

Controls on pH in surface waters of Northwestern European shelf seas

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# Controls on pH in surface waters of northwestern European shelf seas

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## Abstract

We present here a high resolution surface water pH dataset obtained in the Northwest European shelf seas in summer 2011. This is the first time that pH has been measured at such a high spatial resolution (10 measurements  $\text{h}^{-1}$ ) in this region. The aim of our paper is to investigate the carbonate chemistry dynamics of the surface water using pH and ancillary data. The main processes controlling the pH distribution along the ship's transect, and their relative importance, were determined using a statistical approach. The study highlights the impact of biological activity, temperature and riverine inputs on the carbonate chemistry dynamics of the shelf seas surface water. For this summer cruise, the biological activity formed the main control of the pH distribution along the cruise transect. Variations in chlorophyll and nutrients explained 29% of the pH variance along the full transect and as much as 68% in the northern part of the transect. In contrast, the temperature distribution explained ca. 50% of the pH variation in the Skagerrak region. Riverine inputs were evidenced by high dissolved organic carbon (DOC) levels in the Strait of Moyle (northern Irish Sea) and the southern North Sea with consequent remineralisation processes and a reduction in pH. The DOC distribution described 15% of the pH variance along the full transect. This study highlights the high spatial variability of the surface water pH in shelf seawaters where a range of processes simultaneously impacts the carbonate chemistry.

## 1 Introduction

Oceans form an important sink of atmospheric carbon dioxide ( $\text{CO}_2$ ), thereby significantly buffering climate change. About 27% of the anthropogenic  $\text{CO}_2$  emitted between 1959 and 2011 has been taken up by the oceans (Le Quéré et al., 2013). However with increasing atmospheric  $\text{CO}_2$  concentrations, questions arise on whether oceans are able to maintain their current rate of  $\text{CO}_2$  uptake or whether their capacity to absorb  $\text{CO}_2$  is decreasing while ocean waters reach higher dissolved inorganic carbon ( $\text{C}_\text{T}$ )

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levels. The capacity of the oceans to sequester  $\text{CO}_2$  depends on the role of biological (soft tissue and carbonate) and solubility pump processes in altering  $\text{CO}_2$  concentrations in the surface ocean (Volk and Hoffert, 1985). The oceanic carbonate system is controlled by biological and physical processes leading to seasonal and geographical variations. Shelf seas have been recently recognized as a potentially significant sink of  $\text{CO}_2$  ( $0.2 \text{ PgCyr}^{-1}$ ) due to their high biological activity resulting in a net off shelf transport at depth to the adjacent deep ocean regions (shelf sea carbon pump) (Borges et al., 2005; Chen and Borges, 2009; Thomas et al., 2004). However, coastal environments are dynamic, subject to a range of interacting biological and physical processes with contrasting effects on the marine carbonate system and therefore, on the capacity of coastal seas to absorb  $\text{CO}_2$ .

pH is one of the four variables ( $C_T$ , total alkalinity ( $A_T$ ) and partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ )) used to study the carbonate system. The main factors controlling the carbonate chemistry in coastal water are biological activity, temperature changes and discharges of river water (Thomas et al., 2005). Photosynthesis decreases the concentration of  $C_T$  and free protons and leads to an increase in pH, whereas respiration, remineralisation and calcification lead to a decrease in pH. Temperature changes affect the carbonate equilibrium constants and  $\text{CO}_2$  solubility (Mehrbach et al., 1973). A rise in temperature triggers a shift in the marine carbonate system resulting in a decrease in pH. However an increase in temperature will typically also enhance water column stratification and primary productivity (Eppley, 1972). Water column stratification facilitates export of particulate organic matter out of the surface layer and hence results in a net increase in surface water pH. Riverine inputs can have differing effects on pH. Rivers can result in direct changes in coastal carbonate chemistry through the discharge in the North Sea of high  $C_T$  and low  $A_T$  freshwaters (Thomas et al., 2005; Borges and Gypens, 2010; Gypens et al., 2011), thereby lowering pH. Additionally, nutrient supply by rivers can stimulate primary productivity in coastal waters, resulting in an increase in pH, whereas respiration of riverine organic matter will decrease pH (Frankignoulle et al., 1998). Organic matter itself may also directly affect pH depending

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on its composition: for example amines are basic while carboxyl- and keto-groups are acidic. Localised upwelling at shelf breaks of relatively acidic  $C_T$ -rich deep waters will significantly decrease pH while simultaneously enhancing primary productivity through nutrient supply (Feely et al., 2008). Finally, surface water uptake of anthropogenic atmospheric  $CO_2$ , and deposition of  $HNO_3$  and  $H_2SO_4$  aerosols will decrease seawater pH (Doney et al., 2007).

The strong spatial and temporal variability in the surface water carbonate chemistry has led to contradicting estimates of air-sea  $CO_2$  fluxes in coastal seas. Most of the processes affecting the carbonate system are usually occurring simultaneously, making it challenging to understand and determine the main drivers of the carbonate chemistry in coastal seas. This highlights the need for datasets with high spatial and temporal resolution to unravel the various processes and their consequences for the carbonate system.

The carbonate chemistry in the English Channel and the North Sea has been well studied and particularly air-sea  $CO_2$  fluxes using  $pCO_2$  data are widely reported (Thomas and Borges, 2012; Kitidis et al., 2012). The North Sea has been reported to act as a sink for atmospheric  $CO_2$  with export of  $C_T$  to the deep North Atlantic (Thomas et al., 2004). Surface water pH increases in winter and spring/early summer due to temperature decrease (winter) and biological activity (spring) and then decreases in summer and autumn due to temperature increase and remineralisation of organic matter (Gypens et al., 2011).

We present here a new dataset of surface water pH determined in the Northwest European shelf seas in summer 2011. It is the first time that pH has been measured at a high spatial resolution (10 measurements  $h^{-1}$ ) in this shelf sea region. This paper presents a study of the carbonate chemistry dynamics of the shelf sea surface waters using pH and ancillary data. We used a statistical approach to investigate which processes control pH and their relative importance in explaining the observed pH variance along the ship's transect. We explain pH dynamics using solely underway pH, temperature, salinity, and data. The data interpretation is supported by lower resolution surface

water nutrient data, in addition to variables determined only at CTD sampling stations (e.g. DOC).

