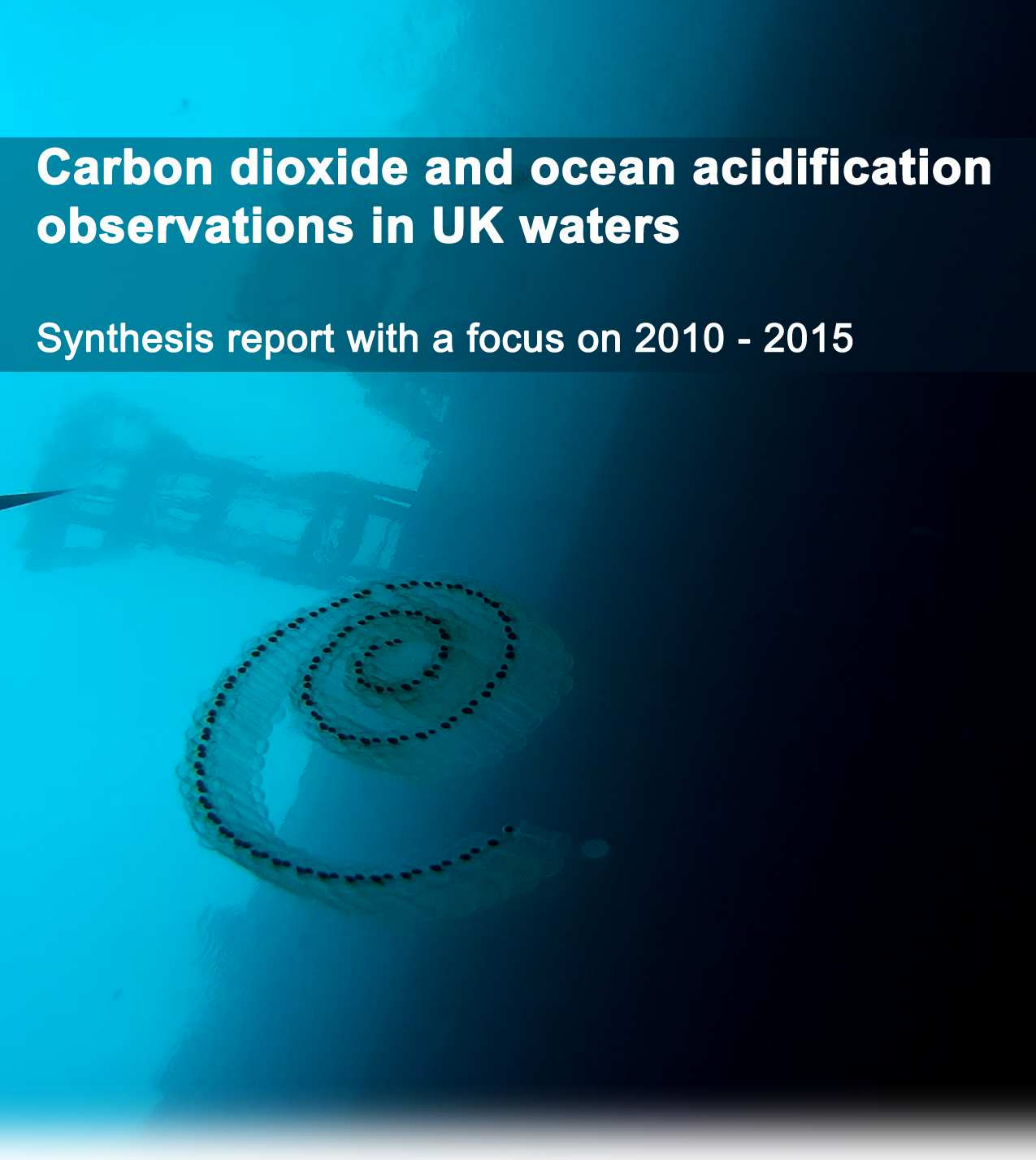
Carbon dioxide and ocean acidification observations in UK waters

Synthesis report with a focus on 2010 - 2015



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UK Ocean Acidification
Research Programme

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Cover photo: *RRS Discovery CTD view of salps.*

June 2016

Carbon dioxide and ocean acidification observations in UK waters

Synthesis report with a focus on 2010 - 2015

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glodap v2
COAS Centre for Ocean and Atmospheric Sciences
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The Scottish Government
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Executive Summary

Key messages:

1.1 The process of ocean acidification is now relatively well-documented at the global scale as a long-term trend in the open ocean. However, short-term and spatial variability can be high.

1.2 New datasets made available since Charting Progress 2 make it possible to greatly improve the characterisation of CO_2 and ocean acidification in UK waters.

3.1 Recent UK cruise data contribute to large gaps in national and global datasets.

3.2 The new UK measurements confirm that pH is highly variable, therefore it is important to measure consistently to determine any long term trends.

3.3 Over the past 30 years, North Sea pH has decreased at 0.0035 ± 0.0014 pH units per year.

3.4 Upper ocean pH values are highest in spring, lowest in autumn. These changes reflect the seasonal cycles in photosynthesis, respiration (decomposition) and water mixing.

3.5 Carbonate saturation states are minimal in the winter, and lower in more northerly, colder waters. This temperature-dependence could have implications for future warming of the seas.

3.6 Over the annual cycle, North-west European seas are net sinks of CO_2. However, during late summer to autumn months, some coastal waters may be significant sources.

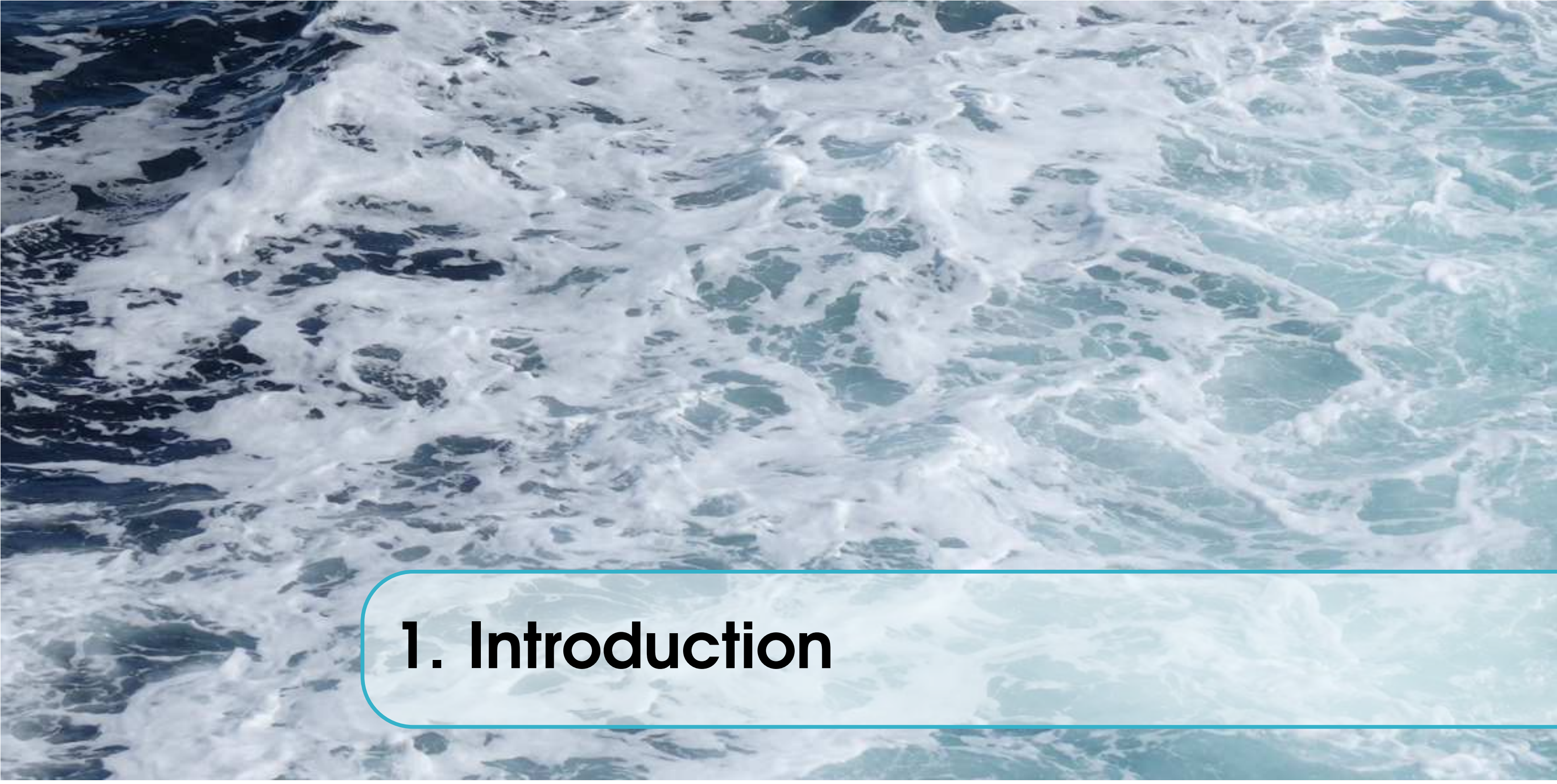
3.7 In seasonally-stratified waters, sea-floor organisms naturally experience lower pH and saturation states; they may therefore be more vulnerable to threshold changes.

