Seasonality and spatial heterogeneity of the surface ocean carbonate system in the northwest European continental shelf

Hartman, S.E.[a], Humphreys, M.P.[b], Kivimäe, C.[a], Woodward, E. M. S[c], Kitidis, V.[c], McGrath, T.[d], Hydes, D.J. [1], Greenwood, N.[e], Hull, T. [e], Ostle, C.[f], Pearce, D.J.[e], Sivyer, D.[e], Stewart, B.M.[g], Walsham, P.[h], Painter, S.C.[1], McGovern, E.[i], Harris,C.[c], Griffiths, A.[b], Smilenova, A.[b], Clarke, J.[b], Davis, C.[j], Sanders, R. [1], Nightingale, P.[c]

[a]National Oceanography Centre, Southampton, UK

[b]Ocean and Earth Science, University of Southampton, Southampton, UK

[c]Plymouth Marine Laboratory, Plymouth, UK

[d]National University of Ireland, Galway, Ireland

[e]Centre for Environment Fisheries and Aquaculture Science (Cefas), Lowestoft, UK

[f]Sir Alister Hardy Foundation for Ocean Science (SAHFOS), Plymouth, UK

[g]Agri-Food and Biosciences Institute (AFBI), Belfast, UK

[h]Marine Scotland Science (MSS), Aberdeen, UK.

[i]The Marine Institute, Galway, Ireland

[j]University of Liverpool, Liverpool, UK

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Key message:

We describe seasonal and regional variability in carbonate chemistry around the north-west European shelf, from a large and unique 1.5 year dataset of biogeochemical sampling combined with underway pCO_2 data. The data has improved understanding of carbonate chemistry in relation to nutrient biogeochemistry, showing seasonal variations between the well-mixed inner shelf and seasonally stratified outer shelf regions.

Abstract

In 2014-5 the UK NERC sponsored an 18 month long Shelf Sea Biogeochemistry research programme which collected over 1500 nutrient and carbonate system samples across the NW European Continental shelf, one of the largest continental shelves on the planet. This involved the cooperation of 10 different Institutes and Universities, using 6 different vessels. Additional carbon dioxide (CO_2) data were obtained from the underway systems on three of the research vessels. Here, we present and discuss these data across 9 ecohydrodynamic regions, adapted from those used by the EU Marine Strategy Framework Directive (MSFD). We observed strong seasonal and regional variability in carbonate chemistry around the shelf in relation to nutrient biogeochemistry. Whilst salinity increased (and alkalinity decreased) out from the near-shore coastal waters offshore throughout the year nutrient concentrations varied with season. Spatial and seasonal variations in the ratio of DIC to nitrate concentration were seen that could impact carbon cycling. A decrease in nutrient concentrations and a pronounced under-saturation of surface pCO_2 was evident in the spring in most regions, especially in the Celtic Sea. This decrease was less pronounced in Liverpool Bay and to the North of Scotland, where nutrient concentrations remained measurable throughout the year. The near-shore and relatively shallow ecosystems such as the eastern English Channel and southern North Sea were associated with a thermally driven increase in pCO_2 to above atmospheric levels in summer and an associated decrease in pH. Non-thermal processes (such as mixing and the remineralisation of organic material) dominated in winter in most regions but especially in the northwest of Scotland and in Liverpool Bay. The large database collected will improve understanding of carbonate chemistry over the North-Western European Shelf in relation to nutrient biogeochemistry, particularly in the context of climate change and ocean acidification.

1.0   Introduction

Continental shelf seas are important net sinks of atmospheric CO_2, occupying only 7% of the global sea surface area (Chen & Borges, 2009). However, there are considerable uncertainties in the contributions of individual shelf seas to regional (and global) carbon budgets (Borges, 2005). Continental shelves have high levels of biological activity due to cross shelf and riverine nutrient supply, and to rapid organic matter recycling from the close pelagic-benthic coupling on the shelf (Liu et al., 2010). The seawater partial pressure of CO_2 (pCO_2) is

59 controlled by seasonal changes in temperature and phytoplankton productivity (Zeebe & Wolf-

60 Gladrow, 2001). Additional factors such as coccolithophore calcification (Harley et al., 2010)

61 can influence seasonal variations in seawater pCO_2.

62   The northeast Atlantic continental shelf is a net CO_2 sink, of about -17 Tg C yr^{-1}

63 (compared with the global estimated shelf sink of -0.2 Pg C yr^{-1}; Laruelle et al., 2014) and thus

64 significant on both a regional and global basis as a hotspot of CO_2 uptake. It comprises both

65 well-mixed and stratified regions, which have different capacities to take up CO_2. Generally

66 the well mixed near-shore heterotrophic ecosystems act as sources of CO_2 to the atmosphere

67 and the seasonally stratified autotrophic continental shelf systems act as sinks of atmospheric

68 CO_2 (Borges, 2005; Chen & Borges, 2009). An example of the former is the southern North

69 Sea (Thomas et al., 2004) and the south western English Channel (Borges, 2005; Marrec et al.,

70 2013, 2015). An example of the latter is the seasonally stratified northern North Sea, which is

71 an order of magnitude stronger CO_2 sink than the well-mixed eastern English Channel (Thomas

72 et al., 2004, 2007). In the boundary between the off-shelf and on-shelf waters, a continuous

73 injection of nutrients can arise due to processes such as internal tides, internal waves, eddies

74 and slope current mixing, which can enhance productivity (Pingree, 1975; Garcia-Soto and

75 Pingree, 1998) and the potential CO_2 sink.

76   Monitoring the seawater total alkalinity (TA) and dissolved inorganic carbon (DIC),

77 along with its pCO_2, will help describe the oceanic carbonate system. The exact definition of

78 TA is complicated but it can be summarised as the stoichiometric sum of bases in solution

79 (Wolf-Gladrow et al., 2007). Many processes can influence TA such as benthic calcification

80 and dissolution, the growth of coccolithophore blooms (Harlay et al., 2010); the contribution

81 of organic matter (Koeve et al., 2012; Hoppe et al., 2012); changes in riverine input (Hydes &

82 Hartman, 2012) and nitrate uptake (Brewer & Goldman, 1976).

83   The anthropogenic increase in atmospheric CO_2 and uptake by seawater is driving a

84 decline in oceanic pH known as ocean acidification (OA) (Caldeira & Wickett, 2003; Doney

85 et al., 2009; Gattuso & Hansson, 2011). It is also important to measure nutrient concentrations

86 as an indication of potential primary production, as this will influence pCO_2 (and therefore

87 seawater pH) through the balance between photosynthesis and respiration.

88   The general features of the annual cycle of nutrient and plankton concentrations on the

89 northwest European shelf have been established for some time (Cushing, 1973; Johnston, 1973;

90 Gerlach, 1988; Nelissen & Stefels, 1988). Within the North Sea, the NERC North Sea

91 Programme in 1988-89, provided the first data set with sufficient information to allow seasonal

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92   changes in nutrient concentrations and plankton biomass to be investigated quantitatively

93   (Howarth et al., 1996). Seasonal variation in carbonate chemistry has also been followed at

94   time series sites (eg: the L4 and Stonehaven sites during the 2008-2010 DEFRApH project,

95   Hydes et al., 2011) or through surveys around the NW European shelf (e.g. Thomas et al., 2004,

96   which was based on 4 surveys of the North Sea).

97   UK-SSB was established in 2014 to improve our understanding of carbon and nutrient

98   cycling within shelf seas. As part of the 'CANDYFLOSS' (Carbon and Nutrient DYnamics

99   and Fluxes Over Shelf Systems) component of UK-SSB, sampling was carried out across the

100   entire NW European continental shelf for DIC, TA and inorganic nutrients. The UK-SSB

101   sampling campaign was a large marine research community effort that started in January 2014

102   and continued for eighteen months, involving the cooperation of 10 institutes and universities

103   and 6 vessels. One aim of the present study was to increase the density and spatial coverage of

104   carbon and nutrient sampling across the entire NW European shelf, using the shelf wide

105   sampling component of the UK Shelf Sea Biogeochemistry research programme (UK-SSB,

106   http://www.uk-ssb.org/). Our aim was to describe how the biogeochemical variables are

107   distributed and interrelated on the shelf, both through the year and across 9 ecohydrodynamic

108   regions, adapted from those used by the EU Marine Strategy Framework Directive (MSFD).

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110   **2.0   Materials and methods**

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112   **2.1   Division of data into Ecohydrodynamic regions**

113   Ecohydrodynamic regions of the NW European Shelf are defined for reporting under

114   the EU Marine Strategy Framework Directive (MSFD). The regions have been adapted from

115   those defined in Charting Progress 2 (UKMMAS, 2010) and Bresnan et al., (2015), with the

116   addition of the Irish Continental Shelf and the Norwegian Trench. They are distinguished by

117   water depth (and seasonal stratification), proximity to the coast, riverine inputs (salinity) and

118   water temperature ranges. These regions and the sampling positions are shown in Figure 1.
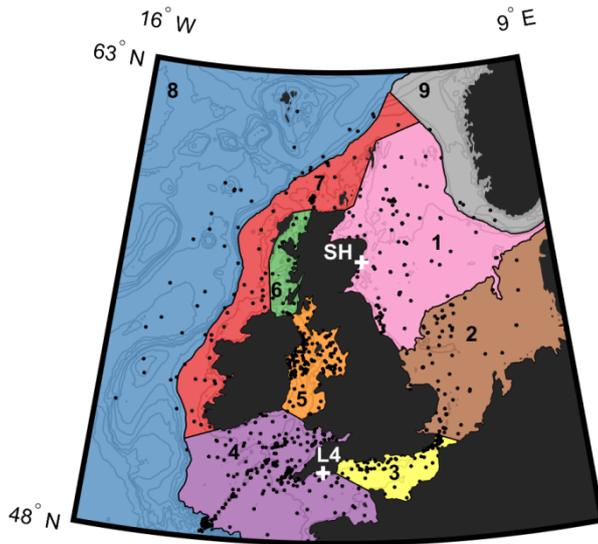
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Figure 1: Map of the sampling positions (black dots) during UK-SSB (2014-2015). Coloured areas 1—9 show the UK ecohydrodynamic regions used for MSFD reporting (adapted from Bresnan et al., 2015 to now include Ireland and the Norwegian Trench and showing the 200m contour). White plusses show the time series sites SH (Stonehaven) and L4.

Complex tidal fronts and topography separate the well-mixed and seasonally stratified waters across the shelf. This will strongly influence the biogeochemical dynamics of the area (as shown by Simpson & Hunter, 1974). The biogeochemical divide along the 50m contour separates the seasonally stratified northern North Sea (region 1) from the shallower, well-mixed southern North Sea (region 2). The North Sea is influenced by the Atlantic Ocean to the North (Huthnance et al., 1997) and by riverine input, especially to the south (Hydes et al., 1999; Bresnan et al., 2015). The northern North Sea acts as a down-welling system (Huthnance et al., 2009). In the southern North Sea the entire water column remains well mixed throughout the year, likewise the eastern Channel (region 3) has shallow (0-100m) and tidally well mixed waters. The deeper western Channel and Celtic Sea (region 4) has strong seasonal stratification with Atlantic influences in the Celtic Sea (Pingree, 1993; Simpson & Hunter, 1974). The relatively shallow and enclosed Irish Sea and especially Liverpool Bay (region 5) have a high influence of fresh water input (Hydes & Hartman, 2012; Greenwood et al., 2011).

