



Distribution and C/N stoichiometry of dissolved organic matter in the North Sea in summer 2011-12

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Abstract. We present the distribution and C:N stoichiometry of dissolved organic matter (DOM) in the North Sea in 2 summers (August 2011 and August 2012), with supporting data from the intervening winter (January 2012). This data
10 demonstrates local variability superimposed on a general pattern of decreasing DOM with increasing salinity, suggesting strong control over broad scale concentrations by mixing between riverine sources and the open North Atlantic. We observe differences in DOC and DON concentrations and gradients between the two summers, leading to an estimated 10-20 Tg difference in the DOM carbon inventory between the 2 years, which is of the same order as the annual uptake of atmospheric CO₂ by the North Sea system, and thus significant for the carbon budget of the North Sea. Differences were particularly
15 pronounced in the bottom layer of the seasonally stratifying Northern North Sea, with higher DOC and lower DON in 2011 and lower C:N ratio and more moderate concentrations of DOC and DON in 2012. Using other data we consider the extent to which these differences in the concentrations and C:N ratio of DOM could be due to differences in the biogeochemistry or physical circulation in the 2 years, or a combination of both. We discuss the implications of these observations for the shelf sea carbon pump and the export of carbon rich organic matter off the shelf.

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1 Introduction

Coastal and shelf seas are generally more productive than the open ocean (Jickells, 1998; Simpson and Sharples, 2012), and through various processes have been proposed as potentially disproportionately important for the drawdown of atmospheric
25 carbon to the deep ocean (Bauer et al., 2013; Regnier et al., 2013; Thomas et al., 2005b; Tsunogai et al., 1999). Our understanding of the mechanisms of such shelf carbon pump processes and their relative importance is limited by observational data, the complexities of shelf circulation and interannual variability of both biological processes and physical drivers, particularly in complex systems such as the North Sea (Bozec et al., 2005; Kühn et al., 2010; Simpson and Sharples, 2012; Thomas et al., 2004, 2005b).



1.1 Dissolved organic matter and the continental shelf pump

One potentially important mechanism of shelf carbon export to the deep ocean is via dissolved organic matter (DOM). Marine DOM is a complex mixture of organic material from various sources both terrestrial and marine, with a spectrum of lifetimes from hours to millennia (Hansell, 2013; Nelson and Wear, 2014; Repeta, 2015). Its reactivity and in particular its availability for breakdown by marine microbes is a key factor controlling in its lifetime in relation to degradation to inorganic carbon (e.g. Jiao et al., 2014) and thus capacity for long-term carbon storage. A recent synthesis of DOC in continental shelf seas observes a strong relationship between distance from rivers and decreasing DOC concentration, with significant enrichment of DOC in nearshore waters relative to the open ocean, leading to inferred global DOM flux across the shelf break ranging between 7 and 29 Pg C yr⁻¹ (Barrón and Duarte, 2015). This is consistent with a long term observational data set from the North Sea (Van Engeland et al., 2010) and results from the Mid Atlantic Bight (Bauer et al., 2002; Vlahos et al., 2002) and Arctic (Wang et al., 2006).

This export flux is composed of a combination of terrestrially-derived organic matter from rivers (allochthonous DOM) and production of autochthonous DOM on the shelf through in-situ autotrophic processes; although the relative importance of the different sources in shelf sea systems is uncertain. The stoichiometry of exported DOM may also be an important indicator of the efficiency of the shelf carbon pump. This stoichiometry is normally compared to the so-called Redfield ratio, and deviations of DOM stoichiometry from Redfield have been observed (Abell et al., 2000; Aminot and K erouel, 2004; Ducklow et al., 2007; Hopkinson and Vallino, 2005; Letscher and Moore, 2015; Pujo-Pay et al., 2011), although it needs to be recognised that the Redfield ratio is not a single fixed ratio even in primary production (Moore et al., 2013). Despite these caveats, a net enrichment of carbon relative to nitrogen as shelf seas process internally-produced organic matter implies possible re-use of the nitrogen to drive further primary production, thus decoupling organic matter processing from the relatively fixed stoichiometry of algal growth. Carbon-rich DOC might be produced by the preferential remineralisation of phosphorus and nitrogen over carbon from DOM by bacteria (e.g. needing to meet their nutrient requirements for growth) (L onborg et al., 2010) or via the ‘overflow production’ of carbon rich organic matter by phytoplankton under situations of nutrient limitation, also referred to as ‘carbon overconsumption’ (Prowe et al., 2009; Toggweiler, 1993). The bioavailability/reactivity of exported DOM is also likely to impact the efficiency of the shelf pump, with e.g. a change to more refractory DOM leading to accumulation in the marine system and subsequent net removal of carbon from the atmosphere. The bioavailability of DOM in shelf environments has been proposed to be linked to nutrient availability, with higher nutrient (specifically, nitrogen) availability leading to greater remineralisation of DOM which has low bioavailability as a result of its high C:N ratio and thus a decrease in microbial carbon pump efficiency (Jiao et al., 2014).



1.2 The North Sea system

The North Sea can be characterised by a shallow, well mixed water column in the south (Emeis et al., 2015), and a deeper seasonally stratifying system to the North (Van Haren and Howarth, 2004; Knight et al., 2002), with the boundary between these systems at roughly 55N and ~40m depth. The North Sea is a highly productive shelf sea, particularly the southern part which fixes 25 – 30 mol C m⁻² yr⁻¹ (Emeis et al., 2015), although as the southern North Sea water column remains well mixed throughout the year, and is highly affected by riverine carbon fluxes, respiration processes may mean it is a net source of carbon to the atmosphere (i.e. net heterotrophic) (Bozec et al., 2005). In contrast, the northern North Sea is thought to be net autotrophic (i.e. accumulates organic matter and is a net sink for inorganic carbon) and through its seasonal stratification and the consequent vertical separation of surface autotrophy and respiration at depth, is a strong net sink for atmospheric CO₂ (~2 mol m⁻² yr⁻¹ taken up at the air-sea interface) (Clargo et al., 2015). Deeper waters in the northern North Sea are thought to exchange with the deep ocean, so the accumulation of respiration products there (i.e. dissolved inorganic carbon, DIC) may be an important mechanism in the shelf carbon pump (Bozec et al., 2005; Thomas et al., 2004). These net DIC exchanges represent small differences between the large carbon fluxes representing primary production and respiration over the seasonal cycle. Recent studies have also noted that there can be important interannual variations of North Sea circulation and exchange with open Atlantic waters linked to cycles such as the North Atlantic Oscillation (NAO, Salt et al., 2013; Sheehan et al., 2017) and possibly longer-term shifts in patterns of production (McQuatters-Gollop et al., 2007) which have the potential to alter the net DIC exchange fluxes.

The role of DOM in the carbon pump of the North Sea is even less clear than that of DIC. Thomas et al. (2005b) observe inflows and outflows to the North Sea which suggest minor net respiration of DOC, based on observations from a single year (spring and autumn cruises). However, Prowe et al. (2009) invoke the production of carbon rich organics via overflow production in the northern North Sea to explain the apparent decoupling of nitrate and DIC drawdown over a seasonal cycle. Various studies also point to strong seasonality in the in-situ production of DOM by algae (especially during the spring bloom) and subsequent slow degradation (time scales of weeks to a month or so), albeit with strong spatial variability and apparent patchiness (Van Engeland et al., 2010; Johnson et al., 2013; Suratman, 2007; Suratman et al., 2008, 2009). At the current level of knowledge and available data it is impossible to determine whether the North Sea is a net source or sink for DOC in a typical year. In order to better understand the dynamics and stoichiometry of DOM, and whether or not there is the potential for an organic matter continental shelf pump for carbon (Barrón and Duarte, 2015; Thomas et al., 2005b), a more detailed understanding on the spatial variability and large-scale controls on DOM concentrations is thus required.

We undertook a spatial survey of the North Sea on cruises of opportunity in two summers (2011 and 2012) and the intervening winter to investigate the broad scale distribution and stoichiometry of DOM, on the working hypotheses that i) the dominant control on DOC/DON concentration would be salinity, and this would represent mixing of riverine or low



5 salinity autochthonous marine DOM (Barrón and Duarte, 2015) with a relatively constant high salinity end-member, characteristic of the North Atlantic; ii) this signal would be complicated, particularly in summer, by internal processes in the open North Sea such as algal production and bacterial degradation (e.g Johnson et al., 2013); iii) that the stoichiometry of DOM in surface waters would show higher C:N than deeper waters due to carbon overconsumption due to nutrient limitation in summer and iv) given that agriculturally-influenced rivers tend to have low C:N DOM, due to high nitrogenous inputs (Mattson et al., 2009), that the C:N ratio would increase with salinity, towards the characteristic C:N of DOM of N. Atlantic winter water of approximately 13-15 (Aminot and Kérrouel, 2004).

2 Study area, sampling and analytical methods

2.1 Study sites and field sampling processes

10 Sampling (Fig. 1) was conducted on 3 cruises of opportunity on board the RV Cefas Endeavour (CEND 14/11, 8th August to 7th September 2011; CEND 02/12, 20th to 31st January 2012; and CEND 13/12, 9th to 21st August 2012). The two summer cruises were the summer surveys of the long-term ICES (International Council for the Exploration of the Sea) international bottom trawl survey, with the primary aim of surveying fish numbers. The sampling grid is determined by the needs of this survey, and aims to occupy one station in each of the ICES survey rectangles, with each station being close to the same location each year (The International Council for the Exploration of the Sea (ICES), 2017). Due to time and weather constraints the more northerly stations of the survey were not sampled in 2012. The winter cruise surveyed a set predominantly of coastal sites in the well mixed southern and western North Sea.

20 Surface and bottom waters were sampled from 10 litre Niskin bottles attached to a CTD rosette. In general, surface and bottom water samples were collected at 2-4 meters below the surface and 5-6 meters above the seabed respectively. Sampling focused on the open waters of the North Sea and did not sample near shore regions with strong riverine influence (minimum observed salinity at DOM sampling points =30.9, 87% of samples had salinity >34.0).

25 Samples were collected at all stations for measurements of DOC and DON, along with dissolved inorganic nutrients (the sum of NO_3^- and NO_2^- (henceforth nitrate), ammonium, phosphate and silicate). Additionally, chlorophyll a, POC and PON samples were collected during the summer 2012 cruises. Standard hydrographic measurements including temperature and salinity were recorded by the ship's water column profiling equipment and processed using standard techniques (Tom Hull, Cefas, pers. comm.).

2.2 Analytical procedures

30 Water samples were filtered immediately on-board upon collection to separate dissolved material (DOC, DON and inorganic nutrients) from particulate material (POC and PON). Filters and most of the filtration unit were combusted in a muffle



furnace before use (Kaplan, 1992; Sharp et al., 1993). Gentle vacuum filtration (~5 kPa) was used through pre-combusted (450 °C, 5 hours) glass fiber filters, 47 mm diameter of nominal pore size 0.7 µm with an ashed (550 °C, 5 hours) glass filtration unit. Filtrates were then collected in polypropylene sample tubes (Fisherbrand™ polypropylene centrifuge tube 50ml, Fisher Scientific, UK) for DOC, TDN and inorganic nutrients analysis. This storage regime has previously been shown to be effectively preserve and not contaminate these analytes (Chaichana, 2017; Suratman, 2007; Tupas et al., 1994). Filters were wrapped in aluminium foils for POC and PON analysis, the water volume recorded. Chlorophyll *a* samples were collected from a separate water sub-sample on the same type of GF/F glass fibre filters (without combustion, gentle vacuum filtration ~10 kPa) and the water volume recorded. All samples were immediately frozen at -20 °C after filtration on board (-60 °C for Chlorophyll *a* samples) until further analysis in the laboratory.

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DOC and total dissolved nitrogen (TDN) were determined by the high temperature catalytic oxidation method coupled with nitrogen chemiluminescence detector system (HTCO-TOC-ND system) using a Skalar Formacs^{HT} combustion TOC/TN analyser (Skalar analytical, Netherlands) coupled with a Skalar nitrogen chemiluminescence detector (ND20, Skalar analytical, Netherlands). The methods involve minor developments of those we have reported previously (Johnson et al., 2013; Suratman et al., 2010). The combustion temperature was 750 °C. The catalyst was a layer of cobalt-chromium (CoCr, ~15 g sitting on quartz wool to prevent loss of the catalyst from the bottom of the combustion tube) and cerium oxide (CeO₂, ~2.5 g on top) in a quartz glass column. Carbon-free, high purity air (Zero grade air, BOC gases, England) was used as carrier gas (240 ml/min). To eliminate inorganic carbon in samples, acidification (adding 100 µl of 10% hydrochloric acid to 6 ml of sample), sparging (using pure air for 240 s) and stirring (180 s) were performed automatically by the TOC/TN analyser. The sample injection volumes was 200 µl (the best 2 injections were chosen automatically from 2 - 4 injections to achieve the coefficient of variation (CV) better than 2 %).