3.8 Large pH changes (0.5 - 1.0 units) can occur in the top 1 cm of sediment; however, such effects are not well-documented.

3.9 A coupled forecast model estimates the decrease in pH trend within the North Sea to be -0.0036 ± 0.00034 pH units per year, under a high greenhouse gas emissions scenario (RCP 8.5).

3.10 Seasonal estimates from the forecast model demonstrate areas of the North Sea that are particularly vulnerable to aragonite undersaturation.

ⓘ If you are viewing this document as a soft-copy, the numbers next to the above key messages are hyper-linked and will take you to the relevant section of the document.



1. Introduction

Take-home messages

> **1.1** The process of ocean acidification is now relatively well-documented at the global scale as a long-term trend in the open ocean. However, short-term and spatial variability can be high

> **1.2** New datasets made available since Charting Progress 2 make it possible to greatly improve the characterisation of CO_2 and ocean acidification in UK waters

1.1 Rationale

Ocean acidification is the large-scale, long-term fall in pH (increase in hydrogen ion concentration) occurring as an inevitable consequence of increasing carbon dioxide (CO_2) in the atmosphere. Other chemical changes include a decrease in carbonate ion concentration, and increase in bicarbonate ions (see **Box 1**, and figure 1.1).

A useful list of frequently asked questions and answers about ocean acidification can be found here **www.epoca-project.eu**

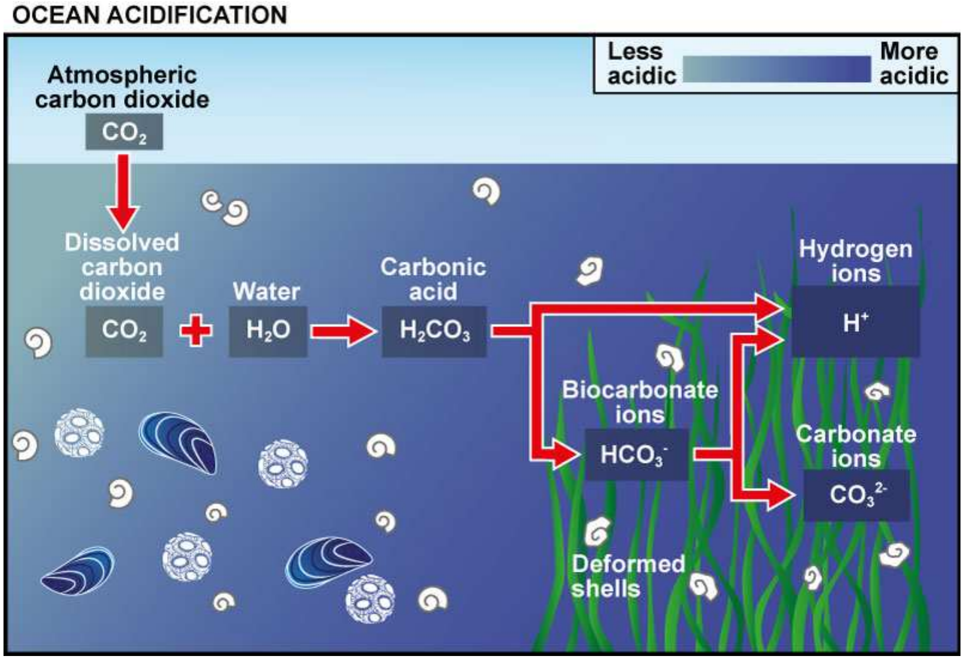


Figure 1.1: Schematic of ocean acidification, adapted from a graphic by the University of Maryland, taken from **www.oceanacidification.org.uk**.

Box 1: What is ocean acidification?

When CO_2 dissolves in seawater, it forms carbonic acid - that then dissociates to release carbonate and hydrogen ions (see figure 1.1). The latter decreases pH (a logarithmic, inverse measure of H^+ concentration), causing acidification. However, most seawater pH is, and will remain, well above 7.0, the chemists' boundary between acidic and alkaline solutions. Associated chemical changes include increased concentrations of bicarbonate ions, but decreased levels of carbonate ions. Reductions in carbonate ions lower the saturation state (Ω) of the two main forms of calcium carbonate, aragonite and calcite, used by many marine organisms for their shells and other external coverings. Low carbonate saturation states can cause the dissolution of these structures, particularly in deeper and/or colder water, where dissolved CO_2 levels are naturally higher (and pH lower). The water depth at which carbonate dissolution occurs is called the saturation horizon.

Since the beginning of the industrial revolution, pH of surface seawater has globally decreased by 0.1 units, which corresponds to an increase in hydrogen ion concentration of around 26% (Stocker *et al.*, 2013). A wide range of other process affect seawater pH at the local and regional level.

The potential for these chemical changes to have serious biological, ecological and socio-economic consequences was first identified 10 - 15 years ago. Many experimental studies have since been carried out on marine species in the laboratory, with focus on the mean pH (and CO_2) values expected to occur in surface seawater in future, under 'business as usual' climate change scenarios – involving a decrease of $\sim$0.4 pH units.

The research effort on ocean acidification increased greatly around 2010, with the implementation of UK, German, US and European programmes. The UK Ocean Acidification research programme (UKOA, 2010 - 16; co-supported by NERC, Defra and DECC) supported *inter alia* experimental studies that investigated interactions of temperature and pH, including for coldwater corals; palaeo-ocean acidification events; regional and global modelling; and observations in European waters and polar seas. The Defra-funded PLACID project at Cefas (Placing Ocean Acidification in a wider Fisheries Context, 2013 - 16) extended the observational studies, and also carried out additional experimental and modelling work.

Measurements made by other groups of decadal-scale changes have confirmed that ocean acidification is a real event globally (IPCC, 2014). However, there is considerable natural variability around the long-term trends for the upper ocean (figure 1.2), with an annual range of up to 0.4 pH units at open ocean sites. Variability at coastal sites may be greater, with additional influences of watershed processes, nutrient inputs, and changes in ecosystem structure (Duarte *et al.*, 2013).

