DISTRIBUTION, COMPOSITION AND TRANSPORT OF DISSOLVED ORGANIC MATTER IN SHELF SEAS

Thesis submitted in accordance with the requirements of the University of Liverpool for the degree of Doctor in Philosophy

By

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March 2018

Abstract

Distribution, composition and transport of dissolved organic matter in shelf seas

Nealy Carr

For their size, shelf seas play a disproportionately large role in the oceanic carbon pump. While accounting for only 7% of the surface ocean, the amount of carbon exported from shelf seas contributes to between 20 and 50% of total oceanic CO_2 storage (Tsunogai et al. 1999). In terms of their socio economic importance, shelf seas support ~ 90% of global fish catches (Pauly et al. 2002), and future projections estimate that up to 4.2 billion people will live within 200 km of the coast by 2030 (Kummu et al. 2016). Shelf seas are the interface between land and ocean and high nutrient inputs and intense physical energy provided mainly by tidal mixing, help to maintain high biological activity on the shelf. Indeed, rates of primary production are up to 3 times greater in shelf seas than in the open ocean (Simpson and Sharples 2012). Through a process known as the continental shelf pump, over 40% of particulate organic matter produced on-shelf is exported to the adjacent ocean (Muller-Karger et al. 2005). The role of dissolved organic matter (DOM) in this pump, in particular, dissolved organic carbon (DOC), is less well understand, despite DOC concentrations in the ocean being 50 times more than carbon in the particulate pool (Eglinton and Repeta 2006), and the amount of carbon in the DOC pool being similar to that of carbon as CO_2 in the atmosphere (Hansell and Carlson 1998).

Here, to add to the growing body of work on the distribution of DOM in shelf seas, the main goals of this thesis were to (a) map the distribution of DOC and dissolved organic nitrogen (DON) across 5 shelf regions across the Northwest European shelf, and the adjacent North Atlantic; (b) to assess the distribution of DOC and DON in different regions over a seasonal cycle to see if they followed a typical seasonal cycle of production, consumption and loss; (c) to characterise the source of DOM in the Celtic Sea and determine how much of the DOC pool was of terrestrial origin; (d) to assess multi-year trends in DOC and DON in the North Sea specifically and finally (e) for the first time, estimate DOC fluxes between the Celtic Sea and North Atlantic, and compare them with DOC fluxes across the Malin-Hebrides Shelf.

DOC and DON distributions across the Northwest European seas were in accordance with global trends, and concentrations decreased with increasing distance from land, highlighting the influence of terrestrially-derived DOM in this region. However, there was large variability within and between regions, highlighting the importance of local controls on DOM production and distribution. In the North Sea, multi-year differences in DOC and DON concentrations showed an overall decline between 2011 and 2015

alongside declines in concentrations of inorganic nutrients, indicating a combination of changing nutrient regimes and variability in the strength of exchange with the North Atlantic. Finally, annual net and springtime surface fluxes from the Celtic Sea to the North Atlantic were significant and higher compared to the Malin-Hebrides Shelf. The estimates were large but within global ranges (Barron and Duarte 2015).

I certify that the work described in this thesis is my own except where otherwise stated and has not previously been submitted for any degree at this or any other University

Nealy Carr

Acknowledgements

Without the support and understanding from my parents, Joan and Tony, I would never have made it to this point. Their continued and unwavering belief in me has motivated me in my undertaking of such a rewarding challenge. Thank you for believing and thank you for the work ethic you instilled in me from a young age, without it I would not be at this point. Also, thank you for looking after Jasper.

A great debt of gratitude is owed to my supervisor Claire Mahaffey, whose guidance and support has both driven and inspired me to learn more about our seas and ocean, and about the stuff that's in them. And, without whom, I might well still be looking for CDOM in the Albert Dock. I would also like to thank my other supervisors, Jo and Jonathan for their help and guidance. I have learned a lot over the course of my PhD, and have understood it better because of them.

Thank you also to my colleagues at Liverpool, to Anu Thompson who taught me how to use a HPLC instrument, a freeze drier and efficiently use a muffle oven. Thank you to Sabena Blackbird for all her work in the lab, and Clare Davis and Calum Preece for their help in collecting and analysing many many samples.

Thank you to my friends and colleagues in room 206 of the Nicholson Building, and a special thanks to Mila for making me understand that time wasted with friends is never time wasted. And to Henio, gracias por tu ayuda and for being there.

Contents

List of figures

List of tables

Chapter 1

Introduction

1.1. Shelf seas

Shallow shelf seas are physically dynamic and biologically active regions of our world's ocean. Despite occupying ~ 7% of the surface ocean and < 1% of its volume (Simpson and Sharples 2012), the impacts of shelf seas are wide reaching and extend into society and economics. For example, up to 50% of the global population live within 200 km of the coast (Kummu et al. 2016), and over 400,000 people are directly employed in marine related activities in UK coastal and shelf seas which contribute to up to 4% of UK GDP (Richardson 2015)**.** Along with being an important part of marine ecosystems, they are a key source of protein and indeed biological production in shelf seas supports over 90% of global fish catches (Pauly et al. 2002).

The main source of energy for intense physical activity in shelf seas is provided by tides, and globally, up to 60% of tidal energy dissipation occurs in shelf seas (Egbert and Ray 2000, Rippeth 2005). Shelf seas connect the terrestrial biosphere to the ocean biosphere and high nutrient inputs from land (Seitzinger et al. 2005, Sharples et al. 2017) and the ocean, and their efficient use (Rippeth 2005), help to sustain primary production that is up to 3 times greater than the rate of primary production in the open ocean (Simpson and Sharples 2012).

Up to 30% of total oceanic primary production (Wollast 1998) and over 40% of global particulate carbon sequestration (Muller-Karger et al. 2005) occurs in shelf seas. Via a mechanism first described by Tsunogai (1999) named the 'continental shelf pump', or shelf pump (Fig.1.1), carbon export from seasonally stratifying shelf seas is proposed to account for between 20 and 50% of the total CO_2 storage in the open ocean (Tsunogai et al. 1999).

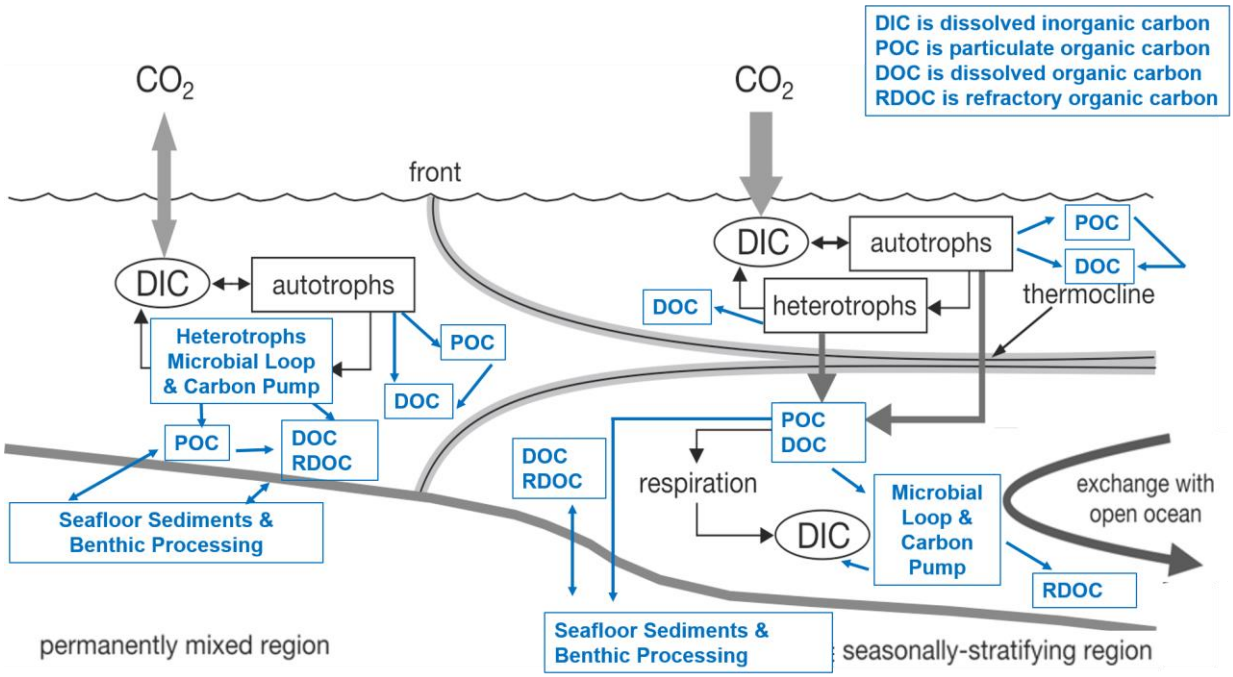

Fig.1.1. Schematic of a simplified shelf pump adapted from Simpson and Sharples (2012) to include more detailed processes and dissolved organic carbon pools. Adaptations are coloured in blue.

1.2. Dissolved organic matter in the marine environment

Operationally, dissolved organic matter (DOM) is defined as organic matter that passes through a glass fibre filter (GF/F) with a nominal pore size of 0.7 μm, thus separating DOM from the particulate organic matter (POM) pool. DOM is a complex mixture of organic molecules containing dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved

organic phosphorous (DOP), of which over 90% of DOM remains uncharacterised (Benner 2002).

The main sources of DOM in shelf seas can be separated into two pools. There is an external or allochthonous pool where terrestrial DOM inputs enter shelf seas via estuaries, rivers and the coastal zone (Liu et al. 2010, Bianchi 2011, Raymond and Spencer 2015). Globally, up to 60% of riverine organic carbon enters the coastal zone annually as DOC (250 Tg C). Riverine DOC is considered to be largely refractory, however, a fraction of the allochthonous DOM pool is degraded over a matter of days to years during mixing with seawater (Cauwet 2002). In addition, recalcitrant DOC can be degraded by microorganisms in the presence of a labile substrate by a priming process, which could explain why so little terrestrial organic carbon is observed in the global ocean (Bianchi 2011, and references therein).

Internally produced or autochthonous marine DOM is produced mainly by phytoplankton in the euphotic zone, and DOM production is most evident during bloom periods (Carlson 2002)**.** DOM is also released during phytoplankton exudation, viral and bacterial cell lysis, and during grazing by zooplankton (Carlson 2002). Global estimates of oceanic DOM production are 7000 Tg C yr^{-1}, and although marine DOM is considered more labile compared to terrestrially derived DOM, up to 17% of newly produced DOC escapes remineralisation and is available for export to the interior ocean (Carlson 2002).

The main biological sink of DOM in the marine environment is when it enters the microbial loop, respired by heterotrophic bacteria and released as CO_2. Figure 1.2, taken from Buchanan et al (2014), illustrates nicely the

processes by which atmospheric carbon (CO_2) enters the surface ocean and is fixed by phytoplankton in the euphotic zone (1), leading to the release of DOM and POM (2), of which, a fraction enters the microbial loop (4) where DOC is respired. While DON and DOP are remineralised by bacteria, a fraction of DOC enters the microbial carbon pump (5) and is transformed into recalcitrant DOC that is resistant to further degradation, and can be stored in the ocean interior for thousands of years (Hopkinson et al. 1997, Ducklow et al. 2001, Jiao et al. 2010, Buchan et al. 2014). However, the mechanisms of production and removal of refractory DOC in the microbial carbon pump are not fully understood (Legendre et al. 2015).

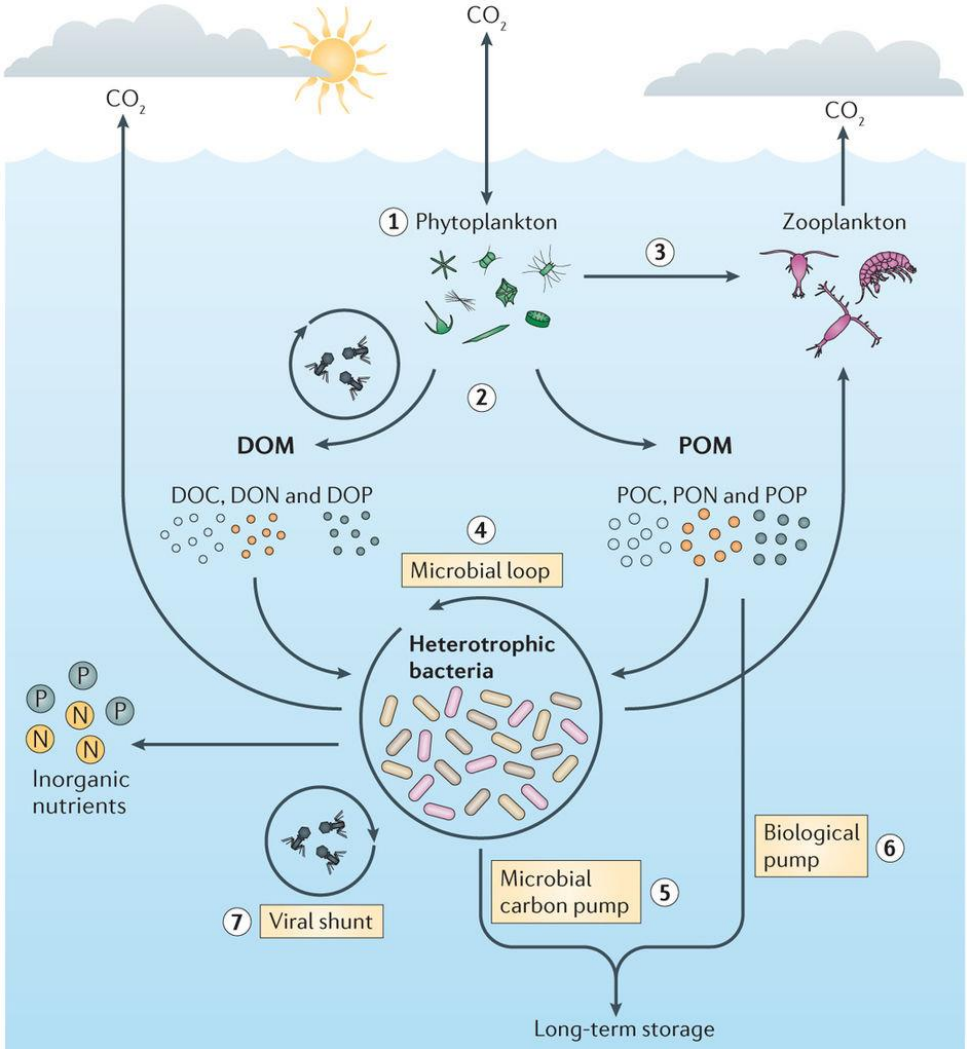

Fig.1.2. Schematic illustrating DOM production, consumption and export processes in the ocean (taken from (Buchan et al. 2014)).

1.3. The role of DOM in the marine environment

Historically, the export of POM from the surface ocean was considered to be the main mechanism for removal of organic carbon to the ocean interior thereby maintaining the vertical gradient in dissolved inorganic carbon (DIC) and enabling continual uptake of atmospheric CO_2 (Hansell et al. 2009). However, due to improvements in the way we measure and characterise DOM, we have gained new insights in the role of DOM in ocean biogeochemistry, for example the role of DON as a nutrient source in nitrogen limiting environments (Sipler and Bronk 2015), and the role of DOC in the biological pump (Hansell et al. 2009) (Fig.1.2). DOC is the second most abundant form of carbon in the marine environment as the DOC pool is up to 50 times larger than the POC pool (Eglinton and Repeta 2006), and DOC concentrations (665 Gt C) are comparable to carbon stored as CO_2 in the atmosphere (Hansell and Carlson 1998).

As hinted at earlier (section 1.2), DOM can be separated by its relative bioavailability. DOM was previously considered largely refractory however, we now know that this is not the case and DOM is much more dynamic than previously believed. Labile DOM has a short lifetime and is cycled on timescales of hours to days. Semi-labile DOM is cycled over timescales of weeks to months, and the refractory DOM pool which can accumulate over millennia (Hansell 2013). Furthermore, by looking at the stoichiometry of DOM (C:N:P), Hopkinson and Vallino (2005) (Fig.1.3.) found that both the labile and refractory DOM pools were substantially larger than that of the Redfield ratio for inorganic nutrients (106:16:1, (Redfield 1934)), and POM, indicating the export of carbon-rich DOM was more efficient compared to

POM export which conformed to Redfield (Hopkinson et al. 1997, Hansell 2013).

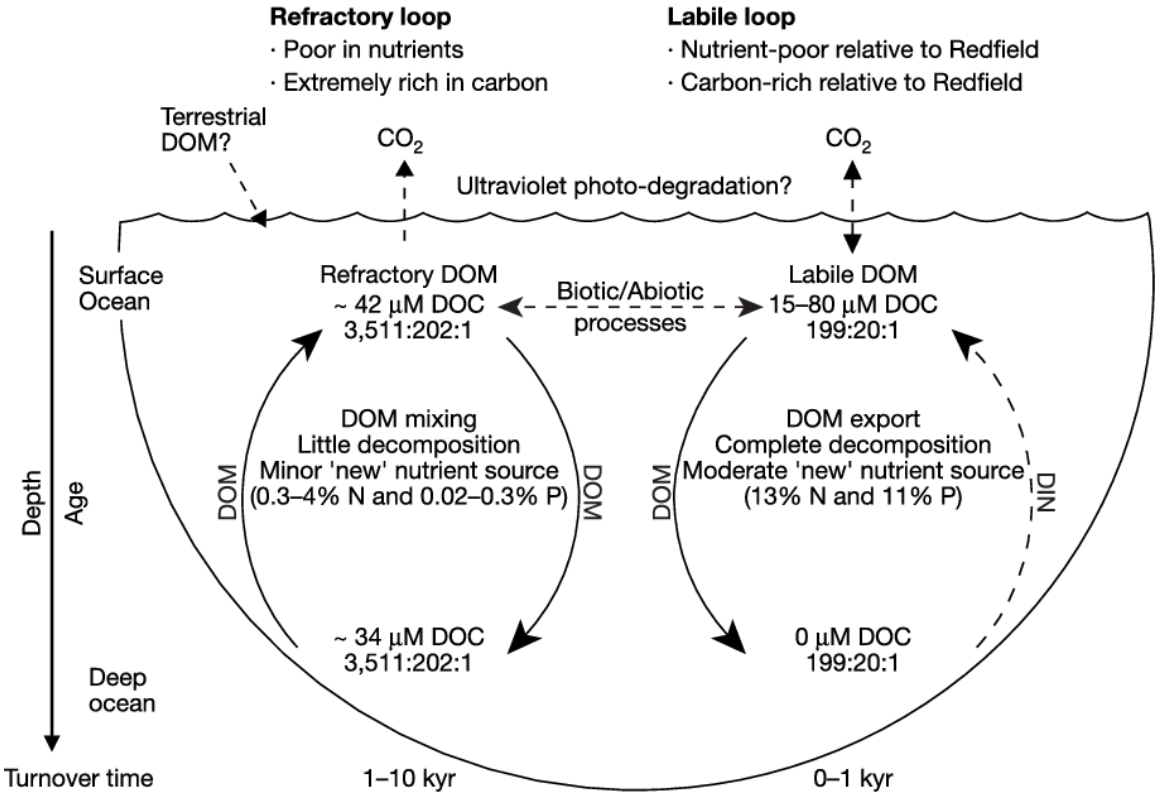

Fig.1.3. Schematic illustrating the cycling of the refractory and labile DOM pools (taken from (Hopkinson and Vallino 2005)).

1.4. Characterising DOM in the marine environment

DOC and DON concentrations are measured using high temperature catalytic oxidation, however, the identification and characterisation of the molecules and compounds in the DOM pool is not as straightforward, indeed as mentioned previously, a large majority of the DOM pool (>90%) remains uncharacterised.

For the identification and characterisation of DOM in terms of source and lability, we can look at specific compounds such as lignin which is a well-established biomarker of terrestrial DOM (Hedges et al. 1997, Fichot et al. 2016). To access the elemental composition of DOM, solid phase extraction and ultra high-resolution Fourier transform ion cyclotron resonance mass

spectrometry (FTICR-MS) can be used to resolve thousands of peaks from a single sample (Stubbins et al. 2014). Although these complex geochemical methods provide valuable insights into the complexities of DOM, they are time consuming thus limiting the number of samples that can be analysed.

Another method for assessing DOM in terms of source and lability is to measure its optical properties. Measuring sample absorbance and fluorescence is straightforward and takes between 2 to 30 minutes for each sample, allowing the analysis of a large number of samples required to capture spatial and seasonal trends in DOM composition during the Shelf Sea Biogeochemistry (SSB) programme.

The coloured fraction of the DOM pool contains chromophores (CDOM) which absorb light (Fig.1.4), and from the resulting absorbance spectrum we are able to quantify the amount of CDOM using an absorbance coefficient (aCDOMλ) (Stedmon et al. 2000, Kowalczuk et al. 2013).

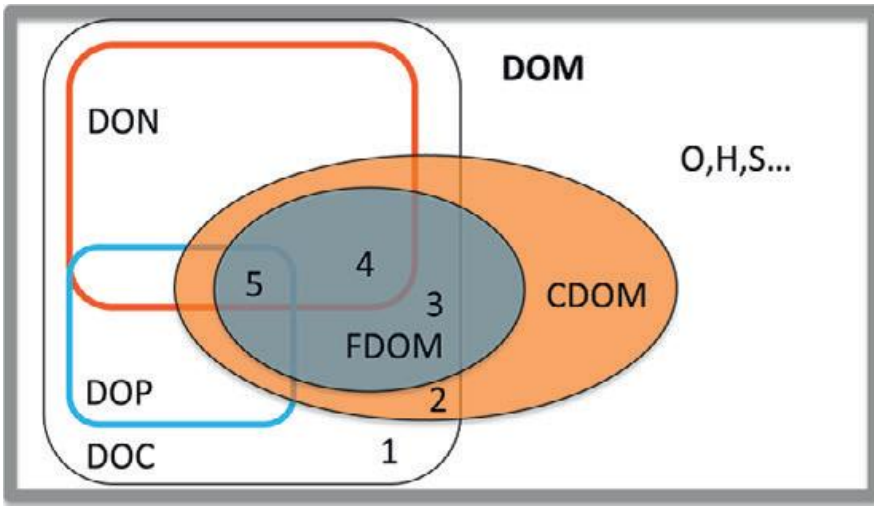

Fig.1.4. Schematic illustrating the fractions of DOM that absorb (CDOM) and fluoresce (FDOM) (taken from (Stedmon and Nelson 2015)).

We can also look at the absorbance spectral slope (Fig.1.5) to characterise the source of CDOM (Kitidis et al. 2006), and at the slope ratio (Fig.1.6) which is an indicator of molecular weight, source and extent of photobleaching (Helms et al. 2008).

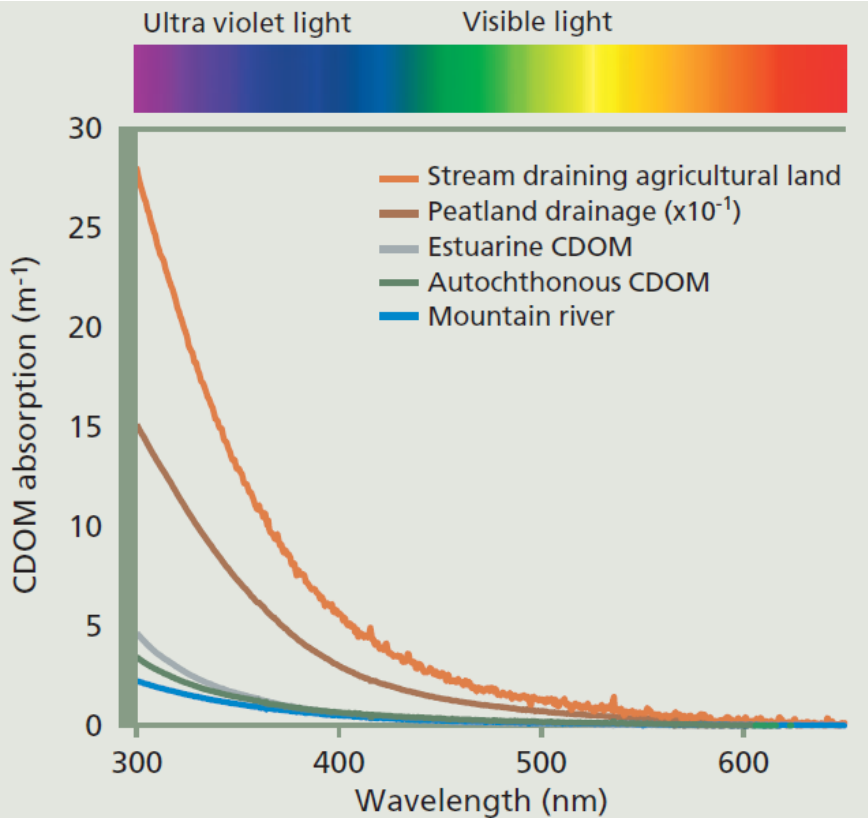

Fig.1.5. CDOM absorbance spectral slope for DOM from differing sources (taken from (Sondergaard and Thomas (2004)).

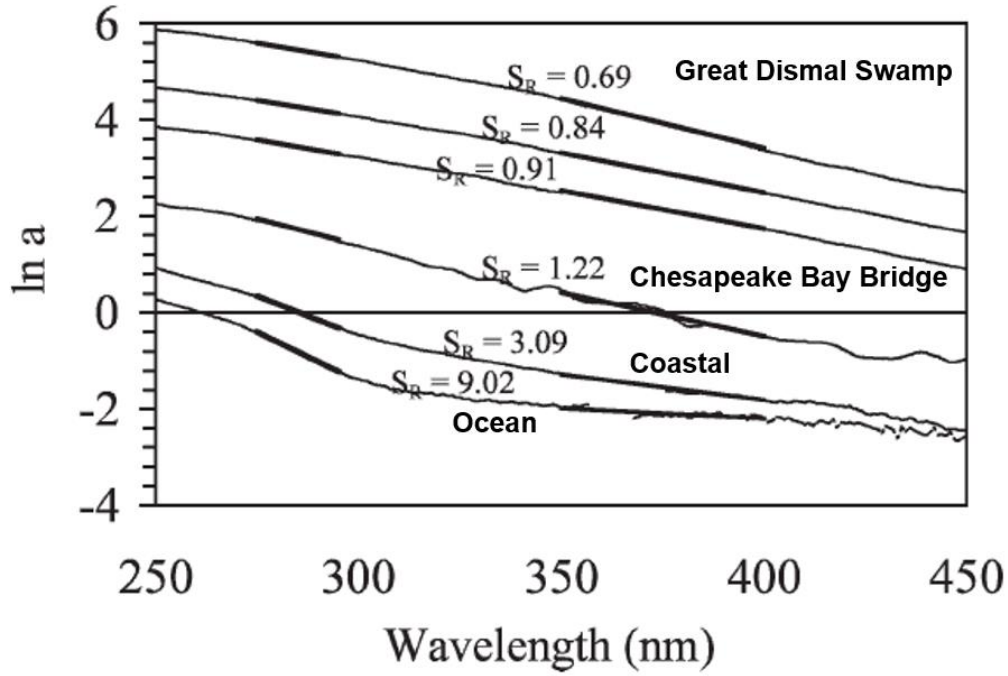

Fig.1.6. Absorbance slope ratio (SR) for DOM from differing sources (a is absorbance; adapted from (Helms et al. 2008)).

A fraction of DOM also fluoresces upon light excitation (FDOM) and by using the DOM fluorescence excitation emission matrices (EEMs) coupled with a statistical decomposition Parallel Factor Analysis model (PARAFAC) the underlying components contributing to the total fluorescence signal can be identified and classified in terms of humic and protein sources (Coble 1996, Stedmon and Bro 2008, Stedmon et al. 2011). Coupled with additional environmental information alongside source characteristics, we can infer lability (Liu et al. 2010, Jorgensen et al. 2011).

1.5. Research aims

In this thesis, I will present findings from the NERC-funded Shelf Sea Biogeochemistry programme, specifically focusing on the dynamics, source and fluxes of dissolved organic carbon and nitrogen in the Northwest

European Shelf region. My overarching hypothesis is that dissolved organic matter plays a major role in the cycling and transport of carbon in shelf sea regions. This hypothesis is addressed via 4 chapters focused on specific aspects of this study.

In **Chapter 2**, for the first time, I used a combination of measurements of DOC concentrations alongside DOM absorbance and fluorescence excitation emission matrices (EEMs) coupled with PARAFAC modelling to assess the source and lability of DOM on seasonal time scales at three physically distinct sites in the Celtic Sea. The goal was to assess the contribution of land-derived DOC to the DOM pool in the Celtic Sea and to determine how lability was affected by productivity events in the Celtic Sea. This work has been published recently in the Shelf Sea Biogeochemistry Special Issue in Progress in Oceanography (Carr et al. 2018).

In **Chapter 3**, data from the shelf-wide sampling programme, conducted as part of the NERC funded Shelf Sea Biogeochemistry (SSB) programme, was analysed to determine how the magnitude of DOC and DON vary on the Northwest European Shelf on annual and seasonal time scales, how DOC and DON dynamics differ between stratified and mixed regions and how these patterns compare with our conceptual understanding of DOC and DON in shelf seas.

In **Chapter 4,** I focused specifically on the North Sea region, firstly examining how DOC and DON behaved during the shelf wide sampling programme in 2014 and 2015. Using published data sets, I then compared the multi-year trends in DOC and DON in August from 2011 and 2016 and

discuss the processes controlling the between year variability in DOC and DON in the North Sea.

In the final data chapter, **Chapter 5**, I quantified the off-shelf seasonal fluxes of DOC in the Celtic Sea and compared them to the annual net fluxes of DOC in the Malin-Hebrides Shelf and Celtic Sea.

Finally, in **Chapter 6**, I report and synthesise the conclusions from each chapter and address the hypothesis related to the importance of DOC in shelf seas.

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Chapter 2

Seasonal and spatial variability in the optical characteristics of DOM in a temperate shelf sea

2.1. Introduction

Dissolved organic matter (DOM) is the largest pool of organic material in the ocean, storing up to fifty times more carbon (C) than that stored in the particulate pool (POC 18 ± 5 x 10^{15} g C (Eglinton and Repeta 2006)). The amount of dissolved organic carbon (DOC) in the ocean (685 x 10^{15} g C) is comparable to the amount of carbon as CO_2 in the atmosphere (Hansell and Carlson 1998, Hansell et al. 2009).

DOM is produced autochthonously by plankton in the surface ocean during primary and secondary production (Hansell and Carlson 2001, Hansell et al. 2009), with substantial amounts being released or exuded by phytoplankton (Hygum et al. 1997, Jiao et al. 2010). Mesozooplankton mediate the release of DOM and up to 50% of suspension filtered food can be released as DOM during grazing activity (Hygum et al. 1997). Viral cell lysis (Suttle 2005, Suttle 2007) and bacteria (Jiao et al. 2010) cause DOM release from particulate organic matter (POM). Rivers are also an important source of externally supplied DOM from terrestrial origin to the marine environment. Syntheses of past and recent global estimates show that rivers, as part of the land-ocean continuum, contribute around 0.25 x 10^{15} g C yr^{-1} to the global ocean as DOC (Hedges et al. 1997, Cai 2011, Raymond and Spencer 2015).

In the upper 100 m of the open ocean, DOC concentrations vary from 34 to 80 µM (Sipler and Bronk 2015). DOC concentrations are higher in coastal and continental shelf regions, reaching up to 140 µM in coastal waters at a salinity greater than 35 (Barron and Duarte 2015). The strong inverse relationship between salinity and DOC in estuarine and coastal environments (Barron and Duarte 2015), continental shelf seas (Mendoza and Zika 2014) and the open ocean (Kowalczuk et al. 2013) highlights the importance of land as a source of DOC in the marine environment. Employing the empirical relationship reported in Barron and Duarte (2015), 9 µM of DOC is lost when salinity increases by 1 unit.

Heterotrophic utilisation and remineralisation is the largest biotic sink of DOC in the aerobic ocean (Hansell et al. 2009). As the most abundant microorganisms in the surface ocean, bacterioplankton help shunt DOM towards the microbial loop where it is remineralised to its inorganic constituents i.e. dissolved inorganic carbon (DIC), DIN and DIP (Hansell and Carlson 2015).

Knowledge of the composition of DOC is important for understanding how DOC is cycled in the water column and identifying the sources and sinks (Hansell and Carlson 2015). However, determining the source, composition and lability of DOC is not straightforward, and requires analytically complex geochemical techniques, for example, to distinguish between high molecular weight compounds and humic substances (Aluwihare et al. 2002, Repeta et al. 2002), or to unravel DOM molecular complexity (Stubbins et al. 2014). A simple approach is to use vertical distributions to infer bulk properties of DOM. In the open ocean, DOC at 1000 m is considered to be refractory and

can thus be subtracted from surface ocean DOC concentrations to reveal the partitioning of DOC into labile, semi-labile, semi-refractory, refractory and ultra-refractory pools (Hansell 2013, Hansell and Carlson 2015). However, in shelf seas, this simple view does not work due to (a) the vertical exchange between the shallow surface mixed layer (SML) and bottom mixed layer (BML) by tides and turbulent mixing which smears out vertical gradients in DOM (b) multiple sources of DOM, for example, from freshwater inputs and sediments and (c) strong productivity events (spring and autumn blooms) or interactions (grazing pressure) that consume or release DOM. Thus, alternative approaches must be used to better understand the dynamics of DOM in shelf seas, as well as its source and lability.

A number of studies (Hopkinson and Vallino 2005, Barron and Duarte 2015) highlight the importance of DOM in biogeochemical nutrient cycling and DOC on global carbon export. However, DOM production and composition in shelf seas and the subsequent export of carbon at continental margins is less well understood (Liu et al. 2010). This study extends the application of EEM and PARAFAC modelling, a technique commonly employed across a wide range of aquatic and marine environments (Stedmon et al. 2003, Yamashita and Tanoue 2003, Yamashita et al. 2011) to the seasonally stratified, temperate Celtic Sea region in the Northwest European Shelf. Here, for the first time, a combination of measurements on DOC concentrations alongside DOM absorbance and fluorescence EEMs coupled with PARAFAC modelling was used to assess the source and lability of DOM on seasonal time scales at three physically distinct sites in the Celtic Sea. The goal was to assess the contribution of land-derived DOC to the

DOM pool in the Celtic Sea and to determine how lability was affected by productivity events in the Celtic Sea.

2.2. Materials and methods

2.2.1. Sampling

As part of a Natural Environment Research Council (NERC) funded SSB programme, cruises were conducted between November 2014 and August 2015 on the Northwest European Shelf region and in the North Atlantic (Fig.2.1), aboard the *RRS Discovery*. Seawater samples were collected during four cruises, November 2014, March 2015, April 2015 and July 2015, representing autumn, winter, spring and summer respectively. Samples were collected from three stations representing on-shelf (Site A), the Central Celtic Sea (CCS) and shelf edge regions (Fig.2.1).

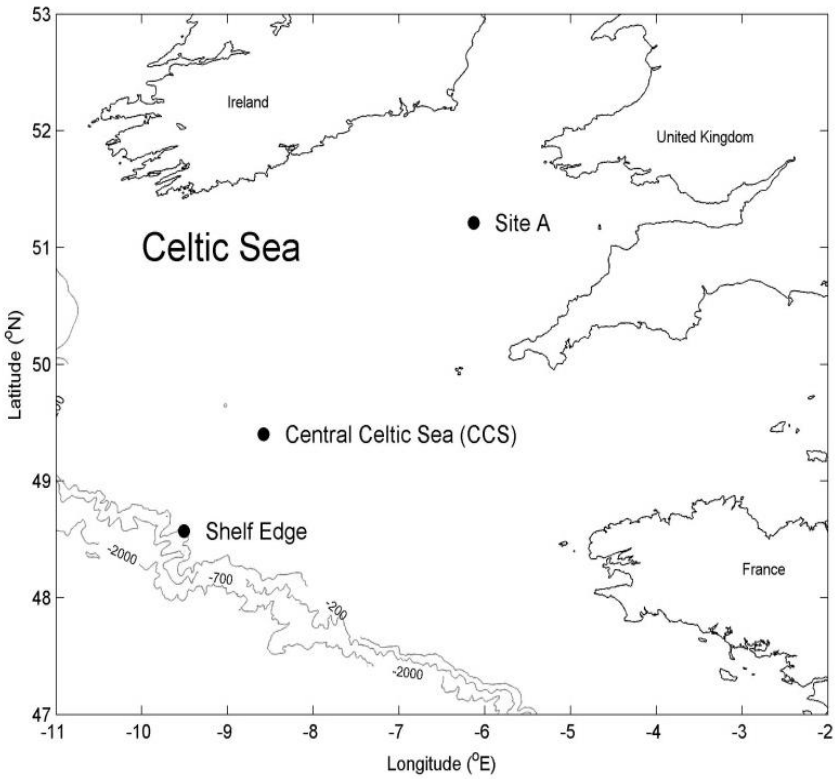

Fig.2.1. Map showing the location of the shelf edge, central shelf (CCS) and on-shelf (Site A) stations sampled during SSB research cruises.

Seawater samples were collected at discrete depths ranging from 3 to 242 m using Niskin bottles attached to a rosette frame with a sensor package consisting of a Sea-Bird conductivity-temperature-depth (CTD) sensors and fluorometer. Sensors were calibrated using discrete samples collected during each cruise and fluorescence was calibrated to chlorophyll *a* mg m^{-3} by analysis of extracted samples filtered through Whatman glass fibre filters (GF/F, nominal pore size 0.7 µm) as described in Mayers et al. (2017). The determination of dissolved inorganic nutrients is described in Humphreys et al. (in press). The depth of the base of the thermocline was defined as the depth at which temperature deviated by > 0.05°C from the lowest temperature. Below the base of the thermocline was defined as the bottom mixed layer (BML) and above the base of the thermocline was defined as the surface mixed layer (SML).

2.2.2. DOC and DOM fluorescence and absorbance

Samples for measurement of DOC were collected by filtering seawater through a combusted glass fibre filter (GF/F) under low vacuum pressure (< 10 mmHg). Samples were preserved with 20 µL of 50% (v/v) hydrochloric acid and analysed onshore using high temperature catalytic oxidation (HTCO) on a Shimadzu TOC-V_{CPN}. The limits of detection for DOC were 3.4 µM with a precision of ± 2.5%. Consensus Reference Materials from the Hansell laboratory, Miami were analysed daily with a mean and standard deviation for DOC of 43.9 ± 1.2 µM (expected range 42 – 45 µM; n=39). DOM samples collected for fluorescence and absorbance measurements were immediately filtered through a GF/F as above. In addition, samples were filtered through 0.2 µm polycarbonate filters under

low vacuum pressure (< 10 mmHg), and stored in the dark at 5 °C until on-board analysis within five days of collection.

2.2.3. Fluorescence and absorbance

2.2.3.1. Excitation Emission Matrices (EEMs)

Water samples were brought to room temperature and fluorescence measurements were obtained using a spectrofluorometer (Horiba FluoroMax-4). Scan settings were configured for emission from 290 to 600 nm at 2 nm increments, excitation between 250 to 450 nm at 5 nm increments and band width set to 5 nm for both excitation and emission monochromators. Fluorescence spectra were acquired in instrument corrected mode (S1c/R1c) at 0.25 s integration time. EEMs were corrected by subtraction with Milli-Q water blank analysed daily, and for inner filter effects using sample absorption spectra measured using a UV-Vis spectrophotometer (Shimadzu 1650PC).

EEMs were calibrated against the area under the water Raman peak (excitation at 350 nm) from Raman scans analysed daily and the resultant spectra are in Raman Units (R.U.). EEM corrections and calibrations were carried out using the drEEM (0.2.0) MATLAB toolbox (Murphy et al. 2013).

2.2.3.2. *PARAFAC modelling*

The three-way EEM spectra of DOM fluorescence are modelled using a multi-way data analysis that decomposes the data matrix into a set of trilinear terms and a residual array (Equation 2.1. The PARAFAC Model). The model was fitted to minimise the sum of squared residuals (Andersson and Bro 2000, Stedmon et al. 2003).

$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + e_{ijk,} \qquad i = 1,\ldots,I;\ j = 1,\ldots,J;\ k = 1,\ldots,K. \quad (2.1)$$

For analysis of EEM spectra, χ_{ijk} is the fluorescence intensity for the *i*th sample at emission wavelength *j* and excitations wavelength *k*. The *f* corresponds to individual PARAFAC components and each component has *a*-values (scores) for each sample, *b*-values (emission loadings) for each emission wavelength and *c*-values (excitation loadings) for each excitation wavelength, where *b* and *c* are scales estimates of emission and excitation spectra at wavelengths *j* and *k,* respectively. Variability within the EEM spectra not captured by the model is contained in the data array e_{ijk}. For a detailed description of employing PARAFAC modelling, principles and approaches, and applying equation 2.1 to three-way data arrays see Bro (1997), Stedmon and Bro (2008) and Murphy (2013).

The fluorescent components of the corrected and calibrated EEM spectra were modelled using Parallel Factor Analysis (PARAFAC) following the methods as described by (Murphy et al. 2013). The PARAFAC modelling was carried out using MATLAB 8.3.0.532 (R2014a) with the DOMFluor toolbox and data sets from each cruise were inserted into the model separately. EEMs were corrected and calibrated using the drEEM (0.2.0) MATLAB toolbox (Murphy et al. 2013).

To reduce random noise introduced from lower wavelengths and secondary Raman and Rayleigh scatter, PARAFAC models were applied to a reduced EEM range of 270 – 450 nm and 290 – 500 nm for excitation and

emission wavelengths respectively. Each data array consisted of between 106 and 198 samples with 37 excitation and 106 emission wavelengths. For each dataset, models were initially fitted using between two and six components, and the number of components were selected when a reasonable fit of above 97% was obtained. To ensure a least squares and global solution, the estimated fluorescent DOM components identified in each dataset were validated using random initialisation and split half analysis (Stedmon and Bro, 2008).

2.2.3.3. *DOM fluorescent component assignment*

3D fluorescense and the resolved excitation and emission spectral loadings of the components identified by the PARAFAC model are shown in Figure 2.2. while Table 2.1 summarises spectral characteristics with references to comparative components identified globally from coastal, shelf sea and oceanic environments. Components were assigned to terrestrial UVC humic material of allochthonous origin (C1), UVA humic-like material of both terrestrial and marine origin (C2), and two protein-like components tyrosine (C3) and tryptophan (C4) of biological autochthonous origin. The DOM pool is a complex mixture of organic molecules in which a fraction absorbs light (CDOM) and a sub-fraction of this absorbing pool emits light as fluorescence (FDOM).

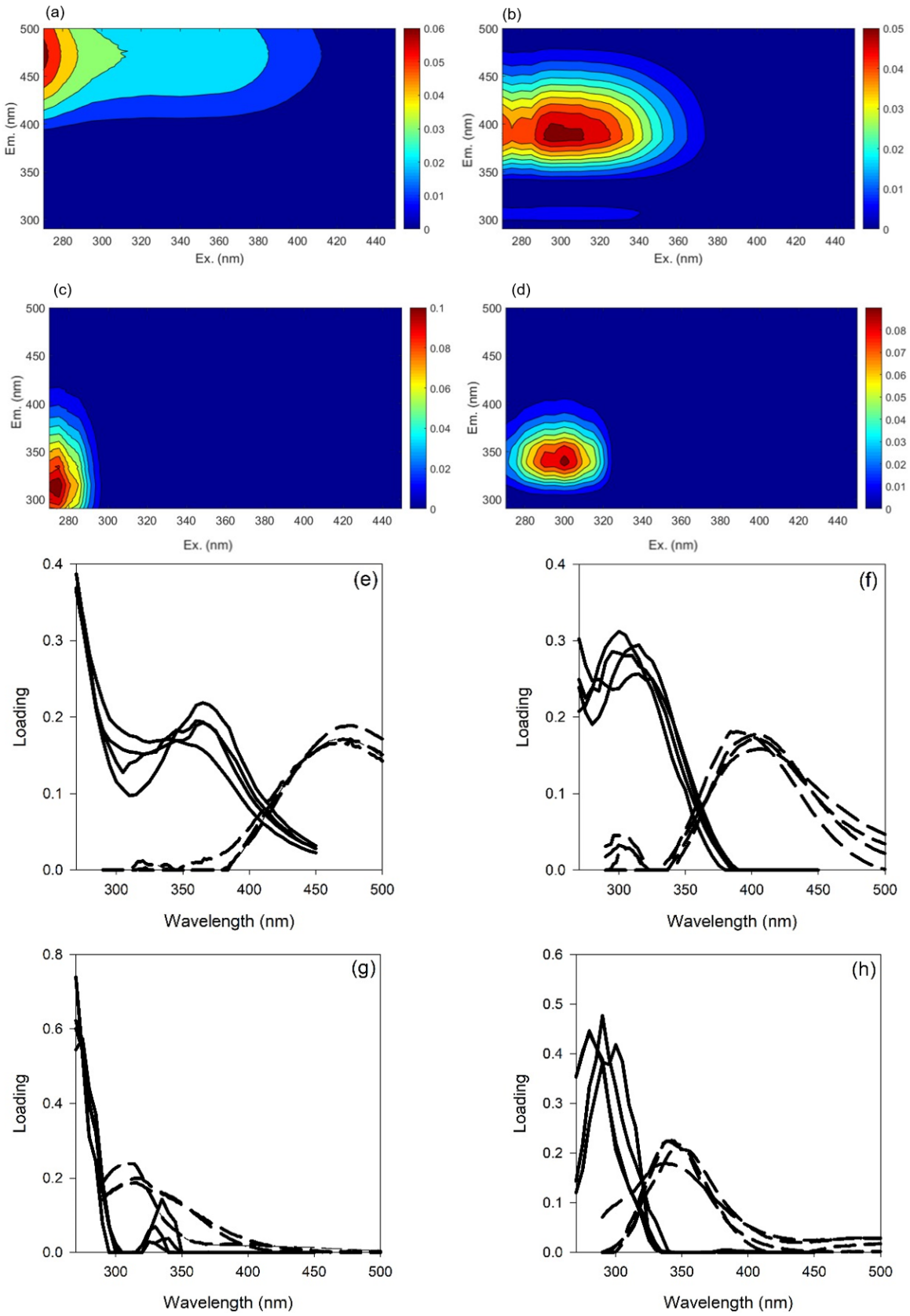

Fig.2.2. Example of the PARAFAC model output and fluorescence signatures of four components identified, C1 (a), C2 (b), C3 (c) and C4 (d). Spectral loadings for each component for all datasets (excitation spectra solid black line and emissions spectra dotted black line), C1 (e), C2 (f), C3 (g) and C4 (h).

Assigning source and lability based on DOM fluorescence alone is challenging as an increasing number of studies have indicated that humic-like fluorescence can result from diagenesis of DOM regardless of source i.e. autochthonous and allochthonous (Lu et al. 2015), as well as production from microalgae (Jorgensen et al. 2011, Bai et al. 2017) and picocyanobacteria produced humic-like fluorescence found in the deep ocean (Zhao et al. 2017). The characterisations assigned to PARAFAC modelled DOM components identified in this study are based on their spectral characteristics and on published comparable studies of component fluorescence spectra, behaviour and distribution, across the freshwater-marine continuum including but not limited to Kowalczuk et al. (2013), Mendoza and Zika (2014) and Pitta et al (2016).

Table 2.1. Peak description of PARAFAC modelled DOM fluorescent components and their source assignment for this study.

Component	Peak max position Ex/Em	Coble Peak*	Source assignment
C1	270/470 - 478	A	UVA humic-like, terrestrial, allochthonous Component 3: 270 (360)/478 (Stedmon et al. 2003) Component 1: <250 (320)/422 (Yamashita et al. 2011) Component 2: 240 (370)/480 (Kowalczuk et al. 2013)
C2	295 - 315/384 - 406	M	UVC marine humic-like, terrestrial, microbial Component 4: <250 (295)/358 (Yamashita et al. 2011) Component 5: 300/408 (Kowalczuk et al. 2013) Component 2(HLC2): 250(310)/410 (Mendoza and Zika 2014) Component 2: 300/402 (Pitta et al. 2016)
C3	270 - 275/310 - 314	B	Tyrosine-like, protein-like, autochthonous, biological, microbial Component 4: 300/408 (Kowalczuk et al. 2013) Component 5(TLC5): 270/305 (Mendoza and Zika 2014) Component OP6: 275/308 (Yamashita et al. 2015)
C4	280 - 300/338 - 344	T	Tryptophan-like, protein-like, autochthonous, biological, microbial Component 6: 280/328 (Murphy et al. 2008) Component 5: 280/334 (Yamashita et al. 2011) Component 6: 295/334(360) (Kowalczuk et al. 2013)

*(Coble 1996)

2.2.3.4. Spectral Indices

Water samples were allowed to reach room temperature and absorbance measurements were obtained using a UV-Vis spectrophotometer (Shimadzu 1650PC). The instrument baseline correction was performed before sample analysis. Chromophoric dissolved organic matter (CDOM) absorbance was measured from 250 to 800 nm at 1 nm increments (2 nm, slit width) with Milli-Q water as the reference blank. Raw absorbance was corrected for instrument drift, temperature effects, scattering and refractive effects by subtracting the average absorbance between 700 and 800 nm from the absorbance spectrum (Green and Blough 1994, D'Sa et al. 1999, Helms et al. 2008). Absorption coefficients were obtained from absorbance spectra as follows:

$$a = 2.303 \frac{A}{l} \quad (2.2)$$

where *a* is the absorption coefficient in m^{-1} at a reference wavelength, A is the raw absorbance at the reference wavelength and *l* is the path length of the cell in metres.

As a measure of CDOM concentrations, the absorption coefficient at 305 nm was chosen for comparison with results from previous work in the Celtic sea region (Kowalczuk et al. 2013). The spectral slope coefficient of CDOM, *S*, is a descriptor of CDOM absorbance spectra and is inversely proportional to molecular weight, and used to characterise DOM composition (Stedmon and Nelson 2015). For this study, *S* was calculated between 300 – 650 nm using

a non-linear regression technique according to (Stedmon et al. 2000). This range was chosen as it is within the wavelength range that captures changes in CDOM composition due to production and photochemical alterations (Nelson and Siegel 2013), and it is relevant to remote sensing applications (Stedmon et al. 2011). The spectral slope ratio (SR) of the absorbance spectra is used as an indicator of the molecular weight (MW), source and photobleaching of CDOM (Helms et al. 2008).

For this study, the slope coefficient values for slopes between 275 and 295 nm, and between 350 and 400 nm were obtained from linear regression of log transformed absorbance spectra using MATLAB 8.3.0.532 (R2014a). The SR was then calculated as the ratio between the two slopes. Low SR values are generally attributed to higher MW DOM of terrestrial origin e.g. ~ 0.7 for terrestrial and ~ 1.1 for estuarine and coastal samples, while increases in SR values can be photochemically induced, while decreases are due to microbial processing (Helms et al. 2008).

The specific ultraviolet absorbance (SUVA) is calculated by normalising decadic absorption to DOC concentrations and has been shown to be positively correlated with molecular weight and an indicator of aromaticity of aquatic humic substances (Weishaar et al. 2003). Here SUVA was calculated at 280 nm ($SUVA_{280}$). The humification index (HIX) was calculated according to (Zsolnay et al. 1999) as the ratio of emission 434 – 480 nm to the peak emission area 300 – 346 nm at 254 nm excitation.

The HIX is an indicator of humic substances and extent of humification of organic matter (Hansen et al. 2016). High HIX is characterised by high molecular weight humic acids (Zsolnay et al. 1999, Kowalczuk et al. 2013) and higher values indicate greater humification of the source material (Ohno 2002). The fluorescence index (FI) was calculated according to (McKnight et al. 2001) as the ratio of emission at 450 nm to emission at 500 nm at 370 nm excitation. The FI is used to differentiate between microbially derived fulvic acids, index value ~ 1.9, and terrestrially derived fulvic acids, index value ~1.4 (McKnight et al. 2001). The biological index (BIX) was calculated according to (Huguet et al. 2009) as the ratio of emission at 380 nm to emission at 430 nm at 310 nm excitation. The BIX is an indicator of freshly produced autochthonous DOM, with higher values indicating a higher proportion of fresh DOM (Huguet et al. 2009, Hansen et al. 2016).

2.2.4. Statistical analysis, correlations and linear regressions

Statistical analysis was performed using SigmaPlot version 13.0, Systat Software, Inc. SigmaPlot for Windows. Paired t-tests were used to determine significant differences for groups of data between sites and seasons, and the Mann-Whitney Rank Sum Test was used when data were not normally distributed. Differences were deemed statistically significant when the p value was < 0.05. Linear regression analysis was used to identify significant correlations between parameters and correlations deemed significant when p values of regression coefficients were < 0.05.

2.3. Results

2.3.1. Seasonal and spatial variation in hydrography, chlorophyll a and inorganic nutrients

The seasonal and vertical variation in salinity, temperature and chlorophyll *a* (Fig.2.3 a-i) and nitrite plus nitrate (N+N) (Fig.2.4 a-c) for the three stations sampled in the Celtic Sea highlight the seasonality observed at each site.

