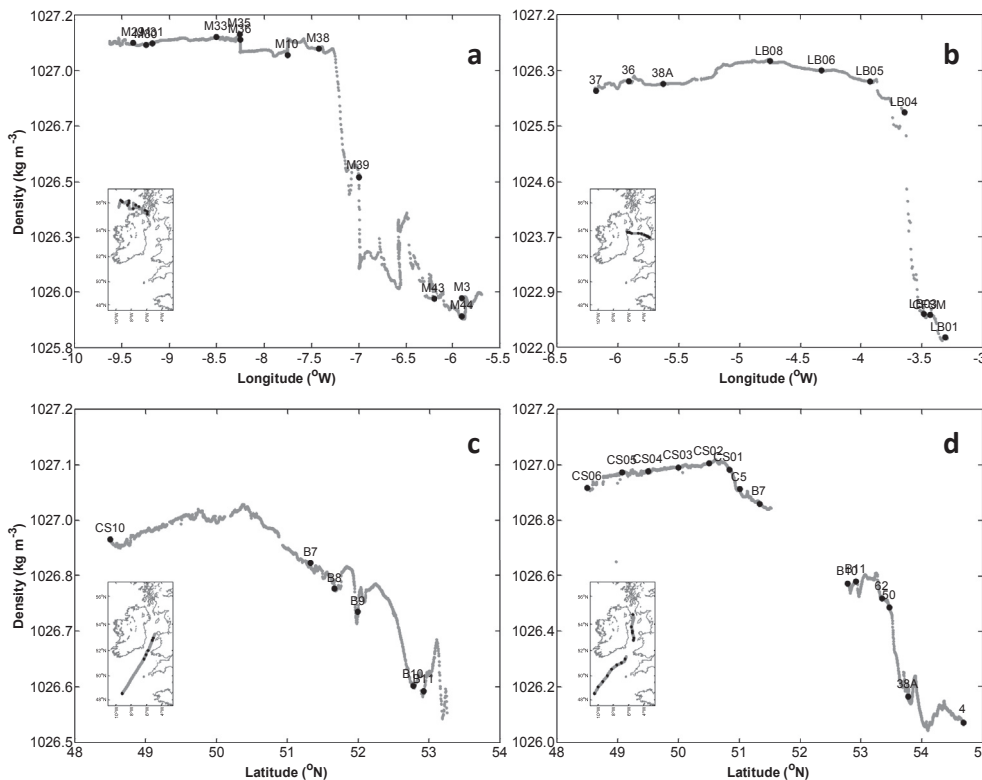
Fig. 2. Near surface (~5 m) density from temperature and conductivity recorded by the thermosalinograph aboard RV Corystes along its track in January 2013. a; east to west transect at the Malin Shelf, b; east to west transect at the Irish Sea, c; south to north transect at the Celtic Sea, d; north to south transect at the Celtic Sea.

most well-known of these is the front extending from Malin Head to the west of Islay, known as the Islay front (Fig. A2). In the winter, the Islay front is manifested as a salinity gradient caused by saline oceanic water from the shelf edge flowing on-shelf (Ellett, 1979). This water merges with fresher Irish Sea and Firth of Clyde water, to form a current flowing northward partly along the east and partly along the west coast of the Outer Hebrides (Ellett, 1979; Hill et al., 1997). During spring and summer the Islay front is more complex and includes a temperature component (Gowen et al., 1998; Hill and Simpson, 1989; Simpson et al., 1979).

There is likely to be limited exchange of water between the western and eastern Irish Sea (Gowen et al., 2002 and references cited therein). These authors observed a strong west to east gradient in salinity caused by the northward flow of more saline Celtic Sea water through the western Irish Sea and by freshwater inflow to the eastern Irish Sea. A similar situation prevailed in January 2013 and there was a pronounced salinity front between stations LB03 and LB04 in Liverpool Bay (Fig. 2b) which separated the ROFI from more saline coastal water.

A density front at St. Georges Channel was recorded in January and February 2000 by Hydes et al. (2004). These authors observed a northward shift in the position of the front during neap tide conditions relative to its position during spring tide conditions. We observed a similar effect of the tide. On the southward leg of the cruise (neap tide conditions) the front was positioned between stations 50 and 38A (Fig. 2d). On the northward leg of the cruise (spring tide conditions) the front was positioned further south between stations B9 and B10 (Fig. 2c).

For the purposes of this paper we used the observed positions of the frontal boundaries (Fig. 2) and the T-S characteristics of the sampling stations (Fig. 3) to divide the sampling area into four hydrodynamic regions of different physical and potentially chemical composition (Fig. A3). These were: 1-Outer Malin Shelf; this region is to the west of the Islay front, as far as the near ocean water of just beyond the Malin Shelf slope, and stations therein had average near surface temperature and salinity 8.8—10.5 °C and >35 g kg^{-1} respectively. 2-W Irish Sea & North Channel; this region is bounded by the Islay front to the north, the St. George's Channel front to the south and the Liverpool Bay front to the east. Stations in this region had average near surface temperature and salinity 8.6—10.1 °C and 33.8—35 g kg^{-1} respectively. 3-Liverpool Bay; this is the ROFI to the east of the Liverpool Bay front and was the region with the lowest average near surface temperature (7.1—8.3 °C) and salinity (~9.6—33.4 g kg^{-1}). 4-Celtic Sea; this region is to the south of St. George's Channel, as far as the near ocean water of just beyond the Celtic Sea shelf slope, and stations therein had average near surface temperature and salinity 10.3—11.9 °C and >35 g kg^{-1} respectively.

3.1.2. Relationship between chemical and physical patterns

To investigate whether the hydrodynamic regions defined above had distinct chemical characteristics, PCA was applied to the 35 stations where all chemical parameters were sampled. The PCA ordination (Fig. 4) showed a gradual transition from coastal to oceanic water, similarly to the T-S plot (Fig. 3), and the probability of occurrence of the observed chemical patterns across all regions assuming no differences between any regions, calculated by the ANOSIM test, was 0.01% (Table 1). The probabilities of occurrence of the observed chemical patterns in pairs of regions assuming no differences between them, calculated by the pairwise ANOSIM tests were of similar magnitude (Table 1), except for the comparison of the Celtic Sea and the Malin Shelf where the probability level was 6.2 %.