## 2 Method

### 2.1 Cruise

5 The data used in this study have been collected between 6 June 2011 and 7 July 2011 during the RRS *Discovery* research cruise D366 in northwest European shelf seas (see cruise track in Fig. 1). The four parameters of the carbonate system ( $C_T$ ,  $A_T$ ,  $pCO_2$  and pH) were determined at a high spatial resolution, thereby over-constraining the carbonate system and facilitating internal data quality verification (Ribas-Ribas et al.,  
10 2014).

#### 2.1.1 Hydrography of the northwest European shelf seas

The northwest European shelf seas are typically shallower than 250 m with the exception of the deep Norwegian Trench (Fig. 1) (Pingree et al., 1978), which extends from the Skagerrak northwards to the open Atlantic Ocean. In the Skagerrak Strait depths reach 700 m. The southern North Sea is shallower than 50 m and increases in depth  
15 towards the north to ca. 150 m. The Celtic Sea and the English Channel increase in depth towards the shelf edge with the Atlantic Ocean. The Irish Sea is semi-enclosed, with a shallow eastern part (generally less than 80 m deep), and a deeper north-south trending trough as deep as 250 m. The Irish Sea communicates with the Atlantic Ocean  
20 via the Malin Sea to the northwest and the Celtic Sea to the southwest.

The current regime in the North Sea is dominated by an anti-clockwise current along the edges, with Atlantic waters coming mainly from the northwest but also to a much lesser extent from the English Channel and leaving along the Norwegian coast via the Norwegian Trench (OSPAR Commission, 2000). Tidal currents can be stronger than the residual current in many areas and cause important mixing in the water column. The  
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water temperature increased by  $0.2^{\circ}\text{C}$  from the ship's intake to the pH instrument. The pH data were corrected to in situ temperature using the  $C_T$  data (Hunter, 1998). For this purpose the pH and  $C_T$  data were used to calculate  $A_T$ . Calculations were made using CO2SYS (Pierrot et al., 2006), on the total pH scale with  $K_1$  and  $K_2$  from Mehrbach et al. (1973), refitted by Dickson and Millero (1987) and  $\text{KHSO}_4$  from Dickson (1990).  $C_T$  and  $A_T$  are not temperature dependent and can therefore be used to calculate pH at the in situ oceanic temperature using thermodynamic relationships. A linear relationship between pH and temperature was derived from this correction and used to calculate pH at in situ temperature where no  $C_T$  value was available. The magnitude of the correction was about  $0.002 \pm 0.001$  pH units. An additional correction of  $+0.004$  pH units has been applied to the pH data to correct for an analysis perturbation due to the inflexion of the light triggered by the density lenses created in the absorption cell (Schlieren effect) (see Rérolle et al., 2013 for more details). The final pH dataset has been submitted to the British Oceanographic Data Centre ([http://www.bodc.ac.uk/projects/uk/ukoa/data\\_inventories/cruise/d366/](http://www.bodc.ac.uk/projects/uk/ukoa/data_inventories/cruise/d366/)).

$p\text{CO}_2$  measurements were made using a PML-Dartcomm *Live*  $p\text{CO}_2$  system with a shower-head equilibrator, pre-equilibrator and an infrared gas analyser (LICOR, LI-840) (Hardman-Mountford et al., 2008), and referenced against NOAA-certified standard  $\text{CO}_2$  gases (0, 251.3 and 446.9 ppmv  $\text{CO}_2$ ). Further details are presented in Ribas et al. (2014).

Continuous seawater temperature ( $T$ ), conductivity and chlorophyll  $a$  fluorescence (Chl) data were obtained from the Sea-Bird Electronics SBE45 ThermoSalinoGraph (TSG) installed on the ship's underway supply.

### 2.2.2 Discrete underway water samples

Discrete seawater samples for  $C_T$ ,  $A_T$  and nutrients were collected every two hours from the underway supply. Discrete water samples for salinity ( $S$ ) were also collected every four hours in order to calibrate the underway conductivity measurements. Discrete salinity samples were analysed using an Autosol salinometer (Guildline).

The  $C_T$  and  $A_T$  samples were collected using standard protocols (Dickson et al., 2007; Bakker and Lee, 2012) in 250 mL glass bottles, poisoned with a saturated mercuric chloride solution, and subsequently analysed for  $C_T$  and  $A_T$  using a VINDTA 3C instrument (Mintrop, 2004). Measurements were calibrated using certified reference material provided by the Scripps Institution of Oceanography.

Analyses of nitrate and nitrite (total oxidised nitrogen, TON), phosphate ( $PO_4^{3-}$ ) and silicate ( $SiO_4^{4-}$ ) were undertaken using a segmented flow auto-analyser (Skalar San+) following methods described by Kirkwood (1989). Samples were stored in 25 mL polycarbonate vials and kept refrigerated at approximately 4 °C until nutrient analysis (within 12 h after sampling).

### 2.2.3 CTD parameters

Dissolved oxygen ( $O_2$ ) was determined by automated Winkler titration with photometric endpoint detection (Carritt and Carpenter, 1966). Samples for DOC were analysed using a high temperature combustion technique (Badr et al., 2003).

## 2.3 Study region

The study area has been split into eleven regions which were defined by geographical and water masses characteristics (Fig. 2). A multivariate analysis of variance (MANOVA) was performed with pH,  $T$  and  $S$  to determine whether the data from the regions were statistically different ( $t$  test,  $p < 0.05$ ). The regions 4 and 11 were relatively small and corresponded to areas where deep water had been locally brought to the surface by storm or shelf mixing. No statistical analysis has been performed with the data from these regions.

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## 2.4 Statistical approach

In order to perform statistical analyses on the data, all the parameters have been transformed using a common logarithm function ( $\log_{10}$ ) to obtain a normal distribution and standardised (centred to 0 and scaled to 1). Distributions of TON was strongly positively skewed, even after transformation. The data analysis has been performed using the software Matlab<sup>®</sup>.

A stepwise multi-linear regression to relate pH data to environmental parameters has first been performed with all the data from the surface samples of CTD stations (< 10 m deep) using the following parameters: DOC, O<sub>2</sub>, *S*, *T*, Chl, SiO<sub>4</sub><sup>4-</sup> and TON. The same stepwise multi-linear regression has been performed again but without O<sub>2</sub>.