At Site A, surface waters were cooler and fresher in winter and spring than in autumn, and remained fresher with increasing temperatures in summer (Fig.2.3 c and f, and Table 2.2). Surface salinity varied seasonally by 0.5. Temperature gradients between the SML and BML in autumn (0.87 °C), winter (0 °C) and spring (1.04 °C) were small indicating either a completely mixed or weakly stratified water column. In contrast, the SML-BML temperature difference was 5.61 °C in summer, indicating a stratified water column. Mean surface chlorophyll *a* concentrations were highest in spring and autumn, respectively, indicative of bloom events, and were lower in summer and winter (Fig.2.3 i and Table 2.2). Subsurface chlorophyll maxima (SCM) were evident in summer, with concentrations reaching 1 mg m^{-3} within the SCM compared to 0.44 mg m^{-3} at the surface. There were strong vertical gradients in nitrate between the SML and BML in autumn (6.0 µM), spring (7.4 µM) and summer (9.5 µM) but gradients were weak in winter (0.11 µM, Fig.2.4 c).

At CCS, surface waters were cooler and fresher in winter and spring than in autumn, with higher temperature and salinity in

summer (Fig.2.3 b and e, and Table 2.2). The water column was stratified in autumn and mixed in winter. Surface salinity varied seasonally by 0.1. The onset of stratification occurred in spring when the difference in temperature between the SML and BML ranged between 0.52 °C and 1.29 °C, compared to 5.91 °C in summer when the water column was strongly stratified. Mean surface chlorophyll *a* concentrations were highest in spring and autumn, respectively, indicating seasonal bloom events, and were lower in summer and winter (Fig.2.3 h and Table 2.2). SCM were evident in the summer, with concentrations reaching 0.73 mg m^{-3} at the peak of the SCM. Again, there were strong vertical gradients in nitrate between the SML and BML in autumn (8.0 μM), spring (5.5 μM) and summer (8.5 μM) but gradients were weak in winter (0.14 μM) and early spring (1.1 μM, Fig.2.4 b).

At the shelf edge site, surface waters were cooler in winter and spring than in autumn, with increased temperature in summer (Fig.2.3 a and d, and Table 2.2). Surface salinity varied seasonally by 0.05. The water column was mixed in winter and stratified in autumn, with weak stratification in spring. In summer, the water column was strongly stratified, with the difference between SML and BML temperatures reaching 4.34 °C, compared to 1.87 °C in autumn and < 1 °C in spring. Surface chlorophyll *a* concentrations were highest in spring at 1.28 mg m^{-3} (mean 0.75 $\pm$ 0.46 mg m^{-3}) and summer 0.86 mg m^{-3}, and lowest in winter at 0.38 mg m^{-3} (Fig.2.3 g and Table 2). SCM were not observed at the shelf edge in summer.

Again, there were strong vertical gradients in nitrate between the SML and BML in autumn (6.0 μM) and summer (9.4 μM) but gradients were weak in winter (0.1 μM) and spring (0.9 μM, Fig.2.4 a).

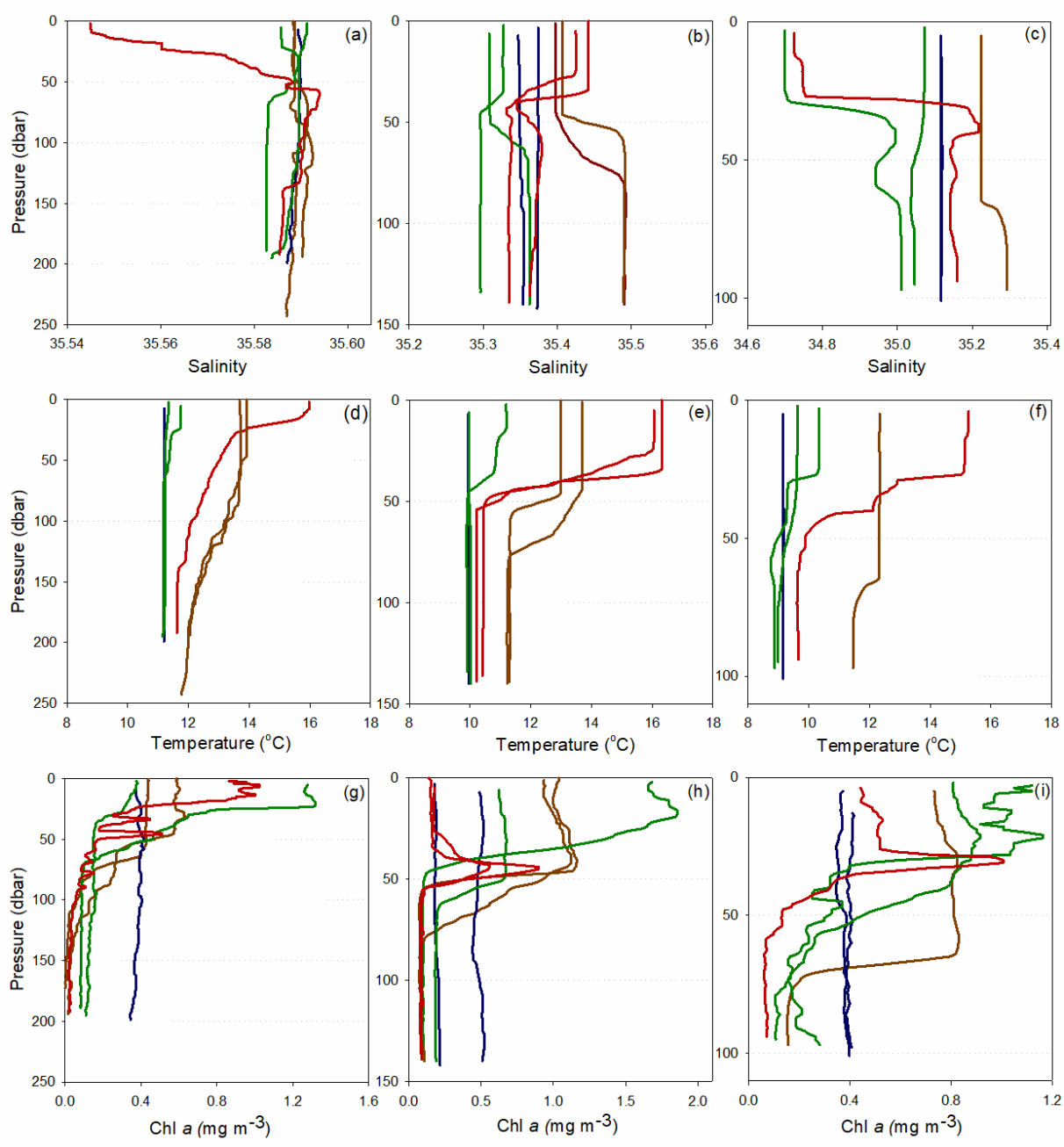

Fig.2.3. Vertical profiles of; salinity at (a) Shelf edge, (b) CCS and (c) Site A; temperature (°C) at (d) Shelf edge, (e) CCS and (f) Site A; and chlorophyll *a* fluorescence (mg m^{-3}) at (g) Shelf edge, (h) CCS and (i) Site A, for autumn (brown line), winter (blue line), spring (green line) and summer (red line), for CTD cast on initial and final visit (where applicable).

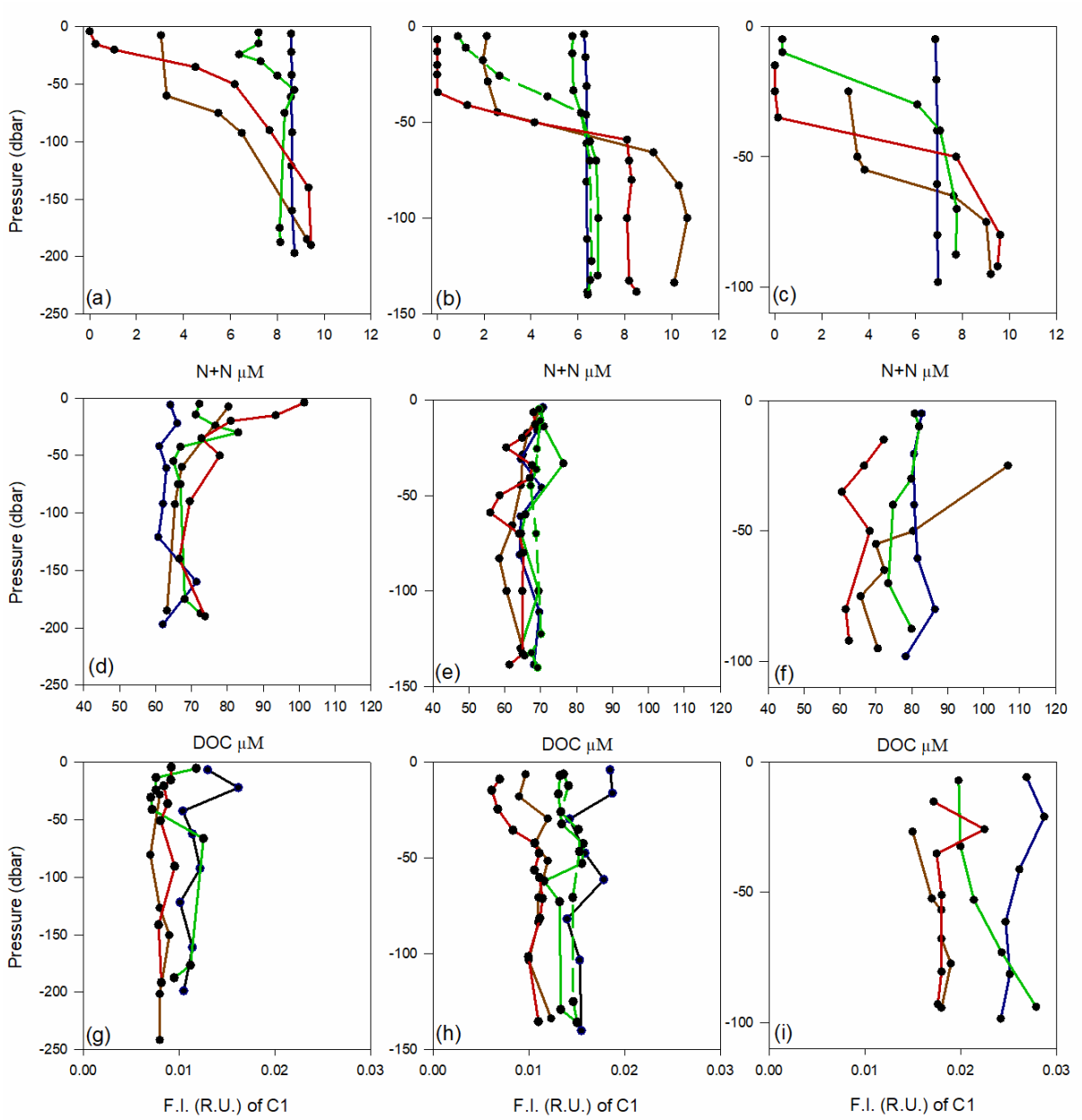

Fig.2.4. Vertical profiles of mean; inorganic nutrients (N+N (µM)) at Shelf edge (a), CCS (b) and Site A (c); DOC at Shelf edge (d), CCS (e) and Site A (f); and PARAFAC model component C1 (F.I. R.U.) at Shelf edge (g), CCS (h) and Site A (i), for autumn (brown line), winter (blue line), spring (green line) and summer (red line).

Surface waters were consistently cooler and fresher at Site A compared to CCS and the shelf edge throughout all seasons (Table 2.2). Cross shelf surface temperature gradients were strongest during winter (by 2.04 °C) and weakest in summer (by 0.71 °C). Conversely, the cross shelf gradient in surface salinity was most

pronounced during summer (0.82) and weakest during autumn (0.36). Surface chlorophyll *a* concentrations were highest at Site A in spring (0.96 mg m^{-3}), at CCS in autumn and during the autumn bloom (1.09 mg m^{-3} and 1.86 mg m^{-3}, respectively) and at the shelf edge in summer (0.86 mg m^{-3}). Surface chlorophyll *a* concentrations were lowest at Site A in winter (0.37 mg m^{-3}), at CCS in summer (0.14 mg m^{-3}) and at the shelf edge in autumn and spring (0.59 mg m^{-3} and 0.36 mg m^{-3}, respectively). There was a strong cross shelf gradient in N+N in the BML, with the highest concentrations (> 10 μM) and lowest concentrations (6.4 μM) at CCS (Fig.2.4 b).

Table 2.2 Mean ± std dev of surface temperature (°C), salinity and chlorophyll *a* concentrations (mg m^{-3}), integrated and depth averaged DOC (µM), and average water column fluorescence intensity of PARAFAC modelled components (C1 – C4 (R.U.)).Table indicates sample size (n) for which means were calculated.

Parameter	Season	Site A	n	Central Celtic Sea (CCS)	n	Shelf Edge	n
Surface temperature (ºC)	Autumn	12.33		13.41		13.91	
	Winter	9.16		10.01		11.2	
	Spring	9.98		10.34		11.5	
	Summer	15.26		16.28		15.97	
Surface salinity	Autumn	35.22		35.4		35.58	
	Winter	35.12		35.36		35.59	
	Spring	34.89		35.32		35.59	
	Summer	34.72		35.42		35.54	
Surface chlorophyll a (mg m^{-3})	Autumn	0.73		1.00		0.59	
	Winter	0.38		0.44		0.38	
	Spring	0.96		0.88		0.75	
	Summer	0.44		0.17		0.86	
DOC (µM)	Autumn	83.9 ± 0.7	6	65.7 ± 0.6	20	67.9 ± 0.9	10
	Winter	80.4 ± 0.9	12	65.2 ± 1.1	16	63.5 ± 1.1	8
	Spring	67.1 ± 1.3	12	68.5 ± 1.3	39	69.4 ± 1.3	14
	Summer	62.7 ± 1.1	6	63.4 ± 1.1	31	73.1 ± 1.1	8
C1 (R.U.)	Autumn	0.018 ± 0.001	6	0.011 ± 0.002	19	0.008 ± 0.001	6
	Winter	0.026 ± 0.002	12	0.016 ± 0.002	26	0.012 ± 0.002	8
	Spring	0.023 ± 0.003	7	0.014 ± 0.002	40	0.010 ± 0.003	18
	Summer	0.018 ± 0.002	6	0.010 ± 0.002	27	0.009 ± 0.001	8
C2 (R.U.)	Autumn	0.016 ± 0.001	6	0.011 ± 0.002	19	0.009 ± 0.000	6
	Winter	0.017 ± 0.001	12	0.011 ± 0.002	26	0.008 ± 0.001	8
	Spring	0.018 ± 0.002	7	0.012 ± 0.002	40	0.007 ± 0.002	18
	Summer	0.018 ± 0.002	6	0.010 ± 0.003	27	0.008 ± 0.001	8
C3 (R.U.)	Autumn	0.019 ± 0.005	6	0.016 ± 0.014	18	0.013 ± 0.005	6
	Winter	0.025 ± 0.009	12	0.033 ± 0.016	26	0.020 ± 0.007	8
	Spring	0.020 ± 0.010	6	0.029 ± 0.016	36	0.031 ± 0.019	15
	Summer	0.017 ± 0.007	6	0.025 ± 0.010	27	0.010 ± 0.010	8
C4 (R.U.)	Autumn	0.015 ± 0.003	6	0.011 ± 0.006	18	0.009 ± 0.003	6
	Winter	0.011 ± 0.002	12	0.019 ± 0.025	26	0.016 ± 0.014	8
	Spring	0.016 ± 0.006	6	0.021 ± 0.009	36	0.015 ± 0.012	17
	Summer	0.020 ± 0.004	6	0.017 ± 0.003	27	0.014 ± 0.003	8

2.3.2. Seasonal and spatial variation in DOC and PARAFAC modelled DOM components

Vertical gradients in DOC were weak except at Site A during autumn and the shelf edge during summer (Fig.2.4 f and d). The spatial and seasonal gradients in DOC were stronger than the vertical gradients and thus, to compare between sites and seasons, DOC measurements were integrated and depth-averaged (Fig.2.5 and Table 2.2). The statistical significance of seasonal and spatial patterns are reported in Appendices Tables 1 and 2.

At Site A, DOC was highest in autumn (84 μM ± 0.7 μM) and lowest in summer (63 μM ± 1.1 μM) (Fig.2.5 and Table 2.2). At CCS, DOC concentrations were highest in spring (69 μM ± 1.3 μM) and lowest in summer (63 μM ± 1.1 μM) (Fig.2.5 and Table 2.2). At the shelf edge DOC concentrations were highest in summer (73 μM ± 1.1 μM) and lowest in winter (64 μM ± 1.1 μM) (Fig.2.5 and Table 2.2). There were strong seasonal cross shelf gradients in DOC, with DOC being higher at Site A and declining towards the shelf edge in autumn (by 19%, $p > 0.05$) and winter (by 21%, $p < 0.05$). In contrast, DOC was higher at the shelf edge and declined towards Site A in spring (by 3%, $p > 0.05$) and summer (by 14%, $p < 0.05$).

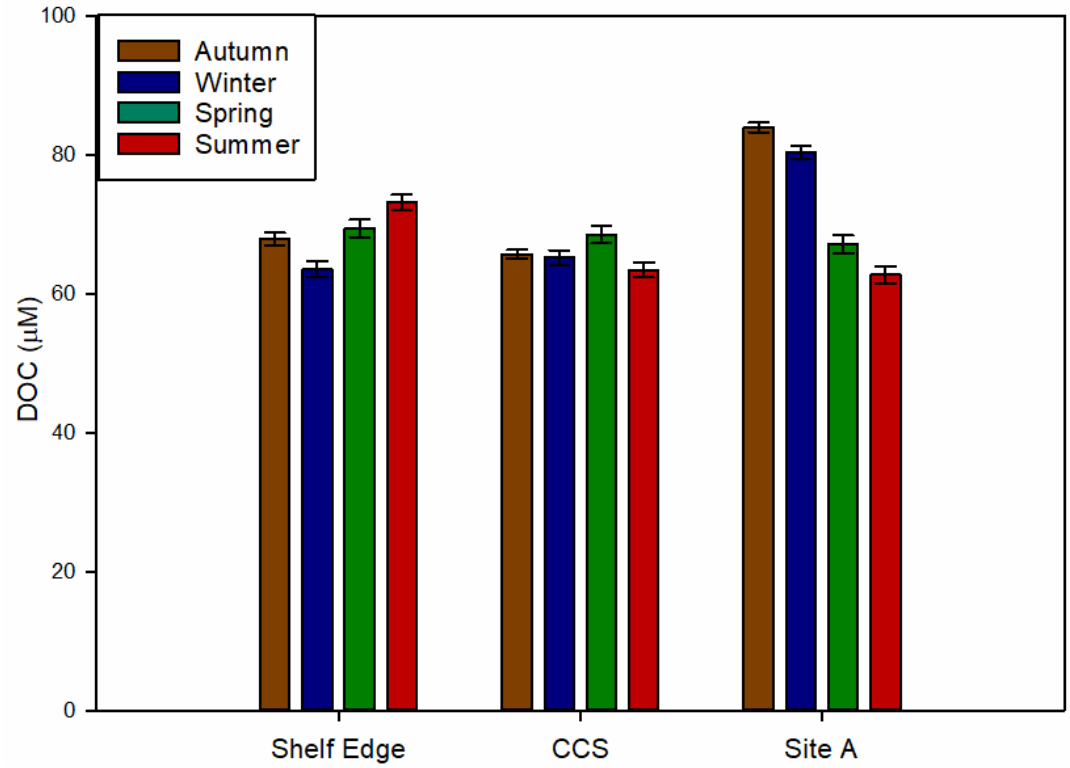

Fig.2.5. Seasonal and cross shelf integrated and depth averaged DOC concentrations (µM). Error bars represent one standard deviation. Autumn (brown bar), winter (blue bar), spring (green bar) and summer (red bar).

As with DOC, vertical gradients in DOM components were weak. Fluorescence intensity of the humic-like components, C1 (Fig.2.4 g, h and i) and C2, was generally lower in the surface at all sites and increased with depth. For example, C1 increased with depth by 41% at Site A during spring, suggesting photodegradation in surface waters. The protein-like components varied with depth similarly to DOC, and were generally higher in the surface than at depth. Overall, components displayed profiles typical to those found globally (Jorgensen et al. 2011). However, seasonal variability (Fig.2.6) and cross shelf gradients were more pronounced (Table 2.2) therefore water column measurements of fluorescence intensity were averaged for comparisons between seasons and sites.

At Site A, CCS and the shelf edge, C1 was highest in winter and lowest in summer, except at the shelf edge, when C1 was lowest in autumn (Fig.2.6 a-c and Table 2). There were no consistent clear seasonal trends at each site for C2, the marine humics component. At Site A, C2 was highest in spring and summer and lowest in autumn but differences were not significant (Fig.2.6 a and b, and Table 2.2). At CCS, C2 was highest in spring and lowest in summer but at the shelf edge, C2 was highest in autumn and lowest in spring (Fig. 2.6 b and c, and Table 2.2).

C1 and C2 were at least two-fold higher at Site A compared to the shelf edge during all seasons, resulting in a strong and significant cross shelf seasonal gradient in humic material (Table 2.2 and Appendices Table 2). The dominance of C1 at Site A indicates the impact of terrestrial organic matter in this region and suggests that the distribution is the result of seasonal variability in the supply and transport and dilution of this component.

There was greater variability in the seasonal rather than cross shelf trends in C3 and C4, the two protein-like components. Overall fluorescence intensity of these components were up to four times greater than the humic-like components (Fig.2.6). At Site A, there were no significant seasonal trends in C3, the tyrosine-like amino acid component. However, C3 increased from 0.020 R.U. nm^{-1} to 0.031 R.U. nm^{-1} at Site A between visits two days apart during winter. This increase was coincident with a 12% increase in surface chlorophyll *a* concentrations (from 0.37 mg m^{-3} to 0.41 mg m^{-3}) and a

21% increase in surface DOC (from 73 μM to 94 μM) at this site over the same period.

At CCS, C3 was highest in winter and more than double that of the lowest values in autumn (Fig.2.6 b and Table 2.2). During the development of the spring bloom, C3 more than doubled from 0.015 ± 0.003 R.U. nm^{-1} to 0.041 ± 0.012 R.U. nm^{-1}, and was coincident with a three-fold increase in surface chlorophyll *a* concentrations (0.62 mg m^{-3} to 1.68 mg m^{-3}). Conversely, C3 decreased by 50% (0.035 ± 0.006 R.U. nm^{-1} to 0.018 ± 0.008 R.U. nm^{-1}) over a two-week period during summer as surface chlorophyll *a* concentrations decreased by 22% (0.18 mg m^{-3} to 0.14 mg m^{-3}).

At the shelf edge, C3 was highest in spring, more than treble that of the lowest values in summer (Fig.2.6 c and Table 2.2). In spring, C3 increased three-fold over a five hour period (0.014 ± 0.003 R.U. nm^{-1} to 0.048 ± 0.009 R.U. nm^{-1}), and more than doubled within a week during the spring bloom period (to 0.037 ± 0.012 R.U. nm^{-1}), when surface chlorophyll *a* concentrations increased nearly three-fold (0.36 mg m^{-3} to 0.99 mg m^{-3}).

At Site A, C4, the tryptophan-like amino acid component, was highest in summer and twice that of the lowest values in winter (Fig.2.6 a and Table 2.2). At CCS, C4 was highest in spring and twice that of the lowest values in autumn (Fig.2.6 b and Table 2.2). Similarly to C3, C4 more than doubled over a three-week period during the development of the spring bloom (0.011 ± 0.002 R.U. nm^{-1} to 0.028 ± 0.007 R.U. nm^{-1}), and decreased by 25% between visits

one day apart in summer. At the shelf edge differences in C4 were only significant between autumn and summer (Fig.2.6 c and Table 2.2). Similarly to C3, there were significant differences during the development of the spring bloom when C4 increased over three-fold (0.006 ± 0.000 R.U. nm^{-1} to 0.022 ± 0.006 R.U. nm^{-1}) within a week. Coincident with C3, C4 increased five-fold between visits only five hours apart (0.006 ± 0.000 R.U. nm^{-1} to 0.030 R.U. nm^{-1}).

Cross shelf gradients in C3 and C4 were not as clear compared to C1 and C2, and the direction of the gradient changed with each season. However, the gradient in C3 was only significant in winter and summer, when C3 was higher at CCS than at the shelf edge by 39% and 60%, respectively (Fig.2.6 b and c, and Appendices Table 2). The cross shelf gradient in C4 was only significant in autumn and summer, when C4 was significantly higher at Site A compared to the shelf edge by 30% and 40%, respectively (Fig.2.6 a and c, and Appendices Table 2). Relative to C1 and C2, C3 dominated at CCS and the shelf edge during periods of high productivity, for example, during the spring bloom, and varied significantly with season, indicating that this protein-like DOM pool is an important autochthonous component of the DOM pool across the shelf.

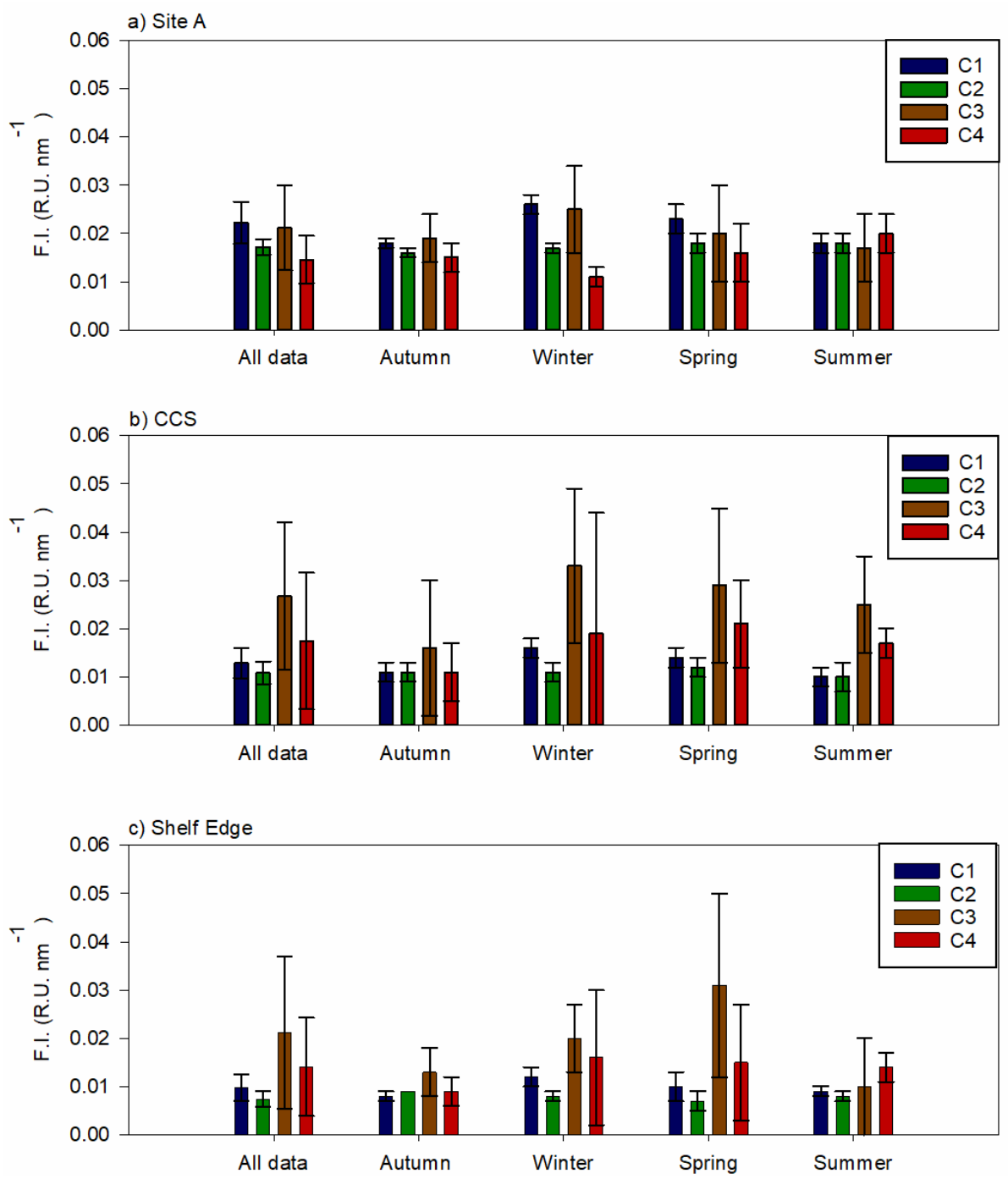

Fig.2.6. Seasonal and cross shelf distribution of fluorescence intensity in Raman Units (F.I. (R.U.)) of the PARAFAC components, a) C1 (blue), b) C2 (green), c) C3 (brown), and d) C4 (red). Bar plots represent the mean water column F.I. for all data. Whiskers are one standard deviation of the mean.

2.3.3. Seasonal and spatial variations in spectral and fluorescent indices

The spectral indices of absorption, the slope ratio (SR), absorption coefficient a305, slope coefficient $S_{300\text{-}650}$ and $SUVA_{280}$, and fluorescence indices, the humification index (HIX), fluorescence index (FI) and biological index (BIX) are summarised in Table 2.3. Except for a305, there were no strong vertical trends in either the spectral or fluorescence indices and thus indices were averaged over the entire water column. Note that absorbance data were not available for Site A in autumn.

For the entire data set, the SR ranged from 0.9 to 4.4 with seasonal means ranging from 1.8 ± 0.1 in summer to 3.1 ± 0.6 in autumn (Table 2.3). These SR values were within the range reported for shelf near-shore and offshore regions (1.7 and 4.6, respectively) (Helms et al. 2008, Kowalczuk et al. 2013, Catala et al. 2015). The lowest value of 0.9 was observed during winter and is indicative of influence of terrestrial DOM (Kowalczuk et al. 2013). Seasonality in the SR at Site A was not significant. At CCS and the shelf edge, the SR was highest in autumn and lowest in summer (Appendices Table 1). Notably the SR increased at the shelf edge during the development of the spring bloom by over 50% (from 2.2 ± 0.4 to 3.3 ± 0.5) (Fig.2.7 insert bar chart).

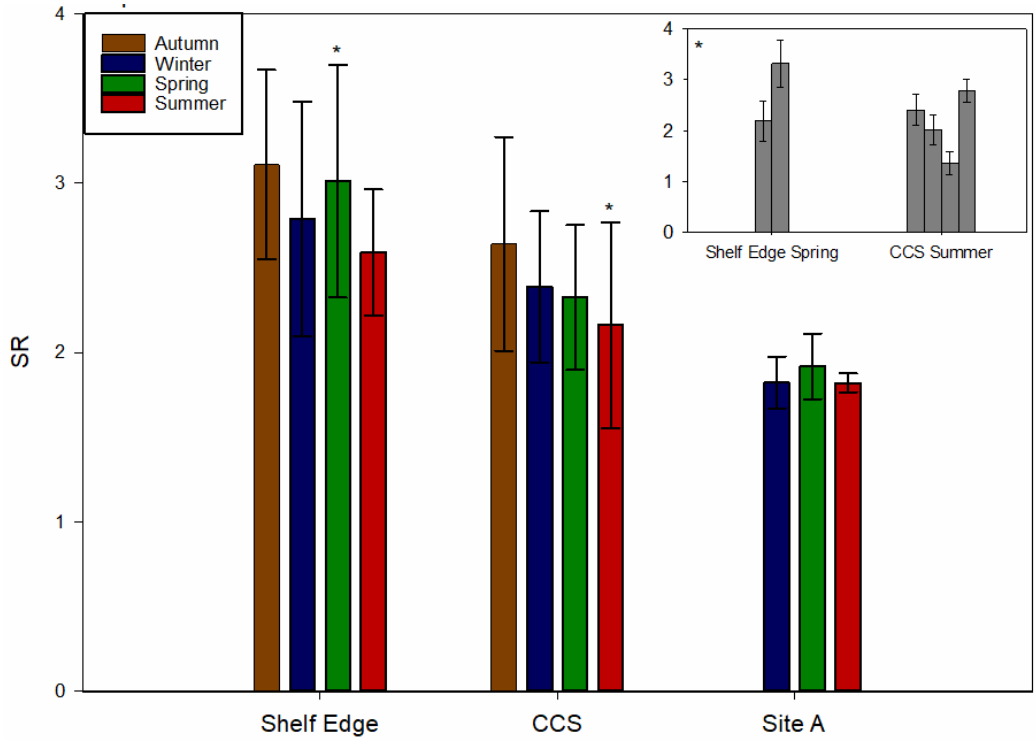

Fig.2.7. Seasonal and cross shelf distribution of spectral slope ratio (SR). Bar plots represent the mean water column SR for all data. Whiskers are one standard deviation of the mean. Autumn (brown), winter (blue), spring (green) and summer (red). *Insert bar charts to show individual vertical profile averages of water column SR for repeat station visits in instances were significant variability between visits and within seasons where identified ($p < 0.05$).

The CDOM absorption coefficient aCDOM(λ), here depicted as a305, ranged across the entire data set from 0.16 to 1.26 m^{-1}, with seasonal means ranging from 0.31 ± 0.10 in winter to 0.74 ± 0.08 in summer (Table 2.3). At Site A, a305 was highest in summer and lowest in winter (Appendices Table 1). There were no clear seasonal trends in a305 at CCS and the shelf edge, but a305 was 23% higher in summer than winter at the shelf edge (Appendices Table 1).

At Site A, variability in $S_{300\text{-}650}$ was low (range of 0.001 ± 0.002) and seasonal differences were not significant. At CCS and the shelf edge, $S_{300\text{-}650}$ was highest in autumn and lowest in summer (Table 2.3 and Appendices Table 1).

At Site A and CCS, $SUVA_{280}$ was highest in summer compared to winter and autumn. Elevated $SUVA_{280}$ in summer coincided with low DOC and humic DOM suggesting that higher molecular weight material is produced in situ during the biodegradation of labile DOM produced during summer and the preceding spring. There were no significant seasonal patterns at the shelf edge.

The SR was higher at the shelf edge site compared to Site A (by 30-36%, $p < 0.05$, Fig.2.7 and Table 2.3), resulting in a strong cross shelf gradient in SR. In contrast, a305 and $SUVA_{280}$ were higher at Site A compared to the shelf edge (by 51% and 49%, respectively, $p < 0.05$), thus reversing the cross shelf gradient in comparison to the SR (Table 2.3).

Although the spectral slope $S_{300\text{-}650}$ values varied significantly between season (see above), the difference in the $S_{300\text{-}650}$ values were only significant in spring between Site A and CCS making it a poor descriptor of DOM composition over the spatial scales in this study.

The absolute values and range in HIX (0.11 and 3.64), FI (0.23 and 2.96) and BIX (0.71 and 1.39) are small in this study in comparison to the complete range that can occur in the natural environment. In isolation, they are of limited value in interpreting the source and dynamics of DOM but in combination with other environmental and optical data, they support our findings of strong

cross shelf gradients in humic DOM but a strong seasonal trend in biologically associated DOM.

At site A and CCS, HIX was highest in autumn (Table 2.3), indicating DOM was more degraded and humified in autumn compared to the rest of the year. HIX was lowest in spring at Site A and lowest in winter at CCS, suggesting DOM was fresher and less humified then. At the shelf edge, HIX was significantly lower in summer than spring (Appendices Table 1). FI was significantly higher at all sites in summer than in spring (Appendices Table 2). The range in averaged BIX was low (0.31 ± 0.16) and generally >1 at all sites except Site A and the shelf edge in summer, and at CCS in autumn. BIX values were in the reported range for DOM of both autochthonous and bacterial origin (Huguet et al. 2009).

The HIX was significantly higher at Site A than at the shelf edge throughout the year apart from spring when differences were not significant (Appendices Table 2). Cross shelf gradients in FI and BIX were less clear and varied seasonally. Results from absorbance and fluorescence indices indicate a gradient in CDOM concentrations and composition persistent on seasonal time scales. High a305 coupled with high $SUVA_{280}$ and higher HIX values suggest that at Site A, there were greater concentrations of CDOM and that this material was higher molecular weight and more aromatic than compared to the shelf edge site, characterised by DOM of lower molecular weight.

Table 2.3 Water column mean ± std dev (representing the water column variability) of the SR, a305 (m^{-1}), $S_{300–650}$ (nm^{-1}) and $SUVA_{280}$ (L mg-C^{-1} m^{-1}), HIX, FI and BIX values at three sites grouped according to season.

Variable	Region	Autumn	Winter	Spring	Summer
Slope Ratio (SR)	Shelf Edge	3.1 ± 0.6	2.8 ± 0.7	3.0 ± 0.7	2.6 ± 0.4
	CCS	2.6 ± 0.6	2.4 ± 0.5	2.3 ± 0.4	2.2 ± 0.6
	Site A	No data	1.8 ± 0.2	1.9 ± 0.2	1.8 ± 0.1
***a305* m^{-1}**	Shelf Edge	0.39 ± 0.11	0.31 ± 0.10	0.45 ± 0.26	0.40 ± 0.05
	CCS	0.41 ± 0.10	0.43 ± 0.08	0.45 ± 0.15	0.44 ± 0.08
	Site A	No data	0.63 ± 0.05	0.68 ± 0.08	0.74 ± 0.08
$S_{300-650}$ (nm^{-1})	Shelf Edge	0.012 ± 0.002	0.016 ± 0.004	0.015 ± 0.006	0.016 ± 0.002
	CCS	0.011 ± 0.003	0.017 ± 0.003	0.015 ± 0.003	0.018 ± 0.004
	Site A	No data	0.018 ± 0.001	0.017 ± 0.002	0.017 ± 0.001
$SUVA_{280}$ (L mg-C^{-1} m^{-1})	Shelf Edge	0.33 ± 0.08	0.42 ± 0.06	0.44 ± 0.14	0.41 ± 0.03
	CCS	0.41 ± 0.07	0.55 ± 0.09	0.48 ± 0.19	0.56 ± 0.11
	Site A	No data	0.56 ± 0.08	0.76 ± 0.30	0.79 ± 0.06
Humification Index (HIX)	Shelf Edge	0.47 ± 0.10	0.56 ± 0.42	0.62 ± 0.30	0.41 ± 0.12
	CCS	1.31 ± 0.38	0.36 ± 0.25	0.75 ± 0.29	0.51 ± 0.29
	Site A	1.74 ± 0.36	1.69 ± 1.11	0.70 ± 0.18	1.39 ± 0.14
Fluorescence Index (FI)	Shelf Edge	1.25 ± 0.04	1.23 ± 0.37	1.08 ± 0.07	1.28 ± 0.05
	CCS	1.22 ± 0.08	1.19 ± 0.39	1.03 ± 0.07	1.30 ± 0.05
	Site A	1.30 ± 0.03	0.96 ± 0.02	0.83 ± 0.27	1.33 ± 0.05
Biological Index (BIX)	Shelf Edge	1.05 ± 0.04	1.24 ± 0.05	1.24 ± 0.05	0.99 ± 0.04
	CCS	0.98 ± 0.16	1.27 ± 0.04	1.26 ± 0.04	1.03 ± 0.05
	Site A	1.02 ± 0.06	1.28 ± 0.03	1.25 ± 0.02	0.97 0.01

2.3.4. Relationships between DOC, DOM components, CDOM spectral indices and salinity

The relationship between parameters was determined by linear regression analysis (Table 2.4). DOC and salinity were negatively correlated in winter and weakly positively correlated in summer. Fluorescence intensity of components C1 and C2 were negatively correlated with salinity throughout the year, the relationships varied seasonally, with the strongest relationships being observed in winter (R^2 = 0.80) (Fig.2.8 a-d and 2.8 e-f, respectively). The C4 component was weakly negatively correlated with salinity during autumn and summer and similarly to C1 and C2, the relationship varied between seasons (Fig.2.8 i-j). C3 was not correlated with salinity.

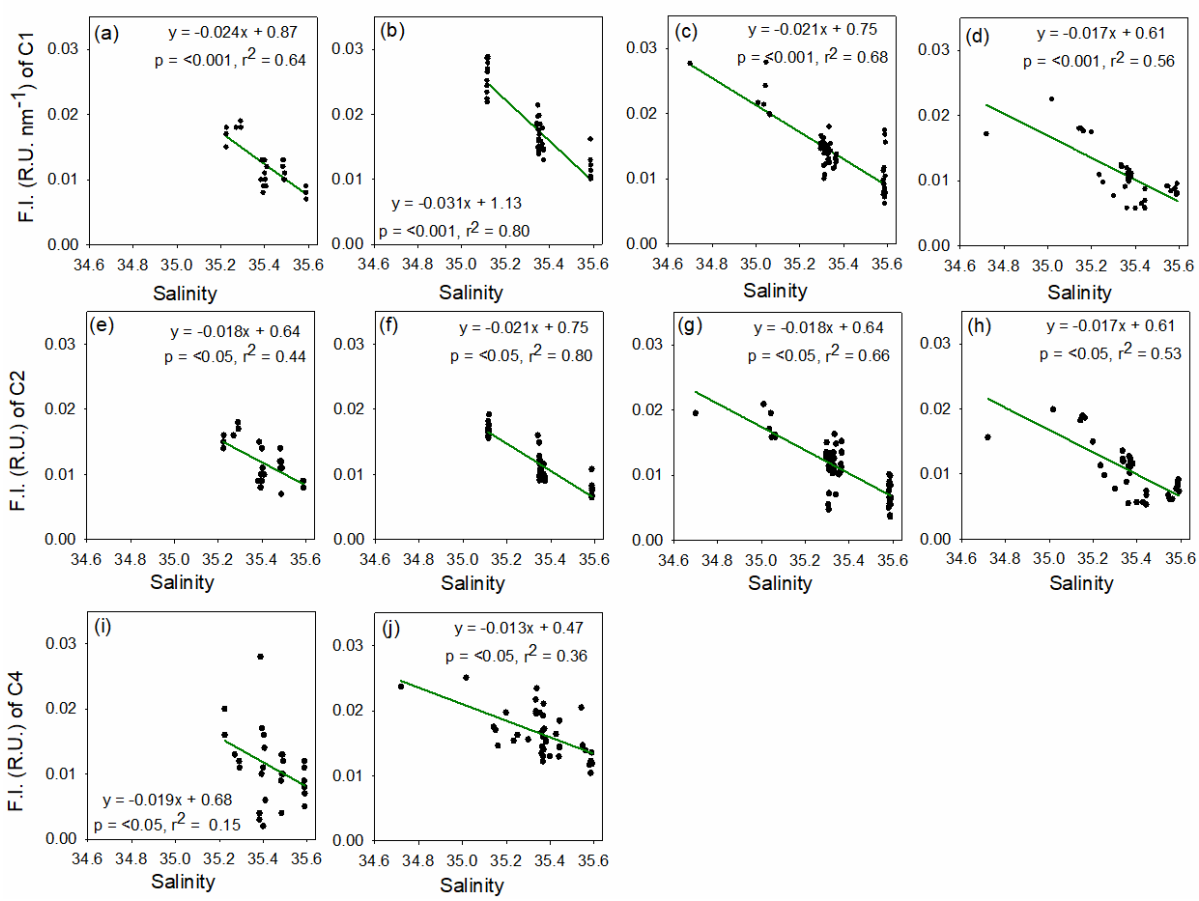

Fig.2.8. Relationships of salinity with fluorescence intensity of PARAFAC components; C1 for a) autumn, b) winter, c) spring, and d) summer; C2 for e) autumn, f) winter, g) spring, and h) summer; C4 for i) autumn, and j) summer.

The SR was weakly positively correlated with salinity, the relationship varied seasonally and was strongest in spring (R^2 = 0.37), and weakest in summer (R^2 = 0.14). HIX and $SUVA_{280}$ were negatively correlated with salinity except in spring, and a305 was negatively correlated with salinity in winter and summer. Although the salinity range sampled across the shelf sea throughout the different seasons was low (< 1), consistent and significant relationships with C1 and C2 indicate the presence of the terrestrially derived end-member.

There were strong positive correlations between DOC and C1 and C2 during winter (R^2 = 0.63 and 0.56, respectively) (Fig.2.9 b and c, respectively). DOC was also positively correlated with C4 (Fig.2.9 a) and $S_{300\text{-}650}$ during autumn, with a305 in winter and negatively correlated with $SUVA_{280}$ in spring and summer (Table 2.4). The relationship between DOC and the SR reversed from negative in winter to positive during spring and summer, with the relationship being strongest in spring (R^2 = 0.27).

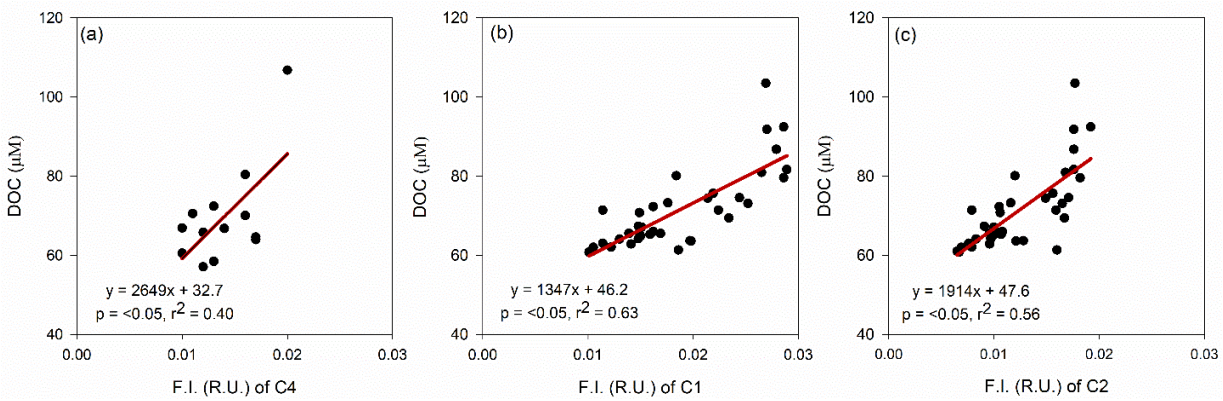

Fig.2.9. Distribution of DOC as a function of fluorescence intensity of fluorescence components a) C4 in autumn, b) C1 in winter, and c) C2 in winter.

DOM components C1, C2 and C4 were correlated to spectral indices to varying strengths and during different seasons (Table 2.4). C1 and C2 were negatively correlated with the SR in winter and spring, positive correlations with the HIX in autumn, winter and summer when the relationships were strongest (R^2 = 0.61), and with $SUVA_{280}$ and a305 in winter and summer. C4 was positively correlated with $SUVA_{280}$ in summer, a305 in spring and summer, with the BIX in autumn and with FI in winter (R^2 = 0.90).

Table 2.4. Results of linear regression analysis between parameters in each season. Regression coefficients, intercept ± standard error (S.E.) and slope ± standard error (S.E.) are significant to $p < 0.05$. * Instances when regression coefficients are not significant $p > 0.05$.

Parameters	Seasons	Intercept ± S.E.	Slope ± S.E.	R^2	Sample size
Salinity vs. C1	Autumn	0.87 ± 0.12	-0.024 ± 0.003	0.64	31
	Winter	1.13 ± 0.08	-0.031 ± 0.002	0.80	46
	Spring	0.75 ± 0.06	-0.021 ± 0.002	0.68	63
	Summer	0.61 ± 0.09	-0.017 ± 0.002	0.56	41
Salinity vs. C2	Autumn	0.64 ± 0.13	-0.018 ± 0.004	0.44	31
	Winter	0.75 ± 0.06	-0.021 ± 0.002	0.80	46
	Spring	0.64 ± 0.06	-0.018 ± 0.002	0.66	63
	Summer	0.62 ± 0.09	-0.017 ± 0.003	0.54	41
Salinity vs. C4	Autumn	0.68 ± 0.30	-0.019 ± 0.008	0.15	30
	Summer	0.47 ± 0.10	-0.013 ± 0.003	0.36	41
Salinity vs. DOC	Winter	1481 ± 252	-40 ± 7	0.48	36
	Summer	-642 ± 286	20 ± 8	0.13	45
Salinity vs. SR	Autumn	-129.5 ± 38.1	3.73 ± 1.1	0.23	42
	Winter	-72.0 ± 15.2	2.1 ± 0.4	0.36	45
	Spring	-76.0 ± 15.3	2.2 ± 0.4	0.37	47
	Summer	-43.6 ± 18.2	1.29 ± 0.5	0.14	40
Salinity vs. HIX	Autumn	118.7 ± 22.5	-3.32 ± 0.6	0.51	28
	Winter	100.3 ± 24.1	-2.82 ± 0.7	0.28	46
	Summer	50.4 ± 11.2	-1.41 ± 0.3	0.34	41
Salinity vs. $SUVA_{280}$	Autumn	21.49 ± 7.7	-0.60 ± 0.2	0.40	13
	Winter	10.53 ± 2.9	-0.28 ± 0.08	0.26	36
	Summer	24.50 ± 3.1	-0.68 ± 0.09	0.62	40
Salinity vs. a305	Winter	24.5 ± 2.6	-0.68 ± 0.07	0.67	46
	Summer	21.6 ± 2.8	-0.60 ± 0.08	0.61	40
C1 vs. DOC	Winter	46 ± 4	1347 ± 178	0.63	36
C1 vs. SR	Winter	3.3 ± 0.2	-56.0 ± 12.4	0.32	45
	Spring	3.6 ± 0.2	-83.3 ± 16.9	0.36	45
C1 vs. FI	Spring	1.22 ± 0.04	-14.95 ± 3.08	0.30	58

C1 vs. HIX	Autumn	0.09 ± 0.27*	97.6 ± 22.16	0.44	27
	Winter	-0.48 ± 0.38*	67.551 ± 20.44	0.20	46
	Summer	-0.28 ± 0.12	83.459 ± 10.72	0.61	41
C1 vs. a305	Winter	0.11 ± 0.03	20.429 ± 1.83	0.74	46
	Spring	0.20 ± 0.08	19.508 ± 5.19	0.20	59
	Summer	0.15 ± 0.03	30.725 ± 2.58	0.79	40
C1 vs. $SUVA_{280}$	Winter	0.39 ± 0.05	7.301 ± 2.53	0.20	36
	Spring	0.20 ± 0.10*	22.232 ± 6.60	0.25	36
	Summer	0.28 ± 0.05	26.289 ± 4.65	0.46	40
C2 vs. DOC	Winter	48 ± 4	1914 ± 291	0.56	36
C2 vs. SR	Winter	3.34 ± 0.24	-84.25 ± 18.66	0.32	45
	Spring	3.30 ± 0.23	-76.33 ± 20.77	0.24	45
C2 vs. HIX	Autumn	-0.03 ± 0.34*	109.76 ± 27.77	0.39	27
	Winter	-0.64 ± 0.37*	115.52 ± 29.5	0.26	46
	Summer	-0.24 ± 0.12	81.46 ± 10.47	0.61	41
C2 vs. $SUVA_{280}$	Autumn	0.74 ± 0.09	-31.92 ± 9.34	0.70	7
	Winter	0.38 ± 0.05	11.68 ± 3.75	0.22	36
	Summer	0.29 ± 0.05	25.43 ± 4.70	0.44	40
C2 vs. a305	Winter	0.12 ± 0.04	30.16 ± 2.86	0.72	46
	Summer	0.19 ± 0.04	27.21 ± 3.38	0.63	40
C4 vs. DOC	Autumn	33 ± 14	2649 ± 969	0.40	13
C4 vs. BIX	Autumn	0.86 ± 0.04	12.97 ± 3.01	0.40	30
C4 vs. FI	Winter	0.87 ± 0.02	16.17 ± 0.83	0.90	46
C4 vs. a305	Spring	0.29 ± 0.05	8.35 ± 2.34	0.20	53
	Summer	0.05 ± 0.07	25.47 ± 4.05	0.51	40
C4 vs. $SUVA_{280}$	Summer	0.18 ± 0.09*	23.01 ± 5.33	0.33	40
DOC vs. SR	Winter	3.95 ± 0.64	-0.02 ± 0.01	0.18	35
	Spring	-0.15 ± 1.04	0.04 ± 0.02	0.27	22
	Summer	0.75 ± 0.61	0.02 ± 0.01	0.13	40
DOC vs. $S_{300-650}$	Autumn	485 ± 7	1642 ± 640	0.29	18
DOC vs. a305	Winter	51 ± 5	42 ± 10	0.37	36
DOC vs. $SUVA_{280}$	Spring	80 ± 3	-24 ± 70	0.48	30
	Summer	88 ± 5	-38 ± 9	0.32	40

SR vs. $SUVA_{280}$	Spring	1.06 ± 0.13	-0.18 ± 0.05	0.32	28
SR vs. $S_{300-650}$	Summer	0.029 ± 0.001	-0.005 ± 0.001	0.68	40
HIX vs. a305	Summer	0.37 ± 0.03	0.17 ± 0.05	0.26	40
FI vs. $SUVA_{280}$	Autumn	1.74 ± 0.38	-1.16 ± 0.33	0.67	8
	Spring	1.29 ± 0.24	-0.79 ± 0.24	0.27	32
a305 vs. $S_{300-650}$	Autumn	0.02 ± 0.002	-0.02 ± 0.004	0.38	42
a305 vs. $SUVA_{280}$	Autumn	0.07 ± 0.06*	0.80 ± 0.12	0.80	13
	Winter	0.29 ± 0.04	0.49 ± 0.08	0.52	36
	Spring	0.04 ± 0.09*	0.93 ± 0.16	0.48	39
	Summer	0.13 ± 0.05	0.91 ± 0.11	0.65	40

2.4. Discussion

2.4.1. Factors driving seasonality in DOC

There was no consistent seasonal trend in DOC at stations sampled in the Celtic Sea. Instead, seasonality was site specific and it is likely that the physical and biogeochemical characteristics at each site were a strong determinant for the patterns observed.