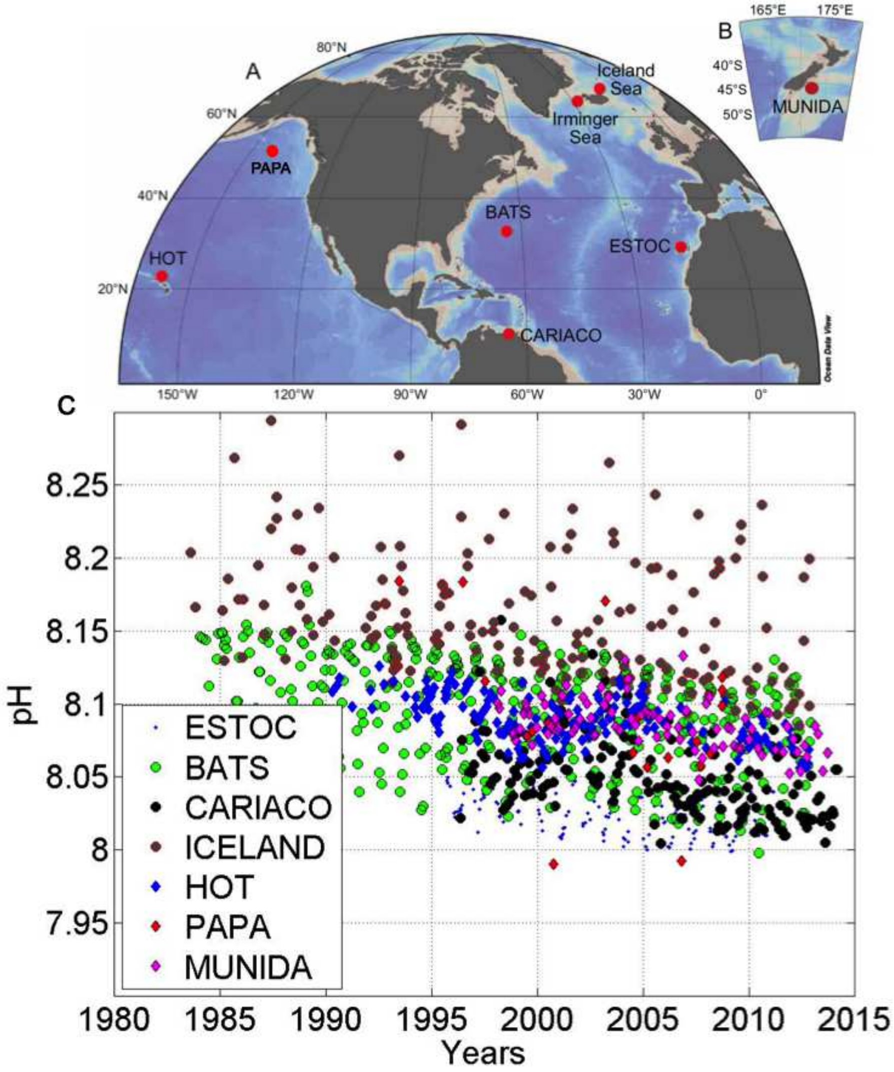


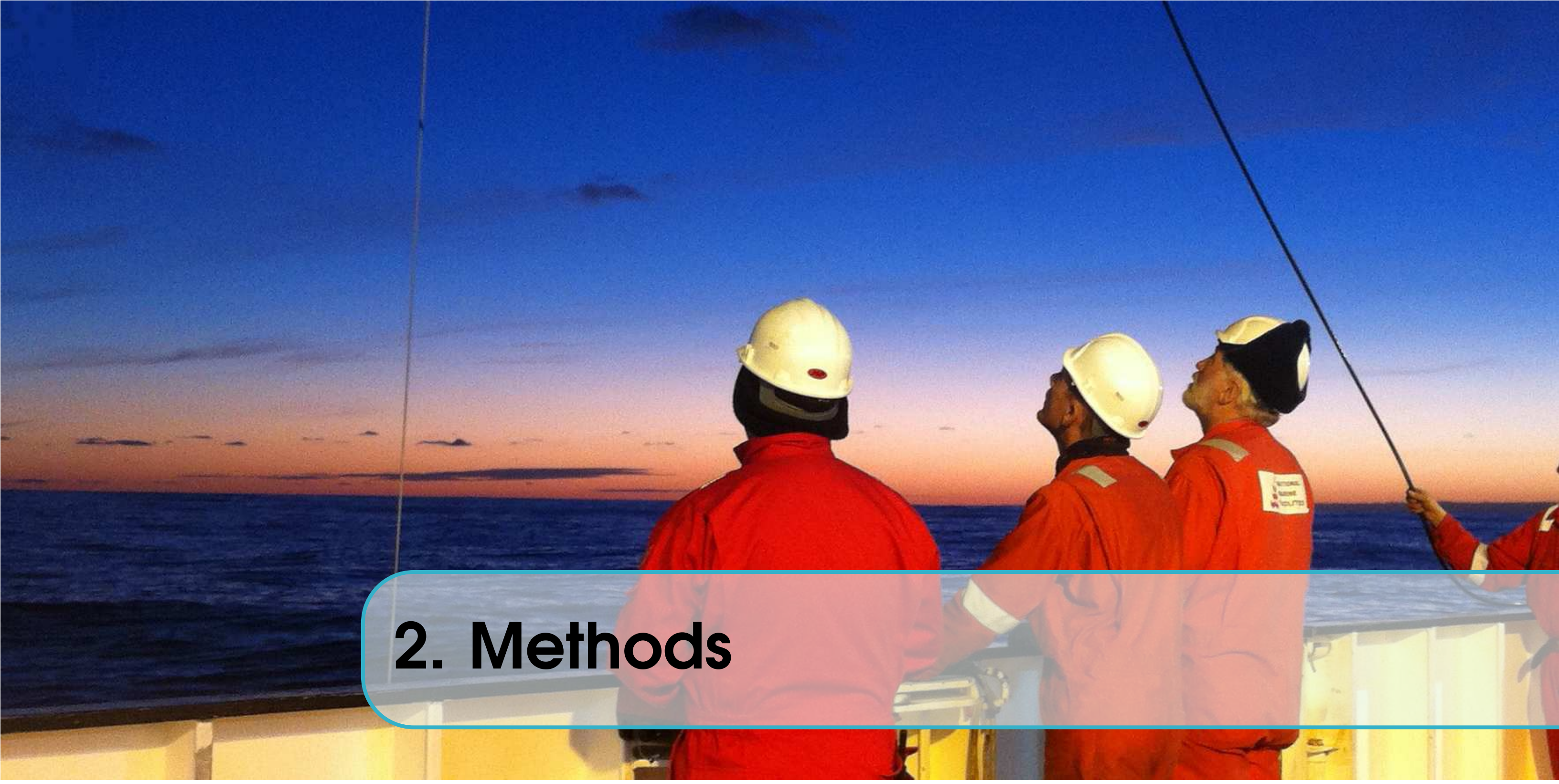
Figure 1.2: pH at seven time series stations, mostly representing open ocean conditions in the Northern Hemisphere: European Station for Time series in the Ocean at the Canary Islands (ESTOC), Bermuda Atlantic Time-series Study (BATS), CArbon Retention In A Colored Ocean (CARIACO), Iceland Sea, Hawaii Ocean Time-series (HOT), Station Papa (PAPA) and Munida (New Zealand). Figure created by Ute Schuster, adapted from Bates *et al.* (2014).

This report brings together relevant data on CO_2 and ocean acidification measurements for UK waters, from UKOA, PLACID and other sources (SOCAT, GLODAP, ICES, SSB, see table 3.1 for details). It updates Charting Progress 2 (Defra, 2010), based on Hydes *et al.* (2011), by focussing on measurements made between 2010 and 2015. Coverage in Charting Progress 2 was limited, with that report stating (p.20): *"Because there are currently no baseline measurement of pH against which changes in UK waters can be judged, it will be some time before we can make accurate judgements about the rate of acidification relative to natural annual and interannual cycles of pH. We also need a better understanding of the physical, chemical and biological processes controlling the ocean's ability to absorb* CO_2*"*.

The current synthesis was initiated in response to policy requirements identified in early 2015 by the Ocean Processes Evidence Group (OPEG), part of the Defra-led UK Marine Monitoring and Assessment Strategy (UKMMAS). Updated information on variability and trends in marine CO_2 and ocean acidification was considered necessary for several upcoming reviews and updates on the status of UK seas. These include the Initial Assessment of the EU Marine Strategy Framework Directive (MSFD) in 2016/2017; UK inputs to future OSPAR (Convention for the Protection of the Marine Environment of the North-East Atlantic) Quality Status Reports for the North Atlantic; and other national reviews of marine climate change; e.g. planned reports of the Marine Climate Change Impacts Partnership (MCCIP) and the Climate Change Risk Assessment (CCRA).

The collection, collation and interpretation of data on ocean acidification and associated marine CO_2 is not a statutory requirement under the EU Marine Strategy Framework Directive (MSFD). Nevertheless, ocean acidification parameters are mentioned in Annex III, with measurement of *"pH,* pCO_2 *profiles or equivalent information used to measure ocean acidification"* included within the *"indicative list of characteristics, pressures and impacts"* (as a *"physical and chemical feature"*).

We do not here provide any assessment of potential biological or socio-economic impacts of the observed changes in water chemistry. Although a wide range of marine organisms are potentially sensitive to ocean acidification (IGBP *et al.*, 2013; CBD, 2014), most adverse impacts occur outside the pH range currently experienced in UK waters. Whilst it is possible that deleterious effects are already underway, it is currently difficult to unambiguously separate the consequences of ocean acidification from other environment changes, such as temperature (Beaugrand *et al.*, 2012), and there is not yet agreement on the most suitable indicator species for pH change (ICES, 2014). Instead, a wide range of biological measurements are considered necessary to assess the ecological response (Newton *et al.*, 2015).



2. Methods

2.1 Carbonate system measurements

Although pH is the parameter of greatest concern for ocean acidification, it is rarely measured directly – since most sensors are not sufficiently accurate. Instead it is usually calculated from measurements of other components of the closely-linked ocean `carbonate system'. These other measurements also give additional ecologically-important information, e.g. on CO_2 levels and carbonate saturation state. There are a number of different methods for measuring carbonate system parameters in seawater, the more widely used methods are well described in Riebesell *et al.* (2011). Briefly, the definitions of the marine carbonate system parameter used within this report, and the common techniques used are given below:

- **pH** can be defined using different scales (Hydes *et al.*, 2013), the more common scale used within seawater is the hydrogen ion scale, therefore for the purpose of this report pH is defined as the negative logarithm of hydrogen ions. pH is commonly calculated from two other carbonate system parameters (see section 2.2). However, it can also be measured directly using electrometric or spectrophotometric determination.
- **pCO_2 and fCO_2** are the sea surface partial pressure of carbon dioxide (pCO_2), and the fugacity of CO_2 (fCO_2), which takes into account the non-ideal nature of the gas. These parameters are most commonly measured using infrared determination.
- **DIC** is the sum of all of the dissolved forms of inorganic carbon, this is

often measured using a coulometric method.

- **TA** is the total alkalinity, which is the balance of all of the ionic charges in the marine carbonate system. TA is usually measured using an acidimetric titration.
- Ω_{ar} is the aragonite saturation state, which is a measure of the potential for carbonate in the form of aragonite to form or dissolve. If Ωar is less than 1 aragonite will readily dissolve. Ωar is most commonly calculated from two measurements of the carbonate system, see section 2.2.

2.2 Calculation of carbonate system parameters

Using two measured carbonate system parameters (DIC, TA, pCO_2/fCO_2 and pH), together with sea surface temperature (SST), salinity, sea level air pressure, silicate and phosphate, the remaining carbonate parameters can be calculated. DIC and TA measurements are most commonly used to calculate the other parameters, as they are relatively easy to collect and preserve for later analysis. However there are advantages/disadvantages and error associated with using different combinations for such calculations (Riebesell *et al.*, 2011). Currently only pH and CO_2 can be measured continuously over time (with appropriate calibration). More compact and reliable sensors to measure pH and CO_2 are currently being developed in the UK and elsewhere.