Despite their geographical separation, the continental slope (200—1000 m isobaths) waters of the Malin Shelf and the Celtic Sea
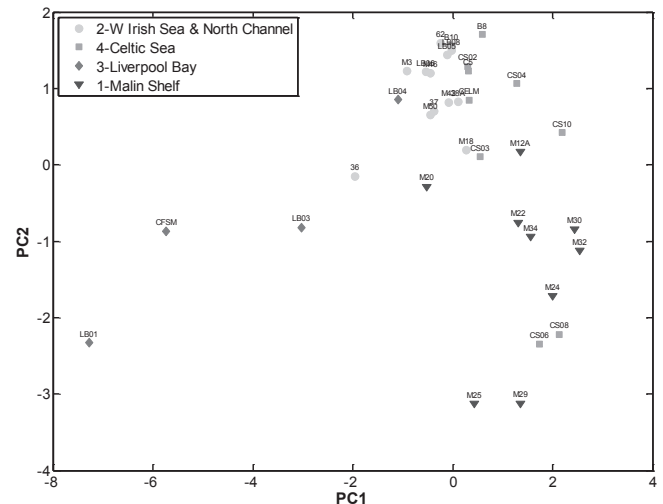

Fig. 4. PCA ordination of all the measured chemical parameters including chlorophyll and phaeopigments at the 35 stations where all parameters were sampled. Points on the plot depict the multivariate chemical composition of the sampled stations on a 2-dimensional space. Distances between points attempt to match the dissimilarity in station chemical composition. PC1 and PC2 together explained 61.6% of the variance. Generally, the pattern on the PCA plot is similar to the pattern in the 2-dimensional space of temperature and salinity depicted by the T-S plot (Fig. 3). To verify this pattern the ANOSIM permutation test was also applied (Table 1).

Table 1
Results of the ANOSIM permutation test. ANOSIM tests the probability that pre-defined multivariate patterns occur in random by permuting the samples numerous times (999 in this instance) and each time comparing the similarity between the randomly created multivariate patterns and the pre-defined ones. Shown are: the probability of occurrence of the observed chemical patterns across all regions, assuming no differences between any regions, calculated by the global test; the probabilities of occurrence of the observed chemical patterns in pairs of regions assuming no differences between them, calculated by the pairwise tests.

Global Test	
Significance level: 0.01%	
Pairwise Tests	
Groups	Significance Level %
2-W Irish Sea & North Channel, 4-Celtic Sea	0.40
2-W Irish Sea & North Channel, 3-Liverpool Bay	1.10
2-W Irish Sea & North Channel, 1-Outer Malin Shelf	0.01
4-Celtic Sea, 3-Liverpool Bay	0.60
4-Celtic Sea, 1-Outer Malin Shelf	6.20
3-Liverpool Bay, 1-Outer Malin Shelf	0.60

are not oceanographically isolated; rather they are connected by the Slope Current. The Slope Current is a northward flow, parallel to the shelf edge, of relatively warm saline water (Burrows and Thorpe, 1999; Hydes et al., 2004; White and Bowyer, 1999) extending from the Bay of Biscay to the North Sea (Pingree et al., 1999). Although the Slope Current can act as a boundary for water exchange between the open ocean and the shelf, it does connect the shelf slope waters of the Celtic, Malin and Hebridean shelves all the way to the North Sea (Booth and Ellett, 1983; Pingree et al., 1999), potentially transporting material such as phytoplankton (e.g. in summer, Gowen et al., 1998) and nutrients. The close resemblance, in multivariate chemical space, of the stations situated between the 200 m and 1000 m isobaths over the shelf slope in both the Celtic Sea and the Malin Shelf is clear on the PCA ordination (Fig. 4), and is perhaps why the pairwise test of these two stations gave a higher probability level, above the guide significance value of 5%. This similarity in chemistry may be created by the slope current transporting material through these stations, or because the biogeochemical processes taking place in these outer

shelf and slope waters are broadly similar, or both.

3.2. Nutrients

3.2.1. Spatial patterns in January 2013

Simple statistics (range, mean, and standard error) for nutrient concentrations averaged over the water column in each hydrodynamic region are presented in Table 2. The highest (3.9 ± 0.2 μmol N L^{-1}) mean total DON concentration was measured in region 2-W Irish Sea & North Channel and the lowest in 1-Outer Malin Shelf (2.3 ± 0.3 μmol N L^{-1}) and 4-Celtic Sea (2.6 ± 0.4 μmol N L^{-1}). Urea, DFAA and DOC concentrations were all highest in region 3-Liverpool Bay (0.7 ± 0.1 μmol N L^{-1}, 0.2 ± 0.04 μmol N L^{-1}, and 106.0 ± 8.3 μmol L^{-1} respectively) and lowest in the 1-Outer Malin Shelf (0.6 ± 0.08 μmol N L^{-1}, 0.1 ± 0.04 μmol N L^{-1}, and 76.6 ± 12.9 μmol L^{-1} respectively) and 4-Celtic Sea regions (0.5 ± 0.04 μmol N L^{-1}, 0.1 ± 0.02 μmol N L^{-1}, and 69.4 ± 2.2 μmol L^{-1} respectively).

Compilations of DOM measurements and individual studies make it possible to put our measurements in global, regional, and local contexts. DOM concentrations in the marine environment tend to decrease along the riverine-oceanic continuum (Antia et al., 1991; Bronk, 2002; Cauwet, 2002; Sipler and Bronk, 2015). With the exception of total DON, DOM concentrations measured in this study support this trend (Table 2). The depth-averaged concentrations of urea, DFAA and DOC decreased from the Liverpool Bay ROFI to the inner shelf waters of the 2-W Irish Sea & North Channel, and to the more ocean influenced waters of the 4-Celtic Sea and 1-Outer Malin Shelf (Table 2). Van Engeland et al. (2010) observed higher DON concentrations at coastal sites compared to open sea sampling stations in the southern North Sea. Similarly, DON concentrations in the inner shelf waters of region 2-W Irish Sea & North Channel were higher than in the more ocean influenced waters of regions 4-Celtic Sea and 1-Outer Malin Shelf (Table 2).