Waters west of Scotland and the Minches (region 6) are made up of North Atlantic Ocean waters and form part of the continental shelf current but are modified by coastal

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influences (Bresnan et al, 2015). The Scottish and Irish continental shelf (region 7) are characterised by seasonal stratification and, as defined here, have a western limit of the 200m depth contour. This region is influenced both by exchanges with the North Atlantic deep water and by water flowing from the south in the shelf edge current (Pingree, 1993; Huthnance, 1995 &1997; Hydes et al 2004). The deep-sea waters beyond the 200m contour are oceanic in origin and the Atlantic Approaches (region 8) encompasses the Rockall Trough and the Faeroe/Shetland Channel. The Norwegian Trench (region 9) is the main outflow path for water leaving the North Sea, and it is permanently stratified (Van Leeuwen et al., 2015).

2.2   Sample collection

Between January 2014 and August 2015, multiple organisations collected samples from the underway water supply of their vessels on a daily basis whenever they were at sea around the NW European shelf (Figure 1). Data were obtained from RRS *Discovery* (8 cruises), RRS *James Cook* (1 cruise), RV *Cefas Endeavour* (34 cruises), RV *Celtic Explorer* (6 cruises), RV *Scotia* (7 cruises), RV *Corystes* (15 cruises), with additional samples from the fixed point monitoring sites Stonehaven in the North Sea and L4 in the English Channel (Figure 1). All data are available from BODC http://www.uk-ssb.org/data/ and as listed in the references from Humphreys et al., 2017 (a-h).

On approximately 1500 occasions, surface samples were collected from the underway seawater supply (nominal 5m depth). For DIC and TA analysis the samples were collected into borosilicate glass bottles (preserved with 0.05 ml saturated mercuric chloride solution following Dickson et al., 2007), and the nutrient samples were filtered and frozen. At the time of sampling the temperature and salinity was recorded from the underway sensors. Additional near surface (0-20 m) samples were taken using a rosette sampler on the UK-SSB cruises in the Celtic Sea, on the RV *Cefas Endeavour* and on a supporting cruise to the Hebrides Shelf (Painter at al., 2016; Hartman et al., 2017).

2.3   Chemical analysis

DIC and TA were mostly (>95%) measured using VINDTA 3C (Marianda, Germany) instruments in our shore based laboratory in Southampton. DIC analysis on the VINDTA involves reaction with 10% phosphoric acid, which converts DIC to CO_2 gas. This is carried

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173   by nitrogen into the coulometer cell where it reacts with monoethanolamine forming a titratable

174   acid, which causes fading of the blue indicator. Responding to the colour change, an electrical

175   current generates base to remove the acid and restore the indicator to the original colour. The

176   amount of CO_2 can be estimated from the total current required (corrected for a blank), and

177   DIC concentration can then be calculated given the sample volume. TA was measured by

178   titration with hydrochloric acid (HCl ~0.10 mol l^{-1}) using an open cell procedure, with a pH

179   half-cell electrode (glass bodied Orion 8101SC, Ross, USA) and an Ag/AgCl reference

180   electrode (model 6.0729.100, Metrohm, Switzerland). A modified Gran plot approach was used

181   to calculate TA (Humphreys, 2015). Approximately 5% of the DIC and TA measurements were

182   conducted using the Apollo SciTech (USA) DIC Analyzer (AS-C3) and Total Alkalinity

183   Titrator (AS-ALK2). The AS-C3 functions similarly to the VINDTA 3C except that the final

184   CO_2 measurement is by infrared absorbance (LI-COR). The AS-ALK2 performs a

185   potentiometric titration with 0.1M HCl to determine the TA.

186   In order to calibrate the results, seawater reference material (RM) obtained from A.G.

187   Dickson (Scripps Institution of Oceanography, USA) were analysed each day (Dickson et al.,

188   2003). Precision was assessed through repeated measurements of pooled seawater samples

189   (n>3) before each batch of sample analysis. The 1σ precision for the whole dataset was

190   estimated as ±2.6 μmol kg^{-1} for DIC and ±2.7 μmol kg^{-1} for TA for VINDTA measurements.

191   For the Apollo measurements, precision was estimated as ±4.0 μmol kg^{-1} and ±3.9 μmol kg^{-1}

192   for DIC and TA respectively (Humphreys et al., 2017, this issue).

193   During the SSB shelf wide sampling, underway pCO_2 was measured on-board the RV

194   *Cefas Endeavour* and on the NERC research vessel RRS *Discovery* using PML-Dartcom

195   systems (Kitidis et al., 2012). Briefly, this comprises of a vented 'showerhead' equilibrator,

196   Peltier cooler for partial drying of the equilibrated gas stream, non-dispersive infrared detection

197   (Licor; LI-840) and associated mechanical/electronic hardware. The system was calibrated

198   against three reference gases (BOC Gases, UK; nominal concentrations 250, 380 and 450 ppmv

199   CO_2 in synthetic air mixtures; changing from 450ppm to 600ppm on the RV *Cefas Endeavour*

200   from November 2014) which were referenced against primary reference gases (National

201   Oceanic and Atmospheric Administration, 244.9 and 444.4 ppm CO_2). A recent at-sea inter-

202   comparison with a similar but independent system, along with other carbonate observations,

203   found the system was precise to within ±4 μatm (Ribas-Ribas et al., 2014). The atmospheric

204   pCO_2 was calculated from monthly averaged pCO_2 measured at Mace Head (53.33° N, 9.90°

205   W) (Humphreys et al., this issue).

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206   Inorganic nutrients were analysed using a 'Bran and Luebbe AA3' segmented flow

207 colorimetric nutrient auto-analyser. The analytical methods were phosphate and silicate using

208 Kirkwood (1989) and nitrate (plus nitrite) with Brewer and Riley (1965) methods. The standard

209 deviation for duplicate measurements was within 2% and quality was assured through daily

210 use of certified reference materials provided by KANSO (Japan). Sampling protocols and

211 methodologies were carried out where possible according to the GO-SHIP nutrient analytical

212 procedures manual (Hydes et al., 2010) including assessment of detection limits (eg: 0.1 µmol

213 kg^{-1} for nitrate).

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215   2.4   Calculations

216   The carbonate system is characterised through knowing any two parameters out of TA,

217 DIC, pCO_2 or pH and then using equilibrium equations and constants (Park, 1969) and the

218 CO_2SYS program (Lewis et al., 1998) to calculate the remaining parameters. The shelf wide

219 UK-SSB measurements of DIC, TA temperature, salinity and nutrient data, were used to

220 calculate pH (free scale, as recommended by Waters & Millero, 2013), pCO_2, calcite (Ω_c) and

221 aragonite (Ω_a) saturation using the CO_2SYS program (Lewis et al., 1998) with the Mehrbach

222 constants (according to Dickson & Millero, 1987). Known uncertainties associated with

223 calculations in CO_2SYS using bottle DIC and TA results as inputs lead to an uncertainty of

224 ±6µatm in the calculation of pCO_2 (eg: Millero et al., 2002). These arise from inaccuracies in

225 the measurements and in the determination of dissociation constants. Calculated pCO_2 values

226 were checked against direct measurements of pCO_2 measured by underway systems on 60

227 occasions on-board the RV *Cefas Endeavour* and RRS *Discovery* research vessels. The average

228 difference was 2 µatm with a variation of up to ±27 µatm between the calculated and measured

229 pCO_2. We calculated pH from DIC and TA, despite this pair not being ideal for this purpose

230 (errors will be ±0.006; Millero et al., 2002), in order to give a general picture of seasonal and

231 regional variations in pH on the shelf.

232   The thermal and non-thermal components of pCO_2 were calculated by assessing the

233 change in pCO_2 relative to the average of all winter data in the survey, the winter mean state

234 (386 µatm), then calculating the thermal component at the mean winter temperature (9.1°C)

235 following Takahashi et al., (2002). The residual between the total and thermal component of

236 change was calculated to assess the non-thermal, or largely biological, component.

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3.0   Results

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239   All results are presented with January to March defined as winter, April-June as spring, July-September as summer and October-December as autumn when describing the seasonal distribution in biogeochemical variables. Table 1 shows the seasonal mean average (and standard deviation) for each variable and region. As the sampling was not distributed evenly in space and time some regions remain under-sampled, especially the Minches (region 6) in autumn and in the Norwegian Trench (region 9), as indicated in Table 1.

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3.1   Hydrographic variability

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247   Figure 2 shows the seasonal variation in sea surface temperature (SST) around an average of 14 °C. The coldest surface waters (average 7.65 °C) were seen in winter, especially in the North Sea (region 1, Table 1a). The warmest surface waters were generally observed to the south and in the summer, (eg: average of 18.27 °C Eastern English Channel (region 3). Warm sea surface temperatures (16.69 °C), were still apparent in the autumn in the Eastern English Channel (region 3). Overall the regional variations were dominated by a decrease in SST to the north (Figure 2).

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(a) Jan—Mar (b) Apr—Jun

(c) Jul—Sep (d) Oct—Dec

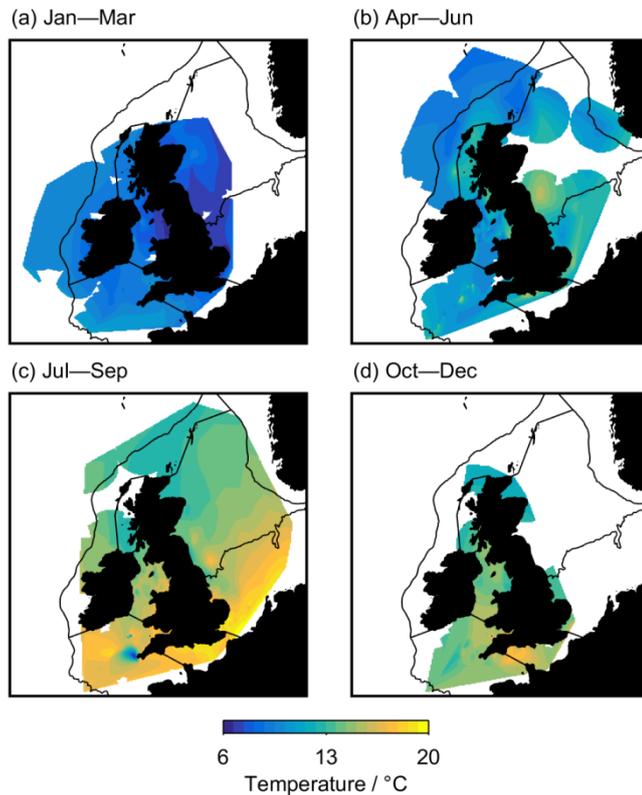6   13   20
Temperature / °C

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Figure 2: Seasonal maps of sea surface temperature (SST), using sensor data taken at the point of sampling on the SSB surveys. Figures 2-9, 12-15 are all mapped from 48 to 62°N, 16°W to 8°E showing winter (Jan-Mar), spring (Apr-Jun), summer (Jul-Sep) and autumn (Oct-Dec).

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Figure 3 shows the seasonal and regional variation in sea surface salinity (SSS). Regional variation dominated over seasonal variability and the shelf waters were fresher than the oceanic waters. The mean SSS for the whole data set was 34.5 with higher salinities from oceanic influence observed to the west on the Atlantic northwest approaches (35.6, region 8). A tongue of high salinity water was observed in the northern North Sea (region 1). This feature was especially prominent in summer (Figure 2, where the average SSS was 34.6, Table 1a), showing the influence of the advection of Atlantic water into this region.