To calculate the carbonate parameters within this report a Matlab toolbox called CO2SYS was used which is based on the program developed by Lewis *et al.* (1998) for DOS and Excel. When using the CO2SYS toolbox there are a number of dissociation constant and formulation options that have to be selected. For this report the dissociation constants for pK_1 were taken from Mehrbach *et al.* (1973) that were refitted by Dickson and Millero (1987), and the dissociation constant for pK_2 was taken from Dickson (1990). Lueker *et al.* (2000) have estimated the root-mean-square-error (RMSE) for pK_1 as ± 0.0055 and for pK_2 as ± 0.01. It is important to note that when calculating carbonate parameters the error associated with each individual measurement input in to CO2SYS and with the dissociation constants used propagates, increasing the uncertainty associated with the output.

A user-friendly seawater-carbon calculator app can be downloaded from here **gcmd.nasa.gov/USGS-CO2calc**

3. Findings

3.1 Sampling locations

Take-home message

> **3.1** Recent UK cruise data contribute to large gaps in national and global datasets ■

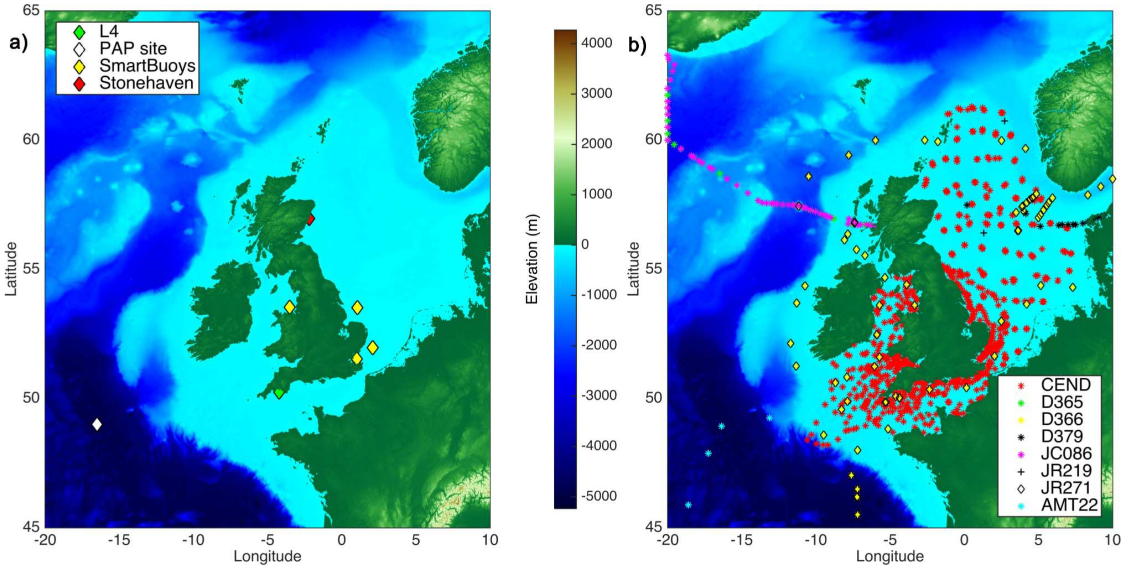


Figure 3.1: Map of the spatial coverage showing the locations of **a)** the fixed-point observatories (coloured diamonds, top-left legend) and **b)** the sampling locations from cruises that took place between 2010 and 2015, with the cruise ID given in the bottom-right legend.

Figure 3.1 shows the region that this report is focussed on, the light blue area of the seas represents shallower waters, and dark blue areas are deeper than $\sim$ 1000 m. Because of the nature of the processes involved, and the relative scarcity of data, it does not make scientific sense to analyse separately for the 8 sub-regions defined in Charting Progress 2 (Defra, 2010). However, additional datasets likely to become available in future (e.g. from the NERC-Defra Shelf Sea Biogeoechemistry programme) are expected to make greater geographical discrimination possible.

Comparisons of the data shown in figure 3.1 with GLODAP (GLobal Ocean Data Analysis Project) V2 data (Key *et al.*, 2015) show that the UK data improves spatial coverage of DIC and TA samples within OSPAR North-East Atlantic regions II (Greater North Sea) and III (Celtic Seas). The temporal coverage is also improved within these regions, as when the GLODAP V2 dataset is combined with the UK cruise data shown in figure 3.1 a complete monthly seasonal pH cycle is resolved. Data used within this report are listed within table 3.1 in section 3.3, with information or links to data access provided.

ⓘ See **www.ospar.org** for an interactive map of the North-East Atlantic OSPAR regions.

3.2 Results

3.2.1 Long-term trends

Take-home messages

> **3.2** The new UK measurements confirm that pH is highly variable, therefore it is important to measure consistently to determine any long term trends ■

> **3.3** Over the past 30 years, North Sea pH has decreased at 0.0035 ±0.0014 pH units per year ■

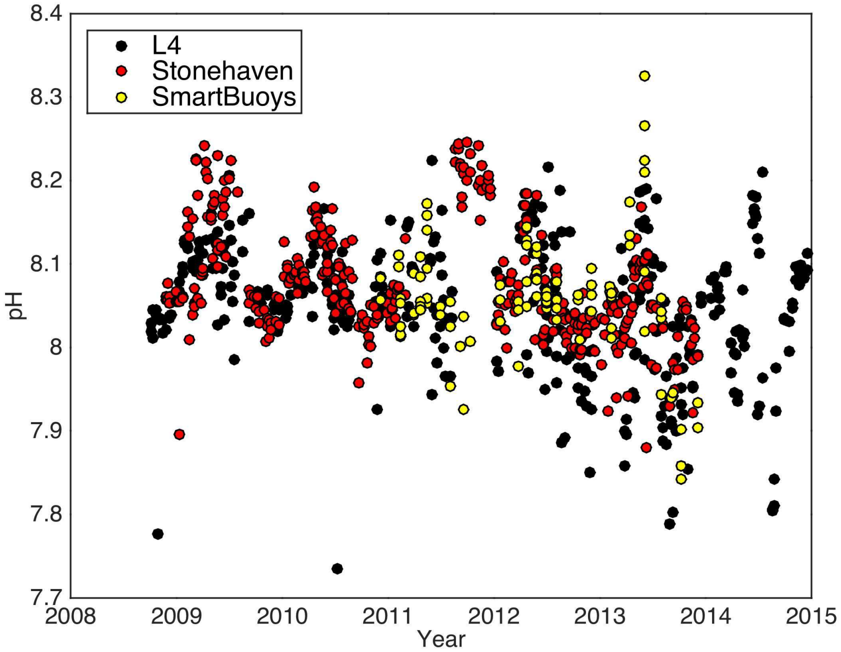


Figure 3.2: pH calculated from DIC and TA samples collected at fixed-point observatories. L4 = black circles, Stonehaven = red circles, SmartBuoys = yellow circles, see figure 3.1 for locations. See table 3.1 for data access and information.

Figure 3.2 shows pH values calculated from DIC and TA samples (see methods section 2.2) collected from three different sources. Although these fixed-point observatories are positioned at different locations around the UK (see figure 3.1), and all show high variability, they compare reasonably well. Thus pH shows clear seasonality, and particularly strong variability in some years; for example 2013 has a larger range in pH than previous years. This variability not only highlights the importance of consistently measuring pH throughout the year to determine any long term trends, but also the measurement of other environmental parameters likely to affect pH (Newton *et al.*, 2015).

One of the longest historical records of pH data (including information for UK waters) can be found on the International Council for the Exploration of the Seas (ICES) (**www.ices.dk**) website. Some of these pH values (measured and calculated) were recorded as far back as 1910; however, there are some difficulties with interpreting this dataset as metadata on how the values were determined are not available. Fay and McKinley (2013) suggest that in order to determine a long-term trend in seawater carbon data, a dataset of >25 years is required. Currently, fixed-point observatory datasets within UK/European waters do not have the temporal coverage to match that difficult to achieve criterion, therefore the ICES dataset considered over the period 1984-2014 provides the best available information to determine a long-term trend in UK/European waters.

Plot 3.3a shows a map of the locations of ICES pH data, with the boundaries of the OSPAR regions shown in black. OSPAR region II (the Greater North Sea, including the English Channel) was the only OSPAR region considered to be adequately sampled. For the purpose of this report, the trend was calculated from 1984 to 2014 using measurements made within the top 20 m (plot 3.3b and 3.3c, covering 31 years of sampling effort). This period was selected for analysis because before 1984 there were not enough pH measurements recorded to obtain annual means. The trend of -0.0035±0.0014 pH units per year (shown in plot 3.3c) is consistent with findings from recent literature (see figure 1.2 and Bates *et al.* (2014)). On the basis of more limited information, Hydes *et al.* (2011) estimated the north west European shelf trend to be between $\sim$ -0.002 to -0.004 pH units per year from 1995 to 2009.