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Calibrations of the instrument were carried out by potassium hydrogen phthalate (KHP) (0-300 µM) and a mixture of ammonium sulphate and potassium nitrate (0 – 50 µM) dissolved in Milli-Q water for DOC and TDN analysis respectively. The system blank was estimated by using acidified and sparged Milli-Q blank injection which was 29.2 ± 4.2 µM (n = 78) for DOC and was 0.6 ± 0.6 µM, (n = 79) for TDN analysis. The value agreed with the system blank reported in other previous studies (Álvarez-Salgado and Miller, 1998; Badr et al., 2003; Benner and Strom, 1993; Hopkinson et al., 1993; Koike and Tupas, 1993; Suzuki et al., 1992). The blank correction was applied to DOC and TDN data. Precision is expressed here as a coefficient of variation (CV) obtained by replicate measurement of the same sample (Miller and Miller, 2010). A continuous run of 40 standards in the same batch provided the analytical precision about 2% and 4% for DOC (used 100 µM) and TDN (used 10 µM standard) analysis, respectively.

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Two types of consensus reference materials (CRM): low carbon water (LCW) and deep seawater reference water (DSR), provided by the Hansell laboratory, the University of Miami (Hansell, 2005), were used to verify the measurement. For DOC



analysis, a consensus value of DOC for LCW is 1 μM . The analysis of LCW in this study yielded a small negative value of DOC concentration as the DOC value for LCW is lower than the system blank value, therefore, sample concentrations was not corrected by the LCW value. Consensus values of DOC for DSR vary in each batch. The analysis of these DSR yielded mean concentration of $42.6 \pm 2.9 \mu\text{M}$ ($n = 98$) and $42.4 \pm 2.6 \mu\text{M}$ ($n = 66$), which were in good accord with the consensus values of 41 – 44 μM (batch 10 lot# 05-10, batch 13 lot# 02-13) and 42 – 45 μM (batch 14 lot# 01-14), respectively. The quantitative recovery of DSR relative to the consensus values is $(100 \pm 7\%, n = 98)$ and $(98 \pm 6\%, n = 66)$. The oxidation efficiency of KHP relative to urea was 93-105% ($100 \pm 3\%, n=50$) and 97 – 108% ($100 \pm 2, n=20$) for 50 μM and 200 μM , respectively. This agreed with previous finding which showed the result $\sim 100\%$ for 200 μM KHP-glycine standard compared to urea (Watanabe et al., 2007). The limit of detection (LOD) estimated as the analyte concentration giving a signal equal to the blank signal plus three standard deviations of the blank (Miller and Miller, 2010) was 6 μM for DOC analysis. The mean of DOC concentrations for DSR SRM is similar between the analyses for the 2 years, with median values differing by less than 1 μM and does not show a significant difference (t-test, $p > 0.05$) between the analysis for summer 2011 and summer 2012 (Fig. S1, supplementary material).

For TDN analysis, the analysis of LCW yielded a concentration 0 μM (no peak areas were detected during TDN analysis), which was in good agreement with the consensus values of 0 μM . The analysis of the DSR yielded a mean concentration of $32.8 \pm 1.7 \mu\text{M}$ ($n = 176$), which was in good agreement with the consensus value of 31 – 33 μM . The quantitative recovery of DSR relative to the consensus values is $102 \pm 5\%$ ($n = 176$). The oxidation efficiency of the mixed standard relative to urea was 92 – 106 ($98 \pm 4, n = 52$) and 94 – 105 ($99 \pm 3, n = 32$) for 10 μM and 50 μM , respectively. The limit of detection for TDN analysis was 1 μM . DON was calculated by subtracting dissolved inorganic nitrogen (DIN) concentration (the sum of nitrogen in the form of nitrate and ammonium) from the TDN concentration. Therefore, the precision of DON is affected by the sum of uncertainties in TDN and DIN analysis. In this study, the precision of TDN, nitrate and ammonium, calculated as a coefficient of variation obtained by replicate measurements of the same samples (Miller and Miller, 2010) were 4%, 3% and 4%, respectively. The resulting uncertainty on DON depends on the relative concentrations of these analytes in a given sample, but where DIN is low (e.g. in surface waters in summer) it roughly equates to the uncertainty on the TDN analysis (4%), whereas where DIN is high and DON is relatively low (e.g. deeper stratified north sea water and all winter samples), uncertainty can be significantly higher, up to $\pm 30\%$ at very low DON concentrations (less than 5 μM). However, in the context of the broad range of concentrations observed in this study, such uncertainties do not affect the findings or conclusions presented here.

Measurements of dissolved inorganic nutrients (nitrate, ammonium, phosphate and silicate) were performed using standard spectrophotometric methods (Kirkwood, 1996) using a Skalar San⁺⁺ autoanalyser (segmented flow analysis and colourimetric chemistry, Skalar analytical, Netherlands). The limit of detection for nitrate, ammonium, phosphate and silicate were 0.1, 0.2, 0.1 and 0.1 μM , respectively. Accuracy was assured by the use of Environment Canada CRMs with



average measured values all within 10% or better of the consensus value. For POC and PON samples, filters were placed overnight (12 hours) in a desiccator saturated with concentrated hydrochloric acid (HCl, 36% w/v) fumes to remove inorganic carbon (carbonate). The filters were then dried for 24 hours at 60 °C. POC and PON were determined by the dry oxidation method using the Exeter Analytical CE440 Elemental analyser (Exeter analytical Ltd.,UK). The precision as the coefficient of variation (CV) was about 1% for C and 4% for N. Chlorophyll *a* filters were extracted by acetone and measured by spectrofluorometric method (Holm-Hansen et al., 1965; Parsons et al., 1985) using spectrofluorometer (Perkin Elmer LS45, USA). The detection limit of the measurement was 0.1 µg/L.

3 Results

3.1 Physical oceanographic conditions

10 During the summer cruises there was a clear difference between southern, well mixed waters and northern, stratified waters in both physical and biogeochemical parameters, as expected. By comparing surface and bottom temperatures we divide the summer cruise data up into 3 sets (henceforth ‘water types’) for further analysis: ‘(southern) well mixed’, ‘(northern) stratified surface layer’ and ‘(northern) stratified bottom layer’. We consider the limited winter cruise data as a whole, on the basis that it is mostly in the permanently well mixed southern part of the North Sea, and given that the whole system is vertically well-mixed in Winter.

Surface waters were generally warmer in summer 2012 than in 2011 (Table 1; Fig S2), and the stratified bottom waters show mostly colder but more variable temperatures in 2011 than in 2012. T-S diagrams (Fig. S2 of supplementary material) of the whole dataset reveal a dominant pattern of mixing of warmer, fresher water with colder, saltier water, with some colder, fresher water observable in the winter data. Although 2011 and 2012 northern bottom waters appear to sit within the same (noisy) mixing line between these end members, there is little overlap in T-S space between the 2 years suggesting considerable renewal of water in the bottom layer between the 2 years. Some of the highest salinities in the dataset are observed relatively close to the coast, in the winter cruise, suggesting possible inflow into the southern North Sea from the English Channel.

25 3.2 Inorganic nutrients

Inorganic nutrient concentrations, summarised in Table 1 show the typical pattern expected for the North Sea, with relatively high concentrations in the winter, and at depth in the northern North Sea, and low concentrations in summer surface waters, presumably due to utilization by phytoplankton. Northern surface waters tend to be more depleted in nutrients than southern well mixed waters, due to the greater re-supply of nutrients from the benthos, river and possibly atmospheric inputs to the latter. Figure 2 presents nitrate, phosphate, ammonium concentrations by cruise and water type. Note that silicate (not



shown) follows a similar pattern to phosphate except for apparently reaching limiting concentrations in all surface waters in both summers.

5 Nitrate and phosphate concentrations and inorganic N:P ratios in the northern bottom waters were significantly higher in 2011 than 2012. This suggests differences between the two years which may reflect differences in water exchange with the open Atlantic, differences in productivity, plankton community and nutrient limitation in the spring and summer before sampling or a combination of all of these.

10 Note that the data are potentially skewed by the more northerly extent of the 2011 cruise sampling waters richer in nitrate and phosphate. However statistical comparison (by t-test, $p < 0.05$) of only the portion of the 2011 cruise south of 59N (i.e. the section covered in both years), reveals a similar, and still statistically significant, difference. The same comparisons have been made for DOC and DON and where we report differences between years these are significant even after comparison on the same basis.

15 Ammonium concentrations have previously been suggested as being diagnostic of the trophic state of the marine system, with periods of decoupling of respiration from photosynthesis leading to accumulation in ammonium concentrations over large areas of the ocean (e.g. Johnson et al., 2007). Ammonium concentrations were high (median values $> 1 \mu\text{M}$) and variable in northern deep waters and not significantly different in the two summers, probably suggesting high levels of remineralisation and heterotrophy in deep waters in both years. In well mixed waters in 2012 most observations were at or below detection limit; however in summer 2011, concentrations were substantially elevated with a median concentration comparable to that of northern bottom waters ($\sim 1.2 \mu\text{M}$), but these high concentrations were generally observed at the bottom of the water column and not in the surface. This is possibly indicative of a strongly net heterotrophic state, either due to remineralisation of sinking organic material, or resuspended benthic material in the southern North Sea in 2011 that was not the case in 2012. These elevated ammonium concentrations coincide with phosphate concentrations being higher in well mixed waters (surface and bottom) in 2011 than 2012. This elevated phosphate is also consistent with greater heterotrophy relative to autotrophy in 2011 than 2012, or the influence of benthic resuspension.

3.3 Dissolved organic carbon and nitrogen concentrations

30 Figure 3 shows the geographic distribution of dissolved organic carbon and nitrogen over the survey area in both summers. Statistical summary of the concentrations is presented in Table 2. In general, higher concentrations were seen in the coastal zones particularly in the Southern Bight, the German Bight and surrounding the East Anglian plume (the Thames estuary, the Humber estuary and the Wash) for both surface and bottom water, and around the coast of Denmark, and lowest concentrations in higher salinity waters in the North. This is consistent with previous observations in the Southern North Sea (Van Engeland et al., 2010) and implies that mixing of riverine/estuarine DOM with open ocean waters is a major control on DOM concentration across the gradient from river to open ocean. Figure 4 presents DOC and DON concentrations with



5 salinity and serves to confirm hypothesis 1 that the gradient in DOM from low salinity, river influenced water to high salinity open-ocean water is a major characteristic of DOM concentrations in the North Sea. Superimposed on the simple mixing relationship is considerable variability which we suggest reflects production and consumption of DOM produced in situ (hypothesis 2). The inverse relationship between salinity and DOC is particularly clear in southern well mixed waters and northern bottom waters, with surface waters in the stratified north showing considerable deviation from the trend, presumably due to in situ consumption and production by microorganisms. The same is the case for DON in summer 2011 but in summer 2012 (Fig. 4d) the salinity relationships is more confused, with northern stratified bottom waters appearing to show a positive relationship with salinity (albeit over a very limited salinity range). The limited winter data (Table 3) show high, but also highly variable DOC concentrations. DON concentration in winter was of a similar magnitude to the summer values but was highly variable. However, the winter data reflects a limited survey area mostly very near to river inputs, so may not reflect conditions in the wider North Sea.

15 DOC average concentrations are an order of magnitude smaller than DIC (e.g. Clargo et al., 2015), and POC average concentrations are 6 times smaller than DOC (Table 2). Hence DIC dominates the carbon inventory in the water. This is not the case for DON, which becomes the dominant form of nitrogen in summer and hence its degradation rate has the potential to influence nutrient availability and phytoplankton productivity. PON is about 3 times smaller than DON in terms of average concentrations, further demonstrating the important role of DON as a nitrogen reservoir in nutrient cycling in shelf environments.