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(a) Jan—Mar (b) Apr—Jun

(c) Jul—Sep (d) Oct—Dec

33.2   34.0   34.8   35.6
Practical salinity
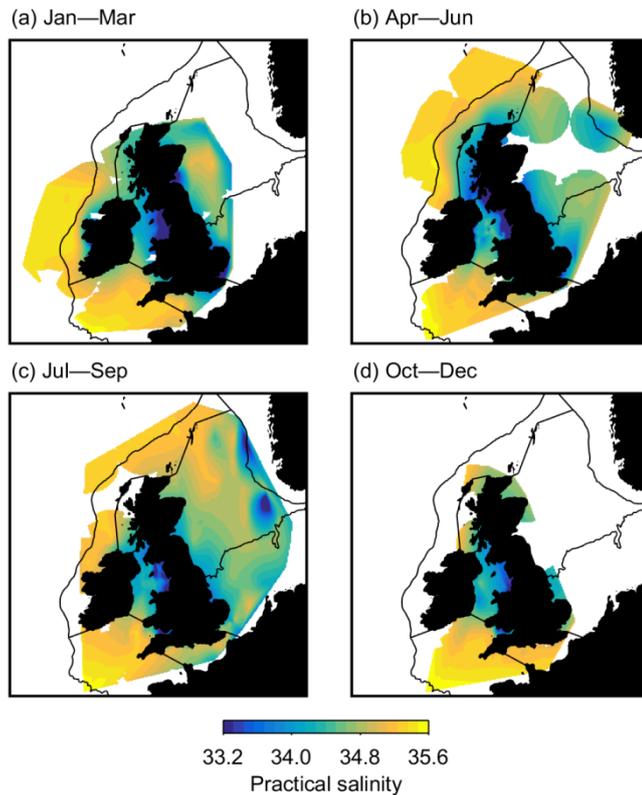
Figure 3: Seasonal maps of sea surface salinity (SSS) as practical salinity, using sensor data taken at the point of sampling on the SSB surveys.

3.2   Chemical variability

3.2.1   Nutrients

Figures 4 and 5 show the seasonal and regional variation in surface inorganic nutrients. Generally nitrate concentrations were relatively high offshore, in the Atlantic waters off shelf (region 7) compared to the inner shelf regions in all seasons. In contrast, the silicate concentrations were generally lower on the outer shelf compared with the inner shelf (see Figure 4 and 5). For example to the west of Ireland (in region 7) the average nitrate concentration in winter was relatively high (7.9 µmol kg $^{-1}$) when the silicate concentrations were relatively low (4.6 µmol kg $^{-1}$) as shown in Table 1.

Seasonally the highest nitrate and silicate concentrations were observed in winter, in all regions (Figures 4 and 5). For example, the winter nutrient concentrations were high in the Irish Sea (region 5) with average winter nitrate and silicate of 9.9 µmol kg $^{-1}$ and 7.5 µmol kg

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284 $^{-1}$ respectively. However, relatively low nitrate concentrations (6.3 µmol kg $^{-1}$) were observed

285 in winter off the Scottish west coast (region 6).

286   In spring the lowest nitrate concentrations were observed in the northern North Sea

287 (average 0.5 µmol kg $^{-1}$, region 1) and the Minches (1.0 µmol kg $^{-1}$, region 6) but remained

288 relatively high offshore to the north of Scotland (6.7 µmol kg $^{-1}$, region 8) and in the Irish Sea

289 (3.9 µmol kg $^{-1}$, region 5) . By summer, nitrate concentrations were depleted in most regions

290 (Figures 4 and 5). However in Liverpool Bay (in region 5), nutrient concentrations were never

291 fully depleted although the largest seasonal changes were observed here, with a winter to

292 summer decrease of 8 µmol kg^{-1} for nitrate and 5 µmol kg^{-1} for silicate (see also Tables 1a and

293 1b). On the Scottish continental shelf (region 7), to the northeast of Scotland, nitrate

294 concentrations also remained above detection (average 1.2 µmol kg^{-1}) into summer. In the

295 autumn, nutrient concentrations had started in increase in Liverpool Bay (in region 5), earlier

296 than in other regions (Figures 4 and 5).

297   Phosphate concentrations were measured but have not been mapped here as they were

298 uniform around the whole of the UK shelf (with a winter mean of 0.55 µmol kg^{-1}, Table 1a),

299 although some deviations in the ratio of nitrate to phosphate are discussed in section 4.1.

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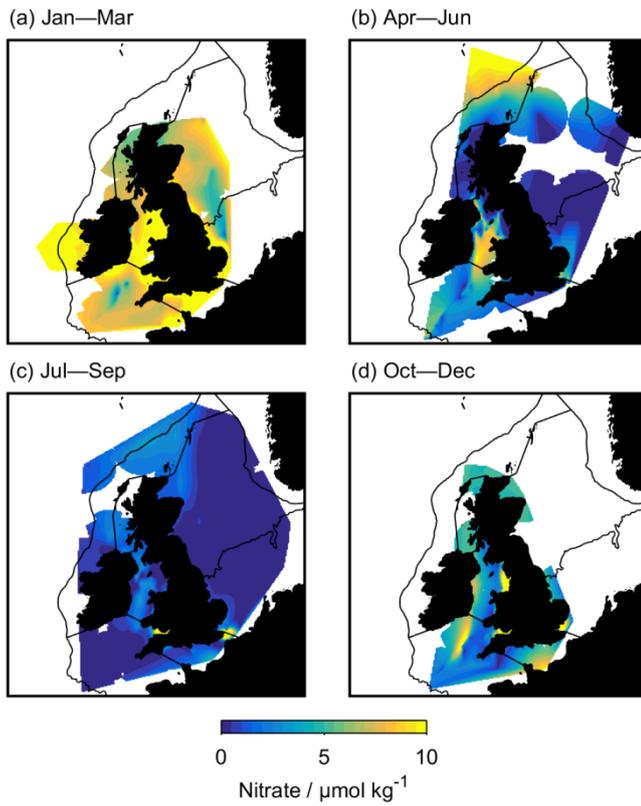
Figure 4: Seasonal maps of sea surface nitrate concentrations, from SSB bottle samples.
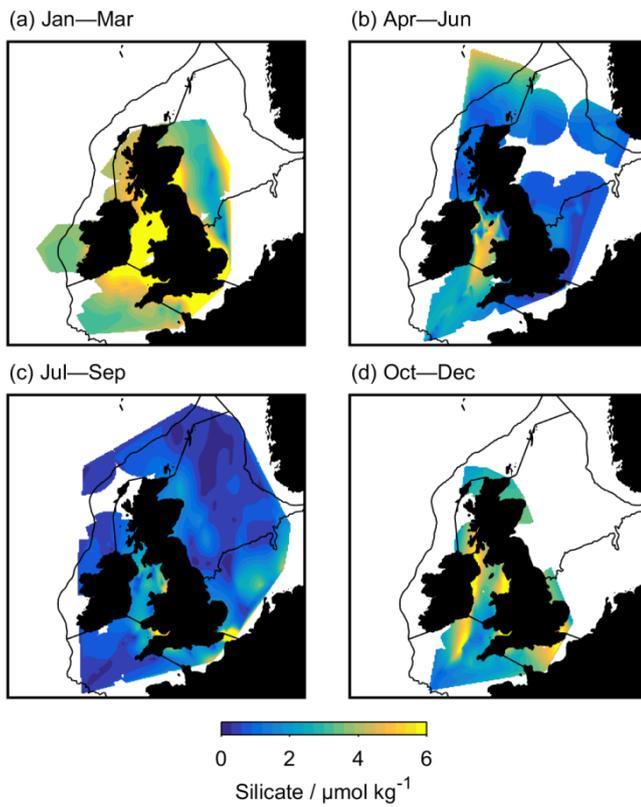
Figure 5: Seasonal maps of silicate concentrations, from SSB bottle samples.

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3.2.2 Total Alkalinity

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307   Figure 6 shows the seasonal and regional TA distribution. The annual mean TA for the

308   whole dataset was 2320 µmol kg^{-1}. There was a relatively large range of values, especially in

309   the northern North Sea (region 1), where the seasonal mean TA increased from 2275 µmol kg^{-1}

310   in spring to 2310 µmol kg^{-1} in winter (Table 1b). In the high salinity Atlantic waters of the

311   northwest approaches (region 8), seasonal mean TA values were relatively high (above 2330

312   µmol kg^{-1}) and the seasonal range was small (Table 1b). Overall, TA distribution was generally

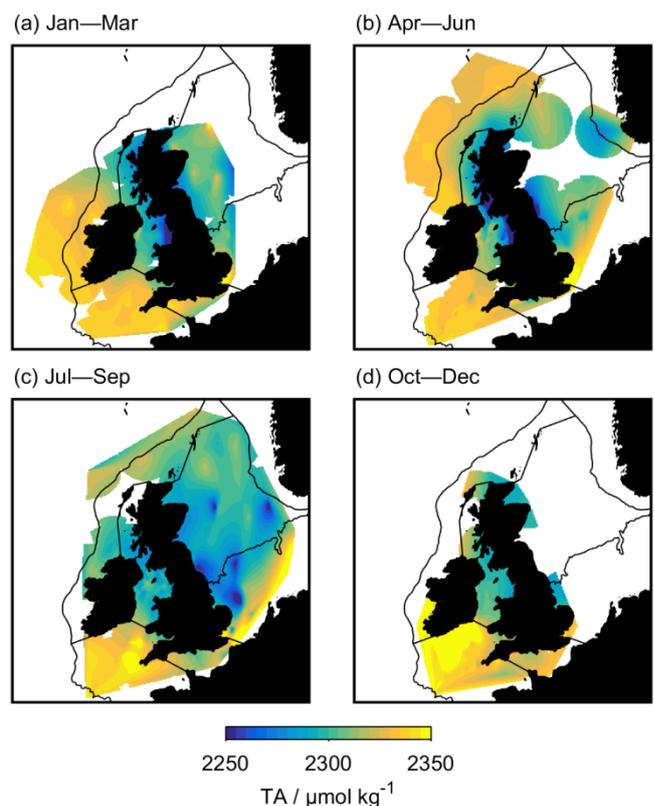313   similar to salinity with higher TA offshore throughout the year and the lowest values on the

314   shelf.

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**Figure 6:** Seasonal maps of total alkalinity (TA) measurements, from SSB bottle samples.

3.2.3 Dissolved Inorganic Carbon

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320   Figure 7 shows the seasonal and regional distribution of DIC. The largest seasonal

321   change in DIC was in the northern North Sea (region 1) where there was over 100 µmol kg^{-1}

322 decrease in the seasonal mean DIC from winter to spring (Figure 7, Table 1b). The lowest DIC

323 concentrations observed were in spring in the northern North Sea (2034 µmol kg^{-1}, region 1)

324 and the Minches (region 6, around 2065 µmol kg^{-1}) and in summer on the continental shelf

325 (region 7, around 2097 µmol kg^{-1}, Table 1b). DIC concentrations peaked in winter and

326 decreased in the spring and summer in all regions (Table 1b), therefore DIC showed a similar

327 distribution to nutrient concentrations.