Across all hydrodynamic regions, the concentrations of total DON measured in January 2013 (3.2 ± 0.2 μmol N L^{-1}), were lower than the average concentration (11.4 ± 7.3 μmol N L^{-1}) for CSS given by Sipler and Bronk (2015), although this is probably because few of the shelf measurements compiled in that study were made during the winter, and bulk DON concentrations are likely to be considerably higher in the warmer months, during the production season (Section 3.2.3). Furthermore, DON as a proportion of TDN ($25.3 \pm 1.8\%$) was below the average ($73.3 \pm 23.2\%$) for CSS given by Sipler and Bronk (2015). This discrepancy is consistent with published data, since DIN typically reaches maximum concentrations in winter (e.g Gowen et al., 1995) and DON reaches maximum concentrations in summer in temperate CSS. These trends are supported by evidence for CSS regionally and locally: for the North Sea (Johnson et al., 2012; Van Engeland et al., 2010) and English Channel (Butler et al., 1979), where seasonal studies have recorded a seasonal pattern in DON concentrations consisting of autumn/winter minima and spring/summer maxima; for region 4-Celtic Sea (Davidson et al., 2013), where concentrations of total DON and DON as a proportion of TDN (in some cases >65%) in summer 2008 were considerably higher than those measured in winter 2013 (Table 2); for the eastern and western Irish Sea (Shammon and Hartnoll, 2002), where DON concentrations were considerably higher in samples taken in June/July than in January 1997 and 1998; and for region 2-W Irish Sea & North Channel from seasonal nutrient measurements presented here (Section 3.2.3).

Urea and DFAA concentrations were within the range reported for other CSS (Sipler and Bronk, 2015). Winter urea concentrations in this study were on average higher than summer concentrations

Table 2

Depth-integrated concentrations of all measured chemical parameters including chlorophyll and phaeopigments. ToxN stands for total oxidised N, that is nitrate and nitrite. Stderr stands for standard error and n is the number of stations at which samples were collected for each parameter in each region.

	4-Celtic Sea				1-Malin Shelf				2-W Irish Sea & North Channel				3-Liverpool Bay				All			
	range	mean	stderr	n	range	mean	stderr	n	range	mean	stderr	n	range	mean	stderr	n	range	mean	stderr	n
DON (μmol N L^{-1})	1.0–3.7	2.6	0.4	9	1.1–3.7	2.3	0.3	9	2.7–5.8	3.9	0.2	13	2.2–5.4	3.8	0.7	4	1.0–5.8	3.2	0.2	35
Urea (μmol N L^{-1})	0.4–0.8	0.5	0.04	9	0.4–1.2	0.6	0.1	9	0.3–1.3	0.6	0.1	14	0.5–1.1	0.7	0.1	4	0.5–1.3	0.6	0.04	35
DFAA (μmol N L^{-1})	0.0–0.3	0.1	0.02	9	0.0–0.4	0.1	0.04	9	0.1–0.2	0.1	0.01	14	0.1–0.3	0.2	0.04	4	0.0–0.4	0.1	0.01	35
DOC (μmol L^{-1})	57.5–79.5	69.4	2.2	9	49.4–177.4	76.6	12.9	9	74.9–116.7	85.7	2.7	14	87.3–127.1	106.0	8.3	4	49.4–177.4	81.6	4.0	35
DIN (μmol N L^{-1})	6.8–12.7	9.1	0.5	15	8.5–13.7	10.2	0.3	24	6.1–9.2	7.4	0.2	30	8.7–29.8	18.1	4.4	4	6.1–29.8	9.2	0.4	74
TDN (μmol N L^{-1})	10.1–14.2	11.8	0.5	9	12.0–18.1	13.7	0.6	15	9.9–12.6	11.2	0.3	14	12.8–31.9	23.7	4.6	4	9.9–31.9	13.4	0.8	35
ToxN (μmol N L^{-1})	5.8–12.5	8.3	0.6	15	8.2–13.6	9.7	0.3	24	5.6–8.8	6.7	0.2	30	7.9–26.2	16.2	3.8	4	5.6–26.2	8.5	0.4	74
Ammonium (μmol N L^{-1})	0.2–1.4	0.8	0.1	24	0.1–1.1	0.5	0.1	24	0.1–1.2	0.7	0.1	24	0.9–3.6	1.9	0.6	4	0.1–3.6	0.7	0.1	74
DIP (μmol L^{-1})	0.5–0.9	0.6	0.03	24	0.6–0.9	0.7	0.01	24	0.5–1.0	0.7	0.02	30	0.7–1.5	1.1	0.2	4	0.5–1.5	0.7	0.02	74
DIS (μmol L^{-1})	2.6–5.5	4.3	0.3	24	3.3–5.7	4.1	0.1	24	4.1–8.8	5.1	0.2	30	6.3–16.1	10.8	2.0	4	2.6–16.1	4.9	0.2	74
Chlorophyll (μg L^{-1})	0.1–0.5	0.3	0.04	15	0.0–0.3	0.2	0.01	24	0.1–0.6	0.3	0.02	30	0.4–0.6	0.5	0.03	4	0.0–0.6	0.3	0.02	74
Phaeopigments (μg L^{-1})	0.0–0.2	0.1	0.01	15	0.0–0.1	0.1	0.01	24	0.1–0.3	0.2	0.01	30	0.2–0.3	0.2	0.04	4	0.0–0.3	0.1	0.01	74
DON as TDN (%)	9.7–35.4	22.9	3.2	9	7.4–27.5	17.1	2.4	9	26.2–45.9	34.8	1.6	13	6.8–31.6	18.6	5.1	4	6.8–45.9	25.3	1.8	35
Urea as DON (%)	10.2–82.7	25.7	7.6	9	12.8–49.0	28.4	3.6	9	6.4–33.9	17.2	2.3	13	9.4–48.6	22.1	9.0	4	6.4–82.7	22.8	2.5	35
DFAA as DON (%)	1.5–26.4	5.3	2.7	9	0.8–11.2	4.5	1.0	9	1.4–6.1	3.5	0.4	13	2.9–14.2	6.3	2.7	4	0.8–26.4	4.5	0.8	35
Urea + DFAA as DON (%)	11.7–109.0	31.0	10.1	9	13.6–53.0	32.8	4.2	9	9.4–36.2	20.7	2.3	13	12.9–62.8	28.4	11.6	4	9.4–109.0	27.3	3.2	35