20 From the DOM vs salinity relationships, it is possible to derive apparent low salinity end-members for DOC and DON and these vary by water type and season (Table 3). The estimated zero-salinity concentrations were 420 μM DOC and 40 μM DON for the combination of two surveys in summer, giving a source C:N ratio of about 10. It is not possible to say from these data whether the high DOM concentrations at low salinities are river-derived (allochthonous) or produced in estuaries or the near-coastal zone (autochthonous), fed by the riverine delivery of inorganic nutrients. Given the low range of salinities observed and the high in-situ variability, the end member values derived here are highly uncertain, but their values are consistent with typical riverine DOC and DON observations (Agedah et al., 2009; Markager et al., 2011; Neal and Robson, 2000). The slope (~ 10) and y intercept (~ 420) for the DOC vs salinity relationship estimated here for the North Sea are also quite similar to those estimated by Bauer et al., 2013 (11.5 slope 455 intercept) for the mid Atlantic Bight region off the US east coast.

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3.4 DOM stoichiometry

The change in C:N ratio with salinity (Fig. 4 e and f) reveals striking differences between 2011 and 2012, with C:N increasing with salinity in 2011 to values above the expected North Atlantic endmember of 13-15, particularly seen in bottom waters of the stratified northern north sea. In 2012 however the C:N ratio decreases to below 10 at high salinities in
5 bottom waters, due to the combination of higher DON and lower DOC than in the previous year. This therefore appears to contradict our hypothesis (iv) of C:N ratio being dominated by mixing line between riverine and open ocean C:N and is investigated further in Section 4.

Plots of DOC vs DON for both summers (Fig. 5) reveal a gradient of between 6.5 and 7. Hopkinson and Vallino (2005)
10 interpret such element/element plots in a study of depth profiles of DOM in the open ocean as indicative of the stoichiometry of DOM breakdown and processing over time. In our dataset, where the concentration of DOM at low salinity is more than an order of magnitude higher than the open ocean concentrations, the slope of this line is, to first order, representative of the stoichiometry of DOM at low salinity (note in Figure 5 that the general pattern is one of increasing salinity with decreasing DOM concentration, particularly in 2011). Thus the gradient could be indicative of autochthonous production of DOM by
15 phytoplankton at or near the Redfield C:N of 6.6:1, in estuarine or coastal waters, driven by riverine nutrient input. However, Mattsson et al., (2009) note in a synthesis of riverine DOM C:N ratios that rivers flowing through catchments with high levels of intensive agriculture commonly have low C:N, likely due to the high inputs of inorganic nitrogen in fertiliser. Thus the C:N of ~7 is potentially consistent with an allocthanous (i.e. terrestrial) DOM source also. More measurements of DOC/N in rivers and estuaries flowing into the North Sea would be a valuable addition to our knowledge of low salinity
20 DOM cycling and production in this region.

3.5 Interannual differences

Consistent with the strong spatial freshwater/seawater mixing gradients, higher DOC concentrations are observed in southern well mixed than northern stratified waters in both 2011 and 2012, although this is not the case in 2012 for DON, where average concentrations in all waters of survey area are very similar (Table 2). In 2011 southern well mixed waters
25 demonstrated statistically significantly (t-test, $p < 0.05$) higher concentrations of DOC and DON than either northern surface or bottom waters (Table 2, Figure 6). In the northern stratified waters DOC and DON concentrations were generally slightly higher in surface waters than at depth. Larger differences in DOM concentrations however, are observed between the 2 years than between surface and bottom concentrations within either of the years.

30 Generally, DOM concentrations were elevated in 2011 compared to 2012. The survey in 2011 presented significantly higher concentrations of DOC and DON than the summer 2012 survey in the whole water data set (all stations) (t-test, $P < 0.05$), each data set separated by the three different water types (t-test, $P < 0.05$), and each data set separated by two water types



(whole surface data and whole bottom data) (t-test, $P < 0.05$). Figure 4 demonstrates that these differences are not related to sampling different salinity ranges on the same DOM/salinity gradient, but rather that concentrations of DOC for all water types, and DON for all but northern bottom waters are elevated in 2011 vs 2012 for a given salinity.

5 Given the challenges associated with DOM analysis it is essential that we demonstrate that this apparent difference cannot be due to a systematic analytical error in DOC measurement. We have demonstrated (Section 2, Fig S1) that repeat measurements of CRMs do not vary systematically in their DOC concentration between the analyses for 2011 and 2012 samples, so we are satisfied that this is not the case and we conclude that this DOC enrichment is a real feature of the North Sea in 2011.

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The C:N ratios of DOM in northern stratified waters show a particularly large difference between the two summers, dominated by the C:N ratio of DOM in the bottom waters. Whilst C:N ratio in the surface is the same in both years (11.3 +/- 1.4 in 2011, 11.7 +/- 2.3 in 2012) the bottom water C:N changes from being higher than surface values in 2011 (13.4 +/- 3.6), to being lower than surface values in 2012 (9.3 +/- 1.8). Thus our working hypothesis iii), that carbon-rich DOM production in surface in summer would lead to enhanced C:N in the surface compared to deep waters is demonstrated to be unfounded. A DOM C:N ratio of 11 is consistent with greater-than-Redfield C:N DOM production, in both years, but the relative C:N is dominated by the bottom water signal.

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3.6 DOM in bottom waters

In order to further investigate bottom water DOM, we investigate the change in DOM concentrations with depth. The relationship between bottom water DOM concentrations and depth (Fig 7) reveals interesting differences between the years, with elevated DOC throughout bottom waters in 2011 (typically 20 to 40 μM higher concentrations than in 2012) and with a pattern of more elevated DOC concentration in shallower regions in 2011, compared to 2012 (in which bottom waters across the survey region appears to have similar DOC concentrations irrespective of depth, except for the shallowest waters). The pattern for DON in bottom waters in 2012 is similar – with little variation with depth of water. However, DON in 2011 behaves very differently, with shallower waters showing enrichment in DON relative to the following year (typically 10 μM compared to 5 μM in 2012), but with deep waters showing similar or even lower DON concentrations than in 2012. Consequently, deep bottom waters with relatively high DOC and low DON in 2011 show elevated C:N ratios (Figure 7c), in a substantial number of cases higher than the typical North Atlantic end member of 13-15 (Aminot and K erouel, 2004).

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4. Discussion

30 The data presented in this paper demonstrate that there is significant complexity in the DOM dynamics in the North Sea both spatially and inter-annually, although through this the expected pattern of decreasing DOM with salinity is still discernible.



The results also demonstrate that there are considerable (and interannually variable) inventories of carbon and nitrogen in DOM in the North Sea. In this discussion, we consider the various potential controls on DOM concentrations, stoichiometry and interannual variability in the following sections, as well as considering the significance of DOM for nitrogen cycling and carbon uptake in the North Sea.

5 4.1 DOM-Salinity relationship

10 The data presented above demonstrates that mixing between high DOM, low salinity estuarine waters and low DOM, high salinity ocean waters is an important component of DOM dynamics in the North Sea. Given the relatively high concentrations of DOM on the shelf relative to the North Atlantic, the DOM data presented here generally supports the suggestion by (Barrón and Duarte, 2015) that shelf sea regions have the potential to export DOC from the continental shelf water to the open ocean. The shelf sea DOC concentrations in the North sea are lower than the global average values compiled by those authors and hence this implies a smaller net DOC flux per unit area of shelf than suggested by those authors. As noted earlier, the DOC salinity relationship seen here is similar to that seen in the North Atlantic Bight, which drains a catchment with some climatological and land use similarities to the North Sea, suggesting that the patterns seen may have wide ranging applicability

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The noisiness of the relationships with salinity demonstrate that there are clearly other controls on concentrations of DOM, consistent with previous data which observes in-situ production and degradation by plankton and bacteria of DOM in the North Sea during spring and summer, and supporting hypothesis 2 (Van Engeland et al., 2010; Johnson et al., 2013; Suratman, 2007; Suratman et al., 2008, 2009), although no direct relationship between either chlorophyll or POC/N (data not shown) was evident. However, as discussed by Johnson et al. (2013) the spring bloom in the North Sea is associated with a DOM maximum which decays away on a timescale of a few months, a situation similar to that described for open ocean and Antarctic systems (Carlson et al., 1994, 1998). Hence by the time of these surveys in late August, the main effects of this seasonal DOM concentration maximum may have decayed away, leaving the river/ocean mixing signal dominant.

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25 4.2 Significance of difference in DOC inventory between 2011 and 2012

The two summers observed appear to be significantly biogeochemically different, not least in the concentration and C:N ratio of DOM observed, but also in nutrient regime, and physical oceanography. The apparent change in DOC concentration across the whole of the North Sea basin between August 2011 and August 2012 is between 20 and 40 μM (Figure 6). Assuming a uniform change throughout the entire North Sea volume of $42.3 \times 10^3 \text{ km}^3$ (the volume used in the carbon budget for the North Sea by Thomas et al. (2005b)), this represents a change in the carbon inventory of the North Sea of approximately 10 to 20 Tg (or about 1 to 2 Tmol). This compares to the estimated strength of the DIC enrichment pump for the North Sea estimated by Thomas et al. (2005b) of $\sim 30 \text{ Tg C yr}^{-1}$. Spread over the entire surface area of the North Sea the

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5 difference in DOC inventory would represent a carbon flux of between 1.5 and 3 mol m⁻², which is the same order of magnitude as our best estimates for annual CO₂ uptake by the Northern North Sea (Thomas et al., 2005a). This change in DOC inventory is, therefore, potentially an important change in the carbon budget of the North Sea, at least for the years concerned. Depending on the source and fate of the DOM, this could represent a substantial change in the magnitude of air-sea CO₂ flux and/or carbon export from the North Sea to the deep ocean between these two years, and is indicative of a system whose carbon cycling demonstrates considerable interannual variability.

10 DOC concentrations observed in winter in shallow coastal stations mostly in the southern part of the North Sea shows among the highest observed in this study, of up to and above 100 μM. These observations also coincide with some of the highest salinities observed in the study (comparable to deep northern North Sea bottom water, Table 1). The salinity distribution (Fig S3a) shows highest salinity waters to the south (presumably inflow from the Channel) and higher salinity waters to the north, with low salinities around the East Anglian Coast. The higher salinities to the north of the winter survey areas were associated with the lowest DOC concentrations observed during the cruise (Fig S3b). This is suggestive of high DOC waters flowing in to the southern North Sea via the Channel and low DOC (35.5 salinity endmember ~50 μM) waters flowing in from the North. This is at odds with the observations of the previous summer, where high salinity northern bottom waters are observed to have DOC concentrations of about 70 μM. This may indicate a flushing and renewal of North Sea waters with N. Atlantic water from the North, whilst the high DOC (75-150 μM), high salinity water flowing in from the South, possibly represents the remnants of summer waters being pushed into the North Sea from the Channel and Western Approaches. If this is so, then the winter exchange in 2011/12 may have been responsible for a significant delivery of DOC to North Atlantic as the shelf system was flushed. Winter 2011/12 had a strongly positive NAO index (Bai et al., 2014; Hurrell, 2017), consistent with a strong shelf-edge exchange and flushing circulation of the North Sea basin (Salt et al., 2013). Given the confused relationship between DOC and salinity (Fig S4), it is likely that other processes played an important role in the DOC concentrations in winter, including riverine inputs and likely interaction with sediments, which are known to be a source of DOM (Fitzsimons et al., 2006).

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4.3 DOM variability, C:N ratio and the seasonal signal

DOC and DON are generally well correlated (Fig 5). Mean C:N ratios of DOM (roughly 9 to 17, Table 2) were comparable to those previously reported in the southern North Sea (10.8 – 14.8) (Van Engeland et al., 2010) and other continental shelf waters (11 – 19) (Bates and Hansell, 1999; Hansell et al., 1993; Hopkinson et al., 1997, 2002; Kim and Kim, 2013; Wetz et al., 2008). There are however some differences in DOC/N relationships with season and location.

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The elevated C:N molar ratio in the winter cruise may be due to the riverine input of high C:N materials as a significant inverse relationship with salinity in C:N molar ratio (R² = 0.15, P < 0.05, n = 60) is seen (Fig S5). However given the



apparent decoupling of DOC and DON concentrations in winter (no statistically significant correlation between DOC and DON were found at the 95% significance level in winter 2011 ($P > 0.05$)), it may be that benthic interactions also play an important role particularly in winter (Suratman et al., 2008).