High DOC observed at Site A in autumn is likely due to local production and external inputs. High C3 and BIX values indicate a predominantly biological and bacterial source of DOM, implying the autumn bloom and/or remineralisation of POM was a source of DOC. In addition, FI values of 1.3 and high HIX values alongside negative correlations between salinity and humic-like DOM and C4 suggests an external terrestrial input which could account for high DOC concentrations at Site A in autumn. DOC was lowest in summer at Site A. This was likely a result of a reduction in DOC production by 1.4-fold compared to the preceding spring (García-Martín et al. 2017, Poulton et al. 2017) as well as reduced discharge and DOC input from the River Severn between winter (242 m^3 s^{-1} and 7699 µM DOC d^{-1} respectively in January 2015) and spring (96 m^3 s^{-1} and 2559 µM DOC d^{-1}, respectively in March 2015) (Leeuwen 2017).

At CCS, high DOC concentrations in spring coincided with the highest DOC production rates (García-Martín et al. 2017). Low DOC in summer coincided with the highest bacterial production and lowest bacterial respiration observed at CCS, implying net consumption of DOC by bacteria at this site (García-Martín et al. 2017). Higher DOC

at the shelf edge site in summer probably reflects net production of DOC during sustained productivity following the spring bloom. Lower DOC in winter may reflect the influence of deep or open ocean waters on the shelf (as noted by (Humphreys et al. in press, Ruiz-Castillo et al. in press), which have lower DOC concentrations relative to shelf waters.

DOC production in autumn, spring and summer at CCS and at the shelf edge was greater than bacterial carbon demand (BCD) (García-Martín et al. 2017), and at CCS DOC:DON ranged from 12.4 ± 0.2 in summer to a maximum of 17.0 ± 3.4 in spring (Davis et al. 2018), greater than the Redfield ratio of 6.6:1 (Redfield 1934). However, Poulton et al. (2017) found that C-overconsumption by phytoplankton was not dominant in the Celtic Sea but instead other biogeochemical processes driven by bacteria and/or zooplankton are likely to create more C-rich material which would contribute to the continental shelf pump. Thus, there is accumulating evidence for the importance of DOM as a vehicle for export of carbon from the shelf sea.

2.4.2. Input of terrestrial OM in the shelf sea

There were strong cross shelf gradients in C1 during all seasons in the Celtic Sea, being consistently higher at Site A and lower at the shelf edge, reflecting input of a terrestrial humic component in the near-shore environment and dilution across the shelf (Murphy et al. 2008, Kowalczuk et al. 2013). Seasonal variation in the inverse relationship between C1 and salinity likely reflects

seasonality in inputs (Leeuwen 2017) alongside seasonal changes in physical transport and hydrography (Ruiz-Castillo et al. in press). Terrestrial humic material is susceptible to photo-degradation and up to 96% of CDOM and 41% of DOC from freshwater sources can be decomposed by solar radiation in the surface mixed layer (Vahatalo and Wetzel 2004). C1 was generally lower in surface waters, however, no distinct vertical gradients were observed in this study.

DOC and salinity were negatively correlated in autumn (not significant) and winter ($R^2 = 0.48$, $p < 0.05$) and positively correlated in spring (not significant) and summer ($R^2 = 0.13$, $p < 0.05$). Reversal of the cross shelf gradients and change in slope reflects seasonality in inputs (see section 2.4.1), seasonality in transport (Ruiz-Castillo et al. in press) and biological production and consumption (García-Martín et al. 2017, Poulton et al. 2017).

Cross shelf gradients in the slope ratio (SR) provides further evidence for the influence of terrestrially-derived DOM in the Celtic sea. The slope ratio (SR) has been shown to be inversely related to CDOM molecular weight (MW) (Helms et al. 2008). The persistent weak positive correlation between SR and salinity implies input of terrestrially-derived higher MW DOM at the freshwater end member in contrast to a fresher low MW or photo-degraded DOM pool at the shelf edge (Stubbins et al. 2012). Correlations between SR and DOC were weak but changed from negative in winter to positive in summer, when DOC and $SUVA_{280}$ were also negatively correlated. Indeed, consistently higher values for a305, $SUVA_{280}$ and HIX at Site

A compared to the rest of the Celtic Sea again provides further evidence for input of terrestrially-derived high MW DOM into the northern Celtic Sea, especially in winter.

In winter, DOC was strongly correlated with C1, when 62% of the DOC distribution was explained by C1 and an intercept value of 46 ± 3 µM indicated that a substantial fraction of DOC (potentially up to 45%) was non-absorbing (Mendoza and Zika 2014). However, when employing the salinity DOC winter regression coefficients, there was a large freshwater end member for DOC (1481 ± 252 µM) of which potentially 815 ± 139 µM of DOC was absorbing. This freshwater end member was over three times greater than the average freshwater end member, 465 ± 12 µM of Barron and Duarte (2015) but within the total range reported for freshwater DOC end members (0 - 2500 µM). Using the slope and intercept values of the relationship between salinity, DOC and C1 (Table 2.4), an estimated maximum of 25 µM of DOC was of terrestrial origin at CCS in winter, representing 35% of the DOC pool (CCS average salinity of 35.4), being 43% at Site A and 24% at the shelf edge. This estimate is high considering that riverine nitrate and nitrite (N+N) only accounts for up to 10% of total N+N at the CCS site Ruiz-Castillo et al. (in press) and that CCS is 200 km from the nearest coast and 400 km from the Bristol Channel. The contribution of terrestrially-derived DOM to the open ocean has not been fully quantified, however new insights into the mechanisms for its transport, transformation and fate are

emerging (Lauerwald et al. 2012, Raymond and Spencer 2015, Osburn et al. 2016).

2.4.3. Biological production of OM in the shelf sea

There were strong temporal variations in the protein-like components, C3 and C4 linked to productivity. For example, C4 increased by 91% from autumn to spring at CCS. Even on shorter timescales of hours to days, when net primary production (NPP) increased 3-fold over a period of four days at CCS (from 154 mmol C m^{-2} d^{-1} to 532.1 mmol C m^{-2} d^{-1}, (Poulton et al. 2017), C3 and C4 increased rapidly. Despite the strong link to biological production, no correlation between C3 or C4 and chlorophyll *a* was observed, possibly due to the patchiness in biological activity as observed in measurements of NPP (Poulton et al. 2017) and gross oxygen production (Seguro et al. 2017). The protein-like components are considered to represent the bioavailable fraction of the DOM pool (Yamashita and Tanoue 2003, Jaffe et al. 2014), and are commonly attributed to autochthonous in situ production by bacterial and phytoplankton (Vantrepotte et al. 2007, Murphy et al. 2008, Mendoza and Zika 2014, Danhiez et al. 2017). Such rapid changes in these components have been observed previously, for example, in the Arctic Ocean following a phytoplankton bloom (Chen et al. 2017) and in the Florida Everglades (Chen and Jaffe 2014).

Winter maxima were observed in the protein-like components, specifically C3 at Site A and CCS and C4 at the shelf edge. The reason for the occurrence of labile DOM in winter in the Celtic Sea is

currently unclear but may be due to remineralisation of POM to dissolved labile compounds over the winter period, or the occurrence of stochastic winter blooms, as observed in the subpolar North Atlantic (Lacour et al. 2017) resulting in release of fresh DOM prior to the spring bloom.

As in other studies (Jorgensen et al. 2011, Kowalczuk et al. 2013, Mendoza and Zika 2014), there was no significant correlation between C3 and salinity, suggesting that the cross shelf distribution of C3 was driven mainly by non-conservative mixing and in situ production. In contrast, C4 was correlated with salinity, as observed elsewhere (Mendoza and Zika 2014, Pitta et al. 2016), and at times followed a terrestrial type distribution (Murphy et al. 2008). C4 also correlated with $SUVA_{280}$, a305, BIX and FI suggest that C4 was produced from substrates of both terrestrial and autochthonous origin.

The increase in a305 and $SUVA_{280}$ from winter to spring to summer indicates that there is an increase in the aromaticity of the DOM, which implies an increase in MW or refractory component of DOM. Rather than being indicative of a terrestrial source, it is postulated that in situ bacterial processing of the DOM pool is likely to have increased the aromaticity of the DOM (Cuss and Gueguen 2015, Hansen et al. 2016), at Site A from winter to summer. These observations highlight the complexity in the DOM pool as both supply and in situ processing operate simultaneously.

2.5. Conclusions

This study demonstrated the strength of a multi-dimensional approach incorporating DOM optical properties alongside measurements of DOC in delineating the complexities of the DOM pool in shelf seas.

Seasonality in DOC concentrations was site specific reflecting contrasting physical and biological conditions at each site. Strong cross shelf gradients in C1, C2, SR, a305, $SUVA_{280}$ and HIX, as well as strong correlations between salinity and DOC, C1, HIX, $SUVA_{280}$ and a305 indicate the input and influence of terrestrially-derived DOM to the DOC pool in the Celtic Sea. Using these correlations, estimates of terrestrial DOM represented 24, 35 and 43% of the total DOC pool at the shelf edge, CCS and Site A, respectively. Significant temporal variation in C3 and C4, also highlighted the importance of biological production and consumption in influencing DOC concentrations in the Celtic Sea over short (hours to days) and longer (seasonal) timescales.

Site A was strongly influenced by inputs from land and the DOM pool reflected this due to the dominance of high MW and humified DOM. In contrast, the shelf edge was characterised by low MW and fresher DOM. Overall, there is accumulating evidence from this study and other studies on bacterial carbon dynamics (García-Martín et al. 2017), phytoplankton carbon dynamics (Poulton et al. 2017) and the stoichiometry of DOM and POM (Davis et al. 2018),

highlighting the potential importance of the DOM pool as a vehicle for transport of C from the shelf.

This study contributes to this emerging idea by providing insight into the seasonality and composition of the DOM pool, thus identifying when the DOM pool is likely to be most efficient at exporting carbon. Further examination is needed on how bacteria and phytoplankton interact with the different DOM pools, both refractory and labile, over the timescales relevant for carbon export from shelf seas. This will help determine the relative magnitude of on-shelf processing versus off shelf export of DOM.

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Chapter 3

DOM across the Northwest European Shelf

3.1. Introduction

In the highly productive continental shelf seas, where rates of primary production are up to 5 times greater than the open ocean (Tweddle et al. 2013), dissolved organic matter (DOM) production and consumption via remineralisation control the magnitude and distribution of dissolved organic carbon, nitrogen and phosphorus (DOC, DON and DOP, respectively; (Liu et al. 2010). As a major carbon reservoir, DOC makes an important contribution to the global carbon cycle (85000 Tg C) (Hansell and Carlson 1998, Hansell et al. 2009). As part of the land-ocean continuum (Liu et al. 2010), the transport and export of DOM from shelf seas could be as important as primary production itself due to DOM residence times on-shelf being shorter than turnover times for deep ocean DOC pools (Hopkinson et al. 1997). Indeed, global estimates of primary production in the coastal zone are ~ 6 Pg C yr^{-1} (Wollast 1998) comparable to estimates of DOC exported from the coastal zone, which range from 4.4 to 27.0 Pg C yr^{-1} (Barron and Duarte 2015). Furthermore, large inputs of DOC from riverine discharge influence the metabolic balance of shelf seas potentially rendering them net heterotrophic if total respiration exceeds production (Liu et al. 2010).

Globally, the distribution of DOC decreases with increasing distance from the coastline and with increasing salinity, with considerable external inputs of 250 Tg C yr^{-1} of generally refractory DOC from land into the coastal ocean (Barron and Duarte 2015). Deep ocean DOC ranges globally from 34 µM in the Pacific Ocean and 48 µM in the North Atlantic (Hansell and Carlson 1998), and is considered to be refractory with turnover times of one to ten thousand years (Hopkinson and Vallino 2005). Similarly, DON concentrations are twice as high in coastal and shelf sea regions (11.4 ± 7.3 µM N) compared to the surface ocean concentrations (5.1 ± 1.7 µM N). The mean DON in the deep ocean is 3.6 ± 2.2 µM N (Sipler and Bronk 2015). Globally, DON exported from rivers is 11.5 Tg N yr^{-1} (Seitzinger et al. 2005), with up to 8 times more bioavailable DON consumed than DOC (Wiegner et al. 2006).

Autochthonous DOC and DON are produced by phytoplankton, bacteria, viruses and microzooplankton. Up to 37% of phytoplankton cell carbon is released as DOC (Strom et al. 1997), with up to 80% being released via excretion and up to 20% via sloppy feeding (Saba et al. 2011). Despite the gradients in concentration in coastal and ocean environments, DON release rates, as a percentage of gross N uptake, are comparable at 36 ± 24% and 29 ± 19%, respectively (Sipler and Bronk 2015).

As the common origins of the elemental components of DOM include primary and autochthonous production, degradation of particulate organic matter (POM) and inputs from terrestrial sources

(Liu et al. 2010), the seasonal cycle of these processes will influence the seasonality of the concentration of DOM. DOC is an important and dynamic part in the ocean carbon cycle, and in the open ocean, DOC seasonality is well understood (Yamanaka and Tajika 1997). Carlson et al. (1994) found that DOC accumulated in surface waters in early spring due to increased primary production during the spring phytoplankton bloom. While a proportion of this DOC was consumed in summer and autumn by heterotrophic bacteria, the unutilised fraction of DOC was exported from surface waters during winter mixing. This export was found to be equal to and even greater than the particulate flux (Carlson et al. 1994) although this is controversial. While we understand the role and seasonal cycling of DOM in the open ocean, in physical and biogeochemically dynamic shelf sea regions, the role of DOM and its seasonal cycle are not clear. We can however conceptualise the seasonal cycling of DOM in shelf seas (detailed in section 3.3.5) to enable comparisons between what is typical, what is observed, and whether different shelf sea regions share similar seasonal patterns.

In this chapter, using a unique data set collected over an 18-month period covering 9 different hydrographic regions located on the northwest European Shelf and adjacent waters of the North Atlantic Ocean (Fig.3.1), I address the following questions;

1) How does the magnitude of DOC and DON vary on the Northwest European Shelf?

2) How does DOC and DON vary seasonally in stratifying and mixed regions on the Northwest European Shelf? And how does this compare with our conceptual understanding of DOM seasonality in shelf seas?

3.2. Materials and methods

3.2.1. Sampling

The shelf wide sampling campaign was in collaboration with UK's Centre for Environment, Fisheries and Aquaculture Science (*CEFAS),* the Marine Institute Ireland, Northern Irelands Agri-Food & Biosciences Institute (AFBI) and Marine Scotland. The campaign was an extension of the NERC funded Shelf Sea Biogeochemistry (SSB) project (for more details visit the UK-SSB website, https://www.uk-ssb.org/).

Samples for DOC, DON, and inorganic nutrients were collected during the SSB and shelf wide sampling campaigns from January 2014 to August 2015 at over 350 locations on the northwest European continental shelf and North Atlantic (Fig.3.1). For SSB, seawater samples were collected from the ship's underway supply and at discrete depths ranging from 3 to 2500 m using Niskin bottles attached to a rosette frame with a sensor package consisting of a Sea-Bird conductivity-temperature-depth (CTD) sensors and fluorometer. Sensors were calibrated using discrete samples collected during each cruise. Chlorophyll fluorescence was calibrated to chlorophyll *a* (units of mg m^{-3}) using filtered, acetone-extracted

samples filtered through Whatman glass fibre filters (GF/F, nominal pore size 0.7 µm) as described in (Mayers et al. 2017). For the shelf wide campaign, surface samples were collected from the ships underway seawater supply (nominal depth 5 m) alongside their corresponding underway temperature and salinity measurements. Subsurface samples were collected from Niskin bottles mounted on a rosette frame with their corresponding temperature and salinity measurements taken from the CTD sensors also mounted on the rosette frame.

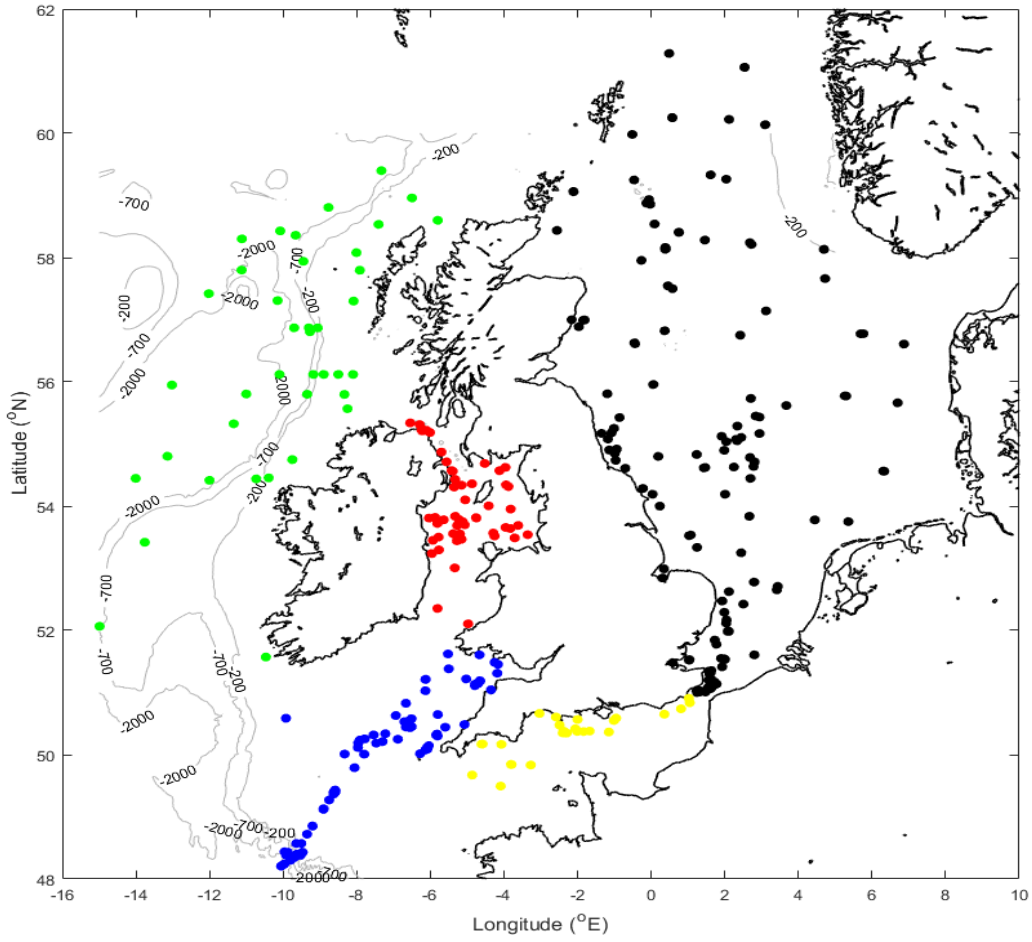

Fig.3.1. Stations sampled during SSB cruises and the Shelf Wide campaign. Regions are colour coded as follows: Irish Sea (red), Celtic Sea (on and off-shelf) (blue), Malin-Hebrides Shelf (on and off-shelf) (green), the English Channel (yellow), and the North Sea (black).

3.2.2. Collection and analysis of inorganic nutrients, DOC and DON

For the SSB cruises, inorganic nutrient analysis, specifically for nitrite, nitrate, ammonium, silicate and phosphate, was performed at sea immediately after sample collection using a 5-channel Bran and Luebbe AIII system (Woodward and Rees 2001). For the shelf wide campaign, samples were stored in HDPE bottles at -20ºC until analysis at the Plymouth Marine Laboratory. Inorganic nutrient analysis is described in detail in Humphreys et al, in press and Hartman et al. (2018).

For SSB cruises, samples for measurement of DOC and DON were collected by filtering seawater through a combusted glass fibre filter (GF/F, nominal pore size 0.7 µm) under low vacuum pressure (< 10 mmHg) using a custom-made glass filtration rig. Samples were preserved with 20 µL of 50% (v/v) hydrochloric acid and analysed onshore using high temperature catalytic oxidation (HTCO) on a Shimadzu TOC-VCPN. The limits of detection for DOC and TDN were 3.4 µM and 1.8 µM respectively, with a precision of 2.5%. Consensus Reference Materials from the Hansell laboratory, Miami were analysed daily with a mean and standard deviation for TDN and DOC of 32.9 ± 1.7 µM (expected range 32.25 to 33.75 µM) and 43.9 ± 1.2 µM (expected range 42 to 45 µM; n=39) respectively. For the shelf wide campaign, samples were collected by either filtering seawater through a combusted glass fibre filter, as above, or using a glass syringe. Samples were collected in pre-cleaned HDPE bottles and stored at -20ºC until analysis at the University of Liverpool.

Concentrations of DON were determined by subtracting the concentration of inorganic nitrogen (nitrate, nitrite, and ammonium) from TDN concentrations.

DOC and DON analysis for the SSB cruises and the shelf wide campaign were performed by Dr. Claire Mahaffey and Sabena Blackbird.

3.2.3. Region division for data analysis

The SSB shelf wide sampling campaign covered the following regions: the Irish Sea and Liverpool Bay, the North Sea, the English Channel, the Celtic Sea, the Malin-Hebrides shelf and the North Atlantic. Region definitions were adapted from the EU Marine Strategy Framework Directive (MSFD) and UK Marine Monitoring and Assessment Strategy Charting Progress 2 (UKMMAS 2010), and their geographic location and boundaries are defined in Table 3.1.

Table 3.1. Geographical location of regional divisions for stations sampled on the Northwest European Shelf and North Atlantic. Sample size and depth range are given for surface mixed layer (SML) and bottom mixed layer (BML) samples.

Region	Location Coordinates (Latitude °N, Longitude °W)	Sample Size (DOC, DON)	Depth Range (m)
The Irish Sea			
Western Irish Sea (WIS)	52.0° to 55.4°N, 4.2° to 6.6°W	44, 36 (SML)	Surface only
Eastern Irish Sea (EIS) including Liverpool Bay	53.0° to 55.0°N, 3.0° to 4.1° W	10, 9 (SML)	Surface only
The North Sea			
Northern North Sea	55.0° to 61.3°N, 2.5°W to 6.9°E	60, 49 (SML) 24, 19 (BML)	Surface - 188
Southern North Sea	51° to 54.9°N, 1.1°W to 6.3°E	85, 58 (SML) 13, 12 (BML)	Surface - 73
The English Channel	49° to 51°N, 5°W to 1.1°E	30, 23 (SML)	Surface only
The Celtic Sea and North Atlantic			
The Celtic Sea On-Shelf	48.4° to 51.2°N, 6.1° to 9.6°W	75, 58 (SML) 45, 39 (BML)	Surface - 199
The Celtic Sea Off-Shelf (North Atlantic)	48.2° to 48.4°N, 9.5° to 10.1°W	20, 19 (SML) 31, 14 (BML)	Surface - 2495
The Malin-Hebrides Shelf			
The Malin Sea On-shelf	51.5° to 59°N, 5.8° to 10.5°W	21, 16 (SML) 7, 4 (BML)	Surface - 125
The Malin Sea Off-shelf (North Atlantic)	52° to 59.4°N, 7.3 to 15°W	23, 17 (SML) 16, 7 (BML)	Surface - 2008

3.2.4. Hydrographic characteristics of regions sampled during the Shelf Wide Sampling campaign

3.2.4.1. The Irish Sea and Liverpool Bay

The Irish Sea, with an area of 54000 km^2 and a volume of 2830 km^3, is a semi-enclosed shelf sea bordered by Ireland to the west and England, Wales and Scotland to the east (Bowers et al. 2013). It is influenced by freshwater inputs, particularly in the eastern region and Liverpool Bay where freshwater stratification is observed (Simpson 1997, Bowers et al. 2013). In the western Irish sea, heated summer water remains above cooled winter water (Huthnance 2010), resulting in summer stratification to the south-west of the Isle of Man, around the coast of Dublin and in the North Channel. However, the Irish Sea is generally mixed throughout the year (Bowers et al. 2013). Moschonas et al. (2015) observed a strong salinity gradient from west to east separated by a density front with limited exchange between the eastern and western parts of the Irish Sea (Gowen and Stewart 2005). Similarly, distinct differences in hydrography during the Shelf Wide sampling campaign were observed. In this study, the Irish Sea was subdivided into the Western Irish Sea (WIS) and Eastern Irish Sea including Liverpool Bay (EIS). The Irish Sea is connected to the Celtic Sea by a northwards residual flow at around 1 cm s^{-1} (Bowers et al. 2013), transporting 0.1 Sv and with a flushing time of about a year for the whole of the Irish Sea (Huthnance 2010). Measurements of DIC from the Shelf Wide sampling campaign

suggest that the Irish Sea is a source of CO_2 to the atmosphere throughout the year (Hartman et al. 2018).

3.2.4.2. The North Sea

The North Sea spans an area of 575300 km^2 with a volume of 42294 km^3 and is surrounded by the British Isles to the west, the European continent to the east and Norway to the northeast. The North Sea is divided along a ~50 m contour at 55°N which separates the deeper and seasonally stratifying northern region from the shallower and permanently mixed southern region. Annual river inputs to the whole North Sea region are between 296 and 354 km^3 which particularly effect the southern region which also receives inputs from the English Channel (Thomas et al. 2005). The northern region also receives freshwater inputs from the Baltic Sea and continuous exchange with North Atlantic Ocean water entering at the northern boundary dominates the water budget (Thomas et al. 2005). In this study, the North Sea was sub divided at the 55°N boundary into the southern North and northern North Sea. Measurements of DIC from the Shelf Wide sampling campaign suggest that the southern North Sea is a source and the northern North Sea a sink of CO_2 to the atmosphere throughout the year (Hartman et al. 2018).

3.2.4.3. The English Channel

The English Channel spans an area of 90450 km^2 with a volume of 4404 km^3 and is bordered by the UK to the north and by France to the south. Although the English Channel receives

freshwater inputs from the Solent and River Seine, their net effect on salinity is small (Huthnance 2010). The Channel is relatively shallow (< 100 m) and the eastern channel is tidally mixed all year round, unlike the western channel along the English coast which is thermally stratified in summer, with the Ushant front separating the well-mixed and stratified waters (Borges and Frankignoulle 2003). The English Channel is connected to the Celtic Sea to the east by weak mean flows which supply 0.1 Sv (Huthnance et al. 2009), while east west flows in the channel transport ~ 0.14 Sv (Southward et al. 2005). Wind driven flows of ~ 1 cm s^{-1} connect the English channel to the North Sea (Pingree and Lecann 1989). Measurements of DIC from the Shelf Wide sampling campaign indicate that the eastern English Channel is a seasonal source of CO_2 to the atmosphere in summer and autumn (Hartman et al. 2018).

3.2.4.4. The Celtic Sea

The Celtic Sea occupies a broad shelf region of 500 km in width, an area of 162340 km^2 and a volume of 17444 km^3. It is bordered by Brittany to the southeast and is south-west of Ireland. Depths range from 30 m in the northern extent to 200 m near the shelf edge (Pingree 1980). The Celtic Sea is seasonally stratified with annual river inputs of 983 m^3 s^{-1} and an ocean-shelf water exchange with the North Atlantic of 3 m^2 s^{-1} (Huthnance 2010). The shelf slope areas of the Celtic and Malin seas are connected through the European slope current, which extends from the Iberian margin and transports Atlantic water northwards to the Norwegian Sea

(White and Bowyer 1997), with a substantial fraction entering the northern North Sea (Marsh et al. 2017). To distinguish between the influence of deep ocean waters and shallow shelf waters in this study, the Celtic Sea was partitioned into an on-shelf region, defined as stations with water depths of < 250 m, and an off-shelf region including North Atlantic ocean waters, defined as stations with water depths > 3000 m. Measurements of DIC from the Shelf Wide sampling campaign indicates that the Celtic Sea is a weak sink of CO_2 throughout the year (Hartman et al. 2018).

3.2.4.5. The Malin-Hebrides Shelf

The Malin-Hebrides Shelf is a narrower shelf, where depths increase from 150 m to 1000 m in a distance of 30 km (Souza et al. 2001). The shelf region encompasses the western Scottish shelf and western Irish shelf with a combined area of 140329 km^2 and volume of 12600 km^3 (Huthnance 2010). The Malin-Hebrides Shelf is seasonally stratified with annual river inputs of 856 $m^3\ s^{-1}$ to the west of Ireland and 1056 $m^3\ s^{-1}$ to the west of Scotland. The combined ocean-shelf water exchange with the North Atlantic is 3.7 $m^2\ s^{-1}$ (Huthnance 2010). Similarly to the Celtic Sea, to distinguish between the influence of deep ocean waters and shallow shelf waters, the Malin-Hebrides Shelf was partitioned into an on-shelf region, defined as stations with water depths of < 200 m, and an off-shelf region including North Atlantic Ocean waters, defined as stations with water depths > 3000 m. Measurements of DIC from the Shelf Wide

sampling campaign suggest that the Malin-Hebrides Shelf was overall, a source of CO_2 throughout the year (Hartman et al. 2018).

Next I will address questions on how DOM varies on the Northwest European Shelf, how DOM varies on seasonal cycles in stratifying and mixed regions, and how this compares to our conceptual understanding of DOM seasonality in shelf seas.

3.3. Results

Data from the shelf wide sampling campaign were used to address questions outlined above. However, before these questions were addressed, it was necessary to consider the temporal and spatial bias in sampling and how this may affect the interpretation of the data set and ability to address the questions outlined above.

3.3.1. Spatial and temporal data distribution of shelf wide data

The full shelf wide data set consists of a total of 985 DOC, 738 DON and 966 N+N data points ranging from near surface waters (~1 m) to a maximum depth of 2495 m. Each nutrient displays a typical vertical distribution, with N+N concentrations being low in the surface and increase with depth, whereas DOC and DON concentrations were higher in the surface and decrease with depth (Fig.3.2).

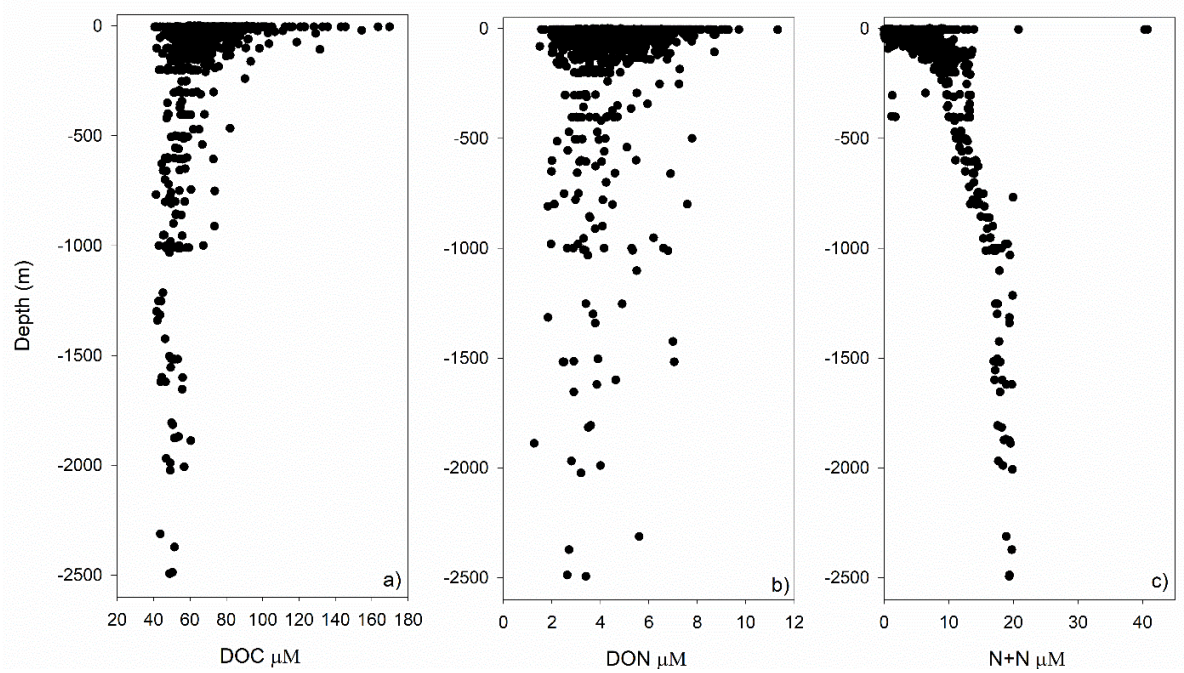

Fig.3.2. Depth distribution of a) DOC (µM), b) DON (µM), and c) Nitrate + Nitrite (N+N (µM)) for the full shelf wide data set.

For some regions, only samples from the surface (< 15m) and bottom waters (typically 20 to 188 m) were collected instead of full vertical profiles at high resolution. Therefore, to allow consistent data comparisons across the on-shelf waters, the shelf wide data set was filtered to consider only a two layer system consisting of the surface mixed layer (SML) and bottom mixed layer (BML). The SML was defined as the top 15 m of the water column, although I acknowledge that the actual SML varies seasonally. Thus, either single data points or averaged data points in the top 15 m of the water column were used to represent SML DOM concentrations. The BML DOM concentration was defined as the data at the deepest depth sampled when the water column was < 250m deep. For the off-shelf bottom waters of the Celtic Sea and Malin-Hebrides Shelf, the deepest depth sampled (typically greater than 400 m) was used to enable

comparisons between shelf sea and deep ocean DOM. Separation of the data into a two layer system reduced the number of data points to 368 in the SML and 134 in the BML. For the southern North Sea region surface data were considered to be representative of the whole water column as this region is permanently mixed.

Sampling was not uniform in space and time during the shelf wide campaign. There were no data collected in December and there were fewer than 20 data points collected in January, February and September (Fig.3.3), with data collection in January and February focused on near-coastal regions, possibly due to adverse weather conditions. There were also biases in regional sampling. For example, in August, the North Sea was sampled systematically but there were no samples collected from the other shelf sea regions during August (Fig. 3.4).

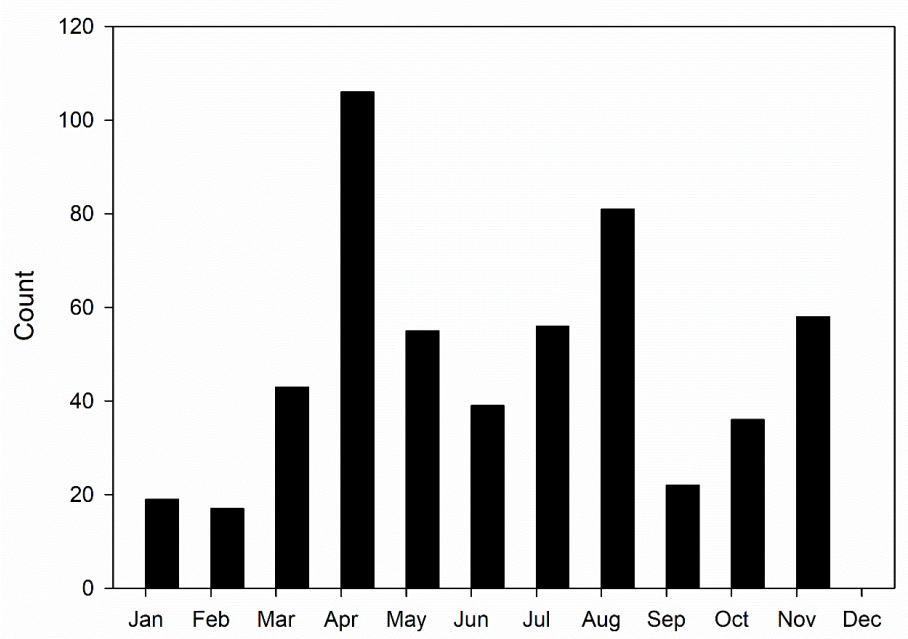

Fig.3.3. Monthly sampling frequency of sampling in 2014 and 2015 during the Shelf Wide sampling campaign. The counts per month represent all data points before separation into a two layer system.

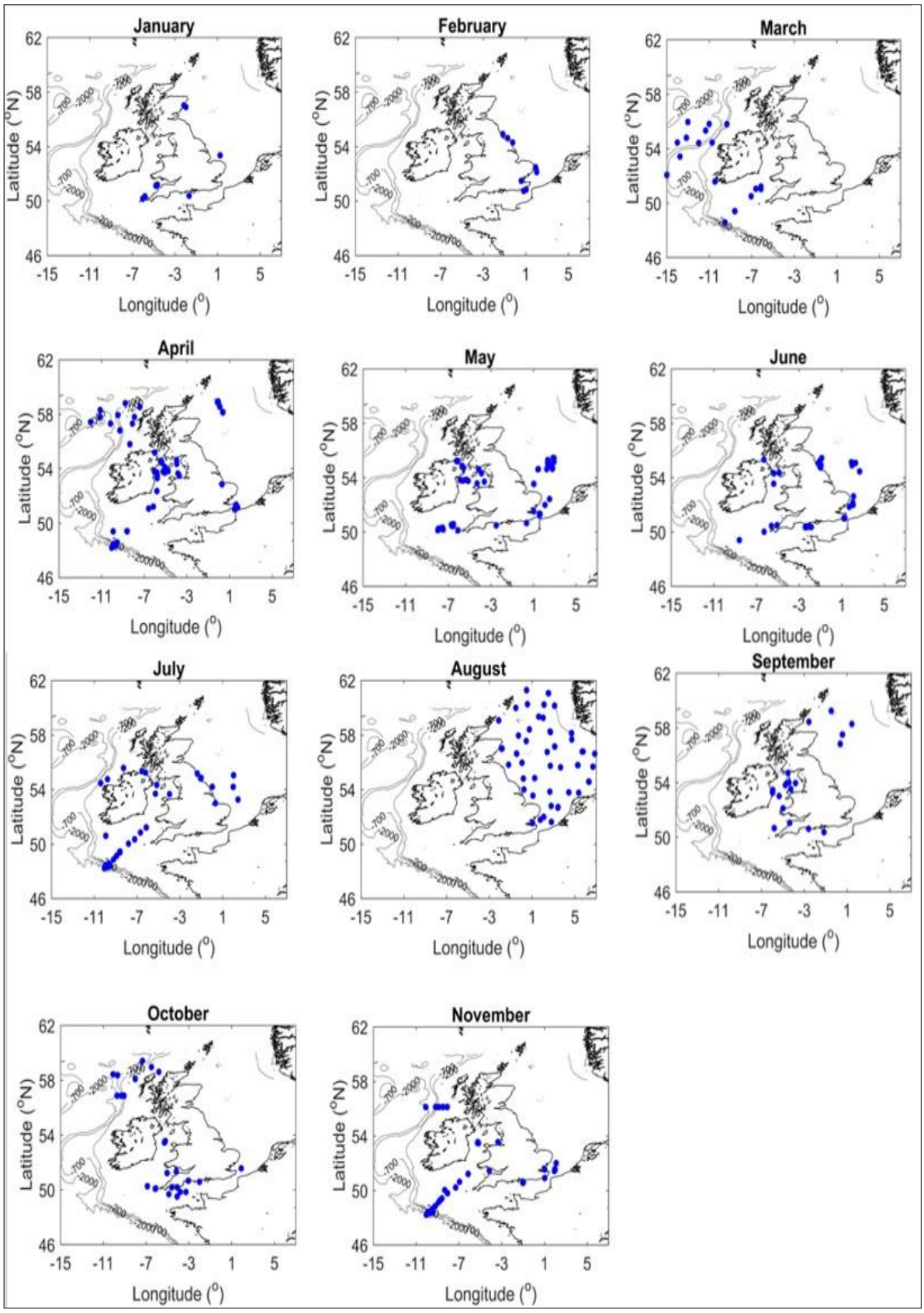

Fig.3.4. Sampling locations by month of sampling during the Shelf Wide sampling campaign.

While the data set is considered to be adequate as a first step in identifying shelf wide DOM distribution, I will focus in this study on seasonality where there is DOC data for winter, spring, summer and autumn. Thus, seasonality was assessed in the English Channel, the Celtic Sea (SML and BML) and the Malin-Hebrides Shelf (SML) (section 3.3.5.1). Seasons were defined as winter (January to March), spring (April to June), summer (July to September) and autumn (October to December).

3.3.2. Hydrography and inorganic nutrients during the Shelf Wide sampling campaign

Samples were collected across a large temperature and salinity range during the entire shelf wide sampling campaign. In the SML, temperature ranged from 7 to 20 °C (Table 3.2). The mean regional temperature was highest in the English Channel and lowest in the off-shelf waters of the Malin-Hebrides Shelf. Salinity ranged from 29.7 to 35.6 (Table 3.2). The mean regional salinity was highest in the off-shelf waters of the Celtic Sea and lowest in the eastern Irish Sea. In the BML in on-shelf waters, the mean temperature ranged from 7 to 17 °C. The mean regional temperature was highest and lowest in the northern North Sea. Salinity ranged from 34.4 to 35.6. The mean regional salinity was highest in the Celtic Sea and lowest in the northern North Sea.

In the SML, N+N concentrations ranged from 0.02 to 21 µM (excluding high data points from Dover Strait stations in the southern

North Sea which were 41 µM) (Table 3.2). The mean regional N+N was highest in the off-shelf waters of the Malin-Hebrides Shelf and lowest in the northern North Sea. On-shelf in the BML, N+N ranged from 0.01 to 14 µM. Mean N+N was typically higher in the BML than in the SML. The highest mean N+N was in the Celtic Sea (8.2 ± 0.2 µM) and lowest was in the northern North Sea (6.5 ± 0.9 µM). N+N concentrations in the deep off-shelf waters (> 400 m) ranged from 9 to 21 µM (Table 3.2). The mean N+N was highest in the off-shelf waters of the Malin-Hebrides Shelf (16.1 ± 0.7 µM) and lowest in the off-shelf waters of the Celtic Sea (15.1 ± 0.9 µM), N+N concentrations in the off-shelf waters are representative of deep North Atlantic water.

The monthly distribution of N+N in the SML, on-shelf BML and off-shelf BML are presented Figure 3.5. Two data points have been omitted where N+N were exceptionally high (> 40 µM, Dover Straits) to avoid obscuring the monthly trends. In the SML, N+N concentrations were low in January (< 10 µM), when sampling was limited to < 10 sites, and increased gradually through March, April and May, before decreasing sharply between June and August (< 5 µM), and then steadily increasing from September to November when they were highest (> 20 µM) (Fig.3.5 a). In contrast, in the BML on-shelf waters, N+N concentrations were more consistent but were generally highest between August and November, and lower between March and July (Fig.3.5 b). In the BML of the off-shelf

waters (North Atlantic), N+N concentrations were also more consistent and never reached levels below 5 µM (Fig.3.5 c).

Table 3.2. Mean temperature (Temp °C), salinity and inorganic nutrients (N+N µM) values in the SML and BML for each region over the whole period sampled. S.E. is the standard error and n is the number of observations.

Region	Mean Temp (°C)	S.E.	Range	n	Mean Salinity	S.E.	Range	n	Mean N+N (µM)	S.E.	Range	n
Celtic Sea												
On-shelf SML	12.4	0.3	9.1 - 17.7	79	35.2	0.04	33.2 - 35.6	78	3.6	0.01	<0.02 - 13.0	69
On-shelf BML	10.5	0.1	8.9 - 12.4	48	35.4	0.02	35.0 - 35.6	48	8.2	0.2	5.8 - 10.7	47
Off-shelf SML	14.2	0.5	10.6 - 17.1	23	35.6	0.01	35.3 - 35.6	23	3.3	0.6	0.2 - 8.6	21
Off-shelf BML	7.6	0.6	3 - 12	32	35.3	0.05	34.9 - 35.6	32	15.1	0.7	6.4 - 20.7	31
Malin-Hebrides												
On-shelf SML	10.8	0.5	8.4 - 15.5	22	35.2	0.06	34.7 - 35.6	20	6.9	0.8	0.3 - 11.3	22
On-shelf BML	11.1	0.6	8.3 - 12.5	7	35.2	0.09	34.8 - 35.4	7	7.8	1.0	4.5 - 12.8	7
Off-shelf SML	10.5	0.2	9.7 - 12.7	24	35.4	0.01	35.3 - 35.4	24	8.7	0.6	2.8 - 11.1	24
Off-shelf BML	7.2	0.6	3.6 - 10.6	16	35.2	0.05	34.9 - 35.5	16	16.1	0.9	10.5 - 19.9	16
English Channel												
Surface Only	15.2	0.5	9.9 - 18.8	22	35.2	0.02	34.9 - 35.4	27	1.7	0.5	0.07 - 8.1	26
Western Irish Sea												
Surface Only	11.9	0.4	8.6 - 16.5	47	34.3	0.03	34 - 34.9	47	5.0	0.6	0.03 - 10.6	43
Eastern Irish Sea												
Surface Only	11.7	1.0	8.2 - 16.8	10	33.7	0.12	33.1 - 34.2	10	5.6	2.2	0.02 - 20.8	10
Northern North Sea												
SML	13.0	0.4	6.8 - 17.5	59	34.5	0.08	32.2 - 35.2	62	1.2	0.3	<0.02 - 6.7	59
BML	9.2	0.4	7.4 - 17.4	31	35.0	0.05	34.4 - 35.4	31	6.5	0.9	0.06 - 13.6	30
Southern North Sea												
SML (Mixed)	14.6	0.4	8 - 20	48	34.4	0.12	29.7 - 35.2	63	2.9	0.9	<0.02 - 40.7* (13.9)	69 (67)

*High N+N (>40 µM) from 2 stations in the southern North Sea are from stations located in the Dover Strait, when these points are excluded the maximum concentration is 13.9 µM and number of observations reduces to 67.

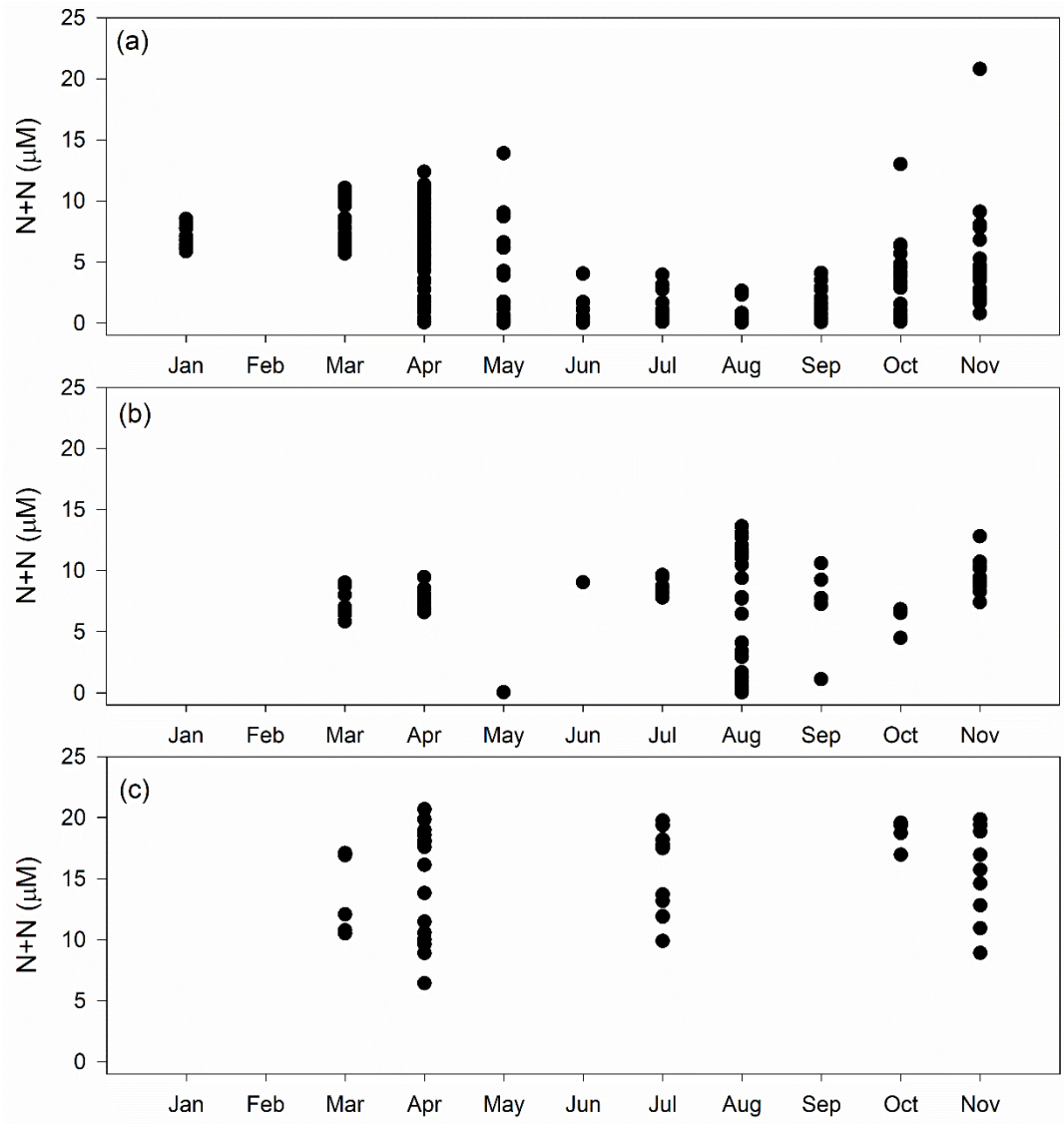

Fig.3.5. Monthly distribution of N+N (µM) for a) SML, b) BML on-shelf, and c) BML off-shelf, during the Shelf Wide sampling campaign.

3.3.3. Distribution of DOC and DON during the shelf wide sampling campaign

The regional means for the whole 12 to 18 month sampling period of DOC, DON and the ratio of DOC to DON (DOC:DON) are shown in Table 3.3, and the mean (± S.E.) concentrations of DOC and DON in the SML and BML are presented in Figure 3.6.

Across the entire shelf wide region sampled, the mean DOC concentrations ranged by ~ 31 μM (Table 3.3). In the SML, mean DOC concentrations were highest in the southern North Sea (83 ± 2 μM) and lowest in the Malin-Hebrides off-shelf region (58 ± 1 μM) (Fig.3.6). Mean DOC concentrations in the BML were highest in the Celtic Sea (68 ± 2 μM). The lowest mean DOC concentrations were observed in off-shelf deep waters (~50 μM), where concentrations (mean of all data > 400 m) were typical of deep ocean values (Hansell and Follows 2008). On average, DOC was 10 ± 4 μM higher in the SML than in the BML (Fig.3.6).

Across the entire shelf wide region sampled, the mean DON concentrations ranged by 3.0 μM (Table 3.3). In the SML, the mean DON concentration was highest in the English Channel (6.0 ± 0.4 μM) and eastern Irish Sea (6.0 ± 0.7 μM), and lowest in the Malin-Hebrides off-shelf region (3.8 ± 0.3 μM) (Fig.3.6). Mean DON concentrations in the BML were highest in the Celtic Sea (4.7 ± 0.2 μM) and lowest DON in the off-shelf waters > 400 m (3.0 ± 0.2 μM) of the North Atlantic, as previously observed (Sipler and Bronk 2015). On average, DON was 1.4 ± 0.4 μM higher in the SML than in the BML (Fig.3.6).