reported for the North Sea (Riegman and Noordeloos, 1998). DFAA concentrations were within the range reported for the Irish and Celtic Seas (Poulet et al., 1991; Riley and Segar, 1970; Williams and Poulet, 1986). In our survey, urea and DFAA concentrations together accounted for an average $27.3 \pm 3.2\%$ of total DON at all stations (Table 2) and their combined depth-averaged concentrations did not exceed 2.0 μmol N L^{-1} at any station [although see Williams and Poulet (1986) and Poulet et al. (1991) for high DFAA concentrations associated with copepods at narrow depth horizons]. This is not surprising since the high lability of these compounds prevents them from accumulating at high concentrations (Sipler and Bronk, 2015).

DOC, and by extension DON, can be conceptually classified into components of differing lability and turnover times (Carlson and Hansell, 2015; Sipler and Bronk, 2015). Urea and DFAA can be classified as labile bio-available DON, which can include a range of other low molecular DON compounds such as purines, pyrimidines, amino sugars, nucleic acids, creatine and ATP, with turnover times of hours to days (Antia et al., 1991; Mulholland and Lomas, 2008). One level down in terms of lability is semi-labile DON with turnover times of weeks to months (e.g. Johnson et al., 2012; Lønborg et al., 2009b), which plays an important role in the annual cycle of N (Section 3.2.3). Finally refractory (turnover times of years to centuries and millennia) DON forms a seemingly ever-present background pool of DON in aquatic environments (e.g. Goldberg et al., 2015). Even though we use this general conceptual classification for the DON fractions measured in this study, we note that it is not universal, as DON lability can be influenced by a number of factors (e.g. depth; Letscher et al., 2013).

DIN concentrations in January 2013 were highest in the region 3-Liverpool Bay (18.1 ± 4.4 μmol N L^{-1}), followed by the ocean influenced waters of the 1-Outer Malin Shelf (10.2 ± 0.3 μmol N L^{-1}) and 4-Celtic Sea (9.1 ± 0.5 μmol N L^{-1}) regions, and the inner shelf waters of region 2-W Irish Sea & North Channel (7.4 ± 0.2 μmol N L^{-1}). DIP and DIS concentrations followed the same trend as urea, DFAA and DOC with concentrations decreasing from region 3-Liverpool Bay (1.1 ± 0.2 μmol L^{-1}, and 10.8 ± 2.0 μmol L^{-1} respectively) to 2-W Irish Sea & North Channel (0.7 ± 0.02 μmol L^{-1}, and 5.1 ± 0.2 μmol L^{-1} respectively), and 1-Outer Malin Shelf (0.7 ± 0.01 μmol L^{-1}, and 4.0 ± 0.1 μmol L^{-1} respectively) and 4-Celtic Sea (0.6 ± 0.03 μmol L^{-1}, and 4.3 ± 0.3 μmol L^{-1} respectively).

In the following section (Section 3.2.2), we use the knowledge gained from the oceanography and the spatial nutrient patterns of the Irish Sea and adjacent shelf to evaluate the oceanic and riverine N inputs to the Irish Sea.

3.2.2. Nutrient inputs

Gowen and Stewart (2005) reasoned that "the Atlantic sets the overall background nutrient levels for the Irish Sea and deviations from Atlantic water concentrations will therefore reflect internal cycling and the influence of anthropogenic nutrient sources". Deep ocean water is rich in inorganic nutrients and poor in organic nutrients relative to the surface (Bronk, 2002; Sipler and Bronk, 2015). As a result, deep Atlantic water mixing to the surface might be expected to elevate inorganic and depress organic nutrient concentrations. The depth of the surface mixed layer over the Celtic Sea shelf slope is typically 300 m in autumn and early winter but is shallower than over the Malin Shelf slope (Hydes et al., 2004), and according to Hydes et al. (2004) this was the reason for their observed differences in nitrate concentration (12.0 and 8.0 μmol N L^{-1} at the Malin Shelf and Celtic Sea slope regions respectively). Any Malin Shelf slope water that flows eastwards onto the shelf appears to be deflected to the north at the Islay front, and does not appear to extend into the Irish Sea (Section 3.1.1). To

the south, the northerly flow of water connects the Irish Sea to the Celtic Sea shelf slope area and as a consequence transport of nutrient rich water to the inner shelf might be expected. However, Pingree et al. (1999) argued that there was limited on-shelf transport of ocean water at the Celtic Sea shelf edge and Hydes et al. (2004) estimated that water from the shelf edge may take 2—6 years to reach the central Irish Sea, an estimate calculated from the deficit of nitrate relative to DIP and known rates of denitrification.

For their calculation, Hydes et al. (2004) used nitrate concentrations in the Celtic and Irish Sea, a shelf slope DIN:DIP ratio of 16.4, a denitrification rate of 0.1 mmol N m^{-2} day^{-1}, and an average water column depth of 100 m. We, also found a deficit in DIN relative to DIP with distance from the Celtic Sea slope region in January 2013, that was manifested as a general decrease in the DIN:DIP ratio along the transect from the outer to the inner Celtic Sea (Fig. A4). For our calculation, we used DIN instead of only nitrate, a DIN:DIP ratio of 16 (measured at the shelf slope in January 2013, Fig. A4), and a denitrification rate of 0.5 mmol N m^{-2} day^{-1}, [the average of the denitrification rate measured by Trimmer et al. (1999) and the rate estimated by Simpson and Rippeth (1998) using the LOICZ procedure].