In addition, multi-linear regressions have been performed to relate the pH data in each individual region with the underway parameters *S*, *T* and Chl. And finally, stepwise multi-linear regressions have been performed with the underway variables *S*, *T*, Chl, SiO<sub>4</sub><sup>4-</sup> and TON which were obtained at a lower spatial resolution.

## 3 Results and discussion

### 3.1 Non-carbonate data distributions

Mean values and standard deviations per regions of surface *S*, *T*, TON, PO<sub>4</sub><sup>3-</sup>, SiO<sub>4</sub><sup>4-</sup> and Chl are presented in Table 1. Salinity varied between 33.2 and 35.8 during the cruise transect apart from the Skagerrak area where salinity was as low as 26.4. Lowest salinities were observed in the Irish Sea (region 1), the southern North Sea (region 7) and the Skagerrak area (region 9). Temperature varied between 10.3 and 17.1 °C with lowest temperatures observed in the Irish and the Malin Seas at the start of the cruise around Ireland (regions 1 and 2 respectively) and south to the Shetlands (region 11). Highest temperatures were observed in the southernmost part of the cruise transect in the Bay of Biscay (region 5), the southern North Sea (region 7) and the

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Skagerrak area (region 9). TON and  $\text{SiO}_4^{4-}$  varied between 0.1 and 5.34  $\mu\text{M}$  with lowest concentrations observed in the Celtic Sea south to Ireland (region 3) and in the northern part of the transect (regions 8, 9 and 10). Highest nutrients concentrations were observed in regions 1, 2 and 11. Chl levels varied between 0.12 and 1.54  $\mu\text{g L}^{-1}$ . Highest levels of Chl were observed in the north west part of the transect regions 2 and 10, whereas the lowest levels were observed in the central North Sea (region 8) and the Skagerrak (region 9).

### 3.2 Distribution of the carbonate chemistry variables

A comprehensive quality check and comparison between the different inorganic carbonate variable datasets can be found in Ribas Ribas et al. (2014). A good agreement was found between all datasets. Comparison of measured pH with pH calculated from a pair of the carbonate variables  $C_T$ ,  $A_T$  and  $p\text{CO}_2$  (e.g.  $\text{pH}_{C_T, p\text{CO}_2}$ ) showed an absolute mean discrepancy between 0.004 and 0.009 pH units.

Surface seawater pH along the transect ranged between 7.995 and 8.210 (Fig. 3), with highest values in the northern North Sea featuring enhanced Chl concentrations (up to 1.6  $\mu\text{g L}^{-1}$ ) and lower temperatures ( $T_{\text{mean, region10}} = 12.5 \pm 0.3^\circ\text{C}$ ). Lowest pH values were observed in the central North Sea in a well-mixed water column with enhanced DOC concentrations (up to 90  $\mu\text{M}$  compared with 65  $\mu\text{M}$  in the northern North Sea) and presumably associated enhanced organic matter respiration with a consequent decrease in pH. Surface  $p\text{CO}_2$  data varied between 220 and 436  $\mu\text{atm}$  (Fig. 4). pH and  $p\text{CO}_2$  variations during the cruise are shown in Fig. 4, and pH displayed a typical anti-correlation with  $p\text{CO}_2$ .

The pH- $p\text{CO}_2$  variations were controlled by temperature variations, biological activity, calcification, gas exchange and dilution processes (e.g. rain fall) as illustrated in Cullison-Gray et al. (2011). The relationship between  $p\text{CO}_2$  and hydrogen ions concentration can be expressed as

$$C_T \approx K_0 K_1 p\text{CO}_2 / [\text{H}^+]. \quad (1)$$

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with  $K_0$  and  $K_1$  the  $\text{CO}_2$  solubility and first dissociation constant for carbonic acid, respectively (Cullison-Gray et al., 2011). This relationship indicates that processes changing the seawater carbonate chemistry will have opposite impacts on pH and  $p\text{CO}_2$ . An increase in  $C_T$  or in the carbonate constants  $K_1$  and  $K_2$ , the first and second dissociation constants of carbonic acid respectively, will result in an increase in  $p\text{CO}_2$  and a decrease in pH.

In the next sections, we consider the effects of various environmental factors on the carbonate equilibrium constants,  $C_T$  and  $A_T$  to determine how each process influences pH.

### pH control by environmental forcings

#### 3.2.1 Surface data from CTD station along the entire transect

The pH data was strongly correlated with dissolved oxygen for the surface samples from the CTD stations along the full transect (correlation coefficient  $Rho = 0.5987$ ,  $p < 0.001$ ,  $n = 62$ ). The stepwise multi-linear regression with DOC,  $\text{O}_2$ ,  $S$ ,  $T$ , Chl,  $\text{SiO}_4^{4-}$  and TON indicated that the correlation of  $\text{O}_2$ ,  $T$  and  $S$  with pH was statistically significant and explained 72 % of pH variance.  $\text{O}_2$ ,  $T$  and  $S$  were found to explain 37 %, 24 % and 11 %, respectively, of the variance in pH. The strong correlation with  $\text{O}_2$  indicated that pH and  $\text{O}_2$  were affected by similar processes and this supports the hypothesis that biological activity and remineralisation played a key role in the pH variations along the transect. The same stepwise multi-linear regression but without  $\text{O}_2$  resulted in  $\text{SiO}_4^{4-}$  (18 %), DOC (15 %) and Chl (11 %) explaining 44 % of the pH distribution along the cruise transect.

#### 3.2.2 Underway data for the 11 regions

The statistical analysis, undertaken using the underway data, indicates the extent to which the pH variance is explained by the various forcing (Tables 2 and 3). The pH

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variability along the transect was mainly determined by biological activity. In most of the regions, the two regressions (with and without nutrients data) resulted with the dominant variables being linked to the same processes. Regions 6 to 8 showed a different pattern, where mixing with outflows from rivers and the Baltic Sea had a strong impact on the carbonate chemistry. Overall between 21 and 79 % of the pH variance can be explained using only salinity, temperature and Chl. This was significantly increased when the nutrient variables were included, resulting in 54 to 95 % of the pH variance being explained. The lowest percentages were obtained in regions where riverine inputs impacted the pH distribution: the Celtic Sea, the Channel and the Southern North Sea (regions 3, 6 and 7 respectively). The low  $R^2$  obtained in the northern part of the transect (region 10) was due to the fact that the impact of primary production was not directly evidenced by a correlation of Chl concentration with pH (see below).