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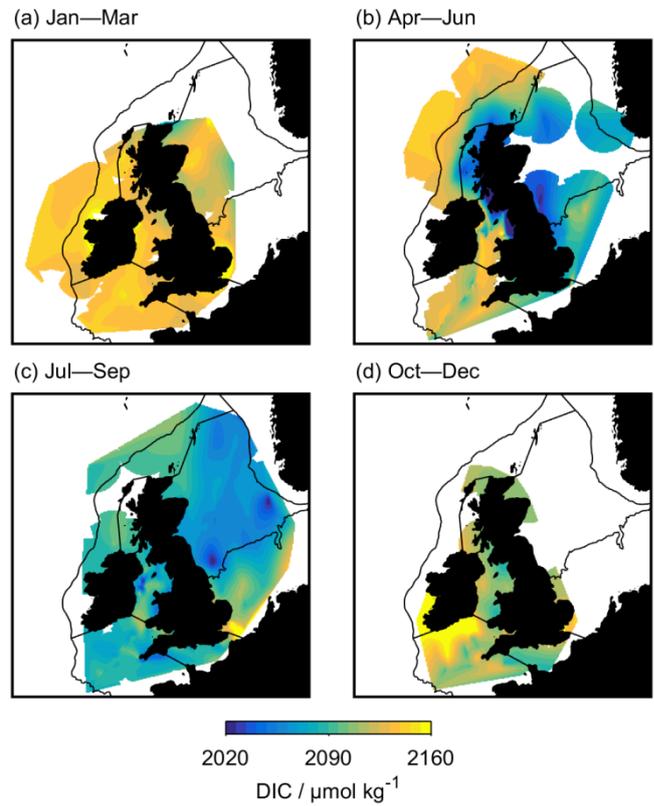
330 **Figure 7:** Dissolved Inorganic Carbon (DIC) measurements, from SSB bottle samples.

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3.2.4   Partial pressure of carbon dioxide

333 Figure 8 shows the seasonal and regional variations in measured and calculated pCO$_2$.

334 Taking an atmospheric pCO$_2$ of 400 µatm (Humphreys et al., this issue) then under-saturated

335 values (relative to atmospheric pCO$_2$) are indicated by the blue colours and over-saturated by

336 the warmer colours in Figure 8. Generally, the highest values were seen in the autumn and the

337 lowest values for each region were in the spring (Figure 8).

338 In the seasonally stratified northern North Sea (region 1) pCO$_2$ values were generally

339 under-saturated from winter (352 µatm, Table 1b) to summer. However, there is some variation

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340   within this region where relatively oversaturated values were observed close to the Scottish

341   coast from autumn to winter (Figure 8). The largest seasonal variation in pCO_2 was observed

342   in the southern North Sea, (region 2) with an increase of over 100 µatm between the spring and

343   autumn (Figure 8, Table 1b).

344   A seasonal over-saturation in CO_2 was especially prominent in the relatively shallow

345   inner shelf regions in summer and autumn (Figure 8 and Table 1b). For example, a marked

346   increase in pCO_2 from spring to summer was observed in the relatively shallow eastern English

347   Channel (region 3, from 333 to 452 µatm, Table 1b).

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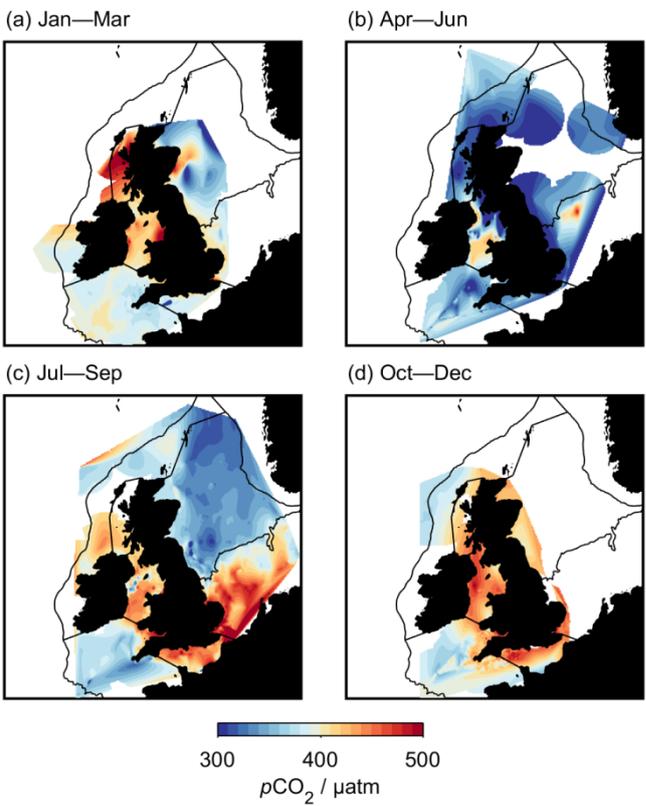
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350   **Figure 8:** Surface pCO_2, calculated from bottle samples analysed for DIC/TA (using

351   CO_2SYS) and measured pCO_2 from underway systems on the RRS *Discovery* and RV *Cefas*

352   *Endeavour* (2014-2015).

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354   In the Celtic Sea (region 4) pCO_2 was predominantly under-saturated throughout the

355   year (Figure 8). However, pCO_2 increased near to the coast in autumn when the average was

356   407 µatm (Table 1b). In contrast, the relatively shallow Irish Sea (region 5) showed a general

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357 year round over-saturation in pCO$_2$ (with seasonal averages above 409 µatm, Table 1b) except

358 for in spring.

359 ### 3.2.5 Calculated pH

360 Figure 9 shows the seasonal and regional variation in calculated pH around the shelf. It

361 is important to note that the colour scale is reversed in Figure 9 for easier comparisons with

362 pCO$_2$ as an inverse relationship is expected. Overall, calculated pH was lowest around the

363 coast in autumn and the highest calculated pH was observed in spring (Figure 9). For example

364 in the northern North Sea (region 1) the seasonal mean pH in spring was 8.19 when pCO$_2$ was

365 low (see Table 1b). In the southern North Sea (region 2) there was a spring to summer decrease

366 in the calculated pH (from 8.15 to 8.05, Table 1b). Likewise, in the eastern Channel (region 3)

367 the pH decreased to a similar extent from spring to summer (Table 1b). In the Irish Sea (region

368 5) and the Minches (region 6) the seasonal mean pH was lowest in winter (when pCO$_2$ was

369 high) and increased in the spring (from 8.06 to 8.18 in region 6, Table 1b).

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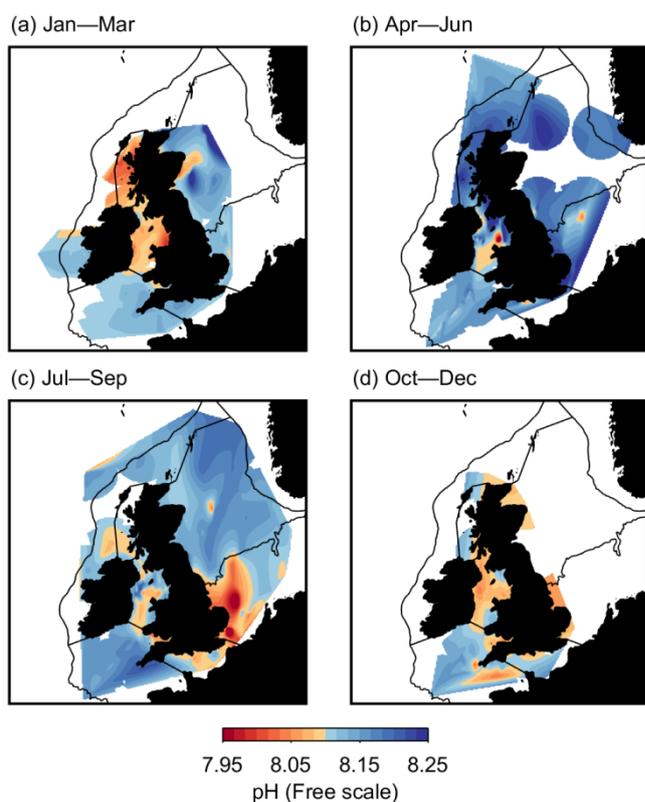
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372 **Figure 9:** pH (freescale), calculated from bottle samples analysed for DIC/TA (using

373 CO$_2$SYS).

4.0 Discussion

4.1 An overview of seasonal variations in relation to regions

Dividing the UK-SSB dataset into 9 ecohydrodynamic regions revealed large regional variations in carbonate chemistry parameters in relation to nutrients and hydrography. Figure 10 illustrates the relationship between hydrography (SST) and surface nutrient concentrations s for each of the regions considered.
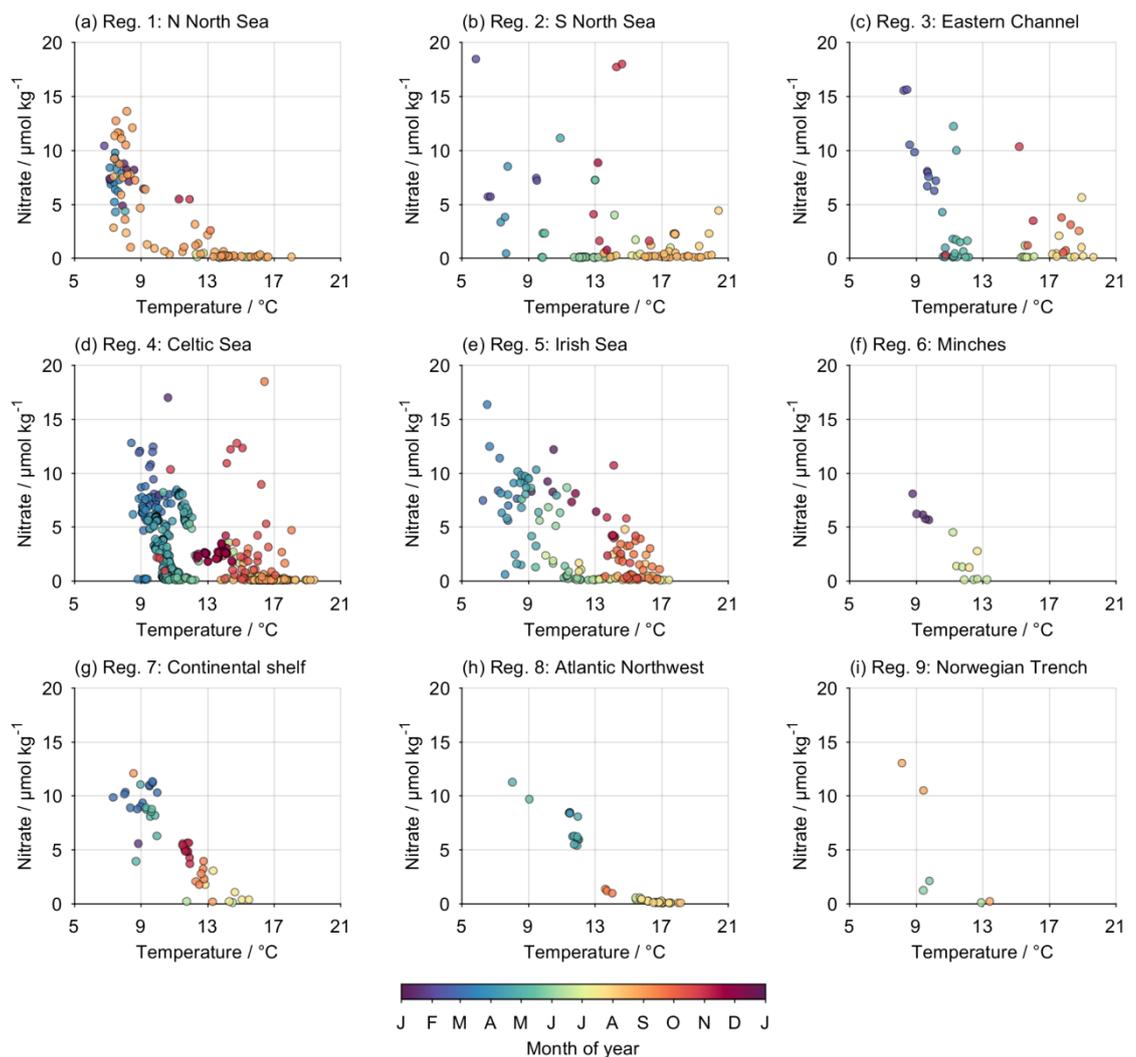
Figure 10: Measured nitrate concentrations and sea surface temperature for each month and region.