We multiplied the average 4-Celtic Sea DIP concentration (0.6 μmol L^{-1}, Table 2) by the shelf slope DIN:DIP ratio of 16 to derive an average 4-Celtic Sea DIN concentration of 9.6 μmol N L^{-1} (assuming no DIN deficit). This value agreed with the range of DIN concentrations measured in January 2013 (Fig. A5). From this value, the minimum and maximum (6.8 μmol N L^{-1}, and 7.8 μmol N L^{-1} respectively) observed DIN concentrations in the inner Celtic Sea (stations CELM, B7, B8, and B9) were subtracted to calculate the minimum and maximum DIN deficits of 1.8 μmol N L^{-1}, and 2.8 μmol N L^{-1} respectively. These values were then multiplied by a denitrification rate of 0.5 mmol N m^{-2} day^{-1} averaged over 100 m to calculate how long it would take for denitrification to create the DIN deficit. Based on these calculations, we estimated that it would take water at the 4-Celtic Sea shelf slope region 1.0—1.5 years before reaching the inner Celtic Sea and entering the Irish Sea. Although our assumptions and overall calculation procedure were the same as those of Hydes et al. (2004), this is a shorter time than theirs because the denitrification rate they used appears to be an underestimate.

Even though our estimate is less than 2 years (the lowest estimate of Hydes et al. (2004) for water to reach the Irish Sea), it is still sufficient time for at least one phytoplankton production season and consequent biogeochemical processes to have modified the shelf slope water. It is also likely that the inner Celtic Sea water will have been influenced by freshwater sources such as the River Severn which flows into the Bristol Channel. Thus, by the time water from the Celtic Sea shelf slope reaches the Irish Sea, its nutrient content will have been modified. Once in the Irish Sea, any further deviations must be the result of internal nutrient cycling in the Irish Sea and anthropogenic nutrient sources.

The main anthropogenic nutrient input to the Irish Sea is via freshwater inflow from surrounding rivers, especially the Alt, Clwyd, Mersey, Ribble and Dee which flow into Liverpool Bay. In January 2013, the lowest salinity (29.6—33.4 g kg^{-1}) and maximum nutrient concentrations (except for total DON) were found in 3-Liverpool Bay. Concentrations of DIN, urea, DFAA, DOC, as well as DIP and DIS were negatively correlated with salinity (Fig. 5), making it possible to use simple linear regression to extrapolate to zero salinity and estimate riverine concentrations. The estimated riverine concentration of DOC (469.1 μmol L^{-1}) was the highest of all nutrients, followed by DIN (226.6 μmol N L^{-1}), and DIS (104.0 μmol L^{-1}). Urea (8.0 μmol N L^{-1}), DFAA (2.1 μmol N L^{-1}), and DIP (8.1 μmol L^{-1}) concentrations were considerably lower. It is clear that nutrient-rich freshwater inflow to the 3-Liverpool Bay
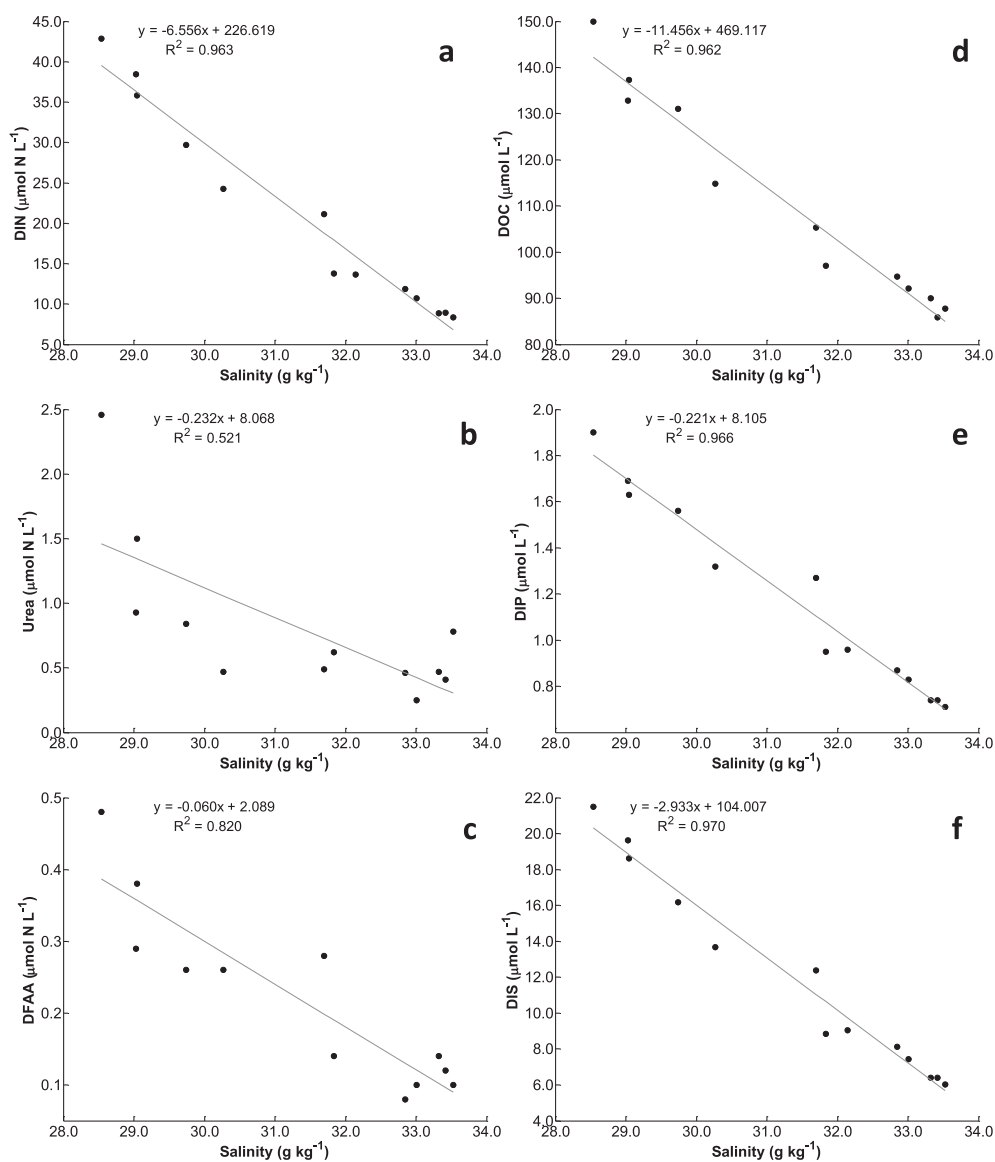
Fig. 5. Relationship between salinity and non-integrated concentrations of (a) DIN, (b) urea, (c) DFAA, (d) DOC, (e) DIP, and (f) DIS in Liverpool Bay. Lines are regression models.