5 In summer 2012 little variation between surface and bottom concentrations of DOC and DON is seen in well mixed southern waters (Figure 6). In 2011, however, these waters show a different pattern, with bottom samples having significantly elevated DOC (and DON) concentrations relative to surface samples, and with a lower C:N ratio. This observation suggests that there is a source of DOC from the shelf sediments in the Southern North Sea in 2011 or remineralisation of accumulated DOM at sufficient rate not to be mixed out by the overturning of the water column. This is consistent with the coincident
10 observations of elevated concentrations of ammonium and phosphate (Figure 2d), suggesting strong remineralisation rates of benthic-derived DOM near the bottom of the water column, potentially associated with a nepheloid layer or similar (Burdige et al., 1999; Burdige and Homstead, 1994; Fitzsimons et al., 2006), either not present or not captured by sampling in 2012.

On the basis of previous observations and the assumption that DOC-rich DOM would be produced in surface waters over the
15 summer and broken down at depth, we predicted that DOC concentrations would be elevated in surface compared to bottom waters in summer. In seasonally stratifying water this seems to be the case in both years, although with a much stronger difference between surface and bottom waters in 2012. The C:N ratio in all surface waters in summer in both years has a rather similar average value of (11.3 ± 1.4 and 11.7 ± 2.3) (Table 2), which is consistent with surface DOM production as
20 previously observed in other studies in the North Sea (Van Engeland et al., 2010) and other continental shelf waters (Bates and Hansell, 1999; Hansell et al., 1993; Hopkinson et al., 1997, 2002; Kim and Kim, 2013; Wetz et al., 2008). However, it is impossible to disentangle local seasonal effects from the broad scale dominance of mixing along the salinity gradient from coast to open ocean.

The substantial differences between surface and bottom waters in the northern stratified part of the surveys in the two years
25 is clear in Figure 6. In 2011 surface DOC is only marginally elevated over bottom DOC, but DON is considerably higher (and less variable) at the surface. In 2012, however, the DOC is much lower in the bottom compared to the surface, but the DON is not significantly different. This leads to differences in C:N in northern bottom waters between 2011 (13.4 ± 3.6) and 2012 (9.3 ± 1.8). The significant difference between the northern bottom waters in the 2 years is explored in Figure 9, which compares DOM stoichiometry in the northern bottom waters in 2011 and 2012 with literature values of the subsurface N.
30 Atlantic end member, representing relatively old water not expected to show interannual variability (e.g. Hopkinson and Vallino, 2005). As low DOM concentrations correspond to high salinities in deep northern waters (Figure 4), we can consider these properties to co-vary with salinity and thus, the location of samples in DOC – DON space can be compared to possible end members as indicated by the subsurface open ocean values from the literature. This indicates that northern bottom waters in 2012 tended towards and were entirely consistent with the N. Atlantic observations of both Álvarez-



Salgado et al. (2001) covering a transect from Ría de Vigo (the eastern North Atlantic upwelling system, 42 – 43°N) and Aminot and K erouel (2004) who considered depth profiles (surface layer – 4000 meters) from the Bay of Biscay (the eastern North Atlantic); other than the surface observations of Aminot and K erouel (2004), defined by those authors as the top 200m, which appear relatively enriched in DOC compared to the 2012 waters.

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Northern bottom waters in 2011, however appear inconsistent with the likely North Atlantic end-member suggesting very different conditions. This may be due to within-year factors such as lower temperatures (inhibiting the remineralisation of DOM), higher primary productivity leading to greater DOM production (nutrient levels in northern bottom waters suggest a greater inorganic nutrient inventory to drive spring phytoplankton growth), stronger N limitation relative to P (as suggested by higher levels of unutilised P in surface waters in 2011) leading to greater overproduction of carbon-rich DOM, greater release from sediment DOC pools, or weaker stratification leading to higher summer productivity (temperature differences between surface and bottom were greater in 2012).

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It may also be possible that there is a multi-year component to this signal. We have seen that the winter data suggests high salinity waters entering the southern North Sea from both the south and north in winter 2011/12 and noted that this winter period was associated with a very high NAO index, which is associated with greater cross-shelf exchange (Salt et al., 2013; Sheehan et al., 2017). Furthermore, higher salinities to the north in the Winter data are associated with much lower DOC concentrations than the previous summer, all suggestive of flushing of the North Sea over the winter of 2011/12. The preceding 3 years were a period of strongly negative NAO index (Bai et al., 2014; Hurrell, 2017), possibly suggesting less exchange between the waters of the NW European Shelf and the North Atlantic over this period. Elevated DOM concentrations throughout the survey in 2011 might then represent the accumulation of DOM over multiple years of productivity, which was then mixed off-shelf in the winter of 2012. Northern bottom waters in 2011 then would be representative of the ‘processing signal’ of organic matter in the North Sea / NW European shelf; and be indicative of DOM carbon-enriching processes. In a period of high shelf-edge exchange associated with NAO this water would be refreshed with water more consistent with the North Atlantic endmember at a similar salinity, resulting in a net export of DOC of approximately the magnitude of the annual CO₂ uptake (section 4.2). Without the full northerly extent of the survey in 2012, however, it is not possible to resolve these details conclusively and further years of summer data are needed to resolve the interannual variability and stoichiometry of DOM processing in the North Sea.

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30 5. Conclusion

The observed DOM concentrations show a strong spatial gradient of decreasing DOC and DON concentrations with distance from land and with decreasing salinity, strongly supporting the conclusions of the data synthesis for global shelf seas of



(Barrón and Duarte, 2015). This gradient may arise in the North Sea from estuarine and coastal DOM production by marine phytoplankton or represent the transport and processing of terrestrially-derived material in the coastal zone. The freshwater end members are consistent with a fluvial source.

5 The spatial pattern dominated by mixing is the same in both years but the actual concentrations are different. High interannual variability appears to dominate the DOC/DON, particularly in the deep bottom waters in the northern North Sea, which are those that are most likely to be leaving the shelf the following winter. The source of elevated DOC concentrations in 2011 is potentially the same as the high DOC signal seen by Thomas et al. (2005b), in their study attributed to onwelling water; but we establish that at least in 2011 the elevated DOC is inconsistent with the open ocean DOC concentration, suggesting an in-situ source (Fig. 8). Simultaneous measurements of DON sheds more light on this than observations of DOC alone– in 2011 at least, high DOC in deep waters appears associated with high C:N ratio (i.e. depleted DON). This is consistent with in-situ production of high DOC organics, and/or the preferential remineralisation of N over C from DOM. Either way this high C:N DOC is potentially a very important component of the shelf carbon pump, allowing greater carbon uptake for a given winter stock of inorganic nutrient than for non-carbon enriched (i.e. Redfieldian) DOM production. The differences between 2011 and 2012 described here suggest important interannual differences in the scale of shelf sea carbon export in his region, and perhaps at other shelf sea boundaries. Further years of data and greater seasonal detail are needed to quantify this effect and understand the role of nutrient limitation in the system.

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References

- Abell, J., Emerson, S. and Renaud, P.: Distributions of TOP, TON and TOC in the North Pacific subtropical gyre: implications for nutrient supply in the surface ocean and remineralization in the upper thermocline, *J. Mar. Res.*, 58(2), 203–222, doi:10.1357/002224000321511142, 2000.
- 5 Agedah, E. C., Binalaiyifa, H. E., Ball, A. S. and Nedwell, D. B.: Sources, turnover and bioavailability of dissolved organic nitrogen (DON) in the Colne estuary, UK, *Mar. Ecol. Prog. Ser.*, 382, 23–33, doi:10.3354/meps07938, 2009.
- Álvarez-Salgado, X. A. and Miller, A. E. J.: Simultaneous determination of dissolved organic carbon and total dissolved nitrogen in seawater by high temperature catalytic oxidation: conditions for precise shipboard measurements, *Mar. Chem.*, 62(3–4), 325–333, doi:10.1016/S0304-4203(98)00037-1, 1998.
- 10 Álvarez-Salgado, X. A., Gago, J., Míguez, B. M. and Pérez, F. F.: Net ecosystem production of dissolved organic carbon in a coastal upwelling system: the Ría de Vigo, Iberian margin of the North Atlantic, *Limnol. Oceanogr.*, 46(1), 135–146, doi:10.4319/lo.2001.46.1.0135, 2001.
- Aminot, A. and Kérouel, R.: Dissolved organic carbon, nitrogen and phosphorus in the N-E Atlantic and the N-W Mediterranean with particular reference to non-refractory fractions and degradation, *Deep Sea Res. I*, 51(12), 1975–1999, doi:10.1016/j.dsr.2004.07.016, 2004.
- 15 Badr, E. S. A., Achterberg, E. P., Tappin, A. D., Hill, S. J. and Braungardt, C. B.: Determination of dissolved organic nitrogen in natural waters using high-temperature catalytic oxidation, *Trends Anal. Chem.*, 22(11), 819–827, doi:10.1016/S0165-9936(03)01202-0, 2003.
- Bai, X., Wang, J., Austin, J. a, Schwab, D. J., Assel, R. a, Clites, A. H., Bratton, J. F., Colton, M., Lenters, J. D., Lofgren, B.
- 20 M., Wohlleben, T., Helfrich, S., Vanderploeg, H., Luo, L. and Leshkevich, G. a: A record-breaking low ice cover over the Great Lakes during winter 2011/2012: combined effects of a strong positive NAO and La Niña, *Clim. Dyn.*, 44(5–6), 1187–1213, doi:10.1007/s00382-014-2225-2, 2014.
- Barrón, C. and Duarte, C. M.: Dissolved organic carbon pools and export from the coastal ocean, *Global Biogeochem. Cycles*, 29, 1725–1738, doi:10.1002/2014GB005056, 2015.
- 25 Bates, N. R. and Hansell, D. A.: A high resolution study of surface layer hydrographic and biogeochemical properties between Chesapeake Bay and Bermuda, *Mar. Chem.*, 67(1–2), 1–16, doi:10.1016/S0304-4203(99)00045-6, 1999.
- Bauer, J. E., Druffel, E. R. M., Wolgast, D. M. and Griffin, S.: Temporal and regional variability in sources and cycling of DOC and POC in the northwest Atlantic continental shelf and slope, *Deep Sea Res. II*, 49, 4387–4419, doi:10.1016/S0967-0645(02)00123-6, 2002.
- 30 Bauer, J. E., Cai, W.-J., Raymond, P. a, Bianchi, T. S., Hopkinson, C. S. and Regnier, P. a G.: The changing carbon cycle of the coastal ocean., *Nature*, 504(7478), 61–70, doi:10.1038/nature12857, 2013.
- Benner, R. and Strom, M.: A critical evaluation of the analytical blank associated with DOC measurements by high-temperature catalytic oxidation, *Mar. Chem.*, 41(1–3), 153–160, doi:10.1016/0304-4203(93)90113-3, 1993.