386   Overall, there was a winter peak in nutrient concentrations, then a rapid decrease in the

387   spring and summer months. The rapid depletion in nitrate (and DIC) concentrations in spring

388   are likely to result from their assimilation in the production of organic material by

389   phytoplankton, during the 'spring bloom' (Frigstad et al., 2015). The dominant pattern on the

390   shelf was for low nitrate concentrations throughout the spring to summer months, in warming

391   water. Then, in the autumn months there was an increase in nitrate concentrations (as the water

392   cools), observed in all regions where data were available (Figure 10). The increase in nitrate

393   concentrations during autumn months is likely to be due to the remineralisation of organic

394   matter, the break down the thermal stratification of the surface waters and the onset of vertical

395   mixing. This seasonal variability is as expected at temperate latitudes (Smith et al., 2014) and

396   gives a triangular distribution to the data points (Figure 10). Similar patterns would be expected

397   for DIC, especially in winter months when seasonal stratification breaks down and nitrate plus

398   DIC accumulates in the surface waters.

399   The winter peak in nutrient (and DIC) concentrations are also likely due to organic

400   matter remineralisation and the convective mixing of colder high nutrient and DIC rich waters

401   from below (Körtzinger et al., 2008). Maximum concentrations were reached just before the

402   return of stratification in spring in all regions (Figure 10). However, in the Northern North Sea

403   the autumn SST is relatively cold and associated with higher nitrate concentrations compared

404   with other regions (Figure 10). The relationship between SST and nitrate concentrations is less

405   clear in the Southern North Sea (region 2, Figure 10). Relatively low salinities were observed

406   in the east of the southern North Sea in summer (region 2, in Figure 3) due to fresh water

407   entering the North Sea from the major European continental rivers (such as the Rhine).

408   Therefore, riverine inputs are likely to have contributed to the higher nitrate concentrations

409   seen in this region.

410   In the well mixed eastern English Channel (region 3) there was a pronounced

411   'triangular' shape in the relative nitrate and SST variability (Figure 10). The nitrate

412   concentrations increased earlier in the year (compared with other regions), starting in the

413   summer whilst SST was still relatively high. This may be due to the continuous injection of

414   nutrients into the euphotic zone that is seen in many well mixed systems (L'Helguen et al.,

415   1996). High nitrate (and silicate, Figure 5) concentrations were observed for most of the year

416   in the eastern Channel (region 3), probably from the remineralisation of organic material in

417   these relatively shallow and well-mixed regions.

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418   In the western English Channel and the Celtic Sea (region 4), an area characterised by

419 seasonal thermal stratification (Smyth et al., 2010; Smith et al., 2014), the highest nitrate

420 concentrations were generally observed in the winter (Figure 10, from January to March). In

421 the central Irish Sea (region 5) nitrate was never depleted, even during spring and summer,

422 possibly due to riverine inputs (Greenwood et al., 2011). The seasonal mean salinity remained

423 relatively low (~33.9, Table 1a) throughout the year in the Irish Sea and Liverpool Bay (region

424 5) showing a high influence of fresh water input to the region (Hydes & Hartman, 2012;

425 Greenwood et al., 2011). Silicate concentrations in the Irish Sea (region 5) were at least 1 μmol

426 kg^{-1} higher than other regions throughout the year (Figure 5), probably due to this riverine

427 influence. Seasonal coverage is relatively poor for the Minches (region 6) and the Norwegian

428 trench (region 9), as seen in Figure 10.

429   In the more open ocean continental shelf (region 7) and Atlantic northwest approaches

430 (region 8) there was a linear relationship between nitrate and temperature, likely due to the

431 spring nitrate depletion and autumn nitrate regeneration (Figure 10). To the far north of

432 Scotland (in region 7) nitrate concentrations remained high (> 5 μmol kg^{-1}) until the summer

433 months (Figure 10), probably due to the general northward delay in bloom timing (Siegel et

434 al., 2002). From the linear relationship seen in Figure 10 the nitrate concentrations could

435 almost be predicted from SST, as shown by Sathyendranath et al., (2001); Henson et al., (2003).

436

437   **4.2 Stoichiometry**

438   Figures 11(a-c) shows the relationship between nitrate and phosphate. These figures

439 confirm the similarity in spatial distributions between nitrate and phosphate, although most of

440 the values were below the open ocean 'Redfield' stoichiometric ratio of 16:1 (Redfield et al.,

441 1963; Anderson and Sarmiento, 1994). In the present study, some especially low nitrate values,

442 relative to phosphate concentrations, were seen in both the southern North Sea (region 2, Figure

443 11a) and the Irish Sea (region 5, Figure 11b). Likewise there is a relatively low N:P in the

444 Celtic Sea (region 4, Figure 11b). The N:P relationship approaches the 16:1 (Anderson and

445 Sarmiento, 1994) ratio in the more Atlantic influenced off shelf areas (regions 6-8, Figure 11c).

446   Nutrient concentrations are likely to be higher near the coast than in the open ocean,

447 particularly where there are riverine inputs. However, a key feature established in the North

448 Sea Project data (Hydes et al., 1999) was that the maximum nitrate concentrations observed in

449 the Central North Sea (Hydes et al., 1999) and in the Irish Sea (Gowen et al., 2002 and 2008)

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450 were below those observed in ocean waters adjacent to the shelf (Hydes et al., 2004). This

451 resulted in low nitrate to phosphate (N:P) ratios (Hydes et al 1999; Gowen et al., 2002),

452 probably from denitrification in the sediments of these relatively shallow (and well mixed) seas

453 (Setzinger and Giblin., 1996). Recently Kitidis et al. (2017) also showed that sediment

454 anaerobic ammonium oxidation and denitrification removed 6-9 % of the nitrate in the Celtic

455 Sea over an annual cycle.

456   Figures 11(d-f) show the relationship between DIC and nitrate. Overall, there was a

457 positive correlation between DIC and nitrate around the northwest European Shelf. However

458 there was large variability in this relationship within and between the regions. For example in

459 the northern North Sea (region 1) most points were above the line shown in Figure 11d (that

460 represents the open ocean C:N of 7.3, Anderson and Sarmiento, 1994). In the southern North

461 Sea (region 2) there was a pronounced variability in the C:N relationship at very low nitrate

462 concentrations (Figure 11d). In the Celtic Sea (region 4) there was a variation in the C:N ratio

463 as the nutrient concentration increased (Figure 11e). However, on the Irish and Scottish shelf

464 (region 7) most of the points followed this line (Figure 11f).

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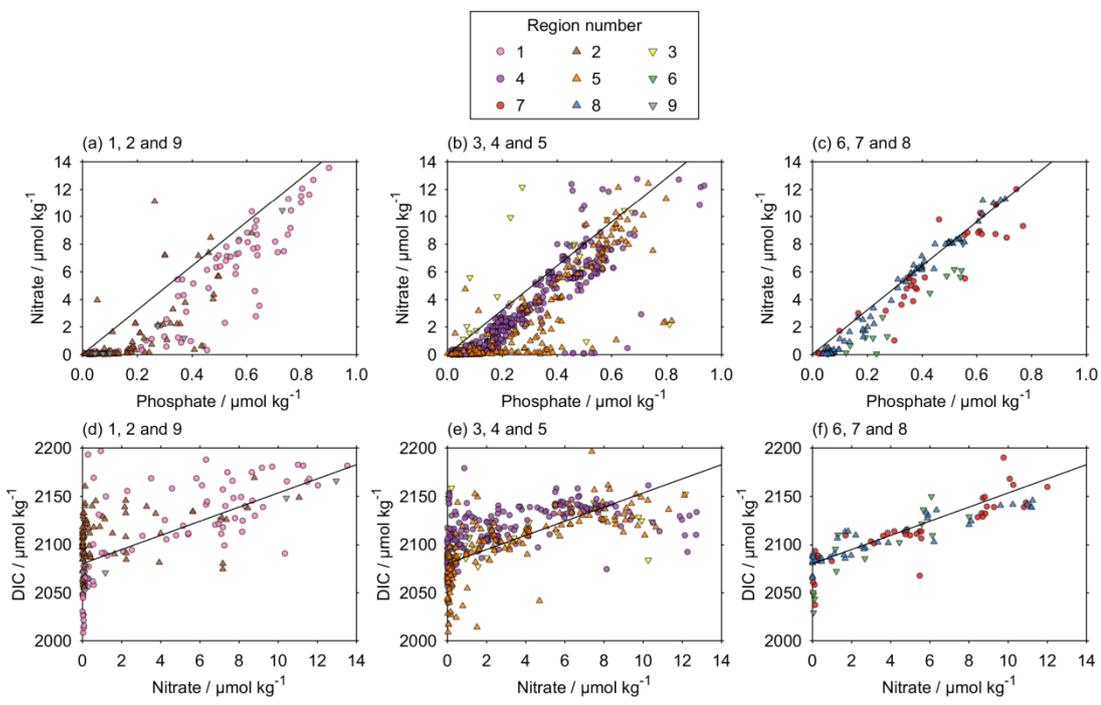
Figure 11: A comparison of the (a-c) nitrate and phosphate concentrations (in groups of 3 regions for ease of viewing) showing the Anderson and Sarmiento (1994) N:P ratio of 16:1 as

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470 a solid line and (d-f) the relationship between DIC and nitrate with the C:N ratio of 7.3 as a
471 solid line (Anderson and Sarmiento, 1994).

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473 A positive correlation was generally observed between DIC and nitrate, as both are
474 influenced by productivity and the breakdown of organic material. Where the variability in the
475 C:N relationship was pronounced at very low nitrate concentrations, for example in the
476 southern North Sea (region 2), this may be a further indication of denitrification. This process
477 is significant in the North Sea (Hydes et al, 1999) and could contribute to the relatively low
478 nitrate values observed in both the N:P and C:N ratios (Figure 11) in this region. However,
479 riverine input can be an additional source of variability in the C:N relationship in the more
480 coastal systems through both nutrient input (Greenwood et al., 2011) and DIC input (McGrath
481 et al., 2016).