The impact of primary production on pH is highlighted by a positive correlation between pH and Chl, and a negative correlation between pH and nutrients. The impact of temperature on pH is evidenced by a negative correlation between these variables. The impact of freshwater inputs by rivers is evidenced by enhanced correlations between pH and salinity, but the sign of the correlation will depend on the total alkalinity (and  $C_T$ ) levels in the river discharges. Here, in the areas impacted by river discharges, the correlation between pH and salinity is positive because the rivers are enriched in  $C_T$  from the important agricultural and industrial activity inland. A positive correlation between pH and nutrients, and a negative correlation with dissolved organic matter can be further indications of riverine inputs supplying high nutrient and DOC fluxes to coastal waters.

The large variability in water masses and environmental conditions sampled in the dynamic shelf system constituted a clear challenge for the data interpretation. A further challenge was that the samples had been collected at various times of the day. The sampling time can have a strong impact on surface water pH, particularly in bloom areas (Thomas and Borges, 2012). Nevertheless, the results of the statistical approach helped to untangle some of the key processes controlling the pH distribution in the

different regions. Biological processes were the dominant control over pH in regions 1, 2, 3, 5, 7 and 10. Temperature was dominant in the central North Sea (region 8) and the Skagerrak (region 9), with still an important contribution by biology on pH in region 8. River inputs seem to have a strong impact on pH in the Channel (region 6) and the southern North Sea (region 7) as well as in the Celtic Sea (region 3).

These observations are in agreement with previous studies investigating the controls on surface water  $p\text{CO}_2$  in the North Sea (Thomas et al., 2005) and the English Channel (Gypens et al., 2011). Indeed, Thomas and co-workers observed that biological activity was the main driver of the seasonal  $p\text{CO}_2$  variability in the northern and central part of the North Sea whereas temperature variations were driving the  $p\text{CO}_2$  variability in the southern part. The fully mixed waters of the southern region were a source of  $\text{CO}_2$  to the atmosphere, but not in spring when primary production was more important in determining  $p\text{CO}_2$  levels than temperature increases. Similarly, Gypens and colleagues observed in their 3-D coupled biogeochemical-hydrodynamic model a seasonal and inter-annual antagonism between biological and temperature effects on  $p\text{CO}_2$  (and pH) in the English Channel and the Southern Bight of the North Sea. They also show that the competition between temperature and biological controls can be strongly affected by riverine nutrient inputs which stimulate biological activity.

### 3.3 pH dynamics

#### 3.3.1 Primary production

The photosynthetic uptake of  $\text{CO}_2$  to form organic matter (biological production) can be expressed as (Sarmiento and Gruber, 2006):



The nitrate uptake to form organic nitrogen results in an increase in  $A_T$ . The formation of organic matter therefore not only decreases  $C_T$  but also increases  $A_T$  proportionally

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An additional riverine impact, in our study area, is the lowering of the buffer capacity due to low  $A_T$ . This could partly explain that the two regions 1 and 7 were sources of  $\text{CO}_2$  to the atmosphere.

### 3.3.4 Mixing

5 Tidal and wind-driven currents are important in the northwest European shelf seas (Huthnance, 1997). These currents can lead to intense mixing of the water column, and includes tidal upwelling which brings bottom water to the surface (Simpson and Sharples, 2012). These deeper waters are typically more acidic, enriched in  $C_T$  and nutrients relative to the surface waters due to remineralisation of organic matter at  
10 depth. Acidified waters brought to the surface by shelf mixing processes have been observed in two regions during the cruise. The first region was to the south of Cornwall, southwest of the Lizard Peninsula (UK) (region 4) (Fig. 7a), where the water column was likely mixed either by strong tidal mixing (Simpson and Sharples, 2012) or storm activity. The mixing of the water column is evidenced on Fig. 8b, where the temperature  
15 gradients showed a typical stratified water column temperature profile on 15 June 2011 and a more homogenised temperature profile on 23 June 2011. This mixing resulted in surface waters with higher concentrations of  $C_T$  ( $+36 \mu\text{mol kg}^{-1}$ ) and TON ( $+2 \mu\text{M}$ ), and lower pH, compared to observation made the previous week (Fig. 7c and d). The second region was south of the Shetland Islands (region 11) where deep water  
20 was brought to surface partly by the advection of Atlantic water through the Orkney–Shetland passage but also by intense tidal mixing around the Orkney and Shetland Isles area (Turrell, 1992) (Fig. 8). Indeed, tidal currents are intensified in the area where the flow is constrained by topography (Pingree et al., 1978). This upwelled water was evidenced by colder temperature ( $-2^\circ\text{C}$ ) and enhanced  $C_T$  ( $+40 \mu\text{mol kg}^{-1}$ ) and TON  
25 ( $+4 \mu\text{M}$ ) concentrations compared to surrounding waters. Higher nutrient concentrations resulted in enhanced primary production but this was not sufficiently pronounced to balance the acidity of the upwelled water.

## 4 Conclusions

The high spatial and temporal resolution of the pH data along with temperature, salinity, chlorophyll *a* fluorescence and nutrients, enabled us to unravel the main processes controlling the carbonate chemistry dynamics of the northwest European shelf sea surface waters. The statistical approach allowed us to determine the main correlations between pH and other variables, and infer the main controlling processes. In agreement with previous studies, the biological activity formed the main control of the pH distribution along the cruise transect for this summer cruise. However, in some regions temperature and riverine inputs balanced or even dominated the impact of primary production. This study highlights the strong variability of the in situ conditions in coastal shelf waters where several processes simultaneously impact the carbonate chemistry. The spatial variability is particularly important in shelf seas with rivers and water column mixing providing a relatively localised impact on the seawater carbonate chemistry. Only datasets with a high spatial and temporal coverage will allow us to obtain more accurate estimates of the air-sea CO<sub>2</sub> fluxes in coastal regions. In order to quantify the main controls on the carbonate chemistry over an annual time scale, the same transect should be sampled using the high resolution pH approach during different seasons.