- Bozec, Y., Thomas, H., Elkalay, K. and De Baar, H. J. W.: The continental shelf pump for CO₂ in the North Sea - Evidence from summer observation, *Mar. Chem.*, 93, 131–147, doi:10.1016/j.marchem.2004.07.006, 2005.
- Burdige, D. J. and Homstead, J.: Fluxes of dissolved organic carbon from Chesapeake Bay sediments, *Geochim. Cosmochim. Acta*, 58(16), 3407–3424, doi:10.1016/0016-7037(94)90095-7, 1994.
- 5 Burdige, D. J., Berelson, W. M., Coale, K. H., McManus, J. and Johnson, K. S.: Fluxes of dissolved organic carbon from California continental margin sediments, *Geochim. Cosmochim. Acta*, 63(10), 1507–1515, doi:10.1016/S0016-7037(99)00066-6, 1999.
- Carlson, C. A., Ducklow, H. W. and Michaels, A. F.: Annual flux of dissolved organic carbon from the euphotic zone in the northwestern Sargasso Sea, *Nature*, 371, 405–408, doi:10.1038/371405a0, 1994.
- 10 Carlson, C. A., Ducklow, H. W., Hansel, D. A., Smith, W. O. and Hansel, D. A.: Organic carbon partitioning during spring phytoplankton blooms in the Ross Sea polynya and the Sargasso Sea, *Limnol Ocean.*, 43, 375–386, doi:10.4319/lo.1998.43.3.0375, 1998.
- Chaichana, S.: Dissolved organic carbon and nitrogen in coastal waters, Ph.D. thesis, School of Environmental Sciences, University of East Anglia., 2017.
- 15 Clargo, N. M., Salt, L. A., Thomas, H. and de Baar, H. J. W.: Rapid increase of observed DIC and pCO₂ in the surface waters of the North Sea in the 2001–2011 decade ascribed to climate change superimposed by biological processes, *Mar. Chem.*, 177, 566–581, doi:10.1016/j.marchem.2015.08.010, 2015.
- Ducklow, H. W., Hansell, D. A. and Morgan, J. A.: Dissolved organic carbon and nitrogen in the Western Black Sea, *Mar. Chem.*, 105, 140–150, doi:10.1016/j.marchem.2007.01.015, 2007.
- 20 Emeis, K. C., van Beusekom, J., Callies, U., Ebinghaus, R., Kannen, A., Kraus, G., Kröncke, I., Lenhart, H., Lorkowski, I., Matthias, V., Möllmann, C., Pätsch, J., Scharfe, M., Thomas, H., Weisse, R. and Zorita, E.: The North Sea - a shelf sea in the anthropocene, *J. Mar. Syst.*, 141, 18–33, doi:10.1016/j.jmarsys.2014.03.012, 2015.
- Van Engeland, T., Soetaert, K., Knuijt, A., Laane, R. W. P. M. and Middelburg, J. J.: Dissolved organic nitrogen dynamics in the North Sea: a time series analysis (1995–2005), *Estuar. Coast. Shelf Sci.*, 89(1), 31–42, doi:10.1016/j.ecss.2010.05.009, 25 2010.
- Fitzsimons, M. F., Millward, G. E., Revitt, D. M. and Dawit, M. D.: Desorption kinetics of ammonium and methylamines from estuarine sediments: consequences for the cycling of nitrogen, *Mar. Chem.*, 101(1–2), 12–26, doi:10.1016/j.marchem.2005.12.006, 2006.
- Hansell, D. A.: Dissolved organic carbon reference material program, EOS Transactions Am. Geophys. Union, 86(35), 318, 30 doi:10.1029/2005EO350003, 2005.
- Hansell, D. A.: Recalcitrant dissolved organic carbon fractions, *Ann Rev Mar Sci*, 5, 421–445, doi:10.1146/annurev-marine-120710-100757, 2013.
- Hansell, D. A., Williams, P. M. and Ward, B. B.: Measurements of DOC and DON in the Southern California Bight using oxidation by high temperature combustion, *Deep Sea Res. I*, 40(2), 219–234, doi:10.1016/0967-0637(93)90001-J, 1993.



- Van Haren, H. and Howarth, M. J.: Enhanced stability during reduction of stratification in the North Sea, *Cont. Shelf Res.*, 24, 805–819, doi:10.1016/j.csr.2004.01.008, 2004.
- Holm-Hansen, O., Lorenzen, C. J., Holmes, R. W. and Strickland, J. D. H.: Fluorometric determination of chlorophyll, *ICES J. Mar. Sci.*, 30(1), 3–15, doi:10.1093/icesjms/30.1.3, 1965.
- 5 Hopkinson, C., Cifuentes, L., Burdige, D., Fitzwater, S., Hansell, D., Henrichs, S., Kihler, P., Koike, I., Walsh, T. and Bergamaschi, B.: DON subgroup report, *Mar. Chem.*, 41(1–3), 23–26, doi:10.1016/0304-4203(93)90103-U, 1993.
- Hopkinson, C. S. and Vallino, J. J.: Efficient export of carbon to the deep ocean through dissolved organic matter, *Nature*, 433, 142–145, doi:10.1038/nature03191, 2005.
- Hopkinson, C. S., Fry, B. and Nolin, A. L.: Stoichiometry of dissolved organic matter dynamics on the continental shelf of the northeastern U.S.A., *Continental Shelf Res.*, 17(5), 473–489, doi:10.1016/S0278-4343(96)00046-5, 1997.
- 10 Hopkinson, C. S., Vallino, J. J. and Nolin, A.: Decomposition of dissolved organic matter from the continental margin, *Deep Sea Res. II*, 49(20), 4461–4478, doi:10.1016/S0967-0645(02)00125-X, 2002.
- Hurrell, J.: The Climate Data Guide: Hurrell North Atlantic Oscillation (NAO) Index (station-based), [online] Available from: <https://climatedataguide.ucar.edu/climate-data/hurrell-north-atlantic-oscillation-nao-index-station-based> (Accessed 29 July 2017), 2017.
- 15 Jiao, N., Robinson, C., Azam, F., Thomas, H., Baltar, F., Dang, H., Hardman-Mountford, N. J., Johnson, M., Kirchman, D. L., Koch, B. P., Legendre, L., Li, C., Liu, J., Luo, T., Luo, Y. W., Mitra, A., Romanou, A., Tang, K., Wang, X., Zhang, C. and Zhang, R.: Mechanisms of microbial carbon sequestration in the ocean - future research directions, *Biogeosciences*, 11(19), 5285–5306, doi:10.5194/bg-11-5285-2014, 2014.
- 20 Jickells, T. D.: Nutrient biogeochemistry of the coastal zone, *Science* (80-.), 281, 217–222, doi:10.1126/science.281.5374.217, 1998.
- Johnson, M., Sanders, R., Avgoustidi, V., Lucas, M., Brown, L., Hansell, D., Moore, M., Gibb, S., Liss, P. and Jickells, T.: Ammonium accumulation during a silicate-limited diatom bloom indicates the potential for ammonia emission events, *Mar. Chem.*, 106(1–2), 63–75, doi:10.1016/j.marchem.2006.09.006, 2007.
- 25 Johnson, M. T., Greenwood, N., Sivy, D. B., Thomson, M., Reeve, A., Weston, K. and Jickells, T. D.: Characterising the seasonal cycle of dissolved organic nitrogen using Cefas SmartBuoy high-resolution time-series samples from the southern North Sea, *Biogeochemistry*, 113, 23–36, doi:10.1007/s10533-012-9738-8, 2013.
- Kaplan, L. A.: Comparison of high-temperature and persulfate oxidation methods for determination of dissolved organic carbon in freshwaters, *Limnol. Oceanogr.*, 37(5), 1119–1125, doi:10.4319/lo.1992.37.5.1119, 1992.
- 30 Kim, T. H. and Kim, G.: Factors controlling the C:N:P stoichiometry of dissolved organic matter in the N-limited, cyanobacteria-dominated East/Japan Sea, *J. Mar. Syst.*, 115–116, 1–9, doi:10.1016/j.jmarsys.2013.01.002, 2013.
- Kirkwood, D. S.: Nutrients: practical notes on their determination in seawater, in *ICES techniques in marine environmental sciences*, no. 17. International Council for the Exploration of Seas, p. 23, Copenhagen., 1996.



- Knight, P. J., Howarth, M. J. and Rippeth, T. P.: Inertial currents in the northern North Sea, *J. Sea Res.*, 47, 269–284, doi:10.1016/S1385-1101(02)00122-3, 2002.
- Koike, I. and Tupas, L.: Total dissolved nitrogen in the Northern North Pacific assessed by a high-temperature combustion method, *Mar. Chem.*, 41(1–3), 209–214, doi:10.1016/0304-4203(93)90121-4, 1993.
- 5 Kühn, W., Pätsch, J., Thomas, H., Borges, A. V., Schiettecatte, L. S., Bozec, Y. and Prowe, A. E. F.: Nitrogen and carbon cycling in the North Sea and exchange with the North Atlantic-A model study, Part II: Carbon budget and fluxes, *Cont. Shelf Res.*, 30(16), 1701–1716, doi:10.1016/j.csr.2010.07.001, 2010.
- Letscher, R. T. and Moore, J. K.: Preferential remineralization of dissolved organic phosphorus and non-Redfield DOM dynamics in the global ocean: impacts on marine productivity, nitrogen fixation, and carbon export, *Global Biogeochem. Cycles*, 29(3), 325–340, doi:10.1002/2014GB004904, 2015.
- 10 Lønborg, C., Álvarez-Salgado, X. A., Martínez-García, S., Miller, A. E. J. and Teira, E.: Stoichiometry of dissolved organic matter and the kinetics of its microbial degradation in a coastal upwelling system, *Aquat. Microb. Ecol.*, 58(2), 117–126, doi:10.3354/ame01364, 2010.
- Markager, S., Stedmon, C. A. and Søndergaard, M.: Seasonal dynamics and conservative mixing of dissolved organic matter in the temperate eutrophic estuary Horsens Fjord, *Estuar. Coast. Shelf Sci.*, 92(3), 376–388, doi:10.1016/j.eess.2011.01.014, 2011.
- 15 McQuatters-Gollop, A., Raitsos, D. E., Edwards, M., Yaswant, P., Mee, L. D. and Lavender, Samantha J Attrill, M. J.: A long-term chlorophyll dataset reveals regime shift in North Sea phytoplankton biomass unconnected to nutrient trends, *Limnol. Oceanogr.*, 52(2), 635–648, doi:10.4319/lo.2007.52.2.0635, 2007.
- 20 Miller, J. N. and Miller, J. C.: *Statistics and chemometrics for analytical chemistry*, 6th ed., Pearson Education Limited, London., 2010.
- Moore, C. M., Mills, M. M., Arrigo, K. R., Berman-Frank, I., Bopp, L., Boyd, P. W., Galbraith, E. D., Geider, R. J., Guieu, C., Jaccard, S. L., Jickells, T. D., La Roche, J., Lenton, T. M., Mahowald, N. M., Maranon, E., Marinov, I., Moore, J. K., Nakatsuka, T., Oschlies, A., Saito, M. A., Thingstad, T. F., Tsuda, A. and Ulloa, O.: Processes and patterns of oceanic nutrient limitation, *Nat. Geosci.*, 6(9), 701–710, doi:10.1038/ngeo1765, 2013.
- 25 Neal, C. and Robson, A. J.: A summary of river water quality data collected within the Land-Ocean Interaction Study: core data for eastern UK rivers draining to the North Sea, *Sci. Total Environ.*, 251–252, 585–665, doi:10.1016/S0048-9697(00)00397-1, 2000.
- Nelson, C. E. and Wear, E. K.: Microbial diversity and the lability of dissolved organic carbon, *Proc. Natl. Acad. Sci. U. S. A.*, 111(20), 7166–7167, doi:10.1073/pnas.1405751111, 2014.
- 30 Parsons, T. R., Maita, Y. and Lalli, C. M.: *A manual of chemical and biological methods for seawater analysis*, Pergamon press, Oxford., 1985.



- Prowe, A. E. F., Thomas, H., Pätsch, J., Kühn, W., Bozec, Y., Schiettecatte, L. S., Borges, A. V. and de Baar, H. J. W.: Mechanisms controlling the air-sea CO₂ flux in the North Sea, *Cont. Shelf Res.*, 29(15), 1801–1808, doi:10.1016/j.csr.2009.06.003, 2009.
- Pujo-Pay, M., Conan, P., Oriol, L., Cornet-Barthaux, V., Falco, C., Ghiglione, J. F., Goyet, C., Moutin, T. and Prieur, L.:
5 Integrated survey of elemental stoichiometry (C, N, P) from the western to eastern Mediterranean Sea, *Biogeosciences*, 8(4), 883–899, doi:10.5194/bg-8-883-2011, 2011.
- Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, Ivan A., Laruelle, G. G., Lauerwald, R., Luysaert, S., Andersson, A. J., Arndt, S., Arnosti, C., Borges, A. V., Dale, A. W., Gallego-Sala, A., Godderis, Y., Goossens, N., Hartmann, J., Heinze, C., Ilyina, T., Joos, F., LaRowe, D. E., Leifeld, J., Meysman, F. J. R., Munhoven, G.,
10 Raymond, P. A., Spahni, R., Suntharalingam, P. and Thullner, M.: Anthropogenic perturbation of the carbon fluxes from land to ocean, *Nat. Geosci.*, 6, 597–607, doi:10.1038/ngeo1830, 2013.
- Repeta, D. J.: Chemical characterization and cycling of dissolved organic matter, in *Biogeochemistry of marine dissolved organic matter*, edited by D. A. Hansell and C. A. Carlson, pp. 22–63, Academic Press, Oxford., 2015.
- Salt, L. A., Thomas, H., Prowe, A. E. F., Borges, A. V., Bozec, Y. and De Baar, H. J. W.: Variability of North Sea pH and
15 CO₂ in response to North Atlantic Oscillation forcing, *J. Geophys. Res. Biogeosciences*, 118(4), 1584–1592, doi:10.1002/2013JG002306, 2013.
- Sharp, J. H., Benner, R., Bennett, L., Carlson, C. a., Dow, R. and Fitzwater, S. E.: Re-evaluation of high temperature combustion and chemical oxidation measurements of dissolved organic carbon in seawater, *Limnol. Oceanogr.*, 38(8), 1774–1782, doi:10.4319/lo.1993.38.8.1774, 1993.
- 20 Sheehan, P. M. F., Berx, B., Gallego, A., Hall, R. A., Heywood, K. J. and Hughes, S. L.: Thermohaline forcing and interannual variability of northwestern inflows into the northern North Sea, *Cont. Shelf Res.*, 138, 120–131, doi:10.1016/j.csr.2017.01.016, 2017.
- Simpson, J. H. and Sharples, J.: *Introduction to the physical and biological oceanography of shelf seas*, Cambridge university press, Cambridge., 2012.
- 25 Suratman, S.: The seasonal distribution and cycling of nitrogen and organic carbon-based nutrient in the North Sea, Ph.D. thesis, School of Environmental Sciences, University of East Anglia., 2007.
- Suratman, S., Jickells, T., Weston, K. and Fernand, L.: Seasonal variability of inorganic and organic nitrogen in the North Sea, *Hydrobiologia*, 610(1), 83–98, doi:10.1007/s10750-008-9424-y, 2008.
- Suratman, S., Weston, K., Jickells, T. and Fernand, L.: Spatial and seasonal changes of dissolved and particulate organic C
30 in the North Sea, *Hydrobiologia*, 628(1), 13–25, doi:10.1007/s10750-009-9730-z, 2009.
- Suratman, S., Weston, K., Greenwood, N., Sivyver, D. B., Pearce, D. J. and Jickells, T.: High frequency measurements of dissolved inorganic and organic nutrients using instrumented moorings in the southern and central North Sea, *Estuar. Coast. Shelf Sci.*, 87(4), 631–639, doi:10.1016/j.ecss.2010.03.001, 2010.