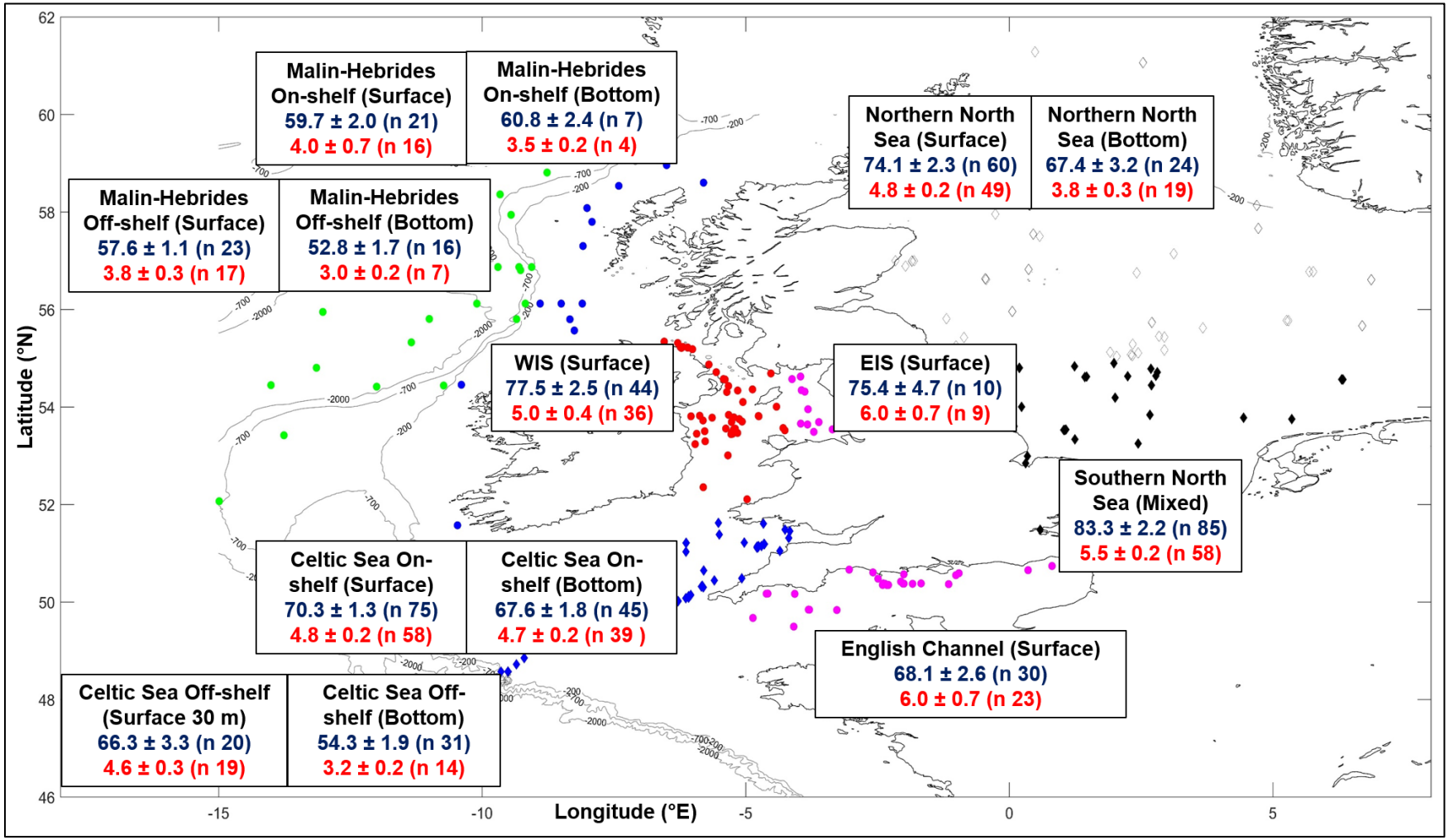

Fig.3.6. Distribution of DOM on the Northwest European Shelf and adjacent North Atlantic (off-shelf regions). Mean ± S.E. of DOC (µM) in blue and DON (µM) in red, n is the number of observations.

Across the entire shelf wide region sampled, the mean ratio of dissolved organic carbon to dissolved organic nitrogen (DOC:DON) ranged by 7 (Table 3.3) and was greater in all regions than the Redfield Ratio of 6.6:1 (Redfield 1934). In the SML, the mean DOC:DON was highest in the western Irish Sea (18 ± 1), and lowest in the English Channel (12 ± 1 (Table 3.3)). The mean DOC:DON in the BML was highest in the northern North Sea (19 ± 2) and lowest in the Celtic Sea on-shelf region (15 ± 1). DOM was typically more carbon rich in the BML in the northern North Sea compared to the SML, while SML and BML values were similar in the Celtic Sea and Malin-Hebrides on-shelf and off-shelf regions (Table 3.3).

Table 3.3. Mean DOC and DON concentrations, and DOM stoichiometry (DOC:DON) values in the SML and BML for each region over the whole period sampled. S.E. is the standard error and n is the number of observations.

Region	Mean DOC (µM)	S.E.	Range	n	Mean DON (µM)	S.E.	Range	n	Mean DOC:DON	S.E.	Range	n
Celtic Sea												
On-shelf SML	70.3	1.3	47.7 - 101.4	75	4.8	0.2	2.6 - 8.6	58	16	0.7	7 - 30	56
On-shelf BML	67.6	1.8	52 - 131.5	45	4.7	0.2	2.2 - 8.7	39	15	0.7	10 - 28	38
Off-shelf SML	66.3	3.3	49.7 - 111.1	20	4.6	0.3	2.4 - 7.4	19	17	2.0	9 - 37	18
Off-shelf BML	54.3	1.9	35.5 - 90.2	31	3.2	0.2	2 - 4.7	14	18	1.3	13 - 31	14
Malin-Hebrides												
On-shelf SML	59.7	2.0	48.6 - 81.5	21	4.1	0.3	2.5 - 7.6	16	15	0.9	10 - 21	16
On-shelf BML	60.8	2.4	52.4 - 68.4	7	3.5	0.2	3.2 - 4	4	17	0.8	15 - 18	4
Off-shelf SML	57.6	1.1	48 - 68.3	23	3.8	0.3	1.7 - 5.9	17	16	1.5	10 - 34	16
Off-shelf BML	52.8	1.7	42.2 - 67.4	16	3.0	0.2	2.0 - 3.8	7	18	1.6	11 - 25	7
English Channel												
Surface Only	68.1	2.6	40.6 - 112.4	30	6.0	0.4	3.2 - 9.7	23	12	0.9	7 - 28	22
Western Irish Sea												
Surface Only	77.5	2.5	54.1 - 143	44	5.0	0.4	2 - 11.3	36	18	1.2	56 - 41	36
Eastern Irish Sea												
Surface Only	75.4	4.7	43.5 - 92.3	10	6.0	0.7	3.1 - 9.3	9	14	1.1	910 - 19	9
Northern North Sea												
SML	74.1	2.3	41.8 - 145.5	60	4.8	0.2	2.2 - 7.6	49	17	0.8	10 - 32	47
BML	67.4	3.2	49 - 118.7	24	3.8	0.3	1.5 - 6.5	19	19	1.8	9 - 36	17
Southern North Sea												
SML	83.3	2.3	45.2 - 169.8	85	5.5	0.2	1.6 - 9.2	58	18	1.4	6 - 59	58

DOC concentrations in the Celtic Sea, Malin-Hebrides shelf and English Channel were typically lower than 70 μM compared to DOC concentrations in the Irish Sea and North Sea which were typically greater than 70 μM (Fig.3.6). DON concentrations were typically lower than 5 μM in the Celtic Sea, Malin-Hebrides shelf and northern North Sea compared to DON concentrations in the Irish Sea, English Channel and southern North Sea which were greater than 5 μM (Fig.3.6). DOM was generally more carbon rich in the western Irish Sea and in the North Sea, the Celtic Sea SML on and off-shelf and off-shelf BML, and the Malin-Hebrides on-shelf BML and off-shelf SML and BML (DOC:DON values > 16), compared to the English Channel, eastern Irish Sea, the BML of the Celtic Sea and SML of the Malin-Hebrides on-shelf regions (DOC:DON values < 16) (Table 3.3). Regional differences in DOC may be explained by influence of rivers and exchange with adjacent ocean regions.

3.3.4. Shelf wide and regional relationship between DOC and salinity

The inverse relationship between salinity and DOC found in estuarine and coastal environments (Barron and Duarte 2015), and in continental shelf seas (Mendoza and Zika 2014) can be used to explain regional differences (Barron and Duarte 2015).

There were strong regional differences in DOC concentrations, with higher DOC concentrations generally observed in regions of relatively low salinities e.g. in the Irish Sea and North Sea (Fig.3.6). Results from linear regression analysis of salinity and

DOC for all data and for each region separately are reported in Table 3.4. During the shelf wide campaign, the freshwater end members were not sampled and therefore I have included additional DOC and salinity data representative of fresh water end members (< 29) from Liverpool Bay, (Yamashita et al. 2011, Moschonas et al. 2015), and the River Mersey (unpublished data). The additional data were included in regressions for the eastern Irish Sea and the shelf wide SML and BML data. For the Celtic Sea and Malin-Hebrides on and off-shelf regions, data for regressions were taken from the top 250 and 200 m, respectively, to include waters that are likely to exchange across the shelf edge. For the North Sea, the SML and BML data were combined.

DOC was consistently inversely correlated with salinity across the entire shelf (slope = -18, R^2 = 0.73 and $p < 0.0001$, Fig.3.7) and within each region (Table 3.4). There was large variability in the strength of the relationship between DOC and salinity between regions as indicated here by the R^2 value. The slope ranged from -3 to -31 (Table 3.4).

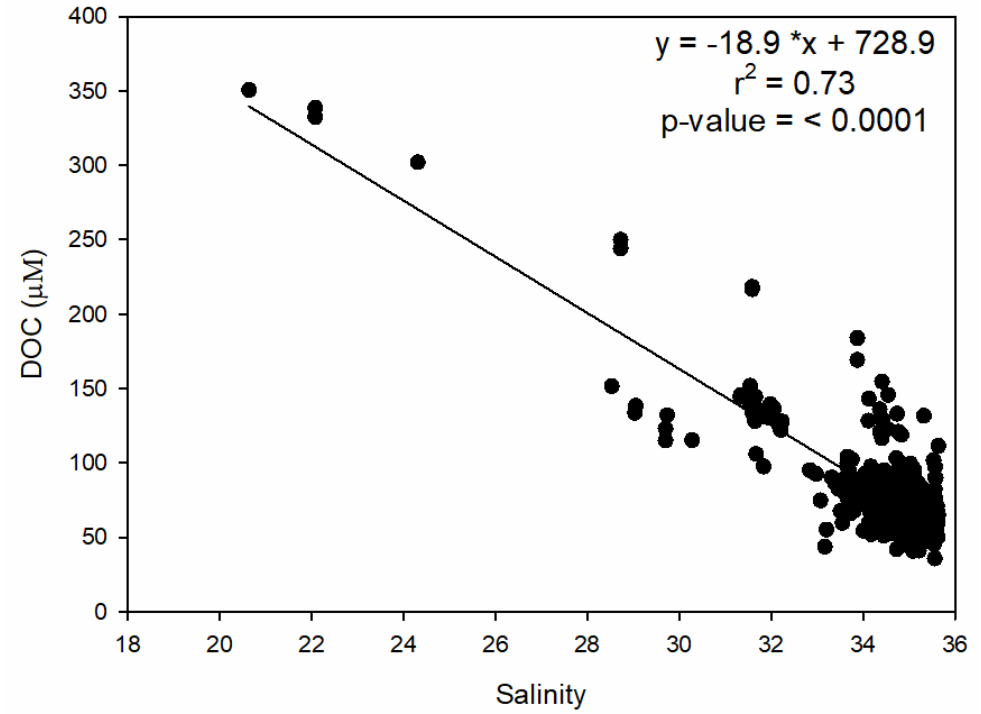

Fig.3.7. Relationship between salinity and DOC (µM) for all SML and BML samples.

Using the inverse relationship between DOC and salinity and simple linear regression, the relationship was extrapolated to zero salinity to estimate the freshwater or riverine DOC contributions. The highest riverine DOC input was into the western Irish Sea (1153 ± 384 µM) followed by the eastern Irish Sea (771 ± 44 µM), the Malin-Hebrides Shelf (561 ± 161 µM), the English Channel (477 ± 734 µM), the southern North Sea (387 ± 84 µM) and the northern North Sea (375 ± 122 µM; Table 3.4). The lowest DOC input estimated from the DOC-salinity relationship was into the Celtic Sea (166 ± 116 µM). However, these estimates should be viewed with caution as the strength of the linear relationships were often very weak ($R^2 < 0.2$) and in instances, were not statistically significant ($p > 0.05$) (Table 3.4).

Table 3.4. Results from linear regression analysis of DOC with salinity (± indicate the standard error (S.E.)). P values are highlighted in bold when relationships were statistically significant.

Region	R^2	Slope	y-Intercept	Sample Size	p - value Slope	p - value Intercept
All Data (SML and BML)	0.73	-18 ± 1	729 ± 18	523	**<0.0001**	**<0.0001**
Celtic Sea						
Surface to 250 m	0.01	-3 ± 3	166 ± 116	143	0.75	0.81
Malin-Hebrides Shelf						
Surface to 200 m	0.16	-14 ± 5	561 ± 161	53	**0.003**	**0.001**
English Channel						
Surface Only	0.01	-12 ± 21	477 ± 734	26	0.58	0.52
Irish Sea						
Western Irish Sea						
Surface Only	0.16	-31 ± 11	1153 ± 384	44	**0.008**	**0.005**
Eastern Irish Sea						
Surface Only	0.79	-20 ± 1	771 ± 44	60	**<0.0001**	**<0.0001**
North Sea						
Northern North Sea						
SML & BML Combined	0.07	-9 ± 4	375 ± 122	83	**0.015**	**0.003**
Southern North Sea						
SML & BML Combined	0.15	-9 ± 2	387 ± 84	75	**0.001**	**<0.0001**

3.3.5. Seasonal distribution of DOM during the Shelf Wide Sampling campaign

In the SML of temperate shelf seas, the seasonal variation in temperature, inorganic nutrients, specifically N+N and DOM should follow a typical and predictable pattern. This pattern is mainly driven by the seasonal heating and cooling of the water column causing periods of mixing and stratification. In parallel, N+N, which is essential for phytoplankton growth and primary production will be consumed in the presence of sufficient light, and regenerated via nitrification. In the absence of lateral transport and advection, a simplified view of this cycle is presented alongside seasonal observational data from the Celtic Sea of temperature, N+N concentrations and chlorophyll *a* (Carr et al. 2018) (Fig.3.8), and idealised DOC and DON concentrations (Fig.3.9).

During winter, the water column is cool and fully mixed and inorganic nutrient concentrations are high and vertically homogenous (Fig.3.8 a and b). DOC and DON are coupled and DOM concentrations are low (Fig.3.9) representing background concentrations of which in winter, in central shelf regions, up to a third of DOC can be of terrestrial origin and therefore considered refractory (Carr et al. 2018). As the temperature increases in spring, a thermocline develops at the onset of stratification. Inorganic nutrients are rapidly assimilated by phytoplankton during the spring bloom (Fig.3.8 a, b and c). DOM production coincides with

phytoplankton growth, resulting in an increase in both DOC and DON concentrations (Fig.3.9).

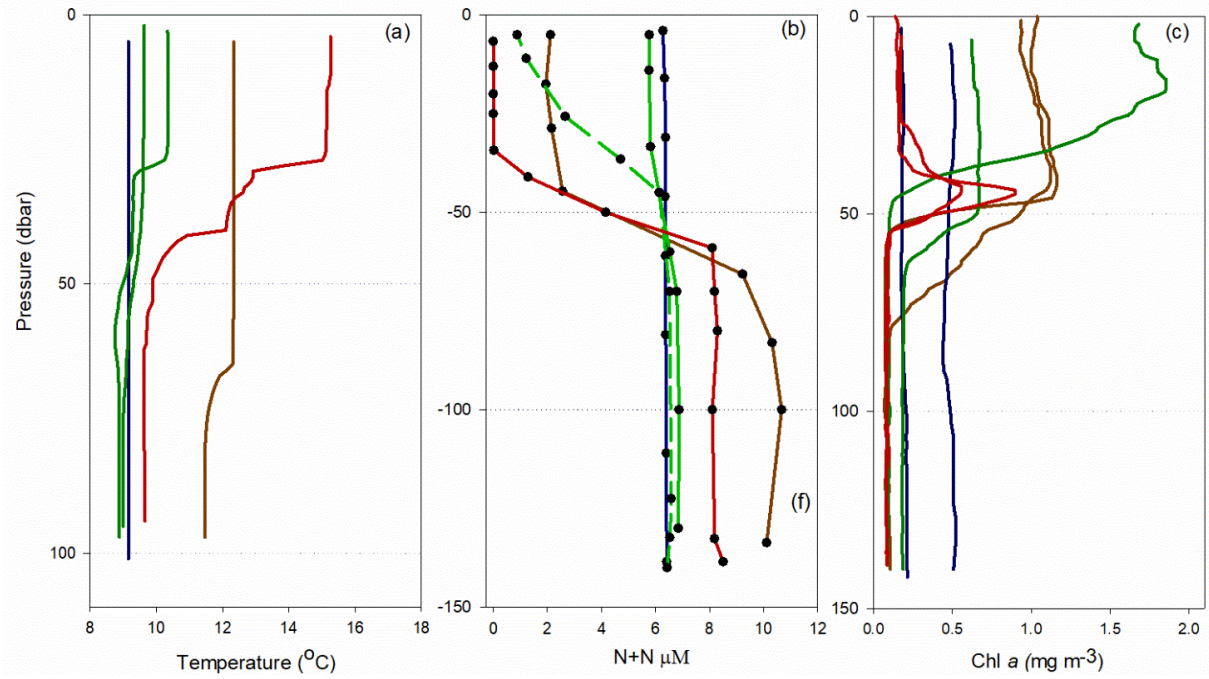

Fig.3.8. Example of a seasonal cycle of a) temperature (°C), b) N+N (µM) and c) chlorophyll *a* (mg m^{-3}), in a stratifying shelf sea. Colours indicate blue for winter, green for spring, red for summer and brown for autumn. Taken from observational data and graphs are adapted from Carr et al. 2018.

Strong stratification in summer results in a strong thermocline which limits vertical mixing and the flux of nutrients from the nutrient-rich BML to the SML. Nutrients in the SML are deplete and phytoplankton growth reduces in the SML and becomes focused in the DCM (Fig.3.8 b and c) (Hickman et al. 2012). DOM production decreases and DOC is consumed by heterotrophic bacteria while DON becomes an important source of nitrogen to microbial communities, and rapidly declines leading to a de-coupling of DOC and DON (Fig.3.9). During autumn, the water column cools and the thermocline deepens allowing phytoplankton access to inorganic

nutrients previously accumulating in the BML (Fig.3.8a, b and c). This results in an autumn phytoplankton bloom and subsequent increases in DOC and DON (Fig.3.9), however, DOC and DON remain de-coupled as DON concentrations take longer to recover from low summer values. The seasonal cycle of nutrients and DOM in regions that are permanently mixed is the same as in seasonally stratifying regions. However, the changes are not as pronounced due to the absence of water column stratification which prevents the accumulation of DOM and depletion of inorganic nutrients in the SML.

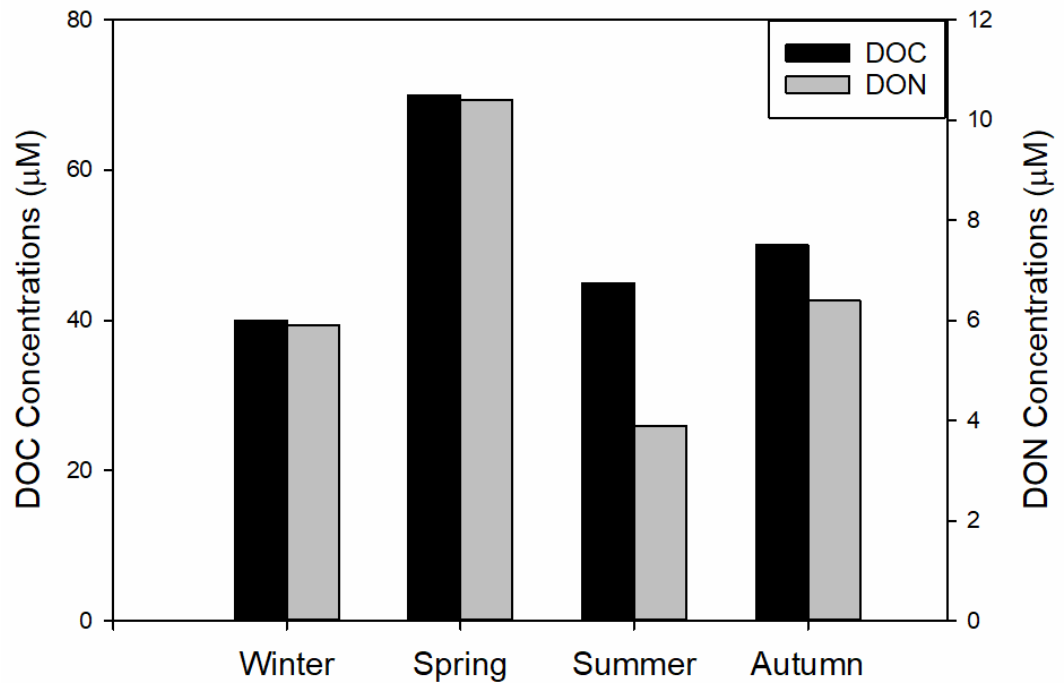

Fig.3.9. Conceptualised seasonal cycle of DOC (black) and DON (grey) distribution in a stratifying shelf sea.

DOC and DON data were not available for all seasons and all regions. Therefore, the regions were grouped according to data availability (Tables 3.10 and 3.11) and seasonality was compared to what we would expect to see as outlined in section 3.3.5. DOC and

N+N data were available in all seasons from the English Channel, the Celtic Sea (SML and BML) and Malin-Hebrides Shelf (SML) and there were DON data for each season from the Celtic Sea and Malin-Hebrides Shelf. DOC and DON data were available for spring and summer only for the eastern and western Irish Sea, allowing comparisons between these two hydrographically different regions.

3.3.5.1. Seasonality in the English Channel, Celtic Sea and Malin-Hebrides Shelf

For each region, seasonal trends in temperature, N+N, DOC and DON concentrations are illustrated using box and whisker plots. The values referred to in the text represent the mean ± standard deviation, unless stated otherwise (Table 3.5 and 3.6). Additional tables for each region detailing further statistics e.g. minimum, maximum, range and sample size are presented in the appendices.

The seasonal distribution of temperature, N+N, DOC and DON in the English Channel are shown in Figure 3.10 and Table 3.5 and 3.6**.** Additional data for DOM stoichiometry and salinity, and statistics are detailed in the appendices (Table 3). Note that there were no DON data for winter.

In the English Channel, temperatures were highest in summer (18.4 ± 0.6 °C), when surface waters were also freshest (35.0 ± 0.2), and lowest in winter (9.9, n=1 (Fig.3.10 a). There were strong seasonal gradients in N+N concentrations, which was highest in winter (6.8 μM) and relatively low in spring (0.3 ± 0.5 μM) before

increasing into summer and autumn (Fig.3.10 b). DOC and DON were uncoupled as DOC concentrations were highest in spring and lowest in winter (74.9 ± 18.6 µM and 63.3 ± 9.2 µM, respectively), and DON concentrations were highest in summer and lowest in spring (7.3 ± 0.1 µM and 5.6 ± 1.6 µM, respectively, Table 3.5). The DOM was more carbon rich in spring (13 ± 6) compared to summer (10 ± 1). While DOC in the English Channel followed a typical seasonal cycle as outlined above, DON did not, with DON being highest in summer and higher in autumn than in spring (Fig.3.10 c and d, and Table 3.6).

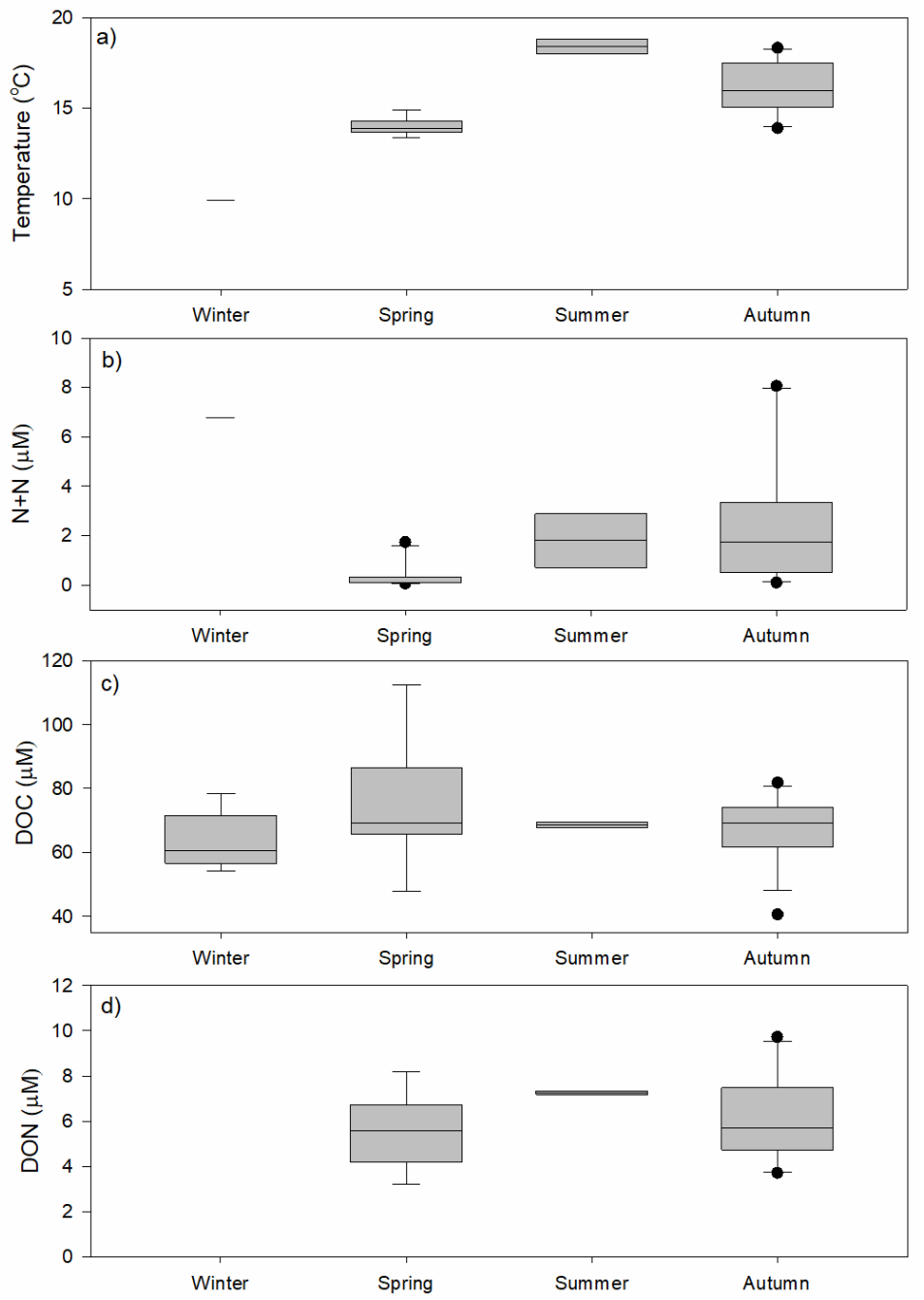

Fig.3.10. The seasonal variation in a) temperature (°C), b) N+N (µM), c) DOC (µM) and d) DON (µM) in the English Channel. The median of the data is represented by the horizontal line within the box, whiskers are the minimum (lower) and maximum (upper) values excluding outliers, and the black dots are outlying values.

The seasonal variation in temperature, N+N, DOC and DON in the SML and BML of Celtic Sea are shown in Figure 3.11 and Table 3.5 and 3.6**.** Additional data for DOM stoichiometry and salinity, and

statistics are detailed in the appendices (Table 4 (SML) and Table 5 (BML)).

In the SML of the Celtic Sea, temperature was highest in summer and lowest in winter (17 ± 0.6 °C and 10 ± 0.9 °C, respectively, Table 3.5). The mean salinity range throughout the year was small (0.2). N+N concentrations were highest in winter and lowest in summer (7.0 ± 0.9 µM and 0.2 ± 0.3 µM, respectively, Table 3.5) and followed a typical seasonal cycle (Fig.3.11 b). DOC and DON were uncoupled and DOC concentrations were highest in spring and lowest in winter (73.0 ± 12.5 µM and 67.3 ± 9.7 µM, respectively, Table 3.6), while DON concentrations were highest in autumn and lowest in spring (5.3 ± 1.3 µM and 4.3 ± 1.2 µM, respectively, Table 3.6). Similarly to the English Channel, DOM was more carbon rich in spring (18 ± 5) compared to winter (13 ± 3). The seasonal DOC distribution in the SML of the Celtic Sea generally followed a typical cycle but DON did not as DON was highest in summer and higher in autumn than in spring (Fig.3.11 c and d).

In the BML of the Celtic Sea, temperature varied from 9.7 ± 0.7 °C in winter to 11.5 ± 0.5 °C in autumn (Table 3.5). The mean salinity range throughout the year was small (0.2). N+N concentrations were highest in autumn (9.5 ± 0.8 µM) when the water column was stratified, and lowest in winter (7.2 ± 1.0 µM) when the water column was mixed (Table 3.5) However, whole water column dissolved inorganic nitrogen (DIN) inventories in winter and autumn were similar (Davis et al. 2018). In contrast to the SML, DOC

in the BML was highest in winter and lowest in autumn (69.4 ± 9.9 µM and 64.3 ± 6.4 µM, respectively, Table 3.6). DON was highest in summer, and lowest in spring and autumn (5.1 ± 2.1 µM and 4.4 ± 1.0, 1.4 µM, respectively, Table 3.6). Similarly to the SML, DOM was more carbon rich in spring relative to winter (17 ± 4 and 13 ± 2, respectively, Table 3.6).

Temperature differences between the SML and BML ranged from 0.62 °C in winter when the water column was mixed to a maximum of 6.23 °C in summer when the water column was strongly stratified. Salinity in the SML and BML ranged from 35.1 to 35.6, with the lowest minimum value of 33.2 occurring in the SML in autumn (Table 3.5). DOC and DON were generally lower in the BML than the SML, and N+N was higher in the BML (Fig.3.11 b, c and d).

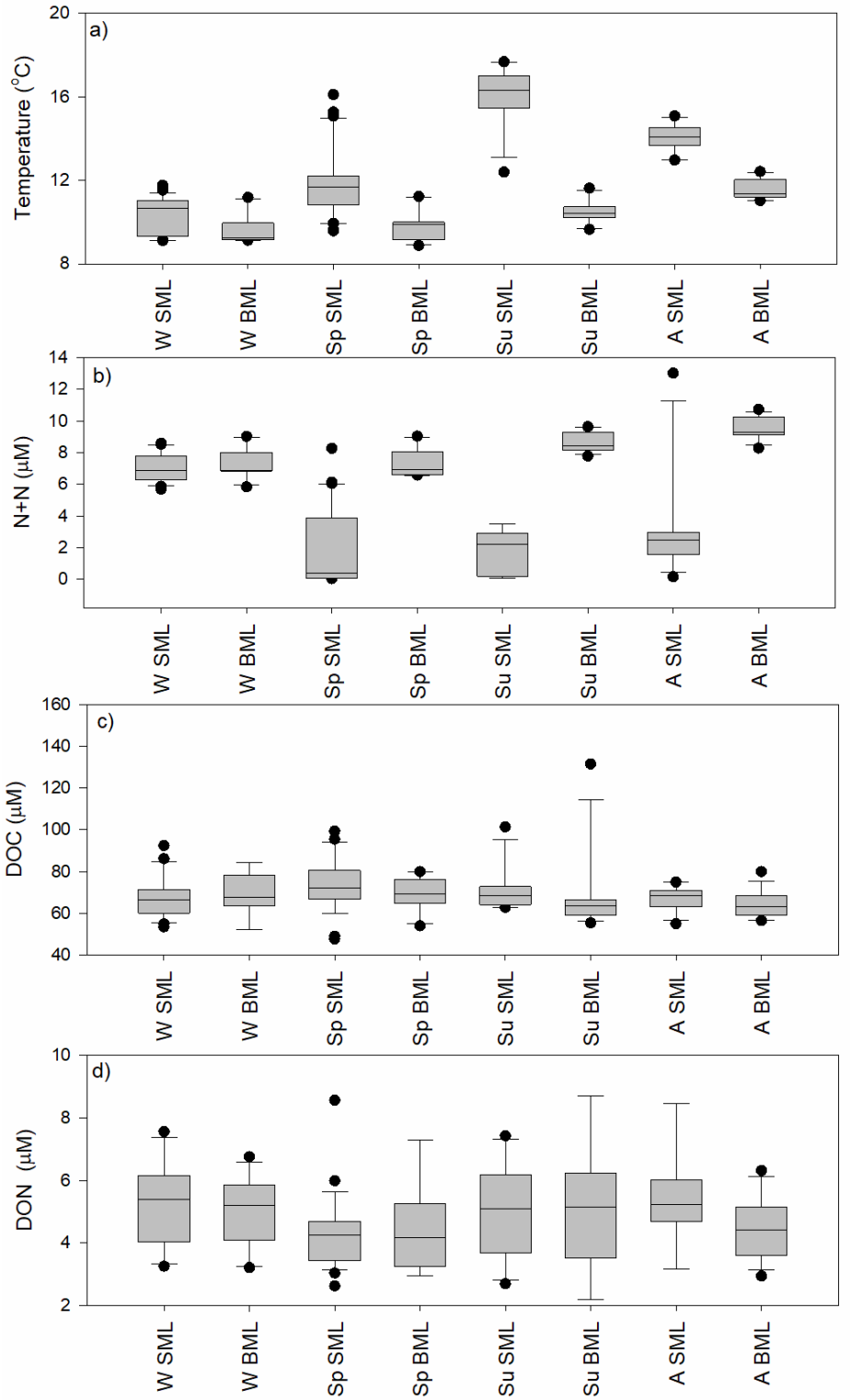

Fig.3.11. The seasonal variation in winter (W), spring (Sp), summer (Su) and autumn (A) in a) temperature (°C), b) N+N (µM), c) DOC (µM) and d) DON (µM) in the on-shelf Celtic Sea (SML and BML) region. The median of the data is represented by the horizontal line within the box, whiskers are the minimum (lower) and maximum (upper) values excluding outliers, and the black dots are outlying values.

The seasonal variation in temperature, N+N, DOC and DON in the Malin-Hebrides on-shelf region are shown in Figure 3.12 and Table 3.5 and 3.6**.** Additional data for DOM stoichiometry and salinity, and statistics are detailed in the appendices (Table 6). Note that there were no DON data for autumn.

In the SML of the Malin-Hebrides on-shelf region, temperatures were highest in summer and lowest in spring (15 ± 0.4 °C and 9 ± 0.6 °C, respectively, Table 3.5). The mean salinity range throughout the year was small (0.1). N+N concentrations were highest in winter and lowest in summer (10.1 ± 1.6 µM and 0.6 ± 0.4 µM, respectively, Table 3.5), following the typical seasonal cycle. DOC concentrations were highest in autumn (66.6 ± 9.5 µM) and DON highest in summer (4.8 ± 1.6 µM). DOC and DON concentrations were lowest in spring (54.5 ± 4.4 µM and 3.5 ± 0.6 µM, respectively, Table 3.6). The DOM pool was more carbon rich in autumn (18) relative to summer (14 ± 3) (Table 3.6). Vertical gradients in temperature were small when the water column was sampled in spring and autumn (0.2 and 0.4 °C, respectively) suggesting that the water column was mixed or weakly stratified when sampled. Minima in salinity were also observed during spring and autumn (34.8 and 34.7, respectively). DOC and DON distribution in the SML of the Malin-Hebrides Shelf did not follow a typical seasonal cycle and although DOC and DON were coupled in spring, DOC was highest in autumn and DON highest in summer (Fig.3.12 c and d).

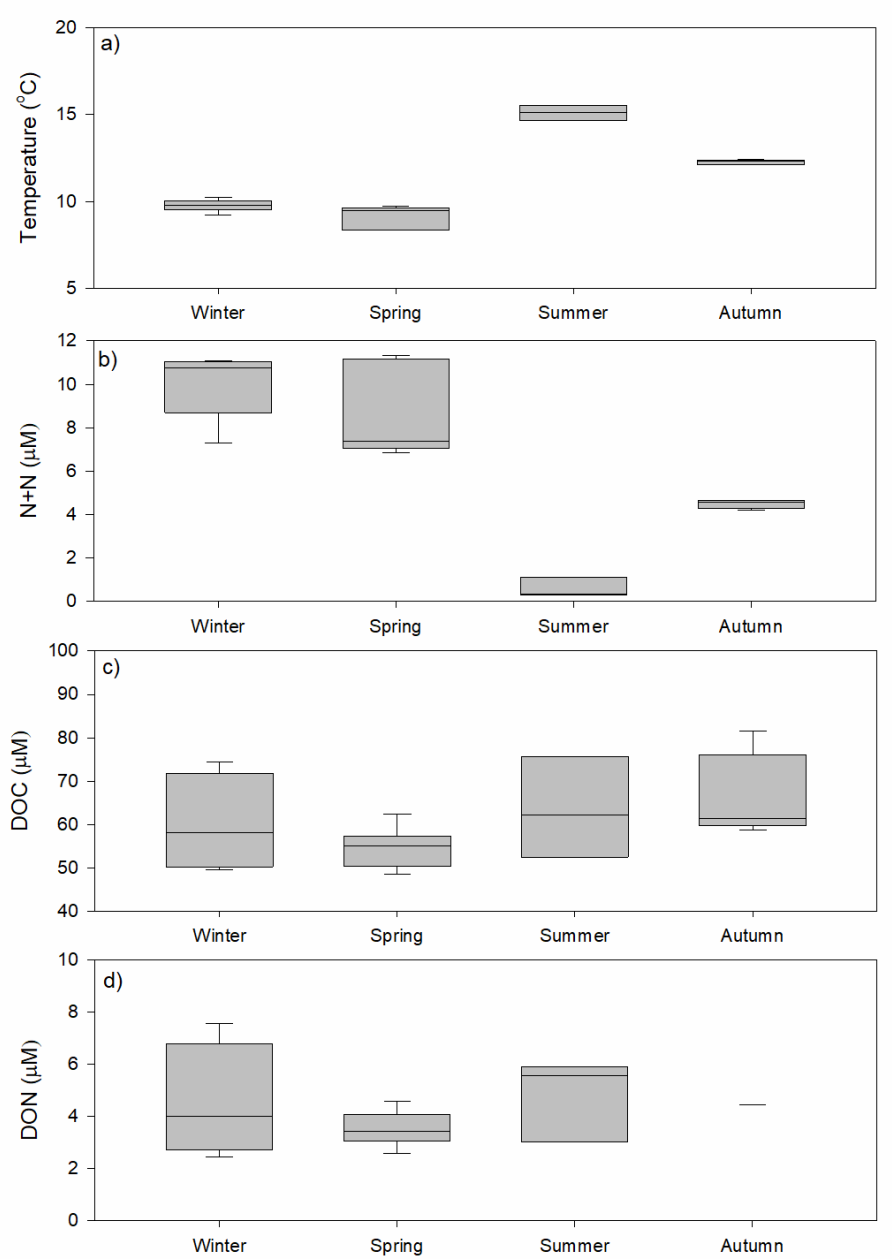

Fig.3.12. The seasonal variation in a) temperature (°C), b) N+N (µM), c) DOC (µM) and d) DON (µM) in the SML of the Malin-Hebrides Shelf. The median of the data is represented by the horizontal line within the box, whiskers are the minimum (lower) and maximum (upper) values excluding outliers.

3.3.5.2. Comparison between the eastern and western Irish Sea in spring and summer

The variation in temperature, N+N, DOC and DON are shown in Figure 3.13 and Table 3.5 and 3.6**.** Additional data for DOM

stoichiometry and salinity, and statistics are detailed in the appendices (Table 7 and 8).

Surface waters were cooler and fresher in the eastern (10.1 ± 2 °C and 33.7) and western (10.0 ± 1 °C and 34.3) Irish Sea in spring compared to summer (16.5 ± 0.4 °C and 34.0 and 14.9 ± 1 °C and 34.4, respectively, Table 3.5). N+N concentrations were higher in spring in the eastern and western Irish Sea (4.9 ± 4.7 μM and 6.4 ± 4.0 μM, respectively) and lower in summer (0.3 ± 0.2 and 2.3 ± 1.5 μM, respectively, Table 3.5).

In contrast, DOC and DON concentrations were higher in summer in the eastern (89.9 ± 3.4 μM and 8.1 ± 1.7 μM, respectively) and western Irish Sea (89.6 ± 27.1 μM and 6.5 ± 1.3 μM, respectively, Table 3.6), compared to spring when DOC and DON were lower in the eastern and western Irish Sea (75.8 ± 9.9 μM and 5.4 ± 1.7 μM, and 73.3 ± 10.5 μM and 4.4 ± 2.3 μM, respectively, Table 3.6). DOM was more carbon rich in spring in the eastern and western Irish Sea (15 ± 3 and 20 ± 8) compared to summer (11 ± 2 and 14 ± 4, respectively), and DOM was more carbon rich in the western Irish Sea compared to the eastern Irish Sea (Table 3.6).

Seasonal variation in nutrients and DOM in the eastern and western Irish Sea regions were similar in spring and summer (Fig.3.13 b, c and d), despite having distinctly different hydrographic regimes (Fig.3.13 a and d). A strong west to east gradient in salinity (Fig.3.14) was observed and was more pronounced in spring when

salinity in the eastern Irish Sea was 0.6 lower than in the west, and temperature in summer was up to 4.6 ºC higher than in the west (Table 3.5 and Fig.3.13 a and d).

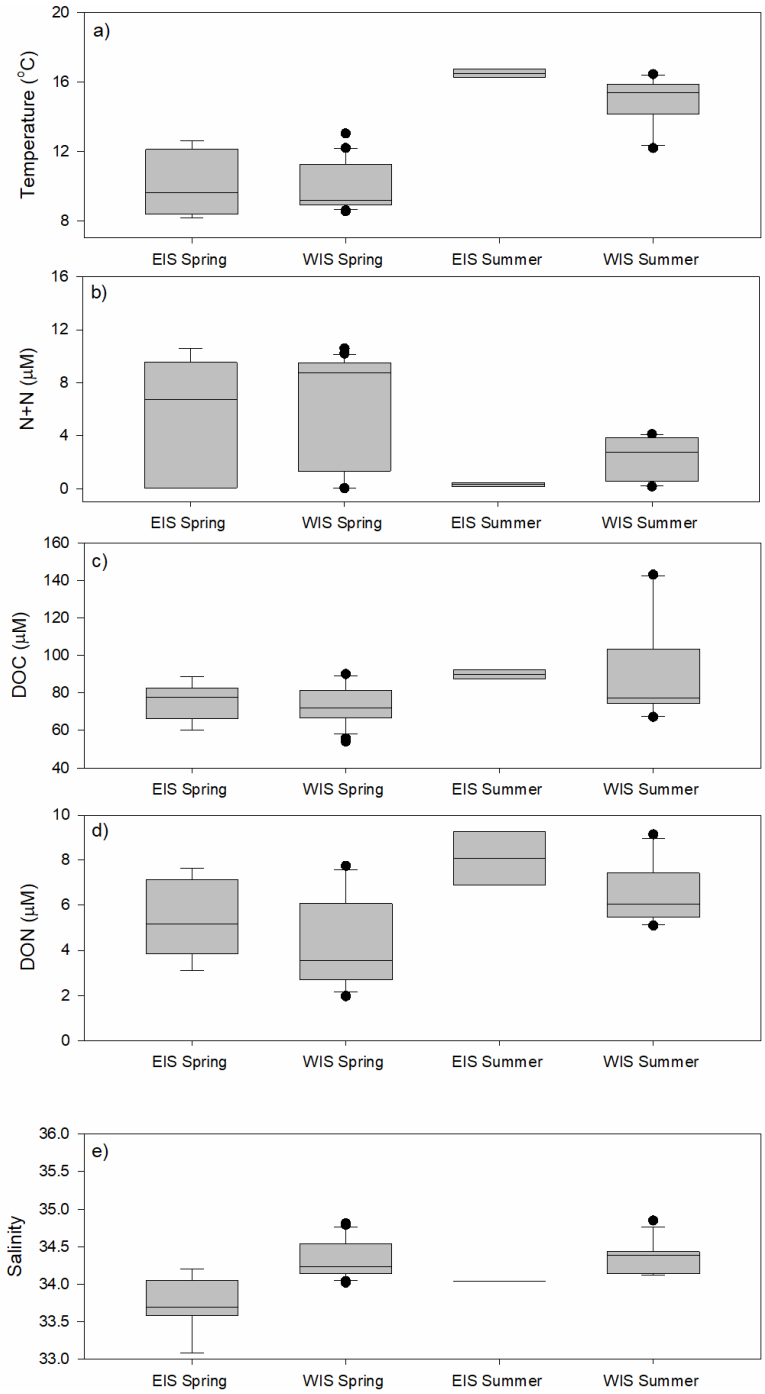

Fig.3.13. Spring and summer variation in temperature (°C), N+N (µM), DOC (µM), DON (µM) and salinity in the eastern (EIS) and western (WIS) Irish Sea. The median of the data is represented by the horizontal line within the box, whiskers are the minimum (lower) and maximum (upper) values excluding outliers, and the black dots are outlying values.

The western Irish Sea is influenced by the Irish rivers, the Boyne and Liffey, and the more saline waters of the northward flowing Celtic Sea (Moschonas et al. 2015). While the eastern Irish Sea is influenced by freshwater inflow from English rivers through Liverpool Bay, including rivers Mersey, Dee and Ribble (Greenwood et al. 2011), with limited exchange between the two regions (Gowen et al. 2002, Moschonas et al. 2015).

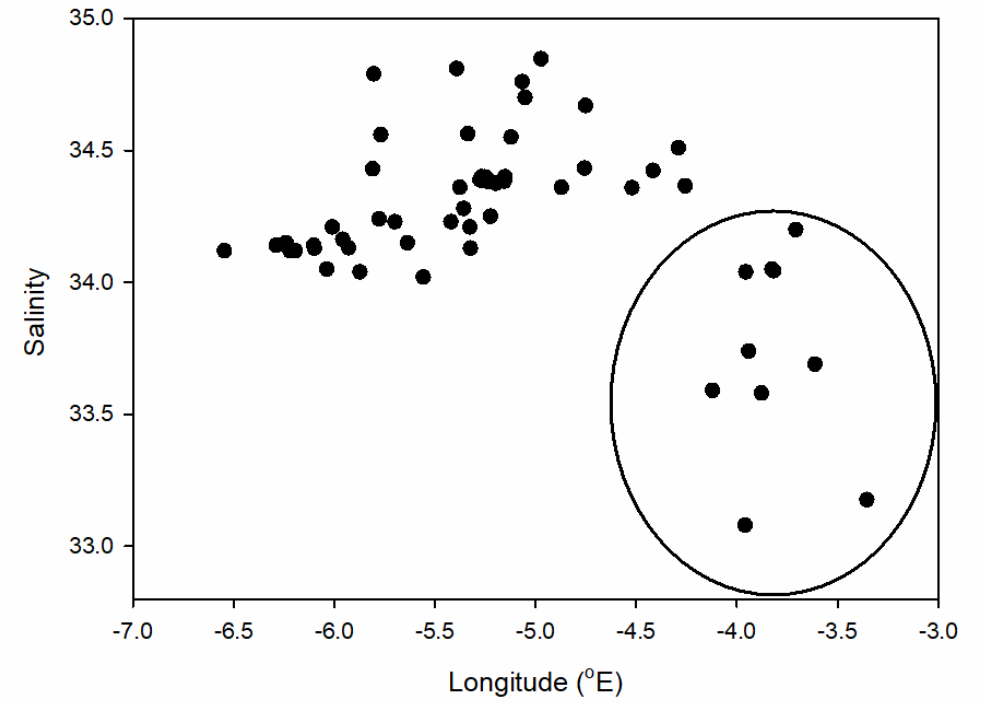

Fig.3.14. Distribution of salinity in the Irish Sea along a west to east transect. Stations in the eastern Irish Sea with lower salinities are circled.

Table 3.5. Seasonal means ± std dev in temperature (Temp °C), salinity and N+N (µM) concentrations. Sample size is indicated below each mean. Red colour indicates in which season N+N concentrations were maximum and blue when they were minimum for each region. X symbol indicates no data.

Region	Temp (°C) Winter	Spring	Summer	Autumn	Salinity Winter	Spring	Summer	Autumn	N+N (µM) Winter	Spring	Summer	Autumn
Section 3.3.5.												
English Channel	9.9 1	14.0 ± 0.5 8	18.4 ± 0.6 2	16.2 ± 1.5 10	35.2 ± 0.0 5	35.2 ± 0.0 8	35.0 ± 0.2 2	35.2 ± 0.1 11	**6.8** 1	**0.3 ± 0.5** 10	1.8 ± 1.5 2	2.6 ± 2.8 12
Celtic Sea (On-shelf SML)	10.3 ± 0.9 23	11.8 ± 1.6 31	16.7 ± 0.6 11	13.9 ± 0.7 14	35.2 ± 0.2 22	35.2 ± 0.2 31	35.3 ± 0.2 11	35.1 ± 0.7 14	**7.0 ± 0.9** 21	1.8 ± 2.5 31	**0.8 ± 1.1** 3	3.1 ± 3.0 14
Celtic Sea (On-shelf BML)	9.7 ± 0.7 11	9.9 ± 0.7 11	10.5 ± 0.6 12	11.5 ± 0.5 14	35.3 ± 0.2 11	35.3 ± 0.2 11	35.4 ± 0.1 12	35.5 ± 0.1 14	**7.2 ± 1.0** 11	7.4 ± 0.9 11	8.6 ± 0.6 12	**9.5 ± 0.7** 13
Malin-Hebrides (On-shelf SML)	9.8 ± 0.4 5	9.1 ± 0.6 9	15.1 ± 0.4 3	12.3 ± 0.1 5	35.3 ± 0.2 3	35.1 ± 0.3 9	35.1 ± 0.1 3	35.2 ± 0.3 5	**10.5 ± 1.6** 5	8.5 ± 2 9	**0.6 ± 0.4** 3	4.5 ± 0.2 5
Western Irish Sea	X	10.0 ± 1.4 28	14.9 ± 1.4 12	14.1 ± 0.0 7	X	34.3 ± 0.2 28	34.4 ± 0.2 12	34.4 ± 0.0 7	X	**6.4 ± 4** 26	**2.3 ± 1.5** 12	4.1 ± 0.1 5
Eastern Irish Sea	X	10.1 ± 1.9 7	16.5 ± 0.4 2	12.8 1	X	33.7 ± 0.4 7	34.0 ± 0.0 2	33.2 1	X	**4.9 ± 4.7** 7	**0.3 ± 0.2** 2	20.8 1
Chapter 4												
Northern North Sea (SML)	6.8 1	10.9 ± 2.9 23	14.5 ± 1.3 35	X	34.0 ± 0.2 4	34.4 ± 0.5 23	34.6 ± 0.6 35	X	X	**2.5 ± 2.8** 24	**0.3 ± 0.4** 35	X
Northern North Sea (BML)	X	X	9.3 ± 2.3 31	X	X	X	35.0 ± 0.3 31	X	X	X	6.5 ± 4.7 30	X
Southern North Sea (SML)	X	13.1 ± 2.4 27	16.9 ± 2.1 19	13.9 ± 0.4 2	33.8 ± 1.7 15	34.6 ± 0.4 27	34.5 ± 0.4 19	34.8 ± 0.1 2	X	3.7 ± 8.9 44	**0.5 ± 0.8** 19	**5.1 ± 2.8** 6
Malin-Hebrides (On-shelf BML)	X	8.9 ± 0.9 2	X	11.9 ± 0.8 5	X	35.2 ± 0.4 2	X	35.2 ± 0.2 5	X	**8.4 ± 1.5** 2	X	**7.6 ± 3.1** 5
Malin-Hebrides (Off-shelf SML)	9.9 ± 0.1 11	9.8 ± 0.0 5	X	12.0 ± 0.5 8	35.4 ± 0.0 11	35.4 ± 0.0 5	X	35.4 ± 0.0 8	10.6 ± 0.4 11	**10.9 ± 0.2** 5	X	**4.9 ± 1.3** 8
Malin-Hebrides (Off-shelf BML)	8.4 ± 2.5 5	7.7 ± 1.3 4	X	6.1 ± 2.8 7	35.3 ± 0.2 5	35.3 ± 0.1 4	X	35.1 ± 02 7	**13.5 ± 3.3** 5	16.0 ± 3.7 4	X	**18.1 ± 2.5** 7
Celtic Sea (Off-shelf SML)	X	11.6 ± 0.4 8	16.4 ± 0.6 9	14.4 ± 0.4 6	X	35.6 ± 0.1 8	35.6 ± 0.0 9	35.6 ± 0.0 6	X	**6.3 ± 2.1** 8	**0.9 ± 0.9** 8	2.2 ± 0.9 5
Celtic Sea (Off-shelf BML)	X	7.9 ± 3.1 13	7.3 ± 3.5 11	7.7 ± 3.5 8	X	35.4 ± 0.2 13	35.3 ± 0.3 11	35.4 ± 0.3 8	X	**14.7 ± 4.8** 13	**15.5 ± 3.5** 11	15.0 ± 3.9 7

Table 3.6. Seasonal means ± std dev in DOC (µM), DON (µM) and DOM stoichiometry (ratio of DOC to DON). Sample size is indicated below each mean. Red colour indicates in which season DOC and DON concentrations were maximum and blue when they were minimum for each region. X symbol indicates no data.