*Acknowledgements.* We would like to thank Mark Stinchcombe for providing the nutrients and dissolved oxygen data used in this work. This work was supported by SENSEnet, a Marie Curie Initial Training Network (ITN) funded by the European Commission Seventh Framework Programme, Contract Number PITN-GA-2009-237868. This work is a contribution to the UK Ocean Acidification Research Programme (UKOA) which was jointly funded by the Department for Environment, Food and Rural Affairs (Defra), the Natural Environment Research Council (NERC) and the Department of Energy and Climate Change (DECC) under grant agreement no. NE/H017348/1.

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**Table 1.** Mean values and standard deviations (Std) of  $S$ ,  $T$ , TON,  $\text{PO}_4^{3-}$ ,  $\text{SiO}_4^{4-}$  and Chl per regions.

Region	Mean $S$	Std $S$	Mean $T$ (°C)	Std $T$ (°C)	Mean TON ( $\mu\text{M}$ )	Std TON ( $\mu\text{M}$ )	Mean $\text{PO}_4^{3-}$ ( $\mu\text{M}$ )	Std $\text{PO}_4^{3-}$ ( $\mu\text{M}$ )	Mean $\text{SiO}_4^{4-}$ ( $\mu\text{M}$ )	Std $\text{SiO}_4^{4-}$ ( $\mu\text{M}$ )	Mean Chl ( $\mu\text{g L}^{-1}$ )	Std Chl ( $\mu\text{g L}^{-1}$ )
1	34.11	0.23	11.06	0.60	1.32	1.15	0.24	0.10	1.51	0.93	0.30	0.11
2	35.14	0.23	11.34	0.11	3.15	1.71	0.21	0.10	2.00	0.64	0.59	0.24
3	35.24	0.14	13.63	0.40	0.10	0.00	0.06	0.06	1.12	0.92	0.20	0.07
4	35.38	0.06	13.59	0.94	0.63	0.92	0.06	0.04	0.58	0.54	0.39	0.20
5	35.65	0.10	14.55	0.59	0.80	0.64	0.08	0.04	1.06	0.24	0.43	0.27
6	35.09	0.11	14.09	0.29	0.90	0.74	0.06	0.03	1.97	0.41	0.38	0.09
7	34.28	0.44	14.99	0.65	1.07	1.58	0.07	0.05	1.56	1.34	0.31	0.16
8	34.86	0.14	13.68	0.26	0.17	0.03	0.04	0.08	0.42	0.33	0.20	0.05
9	30.88	2.09	14.69	1.24	0.18	0.06	0.03	0.03	0.15	0.10	0.30	0.07
10	35.25	0.16	12.50	0.31	0.55	0.71	0.06	0.05	0.44	0.29	0.63	0.41
11	35.31	0.01	10.95	0.10	3.89	0.54	0.33	0.04	1.61	0.44	0.43	0.04

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**Table 2.** Results of the multi-linear regression analysis using  $S$ ,  $T$  and Chl parameters with the underway data divided into 11 regions. The  $R^2$  values express how much of the pH variance is explained by the regression. The component of the pH variance that can be attributed to each parameter is expressed in percentage. The second part of the table details the equation coefficients of each parameter used to describe pH.

	Regions	R1	R2	R3	R5	R6	R7	R8	R9	R10
%	$R^2$	0.79	0.40	0.37	0.58	0.41	0.21	0.65	0.63	0.25
	$S$	5.91	36.65	28.85	31.81	54.67	30.06	6.53	19.99	8.55
	$T$	45.62	12.12	37.26	35.50	29.06	16.41	50.99	73.01	6.11
	Chl	48.47	51.23	33.89	32.69	16.27	53.53	42.47	7.00	85.34
Equation coefficients	Intercept	8.080	8.107	8.112	8.111	8.078	8.080	8.094	8.111	8.161
	$S$	0.002	-0.007	0.010	0.007	0.011	0.005	-0.001	0.005	0.002
	$T$	0.014	0.002	0.013	0.008	-0.006	0.003	-0.011	-0.017	0.001
	Chl	0.015	0.009	0.012	0.007	-0.003	0.010	0.009	0.002	0.018

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**Table 3.** Results of the stepwise multi-linear regression analysis using *S*, *T* and Chl,  $\text{SiO}_4^{4-}$  and TON parameters with the underway data divided into 11 regions. The  $R^2$  values express how much of the pH variance is explained by the regression. The component of the pH variance that can be attributed to each parameter is expressed in percentage. The second part of the table details the equation coefficients of each parameter used to describe pH.

	Regions	R1	R2	R3	R5	R6	R7	R8	R9	R10
%	$R^2$	0.94	0.94	0.54	0.61	0.81	0.61	0.78	0.74	0.79
	<i>S</i>			40.26		72.82	33.33	13.83	17.15	14.22
	<i>T</i>		30.24					42.82	68.49	
	Chl	63.78	26.37		59.60		22.22			36.13
	$\text{SiO}_4^{4-}$	36.22		59.74		27.18	19.29	43.34	14.36	
	TON		43.39		40.40		25.16			49.66
Equation coefficients	Intercept	8.083	8.083	8.111	8.111	8.072	8.086	8.096	8.109	8.163
	<i>S</i>			0.009		0.016	0.033	0.004	0.005	-0.009
	<i>T</i>		-0.017					-0.012	-0.019	
	Chl	0.015	0.015		0.007		0.022			0.022
	$\text{SiO}_4^{4-}$	-0.009				-0.006	-0.019	0.012	0.004	
	TON		-0.025	-0.013	-0.005		-0.025			-0.030