- Suzuki, Y., Tanoue, E. and Ito, H.: A high-temperature catalytic oxidation method for the determination of dissolved organic carbon in seawater: analysis and improvement, *Deep Sea Res.*, 39(2), 185–198, doi:10.1016/0198-0149(92)90104-2, 1992.
- The International Council for the Exploration of the Sea (ICES): ICES statistical rectangles, [online] Available from: <http://www.ices.dk/marine-data/maps/Pages/ICES-statistical-rectangles.aspx>, 2017.
- 5 Thomas, H., Bozec, Y., Elkalay, K. and de Baar, H. J. W.: Enhanced open ocean storage of CO₂ from shelf sea pumping., *Science*, 304(5673), 1005–1008, doi:10.1126/science.1103193, 2004.
- Thomas, H., Bozec, Y., Elkalay, K., De Baar, H. J. W., Borges, A. V and Schiettecatte, L. S.: Controls of the surface water partial pressure of CO₂ in the North Sea, *Biogeosciences*, 2(4), 323–334, doi:10.5194/bg-2-323-2005, 2005a.
- Thomas, H., Bozec, Y., de Baar, H. J. W., Elkalay, K., Frankignoulle, M., Schiettecatte, L.-S., Kattner, G. and Borges, a.
- 10 V.: The carbon budget of the North Sea, *Biogeosciences*, 2(1), 87–96, doi:10.5194/bg-2-87-2005, 2005b.
- Toggweiler, J. R.: Carbon overconsumption, *Nature*, 363, 210–211, doi:10.1038/363210a0, 1993.
- Tsunogai, S., Watanabe, S. and Sato, T.: Is there a “continental shelf pump” for the absorption of atmospheric CO₂?, *Tellus*, 51B(3), 701–702, 1999.
- Tupas, L. M., Popp, B. N. and Karl, D. M.: Dissolved organic carbon in oligotrophic waters: experiments on sample
- 15 preservation, storage and analysis, *Mar. Chem.*, 45(3), 207–216, doi:10.1016/0304-4203(94)90004-3, 1994.
- Vlahos, P., Chen, R. F. and Repeta, D. J.: Dissolved organic carbon in the Mid-Atlantic Bight, *Deep Sea Res. II*, 49, 4369–4385, 2002.
- Wang, D., Henrichs, S. M. and Guo, L.: Distributions of nutrients, dissolved organic carbon and carbohydrates in the western Arctic Ocean, *Cont. Shelf Res.*, 26(14), 1654–1667, doi:10.1016/j.csr.2006.05.001, 2006.
- 20 Watanabe, K., Badr, E., Pan, X. and Achterberg, E. P.: Conversion efficiency of the high-temperature combustion technique for dissolved organic carbon and total dissolved nitrogen analysis, *Int. J. Environ. Anal. Chem.*, 87(6), 387–399, doi:10.1080/03067310701237023, 2007.
- Wetz, M. S., Hales, B. and Wheeler, P. A.: Degradation of phytoplankton-derived organic matter: implications for carbon and nitrogen biogeochemistry in coastal ecosystems, *Estuar. Coast. Shelf Sci.*, 77(3), 422–432,
- 25 doi:10.1016/j.ecss.2007.10.002, 2008.

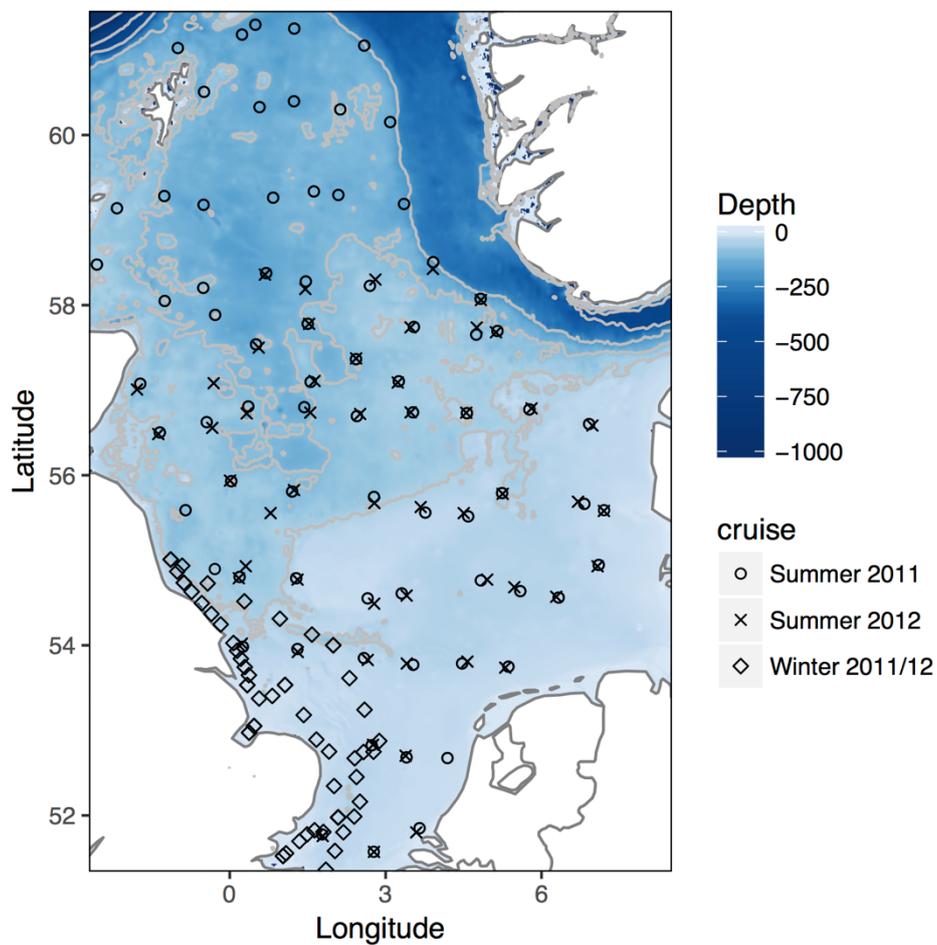
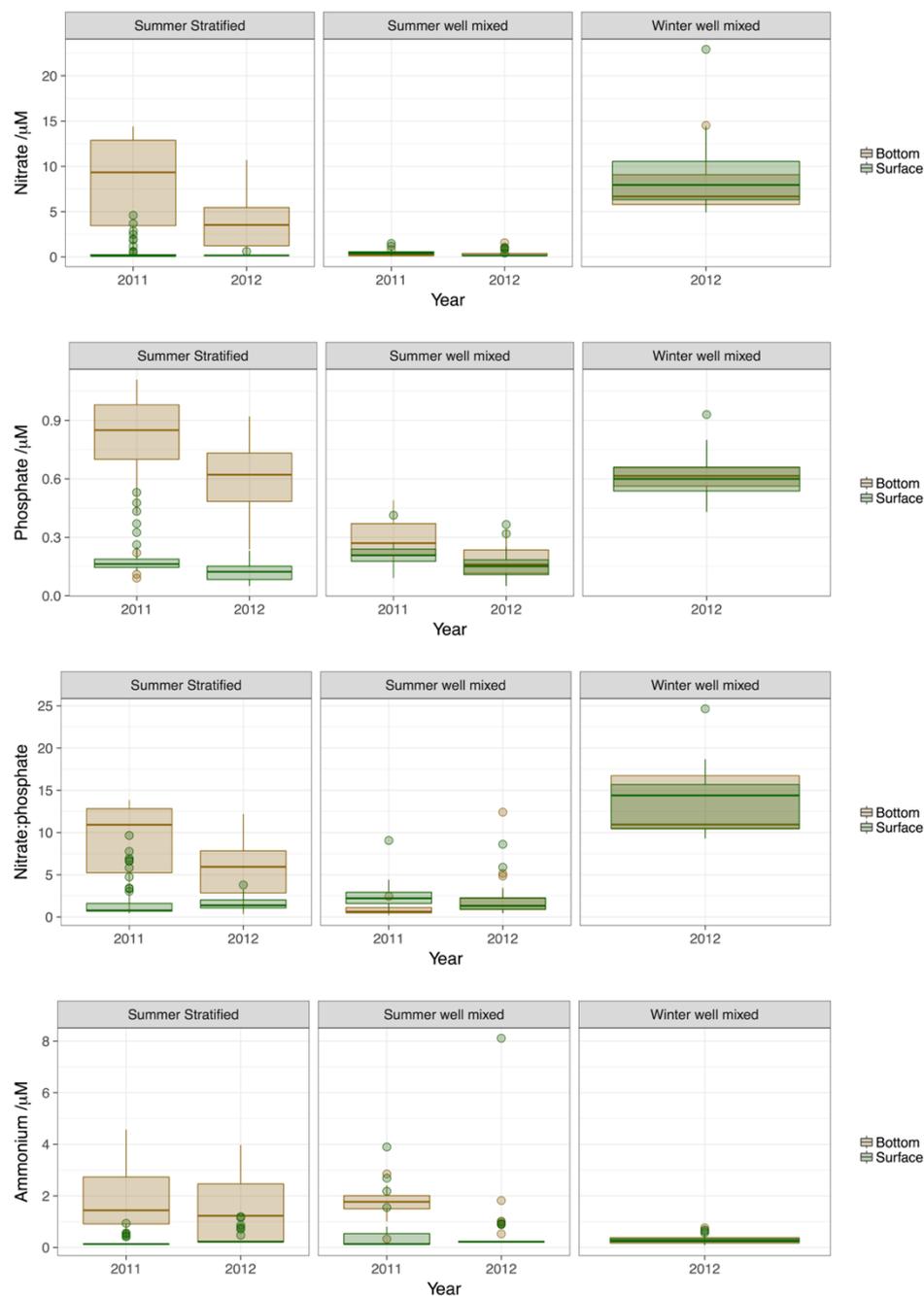


Figure 1: The North Sea study area, showing sampling points from each of the 3 cruises (note that the 2 summer cruises occupy notionally the same stations, each in separate ICES grid square, each year hence the close overlap). Also shown is bathymetry, with 50m, 100m, 200m, 400m, 600m and 1000m contours shown in light grey.



5 Figure 2. Summary of inorganic nutrient observations demonstrating the differences between surface and bottom samples, different mixing regimes, seasons and years. a) nitrate, b) phosphate, c) nitrate to phosphate ratio and d) ammonium concentration.