482 In the Celtic sea (region 4), the points were above the line at low nitrate concentrations
483 and below the line at higher concentrations (> 8μmol kg $^{-1}$, Figure 11e). So, the C:N ratio was
484 initially high in the potentially productive periods (periods of productivity were identified for
485 the Celtic Sea by Hickman et al., this issue), when nitrate concentrations were lower. Then the
486 C:N decreased at high nitrate concentrations. High C:N suggests a more efficient recycling of
487 nitrate compared with carbon and that the organic material exported from the surface would be
488 carbon enriched (Sambrotto et al., 1993). Therefore spatial and seasonal changes in C:N could
489 have a significant impact on carbon cycling and export off the shelf via the continental shelf
490 pump (Gruber and Galloway, 2008; Painter et al., 2017). Variation in the C:N will also have
491 implications for methods that calculate productivity from the depletion in DIC or nitrate
492 (Frigstad et al., 2015 and references therein) using the 'standard' C:N Redfield ratio of 6.6:1
493 (Anderson and Sarmiento, 1994).

494

495 **4.3   Controls on seawater pCO$_2$**

496 The solubility of CO_2 depends mainly on temperature (increased solubility at low
497 temperature, decreased at high temperatures). In turn, biological production processes tend to
498 decrease surface water pCO$_2$, whereas respiration and remineralisation processes tend to
499 increase surface water pCO$_2$ (Shadwick et al., 2011). The dominance of these processes varies
500 through the year and with region (Takahashi et al., 2002; Jiang et al., 2013). To study this
501 further we assessed the physical and biological forcing on pCO$_2$. Figure 12 shows the thermal

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502 component of the change in pCO_2 calculated following Takahashi et al. (2002). Figure 13

503 shows the residual between the total and thermal component of change and represents the non-

504 thermal component, which we assume to be largely biologically driven. This is either through

505 the remineralisation of organic matter in the surface layer, or the addition of remineralised

506 nutrients from the deep layer through vertical mixing. The magnitude of this component may

507 be reduced by any air-sea gas exchange.

508 Our study showed the dominance of thermal control (Figure 12) on the pCO_2 especially

509 in the spring and summer. Temperature can be the main factor influencing the pCO_2 variability,

510 through the control on stratification and stabilisation of the water column triggering production.

511 The spring time decrease in pCO_2, to under saturated levels was seen in all regions and

512 coincided with a large decrease in nutrients in these productive waters (Table 1), as shown by

513 Thomas et al., (2005). Biological production can impact surface pCO_2 in summer in stratified

514 systems by the presence of subsurface phytoplankton blooms below the (shallow) thermocline

515 (Shadwick et al., 2011). Non-thermal or biological control dominated from autumn through to

516 winter (Figure 13) due largely to regeneration from the respiration of organic material.

517 There were clear regional variations in the balance of thermal and non-thermal controls.

518 For example in the central region of the northern North Sea (region 1) there was a thermally

519 driven increase in pCO_2 of about 70 μatm from winter to spring (Figure 12), and a non-thermal

520 decrease of 110 μatm (Figure 13). This region seasonally stratifies and DIC is transported off

521 shelf (Huthnance et al., 2009). Overall, in the seasonally stratified northern North Sea (region

522 1), the control of pCO_2 was predominantly non-thermal (biological, as shown in Figure 13), as

523 has been shown previously (Thomas et al, 2005 & 2006; Van Leeuwen et al., 2015). In contrast,

524 in the well-mixed, shallower southern North Sea (region 2) thermal controls on pCO_2

525 dominated (Figure 12). In this region, water temperature was the dominant control on both

526 pCO_2 and nutrient concentrations (Thomas et al, 2005 & 2006; Van Leeuwen et al., 2015).

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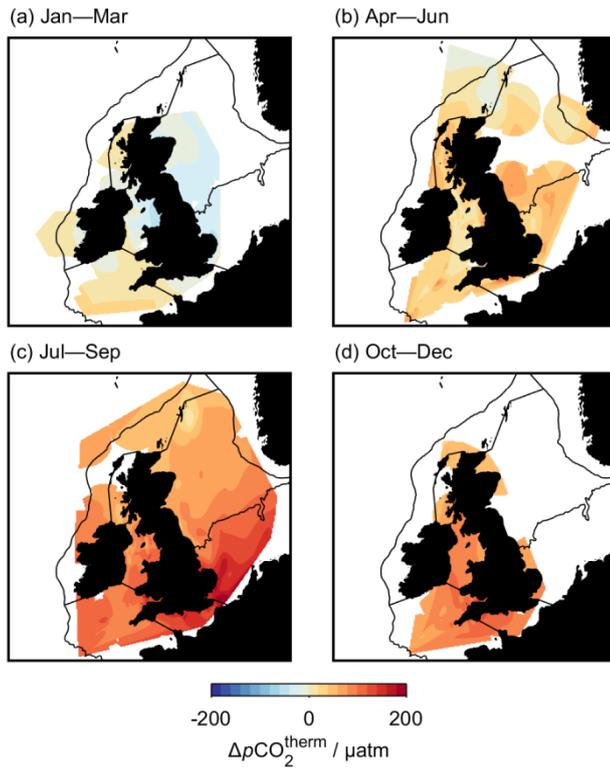
Figure 12: The thermal component of the change in pCO$_2$ calculated following Takahashi et al. (2002).
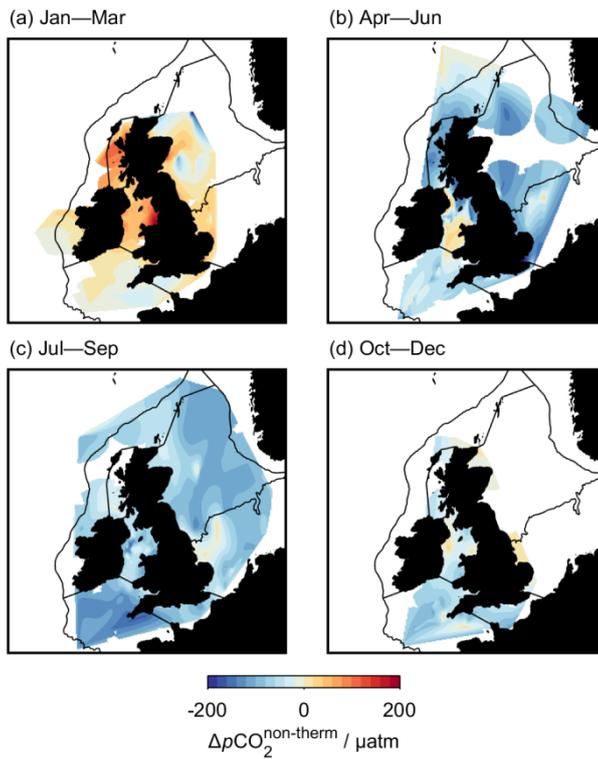
Figure 13: The non-thermal component of the change in pCO$_2$ (calculated following Takahashi et al., 2002 as the residual between the total and thermal component of change).

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535

536   Our study suggested that the eastern English Channel (region 3) was over-saturated in

537   CO_2 in the autumn (Figure 8). This was when non-thermal heterotrophic processes, such as

538   organic matter remineralisation, dominated (Figure 13). An autumnal over-saturation of CO_2

539   has been observed previously in the eastern English Channel (Frankignoulle et al., 1996; Jiang

540   et al., 2013). Borges (2005) also suggested that the permanently well-mixed and shallow

541   ecosystems within the eastern English Channel were seasonally over-saturated and a seasonal

542   source of CO_2.

543   Overall pCO_2 in the Celtic Sea (region 4) was close to the atmospheric pCO_2 for most

544   of the year (Figure 8), with a pronounced under-saturation in spring (to a mean average of 364

545   µatm, Table 1). This is similar to the observations made by Kitidis et al., (2012). The seasonal

546   variations in pCO_2 were dominated by biology rather than advection in the northern part of the

547   western English Channel (Figure 13). In contrast, the data suggested that in the Irish Sea

548   (region 5) pCO_2 was over-saturated for most of the year (Figure 8). There was a dominance of

549   non-thermal controls on pCO_2 in autumn and winter in the Irish Sea (region 5), and the non-

550   thermal influences were especially high near to the coast (Figure 13). pCO_2 remained higher

551   here than if it were in equilibrium with the atmosphere for most of the year (Table 1), except

552   for in the spring when there was a pronounced under-saturation in the surface waters.

553   In the Minches (region 6), the non-thermal component was especially high in winter

554   and had little influence for the rest of the year. In the wider sub-polar Atlantic, the seasonal

555   cycle of pCO_2 was dominated by the mixing of cold water (leading to increased CO_2 solubility).

556   This was seen to the west of Ireland (region 7) where both the thermal and non-thermal

557   components increased pCO_2 in the autumn and winter.

558   In summary, the largest thermal component observed was in the summer to the south

559   of the UK (Figure 12), especially in the southern North Sea (region 2) and the eastern English

560   Channel (region 3) where the highest SST had been observed in summer (Figure 2). The largest

561   non-thermal component observed (Figure 13) was in winter, especially around the coast in

562   Liverpool Bay (region 5) and the Minches (region 6). In all of these well-mixed and shallower

563   regions, it is likely that the decaying bloom, and breakdown of organic material (Carr et al.,

564   this issue), increased the pCO_2 in autumn and winter. As these regions remain mixed the pCO_2

565   super-saturation persists until the next spring.

566   Our seawater pCO_2 data has been used to assess potential sources and sinks around the

567   shelf (Kitidis et al., 2018 in prep.). The direction of air-sea gas fluxes are driven by

568 concentration differences between the seawater and atmosphere. Where pCO_2 in seawater was
569 under-saturated compared with the atmospheric pCO_2 it suggests that this area will be a sink;
570 if it exceeded pCO_2 in air then this suggests the region will be a source to the atmosphere.
571 However, the magnitude of the flux is modulated by other processes, for which wind speed can
572 be used as a proxy (Wanninkhof, 2014). This is explored further in Kitidis et al. (2018, in prep.)
573 and the NW European shelf was found to be net autotrophic and a CO_2 sink over the period of
574 our study.

575   The separation into ecohydrodynamic regions (after Bresnan et al., 2015) was done to
576 distinguish the different hydrographical regions. These separations correspond well to the
577 biogeochemical variability observed from the data. However, if you go further into the details
578 then more complex and dynamic hydrographical systems are observed, such as tidal fronts
579 between the year round well-mixed and seasonally stratified ecosystems, shelf break systems
580 and estuarine systems. The on-shelf tidal frontal zones between the permanently well-mixed
581 and seasonally stratified areas are particularly productive and can influence CO_2 exchange and
582 examples of these frontal regions are seen in the Irish Sea (Simpson & Hunter; 1974) and in
583 the Celtic Sea (Pingree & Griffiths, 1978). For example within the seasonally stratified Celtic
584 Sea (region 4) the southern part of the western English Channel and the waters around Land's
585 End (Marrec et al., 2013), can be distinguished in the hydrography. Within the western Channel
586 and Celtic Sea (region 4) there was a clear division between the northern sub-region, where
587 there was a dominance of non-thermal control of pCO_2 in winter and the southern part where
588 thermal effects dominated (Figure 12).

589

4.4 Changes in alkalinity and pH

591   The TA and salinity distribution is generally similar as both are strongly influenced by
592 evaporation, riverine freshwater inputs and precipitation. TA can be considered as conservative
593 in the open ocean where TA and salinity tend to be linearly related (Lee et al., 2006; Jiang et
594 al., 2014). Near coastal waters, with a strong salinity gradient, are ideal places to get a TA: S
595 linear relationship. However in the current study the real near coastal water area was not
596 assessed, and it was difficult to get see a linear TA:S relationship in such diverse ecosystems
597 although the low salinity water was generally associated with low TA values. The offshore
598 increase in salinity (Figure 3) and TA (Figure 6) dominated over any seasonal variations.