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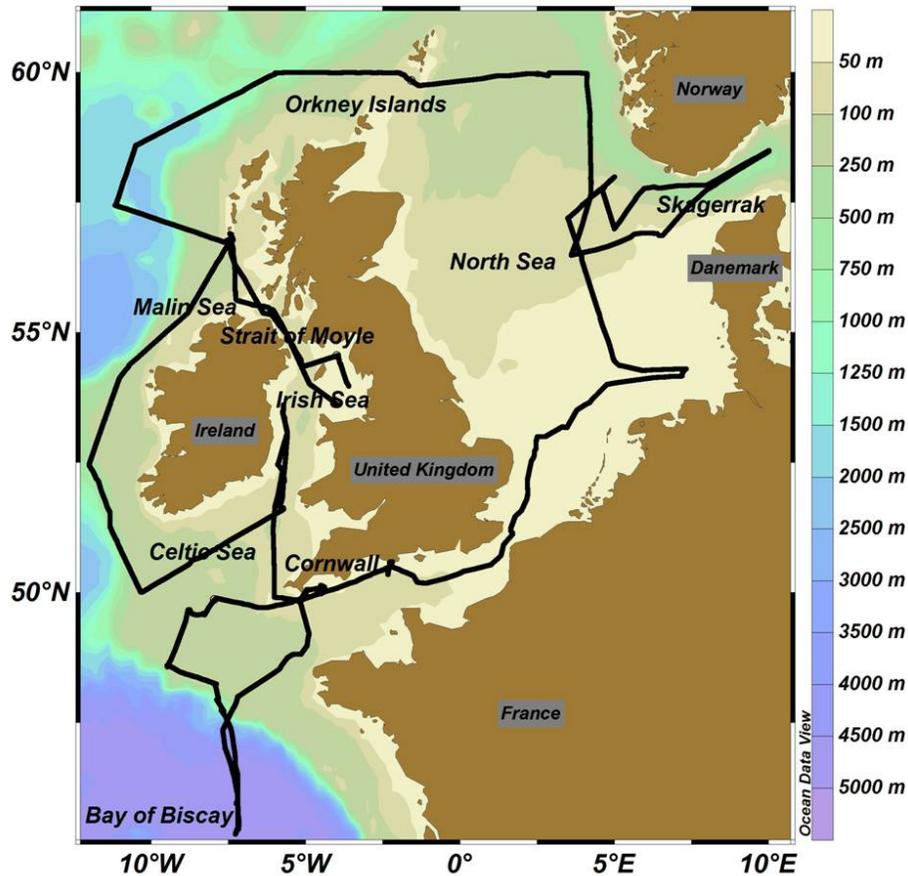
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**Fig. 1.** Map of the D366 cruise track (black line) with bathymetry contours (contour scale).

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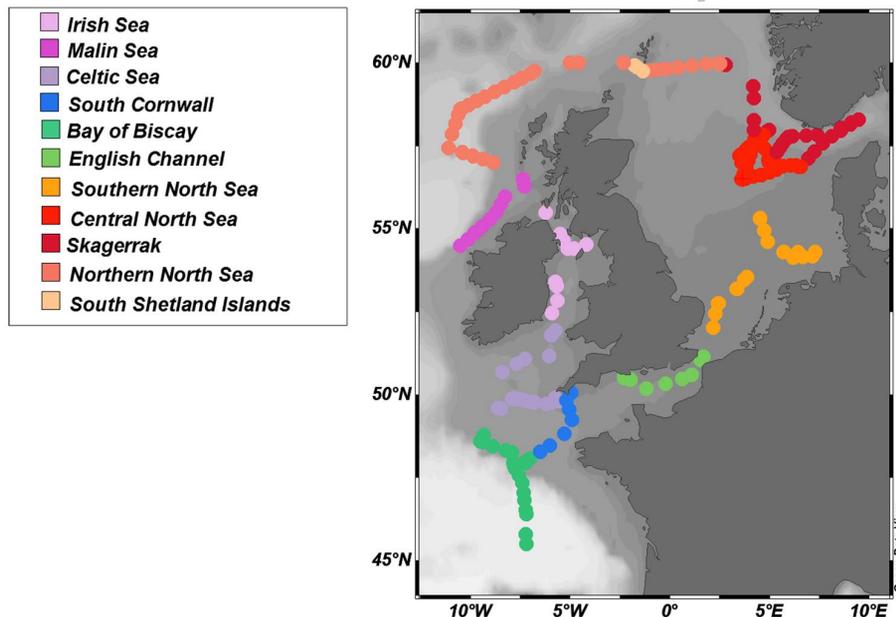
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**Fig. 2.** The 11 regions indicated using colour coding and defined using geographical and water mass ( $T - S$ ) characteristics.