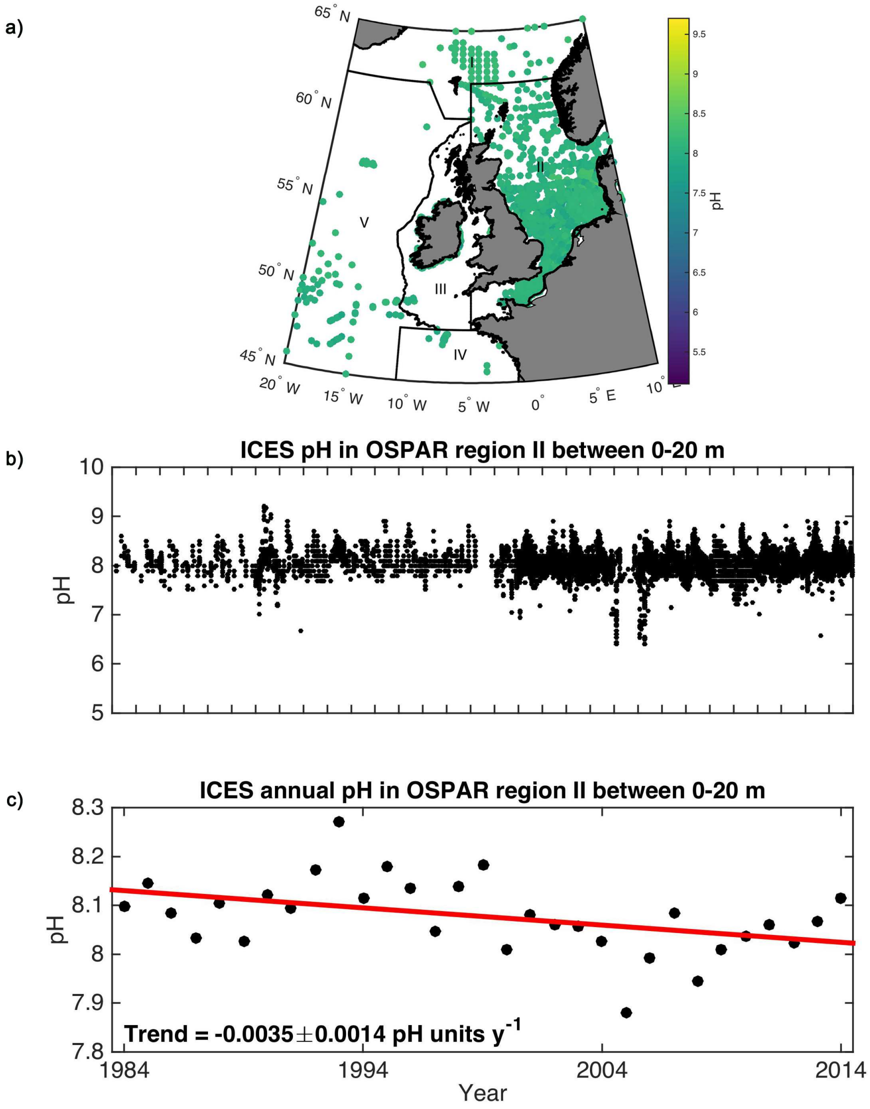


Figure 3.3: a) Map of the ICES pH data with OSPAR boundaries shown. **b)** pH data collected within the top 20 m in OSPAR region II (the greater North Sea) from 1984 - 2014. **c)** The mean annual pH within the top 20 m in OSPAR region II (the greater North Sea) from 1984 - 2014 with the trend and standard deviation shown.

Other analyses of multi-annual changes in North Sea upper ocean carbonate chemistry are provided by Beare *et al.* (2013); Duarte *et al.* (2013); Salt *et al.* (2013); Clargo *et al.* (2015). Beare *et al.* (2013) focussed on ICES data for the central North Sea; their fitted, curvilinear trend for 1963- 2010 indicated an increase in pH until the early 1990s, and a subsequent decline in the following years. Figures in Duarte *et al.* (2013) show a similar pattern for both the southern North Sea (coastal station influenced by river discharge) and Danish Straits, although with the change from increase to decrease occurring earlier, 1985. Additional observations in the southern North Sea, including estuaries (Provoost *et al.*, 2010), indicate that changes in nutrient levels, causing increasing (and subsequently) decreasing eutrophication were probably responsible for the decadal-scale changes occurring in addition to the atmospherically-driven overall trend.

Salt *et al.* (2013) and Clargo *et al.* (2015) both focussed on data since 2001, with the former identifying the North Atlantic Oscillation as an important physical driver, in addition to atmospheric CO_2, through its effects on North Sea water masses.

3.2.2 Seasonal trends

Take-home messages

> **3.4** Upper ocean pH values are highest in spring, lowest in autumn. These changes reflect the seasonal cycles in photosynthesis, respiration (decomposition) and water mixing ■

> **3.5** Carbonate saturation states are minimal in the winter, and lower in more northerly, colder waters. This temperature-dependence could have implications for future warming of the seas ■

> **3.6** Over the annual cycle, North-west European seas are net sinks of CO_2. However, during late summer to autumn months, some coastal waters may be significant sources. ■

The seasonal cycle of pH at Stonehaven and L4 is shown on the following page in figure 3.4. Both fixed-point observatories have a similar seasonal cycle with high pH in the spring (April-June) and low pH in the autumn months (August-October).

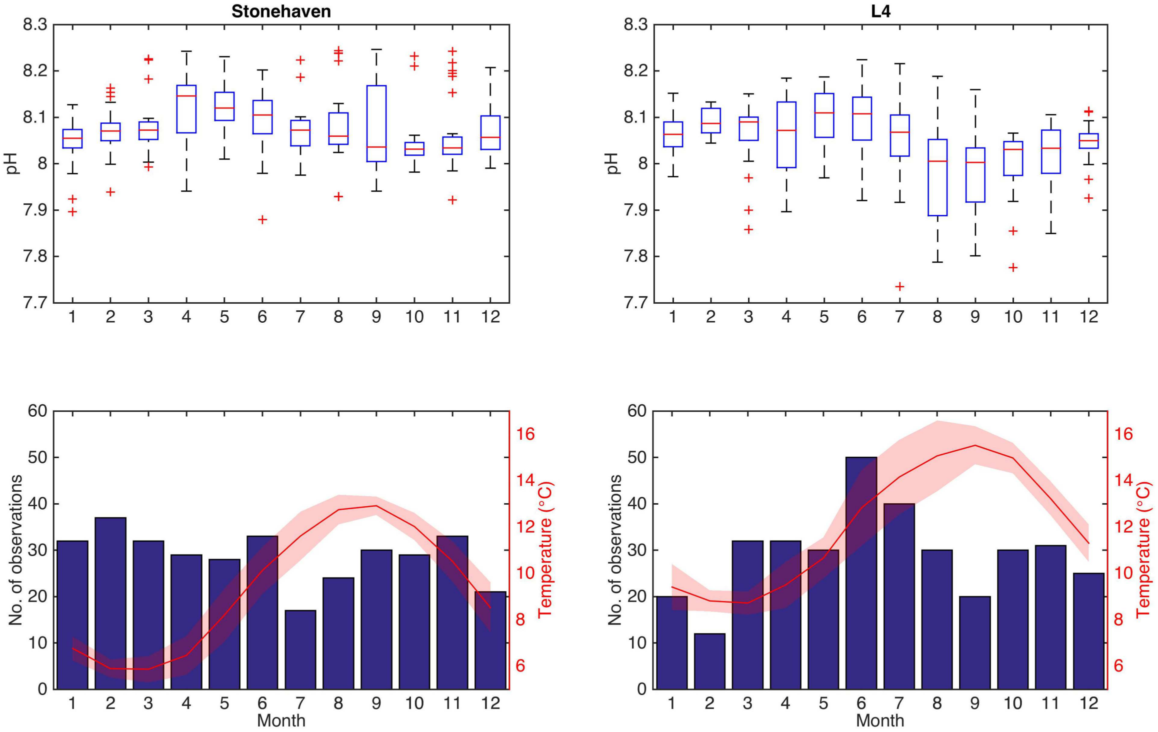


Figure 3.4: Box and whisker plots of calculated pH data within each month from Stonehaven and L4 between 2008 to 2015. The red lines within the boxes represent the median for each month, while the edge of box = 25th and 75th percentile, the whiskers are the extremes (≃2.7 standard deviations) and outliers are outside of this range represented as red crosses. The number of observations within each month are shown in the bottom panel as bar charts, with the mean temperature plotted as a bounded red line with the shaded area showing the standard deviation. See table 3.1 for data access and information.

This increase in pH during the spring is primarily due to the spring bloom of phytoplankton (mostly microscopic algae), with high photosynthetic activity, decreasing the amount of dissolved CO_2 and hence hydrogen ions. The lower pH in the autumn is likely due to the increased abundance and activity of non-photosynthetic marine organisms, including phytoplankton predators (zooplankton), decomposers (mostly bacteria) and benthic invertebrates. Respiration by these organisms returns CO_2 to the seawater, decreasing the pH.