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599   Many processes result in a TA increase in near coastal waters (Cai et al., 2011; Thomas
600   et al., 2007), such as the increase in TA by the oxidation of organic material in marine
601   sediments (Froelich et al., 1979). The southern North Sea (region 2) and the eastern Channel
602   (region 3) both showed large variability in TA compared with other regions as these shallow
603   areas are influenced by high organic material (Salt et al., 2016). Coastal regions are also
604   influenced by riverine input, where the presence of calcareous limestone bedrock can increase
605   TA in shelf waters. For example, the high TA river Liffey near Dublin inputs to the Irish Sea
606   (region 5) although in this case the effects will only be observed near to the coast due to a low
607   riverine discharge (McGrath et al. 2016). Previous studies have shown some seasonality in TA
608   due to productivity, for example Hydes & Hartman (2012) showed higher TA during the spring
609   bloom in the Liverpool Bay sub-region of the Irish Sea (region 5). On the northwest European
610   shelf large coccolithophore blooms can also strongly influence alkalinity and calcification will
611   affect the TA and seawater pCO_2 (Harlay et al., 2010)

612   In the present study, large seasonal variations in pH were observed around the shelf,
613   (up to 0.2 units, Table 1b). The pH range is influenced by DIC, TA and changes in temperature
614   and by the balance between photosynthesis and respiration. There is generally an inverse
615   relationship between pCO_2 and pH, due to the increase in H^+ ions (i.e. decreased pH) when
616   CO_2 dissolves in seawater (Zeebe and Wolf-Gladrow, 2001). pH increased in spring in all
617   regions (Table 1b) when photosynthesis dominated over respiration. pH then decreased in
618   summer in most regions (Table 1b): for example in the Southern North Sea (region 2) pH
619   decreased from spring to summer (8.15 to 8.05, Table1), as respiration became more important
620   (Provoost et al., 2010). Previous studies found similar large seasonal variations in pH (up to
621   0.3) especially off the east coast of Scotland, around the Stonehaven time series site (Hydes et
622   al., 2011; Ostle et al., 2016).

623   In the North Sea (regions 1 and 2) and the eastern Channel (region 3), where
624   temperature control on pCO_2 dominated, there was a winter to summer increase in pCO_2 (and
625   associated pH decrease), possibly influenced by the remineralisation of organic matter in these
626   shallower regions. The pCO_2 increase (and pH decrease) at the end of summer, is likely to be
627   due to the influence of temperature and the remineralisation of organic matter by microbial
628   processes through the sediment-water interface in these relatively shallow regions. The process
629   of denitrification over muddy sediments could also influence pH although we would expect a
630   pH increase due to this process (Froelich et al., 1979; Provoost et al., 2010).

631   The strong pH fluctuations in shelf seas and coastal waters (Duarte et al., 2013; Ostle

632 et al, 2016; Waldbusser & Salisbury, 2014) imply that the concept of ocean acidification (OA)

633 is difficult to transpose to coastal ecosystems, where the rates and variability of OA are higher

634 than in the open ocean (Doney et al., 2009). The occurrence of vibrant biological communities

635 in areas with large regional and seasonal variations in seawater pH imply that they possess an

636 inbuilt tolerance to pH changes (Bates et al., 2014; Kitidis et al., 2017). This tolerance may

637 occur due to the ability of seawater to buffer some of these pH changes through its alkalinity.

638 TA will buffer the hydrogen ions so the buffering capacity of seawater is a direct function of

639 TA as regions with high TA will be less prone to rapid changes in OA. The DIC:TA relationship

640 for example can be strongly linked to different buffer factors (eg: Egleston et al., 2010). Studies

641 such as ours give some indication of the present pH variability over the NW European Shelf,

642 which will be useful in the future in the context of ocean acidification. This study also identified

643 regions where the lowest TA values coincided with the lowest pH, such as the Southern North

644 Sea (region 2, see Table 1). The low TA may suggest regions with a decreased capacity to

645 buffer pH changes in the future.

646   Future OA could have detrimental effects on calcifying organisms (Feely et al., 2009;

647 Riebesell & Tortell, 2011; Doney et al., 2011). In the current study, calcite (Figure 14) and

648 aragonite (Figure 15) were not generally under-saturated. Calcite saturation was always in the

649 range of 1.5 to 4.8 and aragonite was virtually never under-saturated (1.0 to 3.1; about 0.3% of

650 total measurements were <1). Aragonite is the most soluble form of calcium carbonate in the

651 marine environment and saturation will decrease as pH decreases (Feely et al., 2009), giving

652 an indication of susceptibility of a region to ocean acidification. Low saturation coupled with

653 low pH would affect the ability of organisms to form shells and skeletons (Fabry et al., 2008).

654 Model data from Artioli et al., (2014) showed localised potential under-saturation of aragonite

655 in the German Bight by the end of the 21st century. Changes in temperature, pCO_2 and

656 calcification would all further increase the vulnerability of these regions to OA in the future

657 (Bates et al., 2014).

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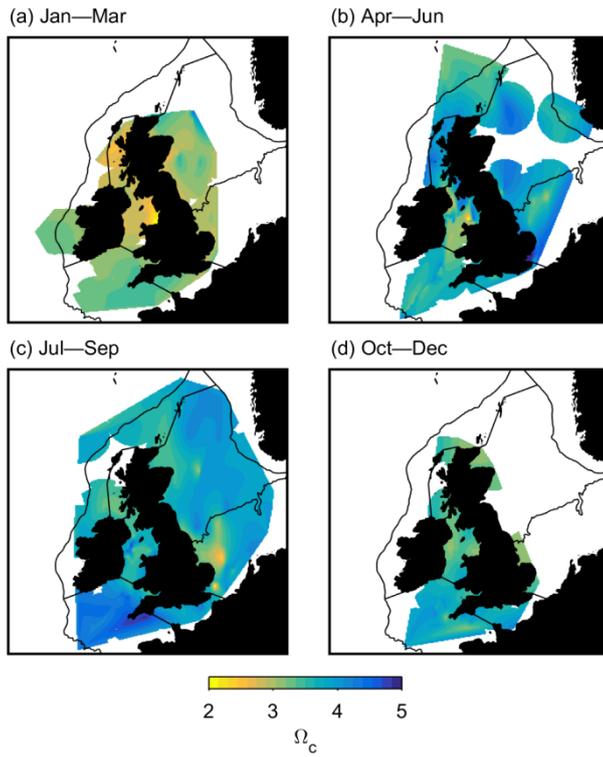
Figure 14: Calcite saturation (Ω_c) calculated from SSB bottle DIC and TA.
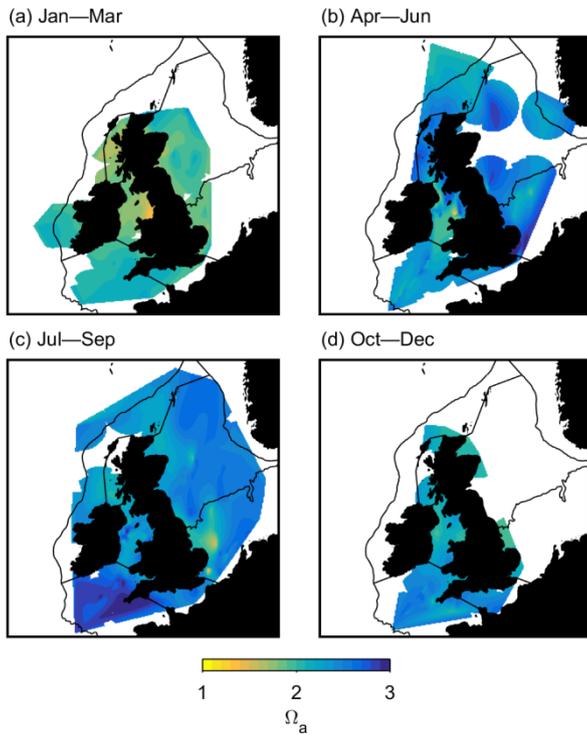
Figure 15: Aragonite saturation (Ω_a) calculated from SSB bottle DIC and TA.

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666   As the seasonal variation in pH can be large (Ostle et al., 2016) long-term time series
667   measurements are required to detect any inter-annual trends (Bates et al., 2014). Ideally, over
668   25 years of consistently measured data are required to detect pH trends (Henson et al., 2016)
669   although ICES studies in the central North Sea (Beare et al., 2013) and southern North Sea
670   (Duarte et al., 2013) have reported a decadal decline in pH. This decline in pH was associated
671   with physical drivers (Salt et al., 2013) and changes in nutrients and eutrophication (Provoost
672   et al., 2010). Hydes et al., (2011) showed a trend of decreasing pH around the NW European
673   Shelf of -0.002 to -0.004 pH units per year between 1995 and 2009. If sample collection were
674   to be continued around the shelf, the present study could be used to extend this emerging time
675   series.

676   **5.0   Conclusions**

677   We have synthesised the spatial distributions of nutrients and carbonate chemistry
678   around the northwest European shelf. The data were divided into 9 ecohydrodynamic regions
679   including well-mixed inner shelf and seasonally stratified outer shelf regions. The general
680   trends in carbon chemistry were related to changes in the hydrography and nutrients
681   (representing biological activity and riverine input). The seasonally stratified regions, (for
682   example off shore on the Continental slope, region 7), showed a clear inverse relationship
683   between SST and surface nitrate (and DIC) concentrations. This was in contrast to the well
684   mixed regions, such as the eastern channel (region 3), where the regeneration of nutrients
685   occurred at higher temperatures. The regional variations in the DIC to nutrient relationship will
686   have implications for calculations of carbon export.

687   The effects of thermal and non-thermal processes influencing pCO_2 have been shown
688   for different seasons and regions. For example in the near-shore and relatively shallow
689   ecosystems such as the eastern English Channel (region 3) and southern North Sea (region 2)
690   there was a thermally driven increase in pCO_2 to above atmospheric levels in summer. Non-
691   thermal processes (such as mixing and the remineralisation of organic material) dominated in
692   winter, especially to the northwest of Scotland (region 6) and in Liverpool Bay (region 5). In
693   all regions, the seawater pCO_2 was under-saturated in spring in respect to the atmospheric
694   equilibrium. In the well-mixed inner shelf regions pCO_2 was over-saturated for the rest of the
695   year whereas pCO_2 remained under-saturated throughout the year in the seasonally stratified
696   regions such as the Celtic sea (region 4). The seasonal variations in under and over saturation
697   of pCO_2 will have implications in calculations of shelf wide net CO_2 flux, presented and

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698 discussed in Kitidis et al., (in prep., 2018). TA concentrations remained relatively constant

699 seasonally and showed a similar distribution to salinity, as both are influenced in part by

700 evaporation and precipitation. However, the lowest TA and lowest pH values were observed at

701 the end of winter in the northern North Sea (region 1). We have shown that calcite saturation

702 values are currently above 1.0 in all regions and such results will be useful for studies of ocean

703 acidification in the future.

704   This synthesis provided a 18 month 'snapshot' of the diverse and dynamic ecosystems

705 around the northwest European shelf. It is complicated to catch the variability of complex

706 ecosystems as the ecohydrodynamic regions studied were very diverse and dynamic. Within

707 each region further subdivisions were identified and the seasonal variation in biogeochemistry

708 within these regions will have implications for using such broad hydrographic divisions to

709 study biogeochemical variations on the northwest European shelf. Incorporating high

710 frequency underway data (as was available for pCO_2 measurements) improved both the

711 seasonal and spatial coverage over what was possible with bottle sampling alone. Generally,

712 the wintertime period was under sampled, as were some regions year round, including the

713 Norwegian Trench (region 9) and the Minches (region 6). Addressing these issues could be the

714 focus for further sampling campaigns. The increased use of autonomous measurements on

715 robust platforms (such as buoys and autonomous surface vehicles) would help in this regard.