	DOC (µM)				DON (µM)				DOC:DON			
Region	**Winter**	**Spring**	**Summer**	**Autumn**	**Winter**	**Spring**	**Summer**	**Autumn**	**Winter**	**Spring**	**Summer**	**Autumn**
Section 3.3.5												
English Channel	**63 ± 9**	**75 ± 19**	69 ± 1	67 ± 11	X	**5.6 ± 1.6**	**7.3 ± 0.1**	6.1 ± 1.9	X	13 ± 6	10 ± 0	12 ± 4
	5	9	2	13		9	2	11		8	2	11
Celtic Sea (On-shelf SML)	**67 ± 10**	**73 ± 13**	70 ± 11	69 ± 8	5.2 ± 1.3	**4.3 ± 1.2**	5.1 ± 1.7	**5.3 ± 1.3**	13 ± 3	18 ± 5	16 ± 6	14 ± 4
	21	29	11	14	11	26	9	12	9	26	9	12
Celtic Sea (On-shelf BML)	69 ± 10	69 ± 7	**69 ± 20**	**64 ± 6**	5.0 ± 1.1	**4.4 ± 1.4**	**5.1 ± 2.1**	4.4 ± 1	13 ± 2	17 ± 4	17 ± 6	15 ± 3
	9	10	12	14	11	9	6	13	9	9	6	13
Malin-Hebrides (On-shelf SML)	60 ± 11	**55 ± 4**	64 ± 12	**67 ± 10**	4.5 ± 2.2	**3.5 ± 0.6**	**4.8 ± 1.6**	4.5	15 ± 6	16 ± 3	14 ± 3	18
	4	9	3	5	4	8	3	1	4	8	3	1
Western Irish Sea	X	**73 ± 11**	**90 ± 27**	76 ± 6	X	**4.4 ± 2.3**	**6.5 ± 1.3**	5.0 ± 1.1	X	20 ± 8	14 ± 4	16 ± 3
		27	10	7		23	10	3		23	10	3
Eastern Irish Sea	X	76 ± 10	**90 ± 3**	**44**	X	**5.4 ± 1.7**	**8.1 ± 1.7**	X	X	15 ± 3	11 ± 2	X
		7	2	1		7	2			7	2	
Chapter 4												
Northern North Sea (SML)	74 ± 6	**73 ± 16**	**75 ± 20**	X	X	**5.5 ± 1.5**	**4.2 ± 1.4**	X	X	14 ± 3	20 ± 6	X
	3	24	33			22	27			22	25	
Northern North Sea (BML)	X	X	**67 ± 16**	X	X	X	3.8 ± 1.5	X	X	X	19 ± 7	X
			24				19				17	
Southern North Sea (SML)	81 ± 22	**87 ± 23**	79 ± 15	**72 ± 8**	X	**5.3 ± 1.7**	**5.9 ± 2.1**	5.7 ± 1	X	19 ± 11	16 ± 9	13 ± 3
	14	46	19	6		38	15	5		38	15	5
Malin-Hebrides (On-shelf BML)	X	**55 ± 4**	X	**63 ± 6**	X	**3.6 ± 0.6**	X	**3.5 ± 0.02**	X	16 ± 1	X	18 ± 1
		2		5		2		2		2		2
Malin-Hebrides (Off-shelf SML)	57 ± 4	**56 ± 8**	X	**60 ± 5**	**3.9 ± 1.4**	3.9 ± 0.5	X	**3.6 ± 0.9**	16 ± 7	16 ± 4	X	19 ± 5
	10	5		8	11	3		3	10	3		3
Malin-Hebrides (Off-shelf BML)	**48 ± 3**	**57 ± 9**	X	53 ± 6	2.9	**2.8 ± 0.2**	X	**3.1 ± 0.8**	12 ± 3	15 ± 5	X	18 ± 6
	5	4		7	1	2		**4**	4	4		4
Celtic Sea (Off-shelf SML)	X	**61 ± 7**	**71 ± 20**	65 ± 3	X	4.7 ± 0.9	**4.2 ± 1.9**	**5.0 ± 1.2**	X	14 ± 4	22 ± 12	14 ± 4
		7	9	4		8	7	4		7	7	4
Celtic Sea (Off-shelf BML)	X	**52 ± 8**	**56 ± 16**	55 ± 6	X	**3.4 ± 1.1**	**3.2 ± 0.5**	**3.2 ± 0.5**	X	19 ± 8	15 ± 5	15 ± 4
		13	11	7		4	6	4		4	9	5

3.4. Discussion

3.4.1. Shelf Wide variability

Overall, sea surface temperatures were coolest in winter and warmest in summer following a typical temperate seasonal cooling and heating cycle. The coolest waters were observed in the SML of the northern North Sea (6.8 °C) which was 3 °C lower than other wintertime SSTs (Table 3.5). The English Channel was between 2 and 4 °C warmer than other regions in summertime (Table 3.5). Overall, surface salinity was lowest in winter with the freshest water observed in the southern North Sea (33.8), a region that receives a significant amount of riverine fresh water (Thomas et al. 2005). Seasonal maxima were region dependent (Table 3.5). In surface waters, N+N concentrations were typically highest in winter and lowest in spring and summer as they were consumed by phytoplankton during primary production. DOC and DON concentrations in surface waters were highest in summer however, there was large regional and seasonal variability (Table 3.6).

To disentangle the overall shelf wide DOM distribution trends, the factors driving their distribution are considered and include, the interplay between seasonality and how the regions compare with the conceptual seasonal DOM cycle, and finally how DOM varies between two regions with different hydrographical regimes.

3.4.2. Factors driving shelf wide DOM distribution

There was clear regional variation in DOM across the Northwest European Shelf and adjacent North Atlantic waters during the 12 to 18 month sampling period. Across the shelf, DOC and DON concentrations varied by ~ 30% and 50%, respectively. DOM concentrations were higher in the regional seas closest to land affected by external inputs of terrestrial DOM supplied to the coasts by rivers, in particular the southern North Sea where the highest DOC concentration (169.8 µM) was measured, and both the western and the eastern Irish Sea, a region of fresh water influence, where the highest DON concentration (9.7 µM) was measured. The strong shelf wide inverse relationship between DOC and salinity was a further indication of the importance of terrigenous inputs of organic matter to shelf seas. DOC and DON concentrations in the off-shelf regions of the Celtic Sea and Malin-Hebrides Shelf were significantly lower (Mann-Whitney, $p < 0.001$) and typical of oceanic values, particularly in the BML of the off-shelf Celtic Sea where the lowest DOC concentration (36 µM) was measured. In the on-shelf waters of these regions DOC and DON had intermediate values (DOC between 59 ± 2.0 µM and 70 ± 1.3 µM, and DON between 3.5 ± 0.2 µM and 4.8 ± 0.2 µM) (Fig.3.6) reflecting the mixing of high DOM inputs from the coastal zone with oceanic waters of lower DOM.

Superimposed on this broad scale pattern of decreasing DOM with increasing distance from land and increasing salinity is local variability in hydrography, nutrient regime, in situ DOM production

and consumption. Similar to other studies, no apparent trends between DOM and temperature were identified (Chaichana et al. in review). However, low concentrations of inorganic nutrients (N+N) were observed in instances when DOC and DON concentrations were high. This was evident in the permanently mixed southern North Sea which is known to be a particularly productive region that fixes up to 3.5 times more carbon annually than the northern North Sea (Emeis et al. 2015), and is a region which was a net source of CO_2 to the atmosphere during the sampling period due to thermally driven increases in pCO_2, unlike the northern region which was a net sink (Hartman et al. 2018).

While data were available regarding riverine inorganic nutrient and DON inputs in our study regions and the Northwest European Shelf as a whole (Artioli et al. 2008, Liu et al. 2010), estimates of riverine DOC inputs in many of the regions are noticeably lacking (Liu et al. 2010), making it difficult to determine any long-term changes in DOC entering the coastal and shelf sea region. However, extensive studies show that for the North Sea, in particular, effective nutrient reduction policies have led to a 20% reduction of inorganic nitrogen since the 1990's (Artioli et al. 2008), the reduction in riverine nutrient inputs has recently been linked to declining levels of primary production in this region (Capuzzo et al. 2018). A general trend of decreasing DON concentrations has also been observed in the North Sea (Suratman et al. 2008, Chaichana et al. in review), which could also be linked to reduced riverine inputs (see Chapter 4).

From this large and unique data set I was able to map the general distribution of DOM across the Northwest European Shelf, and identify regions of relatively higher and lower DOM. To further explore the local and regional controls on the patterns observed, next I will focus on regional trends, seasonality and contrasting hydrographical regimes.

3.4.2.1. Seasonality in the English Channel, Celtic Sea and Malin-Hebrides Shelf

There is a paucity of data on the DOM distribution in the English Channel. Early studies report DON values of 4.6 µM and DOC between 43 to 95 µM (Banoub and Williams 1973), which are comparable with more recent measurements of DOC of 42 to 225 µM (Bodineau et al. 1999), and to this study as DON ranged from 3.2 to 9.7 µM and DOC from 41 to 112 µM.

Model studies of DOM production in the English Channel at the long-term monitoring station, E1 estimate a 34 µM increase in DOC and ~ 2 µM increase in DON during spring (Anderson and Williams 1998), with DON displaying greater variability than DOC (Banoub and Williams 1973). A typical seasonal cycle (refer to section 3.3.5) of DOC in the English Channel was observed and there was a mean increase of 12 µM between winter and spring when DOC concentrations were greatest (Table 3.6). However, DON did not follow a typical seasonal cycle as DON was lowest in spring (in the absence of winter DON data). This could be due to the

utilisation of DON as a nitrogen source as N+N was depleted in spring (0.3 ± 0.5 µM) after consumption during spring bloom development.

The English Channel is a region that receives DOM inputs from surrounding rivers including rivers Exe, Tamar, Seine and Somme. Estimates of DOC riverine inputs from the Seine, which accounts for up to 46% of total freshwater inputs (Borges and Frankignoulle 2003), are the order of magnitude of 0.5 Tg C yr^{-1}, which would make estimates of total freshwater DOC inputs to be ~ 1.1 Tg C yr^{-1}. Furthermore, elevated POC concentrations in bottom waters are attributed to terrigenous inputs which account for between 20 to 50% of total POC (Bodineau et al. 1999). To my knowledge there is no carbon budget for the English Channel, however annual fluxes of DOC in the English Channel have been estimated to be 6.5 Tg C yr^{-1} (Bodineau et al. 1999). An inverse relationship between salinity and DOC in the English Channel was observed, however, it was very weak and not significant (Table 3.4), indicating considerable variation from a simple mixing line. This is likely due to variability in internal processes such as in situ DOM production and consumption in the English Channel, which is a region of high primary productivity, complex frontal structures such as the Ushant front which separates waters of the north eastern and south eastern region, and variability in the spatial and seasonal distribution of dissolved inorganic carbon (Borges and Frankignoulle 2003).

The Celtic Sea and Malin-Hebrides Shelf are influenced by waters originating from the North Atlantic and connected by a northward flowing slope current which extends to the North Sea (Pingree et al. 1999). Ranges in DOC in the Celtic Sea are variable. Previous studies have shown that DOC concentrations range from 45 to 90 μM in the shelf break region (Hydes et al. 2001) and 58 and 80 μM for on-shelf waters, while DON concentrations on the Malin-Hebrides Shelf range from 1.1 to 3.7 μM (Moschonas et al. 2015). In this study, the ranges in DOC and DON for the Celtic Sea (from 47.7 to 101.4 μM and from 2.6 to 8.6 μM, respectively) and Malin-Hebrides Shelf (from 48.6 to 81.5 μM and from 2.5 to 7.6 μM, respectively) were comparable to previous observations. Mean DOC concentrations were higher in the Celtic Sea compared to the Malin-Hebrides Shelf, and DOC and DON were typically higher on-shelf compared to off-shelf in both regions (Table 3.3).

There is little data on DOM seasonality in the Celtic Sea, or indeed the Malin-Hebrides Shelf. However, recent studies within the SSB programme show that DOM dominates the organic matter pool and is typically higher in the SML than the BML (Davis et al. 2018). In general, DOC in the Celtic Sea followed a typical seasonal production cycle and increased in spring during phytoplankton bloom events (Davis et al. 2018). However, DON was decoupled from DOC and was highest in autumn. In a similar manner to the English Channel, DON may have been utilised as a nitrogen source in

nutrient limiting conditions and behaved similarly in a mixed and seasonally stratifying region.

In contrast, DOC and DON were coupled in the SML of the Malin-Hebrides Shelf. However, they were both lowest in spring contrary to the typical seasonal cycle. This could be due to a late on-set of the spring bloom as the temperature differences between SML and BML were small in spring indicating that the water column was not stratified, furthermore, surface water temperatures were similar to winter temperatures (9.1 °C), and surface N+N concentrations were high (Table 3.5). Alternatively, sampling may not have captured spring hydrographical and DOM dynamics that represent this season over the sampling period. There is up to 10 degrees of latitudinal difference (~ 1111 km) between northern stations in the Malin-Hebrides Shelf and southern stations in the Celtic Sea, resulting in warming to the south before the north and thus a potential lag in onset of stratification. In addition, the timing of the onset of the spring bloom here is uncertain. In the Celtic Sea, bloom conditions were observed from the second week of April (Davis et al. 2018), and as all of the samples collected in spring (April to June) in the Malin-Hebrides Shelf were collected during the first week in April, it is most likely that sampling did not capture DOM production resulting from a spring bloom event.

Similarly to the English Channel, the inverse relationship between salinity and DOC in the Celtic Sea was weak and not significant, although this relationship has been shown to change

seasonally (Carr et al. 2018). In contrast and although weak, the relationship in the Malin-Hebrides Shelf was significant (Table 3.4). Regression of this relationship to zero salinity puts estimates of DOC inputs from freshwater sources in the Malin-Hebrides Shelf at 561 ± 161 µM, which is over 100 µM higher than global estimates as reported by (465.7 ±11.6 µM) (Barron and Duarte 2015) but well within the global range (~100 to 2500 µM). Once again, this estimate should be viewed with caution as the relationship was weak and there was considerable variability from a simple 1:1 mixing line.

To my knowledge, no published data were available on the magnitude of total freshwater DOC inputs to the Malin-Hebrides Shelf. However, there are considerable freshwater inputs from a number of sea-lochs, chiefly the Firth of Lorne (ICES 2008) to the western coast of Scotland. There are also freshwater inputs to the west coast of Ireland from the Irish river, the Shannon, and also from the river Severn and Loire (Nolan and Lyons 2006).

3.4.2.2. Comparison of the eastern and western Irish Sea

In comparison to other regional studies, DOC and DON in the Irish Sea ranges from 75 to 127 µM and from 2.2 to 5.8 µM, respectively, with higher DOC values recorded in the eastern Irish Sea and Liverpool Bay, a region of freshwater influence. Exchange between the eastern and western Irish Sea is limited as well as little influence of oceanic N inputs to the western Irish Sea (Moschonas et al. 2015). Riverine DOC inputs are in the order of 1 to 2 Tg yr^{-1} and

export from the Irish Sea to the North Channel is estimated at between 2.5 and 5 Tg yr^{-1} (Bowers et al. 2013).

Overall, DOM observations in this study are comparable with previous measurements, although DON was higher and maximum concentrations of 11.3 µM were recorded in the western Irish Sea (Table 3.3). DON concentrations were also higher in the eastern Irish Sea by between 19 and 20% in spring and summer, respectively, and DOC higher in the eastern Irish Sea by 4% in spring. DOC was similar in both regions and highest in summer, and greater by 32 µM in the western Irish Sea in autumn. However, the difference in autumn was driven by a single low data point for the eastern Irish Sea (Table 3.6). Inorganic nutrients were nearly an order of magnitude greater in the western Irish Sea during summer (2.3 µM) compared to the eastern Irish Sea (0.3 µM), while salinity was lower by 0.3 and temperature higher by 2.5°C. Similarities in DOC concentrations in summer between these two hydrographically different regions could be due to similar production and removal rates as well as comparable inputs of external DOC from surrounding rivers, Irish rivers to the west and English rivers to the east.

The relationships between salinity and DOC in the western and eastern Irish Sea were significant ($p < 0.05$), and strong in the eastern region (R^2, 0.79), and in contrast to what was expected, estimated freshwater inputs were much higher in the western Irish Sea (1153 ± 384 µM) compared to the eastern region (771 ± 44 µM); however the uncertainty in the western region estimates was large

(33%) and the relationship weak (R^2, 0.16). Furthermore, observations of DOM in the eastern and western regions in winter also show similar concentrations (Moschonas et al. 2015).

3.5. Conclusions

The distribution of DOM across 5 shelf seas, and their sub divisions, varies on the Northwest European Continental Shelf and adjacent North Atlantic Ocean waters. The broad scale pattern of DOM distribution fits with global trends (Barron and Duarte 2015), as both DOC and DON concentrations decreased with increasing distance from land and with increasing salinity. These patterns are indicative of the mixing and dilution of riverine DOM with marine and North Atlantic Ocean DOM of lower concentrations. There was however, considerable variability from this broad scale pattern shown by the variations between the salinity and DOC relationships within each region which, in some instances, showed large deviations from a simple 1:1 mixing line rendering the relationships weak and/or not significant.

Superimposed on these broad scale patterns was local variability and seasonality. In the Celtic Sea, Malin-Hebrides Shelf and English Channel, DOM did not adhere to the conceptual view of seasonal distribution. DOC and DON were often uncoupled and while DOC was generally highest in spring during productive periods, DON was not, a further indication that in nutrient limiting conditions

DON is an important nutrient source (Sipler and Bronk 2015). DOM behaved similarly in regions of distinctly different hydrographic regimes, and DOC was highest in spring in both the mixed English Channel region and the seasonally stratifying Celtic Sea. DOM concentrations were also similar in spring and summer in the eastern and western Irish Sea, which has previously been observed for wintertime DOM concentrations (Moschonas et al. 2015).

For the Northwest European Shelf region, there is still a lot that remains unknown or that is unclear regarding DOM dynamics. This hinders our understanding of complex physical and biogeochemical interactions. For example, seasonal changes in lateral transport mechanisms of DOM in both stratified and mixed regions remain unclear as do the annual and interannual variability in these processes. Knowledge of the magnitude and stoichiometry of riverine DOM at source is lacking which hinders the ability to track terrestrial inputs and to characterise DOM from source once transformation and diagenetic processes which alter DOM composition and molecular structure have occurred. Furthermore, microbial re-processing of DOM from differing sources such as marine exudates or dissolution of POM is not well understood.

Shelf seas are an interface between land and the open ocean and regions where complex physical processes such as frontal structures, river inputs and shelf edge processes interplay with biogeochemical nutrient cycles to influence the controls on DOM production, consumption and transport. While this study adds to a

growing body of information on regional and seasonal DOM distribution in shelf seas, much more knowledge is needed on the coupling between DOM and POM, the microbial processing of OM in shelf seas, and exchanges between the inorganic (DIC) and organic nutrient pools (DOM and POM), to better understand the role that DOM in shelf seas plays in global carbon and nitrogen cycles.

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Chapter 4

DOM distribution and multi-year variability in the North Sea

4.1. Introduction

Historically, there have been many studies in the North Sea which have focussed on the physical circulation and exchanges between the North Sea and North Atlantic (Huthnance 1997), the atmosphere (Thomas et al. 2005), the chemistry and distribution of inorganic nutrients (Hydes et al. 1999), and the composition of the biological community (Sintes et al. 2010, Lucas et al. 2016). More recently, concerns regarding eutrophication of the North Sea (Artioli et al. 2008, O'Higgins and Gilbert 2014) have prompted the implementation of a number of EU policies and directives (e.g. the Nitrates Directive and Water Framework Directive) (Artioli et al. 2008) and there has been a specific focus on the consequences of these mitigation policies on primary production (Lenhart et al. 2010).

While the focus of most of the mitigation policies has been on control on inorganic nutrients, the study of the distribution and cycling of dissolved organic matter (DOM) in the North Sea has highlighted their importance as a nutrient source and vehicle of elemental transport (Suratman et al. 2008, Suratman et al. 2009, Sintes et al. 2010, Frigstad et al. 2013, Johnson et al. 2013, Chaichana et al. in review). While these studies have shed invaluable light on DOM

dynamics in shelf seas, there is still some uncertainty about the multi-year variability in DOM and its role in the shelf sea carbon pump in terms of its exchange with the North Atlantic.

While the export of particulate organic matter (POM) is estimated to be responsible for 80% of carbon export to the deep ocean (Hansell and Carlson 2001), advances in methods for measuring DOM since initial measurements (Suzuki et al. 1985, Sugimura and Suzuki 1988), and insights from hydrography (e.g. Joint Global Ocean Flux Study (JGOFS)) and time series (e.g. BATS) programmes have improved our understanding of the role of DOM in the marine environment, in particular in the biological pump (Hansell and Carlson 2001). Repeat measurements from the subtropical North Atlantic reveal that DOM is responsible for 20% to 50% of carbon export (Carlson et al. 2010)**.** In shelf seas, Hopkins and Vallino (2005) revealed that DOM is an efficient vehicle of export through the transfer of carbon rich DOM to the ocean interior. The process for transferring carbon from a shallow shelf sea to the ocean interior is termed the 'continental shelf pump' (Tsunogai et al. 1999), and is highlighted from observations of carbon cycling in the North Sea (Thomas et al. 2004, Thomas et al. 2005, Liu et al. 2010).

According to Thomas et al (2005), the North Sea is a highly efficient continental shelf pump. Over 90% of carbon dioxide (CO_2) absorbed from the atmosphere is exported to the North Atlantic Ocean (Thomas et al. 2005). The carbon budget of the North Sea is controlled by a combination of physical processes, including

exchange fluxes with the North Atlantic, air-sea exchange between the atmosphere and ocean and horizontal exchange with the neighbouring Baltic Sea and riverine inputs (Thomas et al. 2005). The physical contrast between the deeper seasonally stratifying northern and shallower well mixed southern North Sea plays a fundamental role in controlling carbon export in these two regions. Although up to 3 times more carbon is fixed in the southern region, it is the export of carbon from the deeper layers of the northern region to the North Atlantic (Fig.4.1) that make the North Sea a sink of atmospheric carbon (Thomas et al. 2005, Hartman et al. 2018).

The seasonal cycling of DOM (Brockmann et al. 1990) and POM (Thomas et al. 2004) in the stratifying northern North Sea is well established. Surface water OM concentrations increase in spring during phytoplankton production and onset of stratification, then decrease during the summer stratified period as DOM and POM in surface waters are exported below the seasonal thermocline and consumed by bacteria. The excess DIC here is then transported to the North Atlantic during winter flushing. Via a combination of these processes, the northern North Sea is a sink of atmospheric carbon and an autotrophic system (Thomas et al. 2004, Kuhn et al. 2010).

In contrast, the seasonal cycling of DOM in the well mixed waters of the southern North Sea is less clear (Suratman et al. 2010, Van Engeland et al. 2010). Large increases in DOM concentrations have been observed during spring-bloom periods, with DON concentrations doubling relative to the background refractory pool

(Johnson et al. 2013), with rapid, large (up to four-fold) declines in DON eight days following a bloom, implying that DON is being used as a nutrient source (Suratman et al. 2010). However, in the absence of stratification there is weaker net CO_2 removal from surface waters (Thomas et al. 2005) as POM and DOM is recycled in the fully mixed water column that is in contact with the atmosphere (Fig.4.1), making the southern region a heterotopic system and a source of atmospheric CO_2.

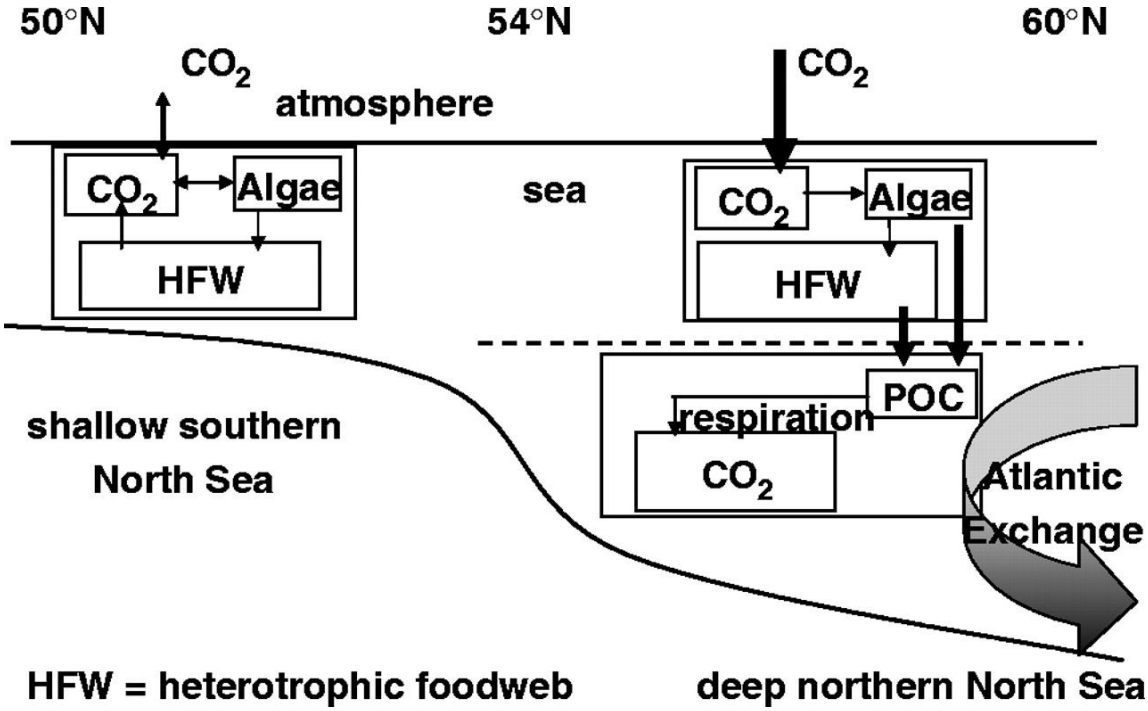

Fig.4.1. Schematic illustrating the North Sea carbon pump in the shallow mixed and seasonally stratifying regions (Taken from (Thomas et al. 2004)).

Despite changes in DOM concentrations having significant implications for regional and global nutrient budgets and the carbon cycle (Hansell and Carlson 2001, Hansell and Carlson 2015, Chaichana et al. in review), studies on DOM variability on multi-year timescales are limited. Studies in the Cariaco Basin indicate DOC

export is affected by interannual variability in coastal upwelling (Lorenzoni et al. 2013). Improved spatial and temporal measurements in Arctic rivers reveal that DOM fluxes from Siberian river systems draining into the Arctic Ocean have been underestimated (Griffin et al. 2011).

Results from long-term monitoring show that changing DOC is a potential indicator of climatic variability locally, for example, in the northern Adriatic where the Adriatic-Ionian Bimodal Oscillating System (BiOS) influences water circulation and hydrographic conditions and furthermore, anthropogenic pressures alter riverine discharge and inputs (Dautovic et al. 2017). Furthermore, on global and geological timescales, changes in the rate of removal of the refractory DOC pool in the ocean interior have been linked to enhanced atmospheric CO_2 during the Neoproterozoic which prevented glaciation over the globe (Hansell and Carlson 2015).

In the North Sea, observations of summertime (August) DOM distribution reveal striking differences of 10-20 Tg C in the DOC inventory between 2 consecutive years, this inventory being equivalent to the North Seas annual uptake of atmospheric CO_2 (Chaichana et al. in review). This stark decline in DOC between years is thought to be driven mainly by the export of bottom layer DOC to the North Atlantic Ocean during wintertime flushing (Chaichana et al. in review).

The North Sea has a long history of long term, multi-decadal studies covering a wide variety of climatological (Salt et al. 2013) and ecological (Aebischer et al. 1990) concerns. The threat of eutrophication in coastal areas due to enhanced nutrient enrichment (Skogen and Mathisen 2009) has been the motivation for many studies and mitigation policies. However, more recently, the effects of the reduction in nutrient inputs into the North Sea have been studied revealing a decline in phosphorous inputs relative to nitrogen has caused a large imbalance in nutrient stoichiometry, with consequences for phytoplankton growth and community composition (Burson et al. 2016).

Long-term studies are important for identifying trends and linking changes to the mechanisms and processes causing them. For example, the continuous plankton recorder survey database holds over 80 years of data on plankton abundance in the North Sea, enabling quantification of the effects of increasing surface water pH and acidity, caused by increasing anthropogenic carbon emissions, on calcifying organisms (Beare et al. 2013).

Following on from Chapter 3, in this chapter I will address the following questions;

1) How do nutrients, DOC and DON behave during the shelf wide sampling programme in the North Sea in 2014 and 2015?

2) What are the multi-year trends in nutrients, DOC and DON in August from 2011 to 2016 in the North Sea?
3) What processes are controlling the between year variability in DOC and DON in the North Sea?

4.2. Materials and methods

4.2.1. Sampling, collection and analysis of inorganic nutrients, DOC and DON

Sampling for the North Sea is as described in Chapter 3, Section 3.2.1, and sample collection and analysis is as described in Chapter 3, Section 3.2.2. To allow comparisons between sampling years, DOC and DON data from 2011 and 2012 was captured from Chaichana et al. (in review) using the software Graphic Click. DOC and DON data from 2016 (LOCATE) was requested from BODC.

4.2.2. Region division for data analysis

The North Sea was divided along the 50 m contour at 55°N, the northern region defined as being north of 55 °N (blue diamonds) and southern region defined as being south of 55 °N (red circles, Fig.4.2). The southern region is permanently mixed, therefore surface measurements were taken as being representative of the whole water column.

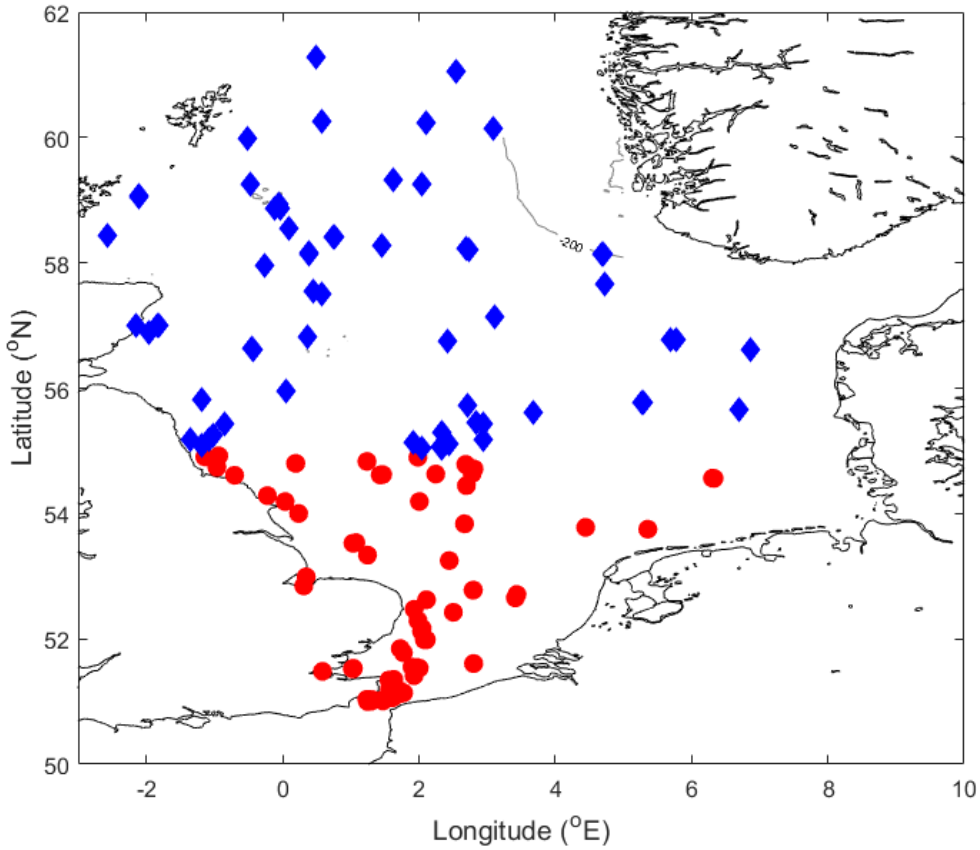

Fig.4.2. North Sea stations sampled between 2014 and 2015 during the Shelf Wide campaign. Regions are colour coded as follows: northern North Sea (blue diamonds) and southern North Sea (red circles).

4.2.3. The North Sea system

The defining characteristic of the North Sea is the differences in water column depth which exerts major controls over physical and biogeochemical properties. The northern North Sea is deeper (~150 m) and seasonally stratifying, enabling particulate organic matter (POM) generated during productive periods to sink below the seasonal thermocline where it is remineralised to DIC and then potentially exported as DIC in deeper layers off shelf to the North Atlantic (Fig.4.1). The northern region is considered to be an oceanic system due to continuous year round exchange with the North Atlantic (Ospar Commission 2000). Terrestrial inputs from the Baltic

Sea and Scandinavian Peninsula play a minor role in the dilution of North Atlantic water. In contrast, the southern North Sea is shallow (~ 50 m, and 20 m around the coast) and permanently mixed with remineralisation of OM occurring in the whole water column preventing the off-shelf transport of DIC. The southern region is strongly affected by riverine inputs from a number of UK and European rivers including the Thames and Rhine, as well as inputs from the Baltic and Wadden Sea (Weston et al. 2004, Dai et al. 2012).

The North Sea has a unique 'U' shaped circulation with major outflows through the Norwegian Trench and transport times estimated at less than one year (Thomas et al. 2005) to between one and two years (Hydes et al. 2004). DOM seasonality in the northern region is well defined while in the southern region, observations vary from no clear seasonal signal (Suratman et al. 2008, Van Engeland et al. 2010), to a 'sawtooth' DON cycle (Johnson et al. 2013). Measurements of DIC from the Shelf Wide sampling campaign suggest that the southern North Sea is a source of CO_2 to the atmosphere throughout the year, and the northern North Sea a sink of atmospheric CO_2 (Hartman et al. 2018).

Next I will address questions on how nutrients, DOC and DON behave in the North Sea during 2014 and 2015, what the multi-year trends in August are, and what processes are controlling between year variability.

4.3. Results

4.3.1.1. Data distribution in the northern and southern North Sea

Between January 2014 and November 2015, there were 179 stations sampled for nutrients, DOC and DON, resulting in 167 DOC values and 126 DON values. However, the data were not evenly spaced in time or space (see Chapter 3, section 3.3.1). In the southern North Sea, data were collected during 9 months and covered all seasons (Fig.4.3), but in the northern North Sea, sampling was biased towards August, with no data for autumn and generally < 10 samples for other months. Therefore, in this chapter, I will describe the seasonality in hydrography, nutrients, DOC and DON in the southern North Sea, and compare the southern and northern North Sea regions for August only.

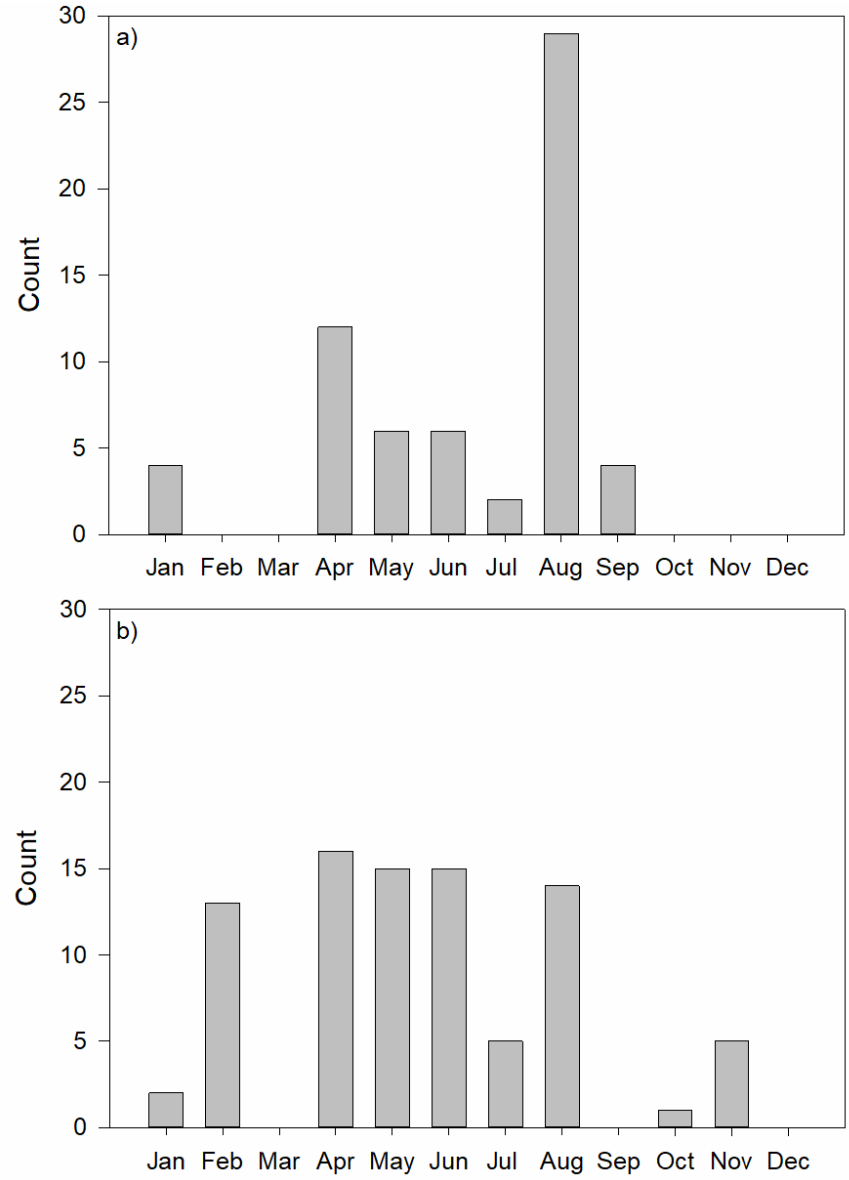

Fig.4.3. Monthly sampling frequency for 2014 and 2015 in the a) northern North Sea and b) southern North Sea. The counts per month represent all data points before separation into a two layer system in the northern North Sea.

4.3.1.2. Seasonal variation in hydrography, nutrients and DOM in the southern North Sea

The variation in temperature, N+N, DOC and DON are illustrated using box and whisker plots (Fig.4.4). The values referred to in the text represent the mean ± standard deviation, unless stated otherwise, and are presented in Table 4.1. An additional table

detailing further statistics e.g. minimum, maximum and range are presented in the appendices (Table 9).

Temperature was typically lowest in winter and highest in summer (7.9 ± 0.9 and 16.9 ± 2.1 °C, respectively, Table 4.1 and Fig.4.4). The range in salinity throughout the year was relatively large (~1) and was highest in autumn and lowest in winter (34.8 ± 0.1 and 33.8 ± 1.7, respectively). N+N generally followed a typical seasonal distribution and concentrations were highest in winter and autumn, and lowest in summer (4.7 ± 1.1 µM and 5.1 ± 2.8 µM, and 0.5 ± 0.8 µM, respectively). The seasonal distribution of DOM in the southern North Sea did not follow the typical cycle for a mixed region. DOC concentrations were highest in spring and lowest in autumn (87 ± 23 µM and 72 ± 8 µM, respectively). In the absence of winter DON data, there were no clear seasonal trends in DON concentrations, which were between 5 and 6 µM throughout the year (Table 4.1). DOM was more carbon rich in spring (19 ± 11) relative to autumn (13 ± 3).

Table 4.1. Seasonal mean ± std dev in the southern North Sea for temperature (°C), salinity, N+N (µM), DOC (µM), DON (µM) and DOM stoichiometry (DOC:DON), n indicates sample size.

Southern North Sea	Winter	Spring	Summer	Autumn
Mean Temp (°C)	7.9 ± 0.9*	13.1 ± 2.4	16.9 ± 2.1	13.9 ± 0.4
Mean Salinity	33.8 ± 1.7	34.6 ± 0.4	34.5 ± 0.4	34.8 ± 0.1
Mean N+N (µM)	4.7 ± 1.1*	3.7 ± 8.9	0.5 ± 0.8	5.1 ± 2.8
Mean DOC (µM)	81 ± 22	87 ± 23	79 ± 15	72 ± 8
Mean DON (µM)	X	5.3 ± 1.7	5.9 ± 2.1	5.7 ± 1
Mean DOC:DON	X	19 ± 11	16 ± 9	13 ± 3

*Temperature and N+N data for winter taken from (Hartman et al. 2018) (Table 1a and 1b).

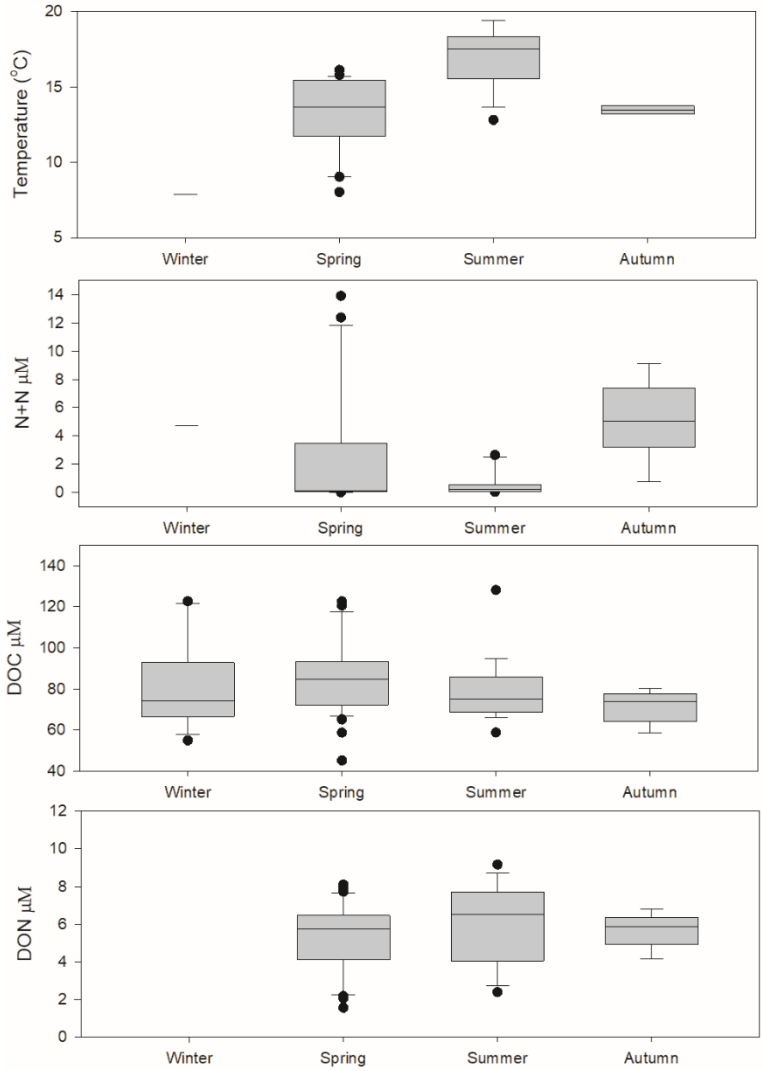

Fig.4.4. The seasonal variation in a) temperature (°C), b) N+N (µM), c) DOC (µM) and d) DON (µM) in the southern North Sea. The median of the data is represented by the horizontal line within the box, whiskers are the minimum (lower) and maximum (upper) values excluding outliers, and the black dots are outlying values.

As previously observed in other regions on the Northwest European Shelf, there were seasonal variations in the inverse relationship between salinity and DOC (Carr et al. 2018). The slope and intercept ranged from -9 in winter to -18 in spring, and from 390 μM in winter to 699 μM in spring, respectively (Table 4.2). This enhanced input of DOC in spring, as suggested from the higher zero salinity intercept, may be the cause of higher mean DOC concentrations in spring (87 ± 23 μM) compared to other seasons (Table 4.1). There was considerable variability from a simple mixing line, particularly in spring and summer when the relationships were significant but weak ($R^2 < 0.2$, Table 4.2).

Table 4.2. Results from linear regression analysis of salinity and DOC (± indicate the standard error). Statistically significant values are highlighted in bold.

Region	R^2	Slope	y - intercept	Sample Size	p - value (slope)	p - value (intercept)
Southern North Sea						
All data	0.24	-9 ± 2	398 ± 74	62	**<0.0001**	**<0.0001**
Winter	0.53	-9 ± 3	390 ± 84	13	**0.003**	**<0.001**
Spring	0.15	-18 ± 9	699 ± 300	27	**0.05**	**0.003**
Summer	0.16	-16 ± 9	647 ± 311	19	0.08	**0.05**
Autumn (N.D)						

4.3.2. Spatial and multi-year comparison between the northern and southern North Sea regions

To compare the broad scale patterns in hydrography, nutrients, DOC and DON, I will first present data collected in August 2014 and August 2015 between the northern and southern North

Sea (Fig.4.5). I will then address multi-year variations in hydrography, nutrients, DOC and DON from August 2011 to August 2016.

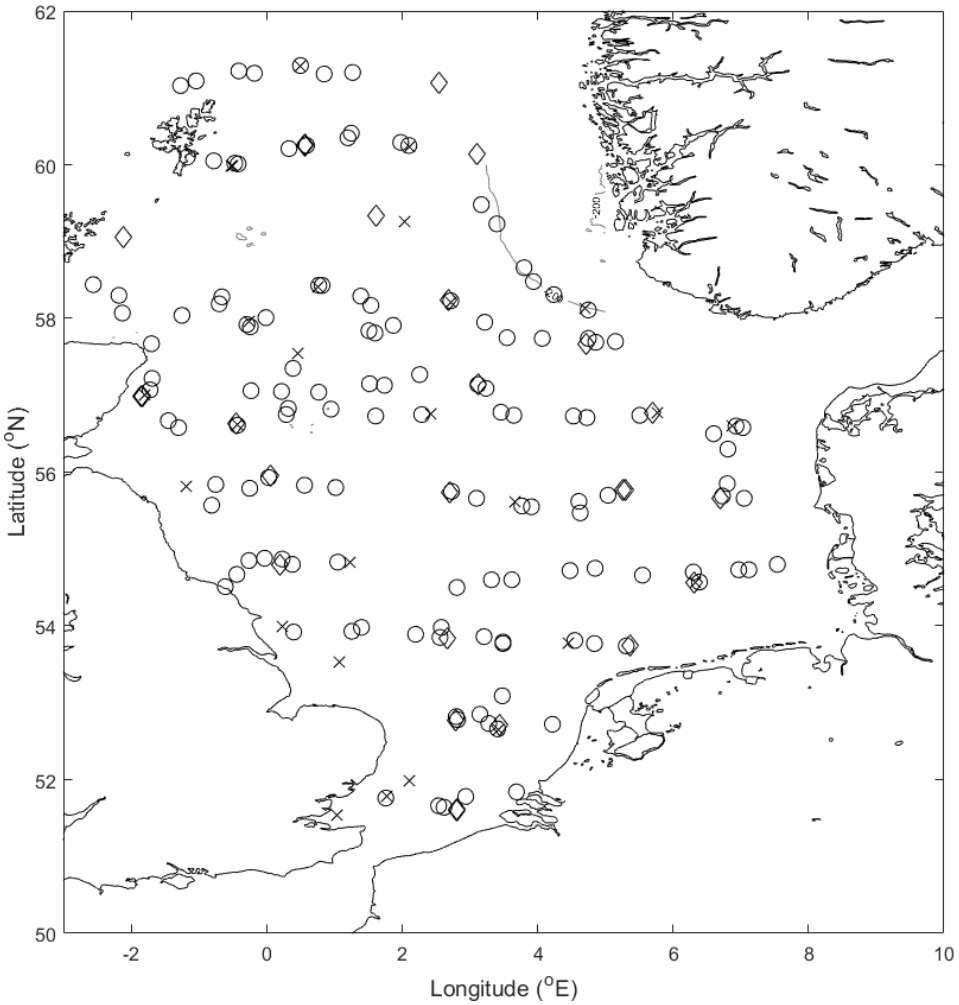

Fig.4.5. North Sea stations sampled in August 2014 (diamonds), August 2015 (crosses) and August 2016 (circles) from LOCATE dataset (Painter et al. 2018).

4.3.2.1 Hydrography in August 2014 and August 2015

There were differences in physical and biogeochemical properties between the surface and bottom waters in the northern North Sea, between the northern stratifying region and southern mixed regions and between years spanning 2014 to 2015.

As expected, in the northern North Sea, SML waters were generally warmer than BML waters, and southern waters were generally warmer than northern waters (Fig.4.6 a). In both years, temperatures in the southern region were on average between 2 and 4 °C higher than in the northern region (Table 4.3). Over the entire North Sea, surface waters were generally warmer (by 0.3 to 2°C) in 2014 compared to 2015 (Table 4.3 and Fig.4.6 a), with these between year differences being most pronounced in the southern North Sea (Figure 4.6 d and e).

Surface waters of the northern region were fresher compared to BML waters, and the southern region was generally fresher. In both years, salinity was lower in the southern region compared to the BML of the northern region by on average 0.4, and similar in 2014 to the northern SML (34.5 and 34.4, respectively, Table 4.). Over the entire North Sea, surface waters were fresher (by 0.1 to 0.5) in 2014 compared to 2015 (Table 4.3 and Fig.4.6 a), with these between year differences being most pronounced in the northern North Sea (Fig.4.6 b and c).

T-S diagrams for August 2014 and 2015 of the whole North Sea region and northern and southern regions show a general pattern of mixing between warmer and fresher, with colder and saltier water (Fig.4.6 a - e), as previously observed in 2011 and 2012 (Chaichana et al. in review). There was overlap between years although some differences were apparent, for example, in surface waters of the southern North Sea (Fig.4.6 d). However, salinity was

similar between years therefore these differences were probably due to warmer surface temperatures in 2014 compared to 2015. In addition, in the SML of the northern North Sea, there were a number of stations with noticeably higher salinities (> 35) in 2015 compared to 2014 when salinities were < 35.

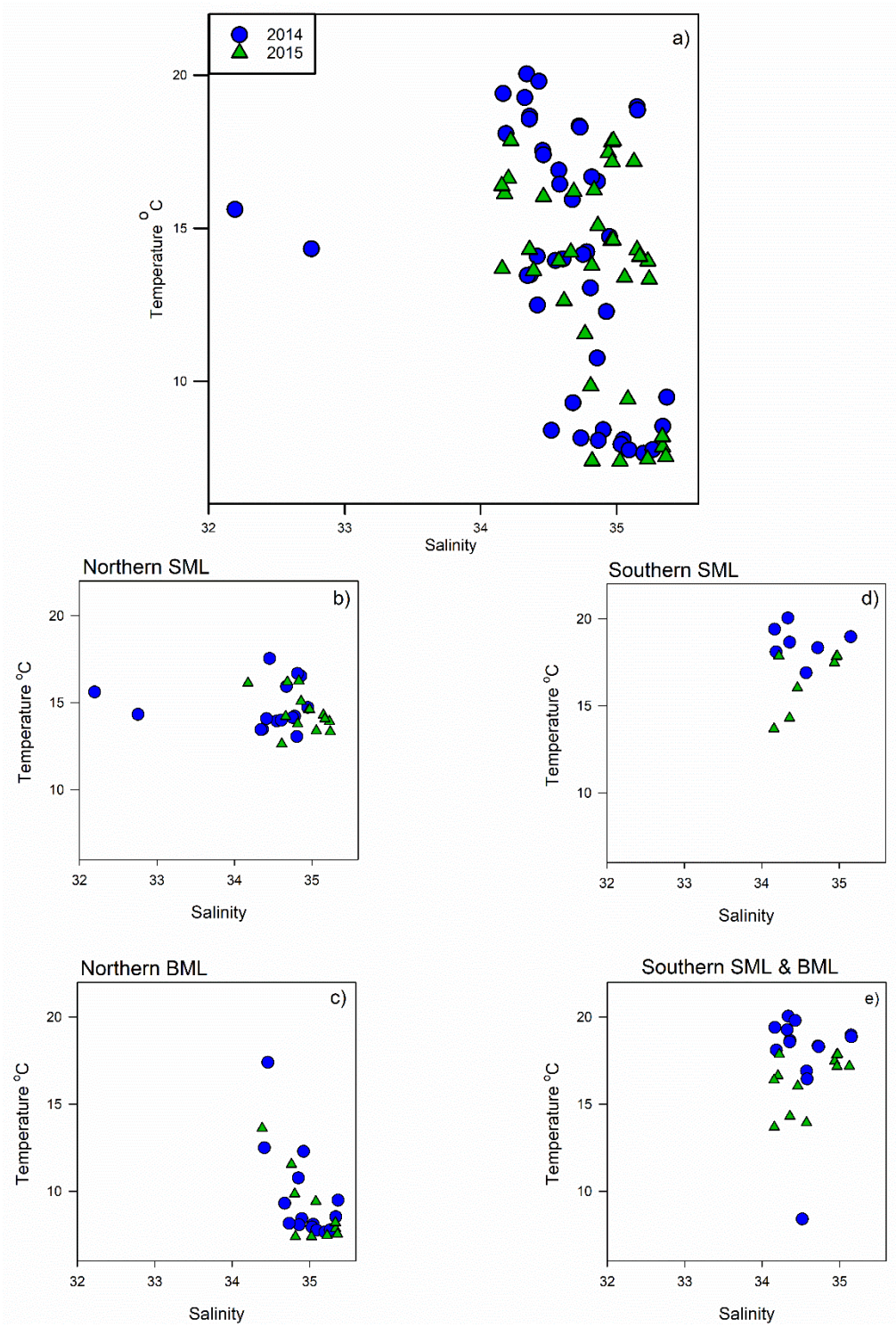

Fig.4.6. T-S plots for 2014 (blue dots) and 2015 (green triangles) for a) All North Sea, b) Northern SML, c) Northern BML, d) Southern SML and e) Southern SML and BML combined.