ROFI elevates this region's nutrient concentrations relative to the Atlantic influenced water flowing into the Irish Sea from region 4-Celtic Sea.

Less clear, however, is the effect of river inflow on nutrient concentrations in region 2-W Irish Sea & North Channel. In this study, mean DIP and DIS concentrations were higher in this region compared to region 4-Celtic Sea, but mean DIN concentrations were higher in region 4-Celtic Sea. Also, no nutrient was significantly correlated with salinity, although DIN, DIP, and DIS concentrations were generally higher in the North Channel where salinity was lower than in the western Irish Sea (Fig. 3, Figs. A5—A7) likely reflecting high concentrations of these nutrients in the runoff of adjacent rivers. Gowen and Stewart (2005) evaluated riverine inputs of inorganic nutrients to the western Irish Sea by comparing plots of DIN, DIP and DIS concentrations against salinity with theoretical mixing lines between winter nutrient concentrations in freshwater and Celtic Sea shelf break end members. DIP and DIS concentrations fell close to their respective theoretical mixing lines, meaning that their concentrations were elevated in accordance with freshwater inflow. DIN concentrations, however, fell below

their theoretical mixing line and Gowen and Stewart (2005) suggested that this was due to denitrification.

DON concentrations, similarly to those of DIN, DIP and DIS, were also higher in the western Irish Sea than in region 4-Celtic Sea, and increased more in the North Channel (Fig. A8), although as with DIN, DON concentrations in the western Irish Sea cannot entirely be accounted for by freshwater inflow as is evident from the seasonal study at station 38A (Section 3.2.3).

River-borne DOM can be an important vector of nutrients to coastal water bodies, either directly, or through its remineralisation to DIN and DIP (Stepanauskas et al., 2002). Furthermore, depending on the residence time of the receiving water body, these nutrients can be exported from coastal waters to the shelf and the open ocean (Lønborg et al., 2009b; Seitzinger and Sanders, 1997). Even though DON accounts for more than 50% of TDN transported by rivers worldwide (Meybeck, 1982; Sipler and Bronk, 2015), to our knowledge, the published scientific literature contains limited information on riverine concentrations of DON in UK rivers.

More research is needed on the riverine transport of DON and its fate within the areas of discharge in UK waters. This need is

highlighted by the estimated concentrations of urea (8.0 μmol N L^{-1}) and DFAA (2.1 μmol N L^{-1}) in rivers discharging to 3-Liverpool Bay (concentrations at the high end of the ranges reported in the studies cited above), and the lack of correlation between total DON and salinity, which prevented us from calculating the riverine concentration. It is likely that less well studied biogeochemical processes in estuaries (Tappin et al., 2010) and in Liverpool Bay modify concentrations of bulk DON to mask the expected gradient with salinity. Stepanauskas et al. (2002) found no correlation between the bacterial bioavailability of river-borne DON and concentrations of urea and DFAA. One interpretation of this finding is that the processes that influence highly labile DON in the form of urea and DFAA are somehow uncoupled by those influencing semi-labile DON.

In summary, it appears that Atlantic influenced water entering the Irish Sea from the south has already been modified for at least 1 year by denitrification and other biogeochemical processes, and is further modified to varying extents in the eastern and western Irish Sea by river runoff and denitrification. As this water flows northwards, exiting the Irish Sea through the North Channel, it likely receives more freshwater and a nutrient 'top up' from local riverine sources. In the following section (Section 3.2.3), the knowledge gained from the physical oceanography, spatial nutrient patterns, and nutrient inputs to the Irish sea is combined with a seasonal study of N in the western Irish Sea to quantify the N budget of this region and the role of DON.

3.2.3. N budget for the western Irish Sea

Station 38A is situated in a region of the western Irish Sea that seasonally stratifies, and where the production season starts in April/May and lasts ~3−4 months (Gowen and Bloomfield, 1996). The general view is that once stratification is established, a near surface circulation (gyre) develops which restricts exchange between the western Irish Sea and the greater Irish Sea (Gowen and Stewart, 2005 and references therein). Also, as a result of stratification, the difference between surface and bottom N concentrations (especially of DIN) becomes larger (Fig. 6 a, b, c). For the purpose of this section, water column average concentrations of DIN (Fig. 6d), PON (Fig. 6e), and DON (Fig. 6f) were used to quantify the annual N budget of the western Irish Sea. Data collected during the seasonal study show that there was a distinct seasonal pattern to concentrations of DIN (Fig. 6d). Maximum concentrations were measured in March (8.6 ± 0.8 μmol N L^{-1}) and deceased to a minimum of 3.5 ± 1.0 μmol N L^{-1} in July. Thereafter, the concentration increased back to the winter maximum. PON and DON followed the opposite trend. PON concentrations were lowest (1.0 ± 0.4 μmol N L^{-1}) in February and highest (2.4 ± 0.2 μmol N L^{-1}) in July (Fig. 6). DON concentrations were lowest (4.3 ± 0.3 μmol N L^{-1}) in March and highest (7.8 ± 0.3 μmol N L^{-1}) in June (Fig. 6f).