716   The data have sufficient coherence and breadth of coverage to develop models that

717 would link physical and biogeochemical processes. The SSB data set could also be used to

718 extend existing studies to create a time series. Once we have a longer time series, we could

719 use this data set to quantify trends in pH and pCO_2, so we recommend that the sampling

720 continue to quantify year-to-year variability and elucidate trends in the data. In conclusion, the

721 large database collected as part of the shelf wide sampling within the SSB project will improve

722 the understanding of carbonate chemistry in relation to nutrient biogeochemistry over the

723 North-Western European Shelf, particularly in the context of climate change and ocean

724 acidification.

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Table 1 a) The mean average (and standard deviation) for the hydrograph and nutrient data in winter (jan-mar), spring (apr-jun), summer (jul-sep) and autumn (oct-dec) for each of the 9 ecohydrographic regions (numbered 1-9). Where insufficient samples exist, n/a has been used.

	Temperature (°C)				Practical salinity				Phosphate (μmol kg^{-1})				Silicate (μmol kg^{-1})				Nitrite (μmol kg^{-1})			
	jan-mar	apr-jun	jul-sep	oct-dec	jan-mar	apr-jun	jul-sep	oct-dec	jan-mar	apr-jun	jul-sep	oct-dec	jan-mar	apr-jun	jul-sep	oct-dec	jan-mar	apr-jun	jul-sep	oct-dec
1	7.65	13.78	14.36	11.65	33.26	34.11	34.61	34.78	0.54	0.08	0.09	0.36	3.59	0.95	0.75	3.07	0.12	0.03	0.06	0.18
	(0.52)	(2.44)	(1.27)	(0.45)	(3.9)	(0.40)	(0.61)	(0.02)	(0.08)	(0.11)	(0.08)	(0.01)	(1.55)	(0.57)	(0.60)	(0.49)	(0.08)	(0.07)	(0.10)	(0.01)
2	7.86	12.40	17.69	14.24	34.08	34.56	34.43	34.67	0.35	0.10	0.16	0.50	2.13	0.80	1.92	3.72	0.14	0.02	0.10	0.59
	(0.85)	(1.27)	(1.67)	(1.28)	(1.53)	(0.36)	(0.42)	(0.34)	(0.12)	(0.07)	(0.13)	(0.44)	(1.48)	(0.53)	(1.77)	(2.13)	(0.10)	(0.05)	(0.15)	(0.46)
3	9.44	12.25	18.27	16.69	34.95	30.64	34.86	35.15	0.53	0.08	1.91	0.35	5.10	2.88	3.62	3.76	0.10	0.11	0.09	0.19
	(0.70)	(1.93)	(0.80)	(1.25)	(0.54)	(10.81)	(0.29)	(0.11)	(0.05)	(0.07)	(6.46)	(0.26)	(2.33)	(9.18)	(5.72)	(1.44)	(0.06)	(0.25)	(0.13)	(0.14)
4	9.48	11.32	16.63	15.84	35.22	35.27	34.12	33.39	0.53	0.21	0.09	0.27	4.23	2.14	0.80	2.27	0.10	0.07	0.08	0.23
	(0.57)	(1.56)	(2.68)	(5.89)	(0.14)	(0.17)	(4.42)	(6.43)	(0.12)	(0.16)	(0.16)	(0.23)	(0.90)	(0.93)	(1.17)	(1.62)	(0.08)	(0.05)	(0.29)	(0.17)
5	8.00	10.53	15.37	14.06	33.80	33.81	34.02	34.19	0.64	0.36	0.25	0.95	7.54	3.00	2.13	5.31	0.13	0.11	0.15	0.23
	(1.40)	(1.84)	(1.14)	(0.89)	(0.78)	(0.81)	(0.46)	(0.36)	(0.22)	(0.21)	(0.18)	(2.15)	(3.34)	(2.30)	(1.19)	(5.59)	(0.18)	(0.09)	(0.23)	(0.36)
6	9.35	12.14	12.47	n/a	34.45	34.00	34.24	n/a	0.53	0.19	0.24	n/a	4.53	1.29	1.43	n/a	0.06	0.10	0.25	n/a
	(0.39)	(0.73)	(0.35)	n/a	(0.09)	(0.35)	(0.16)	n/a	(0.02)	(0.12)	(0.03)	n/a	(0.32)	(0.78)	(0.39)	n/a	(0.01)	(0.07)	(0.18)	n/a
7	8.74	9.70	14.01	18.41	34.53	34.94	35.11	34.87	0.59	0.42	0.13	0.36	4.56	1.54	0.48	2.65	0.27	0.23	0.06	0.31
	(0.58)	(1.80)	(1.05)	(10.87)	(0.50)	(0.42)	(0.27)	(0.2)	(0.04)	(0.27)	(0.11)	(0.03)	(1.01)	(0.79)	(0.29)	(0.43)	(0.13)	(0.14)	(0.05)	(0.18)
8	9.88	11.31	16.16	14.12	35.39	35.65	35.54	35.58	0.62	0.43	0.10	n/a	3.30	2.25	0.36	n/a	0.07	0.17	0.04	n/a
	(0.15)	(1.49)	(1.69)	(0.39)	(0.04)	(0.99)	(0.15)	(0.00)	n/a	(0.18)	(0.07)	n/a	n/a	(1.39)	(0.17)	n/a	n/a	(0.06)	(0.05)	n/a
9	n/a	10.75	14.03	n/a	n/a	34.26	34.65	n/a	n/a	0.17	0.04	n/a	n/a	1.29	0.42	n/a	n/a	0.16	0.01	n/a
	n/a	(1.91)	(0.80)	n/a	n/a	(0.61)	(0.43)	n/a	n/a	(0.14)	(0.02)	n/a	n/a	(0.56)	(0.29)	n/a	n/a	(0.26)	n/a	n/a

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1091 Table 1 b) The mean average (and standard deviation) for nitrate and carbonate data in winter (jan-mar), spring (apr-jun), summer (jul-sep) and
1092 autumn (oct-dec) for each of the 9 ecohydrographic regions (numbered 1-9). Where insufficient samples exist, n/a has been used.

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	Nitrate (μmol kg^{-1})				DIC (μmol kg^{-1})				TA (μmol kg^{-1})				pH				pCO$_2$ (μatm)			
	jan-mar	apr-jun	jul-sep	oct-dec	jan-mar	apr-jun	jul-sep	oct-dec	jan-mar	apr-jun	jul-sep	oct-dec	jan-mar	apr-jun	jul-sep	oct-dec	jan-mar	apr-jun	jul-sep	oct-dec
1	7.40	0.51	0.33	5.42	2133.27	2033.72	2063.51	2110.95	2309.71	2275.17	2291.11	2294.62	8.18	8.19	8.15	8.09	351.51	331.07	362.89	427.
	(1.52)	(1.42)	(0.56)	(0.01)	(23.38)	(31.65)	(17.24)	(0.45)	(29.42)	(28.38)	(19.02)	(7.21)	(0.15)	(0.06)	(0.04)	(0.01)	(81.80)	(52.03)	(73.54)	(8.7
2	4.60	1.11	0.66	6.10	2147.12	2097.67	2110.98	2144.89	2319.90	2314.85	2316.10	2331.90	8.12	8.15	8.05	8.06	382.05	376.22	483.40	469.
	(3.22)	(2.70)	(1.06)	(7.39)	(44.05)	(18.89)	(37.72)	(24.54)	(31.15)	(29.59)	(42.68)	(32.12)	(0.03)	(0.07)	(0.10)	(0.01)	(31.20)	(58.66)	(79.58)	(11.
3	9.56	4.13	3.77	3.45	2133.52	2102.09	2089.84	2102.80	2326.21	2341.57	2316.24	2323.77	8.13	8.19	8.09	8.10	377.89	333.08	452.43	436.
	(3.51)	(10.42)	(9.91)	(3.24)	(8.08)	(36.38)	(14.69)	(10.39)	(14.26)	(26.17)	(12.97)	(10.25)	(0.02)	(0.06)	(0.02)	(0.04)	(19.73)	(54.69)	(29.21)	(48.
4	6.55	2.05	0.49	3.37	2140.49	2111.78	2086.91	2116.19	2332.68	2333.32	2335.20	2337.16	8.12	8.17	8.14	8.12	388.10	354.57	389.88	405.
	(3.69)	(2.44)	(2.28)	(4.06)	(7.93)	(23.78)	(18.09)	(21.57)	(9.60)	(10.09)	(14.97)	(16.05)	(0.01)	(0.03)	(0.04)	(0.04)	(13.26)	(31.18)	(49.11)	(44.
5	9.86	3.94	1.03	5.27	2143.20	2095.01	2076.72	2110.78	2298.23	2294.04	2293.79	2305.37	8.07	8.14	8.12	8.08	435.29	364.82	409.35	446.
	(6.09)	(3.86)	(1.25)	(4.54)	(18.26)	(52.36)	(25.23)	(12.83)	(26.64)	(30.14)	(12.89)	(10.68)	(0.04)	(0.10)	(0.05)	(0.03)	(40.78)	(62.10)	(54.79)	(28.
6	6.31	0.99	1.94	0.00	2129.04	2065.03	2090.22	n/a	2287.09	2294.17	2286.60	n/a	8.06	8.18	8.11	n/a	452.97	333.27	402.89	n/a
	(0.99)	(1.50)	(1.07)	(0.00)	(15.18)	(30.84)	(7.20)	n/a	(10.89)	(10.11)	(7.31)	n/a	(0.05)	(0.05)	(0.03)	n/a	(62.04)	(43.92)	(27.48)	n/a
7	7.88	5.53	1.21	4.91	2117.70	2112.53	2090.19	2127.98	2320.55	2323.43	2301.07	2316.16	8.16	8.17	8.11	8.10	347.37	342.94	411.17	418.
	(3.37)	(4.11)	(1.27)	(0.64)	(47.20)	(30.49)	(15.82)	(27.17)	(31.78)	(14.33)	(8.49)	(26.90)	(0.05)	(0.04)	(0.04)	(0.02)	(51.67)	(29.78)	(41.43)	(19.
8	10.23	6.71	0.59	n/a	2138.65	2129.34	2089.56	n/a	2332.34	2335.43	2329.87	n/a	8.12	8.15	8.15	n/a	386.80	369.86	372.79	n/a
	n/a	(2.99)	(1.00)	n/a	(2.94)	(16.17)	(11.36)	n/a	(8.47)	(6.30)	(17.18)	n/a	n/a	(0.03)	(0.03)	n/a	n/a	(24.80)	(32.84)	n/a
9	n/a	0.67	0.14	n/a	n/a	2070.94	2060.83	n/a	n/a	2298.60	2294.63	n/a	n/a	8.19	8.16	n/a	n/a	325.05	355.18	n/a
	n/a	(0.91)	n/a	n/a	n/a	(0.13)	(12.05)	n/a	n/a	(35.53)	(0.06)	n/a	n/a	(0.03)	(0.04)	n/a	n/a	(12.54)	(38.98)	n/a

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