Table 4.3. Mean ± std dev and range in temperature (°C), salinity, DIN (µM), DOC (µM), DON (µM), DOC:DON and N:P ratios for August 2011 and 2012 (Chaichana et al. in review), Shelf Wide Sampling August 2014 and 2015, and August 2016 from LOCATE dataset (Painter et al. 2018).

Region/Year	Temp (°C)	Salinity	DIN (µM)	DIP (µM)	DOC (µM)	DON (µM)	DOC:DON	N:P
Southern well mixed				**Mean ± Std Dev**				
August 2011*	15.5 ± 1.7	34.3 ± 0.5	1.5 ± 1.1	0.2 ± 0.1	97.5 ± 13.7	9.0 ± 1.8	11 ± 2	N.D.
August 2012*	16.2 ± 1.7	34.5 ± 0.5	0.8 ± 1.2	0.2 ± 0.1	65.5 ± 16.4	5.3 ± 1.3	13 ± 3	N.D.
August 2014	18.6 ± 1.0	34.5 ± 0.3	0.1 ± 0.1	0.1 ± 0.1	77.5 ± 10.9	5.9 ± 1.9	14 ± 4	1.5 ± 1.2
August 2015	16.4 ± 1.8	34.6 ± 0.4	1.0 ± 1.1	0.2 ± 0.1	73.3 ± 10.2	5.3 ± 2.0	17 ± 9	4.6 ± 3.1
August 2016**	17.0 ± 1.3	34.3 ± 0.5	0.7 ± 1.5	0.1 ± 0.1	120.0 ± 15.0	8.1 ± 2.5	16 ± 3	2.2 ± 2.8
Northern SML								
August 2011*	14.2 ± 1.0	34.3 ± 1.0	0.7 ± 1.1	0.2 ± 0.1	73.8 ± 11.6	6.6 ± 1.0	11 ± 1	N.D.
August 2012*	16.3 ± 0.8	34.3 ± 1.0	0.5 ± 0.3	0.1 ± 0.0	60.7 ± 13.0	5.3 ± 1.1	12 ± 2	N.D.
August 2014	14.8 ± 1.4	34.4 ± 0.8	0.3 ± 0.6	0.1 ± 0.1	83.7 ± 26.7	4.3 ± 1.7	21 ± 7	3.0 ± 1.9
August 2015	14.5 ± 1.1	34.9 ± 0.3	0.2 ± 0.2	0.1 ± 0.1	67.1 ± 5.1	3.9 ± 0.8	18 ± 5	4.1 ± 3.8
August 2016**	14.9 ± 1.1	34.6 ± 0.6	0.5 ± 0.7	0.1 ± 0.2	104.7 ± 10.4	6.0 ± 0.9	18 ± 2	1.8 ± 1.4
Northern BML								
August 2011*	8.4 ± 1.6	35.1 ± 0.2	9.9 ± 4.4	0.6 ± 0.1	73.8 ± 14.7	5.9 ± 2.1	13 ± 4	N.D.
August 2012*	8.8 ± 0.6	35.0 ± 0.2	5.5 ± 3.0	0.6 ± 0.2	46.9 ± 6.8	5.2 ± 1.0	9 ± 2	N.D.
August 2014	9.6 ± 2.7	34.9 ± 0.3	6.4 ± 4.2	0.6 ± 0.2	62.9 ± 9.6	3.2 ± 1.6	22 ± 9	8.9 ± 5.1
August 2015	9.0 ± 2.0	35.0 ± 0.3	6.9 ± 5.6	0.6 ± 0.3	60.8 ± 7.9	3.9 ± 1.5	17 ± 7	8.7 ± 5.6
August 2016**	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Southern well mixed				**Range (Min-Max)**				
August 2011*	(10.4-17.8)	(33.0-34.9)	(0.2-4.7)	(0.1-0.5)	(77.1-134.5)	(6.1-13.7)	(8-14)	N.D.
August 2012*	(11.0-18.5)	(33.1-35.1)	(0.4-8.3)	(0.1-0.4)	(36.3-124.4)	(2.8-9.8)	(9-21)	N.D.
August 2014	(16.9-20.0)	(34.2-35.2)	(0.03-0.3)	(0.02 -0.2)	(58.8-91.2)	(3.8-8.4)	(10-18)	(0.3-3.7)
August 2015	(13.7-17.9)	(34.2-35.0)	(0.1-2.6)	(0.04 -0.4)	(66.2-94.9)	(2.4-7.1)	(10-31)	(1.1-9.6)
August 2016**	(14.0-19.6)	(32.5-35.1)	(0.1-9.3)	(0.02-0.4)	(100.8-161.7)	(5.5-16.4)	(8-21)	(0.4-14.3)
Northern SML								
August 2011*	(12.2-16.0)	(31.8-35.4)	(0.2-4.7)	(0.1-0.5)	(51.2-104.2)	(4.8-8.7)	(8-15)	N.D.
August 2012*	(13.2-17.4)	(30.9-35.2)	(0.4-1.5)	(<LOD-0.2)	(32.7-99.5)	(3.0-7.5)	(7-16)	N.D.
August 2014	(13.1-17.5)	(32.2-34.9)	(0.04-2.3)	(0.02-0.3)	(52.3-145.5)	(2.2-7.2)	(11-32)	(0.7-8.1)
August 2015	(12.6-16.3)	(34.2-35.2)	(0.06-0.5)	(0.01-0.2)	(60.1-77.2)	(2.3-4.5)	(14-30)	(0.7-15.8)
August 2016**	(12.1-16.9)	(32.2-35.2)	(0.08-3.3)	(0.02-1.1)	(84.2-135.8)	(3.5-8.2)	(12-26)	(0.4-9.2)
Northern BML								
August 2011*	(6.7-12.4)	(34.6-35.4)	(0.9-16.2)	(0.1-1.1)	(53.3-120.1)	(3.0-11.7)	(7-23)	N.D.
August 2012*	(7.5-10.5)	(34.6-35.4)	(0.4-11.2)	(0.2-0.9)	(36.8-61.2)	(3.5-7.5)	(6-14)	N.D.
August 2014	(7.7-17.4)	(34.4-35.4)	(0.06-12.1)	(0.1-0.8)	(50.8-80.9)	(1.5-6.5)	(11-36)	(0.8-15.0)
August 2015	(7.4-13.6)	(34.4-35.4)	(0.5-13.6)	(0.2-1.2)	(49.0-72.1)	(2.3-6.3)	(9-31)	(2.0-15.1)
August 2016**	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

*DIN for August 2014 and 2015 does not include ammonium (nitrate plus nitrite only). **Data used for 2016 in this study were supplied by the Land Ocean Carbon Transfer (LOCATE) project supported by Natural Environment Research Council grant NE/N018087/1.

4.3.2.2. Inorganic nutrients in August 2014 and August 2015

In the northern North Sea, N+N concentrations in surface waters were, as expected, typically lower by over an order of magnitude, compared to BML waters. N+N in southern waters were also low and similar to concentrations in the SML waters in the northern region. (Table 4.3 and Fig.4.7). N+N concentrations were generally higher in surface and bottom waters in 2015 compared to 2014 (Table 4.3 and Fig.4.7). In the southern region, N+N concentrations were an order of magnitude higher in 2015 compared to 2014 (1.0 ± 1.1 µM and 0.1± 0.1 µM, respectively, Table 4.3, Mann-Whitney, p 0.02). In the BML of the northern region, N+N concentrations were only ~ 10% higher in 2015 compared to 2014 (Table 4.3).

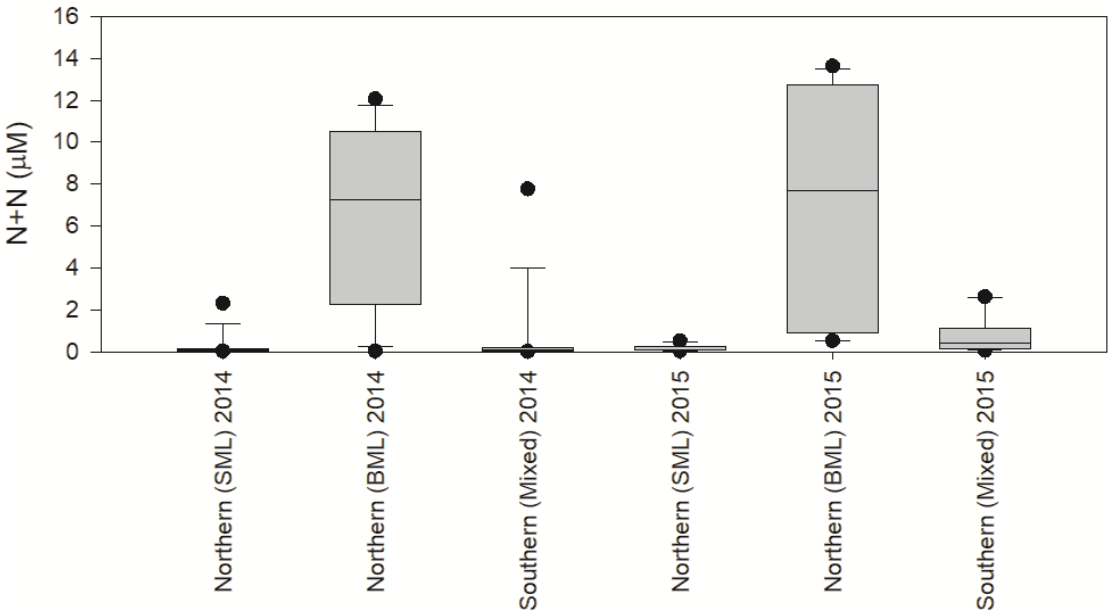

Fig.4.7. Variation in N+N (µM) the northern North Sea SML and BML, and southern North Sea between 2014 and 2015. The median of the data is represented by the horizontal line within the box, whiskers are the minimum (lower) and maximum (upper) values excluding outliers, and the black dots are outlying values.

Phosphate concentrations (DIP), were between 3 and 6 times higher in the BML of the northern region, compared to the SML and to the southern region (Table 4.3). DIP in the northern North Sea did not vary between 2014 and 2015, however DIP concentrations doubled in the southern region between 2014 and 2015 (from 0.1 ± 0.1 µM to 0.2 ± 0.1 µM, respectively, Table 4.3). The elemental ratio of N to P was also greater in the BML of the northern North Sea (~ 9) compared to the SML (~ 2 to 4). The N:P ratio of nutrients was also 2 to 3 times higher in 2015 in the SML of the northern region and the southern region compared to 2014 (Table 4.3).

4.3.2.3. DOM in August 2014 and August 2015

In the northern North Sea, DOC concentrations in surface waters were higher compared to BML waters, while DOC in the southern region was higher than northern waters. Over the whole North Sea region, mean DOC concentrations in 2014 were significantly higher by an average of 11 µM compared to 2015 (Fig.4.8 a and Table 4.3, Mann-Whitney, p 0.02). DOC was highest in the SML of the northern region in 2014 and highest in the southern region in 2015 (Table 4.3). DOC concentrations in the SML and BML of the northern region in 2014 were on average 21 µM and 6 µM higher than in 2015 (Table 4.3), however, the differences were not significant (SML Mann-Whitney, p 0.06 and BML t-test, p 0.6). In the southern region, DOC in 2014 was on average 4 µM higher than in 2015 (Table 4.3), however, as in the northern region, the difference was not significant (t-test p 0.5). The interannual DOC differences

between 2014 and 2015 in surface and bottom waters were not as striking as those reported by Chaichana et al. (in review), who observed differences of between 20 and 40 µM in the BML of the northern region.

Similarly to DOC, DON concentrations in surface waters of the northern North Sea were higher compared to BML waters, and DON was higher in the southern region. DON concentrations for the whole North Sea region were on average 0.3 µM higher in 2014 than in 2015 (4.7 µM and 4.4 µM, respectively, Table 4.3 and Fig.4.8 b) but the small difference was not statistically significant (t-test, p 0.6). DON in the southern region was higher in both 2014 and 2015 compared to the northern region (Table 4.3), and increased by 18% in the BML of the northern region in 2015 (Table 4.3), however, DON regional differences were not significant (t-test, p 0.5). As with DOC, the interannual DON differences between 2014 and 2015 in surface and bottom waters were not as large as those reported by Chaichana et al. (in review), who observed differences of 5 µM in the southern region, but similar concentrations in the BML of the northern region in 2011 and 2012.

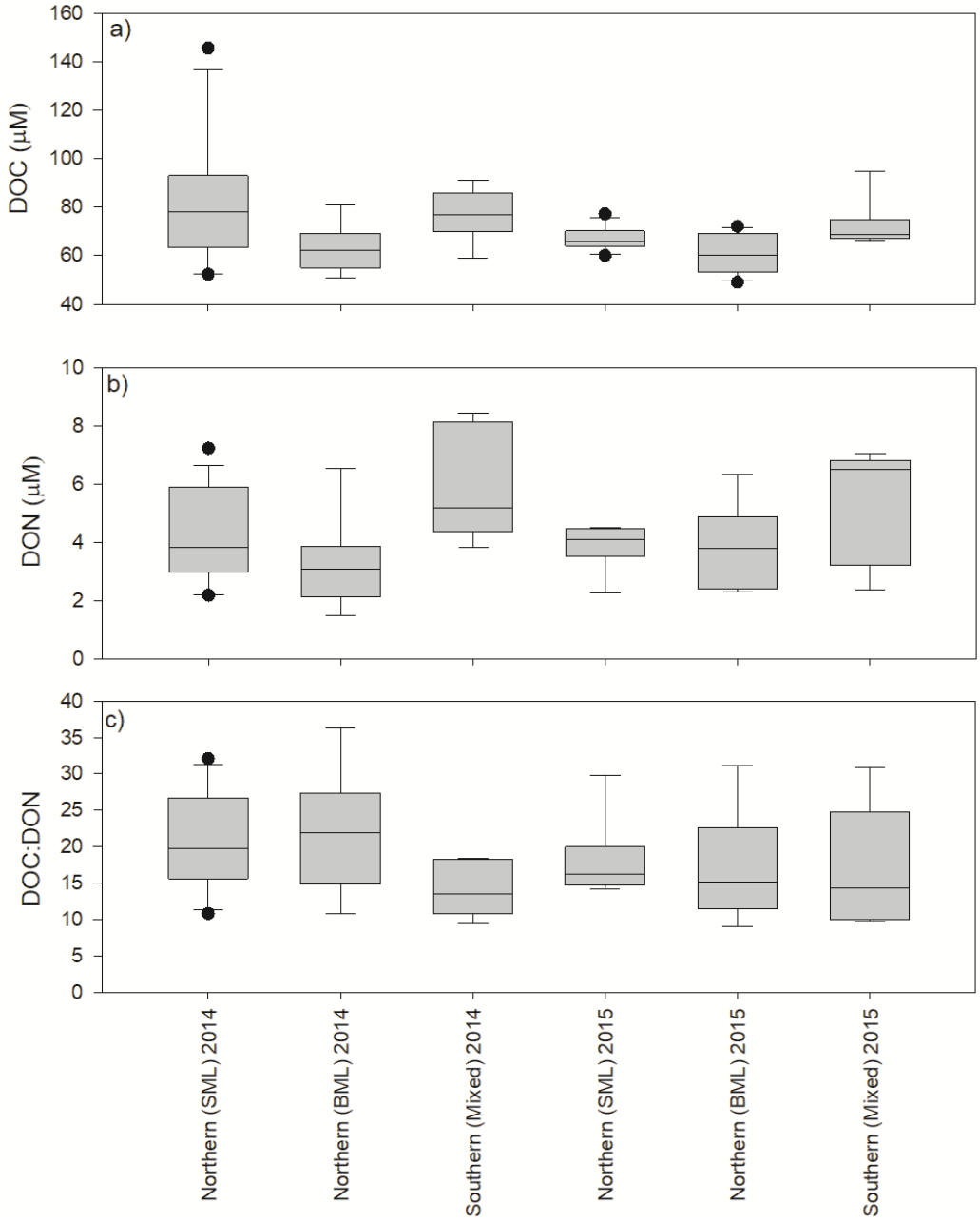

Fig.4.8. The variation in a) DOC (µM), b) DON (µM) and c) DOC:DON, in the northern region SML and BML and southern (mixed) region in August 2014 and 2015. The median of the data is represented by the horizontal line within the box, whiskers are the minimum (lower) and maximum (upper) values excluding outliers, and the black dots are outlying values.

4.3.2.4. North Sea relationship between salinity and DOC (August 2014 and August 2015)

Inverse relationships were observed between salinity and DOM (Fig.4.9) despite the limited number of coastal sites sampled.

However, in many instances the relationships were weak ($R^2 < 0.2$) and not significant ($p > 0.05$, Table 4.4). For DOC, the slope ranged from between -2 and -19, and for DON by between -0.1 and -3 (Table 4.4). There was considerable deviation from the simple theoretical mixing line between freshwater riverine DOM and open ocean DOM in both regions, in particular in the SML of northern North Sea where the DOC salinity and DON salinity slope values were nearly an order of magnitude lower in 2015 than in 2014 (DOC -2 and -19, and DON -0.1 and -0.9, respectively, Table 4.4).

From extrapolation to zero-salinity, estimates of freshwater DOC inputs into surface waters of the North Sea (northern SML and southern mixed region) were over two-fold higher in 2014 compared to 2015 (1341 ± 764 µM and 549 ± 575 µM, respectively), and nearly two-fold lower in 2015 compared to 2016 (1032 ± 201 µM, LOCATE data not shown).

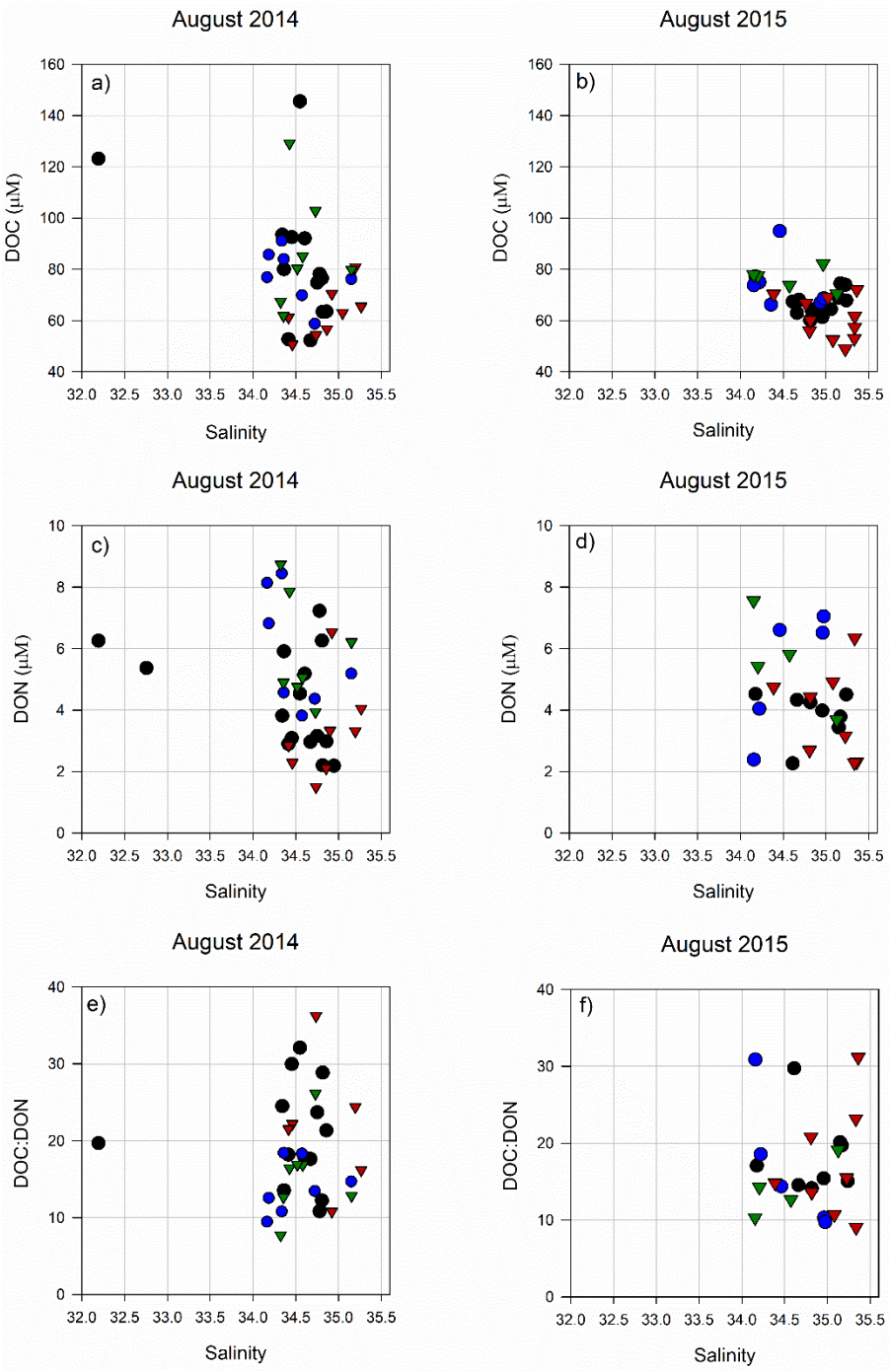

Fig.4.9. Salinity relationship with DOC (a and b), DON (c and d) and DOC:DON (e and f) for the different regions in 2014 and 2015. SML of the northern (filled black circles) and southern (filled blue circles), and BML of the northern (filled red triangles) and southern (filled green triangles) North Sea.

DOC data for the preceding winter (2013/2014) showed slightly elevated concentrations compared to summer 2014 in the southern region (81 ± 22 µM and 78 ± 11 µM, respectively, winter

data not shown). The salinity DOC relationship in the North Sea in winter was strong and significant (Table 4.4). In addition, the highest winter DOC concentrations were observed at stations located at the mouth of the River Thames and north of the River Tees, suggesting winter inputs of riverine DOC could account for these differences. In contrast to the study by Chaichana et al. (in review), DOC concentrations > 70 µM in the BML of the northern region were not observed and the differences between the 2014 and 2015 were small (2 µM).

Furthermore, higher salinity waters were not necessarily associated with higher DOC concentrations (Fig.4.9 a and b). The observations suggest that a similar renewal of North Sea water with low DOC North Atlantic water, or a flushing event between 2014 and 2015 was not observed or captured, as proposed in the study by Chaichana et al. (in review) between 2011 and 2012.

By employing the inverse relationships between DOM and salinity, estimates of freshwater inputs into surface waters for 2014 and 2015 at the zero salinity end member were 1068 µM for DOC and 151 µM for DON, giving a source C:N ratio of 7, which was lower than the estimate reported by Chaichana et al. (in review) of 10 for the 2011 and 2012 surveys. However, these estimates should be viewed with caution given the limited salinity range sampled and the variability in the salinity DOM relationships. The freshwater end member values estimated here are highly uncertain although

consistent with riverine DOC:DON observations (Mattsson et al. 2009, Markager et al. 2011).

Table 4.4. Results from linear regression analysis of salinity with DOC and DON. Errors reported represent the standard error (SE) and statistically significant values are highlighted in bold.

Parameters	Surveys	Region	R^2	Slope	SE	y-Intercept	SE	Sample Size	Slope p-value	Intercept p-value	Significant
DOC	Winter 2013/2014	Southern (Mixed)	0.53	-9	3	390	85	14	**0.003**	**<0.001**	Y/Y
	August 2014	All North Sea 2014	0.24	-19	6	722	223	29	**0.007**	**0.003**	Y/Y
		Northern SML	0.25	-19	10	741	346	13	0.08	0.06	N/N
		Southern (Mixed)	0.24	-15	12	600	418	7	0.3	0.2	N/N
	August 2015	All North Sea 2015	0.21	-11	4	458	137	32	**0.008**	**0.002**	Y/Y
		Northern SML	0.01	-2	5	122	175	14	0.8	0.5	N/N
		Northern BML	0.12	-9	8	363	273	11	0.3	0.2	N/N
		Southern (Mixed)	0.14	-10	12	427	400	7	0.4	0.3	N/N
DON	Winter 2013/2014	Southern (Mixed)	No Data								
	August 2014	All North Sea 2014	0.10	-0.9	0.5	36	18	30	0.09	0.06	N/N
		Northern SML	0.17	-0.9	0.5	34	18	15	0.1	0.08	N/N
		Southern (Mixed)	0.32	-3.0	2.0	111	69	7	0.2	0.2	N/N
	August 2015	All North Sea 2015	0.00	-0.1	0.9	7	30	21	0.9	0.8	N/N
		Northern SML	0.00	-0.1	0.9	6	30	8	0.9	0.8	N/N
		Northern BML	0.04	-0.9	1.7	35	59	8	0.6	0.6	N/N

4.3.2.5. DOM stoichiometry in August 2014 and August 2015

The C:N stoichiometry of DOM (DOC:DON) were similar in the SML and BML of the northern North Sea, and the DOC:DON ratio was lower in the southern region compared to the northern region (Fig.4.8 c and Table 4.3), implying nitrogen rich DOM in the southern region compared to the northern region. Over the whole of the North Sea region, DOC:DON values in 2014 and 2015 were consistently higher than Redfield (6.6) (19 ± 4 and 17 ± 1, respectively), and higher than 2011 and 2012 (12 ± 1 and 11 ± 2, respectively), indicating DOM was more carbon rich in 2014 and 2015 compared to 2011 and 2012. There was no significant difference between 2014 and 2015 (19 ± 4 and 17 ± 1, respectively, Mann-Whitney, p 0.4).

In the northern North Sea, although DOM was more carbon-rich in 2014 in the SML (21 ± 7) and BML (22 ± 9) compared to 2015 SML (18 ± 5) and BML (17 ± 7) (Table 4.3), the differences were not significant (SML t-test, p 0.4, and BML t-test, p 0.3). In the southern North Sea, DOM was more carbon-rich in 2015 (17 ± 9) relative to 2014 (14 ± 4), respectively), but the differences were not statistically significant (Mann-Whitney, p 0.9).

There were differences in the DOC:DON ratio versus salinity relationship between 2014 and 2015 (Fig.4.9 e and f). In the northern North Sea, the ratio was generally higher in the SML and BML at higher salinities in 2014 (> 20) compared to 2015 (< 20), implying the marine end member was more carbon rich in 2014. In the southern

North Sea, the DOC:DON ratio was similar in both years and generally < 20. Lastly, DOC:DON ratios above the typical North Atlantic end members (13 to 15) (Chaichana et al. in review) were more frequent in 2014 than 2015 in both regions, indicating more carbon rich DOM in 2014 and relatively carbon poor DOM in 2015.

The gradient between DOC and DON was lower than the expected Redfield ratio of 6.6, being 2.3 in 2014 and 4.3 in 2015 (Fig.4.10 a and c). These values are also lower than previously reported by Chaichana et al (in review) for 2011 (6.54) and 2012 (6.94). Interpreting these gradients is not straightforward. To first order, the slopes of the regression line are an indication of organic matter decomposition (Hopkinson et al. 1997), as well as an indication of DOM stoichiometry at low salinity (Chaichana et al. in review), whereby an increase in the gradients is linked to autochthonous DOM production, while lower gradients are due to allochthonous inputs with heavy inorganic nitrogen loads.

The observed low gradient values would therefore suggest either a considerable input of riverine DON and inorganic nitrogen over both regions and more so in 2015, or relatively higher consumption of DOC. However, a corresponding increase in inorganic nutrient concentrations which would accompany high DON inputs was not observed, possibly due to nitrate removal via denitrification in sub oxic rivers and estuaries. The low gradients would also suggest that respiration by heterotrophic bacteria is reducing DOC concentrations while increasing DIC concentrations.

However, DIC measurements for the North Sea during the same sampling period indicate that DIC concentrations decreased during summer (Hartman et al. 2018). To add to the complexity, the gradient for DOC and DON for the northern North Sea in 2014 was at Redfield (6.6, Fig.4.10 b) but this was not the case for the other regions. With a limited salinity range sampled and no data on respiration rates, it is difficult to determine what processes here are causing such low gradients in DOC:DON relationships.

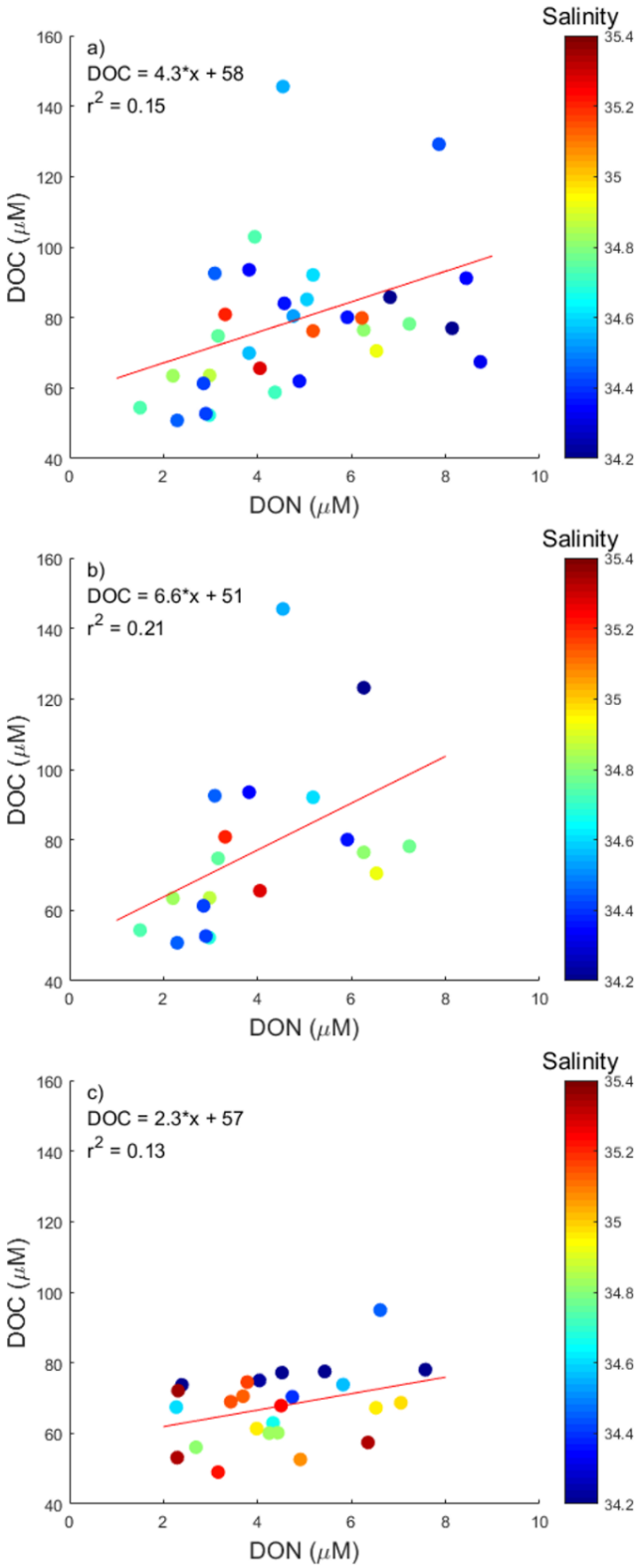

Fig.4.10. Plots of DON vs DOC for the North Sea a) August 2014, b) Northern North Sea August 2014, and c) the North Sea August 2015. Points are coloured by salinity and the equation from results of linear regression are quoted on the plots.

4.3.2.6. Interannual differences and DOM inventories in the North Sea

Differences in the biogeochemistry, hydrography and nutrient regime between 2014 and 2015 appear to be significant although small in some instances. The changes in DOC and DON concentrations across the whole North Sea between August 2014 and August 2015 were on average 11 ± 3 µM and 0.2 ± 0.1 µM, respectively. Given the volume of the North Sea as 42.3 x 10^3 km^3 (Thomas et al. 2005) and assuming a uniform change, this would represent an annual difference of 5.4 ± 1.6 Tg C and 0.12 ± 0.06 Tg N. The differences for DOC were significant (Mann-Whitney, p 0.03) and represent ~ 18% of the yearly estimates of DIC enrichment (~ 30 Tg C yr^{-1}) for the North Sea (Thomas et al. 2005). In contrast, the DON differences were not significant (t-test, p 0.6). Therefore, I will now focus on DOC only.

In contrast to observations reported by Chaichana et al. (in review), in which the differences in DOC in the northern bottom waters were between 20 and 40 µM higher in 2011 than 2012, the differences in DOC between 2014 and 2015 were only 2 µM (Table 4.3) and not significant (Mann-Whitney, p 0.5). However, DOM was more carbon-rich in the northern region SML and BML in 2014 (21 ± 7 and 22 ± 9, respectively) compared to 2015 (18 ± 5 and 17 ± 7, respectively), and the total DOC difference for the whole North Sea was driven mainly by DOC differences in the SML of the northern region (Table 4.3).

4.3.3. Multi-year variations in hydrography, nutrients, DOC and DON in the North Sea from August 2011 to August 2016

4.3.3.1. General trends

Alongside this study for 2014 and 2015, there was hydrographical, inorganic nutrient and DOC and DON data available for 2011 and 2012 (Chaichana et al. in review), and from the LOCATE programme for 2016 (Painter et al. 2018). To compare multi-year trends in August of DOC and DON distribution and explore the processes controlling them, the data from August 2011 to August 2016 are compared in the following section. It is important to note that data collected in each year is not necessarily from the exact same locations. However, data covers both the northern and southern regions, and is therefore broadly representative of hydrography and nutrient dynamics for August of each year.

For the whole of the North Sea, including northern SML and BML and the southern mixed region, there was an overall increase in temperature in August between 2011 and 2016, although salinity was similar across the whole region over the same time period (Table 4.3). In contrast to temperature, DIN and DON concentrations decreased over the whole region between 2011 and 2016, and while DOC concentrations also decreased between 2011 and 2015, then increased in surface waters in 2016 (Table 4.3). DOC:DON ratios increased between 2011 and 2016 (Table 4.3).

T-S diagrams for 2011 to 2016 showed clear patterns of mixing between warmer and fresher with cooler and saltier water over the whole North Sea basin. Surface waters were warmer in the southern region compared to the northern region in all years (Fig.4.11 a - e). Surface waters were fresher in the northern region in 2011, 2012, and 2016 compared to the southern region, but this pattern was less clear in 2014 and 2015 (Fig.4.11 a - e). Northern bottom waters were consistently cooler and saltier in all years, compared to surface waters and to the southern region (Fig.4.11 a - e).

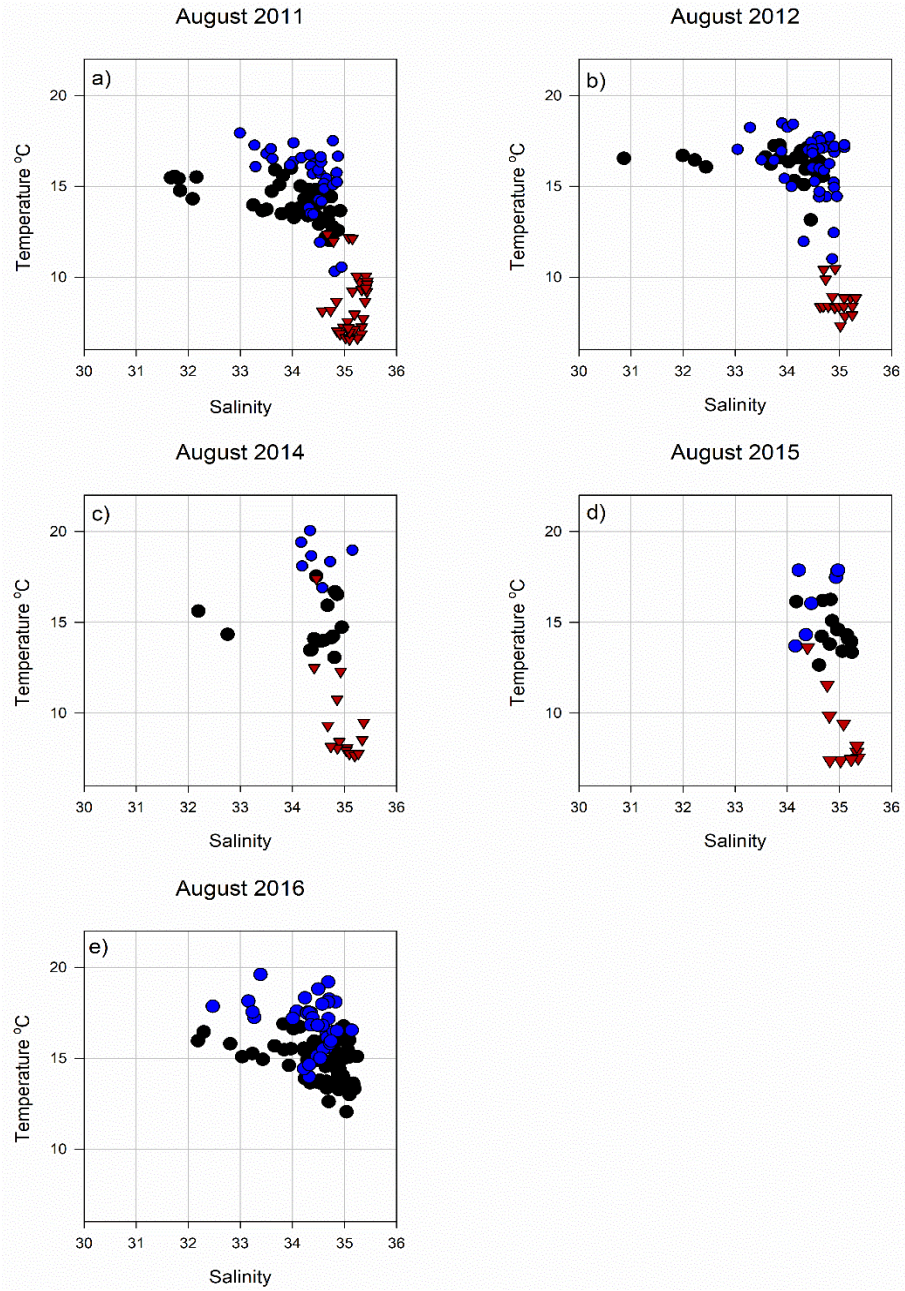

Fig.4.11. T-S plots for August a) 2011, b) 2012, c) 2014, d) 2015 and e) 2016. Regions are coded as follows; northern surface waters (black dots), southern surface waters (blue dots) and northern bottom waters (red triangles).

From the relationship between salinity and DOC, there was an overall pattern of decreasing DOC concentrations with increasing salinity over the whole North Sea basin in all years. However, the relationships were not conservative and varied considerably between years (Fig.4.12 a - e). In surface waters, slopes were generally

steeper in the southern region and ranged from -10 in 2015 to -19 in 2012 (Fig.4.12 d and b). In the northern region, slopes were more variable between years compared to the southern region, and ranged from -2 in 2015, when the salinity range sampled was narrower compared to other years, to -19 in 2014 (Fig.4.12 d and c). There was also variability in the zero-salinity end members (or intercepts), which were consistently higher in surface waters of the southern region in all years compared to the northern region (Fig.4.12 a-e). Freshwater DOC inputs, calculated from the zero-salinity end member, were between 2 and 3.5 times greater in the southern region compared to the northern region (Fig.4.12 d), except for 2016, when freshwater inputs were similar (Fig.4.12 e)

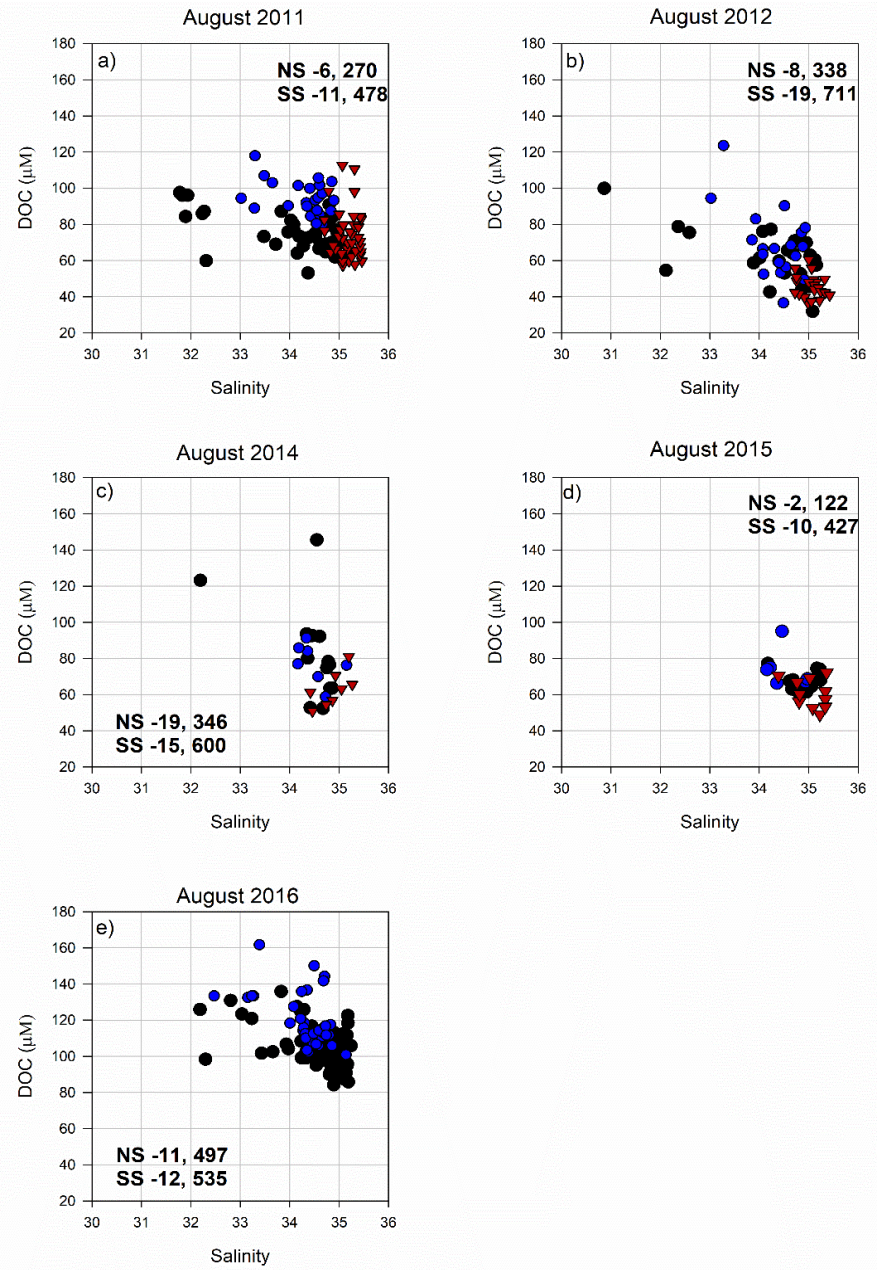

Fig.4.12. Salinity relationship with DOC for August a) 2011, b) 2012, c) 2014, d) 2015 and e) 2016. Regions are coded as follows; northern surface waters (black dots), southern surface waters (blue dots) and northern bottom waters (red triangles). Slope and intercept values are indicated on each plot for the northern North Sea ((NS) and southern North Sea (SS), with the slope (negative number) and intercept (in μM) reported.

Similarly to DOC, the relationship between salinity and DOM stoichiometry was not conservative and variable between years. In general, DOC:DON ratios decreased with increasing salinity (Fig.4.13), indicating that DOM was relatively more carbon rich at the

fresher water end member compared to the higher salinity marine end member. There was large variability in DOC:DON ranges. For example, in 2014 and 2015, DOC:DON ratios ranged by ~ 30 between a salinity range of ~ 3 (Fig.4.13c), compared to 2011, 2012 and 2016 when ratios ranged by < 20 over the same salinity range (Fig.4.13 b). DOC:DON ratios were generally more variable in the bottom waters of the northern sea (Fig4.13 a - d).

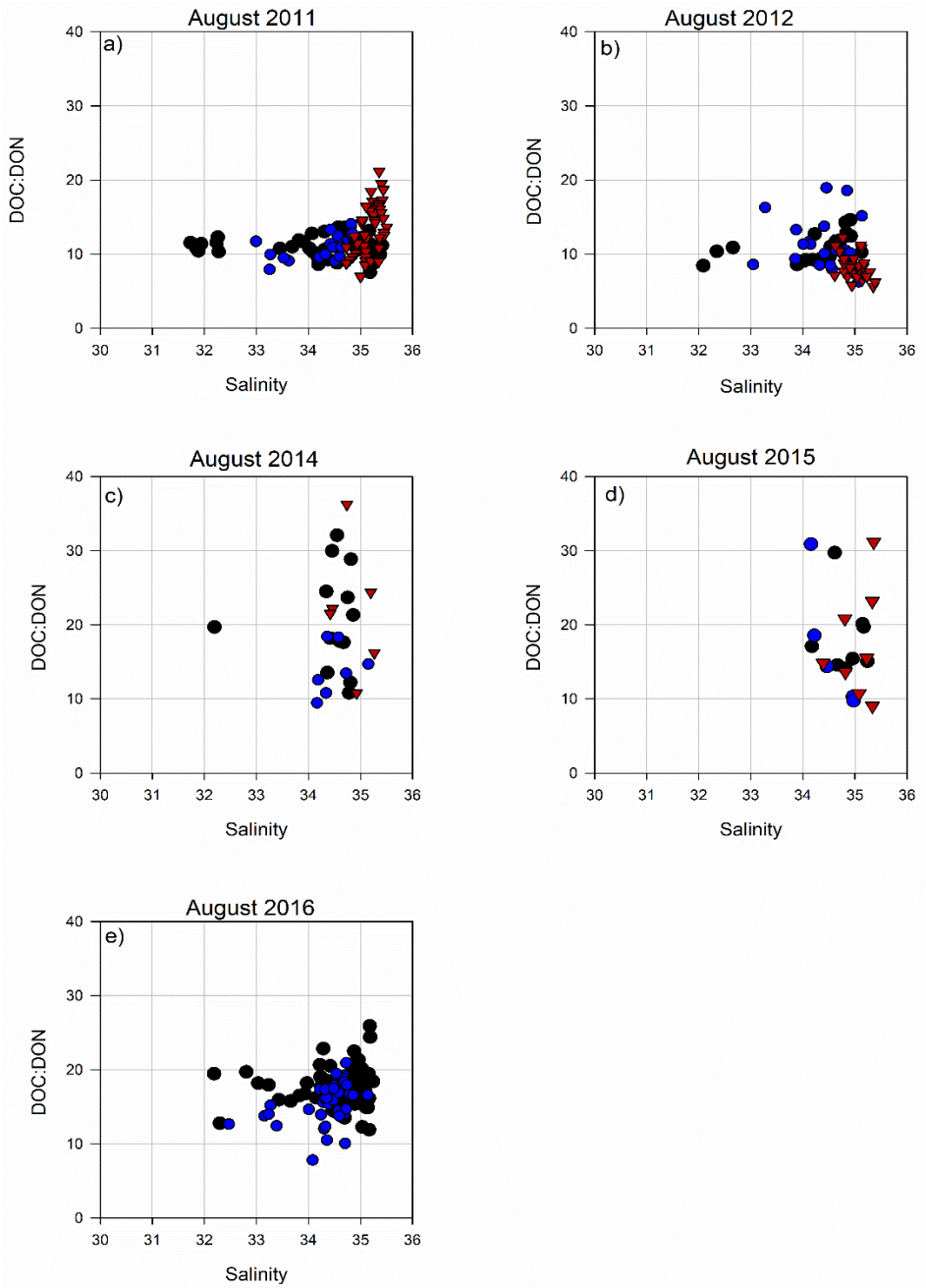

Fig.4.13. Salinity relationship with DOC:DON for August a) 2011, b) 2012, c) 2014, d) 2015 and e) 2016. Regions are coded as follows; northern surface waters (black dots), southern surface waters (blue dots) and northern bottom waters (red triangles).

4.3.3.2. Regional Trends

In the SML of the northern North Sea, temperature and salinity increased overall, and were on average 0.7 °C and 0.3 higher, respectively, in 2016 compared to 2011. Increases in temperature were most pronounced between 2011 and 2012, when surface

waters were over 2 °C warmer in 2012 compared to 2011 (Table 4.3). Increases in salinity were most pronounced between 2014 and 2015, when surface salinity was 0.3 higher in 2015 compared to 2014 (Table 4.3). DIN concentrations decreased overall and were ~ 30% lower in surface waters in 2016 compared to 2011. However, DIN concentrations more than doubled between 2015 and 2016, but remained lower than in 2011 (Fig.4.14 a and Table 4.3).

DOC concentrations generally decreased and were ~ 10% lower in 2015 compared to 2011 (Fig.4.14 b and Table 4.3). DOC increased between 2015 and 2016, and mean concentrations were 38 µM higher in 2016 compared to 2015 (Table 4.3). Similarly to DIN, DON concentrations decreased overall and were ~ 10% lower in 2015 compared to 2011. Similarly to DOC, DON increased between 2015 and 2016, and was 2 µM higher in 2016 compared to 2015 (Fig.4.14 c and Table 4.3). DOC:DON ratios were ~ 60% higher in 2016 than in 2011, indicating DOM was more carbon rich in 2016. Increases in DOC:DON were most pronounced between 2012 and 2014 when values in 2014 were higher by 9 compared to 2012 (Table 4.3).

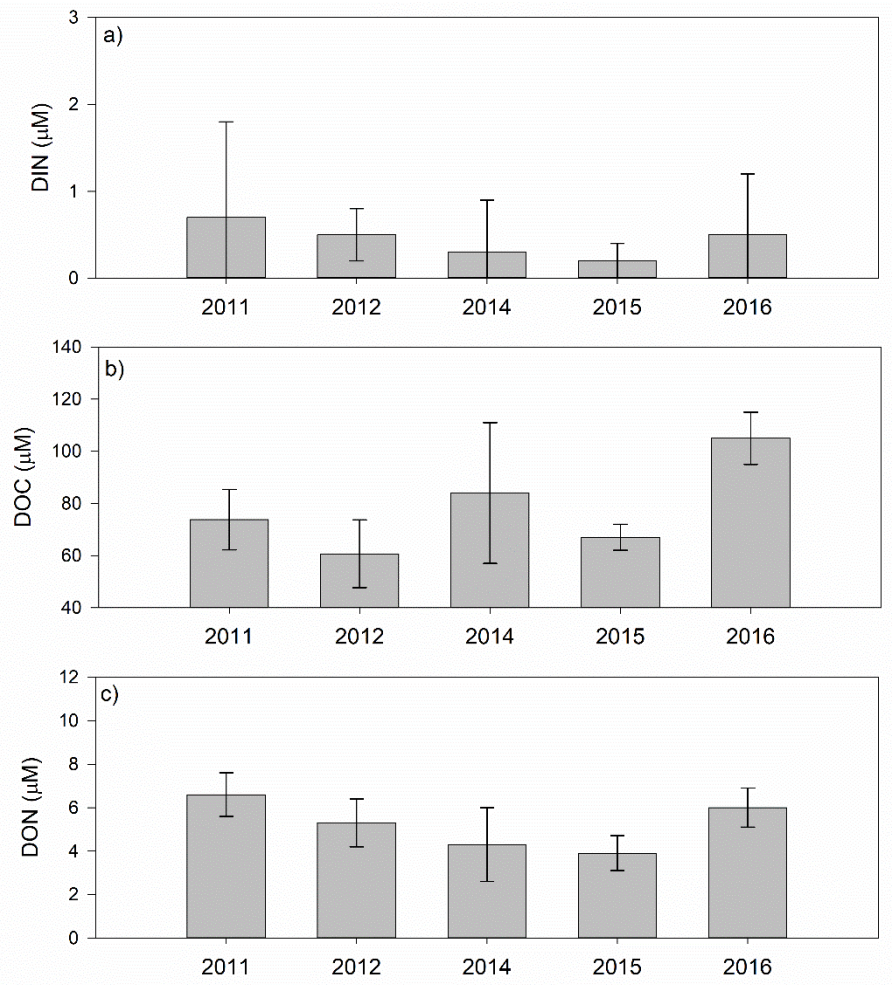

Fig.4.14. The variation in mean ± std dev of a) DIN (µM), b) DOC (µM), and c) DON (µM), in the northern North Sea SML. 2011 and 2012 (Chaichana et al. in review), this study 2014 and 2015, and 2016 LOCATE data (Painter et al. 2018).

In the BML of the northern North Sea, mean temperature increased overall and was 0.6 °C higher in 2015 compared to 2011. Temperature increases were most pronounced between 2011 and 2014, when bottom waters were over 1.2 °C warmer in 2014 compared to 2011 (Table 4.3). The salinity range between 2011 and 2015 was small (0.2) and salinity was similar between 2011 and 2015 (35.1 ± 0.2 and 35.0 ± 0.3, respectively) (Table 4.3). Mean DIN concentrations decreased overall and were ~ 30% lower in bottom waters in 2015 compared to 2011 (Fig.4.15 a and Table 4.3).

Decreases in DIN were most pronounced between 2011 and 2012 when concentrations reduced by nearly half (9.9 ± 4.4 µM and 5.5 ± 3.0 µM, respectively).