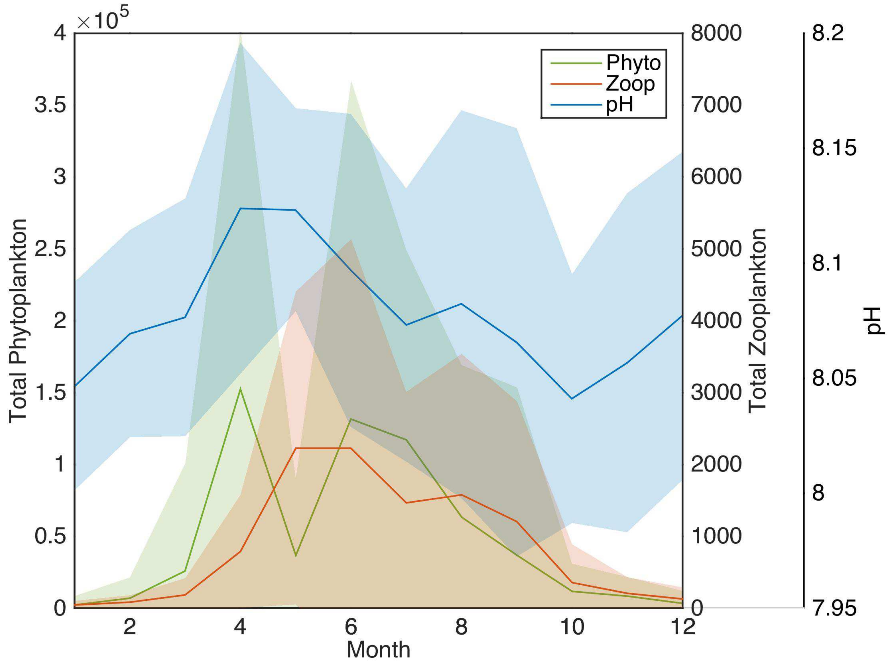


Figure 3.5: Monthly mean total phytoplankton counts = green, and total zooplankton counts = red, from Continuous Plankton Recorded (CPR) data (**doi:10.7487/2014.44.1.10**) collected within 5° radius of L4, and calculated pH at L4 = blue (Cummings *et al.*, 2015) from 2008 to 2013. The shaded area around each mean represents the standard deviation.

The succession between the spring and the summer/autumn bloom of phytoplankton and zooplankton at L4 can be seen in figure 3.5. Stratification starts to break down during autumn, deepening the mixed layer and mixing carbon rich waters to the surface which continues to lower the pH. The above interpretation is supported by findings from Kitidis *et al.* (2012) and Marrec *et al.* (2013), who demonstrated that the seasonal changes in carbonate chemistry in the western English Channel are dominated by changes in biology, rather than advection.

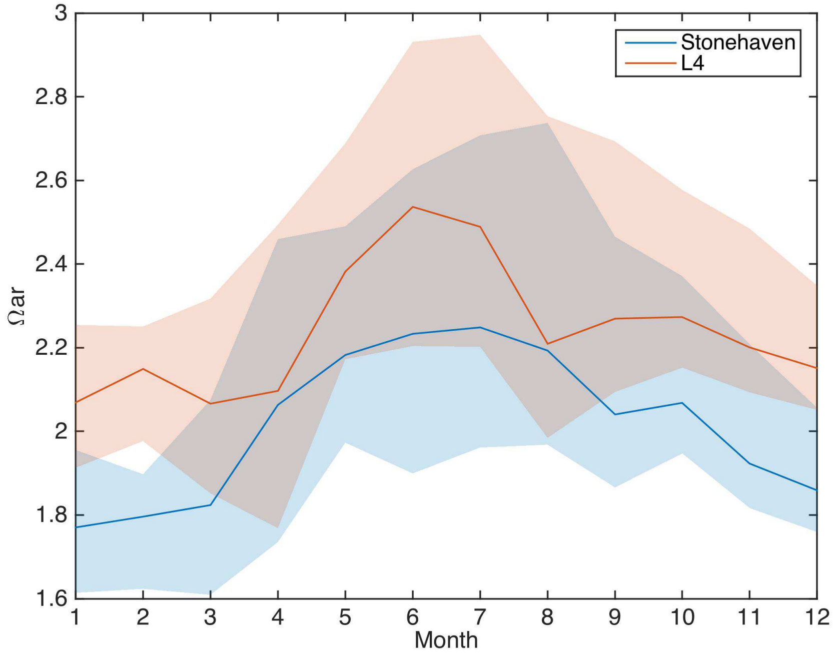


Figure 3.6: Monthly mean saturation state for aragonite (Ωar) calculated from DIC and TA samples between 2008 to 2015, collected at Stonehaven = blue, and L4 = red. The shaded area around each mean represents the standard deviation. See table 3.1 for data access and information.

The mean seasonal cycle of carbonate (aragonite) saturation state at L4 and Stonehaven are shown in figure 3.6. The saturation state is highest during the summer months and lowest during winter at both sites, with Stonehaven having a lower monthly mean saturation state than L4. Whilst this seasonality in aragonite saturation state is primarily driven by the summer decrease in DIC as primary production by phytoplankton increases, it is re-inforced by the seasonal change in temperature. Thus saturation state is higher at warmer temperatures due to lower solubility, which explains the difference between the two sites: water temperatures at Stonehaven are ∼3.1°C cooler than L4 throughout the year. Future warming could therefore reduce the impact of increased CO_2 on saturation state and the depth at which aragonite or calcite dissolves; however, models that take account of both factors indicate that directly-driven CO_2 effects predominate.

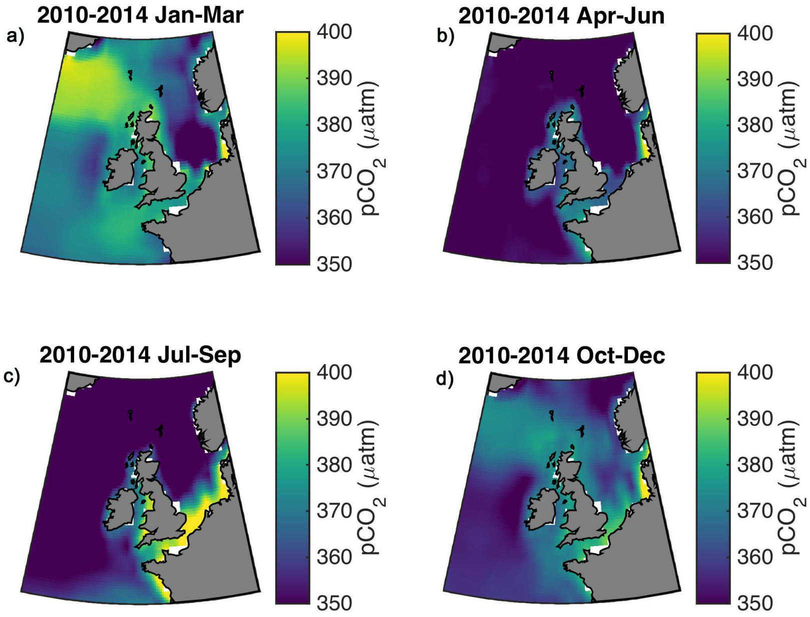


Figure 3.7: Mean seasonal surface ocean pCO_2 between 2010 and 2014. Estimated using SOCAT V3 pCO_2 data (Bakker *et al.*, 2014, 2016) interpolated using the ETH SOM-FFN method (Landschützer *et al.*, 2015a,b).

Figure 3.7 describes the seasonal cycle of CO_2 in surface waters of the north-west European shelf and adjacent Atlantic Ocean. These maps are based on direct observations of upper ocean CO_2, that are interpolated using the ETH SOM-FNN method (using additional indirectly-derived information on sea surface temperature, chlorophyll and mixed layer depth) (Landschützer *et al.*, 2015a,b). High concentrations of CO_2 are indicated off the south coast of Iceland and around the UK during the winter months, with the mixing of high carbon deep waters considered to be the main driver of such effects. During the spring and summer months the concentration of CO_2 decreases, due to increased productivity by phytoplankton taking up CO_2 via photosynthesis. In the autumn (figure 3.7c) there are high concentrations of CO_2 around the coast of the UK and in the south North Sea: This is likely to be an effect of marine respiration and decomposition, as previously noted for L4 and riverine contribution, from watershed run off of high carbon waters and organic matter inputs (Kitidis *et al.*, 2012).

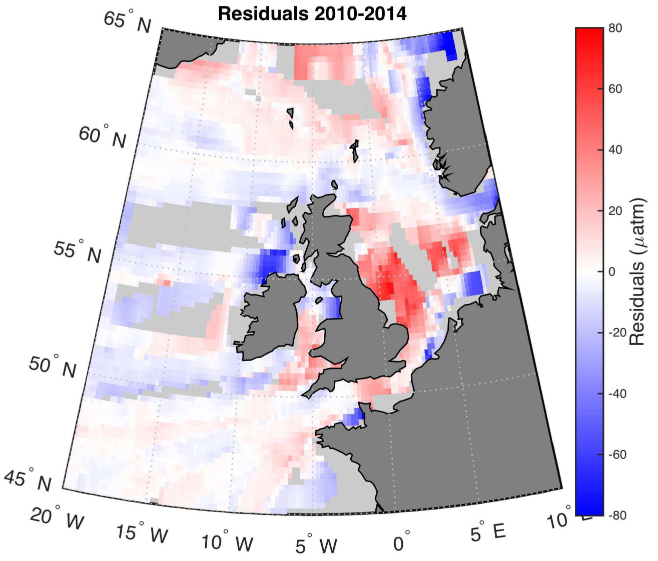


Figure 3.8: Mean residuals (difference) between monthly surface ocean pCO_2 interpolated using the ETH SOM-FFN method (Landschützer *et al.*, 2015a,b) and monthly SOCAT V3 pCO_2 data (Bakker *et al.*, 2014, 2016) between 2010 and 2014. Light grey areas of the map are where no data were available.