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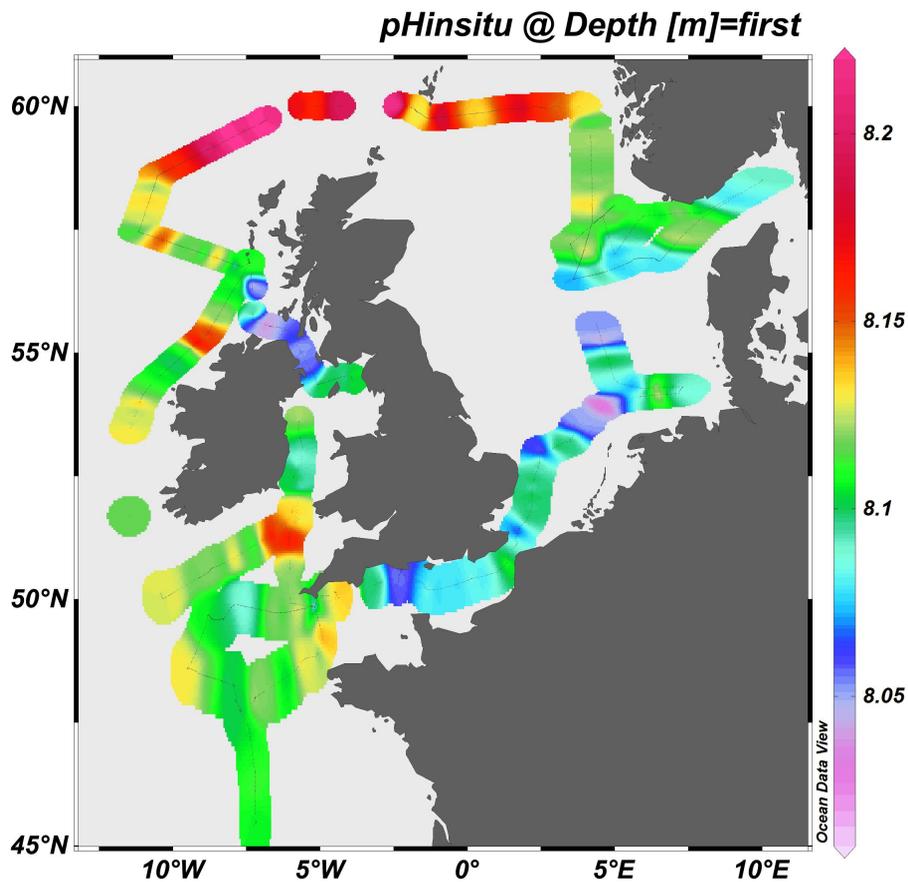
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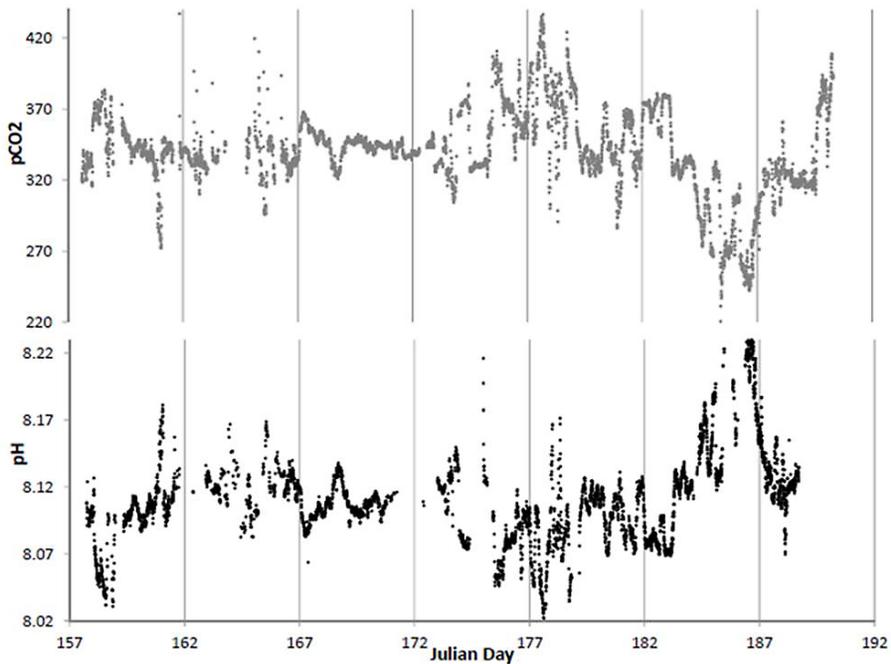
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**Fig. 3.** Map of surface water pH<sub>T</sub> in European shelf seas for the cruise D366 with colour bar indicating pH<sub>T</sub> values.



**Fig. 4.** Time series of sea surface  $p\text{CO}_2$  and pH for the cruise D366 with the variables plotted against Julian day.

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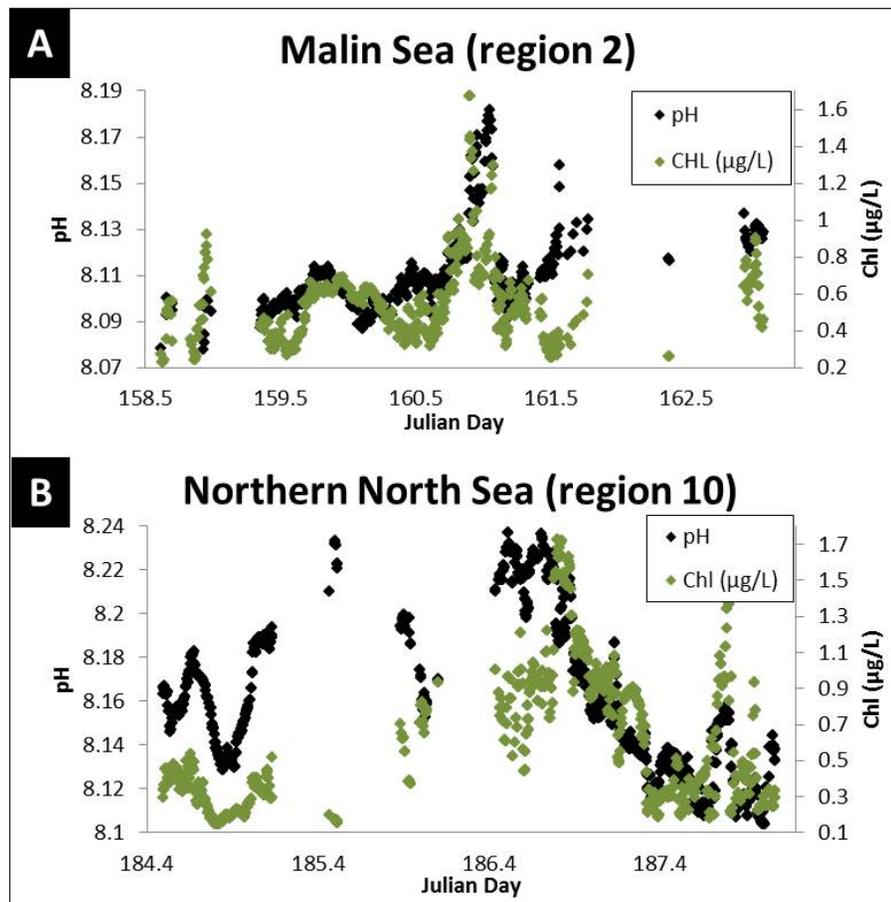
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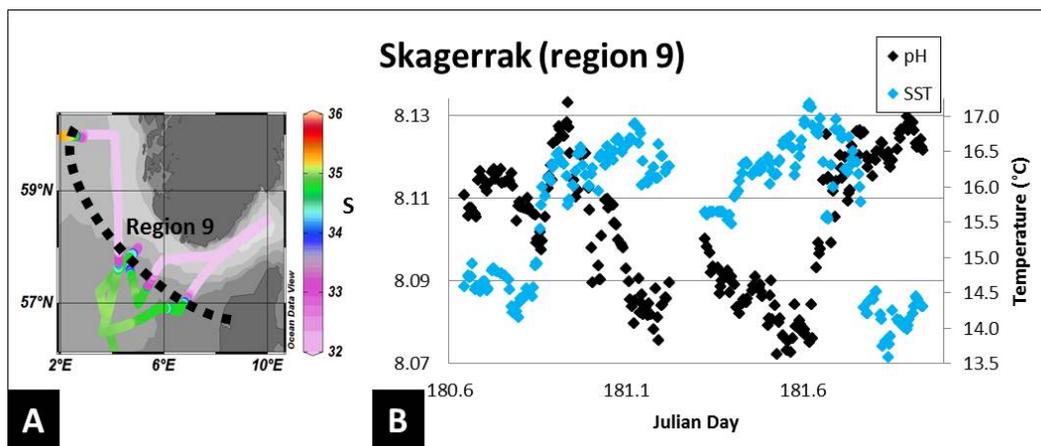




**Fig. 5.** Observed sea surface pH and Chl concentrations plotted against Julian day for **(A)** the Malin Sea (region 2) and **(B)** the northern North Sea (region 10).