Similarly to DIN, mean DOC concentrations decreased overall and were 18% lower in 2015 compared to 2011. Decreases in DOC were most pronounced between 2011 and 2012 when concentrations were 27 µM lower in 2012 compared to 2011 (Fig.4.15 b and Table 4.3). Similarly to DIN and DOC, mean DON concentrations decreased overall and were ~ 35% lower in 2015 compared to 2011. Similar decreases in DON were observed between 2012 and 2014 when concentrations were 2 µM lower in 2014 compared to 2012 (Fig.4.15 c and Table 4.3). In contrast to DIN, DOC and DON, mean DOC:DON ratios increased overall and were 30% higher in 2015 compared to 2011, indicating DOM was more carbon rich in bottom waters in 2015. Increases in DOC:DON values were most pronounced between 2012 and 2015 when values were higher by 13 in 2014 compared it 2012 (Table 4.3)

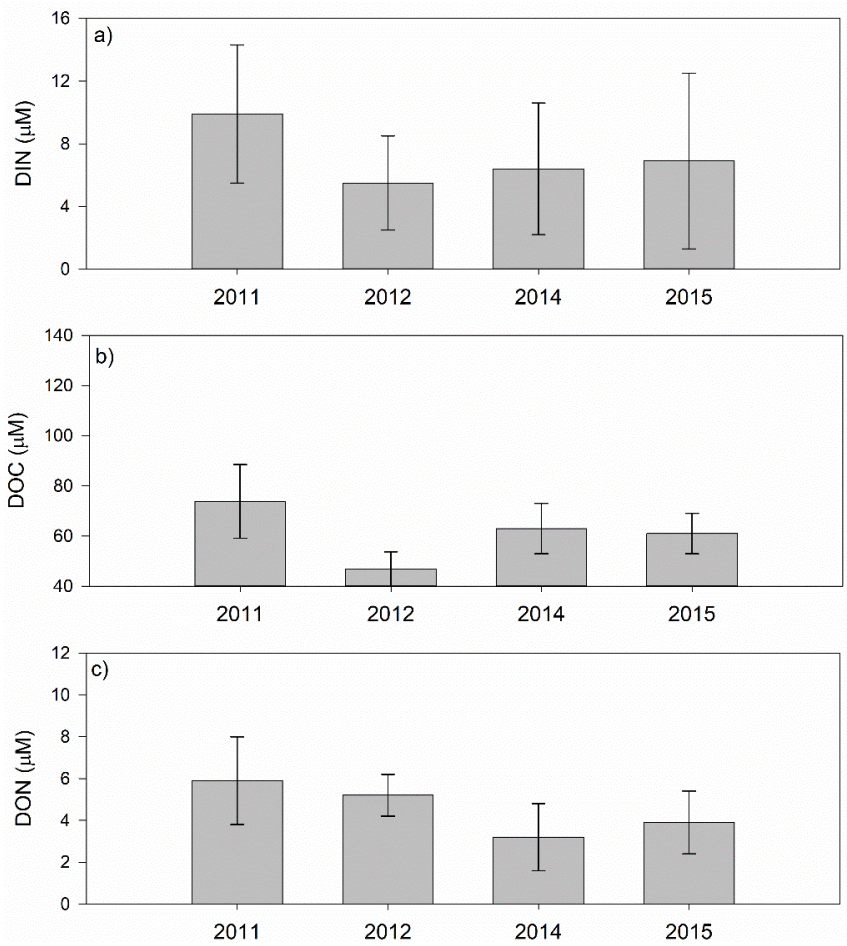

Fig.4.15. The variation in mean ± std dev of a) DIN (µM), b) DOC (µM), and c) DON (µM), in the northern North Sea BML. 2011 and 2012 (Chaichana et al. in review), this study 2014 and 2015.

In the mixed southern North Sea, mean temperature was 1.5 °C higher in 2016 compared to 2011. Increases in temperature were most pronounced between 2011 and 2014, when the southern North Sea was over 3 °C warmer in 2014 compared to 2011 (Table 4.3). There was an overall increase in salinity between 2011 and 2016, however the salinity range was small (0.3) and salinity was the same in 2011 and 2016 (34.3 ± 0.5) (Table 4.3). Mean DIN concentrations decreased overall and were over 50% lower in 2016 compared to 2011 (Fig.4.16 a and Table 4.3). Decreases in DIN were most

pronounced between 2011 and 2012 when concentrations reduced by over half (1.5 ± 1.1 µM and 0.8 ± 1.2 µM, respectively).

Mean DOC concentrations decreased overall and were ~ 25% lower in 2015 compared to 2011. However, DOC increased between 2015 and 2016, and mean concentrations were nearly 50 µM higher in 2016 compared to 2015 (Fig.4.16 b and Table 4.3). Similarly to DIN and DOC, mean DON concentrations decreased overall and were ~ 10% lower in 2016 compared to 2011. Similarly to DOC, DON increased between 2015 and 2016, and concentrations were ~ 3 µM higher in 2016 compared to 2015 (Fig.4.16 c and Table 4.3). Mean DOC:DON ratios increased overall and were ~ 50% higher in 2016 than in 2011, indicating DOM was more carbon rich in 2016. Increases in DOC:DON were most pronounced between 2011 and 2015 when values in 2015 were higher by 6 compared to 2011 (Table 4.3).

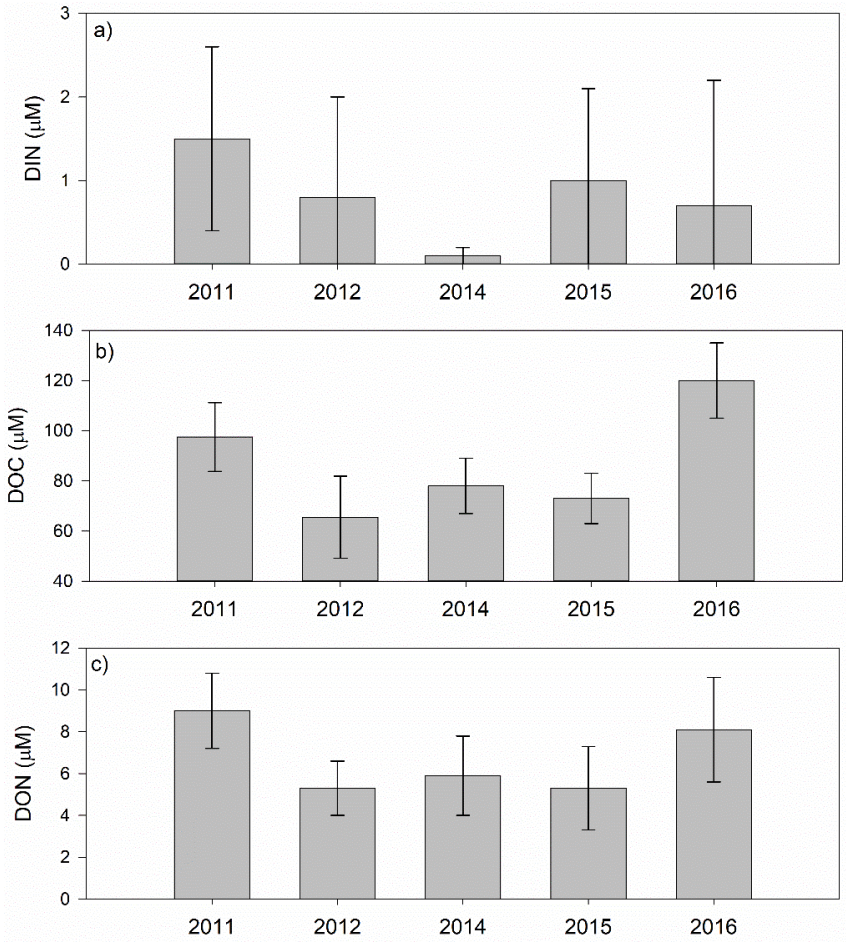

Fig.4.16. The variation in surface a) DIN (µM), b) DOC (µM), and c) DON (µM), in the southern North Sea. 2011 and 2012 (Chaichana et al. in review), this study 2014 and 2015, and 2016 LOCATE data (Painter et al. 2018).

4.4. Discussion

Comparison of nutrients, DOC and DON in the month of August from 2011 to 2016 reveals a broad decline in DIN, DOC and DON. Overall, DIN decreased by 30% in the northern North Sea and 50% in the southern North Sea between 2011 and 2016. DOC and DON concentrations decreased by between 10 and 25% and 10 and 35%, respectively, between 2011 and 2015, but increased in 2016. The nutrient, DOC and DON concentrations measured during the observational campaigns represents the net of processes that supply

and remove these dissolved properties to and from the environment. In the North Sea, there are three principle processes that control the distribution and variability in nutrients, DOC and DON, specifically (a) input of nutrients, DOC and DON from rivers, (b) exchange with the North Atlantic and (c) internal processes that retain, add or remove nutrients, DOC and DON from the marine environment. Previous studies have explained the north-south gradient in DOM as being due to input of terrestrially-derived DOM in the southern region, thus elevating DOM concentrations. Here, I will discuss these processes further.

4.4.1. Riverine inputs of nutrient, DOC and DON to the North Sea

Previous observations of DOM in the North Sea have shown a concentration gradient between higher DOM in the southern well mixed region, particularly around coastal areas, and lower DOM in the northern seasonally stratified region (Suratman et al. 2008, Suratman et al. 2009, Moschonas et al. 2015, Chaichana et al. in review, Painter et al. 2018). The southern North Sea receives the majority of the 300 km^3 of annual freshwater inputs from surrounding rivers such as the Thames, the Rhine, and the Elbe as well as exchanges with the English Channel (Thomas et al. 2005).

These riverine inputs mean that the southern North Sea is strongly affected by the terrestrial inputs of organic and inorganic nutrients (Weston et al. 2004, Skogen and Mathisen 2009), as indicated by a significant inverse relationship between DOM and

salinity (R^2 = 0.24, Table 4.2). In the southern region, DOC concentrations range from 68 to 318 µM and over 400 µM in areas close to the coast in the Wadden Sea (Suratman et al. 2009). Similarly, DON is also generally higher at coastal regions and concentrations range from 4.7 to 15.2 µM (Suratman et al. 2008). In contrast, the seasonally stratified northern region is strongly influenced by higher salinity North Atlantic Ocean water (Thomas et al. 2004, Thomas et al. 2005, Thomas et al. 2009). Summertime DOC and DON concentrations in the SML of the northern North Sea range from 51 to 104 µM and 3.0 to 8.7 µM, respectively, and by between 53 and 120 µM and 3.0 to 11.7 in the BML (Chaichana et al. in review).

Estimates of freshwater inputs at zero-salinity were extrapolated from salinity DOM relationships to assess the seasonality in DOC and DON inputs in the southern North Sea, and the inter-annual variability in inputs in 2014 and 2015, as well as over the longer time period assessed. Although there was no clear seasonal DOM cycle observed during the period sampled, seasonality in freshwater DOC inputs were evident. For example, in the southern North Sea were freshwater inputs were significantly greater in spring and summer compared to winter (p (intercept) < 0.05)). The spring input of DOM is also reflected in elevated DON concentrations observed at coastal stations affected by discharges from the river Rhine (Van Engeland et al. 2010).

Although DOC and DON concentrations for the August 2011-2012 and 2014-2015 periods were similar (Table 4.4), the freshwater source C:N ratio for the combined surveys of 2011- 2012 was higher than the 2014-2015 surveys (10 and 7, respectively), suggestive of interannual variability in DOC and DON freshwater inputs. Indeed, estimates of freshwater DOC inputs into surface waters of the North Sea were over two-fold higher in 2014 than in 2015. This wide range (from 549 to 1341 μM) in freshwater inputs highlights the inter-annual variability in potential carbon input into the North Sea from rivers and thus control this may have on DOC concentrations in the North Sea.

Although to first order, the slope of DOC DON element-element plots indicate the stoichiometry of DOM production and consumption (Hopkinson et al. 1997). Chaichana et al. (in review), noted there were striking differences in the gradients between salinity and DOC:DON ratio between years sampled, and in 2011 the ratio increased with increasing salinity from 7 to values of 23, which were higher than typical North Atlantic end members of 13 to 15. In contrast, the DOC:DON ratio decreased to below 10 at high salinities in the BML in 2012, thus reflecting the impact of riverine inputs on altering the DOC:DON ratio in the North Sea.

Following the OSPAR convention of 1992, the OSPAR commission was established and adopted strategies in 1998 to assess eutrophication of European surface waters. In the North Sea a number of Ecological Quality Objectives were identified to assess eutrophication, and a target of a 50% reduction in inorganic nitrogen

and phosphate in coastal areas from 1985 levels was recommended (Skogen and Mathisen 2009). Following the implementation of a number of EU Directives (e.g. The Water Framework Directive 2000/60/EC and The Nitrates Directive 1991) the coastal North Sea contemporary riverine nitrogen and phosphate fluxes have decreased since eutrophication periods by 21% and 60%, respectively (Artioli et al. 2008).

The decreasing DIN trend observed between 2011 and 2016 may be due to the effectiveness of these water quality policies. However, inputs to the coastal North Sea from rivers have remained the same (Artioli et al. 2008), indicating that reducing river loads has a small effect on nutrients in open ocean sites (Skogen and Mathisen 2009). On longer timescales, reduced DOM in the Wadden Sea has been linked to a decline in primary production resulting from a reduction in inputs of riverine nitrogen loads (van Beusekom and de Jonge 2002). The gradual carbon enrichment of DOM between 2011 and 2016 may be an indirect result of a decline in riverine nitrogen inputs, leading to a loss of DON due to onset of nitrogen-limiting conditions.

4.4.2. Exchange between the North Sea and North Atlantic

Although concentrations of both DOC and DON in August decreased similar to DIN, the long-term trends were more variable (Fig.4.14, 4.15 and 4.16). There was a marked increase in DOC to > 100 μM and DON to > 6 μM in 2016 (Table 4.3). However, one of the

most striking features was the difference in the DOC inventories between August 2011 and August 2012, as reported by Chaichana et al. (in review). Across the whole North Sea basin (including northern North Sea SML and BML, and the southern region) there was a difference in DOC of between 20 and 40 µM, equivalent to between 10 and 20 Tg C. This was comparable to the strength of North Sea DIC enrichment pump of 30 Tg C yr^{-1} and of the same order of magnitude for annual CO_2 uptake in the northern North Sea (Thomas et al. 2005). The between year differences in DOC were statistically significant and Chaichana et al. (in review) proposed that the differences were driven mainly by wintertime flushing of the North Sea with low DOC North Atlantic water, and the export of high North Sea DOC to the North Atlantic during strong shelf edge exchange, as the NAO index was strongly positive in the intervening winter (2011/2012).

Given the volume of the entire North Sea (42.3 x 10^3 km^3), the transport required to flush the whole basin over the 90 day winter period is 5.4 Sv (1 Sv = 10^6 m^3 s^{-1}). This is three times higher than the modelled estimates of yearly transport in the outflow from the Norwegian trench (1.5 Sv) between 1995 and 1996 (Kuhn et al. 2010). However, flushing or turnover times vary throughout the North Sea and vary with changes in wind forcing (Prandle 1984). Under average wind conditions, turnover times for the southern regions (see sub-regions 3, 4, 5 and 8 in Prandle 1984) range from between 58 to 109 days. For the northern region (see sub-regions 1, 2, 3, 6, 7, and

8 in Prandle 1984) turnover times range from between 72 and 159 days. Under wintertime conditions, turnover times are reduced considerably and water mass renewal of the whole North Sea basin can occur within between 20 and 60 days (ICES 1983). Thus, it is possible that a relatively rapid exchange between the North Sea and the North Atlantic could essentially 'reset' the biogeochemical properties in the North Sea. However, sampling on the Cefas survey takes place in August and thus represents the remnants of this flushing after biological activity has modified the signals during the spring bloom and summer stratified period. To accurately capture these flushing events and their impact on the physical and biogeochemical properties of the North Sea, a similar sampling campaign would need to be conducted in winter and/or spring.

DOC was on average 11 ± 2 µM lower in 2015 than 2014, equivalent to 5.4 ± 1.1 Tg C which is ~ 18% of the yearly estimates of DIC enrichment. Differences in the DOC inventories between 2014 and 2015 were significant (Mann-Whitney, p 0.03) but were lower than differences observed between 2011 and 2012. There is no data for the intervening winter (2014/2015), however DOC concentrations in the southern North Sea for the preceding winter (2013/2014) were similar to August 2014 concentrations (81 µM and 78 µM, respectively, Table 4.3). As in the winter of 2011/2012, the NAO was strongly positive in 2013/2014 (3.6) (Hurrell 2017), which would indicate strong shelf edge exchange between 2014 and 2015,

resulting in exchange of high North Sea DOC with renewal of low North Atlantic DOC.

DIN and the inorganic N:P ratios in the BML of the northern region were notably lower in 2012 compared to 2011, reflecting differences in water exchange with the North Atlantic as well as internal variability in productivity, plankton community structure and nutrient limitation. In contrast, differences in nutrient (N+N and silicate (data not shown)) concentrations in the BML in 2014 and 2015 were small (0.5 µM and 1.4 µM, respectively), and N:P ratios were the same (9), supporting the suggestion of limited renewal of BML waters from exchange with the North Atlantic.

Finally, it is worth considering that the winter NAO index was negative in the two years preceding 2011 (Hurrell 2017), which would suggest less wind forcing and limited exchange between the North Atlantic and North Sea and reduced water mass renewal, thus allowing DOM to accumulate in the North Sea over multi-year timescales, before flushing during winter 2011/2012. In contrast, the NAO index was strongly positive in winter 2013/2014 and 2014/2015 (3.6 and 4.6, respectively (Hurrell 2017)), therefore strong shelf exchange in the intervening winters would have prevented the inter-annual accumulation of DOM, and subsequent changes in concentrations would be relatively small.

However, the NAO was also positive (1.8) in the winter preceding the high DOC and DON concentrations observed in

August 2016 (Painter et al., 2017), suggesting a combination of external inputs, internal production and removal processes alongside DOM loss via transport contribute to the inter-annual variability in DOM observed between 2011 and 2016.

4.4.3. Role of biological processes in controlling nutrients, DOC and DON in the North Sea

The North Sea DIN pool can also be strongly reduced during high loss by transport out of the North Sea via the Norwegian Trench (Lenhart et al. 2004) and interannual variability in nutrient concentrations are also correlated with the NAO index, while increases in primary production also lead to a decline in nutrient concentrations (Frigstad et al. 2013), Furthermore, denitrification in the southern North Sea can account for the loss of between 20 and 60% of winter nitrate concentrations (Hydes et al. 1999).

Temperature in the southern North Sea is characteristically higher than surface waters of the northern region (Clargo et al. 2015), due to the contrasting heating and cooling regimes of the southern shallow (50 m) well-mixed water column which warms faster than the deeper (> 150 m) northern seasonally stratifying water column (Thomas et al. 2005). There were significant differences in temperature (t-test, p 0.02) between 2014 and 2015, when waters were on average 2.2 °C cooler in the southern region (Table 4.3). Cooler years have a deeper mixed layer which would delay the onset of stratification and subsequent phytoplankton bloom (Bernardello et

al. 2012) and subsequently DOM production. In the northern North Sea, a sea surface temperature change of 2 °C is suggested to have led to reduction of primary production of 25% due to enhancement of stratification over the shelf break and thus nutrient limitation due to reduced advection from the North Atlantic (Emeis et al. 2015). However, these responses to changing temperatures would be more evident in the stratifying northern region.

A recent synthesis of data from the North sea found that sea surface warming as well as changes to anthropogenic nutrient inputs have resulted in a decline in primary production by between 33% and 50% from the 1990s to 2013 (Capuzzo et al. 2018). Although the main nutrient source is inflow of North Atlantic water, riverine nutrient inputs can increase new potential production, estimated from nutrient inventories, by over four-fold in the southern region from 100 g C m^{-2} yr^{-1} to 430 g C m^{-2} yr^{-1} (Emeis et al. 2015). Another mechanism for the loss of DOC and DON, is the complexation and coagulation of DOM to larger size molecules which are then functionally larger than operational definition separating dissolved (0.7 µm) from particulates (> 0.7 µm), however, this is more likely to occur in coastal areas and estuaries when flocculation occurs as terrestrial humic DOM crosses salinity boundaries (Frigstad et al. 2013).

While many studies have focussed on the seasonal cycling of DON in the North Sea, much less is known about how DOC varies seasonally in the southern mixed region. Reinthaler et al. (2005) found DOC was highest during winter and twice that of spring

concentrations (187 µM and 87 µM, respectively). However, no clear trends were discernible over a seasonal cycle. In contrast, Van Engeland et al. (2010) found that nearly 50% of DOC variability in the southern North Sea away from coasts could be explained by seasonality, whereas DON variability was controlled by processes occurring on timescales shorter than seasons.

In this study, there were no clear seasonal trends in DOC and DON, concentrations did vary between seasons and although DOC was highest in spring and DON highest in summer, differences between seasons were not significant (t-test and Mann-Whitney, $p > 0.05$). DOC and DON were uncoupled, and DOC was highest and DON lowest in spring. This is contrary to other studies that found that DON increased by 5 µM during spring and was minimum in autumn and winter (Johnson et al. 2013). As with observations for the English Channel and Celtic Sea (Carr et al. 2018), the uncoupling of DOC and DON in spring is indicative of the use of DON as a nitrogen source further indicated by the spring maximum of DOC:DON ratios (Table 4.3). Bacteria and phytoplankton both compete for labile DON and indeed, it has been shown that under high biomass and low nutrient conditions, phytoplankton can account for up to 80% of DON uptake, with bacterial DON uptake dominating during autumn and winter (Moneta et al. 2014).

4.5. Conclusions

Given the complex nature of DOM and the dynamical physical and biogeochemical processes governing its production, consumption and transport, capturing long-term trends in its distribution is problematic. Even when datasets are complete and collected at the same spatial resolution at the same time of year, and cover a period of a decade, often no discernible trends can be identified (Van Engeland et al. 2010), suggesting that variability in DOM is driven on shorter, seasonal or interannual, timescales.

The North Sea is a well-studied region of the Northwest European Shelf, and as in the other regions studied (Chapter 3), the broad scale pattern of DOM distribution in the North Sea fits with global trends. DOC and DON concentrations were higher in the southern region reflecting the influence of terrestrial inputs and riverine supply of organic and inorganic nutrients, and lower in the northern region due to inputs of oceanic DOM. In the well-mixed waters of the southern region, a clear seasonal cycle of inorganic nutrient distribution was observed. However, there was no clear trend in seasonal DOC and DON production. DOC and DON were decoupled, and although maximum DOC concentrations were observed during spring, differences between seasons were not statistically significant.

As part of the long-term ICES international bottom trawl surveys, data from the annual summer Cefas cruises provide an

excellent opportunity for assessing changes in the marine environment that have significant regional and global implications on annual and interannual scales. The change in DOC inventories between 2011 and 2012 identified by (Chaichana et al. in review) was of the same order of magnitude as northern North Sea yearly CO_2 uptake. The change in DOC inventories in the years following (2014 and 2015) was much less by comparison, however, it was still significant, representing around 18% of yearly North Sea DIC enrichment, and further illustrating the dynamic nature of DOM on annual timescales.

Identifying long-term DOM trends was not straightforward, and although DOC and DON concentrations showed an overall decline, the declining trends were not uniform between years and concentrations were exceptionally high in 2016 compared to other years. However, variability in DOM distributions both seasonally and interannually could be linked to key processes. These included external inputs from rivers, autochthonous production, in particular of DOC which peaked in spring presumably due to phytoplankton productivity, and its removal driven by biological processes such as respiration, and physical processes which transport DOM to surrounding regions, in particular the North Atlantic where enhanced exchanges with the North Sea are linked to positive phases of the NAO enabling the transport required (5.4 Sv) for wintertime flushing of the whole the North Sea basin.

The North Sea is considered a highly efficient shelf pump via the removal of CO_2 through the export of DIC in the BML of the stratified northern region, with the role of organic matter considered negligible in this export (Thomas et al., 2004, Thomas et al., 2005). However, from observations of inter-annual changes in DOC stock between August 2011 and 2012, and August 2014 and 2015, estimates of DOC export during winter-time flushing can account for between 18 and 67% of the annual DIC enrichment pump. Measurements of DOM alongside water movement i.e. transport, in particularly in the BML of the northern North Sea, are needed to constrain these estimates, and better understand the role of DOM in the North Sea shelf sea pump.

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Chapter 5

Seasonal and annual DOC fluxes across the Northwest European Shelf

5.1. Introduction

In the open ocean, the export of carbon fixed into organic biomass maintains a vertical gradient in DIC concentrations which in turn helps to regulate atmospheric CO_2 levels (Carlson et al. 1994). Organic matter export is considered as the fraction of particulate organic matter (POM) and dissolved organic matter (DOM), that is produced primarily by phytoplankton in the stratified surface layer, that either sinks as POM or is advected and mixed into the ocean interior as DOC, where it is consumed and respired by heterotrophic bacteria. Only ~1% of POM leaving the surface reaches the seabed (Ducklow et al. 2001) with contributions to this export from various phytoplankton size classes (Richardson and Jackson 2007).

Shelf seas are much shallower (< 200 m) than open ocean systems (> 3000 m). Thus, the shallow water column and intense physical exchange between the surface mixed layer (SML) and bottom mixed layer (BML) means that vertical export is more difficult to define in a shelf sea. POM that sinks to the BML is often resuspended many times by tides before it is incorporated into sedimentary cycling. For DOC, the vertical gradient is weak because

exchange at the thermocline erodes the gradient created by net production in the SML and net consumption in the BML. DOC in excess of heterotopic carbon demand and DOC that is respired to DIC is retained in surface waters during winter mixing and convective overturning (Thomas et al. 2005, Simpson and Sharples 2012). Therefore, rather than a vertical flux, DOC fluxes and export in shelf seas require a horizontal flux or movement from on-shelf to off-shelf waters which can occur in both surface waters as DOC, or in bottom waters as DOC or DIC (Huthnance 1997, Thomas et al. 2005, Huthnance 2010, Sharples et al. 2017). Furthermore, shelf seas are the interface between land and the ocean and receive substantial inputs of external or terrestrial DOC via rivers, estuaries and the coastal zone (Seitzinger et al. 2005, Seitzinger and Harrison 2008, Raymond and Spencer 2015).

There are a number physical processes that facilitate exchange between shelf seas and the open ocean (Pingree 1980, Pingree and Lecann 1989, Huthnance et al. 2009, Sharples et al. 2009). For example, globally, deep ocean bottom water can be transported on-shelf through upwelling and wind-driven Ekman transport (Ruiz-Castillo et al. in press). Conversely, dense on-shelf bottom water can cascade off-shelf as observed in the Malin-Hebrides Shelf (Hill et al. 1998) and the Gulf of California (Lavin et al. 2014) and via Ekman drain (Souza et al. 2001). Internal tides in stratifying shelf seas provide a mechanism for exchange along the seasonal thermocline and can travel on-shelf for distances > 150 km

(Sharples et al. 2001, Inall et al. 2011). And in surface waters, wind forcing provides the main mechanism for cross-shelf exchange (Huthnance 2010).

For quantifying DOC fluxes from shelf seas, we can use the gradient between DOC concentrations on-shelf and off-shelf and apply an exchange term to incorporate waters exchanging between shelf seas and the off-shelf waters to estimate fluxes (Barron and Duarte 2015). Furthermore, by looking at the optical properties of DOM, we can identify the marine and terrestrial end members and through characterisation of the likely source (Coble 1996, Stedmon et al. 2000, Murphy et al. 2008, Stedmon et al. 2011), we can estimate the contribution of terrestrially-derived DOC to the flux (Carr et al. 2018).

In this final chapter, I will quantify the seasonal fluxes of DOC in the Celtic Sea and compare the annual net fluxes of DOC between the North Atlantic and the Malin-Hebrides Shelf and Celtic Sea.

5.2. Materials and methods

5.2.1. Sampling, collection and analysis of inorganic nutrients, DOC and DON

The sampling programme for the Malin-Hebrides Shelf, Celtic Sea and off-shelf regions is as described in Chapter 3, Section 3.2.1, and sample collection and analysis is as described in Chapter 3, Section 3.2.2.

5.2.2. Region division for data analysis

On-shelf and off-shelf regions were separated by the 200 m contour for both the Malin-Hebrides Shelf and Celtic Sea (Fig.5.1). On-shelf stations were defined as stations where water column depths were < 200 m (Fig.5.1. green dots and diamonds), and off-shelf water column depths > 200 m (black dots and diamonds).

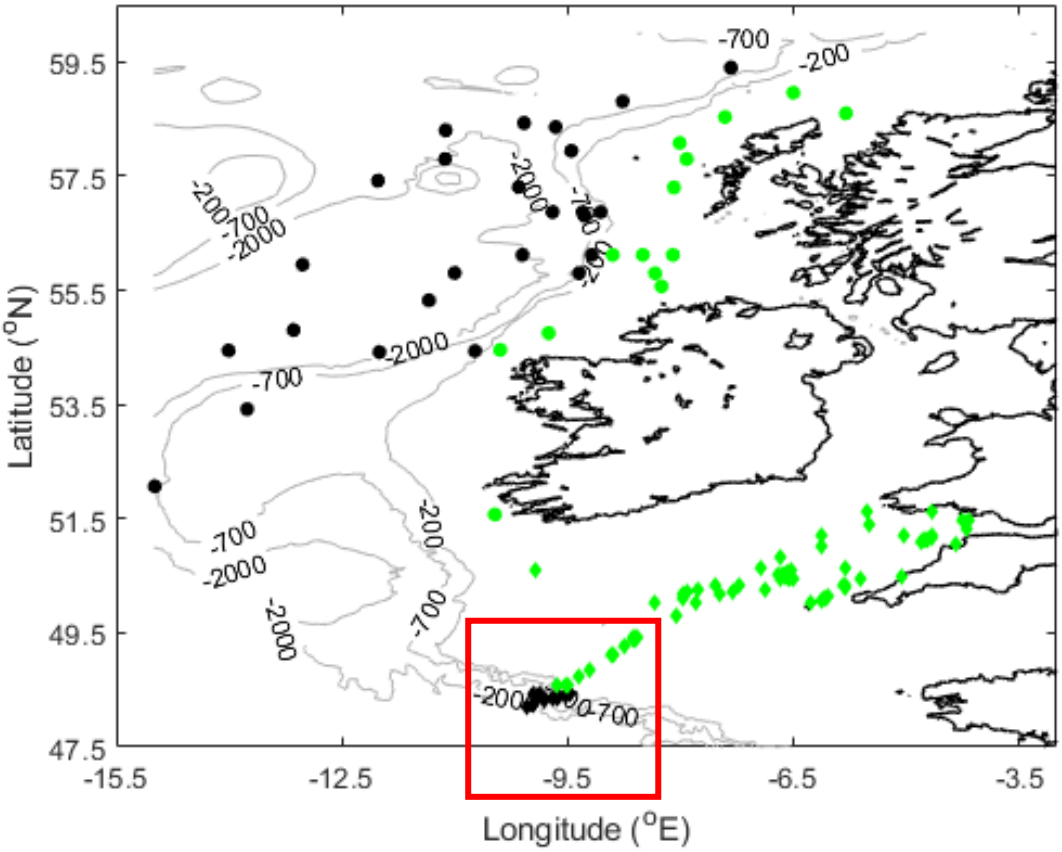

Fig.5.1. Stations sampled on the Malin-Hebrides on-shelf (green dots) and off-shelf in the North Atlantic (back dots), and Celtic Sea on-shelf (green diamonds) and off-shelf in the North Atlantic (back diamonds). Red box highlights the region south of the central Celtic Sea (CCS).

5.2.3. Seasonal surface and annual water column flux calculations

The mean DOC concentration in the upper 30 m of the water column was used in order to enable comparisons between on-shelf

and off-shelf regions and for estimates of seasonal surface DOM flux calculations in the Celtic Sea. The surface 30 m incorporates the productive surface layers in both the on-shelf and off-shelf regions, and is the approximate depth at which the seasonal thermocline at the shelf break of the Celtic Sea station was positioned during the sampling period (Carr et al. 2018). However, there is great uncertainty about how much of the shelf sea, especially the Celtic Sea, physically exchanges with the open ocean. Therefore, two estimates for DOC fluxes from the Celtic Sea are provided. The first includes the mean DOC for the entire on-shelf region sampled in the Celtic Sea. The second estimate considers the mean DOC concentration south of the Central Celtic Sea (CCS) and assumes that only this part of the Celtic Sea exchanges with the North Atlantic (Fig.5.1).

For overall comparisons between on-shelf and off-shelf regions, and for annual flux calculations, the mean DOC concentration for the whole on-shelf shelf water column was included to incorporate waters that are likely to exchange in both the surface layer and bottom layer, and thus represent the net flux. The deepest depths sampled for the Malin-Hebrides was at ~130 m, and at ~ 200 m for the Celtic Sea.

Each nutrient displayed a typical vertical distribution in both the Malin-Hebrides on and off-shelf and Celtic Sea on and off-shelf regions. N+N concentrations were low in the surface and increased

with depth, and DOC and DON concentrations were highest in the surface and decreased with depth (Fig.5.2).

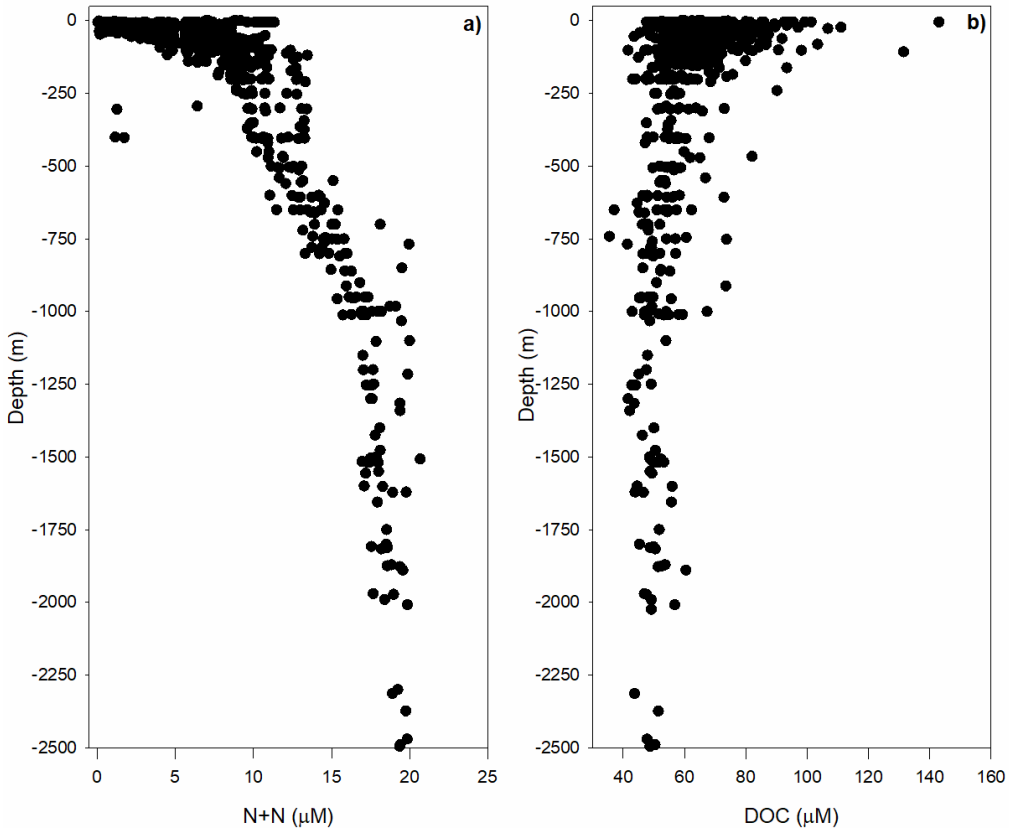

Fig.5.2. Profiles of a) N+N (µM) and b) DOC (µM) for the Celtic Sea and Malin-Hebrides Shelf.

The fluxes of DOC from the Celtic Sea and Malin-Hebrides Shelf to the North Atlantic were calculated from a simple equation (5.1) proposed by Barron and Duarte (2015) for estimating global DOC export from the coastal to the open ocean:

$$\text{DOC export} = (DOC_{On} - DOC_{Off}) \times E \qquad (5.1)$$

where DOC_{On} represents the mean DOC concentrations on-shelf and DOC_{Off} represents the mean DOC concentrations off-shelf (µM), and *E* is the annual water exchange between the on-shelf and off-shelf regions taken from (Huthnance et al. 2009, Barron and Duarte 2015,

Painter et al. 2016). The errors in the estimates are calculated from the mean of the combined coefficient of variation (CV) for each difference. Concentrations have been converted to Gg C yr^{-1} to enable comparisons with global export estimates.

5.3. Results

5.3.1. Seasonality in DOC distribution

5.3.1.1. Hydrography and inorganic nutrients

In the absence of summer data for the Malin-Hebrides and winter data for the Celtic Sea off-shelf regions, the following section compares seasonality between the on and off-shelf and Malin-Hebrides and Celtic Sea regions.

Overall, waters were cooler and fresher on-shelf compared to off-shelf. Mean temperatures on-shelf ranged from 9.1 °C to 16.1 °C and were highest in summer in the Celtic Sea and lowest in spring on the Malin-Hebrides Shelf (Table 5.1). Off-shelf, the mean temperature ranged from 9.8 °C to 16.2 °C and were highest in summer off-shelf of the Celtic Sea and lowest in spring in the Malin-Hebrides off-shelf region (Fig.5.3 a and Table 5.1). Mean salinity ranged from 35.1 to 35.3 on-shelf and was highest in winter in the Celtic Sea and lowest in both regions during different seasons (Table 5.3). Off-shelf, mean salinities ranged from 35.4 and 35.6 and were highest in summer in the Celtic Sea and lowest in spring in the Malin-Hebrides off-shelf region (Table 5.1). Both temperature and salinity

were more variable on-shelf in the Celtic Sea and ranged by up to 7 °C in spring, and salinity by over 1.4 in summer, compared to 1.4 °C and 0.9 for the same seasons in the Malin-Hebrides Shelf (Table 5.1).

Overall, N+N concentrations were higher off-shelf compared to on-shelf (Fig.5.3b). Mean on-shelf N+N ranged from 0.6 µM to 10.1 µM and was highest in winter and lowest in summer in the Malin-Hebrides Shelf (Table 5.1). Off-shelf, mean N+N ranged from 1.1 µM to 10.6 µM and was highest in winter in the Malin-Hebrides off-shelf region and lowest in summer off-shelf of the Celtic Sea (Table 5.1). N+N concentrations were more variable on-shelf in the Celtic Sea and ranged by 8.3 µM in spring, compared to 4.5 µM for the same season in the Malin-Hebrides Shelf (Table 5.3).

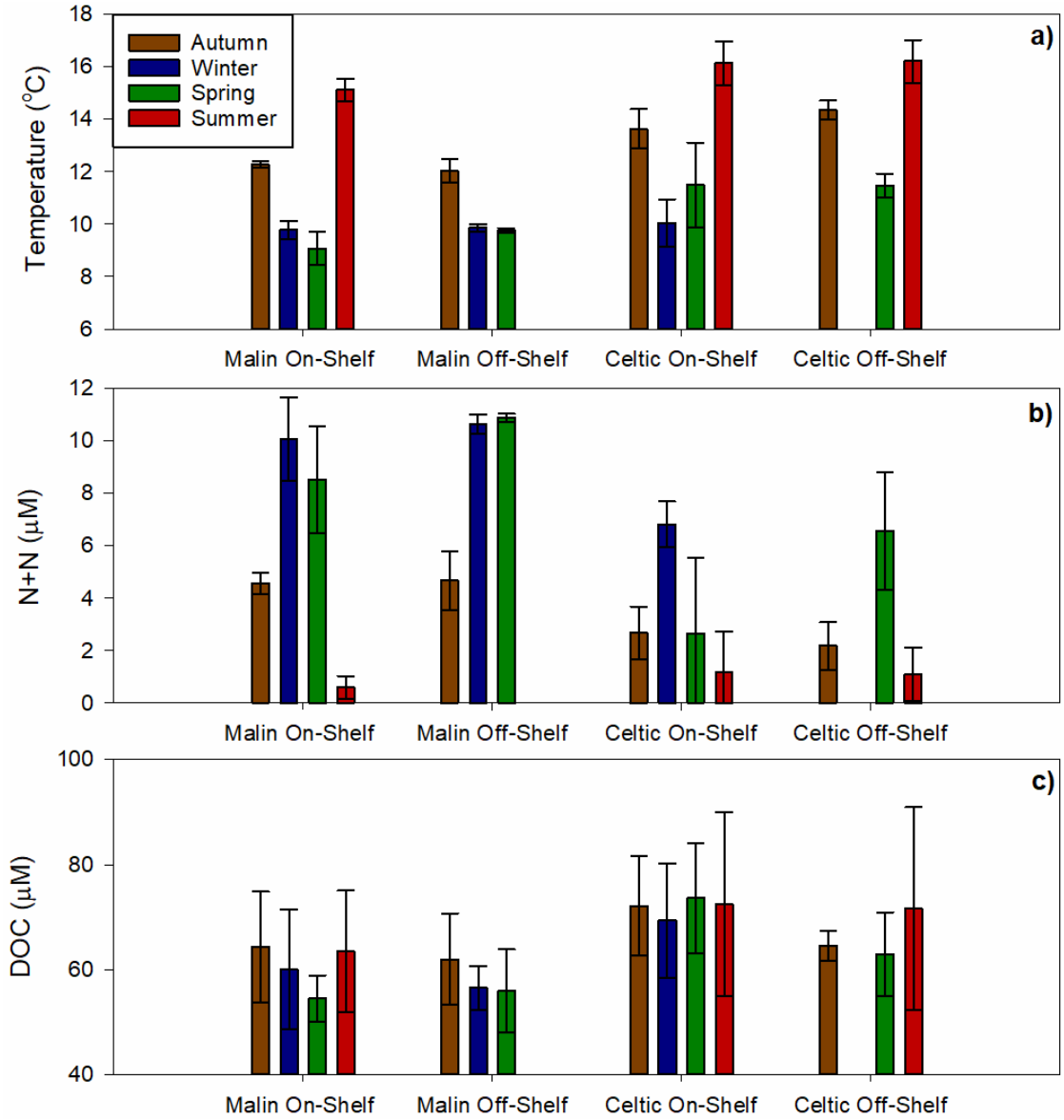

Fig.5.3. Mean ± std dev of a) temperature (°C), b) N+N (µM) and c) DOC (µM), in the Malin-Hebrides and Celtic Sea on and off-shelf regions. Seasons are colour coded as follows; autumn (brown), winter (blue), spring (green) and summer (red).

Table 5.1. Seasonal means ± std dev (S.D.) in temperature (°C), salinity, N+N (µM) and DOC (µM) in the surface 30 m Malin-Hebrides on and off-shelf regions and Celtic Sea on and off-shelf regions. N is the number of observations.

Surface	Malin-Hebrides On-Shelf			Malin-Hebrides Off-Shelf			Celtic Sea On-Shelf			Celtic Sea Off-Shelf		
0-30 m	Mean ± S.D.	Range	N	Mean ± S.D.	Range	N	Mean ± S.D.	Range	N	Mean ± S.D.	Range	N
Autumn												
Temperature (°C)	12.3 ± 0.1	0.3	10	12.0 ± 0.5	1.3	14	13.6 ± 0.8	2.8	28	14.3 ± 0.4	1.0	6
Salinity	35.2 ± 0.2	0.62	10	35.4 ± 0.0	0.1	14	35.1 ± 0.5	1.2	28	35.6 ± 0.00	0.0	6
N+N (µM)	4.6 ± 0.4	1.4	10	4.7 ± 1.1	3.6	14	2.7 ± 1.0	4.0	25	2.2 ± 0.9	2.1	5
DOC (µM)	64.3 ± 10.6	33.7	10	62.0 ± 8.7	34.2	14	72.1 ± 9.5	44.1	27	64.5 ± 2.9	6.9	4
DOC (µM)*							69.9 ± 6.9	25.0	12			
Winter												
Temperature (°C)	9.8 ± 0.4	1.0	5	9.9 ± 0.1	0.4	11	10.1 ± 0.9	2.6	21	N.D.	N.D.	N.D.
Salinity	35.3 ± 0.2	0.4	3	35.4 ± 0.0	0.1	11	35.3 ± 0.2	0.5	21	N.D.	N.D.	N.D.
N+N (µM)	10.1 ± 1.6	4.0	5	10.6 ± 0.4	1.3	11	6.8 ± 0.9	2.9	21	N.D.	N.D.	N.D.
DOC (µM)	60.1 ± 11.4	24.9	4	56.5 ± 4.1	11.4	10	69.3 ± 10.9	38.9	19	N.D.	N.D.	N.D.
DOC (µM)*							66.5 ± 6.9	22.9	9			
Spring												
Temperature (°C)	9.1 ± 0.6	1.4	9	9.8 ± 0.1	0.2	5	11.5 ± 1.6	6.9	49	11.5 ± 0.5	1.5	12
Salinity	35.1 ± 0.3	0.8	9	35.4 ± 0.0	0.1	5	35.3 ± 0.2	0.9	49	35.6 ± 0.1	0.3	12
N+N (µM)	8.5 ± 2	4.5	9	10.1 ± 0.2	0.4	5	2.7 ± 2.9	8.3	49	6.6 ± 2.2	6.5	12
DOC (µM)	54.5 ± 4.4	13.8	9	55.9 ± 7.9	19.7	5	73.6 ± 10.5	51.7	46	62.9 ± 8.0	24.4	12
DOC (µM)*							72.3 ± 4.7	17.9	22			
Summer												
Temperature (°C)	15.1 ± 0.4	0.9	3	N.D.	N.D.	N.D.	16.1 ± 0.8	4.9	30	16.2 ± 0.8	2.5	10
Salinity	35.1 ± 0.1	0.2	3	N.D.	N.D.	N.D.	35.2 ± 0.4	1.41	30	35.6 ± 0.0	0.1	10
N+N (µM)	0.6 ± 0.4	0.8	3	N.D.	N.D.	N.D.	1.2 ± 1.5	4.0	8	1.1 ± 1.0	2.5	9
DOC (µM)	63.5 ± 11.6	23.1	3	N.D.	N.D.	N.D.	72.5 ± 17.5	90.2	29	71.7 ± 19.3	61.4	10
DOC (µM)*							69.5 ± 12.9	48.6	15			

*Seasonal means ± std dev of DOC concentrations south of CCS

5.3.1.2. Seasonal distribution of DOC

Overall, DOC concentrations were higher on-shelf compared to off-shelf (Fig.5.3 c). Mean on-shelf DOC ranged from 54.5 µM to 73.6 µM and was highest and lowest in spring in the Celtic Sea and Malin-Hebrides Shelf, respectively (Table 5.1). Off-shelf, mean DOC ranged from 55.9 µM to 71.7 µM and was highest in summer and lowest in spring in the Celtic Sea and Malin-Hebrides off-shelf regions, respectively (Table 5.1). DOC concentrations were more variable on-shelf in the Celtic Sea and ranged by 90.2 µM in summer when the whole shelf was considered, or 48.6 µM when the region south of the Central Celtic Sea (CCS) was considered, compared to 23.1 µM for the same season on the Malin-Hebrides Shelf (Table 5.1). Differences in DOC concentrations between the Celtic Sea on and off-shelf regions were significant for all seasons when the whole shelf was considered. However, for the area south of CCS, DOC differences were only significant in spring (Table 5.2).

Table 5.2. Results from statistical analysis of the differences between DOC between regions and between seasons in the Celtic Sea. Data were not normally distributed therefore tests were performed using the Mann-Whitney Rank Sum test. P values are highlighted in bold when differences were statistically significant.

Region	P Value
Whole Shelf	
Malin On-Shelf Vs Malin Off-Shelf	**0.048**
Malin On-Shelf Vs Celtic Sea On-Shelf	**< 0.002**
Malin Off-Shelf Vs Celtic Sea Off-Shelf	**0.05**
Celtic Sea On-Shelf Vs Celtic Sea Off-Shelf	**< 0.001**
Celtic Sea South of CCS	
Celtic Sea On-Shelf Vs Celtic Sea Off-Shelf	**< 0.001**
Celtic Sea Seasons	
Whole Celtic Sea Shelf	
Autumn	**0.04**
Winter	N.D.
Spring	**<0.001**
Summer	1.0
Celtic Sea South of CCS	
Autumn	0.1
Winter	N.D.
Spring	**0.003**
Summer	0.7

5.3.2. Contrasting regions on-shelf and off-shelf regions of the Malin-Hebrides Shelf and the Celtic Sea

5.3.2.1. Hydrography and inorganic nutrients in the Malin-Hebrides Shelf and Celtic Sea

Waters were generally fresher and cooler on the Malin-Hebrides Shelf region compared to the Celtic Sea (Table 5.1). Temperature was highest in the Celtic Sea and lowest in the Malin-Hebrides off-shelf regions (12.6 ± 1.7 °C and 10.8 ± 1.1 °C, respectively, Table 5.1). Salinity was highest off-shelf of the Celtic Sea and lowest in the Malin-Hebrides on-shelf region (35.6 ± 0.1 and 35.2 ± 0.2). Both temperature and salinity were more variable in the Malin-Hebrides and Celtic Sea on-shelf regions and ranged by 7.3 °C and 0.81 and 8.8 °C and 1.5, respectively, compared to 3.1 °C and

0.14 and 7.2 °C and 0.1 off-shelf, respectively (Table 5.3). N+N concentrations were typically higher in off-shelf regions and highest in the off-shelf Malin-Hebrides region and lowest on-shelf in the Celtic Sea (8.4 ± 3.0 µM and 5.7 ± 3.0 µM, respectively, Table 5.3). N+N was more variable in the Malin-Hebrides and Celtic Sea on-shelf regions and ranged by 13.1 µM and 10.7 µM, respectively, compared to the off-shelf regions (9.8 µM and 10.0 µM, respectively (Table 5.3)).

5.3.2.2. Distribution of DOC in the Malin-Hebrides Shelf and Celtic Sea

DOC concentrations were significantly higher on-shelf compared to off-shelf in both the Malin-Hebrides and Celtic Sea (61.9 ± 9.7 µM and 58.0 ± 7.4 µM, and 69.0 ± 10.6 µM and 61.8 ± 11.3 µM, respectively, Table 5.2 and Table 5.3). DOC was highest on-shelf in the Celtic Sea and lowest in the Malin-Hebrides off-shelf region (69.0 ± 10.6 µM and 58.0 ± 7.4 µM, respectively, Table 5.3). Differences in DOC concentrations between the Celtic Sea and Malin-Hebrides on and off-shelf regions were significant (Table 5.2). DOC concentrations were more variable in the Celtic Sea on and off-shelf regions and ranged by 95.4 µM when the whole shelf was considered, and 50.8 µM when only the region south of the central Celtic sea was considered, compared to 69.5 µM in off-shelf waters (Table 5.3). The range in DOC was much lower in the Malin-Hebrides Shelf region, and DOC ranged by 38.8 µM on-shelf and by 36.9 µM off-shelf (Table 5.3).

Table 5.3. Mean ± std dev (S.D.) in temperature (°C), salinity, N+N (µM) and DOC (µM), in the top 130 m for the Malin-Hebrides Shelf regions and 200 m in the Celtic Sea regions. N is the number of observations.

	Malin-Hebrides On-Shelf			Malin-Hebrides Off-Shelf		
	Mean ± S.D.	**Range**	**N**	**Mean ± S.D.**	**Range**	**N**
Temp (°C)	11.2 ± 1.8	7.3	57	10.8 ± 1.1	3.1	51
Salinity	35.2 ± 0.2	0.8	55	35.4 ± 0.0	0.1	51
N+N (µM)	6.5 ± 3.0	13.1	57	8.4 ± 3.0	9.8	51
DOC (µM)	61.9 ± 9.7	38.8	54	58.0 ± 7.4	36.9	50
	Celtic Sea On-Shelf			**Celtic Sea Off-Shelf**		
	Mean ± S.D.	**Range**	**N**	**Mean ± S.D.**	**Range**	**N**
Temp (°C)	11.7 ± 2.1	8.8	336	12.6 ± 1.7	7.2	104
Salinity	35.3 ± 0.2	1.5	336	35.6 ± 0.1	0.3	104
N+N (µM)	5.7 ± 3.0	10.7	298	6.5 ± 3.0	10	101
DOC (µM)	69.0 ± 10.6	95.4	321	61.8 ± 11.3	69.5	91
DOC (µM)*	66.5 ± 7.1	50.8	195			

*Mean ± std dev of DOC concentrations south of CCS.

5.3.4. Seasonal DOC fluxes in the Celtic Sea

The method for calculating seasonal DOC fluxes is as detailed above (5.2.3). For surface fluxes, the top 30 m of the water column was used to calculate mean DOC. Previous observations of the depth of the spring and summer thermocline at the shelf edge station indicated that the SML was at ~ 30 m (Carr et al. 2018). Therefore, to obtain fluxes between comparable productive surface layers the top 30 m from on-shelf and off-self stations were considered.