The seasonal patterns in PON and DIN are consistent with the annual cycle of production in temperate seasonally stratifying coastal waters and shelf seas (Joint and Pomroy, 1993; Miller and Wheeler, 2012; Tett et al., 1986). DIN is taken up by the microbial community and converted to PON in microbial biomass. In turn when these microbes die, PON is remineralised to DIN. If N uptake and remineralisation occurred at equal rates throughout the year, the concentrations of PON and DIN would remain constant. Therefore, changes in their concentrations must reflect uncoupling between uptake and remineralisation. In autumn and winter phytoplankton growth is limited by light availability, and the rate of N uptake is lower than the rate of N remineralisation, resulting in PON decreasing and DIN increasing. Conversely, spring and summer conditions favour phytoplankton growth and the rate of N uptake exceeds that of remineralisation, resulting in DIN decreasing

and PON increasing. However, the role of the DON pool is missing from this 'textbook' (Miller and Wheeler, 2012) description of the annual cycling of N.

Time-series of DON concentrations in temperate CSS including, but not limited to, the North Sea (Johnson et al., 2012; Suratman et al., 2008; Van Engeland et al., 2010), the English Channel (Butler et al., 1979), Scottish sea-lochs (Lønborg et al., 2009b; Solórzano and Ehrlich, 1977), and English estuaries (Badr et al., 2008) show a seasonal pattern in which DON is produced during spring and summer, at the same time or following the drawdown of DIN. Given that semi-labile DON constitutes an 'extra' N pool in the yearly N cycle, it is important to quantify it relative to PON and DIN, something that it is possible to do for the western Irish Sea.

The annual N budget of the western Irish Sea will reflect a balance between the oceanic inputs, riverine inputs, and internal cycling (Gowen and Stewart, 2005). Atlantic water from the 4-Celtic Sea shelf slope is already modified by the time it reaches the southern entrance to the Irish Sea (Section 3.2.2), and the inner Celtic Sea contains similar concentrations as the western Irish Sea (Fig. A5, A8). So, it is unlikely that inflow of this water into the western Irish Sea has a sizable effect on N concentration. In contrast, freshwater inflow from local rivers has the potential to substantially raise the N concentration of the western Irish Sea. Yearly average salinity at station 38A is ~34.4 g kg^{-1} and assuming a mean near ocean salinity of 35.5 g kg^{-1} (Hydes et al., 2004), gives a freshwater contribution of 3% from river runoff. The Irish rivers Boyne and Liffey are the main freshwater source to the western Irish Sea. Between years 2000 and 2003, the average DIN concentration in the Boyne and Liffey was 180.3 μmol N L^{-1} (OSPAR, 2005, 2004, 2003, 2002), 3% of which is 5.4 μmol N L^{-1}. No published DON data from these rivers exists to our knowledge, but taking the average concentration for selected rivers worldwide of 23.8 μmol N L^{-1} (Sipler and Bronk, 2015), 3% of this is 0.7 μmol N L^{-1}. So, we estimate that the Boyne and Liffey could contribute a total 6.1 μmol N L^{-1} dissolved N to Station 38A per year.

Any N entering the western Irish Sea in river runoff must be removed by N cycling processes, since Gowen et al. (2002) concluded that N concentrations in the Irish Sea have remained stable since the 1970's. Denitrification rates averaged over the water column at Station 38A were 0.6−4.5 μmol N L^{-1} yr^{-1} (Trimmer et al., 1999), and in possible combination with other processes, likely removed an average 6.1 μmol N L^{-1} yr^{-1}.

Since oceanic inputs to the western Irish Sea are unlikely to have a sizable effect on N concentration (Section 3.2.2), and much of the riverine input is likely to be removed by natural processes, seasonal changes in concentrations must reflect cycling of N between DIN, PON, and DON. Between March and June, when DON concentrations reached maxima and minima respectively, and DIN and PON concentrations approached their seasonal maxima and minima (Fig. 6), the change in N concentration (absolute value) was highest in DIN (5.0 ± 1.3 μmol N L^{-1}), followed by DON (3.6 ± 0.4 μmol N L^{-1}), and PON (0.8 ± 0.2 μmol N L^{-1}). Clearly DON plays an important role in the annual N cycle as, on average, 38% of the change in N was accounted for by DON, compared to 53% by DIN and only 9% by PON.