The model-derived interpolated data of figure 3.7 was subtracted from the directly observed data (residuals) to indicate areas of greater uncertainty (figure 3.8). In most areas the interpolated data agrees well with the observational data, there is a good fit between the observations and the model-derived data in the open ocean, but less so in the shelf regions as the south North Sea and coastal areas show larger uncertainty.

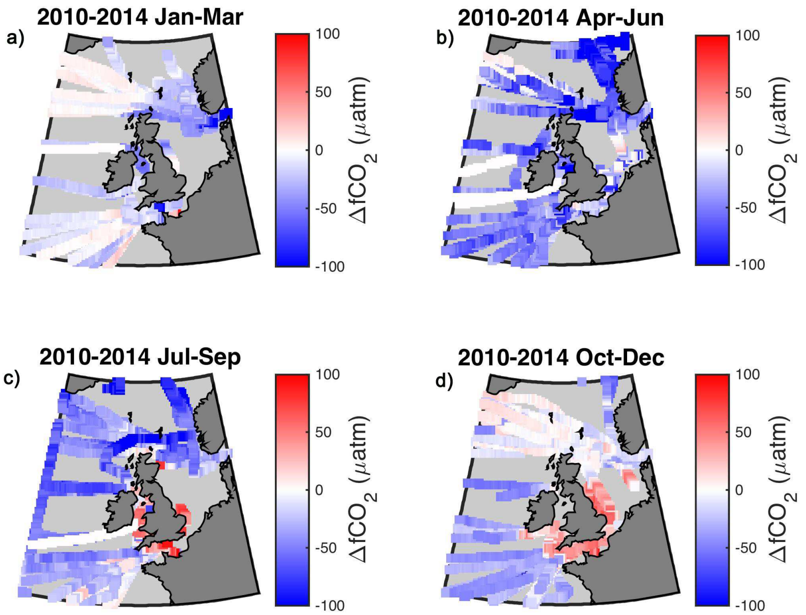


Figure 3.9: Mean seasonal surface ocean ΔfCO_2 (fCO_2 in seawater - fCO_2 in atmosphere) between 2010 and 2014. Estimated using SOCAT V3 fCO_2 data (Bakker *et al.*, 2014, 2016). Red = CO_2 source, blue = CO_2 sink. Light grey areas of the maps are where no measurements were available (in SOCAT).

The seasonal ΔfCO_2 maps shown in figure 3.9 indicate that throughout most of the year the north-east Atlantic is a sink for CO_2, i.e. net uptake. During July to December there is a region of high CO_2 that creates a source of CO_2 to the atmosphere around the south coast of the UK (subplots 3.9c and 3.9d). This is likely due to the high riverine run-off that occurs during this period, creating high concentrations of CO_2 (seen in figure 3.7). Note that information for some UK waters is sparse or lacking for this analysis, based on different sources from those shown in figure 3.1. Additional coverage for the period 2014-2016 is expected to become available through the Shelf Sea Biogeochemistry programme.

3.2.3 Depth distributions

Take-home messages

> **3.7** In seasonally-stratified waters, sea-floor organisms naturally experience lower pH and saturation states; they may therefore be more vulnerable to threshold changes ▪

> **3.8** Large pH changes (0.5 - 1.0 units) can occur in the top 1 cm of sediment; however, such effects are not well-documented ▪

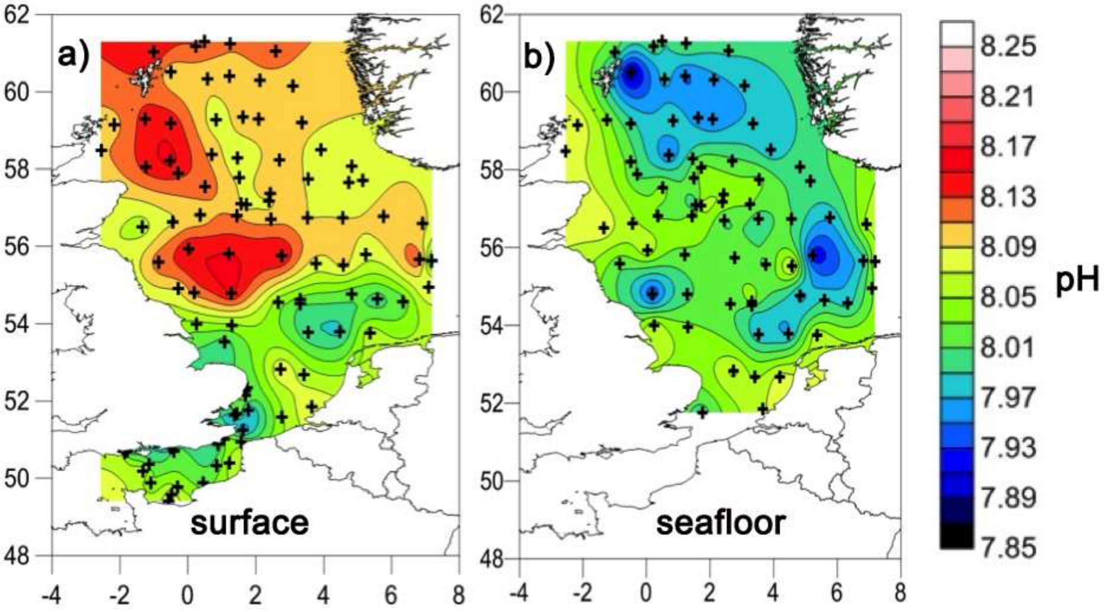


Figure 3.10: In stratified waters, pH values at the **a)** sea surface can be ~0.2 units higher than at the **b)** seafloor, as shown here for a North Sea survey in summer 2011. Figure created by Naomi Greenwood (Greenwood *et al.*, 2012).

The data considered so far overwhelmingly relates to the upper ocean (0 - 20 m), where most ocean acidification measurements have been made. But marine organisms of commercial and ecological significance live throughout the water column, and seafloor habitats in UK waters are of particular importance, supporting both high biomass and high biodiversity. Wherever seasonal stratification occurs (typically at water depths > 50 m for UK waters, e.g. northern North Sea and deeper parts of the Celtic Sea), strong vertical gradients in pH and other carbonate chemistry parameters develop during the summer (figure 3.10, figure 3.11).

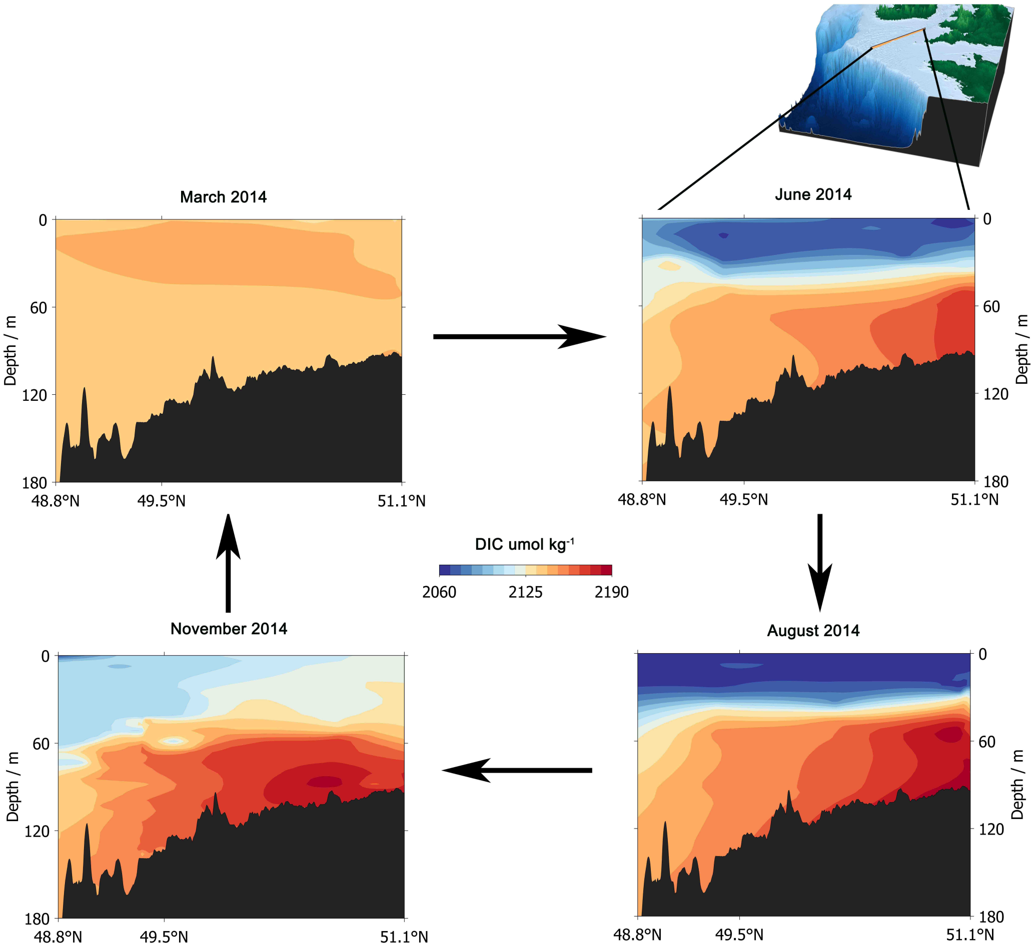


Figure 3.11: Seasonal depth profiles of dissolved inorganic carbon (DIC) from a transect within the Celtic Sea for the year 2014. Figure adapted from Humphreys *et al.* (2015).