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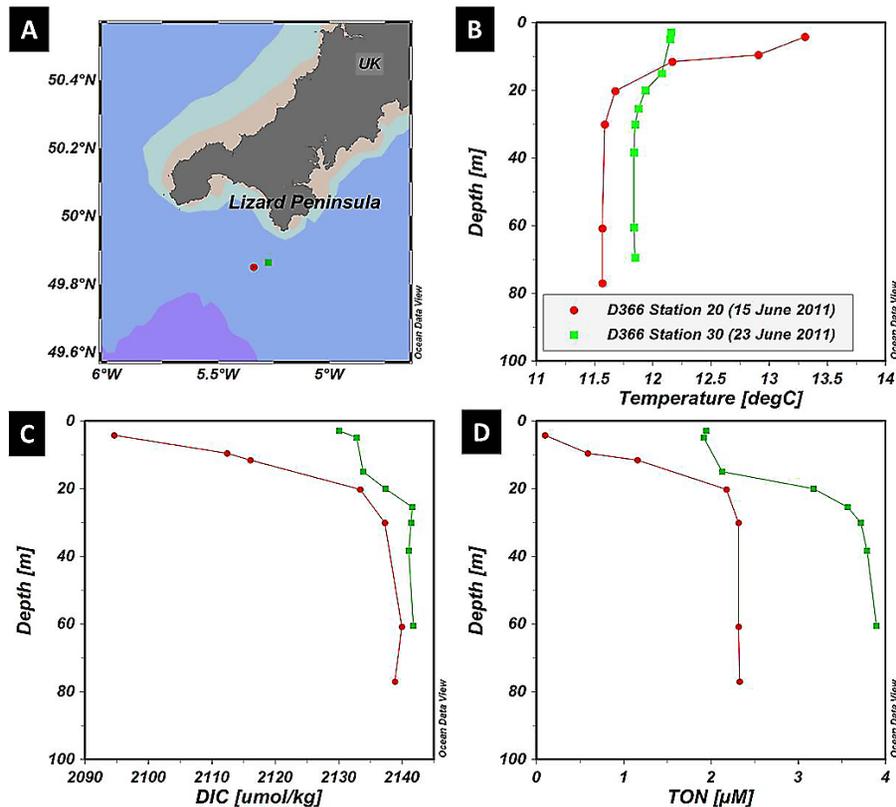


**Fig. 6.** Impact of temperature on sea surface pH distribution. **(A)** map of sea surface salinity observed during the cruise D366 in the Skagerrak region (region 9). The dotted line shows the limit of region 9. **(B)** sea surface pH and temperature plotted vs. Julian day for the Skagerrak region.

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**Fig. 7.** Impact of storm mixing on sea surface pH (region 4). **(A)** location of station 20 sampled on the 15 June 2011 (red) and station 30 sampled on the 30 June 2011 (green) south of Cornwall (UK). **(B–D)** depth profiles of temperature, DIC and TON at the two stations.

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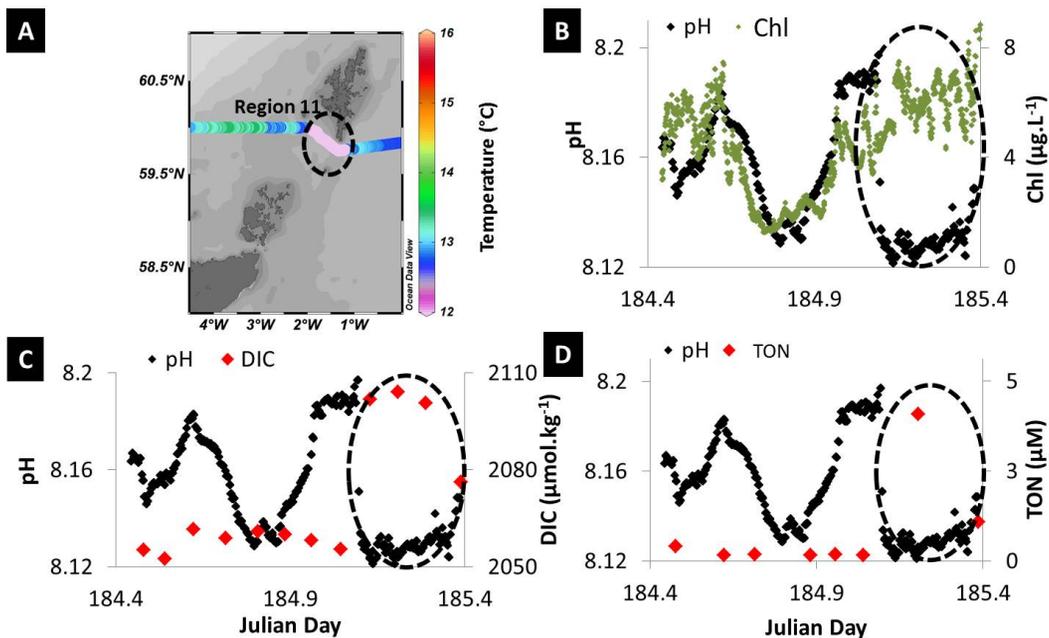
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**Fig. 8.** Impact of tidal shelf mixing on sea surface pH (region 11). **(A)** sea surface temperatures observed in region south of the Orkney Islands. Time series plots of sea surface pH and **(B)** Chl, **(C)** DIC and **(D)** TON concentrations, plotted against Julian day. The encircled part of the plots denotes data observed in region 11.

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