In addition to the importance of semi-labile DON in the annual N cycle of the western Irish Sea, labile DON could potentially fuel primary production at different times during the phytoplankton production season. Within the constraints of uncertainty resulting from natural variability and measurement errors, we attempted to estimate the concentration of labile DON in January 2013 which could contribute a substantial amount of N to spring bloom production. Assuming that the average winter DON concentration (~1.7 ± 0.7 μmol N L^{-1}) that we measured below 200 m in the shelf
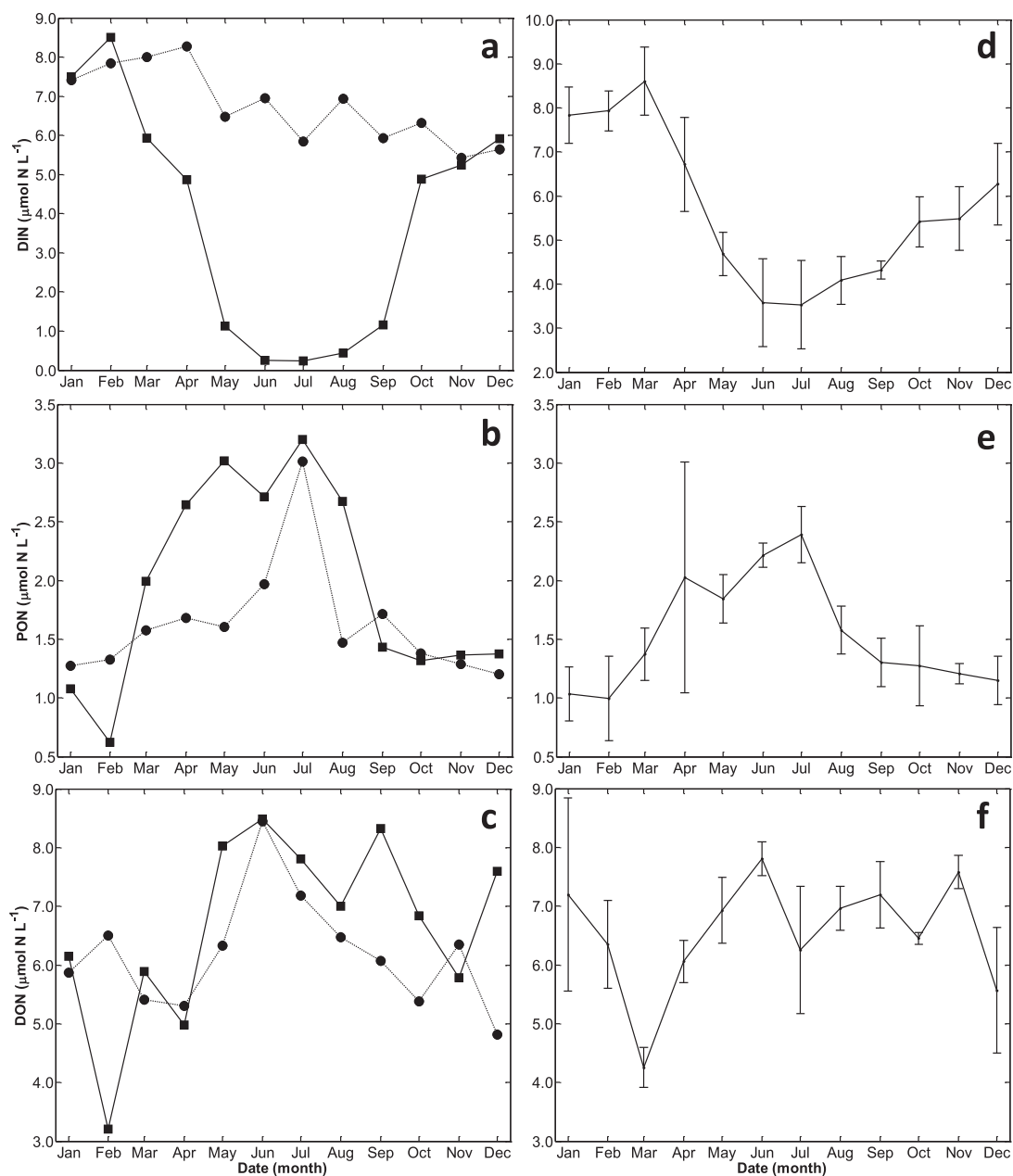
Fig. 6. Monthly surface (<3 m, filled circles) and bottom (80–95 m, filled squares) concentrations of (a) DIN, (b) PON, and (c) DON, and monthly water column averaged concentrations of (d) DIN, (e) PON, and (f) DON between 1999 and 2004 at Station 38A in the western Irish Sea. Error bars are standard errors. Error bars in the surface/bottom concentration plots have been omitted for clarity.

break region of the Celtic Sea and Malin Shelf was typical of deep ocean water in being largely refractory (Carlson and Hansell, 2015), then this represents the minimum background concentration of DON in the Irish Sea. When subtracted from the January 2013 average DON concentration (3.9 ± 0.2 µmol N L^{-1}), in region 2-W Irish Sea & North Channel this gives a potential 2.2 ± 0.7 µmol N L^{-1} of labile and semi-labile DON. Between January and March (data collected between 2000 and 2004) at Station 38A, DIN increased by 0.8 µmol N L^{-1} (Fig. 6d) which is consistent with the increase of 0.8 ± 1.0 µmol N L^{-1} measured over the same time period in the western Irish Sea in previous investigations (Gowen et al., 2002; Gowen and Stewart, 2005). If this increase in DIN was accounted for by a decrease in DON, it would leave 1.4 ± 1.2 µmol N L^{-1} of labile and semi-labile DON in March of

which ~0.7 ± 0.1 µmol N L^{-1} would be labile DON in the form of urea and DFAA (Table 2). This would leave 0.6 ± 1.2 µmol N L^{-1}, which could be semi-labile DON or other labile compounds that we did not measure in this study. Bronk (2002) gave concentrations of dissolved combined amino acids, nucleic acids, and methylamines that summed could exceed 0.6 µmol N L^{-1}, making it possible that all 1.4 ± 1.2 µmol N L^{-1} is labile DON and potentially available to phytoplankton.

4. Synthesis & conclusion

In this study, we investigated the role of DON in the N dynamics of the Irish Sea and adjacent shelf waters, by combining spatial data from January 2013 across the shelf and seasonal data between 1999

and 2004 from the western Irish Sea. In January 2013, the Celtic Sea, Malin Shelf, Irish Sea, and Liverpool Bay regions were divided by three density fronts into hydrographically and chemically homogeneous regions. Concentrations of DON exhibited spatial and seasonal patterns in agreement with data from other temperate CSS. Spatially, winter DON concentrations generally decreased from the Liverpool Bay ROFI to the oceanic waters of the Celtic Sea and Malin Shelf. Seasonally, DON and PON concentrations in the western Irish Sea reached maxima in mid-summer and minima in late winter/early spring, while the opposite was true for DIN. We evaluated oceanic and riverine N inputs to the western Irish Sea and concluded that oceanic inputs are unlikely to have a substantial effect on N concentrations, whereas riverine inputs that could have a considerable effect are likely removed by N cycling processes. DON contributed a notable 38% to the internal N cycling between inorganic, particulate and organic N components in the western Irish Sea, and winter DON was estimated to potentially contribute as much as 1.4 ± 1.2 μmol N L^{-1} labile N to spring bloom production. Clearly, DON is important in the N dynamics of the Irish Sea and adjacent shelf waters and should not be ignored in biogeochemical studies and monitoring programmes, especially at a time when the CSS biogeochemical cycles are under threat from anthropogenic pressures (Jickells, 1998).

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ecss.2015.07.030.

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