When the entire shelf is considered, seasonal DOC flux estimates in the SML ranged from 303 ± 46 Gg C yr^{-1}, using conservative exchange terms, to 8106 ± 1094 Gg C yr^{-1} using the higher exchange term, and were an order of magnitude lower in

summer than in both autumn and spring (Table 5.4). Differences between DOC concentrations on and off-shelf in autumn and spring were significant (Table 5.2) and the flux was off-shelf indicating export to the North Atlantic. When the region south of CCS is considered, DOC differences were not significant in autumn and summer, and the flux was on-shelf in summer (Table 5.2). The seasonal flux in spring was significant but lower, and DOC flux estimates ranged from 3560 ± 342 Gg C yr^{-1} to 7121 ± 684 Gg C yr^{-1} when using the conservative and higher exchange term, respectively (Table 5.4).

Table 5.4. Estimates of seasonal surface DOC fluxes for the Celtic Sea for the whole shelf and south of the central Celtic Sea (CCS). Values in red indicate on-shelf flux.

Season	Exchange Sv	Mean Difference DOC ± CV (µM)	DOC Export Gg C yr^{-1} ± error (Gg C)
Whole Celtic Sea			
Autumn			
Surface 0-30 m	0.1	7.6 ± 0.7	2879 ± 255
	0.2	7.6 ± 0.7	5757 ± 509
Spring			
Surface 0-30 m	0.1	10.7 ± 1.4	4053 ± 547
	0.2	10.7 ± 1.4	8106 ± 1094
Summer			
Surface 0-30 m	0.1	0.8 ± 0.2	303 ± 46
	0.2	0.8 ± 0.2	606 ± 91
South of CCS			
Autumn			
Surface 0-30 m	0.1	5.4 ± 0.4	2045 ± 147
	0.2	5.4 ± 0.4	4091 ± 294
Spring			
Surface 0-30 m	0.1	9.4 ± 0.9	3560 ± 342
	0.2	9.4 ± 0.9	7121 ± 684
Summer			
Surface 0-30 m	0.1	**-2.2 ± 0.5**	**-833 ± 189**
	0.2	**-2.2 ± 0.5**	**-1667 ± 379**

Up to 24% of the DOC pool at the Celtic Sea shelf break in winter was found to be humic and of terrestrial origin and is therefore considered more refractory (Carr et al. 2018). At the lower end, seasonal estimates of off-shelf exports of humic DOC (24%), when the entire shelf is considered, ranged from 73 ± 11 Gg C yr^{-1} to 145 ± 22 Gg C yr^{-1} in summer, from 691 ± 61 Gg C yr^{-1} to 1382 ± 122 Gg C yr^{-1} in autumn, and from 923 ± 132 Gg C yr^{-1} to 1945 ± 263 Gg C yr^{-1} in spring. When the region south of CCS is considered, off-shelf exports of humic DOC in spring ranged from 854 ± 82 Gg C yr^{-1} to 1709 ± 164 Gg C yr^{-1} when using the conservative and higher exchange term, respectively (Table 5.4).

5.3.5. Net annual DOC fluxes for the Malin-Hebrides Shelf and Celtic Sea

The method for calculating seasonal DOC fluxes is as detailed above (5.2.3). However, for annual fluxes, the whole depth of the on-shelf water column of each region was used to calculate mean DOC, to incorporate waters that are likely to exchange in both the surface layer and bottom layer, and thus represent the net flux.

When the entire Celtic Sea was considered, the annual net DOC flux estimates for the Celtic Sea ranged from 2651 ± 445 Gg C yr^{-1}, using the conservative estimate of exchange (0.1 Sv) from Barron and Duarte (2015), to 5303 ± 891 Gg C yr^{-1} using the higher exchange term (0.2 Sv, Table 5.5 (Huthnance et al. 2009)). The estimates were significant (Table 5.2) and off-shelf to the North

Atlantic. When the region south of the central Celtic Sea was considered, the annual net DOC flux estimates were lower and ranged from 1773 ± 257 Gg C yr^{-1} to 3546 ± 514 Gg C yr^{-1}.

Annual DOC flux estimates for the Malin-Hebrides Shelf were lower compared to the Celtic Sea and ranged from 1477 ± 210 using the conservative estimate of exchange (0.1 Sv) from Barron and Duarte (2015), to 2954 ± 420 Gg C yr^{-1} using the exchange term calculated for the top 200 m (0.2 Sv, Table 5.5 (Painter et al. 2016)). The estimates were significant (Table 5.2) and off-shelf to the North Atlantic.

Table 5.5. Estimates of net annual DOC fluxes for the Celtic Sea (whole shelf and south of the central Celtic Sea (CCS), and Malin-Hebrides Shelf.

Region	Exchange Sv	Mean Difference DOC ± error (µM)	DOC Export Gg C yr^{-1} ± error (Gg C)	Shelf Length (km)	Water Exchange References
Celtic Sea					
Whole Shelf					
Surface 0-200 m	0.1	7.0 ± 1.2	2651 ± 445	100	(Barron and Duarte 2015)
	0.2	7.0 ± 1.2	5303 ± 891	100	(Huthnance et al. 2009)
South of CCS					
Surface 0-200m	0.1	4.7 ± 0.7	1773 ± 257	100	(Barron and Duarte 2015)
	0.2	4.7 ± 0.7	3546 ± 514	100	(Huthnance et al. 2009)
Malin Shelf					
Surface 0-130 m	0.1	3.9 ± 0.6	1477 ± 210	100	(Barron and Duarte 2015)
	0.2	3.9 ± 0.6	2954 ± 420	100	(Painter et al. 2016)

By using the same approach as employed for calculating humic, terrestrially derived DOC concentrations in seasonal fluxes, and assuming seasonal and spatial uniformity in on-shelf terrestrially derived DOC concentrations. Estimates of off-shelf exports of humic DOC (24%) from the Malin-Hebrides Shelf ranged from 354 ± 50 Gg C yr^{-1} to 708 ± 100 Gg C yr^{-1}. For the Celtic Sea, when the whole shelf was considered, estimates of off-shelf exports of humic, terrestrially-derived DOC was nearly double that of the Malin-Hebrides Shelf and ranged from 636 ± 107 Gg C yr^{-1} to 1272 ± 214 Gg C yr^{-1}. When the region south of the central Celtic Sea was considered, estimates of off-shelf exports of humic DOC (24%) from the Celtic Sea ranged from 426 ± 62 Gg C yr^{-1} to 852 ± 123 Gg C yr^{-1}.

5.4. Discussion

5.4.1. On-shelf and Off-shelf DOC production

Rates of primary production in shelf seas are ~ 3 times greater than in the open ocean (Simpson and Sharples 2012), and globally, rates of organic carbon production on-shelf (230 g C m^{-2} yr^{-1}) are between 1.5 and 2.4 greater than the rates of organic carbon production on the shelf slope and in the open ocean, of which an estimated 36% is exported (Wollast 1998). Thus, cross shelf gradients in DOM between the shelf seas and open ocean are largely driven by the differences in productivity in these two regions.

In contrast, DOM in the deep ocean is thought to be largely refractory and representative of the background pool consisting of DOM that is carbon-rich and nutrient-poor with an average age of 4 thousand years (Hopkinson and Vallino 2005). For the deep waters of the North Atlantic (1100 – 4800 m) DOC concentrations are around 45.1 ± 0.4 µM and differences between ocean basins are driven by differences in the thermohaline circulation (Hansell and Carlson 1998).

As with global and basin scale trends, cross shelf gradients in DOC were observed. For the surface waters mixing over the shelf break, DOC was greater on-shelf in autumn in the Celtic Sea by between 8 and 11%, and by between 13 and 15% in spring. DOC was similar on-shelf versus off-shelf in summer, with only a 1% difference, within the error of analysis. Overall, the ranges in DOC concentrations in whole on-shelf water column, for both the Malin-Hebrides and Celtic Sea were greater on-shelf (38.8 µM and 95.4 µM, respectively) compared to off-shelf (between 36.9 µM and 69.5 µM, respectively) (Table 5.3), suggesting that DOC production was more variable on-shelf compared to off-shelf.

The gradients in DOC between on-shelf and off-shelf waters result from a combination of enhanced primary production, and in turn DOC production, which is facilitated by the supply of nutrients to the surface layer via vertical nutrient fluxes driven by internal tides, in particular at shelf edge sites (Sharples et al. 2013). The trends observed were in agreement with global and regional trends and

evidence for external DOC inputs are indicated by the inverse relationships between salinity and DOC (chapter 3, Table 3.4).

A north south gradient in DOC and N+N concentrations was observed in the top 130 – 200 m of North Atlantic waters in the off-shelf regions of the Malin-Hebrides and Celtic Sea. Higher DOC concentrations were observed off-shelf of the Celtic Sea, while higher N+N concentrations were observed in the off-shelf region of the Malin-Hebrides Shelf (Table 5.3). Differences in nutrient concentrations are attributed to the changes in the depth of the average winter mixed layer between the two regions which increases from south to north (Hydes et al. 2004).

The entrainment and mixing of surface DOC to deeper depths in the Malin-Hebrides off-shelf region during winter could explain the south to north gradient in DOC concentrations observed between the two regions. Furthermore, direct exchange of surface shelf waters and ocean water is more limited in the Malin-Hebrides Shelf compared to the Celtic Sea (Hydes et al. 2004) which would reduce the amount of allochthonous and autochthonous DOC being exported off-shelf to the North Atlantic from the Malin-Hebrides Shelf. Differences in DOC concentrations could also be due to variations in primary production, however, no data were available for direct comparisons of net primary production between the two regions. Estimates of annual net primary production for the Hebrides Shelf west of Scotland are 200 g C m^{-2} yr^{-1} (Painter et al. 2016), and while no annual primary production estimates are available for the Celtic

Sea, primary production in summer is estimated to be between 0.17 and 0.39 g C m^{-2} d^{-1} (Hickman et al. 2012). However, during the peak of the spring bloom primary production can reach up to 12 g C m^{-2} d^{-1} (Poulton et al. 2017).

5.4.2. Seasonal DOC Fluxes from the Celtic Sea

The seasonal cycle of primary production and atmospheric uptake of carbon in shelf seas are well established (Tsunogai et al. 1999, Thomas et al. 2004, Thomas et al. 2005), but the seasonal trends in DOM production are less clear (chapter 3). However, DOC distribution in the Celtic Sea did follow a typical seasonal cycle (chapter 3, section 3.3.5.1) and DOC concentrations were highest in spring and lowest in winter. Due to the absence of winter DOC data for the off-shelf Celtic Sea region estimates of DOC fluxes are not provided.

The seasonal fluxes of DOC are not net estimates but represent gross estimates due to the potential for DOC exported off-shelf to return on-shelf by an on-shelf flow in either surface or bottom waters. For flux calculations including the whole shelf, estimates of surface DOC fluxes were seasonally variable, with spring DOC fluxes being significantly higher (~1.5) than the net annual flux (Table 5.4 and Table 5.5). In contrast, summer DOC fluxes were over an order of magnitude lower than net annual flux, and autumn DOC fluxes were similar to the net annual flux (Table 5.4 and Table 5.5). Thus, annual DOC fluxes were driven by the large fluxes in springtime.

When the region south of CCS is considered, springtime surface DOC fluxes were still significant higher (~2) than the annual net flux (Table 5.4 and Table 5.5).

Greater surface fluxes in spring compared to other periods could be due to two main reasons. Firstly, spring is the most productive season in terms of primary production, therefore more DOC will be produced especially during phytoplankton bloom periods, and subsequent DOC release during grazing (Hygum et al. 1997). As the shelf is more productive the gradient in DOC from higher on-shelf to lower off-shelf concentrations is larger. The DOC pool measured represents the net DOC, and DOC production during spring was in excess of bacterial carbon demand, not only during spring, but throughout the year (García-Martín et al. 2017), indicating surplus DOC was available for transport.

Secondly, river DOC inputs would increase on-shelf DOC concentrations thereby enhancing the gradient between on and off-shelf. Rivers discharging into the Celtic Sea, such as the Severn, follow a seasonal cycle of highest discharge and DOC inputs in winter, and reducing by more than half in spring (chapter 2, section 2.4.1). However, although inputs are lower in spring, DOC inputs from the River Severn in March are still substantial 2559 µM DOC d^{-1} (Leeuwen 2017). Furthermore, the Celtic Sea is a broad shelf with a distance of ~ 500 km from the UK mainland and Bristol Channel. Surface flows around the Isles of Scilly reach a maximum of 0.09 m^{-1} in spring (Pingree et al. 1999). Therefore, by assuming flow speeds

are uniform, river inputs of DOC from preceding seasons (e.g. winter) could impact on-shelf DOC concentrations in spring, given transport is ~ 8 km per day, and depending on flow direction, transit time to the shelf edge would be 63 days.

While the mechanisms for facilitating off-shelf transport of DOC will not be discussed in depth here, cross-shelf exchange could be enhanced in spring by off-shelf surface flows. Indeed, surface flows around the Isles of Scilly are marginally slower in spring than summer maximums at the Goban Spur (0.09 m s^{-1} and 0.10 m s^{-1}, respectively (Pingree et al. 1999), and at the shelf break flow reversals occur in early spring through April and are along slope and equatorward (Pingree et al. 1999). Another mechanism is wind forcing, which accounts for up to a third of total ocean-shelf water exchange in the Celtic Sea (Huthnance 2010). In addition, internal tides that occur during stratified periods facilitate on-off shelf exchange, and supply mixing which drives turbulent fluxes of nitrate into surface waters in areas over 100 km from the shelf break (Sharples et al. 2009).

5.4.3. Net Annual DOC Fluxes

By employing a simple equation derived from the gradient in DOM concentrations between on-shelf and off-shelf regions, estimates of the annual net DOC flux from the Malin-Hebrides Shelf ranged from 14.5 ± 2.1 to 29.5 ± 4.2 Gg C yr^{-1} per km of shelf, respectively (Table 5.4). These ranges were within the range

reported by Barron and Duarte (2015) which were 1.4 to 66.1 Gg C yr^{-1} per km of shelf break. However, previous estimates of DOC fluxes from the Malin-Hebrides Shelf over a 30 day period in autumn were around half of the estimates here at 7.6 Gg C yr^{-1} per km of shelf break (calculated from quoted concentrations of 0.13 Tg C d^{-1} over 516 km length of shelf for 30 day period) (Painter et al. 2016) (Table 5.4).

Assuming DOC fluxes in shelf seas are constant and independent of season, extrapolation of the autumn flux reported in Painter et al. (2016) would be 92.5 Gg C yr^{-1} per km of shelf break, which is between 3 to 7 times greater than estimates here. However, from the variability observed in the seasonal fluxes in the Celtic Sea, we know that this assumption is incorrect and probably responsible for the much larger estimate of DOC flux from the extrapolation from autumn only.

Estimates of the annual net DOC flux from the Celtic Sea were 2 times larger than the Malin-Hebrides Shelf, and ranged from 26.5 ± 4.5 to 53.0 ± 8.9 Gg C yr^{-1} per km of shelf when the whole shelf was considered and by 17.7 ± 2.6 to 35.5 ± 5.1 Gg C yr^{-1} per km of shelf when the shelf south of CCS was considered. These estimates are also within the mean regional ranges quoted by Barron and Duarte (2015). To my knowledge, these are the first estimates of DOC fluxes in the Celtic Sea region. Estimates of POC export from the Goban Spur area, in shelf break waters close to the transect of SSB stations sampled, were estimated to be 1.5 Gg C km^{-1} yr^{-1} (Wollast and Chou

2001), making the net annual flux of DOC from the Celtic Sea between 18 and 35 times greater compared to POC export.

In addition, estimates of DOC export from surface waters of the North Atlantic into the interior are 0.081 Pg C yr^{-1}, which is 81,000 Gg C yr^{-1}, over an area of around 7659 km (6ºS to 63ºN) (Carlson et al. 2010). By comparing export flux per km, then interior export is 11 Gg C yr^{-1} per km, which is between 2 and 5 times lower than the net annual off-shelf fluxes of DOC from the Celtic Sea. This would suggest that the Celtic Sea is an important site of carbon export as DOC to the North Atlantic.

Globally, mean air-sea CO_2 fluxes from the atmosphere into the surface ocean in continental shelf seas are estimated to be between 180 and 450 Tg C yr^{-1} (Cai et al. 2006, Laruelle et al. 2014). The Northwest European Shelf is considered to be a net sink of atmospheric carbon, with annual fluxes of 17 Tg C yr^{-1} (Hartman et al. 2018). If we consider a combined length of the Malin-Hebrides (~ 600 km) and Celtic Sea (~ 700 km) shelf-break to be ~ 1300 km, the annual net DOC flux across the entire length of shelf adjacent to the North Atlantic is between 21 ± 3 Tg C yr^{-1} and 43 ± 6 Tg C yr^{-1}, for 0.1 Sv and 0.2 Sv of exchange, respectively. These estimates of the annual DOC flux is of the same order of magnitude as the air-sea flux of CO_2, but double the air-sea flux if we consider the higher end of the range.

This may be due to a number of assumptions made in this calculation. I have assumed that the cross shelf DOC gradient is constant across the entire shelf region and that DOC is transported at the same rate along the entire shelf edge system. However, I have not included cross shelf exchange between the North Sea and the North Atlantic, which would only increase this estimate of DOC flux from the Northwest European Shelf region. Thus, while these simplified calculations provide a first order estimate on the DOC transfer between the Northwest European Shelf, which are in line with other shelf sea regions, such as the Mid Atlantic Bight (Barron and Duarte 2015), they need to be critically evaluated with a better understanding of the variability in physical fluxes at the shelf edge.

5.5. Conclusions

Fitting with global trends, DOC concentrations were significantly higher on the Malin-Hebrides Shelf and in the Celtic Sea compared to the off-shelf waters of the North Atlantic. In contrast, the variability in DOC concentration was higher on-shelf compared to off-shelf. Annual net fluxes of DOC were off-shelf and within global ranges. The first estimates of DOC flux from the Celtic Sea indicate that nearly twice as much DOC was exported off-shelf from the Celtic Sea compared to the Malin-Hebrides Shelf. In the Celtic Sea, DOC seasonal surface fluxes were 50% higher in spring compared to the annual flux, and up to a quarter of DOC available for export from the

Celtic Sea in winter was humic material and thus likely to be of terrestrial origin (Chapter 2).

The magnitude of the annual net and seasonal surface fluxes of DOC from the Malin-Hebrides Shelf and Celtic Sea has wide implications for the carbon budgets in these regions and the neighbouring North Atlantic. While the processes acting on DOC once it leaves shelf waters are not discussed here, up to a quarter is considered terrestrially derived and therefore may contribute to the deep ocean pool of refractory DOC which has implications for the global carbon cycle on decadal to millennial time-scales.

Observations from the SSB programme and Shelf Wide sampling campaign provided invaluable insights covering a wide range of key shelf sea processes such as the seasonal variability in physical circulation and transport, plankton community respiration and bacterial metabolism, distribution, production and supply of inorganic and organic nutrients, as well as identifying areas of the northwest European Shelf which are sources and sinks of atmospheric CO_2.

However, in order to accurately assess and quantify the magnitude and variability of DOC fluxes from the shelf to the adjacent open ocean more observations are needed, for example on how the DOC gradient varies around the whole shelf break, and indeed how shelf wide exchange varies. Furthermore, key processes determining the ultimate fate of shelf sea DOC remain unclear or unknown, for example, coupling or de-coupling between the POM

and DOM pools. The fate of vertically exported POC, which is subject to microbial reprocessing to DOC in the water column, or reaches the sea floor where benthic processes control its recycling, remineralisation and burial of OM are also unclear in shelf seas. Physical processes that lead to re-suspension of OM, in particularly in the shelf slope region are not well documented, nor is the magnitude of OM re-introduced in the water column during these events. Finally, the fate of DOC once it has left the shelf seas remains unknown, and DOC advected off-shelf can only be considered lost to the dynamic and exchanging carbon pool if it reaches depths greater than that of winter mixing (~ 500 m in the North Atlantic).

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Chapter 6

Conclusions and synthesis

As the largest exchangeable reservoir of organic material on the planet, DOM in the marine environment plays an important role in many key processes. However, despite being the most variable and dynamic pool, it is least understood in terms of composition and reactivity, and the contribution it makes to the shelf sea carbon pump. While we now understand the spatial trends in DOM distribution globally (Barron and Duarte 2015), local processes that contribute to the production, consumption and alteration of DOM, which occur on shorter spatial and timescales are less understood. In addition, the magnitude, variability and composition of allochthonous DOM inputs are unclear, and gaps remain in our ability to track terrestrial DOM to the open ocean (Bianchi 2011).

The Global Ocean Observing System (GOOS) expert panel have identified DOC as an Essential Ocean Variable (EOV) that contributes up to 20% to the ocean's biological pump. DOC also plays a key role in the microbial loop by providing a substrate for bacterial production that is either remineralised back to DIC, or enters the MCP where it can be transformed into recalcitrant DOC and stored in the ocean interior on long time-scales.

Our understanding of the role of DOM in the marine environment has vastly improved in the past decade due to the

advent of new techniques (Coble 1996, Bro 1997, Hopkinson et al. 1997), our new understanding of microbial processing of DOM (Carlson 2002, Buchan et al. 2014) and synthesis of large data sets that highlight global trends in the open ocean (Hansell et al. 2009, Liu et al. 2010) and shelf seas (Barron and Duarte 2015). Using the NERC-funded Shelf Sea Biogeochemistry sampling platform, I have assessed the dynamics of DOM in the Northwest European Shelf region. My findings contribute to the growing evidence that DOM plays an important role in the global carbon cycle, especially in shelf seas. Here, I highlight the findings in each chapter, their implications and the information we need to better understand DOM in the marine environment.

In **Chapter 2,** I demonstrated the strength of using multi-dimensional approach by incorporating DOM optical properties alongside measurements of DOC to delineate the complexities of the DOM pool in shelf seas. I found that the seasonality in DOC concentrations was site specific reflecting contrasting local physical and biological conditions. Strong cross shelf gradients in humic-like DOM, and their correlation with salinity indicated the importance of the input and influence of terrestrially-derived DOM to the DOC pool in the Celtic Sea. I estimated that terrestrial DOM represented 24, 35 and 43% of the total DOC pool at the shelf edge, in the central Celtic Sea and at the on-shelf station, respectively. Significant temporal variation in protein-like DOM fractions also highlighted the importance of biological production and consumption in influencing

DOC concentrations in the Celtic Sea over short (hours to days) and longer (seasonal) timescales.

Overall, there is accumulating evidence from this study and other CANDYFLOSS studies on bacterial carbon dynamics (García-Martín et al. 2017) phytoplankton carbon dynamics (Poulton et al. 2017) and the stoichiometry of DOM and POM (Davis et al. 2018) that show that there is excess organic carbon in the shelf seas after bacterial consumption or remineralisation, leaving the DOM pool carbon rich and available for off-shelf transfer.

Further examination is needed on how bacteria and phytoplankton interact with the different DOM pools, both refractory and labile, over the timescales relevant for carbon export from shelf seas. This will help determine the relative magnitude of on-shelf processing versus off-shelf export of DOM. Interactions could be assessed by the separation of DOM into fractions (e.g. on basis of MW using size exclusion chromatography (Piccolo et al. 1996, Romera-Castillo et al. 2014), followed by a series of addition experiments and measurement of uptake and production rates in both phytoplankton and microbial communities.

Results from addition experiments could also give a quantitative measure of the priming effect (Chapter 1). In addition, the use of biomarkers for specific terrestrial OM, such as lignin, would confirm the presence of and provide a quantitative estimate of terrestrial DOM across the Celtic Sea, over the shelf break and into

the North Atlantic. Furthermore, measurement of the optical properties would also help delineate humic signals from reprocessed DOM and terrestrial DOM.

Benthic and pelagic coupling was beyond the scope of this PhD, and vertical DOM/POM export was not considered here. However, both processes need to be incorporated into carbon budgets and inventories on seasonal and annual timescales, to account for inputs from and losses on shelf, particularly in physically active areas, such as the shelf break, where for example, reintroduction of DOM into the BML may be significant.

In **Chapter 3**, I assessed the distribution of DOM in 5 shelf seas across the Northwest European Continental Shelf and adjacent North Atlantic Ocean waters. The broad scale pattern of DOM distribution was in fitting with global trends (Barron and Duarte 2015), as both DOC and DON concentrations decreased with increasing distance from land and with increasing salinity. These patterns are indicative of the mixing and dilution of riverine DOM with marine and North Atlantic Ocean DOM of lower concentrations. The deviation from this broad scale pattern, e.g. from the 1:1 mixing line, highlights the importance of local processes and seasonality in controlling DOM dynamics. DOM did not conform to the conceptual view of seasonal distribution in the Celtic Sea, Malin-Hebrides Shelf and the English Channel, with DOC and DON often being decoupled. This was especially evident during productive periods, when DON was drawndown to low concentrations, highlighting its importance as a

source of nitrogen when inorganic nutrients become limiting. In contrast, DOC behaved similarly in regions of distinctly different hydrographic regimes (e.g. mixed English Channel versus the seasonally stratifying Celtic Sea), highlighting the complexity and unpredictable nature of DOC specifically.

This chapter highlighted that shelf seas, which are the interface between land and the open ocean, are subjected to complex physical processes such as frontal structures, river inputs and shelf edge processes which together influence DOM production, consumption and transport. However, it also highlighted the need to better understand the role of local processes in controlling DOM in small spatial (10's of km) and temporal (days) scales to better understand the broad scale patterns.

Any future work in these regions should include observations of the freshwater DOM and POM end members i.e. river and estuary input measurements as well as composition, including DOM/POM stoichiometry. This would provide a more accurate starting point for tracking terrestrial DOM/POM inputs. Data are already available in some regions e.g. Celtic and Irish Sea, however expanding this dataset to cover more of the major rivers which discharge into the regional seas, as well as the major estuaries would provide much needed information (e.g. how the magnitude, composition and stoichiometry of riverine DOM and POM varies over a seasonal cycle).

Furthermore, a shelf wide freshwater input dataset would be useful in assessing longer term changes in discharge and inputs that may be driven by accelerated climate change. A warmer climate is likely to be a wetter one which would increase land run-off, and changes in inputs could affect nutrient loads around the coasts and in shelf seas. Increased nutrient loads and OM inputs could enhance eutrophication, which would alter the metabolic balance and could lead to the risk of oxygen deficit regions.

Future work should also provide a better understanding of transport and connectivity between the 5 shelf sea regions and the North Atlantic to constrain lateral DOM transport and export pathways. The use of automated platforms such as gliders, shipboard observations (underway and CTD), along with a regional model would be useful in determining shelf wide circulation.

In **Chapter 4,** I focused specifically on DOM cycling in the North Sea by contrasting the northern and southern regions of the North Sea, seasonal cycling of DOM in the southern North Sea and then assessing the multi-year trends in August in nutrients and DOM from 2011 to 2016. Higher DOC and DON concentrations in the southern North Sea reflected the impact of terrestrial inputs and riverine supply of organic and inorganic nutrients. In contrast, lower inorganic and organic nutrients in the northern North Sea reflected reduced riverine inputs as well as dilution of surface waters with oceanic nutrients and DOM. Using published data sets alongside those collected during the Shelf Wide sampling campaign in 2014

and 2015, I found that August nitrate and DON concentrations declined from 2011 to 2016, and DOC declined from 2011 to 2015 before increasing again in 2016. This decline in nitrogen may be due to effective wastewater management and indeed the implications on North Sea productivity have been noted (Capuzzo et al. 2018).

DOC concentrations were more variable, with the largest change in the DOC inventory being observed between 2011 and 2012, as reported by (Chaichana et al. in review). This change in DOC was of the same order of magnitude as northern North Sea yearly CO_2 uptake. The change in DOC inventories in the years following (2014 and 2015) was much less in comparison, however, it was still significant, representing around 18% of yearly North Sea DIC enrichment, and further illustrating the dynamic nature of DOM on annual timescales. I assessed the potential for physical exchange between the North Sea and North Atlantic in explaining these changes in DOC inventory between years and concluded that it is possible to flush the entire North Sea under specific climatic conditions, e.g. under a positive NAO index.

Furthermore, little is known about the internal changes in DOC stocks in the North Sea, and more work is needed to assess any inter-annual variability in the biological processing of DOM which controls how much DIC accumulates in the BML and is available for exchange with the North Atlantic in the northern region. In the southern region, more consideration should be given to benthic-pelagic interactions. This shallower region is permanently mixed with

the benthos potentially being a significant source of re-processed DOM, of which the composition remains largely unknown.

Given the complex nature of DOM and the dynamical physical and biogeochemical processes governing its production, consumption and transport, capturing long-term trends in its distribution is problematic, even when data sets are complete and collected at the same spatial resolution and at the same time of year. The multi-year trends highlighted here demand that a consistent sampling regime is maintained over decadal timescales. However, as noted in chapter 4, to better understand the potential role of winter mixing, a consistent sampling regime in winter and or spring would be required to assess the role of physical exchange prior to modification of the biogeochemistry of the water during the spring bloom period. While sampling the North Sea in winter may be challenging due to weather, the use of autonomous sampling platforms and moorings may help in this regard.

Following on from directives introduced in the 1990's to reduce the risk of eutrophication in the North Sea, a current work package within the AlterEco project (http://altereco.ac.uk/work-packages) investigates the controls on oxygen deficiency in the BML of the North Sea. The results from this project should provide some answers regarding the physical structure, changes in thermal stratification as well as vertical and horizontal fluxes and transport. In addition, organic matter remineralisation in the BML and productivity in the SML will be resolved on seasonal and spatial scales to assess

the contribution of both physical and biological drivers of oxygen deficiency in the North Sea.

In **Chapter 5,** I assessed the cross shelf gradients in DOC and estimated the seasonal and annual fluxes of DOC in the Celtic Sea and Malin-Hebrides Shelf regions. Annual net fluxes of DOC were off-shelf and within global ranges previously reported by Barron and Duarte (2015). To my knowledge, these are the first estimates of DOC fluxes from the Celtic Sea. Interestingly, annual DOC fluxes from the Celtic Sea are twice as high as the DOC fluxes from the Malin-Hebrides Shelf. In the Celtic Sea, DOC seasonal surface fluxes were 50% higher in spring compared to the annual flux, and up to a quarter of DOC available for export from the Celtic Sea in winter was humic matter and thus likely to be of terrestrial origin.

The magnitude of the annual net and seasonal surface fluxes of DOC from the Malin-Hebrides Shelf and Celtic Sea has wider implications for the carbon budgets in these regions and the neighbouring North Atlantic. While the processes acting on DOC once it leaves shelf waters are not discussed in this thesis, up to a quarter is considered humic and terrestrially derived. We currently lack knowledge on the bioavailability of this DOC pool and how it contributes to the carbon pool in the deep ocean. If this DOC is largely refractory, then it may be stored in the deep ocean for decadal to millennial time-scales. Thus, a better understanding of the composition and lability of the DOC that is transported off shelf is

required to quantify its role in the deep ocean carbon cycle and define if this carbon represents a ‘sequestered’ pool of carbon.

There is much scope from the results here to reduce the uncertainty and provide a more accurate estimate of DOC fluxes between the Celtic Sea and Malin-Hebrides Shelf with the North Atlantic, and this work is currently in progress. The methodology will be improved to take into consideration the regions where exchange is likely to occur, as well as the distance on-shelf from which waters will exchange, namely 100 to 170 km from the shelf break (Inall et al. 2011, Ruiz-Castillo et al. in press).

Future work to determine the role of DOC in the shelf pump across the whole northwest European Shelf should consider the mechanisms of lateral exchange, for which observations from gliders located in key areas (e.g. on-shelf and off-shelf) and during key seasonal events would provide an estimate of the magnitude and variability of transport. Furthermore, a glider sensor package including an optical array (specifically absorbance) alongside ship board DOC sampling would provide SUVA concentrations for determining DOC gradients from which flux calculations could be retrieved. DOM composition analysis using specific biomarker and/or the ratio of ^{13}C and ^{12}C ($\delta^{13}C$) would help in confirming the presence of and accurately estimating terrestrial DOC fluxes.

We now have a better understanding of the variability in bacterial metabolism and plankton respiration in the Celtic Sea

(Garcia et al. 2017). However, for processes acting on more local scales, a better understanding of the role of DOC in the microbial carbon pump is needed. In addition, vertical fluxes of and DOM/POM coupling, and benthic pelagic interactions should also be considered and quantified.

While the Shelf Sea Biogeochemistry programme provided an excellent sampling platform and improved our understanding in DOM in shelf seas, there are gaps in our knowledge that need to be addressed to provide a complete understanding of DOM in shelf seas. The shelf wide programme ignored near coastal, low salinity regions, which hampered our understanding of the concentration, composition and bioavailability of land-derived DOM. Measurement of riverine DOM would also have helped to define the freshwater end members and the riverine DOM stoichiometry to compare with marine derived DOM stoichiometry to better define end members.

The Shelf Wide Sampling programme was opportunistic and thus the sampling locations were based on other priorities rather than defining DOM dynamics. In order to capture the gradients in DOC for constraining flux estimates, a sampling campaign specifically designed with knowledge of the temporal and spatial scales over which exchanges processes act to transfer DOC would improve our understanding of this potentially important flux of DOC. As above, understanding the fate of the DOC transported off shelf would also better define the importance of this flux into the deep ocean.

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APPENDICES

Table 1

Chapter 2 Appendices Table 1. Results of statistical analysis. Differences for groups of data from three sites (Shelf Edge, CCS and Site A) between seasons

Table 2

Chapter 2 Appendices Table 2. Results of statistical analysis. Between site and seasons

Table 3

Chapter 3 Appendices Table 3. English Channel – Seasonal distributions

Table 4

Chapter 3 Appendices Table 4. Celtic Sea on-shelf SML – Seasonal distributions

Table 5

Chapter 3 Appendices Table 5. Celtic Sea on-shelf BML – Seasonal distributions

Table 6

Chapter 3 Appendices Table 6. Malin-Hebrides on-shelf SML – Seasonal distributions

Table 7

Chapter 3 Appendices Table 7. Eastern Irish Sea – Seasonal distributions

Table 8

Chapter 3 Appendices Table 8. Western Irish Sea – Seasonal distributions

Table 9

Chapter 4 Appendices Table 9. Southern North Sea – Seasonal distributions

Chapter 2 Carr et al. 2018

Chapter 2 Appendices Table 1. Results of statistical analysis. Paired t-tests (T) or Mann-Whitney Rank Sum Test (MW), when data were not normally distributed, were used to determine significant differences for groups of data from three sites (Shelf Edge, CCS and Site A) between seasons. Differences were deemed statistically significant when the p value was < 0.05.

Variable	Region	Autumn-Winter	Autumn-Spring	Autumn-Summer	Winter-Spring	Winter-Summer	Spring-Summer
C1	Shelf Edge CCS Site A	MW, <0.001 MW, <0.001 T, <0.001	T, < 0.001 T, 0.003		MW, 0.03 T, < 0.001	MW, <0.001 T, < 0.001 T, < 0.001	T, < 0.001 T, 0.012
C2	Shelf Edge CCS Site A	MW, 0.029	MW, 0.016	MW, 0.043	MW, 0.005		MW, 0.024
C3	Shelf Edge CCS Site A	MW, < 0.001	MW, 0.024 MW, 0.002	MW, 0.003		MW, 0.05	MW, 0.005
C4	Shelf Edge CCS Site A	T, 0.019	MW, < 0.001	T, 0.008 MW, < 0.001 T, 0.043	MW, 0.013 T, 0.018	MW, 0.043 T, < 0.001	
Slope Ratio	Shelf Edge CCS Site A		T, 0.048	T, 0.022 T, 0.013			
DOC	Shelf Edge CCS Site A	MW, 0.012	MW, < 0.001	T, 0.05 MW, 0.041	T, 0.005 T, 0.01	T, 0.003 T, 0.025 T, 0.002	T, 0.032 MW, < 0.001
Slope (300-650)	Shelf Edge CCS Site A	T, 0.003 T, < 0.001 N.D.	T, 0.037 T, < 0.001 N.D.	T, <0.001 MW, < 0.001 N.D.	T, 0.003		MW, 0.003
a305	Shelf Edge CCS Site A	N.D.	N.D.	N.D.		T, 0.04 T, 0.003	
SUVA280	Shelf Edge CCS Site A	T, 0.049 T, < 0.001 N.D.	N.D.	T, 0.027 MW, 0.001 N.D.		T, < 0.001	
HIX	Shelf Edge CCS Site A	MW, < 0.001	T, < 0.001 MW, 0.02	T, < 0.001	MW, < 0.001 MW, 0.028		MW, 0.026 MW, 0.02 T, < 0.001
FIX	Shelf Edge CCS Site A	MW, 0.02 MW, < 0.001	T, < 0.001 T, < 0.001 MW, 0.001	MW, < 0.001	MW, 0.006 MW, 0.010	MW, < 0.001 MW, < 0.001	T, < 0.001 MW, < 0.001 MW, 0.001
BIX	Shelf Edge CCS Site A	T, < 0.001 MW, < 0.001 T, < 0.001	T, < 0.001 MW, < 0.001 MW, 0.001	T, 0.008	T, < 0.001	T, < 0.001 MW, < 0.001 T, < 0.001	T, < 0.001 MW, < 0.001 T, < 0.001

Chapter 2 Appendices Table 2. Results of statistical analysis. Between site and season differences were deemed statistically significant when the p value was < 0.05.

Variable	Season	Between Shelf Edge and CCS	Between Shelf Edge and Site A	Between CCS and Site A
C1	Autumn	MW, <0.001	T, <0.001	T, <0.001
	Winter	MW, <0.001	T , <0.001	T, <0.001
	Spring	MW, <0.001	MW, <0.001	MW, <0.001
	Summer		MW, <0.001	T, <0.001
C2	Autumn	MW, 0.038	T, <0.001	MW, <0.001
	Winter	MW, <0.001	T, <0.001	MW, <0.001
	Spring	MW, <0.001	T, <0.001	MW, <0.001
	Summer	MW, 0.039	T, <0.001	MW, <0.001
C3	Autumn			
	Winter	MW, 0.007		
	Spring			
	Summer	MW, 0.003		
C4	Autumn		T, 0.006	
	Winter			
	Spring			
	Summer	MW, 0.013	T, 0.008	T, 0.040
Slope Ratio	Autumn	T, 0.0152		
	Winter		MW, 0.004	MW, <0.001
	Spring	T, <0.001	T, <0.001	
	Summer		T, <0.001	
DOC	Autumn			MW, 0.002
	Winter	MW, 0.035	MW, <0.001	MW, <0.001
	Spring			
	Summer	MW, <0.001	T, 0.019	
Slope (300-650)	Autumn		N.D.	N.D.
	Winter			
	Spring			T, 0.034
	Summer			
a305	Autumn		N.D.	N.D.
	Winter	T, <0.001	T, <0.001	T, <0.001
	Spring		MW, 0.003	MW, <0.001
	Summer		T, <0.001	T, <0.001
SUVA280	Autumn		N.D.	N.D.
	Winter	MW, <0.001	T, <0.001	
	Spring		T, 0.008	T, 0.005
	Summer	MW, <0.001	MW, 0.002	0.002
HIX	Autumn	MW, <0.001	MW, 0.002	T, 0.03
	Winter		MW, 0.023	MW, <0.001
	Spring			
	Summer		T, <0.001	MW, <0.001
FIX	Autumn		T, 0.033	MW, 0.016
	Winter		MW, 0.02	MW, <0.001
	Spring		MW, 0.001	MW, <0.001
	Summer			
BIX	Autumn			
	Winter			
	Spring		MW, 0.001	
	Summer	MW, 0.021		MW, 0.001

Chapter 3 Appendices Table 3. English Channel – Seasonal distributions

ENGLISH CHANNEL Surface only	DOC (µM)	DON (µM)	DOC:DON	N+N (µM)	Temp (°C)	Sal
WINTER						
Average	63.3			6.8	9.9	35.2
Std Dev	9.2					0.0
CV %	15					0
Std Error	4.1					0.0
Min	54.2			6.8	9.9	35.1
Max	78.5			6.8	9.9	35.2
Range	24.3			0.0	0.0	0.1
Sample Size	5			1	1	5
SPRING						
Average	74.9	5.6	12.9	0.3	14.0	35.2
Std Dev	18.6	1.6	6.1	0.5	0.5	0.0
CV %	25	29	47	164	3	0
Std Error	6.2	0.5	2.2	0.2	0.2	0.0
Min	48.0	3.2	8.9	0.1	13.4	35.2
Max	112.4	8.2	27.6	1.7	14.9	35.3
Range	64.4	4.9	18.7	1.7	1.5	0.1
Sample Size	9	9	8	10	8	8
SUMMER						
Average	68.6	7.3	9.5	1.8	18.4	35.0
Std Dev	1.2	0.1	0.0	1.5	0.6	0.2
CV %	2	1	0	85	3	0
Std Error	0.9	0.1	0.0	1.1	0.4	0.1
Min	67.8	7.2	9.4	0.7	18.0	34.9
Max	69.5	7.3	9.5	2.9	18.8	35.1
Range	1.7	0.1	0.1	2.2	0.8	0.2
Sample Size	2	2	2	2	2	2
AUTUMN						
Average	67.2	6.1	12.3	2.6	16.2	35.2
Std Dev	10.5	1.9	3.5	2.8	1.5	0.1
CV %	16	32	28	107	9	0
Std Error	2.9	0.6	1.0	0.8	0.5	0.0
Min	40.6	3.7	6.4	0.1	13.9	35.0
Max	81.9	9.7	17.9	8.1	18.3	35.4
Range	41.3	6.0	11.4	8.0	4.4	0.4
Sample Size	13	11	11	12	10	11

Chapter 3 Appendices Table 4. Celtic Sea on-shelf SML – Seasonal distributions

CELTIC SEA ON-SHELF SML	DOC (µM)	DON (µM)	DOC:DON	N+N (µM)	Temp (°C)	Sal
WINTER						
Average	67.3	5.2	13.4	7.0	10.3	35.2
Std Dev	9.7	1.3	3.2	0.9	0.9	0.2
CV %	14	26	24	13	8	1
Std Error	2.1	0.4	1.1	0.2	0.2	0.05
Min	53.5	3.3	9.7	5.7	9.1	34.8
Max	92.4	7.6	19.6	8.6	11.8	35.6
Range	38.9	4.3	9.9	2.9	2.6	0.8
Sample Size	21	11	9	21	23	22
SPRING						
Average	73.0	4.3	18.2	1.8	11.8	35.2
Std Dev	12.5	1.2	4.9	2.5	1.6	0.2
CV %	17	27	27	144	13	0
Std Error	2.3	0.2	1.0	0.5	0.3	0.03
Min	47.7	2.6	8.7	0.0	9.6	34.7
Max	99.3	8.6	29.3	8.3	16.1	35.6
Range	51.7	5.9	20.6	8.2	6.5	0.9
Sample Size	29	26	26	31	31	31
SUMMER						
Average	70.4	5.1	15.6	0.8	16.7	35.3
Std Dev	10.9	1.7	6.2	1.1	0.6	0.2
CV %	15	34	40	137	4	0
Std Error	3.3	0.6	2.1	0.6	0.2	0.1
Min	62.9	2.7	9.0	0.1	16.0	34.9
Max	101.4	7.4	23.6	2.0	17.7	35.5
Range	38.6	4.7	14.7	1.9	1.7	0.6
Sample Size	11	9	9	3	11	11
AUTUMN						
Average	69.2	5.3	14.0	3.1	13.9	35.1
Std Dev	7.8	1.3	3.8	3.0	0.7	0.7
CV %	11	24	27	96	5	2
Std Error	2.1	0.4	1.1	0.8	0.2	0.2
Min	55.0	3.2	7.4	0.2	12.4	33.2
Max	89.4	8.5	21.6	13.0	15.1	35.6
Range	34.5	5.3	14.2	12.8	2.7	2.4
Sample Size	14	12	12	14	14	14

Chapter 3 Appendices Table 5. Celtic Sea on-shelf BML – Seasonal distributions

CELTIC SEA ON-SHELF BML	DOC (µM)	DON (µM)	DOC:DON	N+N (µM)	Temp (°C)	Sal
WINTER						
Average	69.4	5.0	13.4	7.2	9.7	35.3
Std Dev	9.9	1.1	2.2	1.0	0.7	0.2
CV %	14	23	17	13	8	0
Std Error	3.3	0.3	0.7	0.3	0.2	0.0
Min	52.0	3.2	10.5	5.8	9.1	35.1
Max	84.2	6.8	16.8	9.0	11.2	35.6
Range	32.1	3.5	6.3	3.2	2.0	0.5
Sample Size	9	11	9	11	11	11
SPRING						
Average	69.1	4.4	17.2	7.4	9.9	35.3
Std Dev	7.4	1.4	4.1	0.9	0.8	0.2
CV %	11	32	24	12	8	1
Std Error	2.4	0.5	1.4	0.3	0.2	0.1
Min	54.0	3.0	10.4	6.6	8.9	35.0
Max	79.9	7.3	22.6	9.0	11.2	35.6
Range	25.9	4.3	12.2	2.5	2.3	0.6
Sample Size	10	9	9	11	11	11
SUMMER						
Average	68.8	5.1	16.5	8.6	10.5	35.4
Std Dev	20.3	2.1	6.4	0.6	0.6	0.1
CV %	29	42	39	7	5	0
Std Error	5.9	0.9	2.6	0.2	0.2	0.0
Min	55.3	2.2	11.8	7.8	9.7	35.2
Max	131.5	8.7	28.4	9.6	11.6	35.6
Range	76.2	6.5	16.6	1.8	2.0	0.4
Sample Size	12	6	6	12	12	12
AUTUMN						
Average	64.3	4.4	15.2	9.5	11.5	35.5
Std Dev	6.4	1.0	3.1	0.7	0.5	0.1
CV %	10	23	20	7	4	0
Std Error	1.7	0.3	0.9	0.2	0.1	0.0
Min	56.5	2.9	9.8	8.3	11.0	35.3
Max	79.9	6.3	20.3	10.7	12.4	35.6
Range	23.4	3.4	10.4	2.4	1.4	0.3
Sample Size	14	13	13	13	14	14

Chapter 3 Appendices Table 6. Malin-Hebrides on-shelf SML – Seasonal distributions

MALIN-HEBRIDES ON-SHELF SML	DOC (µM)	DON (µM)	DOC:DON	N+N (µM)	Temp (°C)	Sal
WINTER						
Average	60.1	4.5	15.1	10.1	9.8	35.2
Std Dev	11.4	2.2	5.5	1.6	0.4	0.2
CV %	19	49	37	16	4	1
Std Error	5.7	1.1	2.8	0.7	0.2	0.1
Min	49.6	2.5	9.8	7.3	9.2	35.0
Max	74.5	7.6	21.3	11.1	10.2	35.4
Range	24.9	5.1	11.5	3.8	1.0	0.4
Sample Size	4	4	4	5	5	3
SPRING						
Average	54.5	3.5	15.8	8.5	9.1	35.1
Std Dev	4.4	0.6	2.6	2.0	0.6	0.3
CV %	8	18	16	24	7	1
Std Error	1.5	0.2	0.9	0.7	0.2	0.1
Min	48.6	2.6	12.7	6.9	8.4	34.8
Max	62.4	4.6	19.8	11.3	9.8	35.6
Range	13.8	2.0	7.1	4.5	1.4	0.8
Sample Size	9	8	8	9	9	9
SUMMER						
Average	63.5	4.8	13.7	0.6	15.1	35.1
Std Dev	11.6	1.6	3.2	0.4	0.4	0.1
CV %	18	32	23	74	3	0
Std Error	6.7	0.9	1.8	0.3	0.2	0.1
Min	52.5	3.0	11.2	0.3	14.7	35.0
Max	75.6	5.9	17.3	1.1	15.5	35.3
Range	23.1	2.9	6.1	0.8	0.9	0.2
Sample Size	3	3	3	3	3	3
AUTUMN						
Average	66.6	4.4	18.3	4.5	12.3	35.2
Std Dev	9.5			0.2	0.1	0.3
CV %	14			4	1	1
Std Error	4.3			0.1	0.1	0.1
Min	58.7	4.4	18.3	4.2	12.1	34.7
Max	81.5	4.4	18.3	4.7	12.4	35.4
Range	22.8	0.0	0.0	0.5	0.3	0.6
Sample Size	5	1	1	5	5	5

Chapter 3 Appendices Table 7. Eastern Irish Sea – Seasonal distributions

EIS Surface only	DOC (µM)	DON (µM)	DOC:DON	N+N (µM)	Temp (°C)	Sal
WINTER	N.D.					
SPRING						
Average	75.8	5.4	14.9	4.9	10.1	33.7
Std Dev	9.8	1.7	3.2	4.7	1.9	0.4
CV %	13	32	22	96	19	1
Std Error	3.7	0.7	1.2	1.8	0.7	0.1
Min	60.3	3.1	10.5	0.0	8.2	33.1
Max	88.8	7.6	19.4	10.6	12.6	34.2
Range	28.5	4.5	8.9	10.6	4.5	1.1
Sample Size	7	7	7	7	7	7
SUMMER						
Average	89.9	8.1	11.3	0.3	16.5	34.0
Std Dev	3.3	1.7	1.9	0.2	0.4	0.0
CV %	4	21	17	64	2	0
Std Error	2.4	1.2	1.4	0.1	0.3	0.0
Min	87.6	6.9	9.9	0.2	16.3	34.0
Max	92.3	9.3	12.7	0.5	16.8	34.0
Range	4.7	2.4	2.8	0.3	0.5	0.0
Sample Size	2	2	2	2	2	2
AUTUMN						
Average	43.5			20.8	12.8	33.2
Std Dev						
CV %						
Std Error						
Min						
Max						
Range						
Sample Size	1			1	1	1

Chapter 3 Appendices Table 8. Western Irish Sea – Seasonal distributions

WIS Surface only	DOC (µM)	DON (µM)	DOC:DON	N+N (µM)	Temp (°C)	Sal
WINTER	N.D.					
SPRING	73.3	4.4	20.0	6.4	10.0	34.3
Average	10.5	2.3	7.9	4.0	1.4	0.2
Std Dev	14.3	51.8	39.5	63.0	13.8	0.7
CV %	2	0	2	1	0	0
Std Error	54.1	2.0	5.9	0.0	8.6	34.0
Min	90.1	11.3	40.9	10.6	13.0	34.8
Max	36.0	9.4	35.0	10.6	4.5	0.8
Range	27	23	23	26	28	28
Sample Size						
SUMMER						
Average	89.6	6.4	14.0	2.3	14.9	34.4
Std Dev	27.1	1.3	3.7	1.5	1.4	0.2
CV %	30	19	26	66	9	1
Std Error	8.6	0.4	1.2	0.4	0.4	0.1
Min	67.2	5.1	9.4	0.2	12.2	34.1
Max	143.0	9.1	23.3	4.1	16.5	34.8
Range	75.8	4.0	13.9	3.9	4.3	0.7
Sample Size	10	10	10	12	12	12
AUTUMN						
Average	76.1	5.0	15.7	4.1	14.1	34.4
Std Dev	5.5	1.1	2.5	0.1	0.1	0.0
CV %	7	22	16	2	0	0
Std Error	2.1	0.6	1.5	0.0	0.0	0.0
Min	71.7	4.2	13.1	4.0	14.0	34.4
Max	85.9	6.2	18.1	4.2	14.2	34.4
Range	14.2	2.0	5.0	0.2	0.2	0.0
Sample Size	7	3	3	5	7	7

Chapter 4 Appendices Table 9. Southern North Sea – Seasonal distributions

SOUTHERN NORTH SEA	DOC (µM)	DON (µM)	DOC:DON	N+N (µM)	Temp (°C)	Sal
WINTER						
Average	81.1					33.8
Std Dev	22.2					1.7
CV %	27					5
Std Error	5.9					0.4
Min	55.0					29.7
Max	122.8					35.0
Range	67.8					5.3
Sample Size	14					15
SPRING						
Average	87.3	5.3	18.7	3.7	13.1	34.6
Std Dev	23.0	1.7	11.2	8.9	2.4	0.4
CV %	26	33	60	242	18	1
Std Error	3.4	0.3	1.8	1.3	0.5	0.1
Min	45.2	1.6	5.7	0.0	8.0	33.6
Max	169.7	8.1	58.5	40.7	16.1	35.1
Range	124.6	6.5	52.8	40.7	8.1	1.5
Sample Size	46	38	38	44	27	27
SUMMER						
Average	79.1	5.9	16.2	0.5	16.9	34.5
Std Dev	15.2	2.1	9.3	0.8	2.1	0.4
CV %	19	36	57	145	12	1
Std Error	3.5	0.5	2.4	0.2	0.5	0.1
Min	58.8	2.4	9.5	0.0	12.8	33.7
Max	128.2	9.2	42.8	2.6	20.0	35.2
Range	69.4	6.8	33.3	2.6	7.2	1.4
Sample Size	19	15	15	19	19	19
AUTUMN						
Average	71.6	5.7	13.1	5.1	13.5	34.8
Std Dev	7.9	1.0	3.0	2.8	0.4	0.1
CV %	11	17	23	54	3	0
Std Error	3.2	0.4	1.4	1.1	0.3	0.1
Min	58.7	4.2	9.9	0.8	13.2	34.7
Max	80.1	6.8	17.8	9.1	13.8	34.9
Range	21.4	2.6	7.9	8.3	0.5	0.2
Sample Size	6	5	5	6	2	2