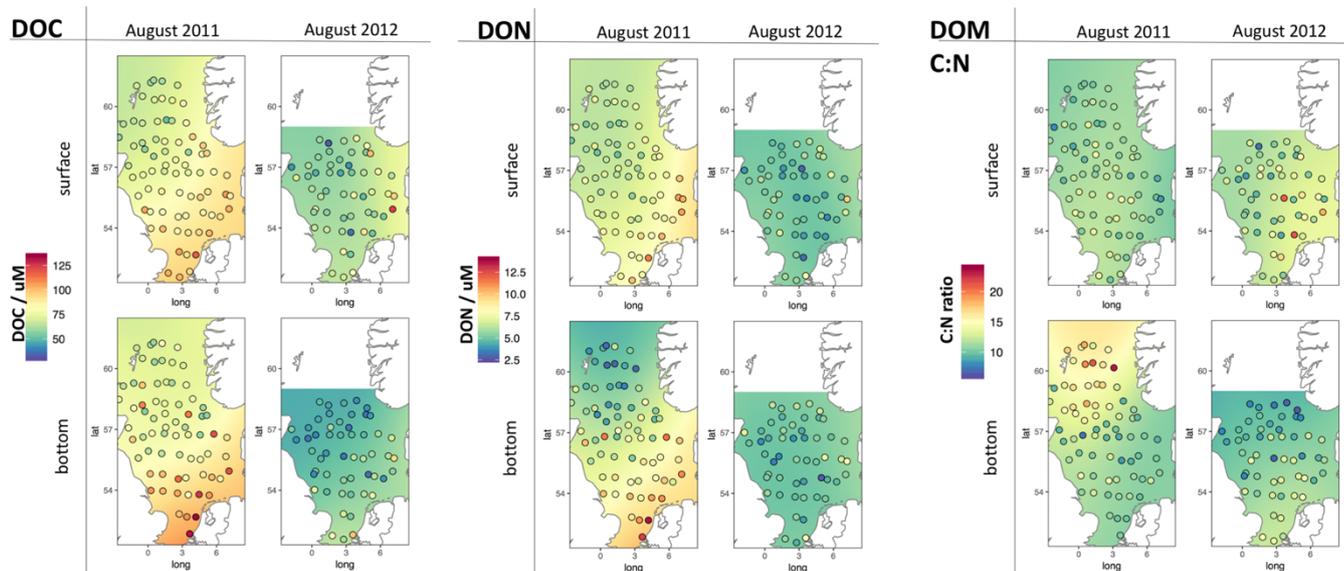
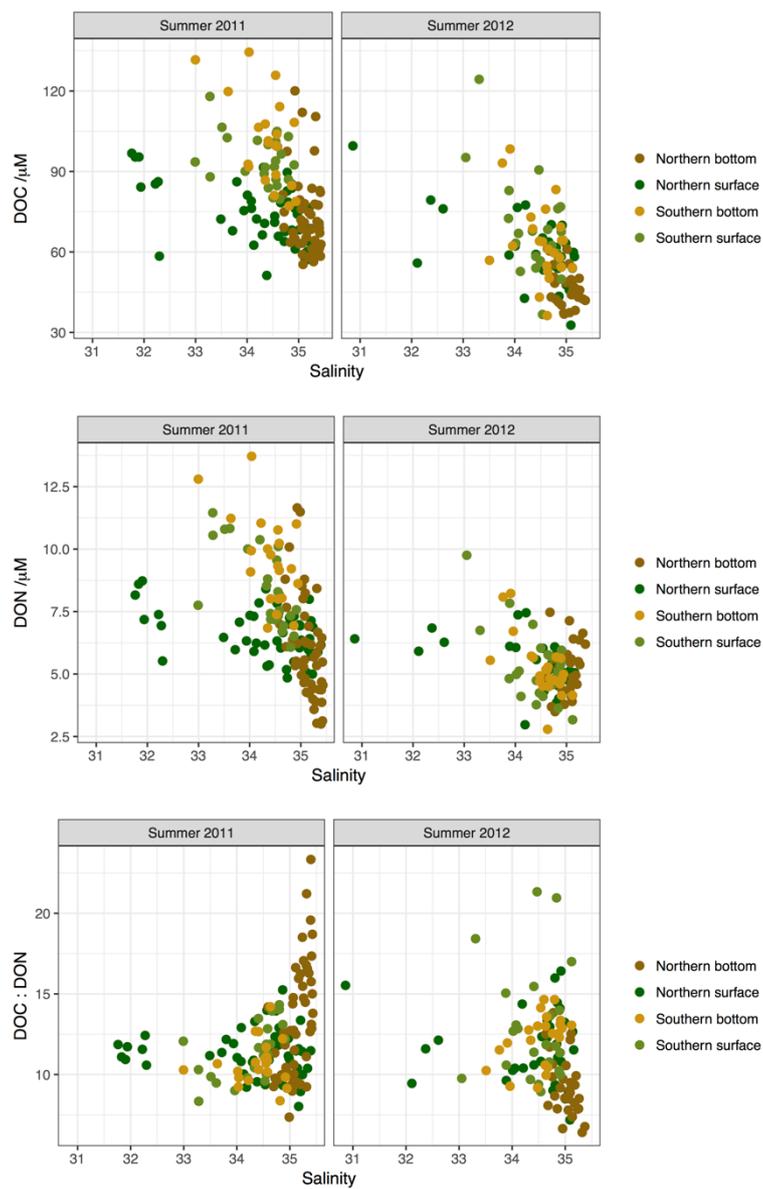


Figure 3. Distribution of DOC and DON and C:N ratio of DOM for surface and bottom waters in summer 2011-2012. Points represent discrete observations and the underplotted colour gradient is a 2-dimensional Gaussian smooth of the discrete data to demonstrate the spatial trend.

5



5 Figure 4. Property-salinity plots for a) DOC and b) DON c) C:N ratio of DOM for both summer cruises.

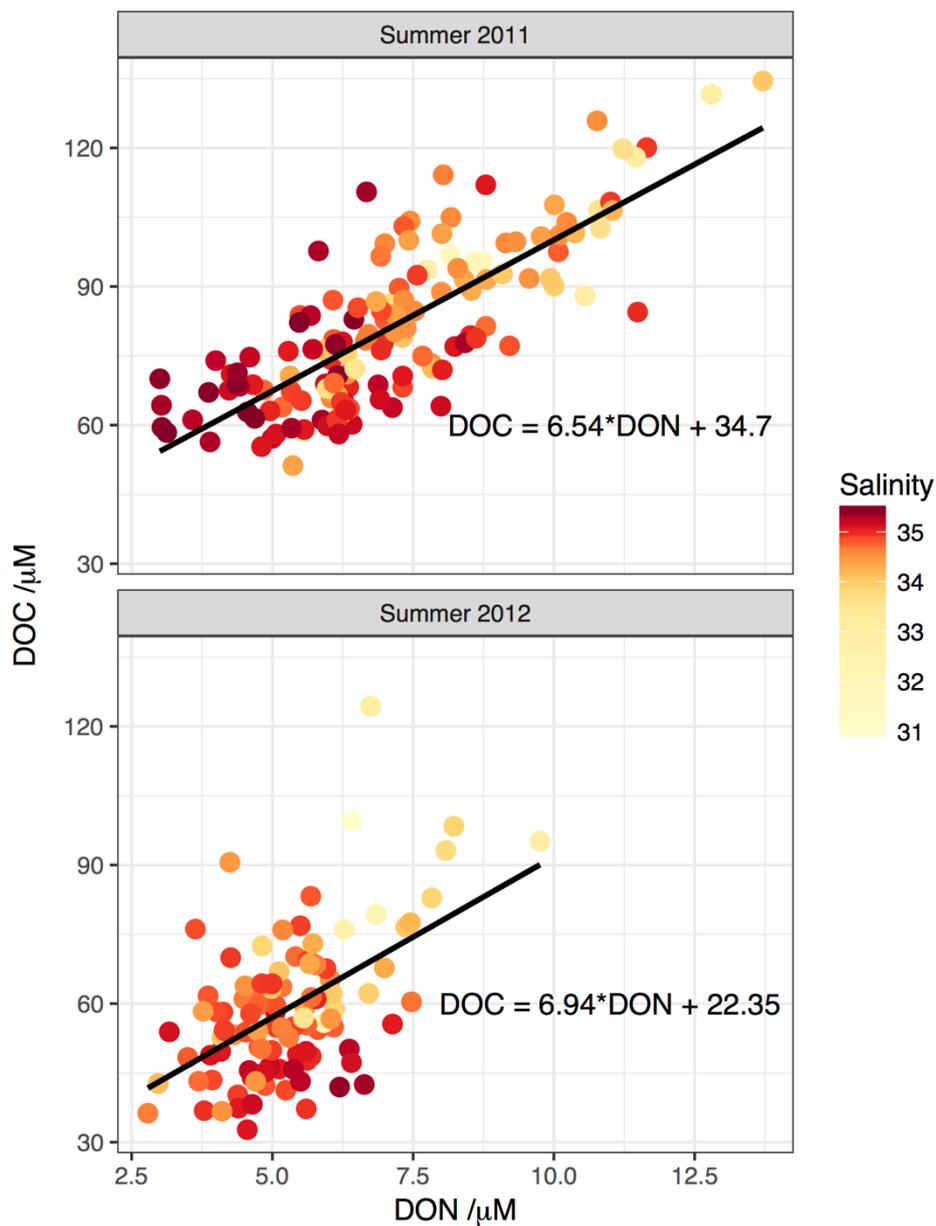


Figure 5. Element-element plots of DOC vs DON for summer surveys a) August 2011; b) August 2012. Points are coloured by salinity. Lines represent application of standard linear least squares regression models to the relevant data; equations for which are quoted on the plots.

