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

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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 ± 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 ± 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

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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 onboard 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

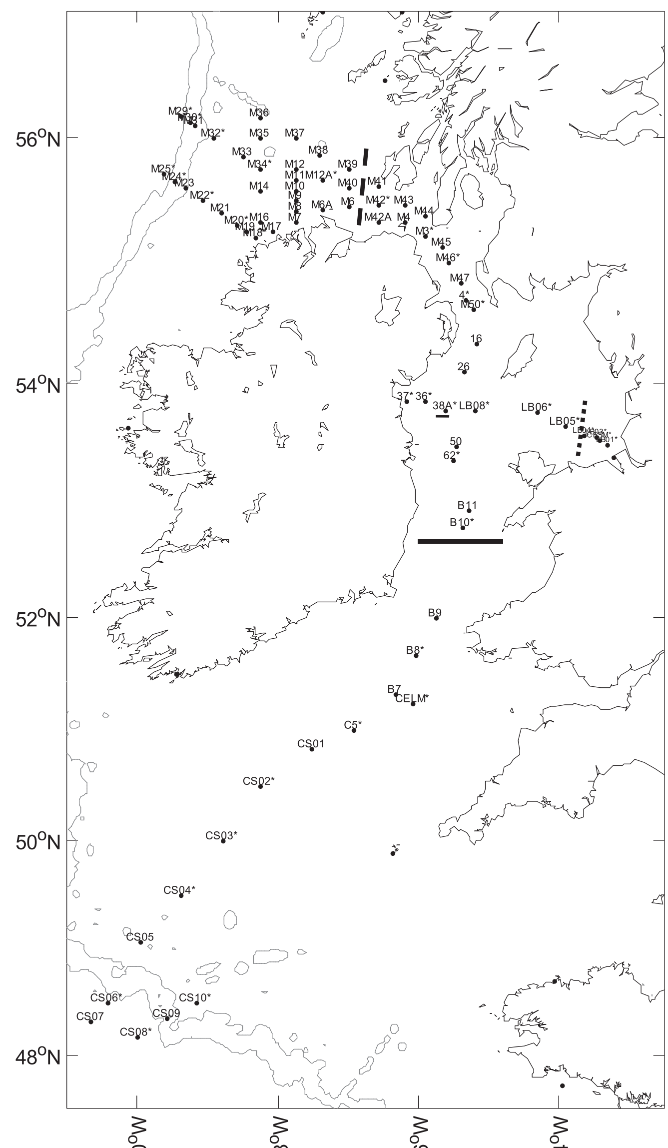

Fig. 1. A map of the western shelf region showing the positions of the stations sampled in January 2013 and the approximate positions of the observed fronts (see text). Superscripted asterisks denote stations where DON was sampled. Station 38A, the location of the seasonal study, is underlined. Contour 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).