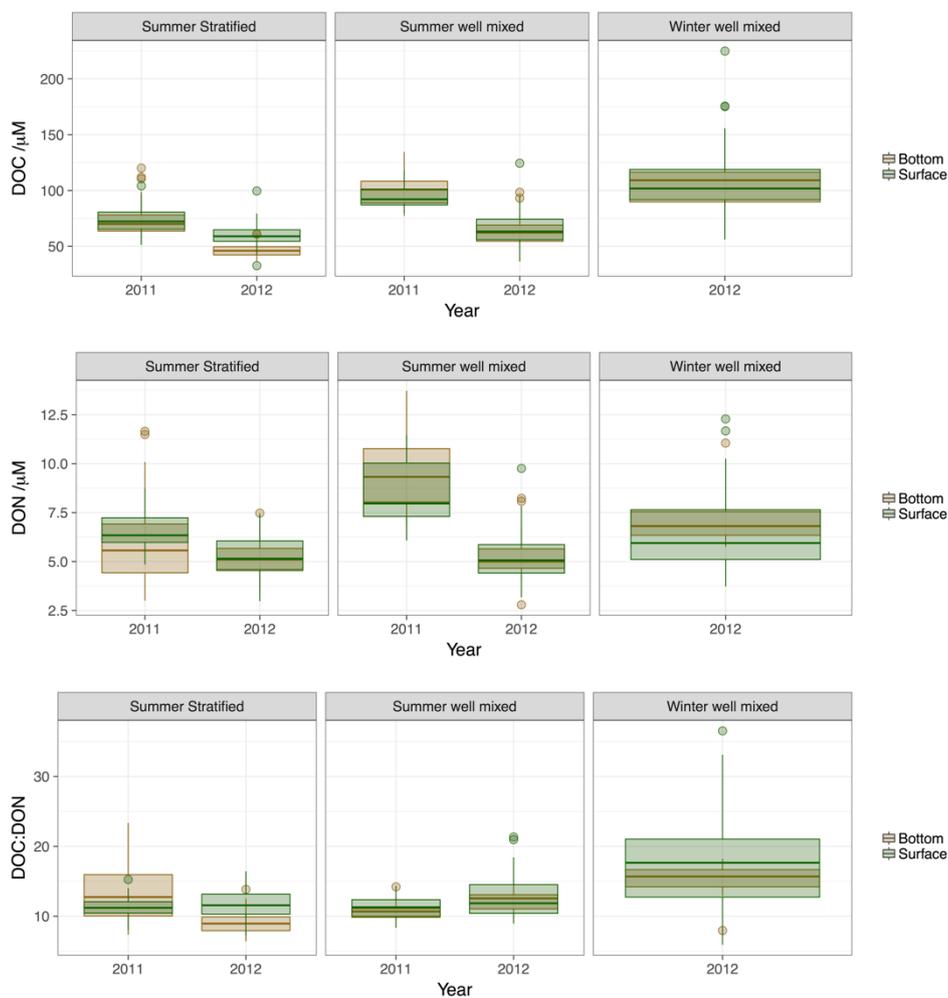


Figure 6. Summary of DOM concentrations a) DOC, b) DON, c) DOM C:N ratio

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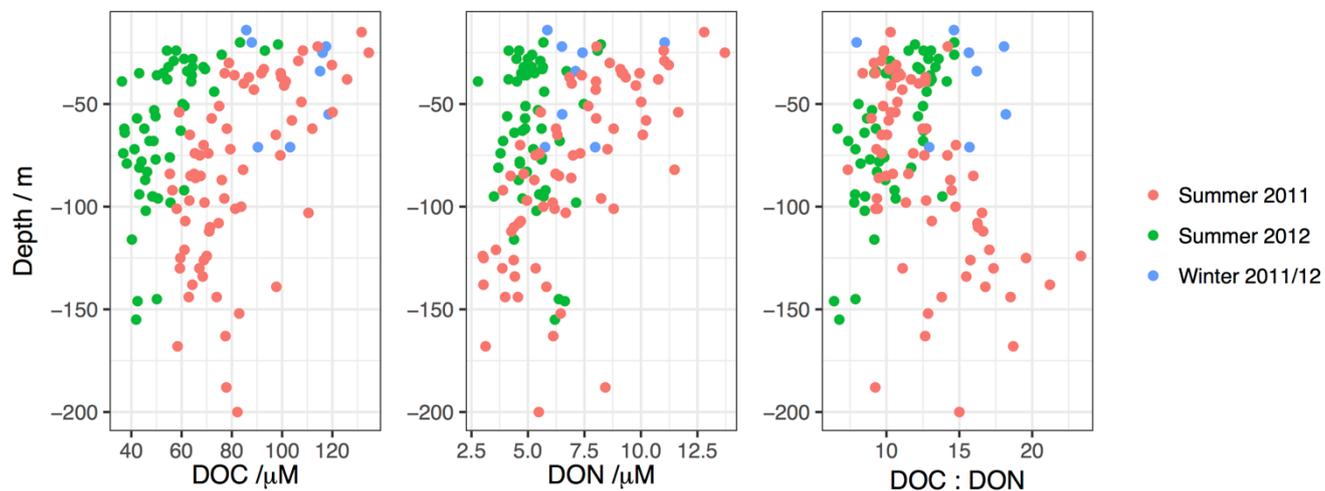
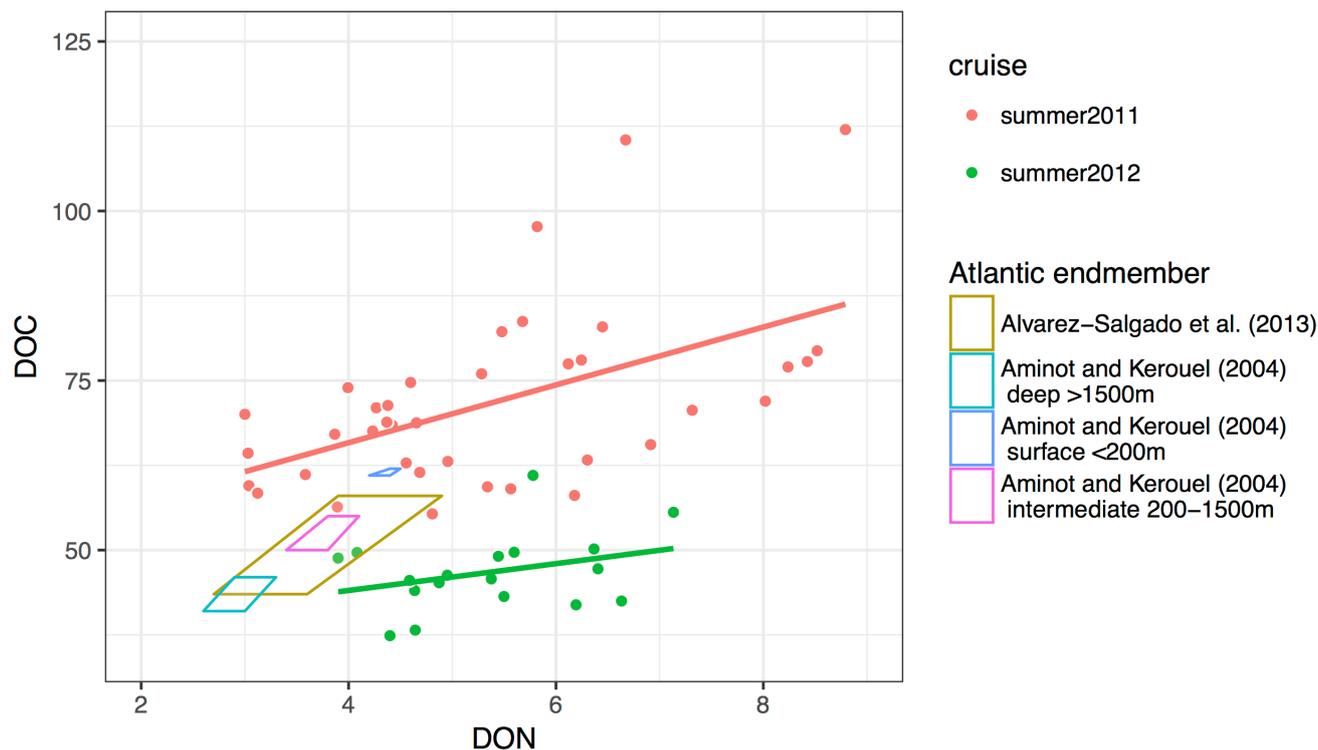


Figure 7. DOC, DON and DOM carbon to nitrogen ratios in bottom water samples, plotted against sampling depth (approximately 10m less than total water column depth). Red points from summer 2011, green points from summer 2012, blue from the intervening winter cruise

5



5 **Figure 8.** DOM stoichiometry from northern stratified bottom water samples in 2011 (red) and 2012 (green), compared with open North Atlantic concentrations from Alvarez-Salgado et al., (2013) and Aminot and Kerouel (2004). These ‘end member’ ranges were constructed in DOC/DON space based on the ranges of concentrations of DOC and DON quoted in the relevant papers, constrained by limiting possible combinations of DOC and DON that were consistent with the quoted range of observed C:N ratios (in the absence of the full dataset). Effectively the full range of DOC concentrations observed in the studies is covered by these derived end-members, and the large majority of the DON concentrations.

10

**Table 1. Summary of physical and inorganic nutrient parameters during the 3 cruises.**

	Temperature (°C)	Salinity	DIN ($\mu\text{mol l}^{-1}$)	DIP ($\mu\text{mol l}^{-1}$)	DISi ($\mu\text{mol l}^{-1}$)
August 2011					
Southern well mixed	15.5 ± 1.7 (10.4-17.8)	34.3 ± 0.5 (33.0- 34.9)	1.5 ± 1.1 (0.2-4.7)	0.2 ± 0.1 (0.1-0.5)	2.2 ± 1.5 (0.4-7.7)
Northern SML	14.2 ± 1.0 (12.2-16.0)	34.3 ± 1.0 (31.8- 35.4)	0.7 ± 1.1 (0.2-4.7)	0.2 ± 0.1 (0.1-0.5)	1.3 ± 0.6 (0.5-3.7)
Northern BML	8.4 ± 1.6 (6.7-12.4)	35.1 ± 0.2 (34.6- 35.4)	9.9 ± 4.4 (0.9-16.2)	0.8 ± 0.3 (0.1-1.1)	4.5 ± 1.6 (0.3-6.8)
January 2012					
Southern well mixed	7.2 ± 0.9 (5.7-8.7)	34.8 ± 0.4 (33.3- 35.4)	8.8 ± 3.3 (5.3-23.0)	0.6 ± 0.1 (0.4-0.9)	5.4 ± 1.0 (4.1-8.9)
August 2012					
Southern well mixed	16.2 ± 1.7 (11.0-18.5)	34.5 ± 0.5 (33.1- 35.1)	0.8 ± 1.2 (0.4-8.3)	0.2 ± 0.1 (0.1-0.4)	1.5 ± 1.0 (0.3-5.2)
Northern SML	16.3 ± 0.8 (13.2-17.4)	34.3 ± 1.0 (30.9- 35.2)	0.5 ± 0.3 (0.4-1.5)	0.1 ± 0.0 (<LOD-0.2)	0.9 ± 0.5 (0.1-1.6)
Northern BML	8.8 ± 0.6 (7.5-10.5)	35.0 ± 0.2 (34.6- 35.4)	5.5 ± 3.0 (0.4-11.2)	0.6 ± 0.2 (0.2-0.9)	3.2 ± 0.8 (1.2-5.1)

Mean values are presented in mean ± SD, SD is standard deviation. Range values are showed in parentheses. Limit of detection (LOD) is 0.1 μM for phosphate in August 2012 samples. For parameters presented < LOD, the half of detection limit was used to calculate the mean value.

**Table 2. Summary of organic carbon and nitrogen observations during the 3 cruises.**

	DOC ($\mu\text{mol l}^{-1}$)	DON ($\mu\text{mol l}^{-1}$)	DOC:DON	POC ($\mu\text{mol l}^{-1}$)	PON ($\mu\text{mol l}^{-1}$)	POC:PON
August 2011						
Southern well mixed	97.5 ± 13.7 (77.1-134.5)	9.0 ± 1.8 (6.1- 13.7)	11.1 ± 1.6 (8.3-14.3)	-	-	-
Northern SML	73.8 ± 11.6 (51.2-104.2)	6.6 ± 1.0 (4.8-8.7)	11.3 ± 1.4 (8.0-15.3)	-	-	-
Northern BML	73.8 ± 14.7 (53.3-120.1)	5.9 ± 2.1 (3.0- 11.7)	13.4 ± 3.6 (7.4-23.3)	-	-	-
January 2012						
Southern well mixed	107.5 ± 29.6 (56.2-224.8)	6.7 ± 2.0 (3.7- 12.3)	17.3 ± 6.2 (5.9-36.5)	-	-	-
August 2012						
Southern well mixed	65.5 ± 16.4 (36.3-124.4)	5.3 ± 1.3 (2.8-9.8)	12.6 ± 2.8 (8.9-21.3)	16.0 ± 9.3 (5.8-43.8)	2.2 ± 1.3 (0.6-5.9)	7.7 ± 1.8 (5.0-13.2)
Northern SML	60.7 ± 13.0 (32.7-99.5)	5.3 ± 1.1 (3.0-7.5)	11.7 ± 2.3 (7.2-16.4)	10.5 ± 4.2 (2.7-21.8)	2.0 ± 0.7 (0.6-2.9)	5.9 ± 3.1 (1.1-14.2)
Northern BML	46.9 ± 6.8 (36.8-61.2)	5.2 ± 1.0 (3.5-7.5)	9.3 ± 1.8 (6.4-13.8)	7.3 ± 3.5 (1.1-16.2)	1.5 ± 0.7 (0.3-2.7)	6.0 ± 3.9 (0.7-16.8)

Mean values are presented in mean ± SD. Range values are showed in parentheses.



Table 3. Regression analysis of DOC, DON, POC and PON with salinity in each water mass. Note only significant correlation (at the 0.05 confidence level) is presented.

Parameters	Surveys	Water mass ^a	R-square (R ²)	Slope	y-Intercept ± uncertainty	n ^b
DOC	Summer 2011	NS	0.2594	-5.7	270.1 ± 47.9	50
		SM	0.1661	-11.1	477.7 ± 129.9	45
	Winter 2011	SM	0.0830	-20.0	805.5 ± 304.6	60
	Summer 2012	NS	0.4062	-8.1	338.3 ± 63.5	30
		SM	0.2871	-18.7	711.0 ± 153.4	46
DON	Summer 2011	NS	0.1973	-0.4	20.6 ± 4.1	50
		NB	0.3009	-5.1	183.7 ± 39.5	49
		SM	0.3037	-1.9	75.3 ± 15.3	45
	Summer 2012	NS	0.2535	-0.5	23.4 ± 5.9	30
		SM	0.4047	-1.8	67.1 ± 11.3	46
POC	Summer 2012	SM	0.1004	-6.3	233.6 ± 98.2	46
PON	Summer 2012	SM	0.1469	-1.0	37.8 ± 12.9	46

5 ^a Water masses: NS = stratified northern surface water, NB = stratified northern bottom water, SM = southern well-mixed water

^b Number of sample (n)