The full annual cycle is shown for dissolved inorganic carbon (DIC) in the Celtic Sea for the year 2014 (figure 3.11) – from complete mixing (April) to the onset of stratification (June), its strengthening (August) and subsequent, wind-driven breakdown and beginning of re-mixing (November) (Humphreys *et al.*, 2015).

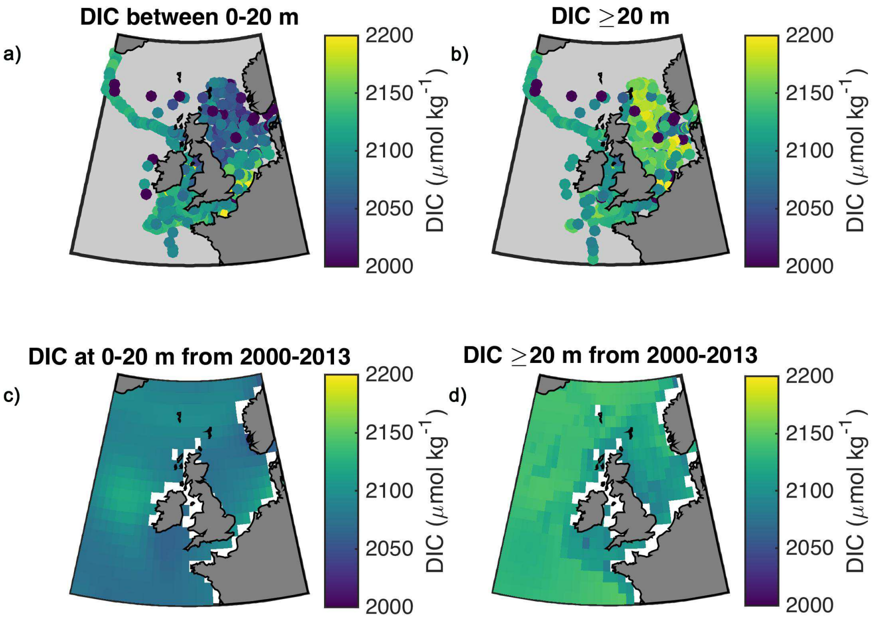


Figure 3.12: Maps of surface dissolved inorganic carbon (DIC) and DIC at depth below 20 m. **a)** DIC from UK cruise data from 2010 to 2015 (see figure 3.1 for sampling locations) between 0 m and 20 m **b)** DIC from UK cruise data from 2010 to 2015 deeper than 20 m. **c)** DIC from GLODAP V2 climatology (Lauvset *et al.*, 2016) from 2000 to 2013 between 0 m and 20 m. **d)** DIC from GLODAP V2 climatology (Lauvset *et al.*, 2016) from 2000 to 2013 deeper than 20 m. Light grey areas of the maps are where no data were available.

The increased concentration of DIC at depth seen in figure 3.11 can also be seen in the maps of the cruise data DIC measurements and the estimates from GLODAP V2 (Lauvset *et al.*, 2016) shown in figure 3.12. The GLODAP V2 (Lauvset *et al.*, 2016) climatology agrees well with the cruise data.

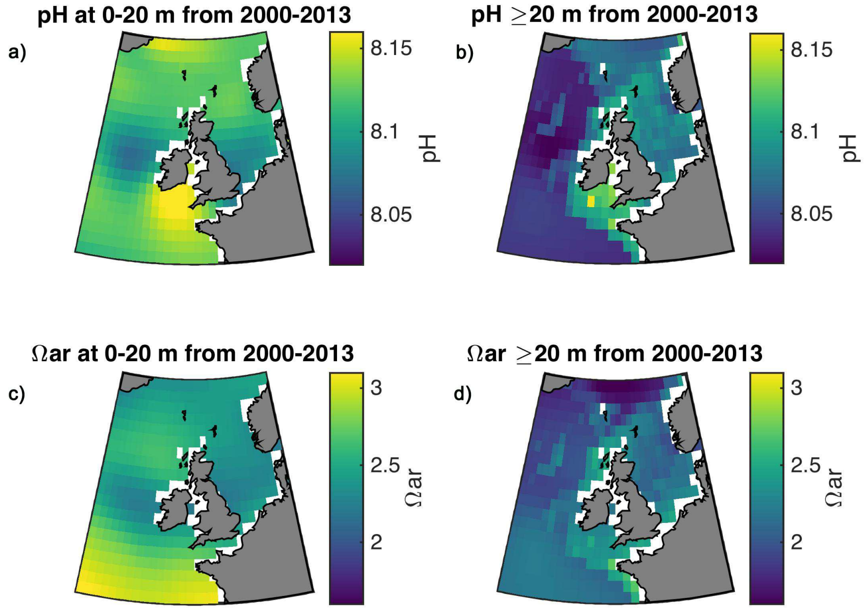


Figure 3.13: Maps of pH and aragonite saturation state (Ωar) from GLODAP V2 climatology (Lauvset *et al.*, 2016). **a)** pH from 2000 to 2013 between 0 m and 20 m. **b)** pH from 2000 to 2013 deeper than 20 m. **c)** Ωar from 2000 to 2013 between 0 m and 20 m. **d)** Ωar from 2000 to 2013 deeper than 20 m.

There are lower pH values at depth compared with surface measurements (see figure 3.13) particularly off the shelf where the depth increases (figure 3.1). The saturation states are also lower at depth, however the spatial distribution is different to that of pH because saturation state is more influenced by temperature, therefore the region between Iceland and Norway has the lowest saturation states of aragonite as temperatures are coldest here (subplot 3.13d).

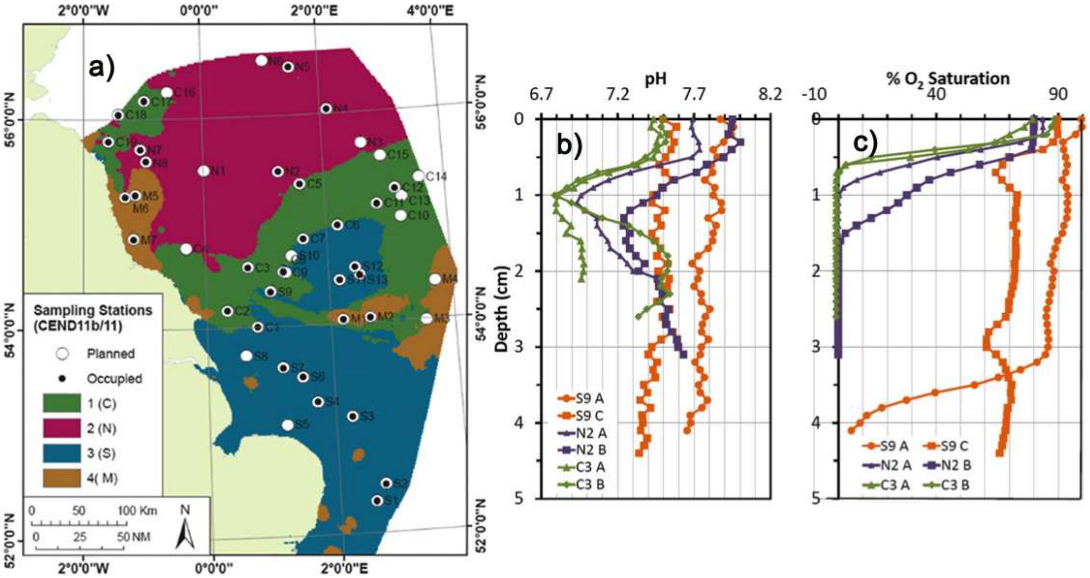


Figure 3.14: Sediment profiles from the North Sea. **a)** S = Southern region (blue), N = Northern region (pink), C = central region (green), M = Mud (brown), as determined by EHUs (Eco Hydrodynamic Units) calculated from Sediment (% fines), depth and temperature difference (stratification). Selected **b)** pH and **c)** oxygen profiles from contrasting stations in the North Sea. Figure adapted from Parker *et al.* (2012) and Greenwood *et al.* (2012).

At the seafloor itself, further pH and carbonate chemistry gradients occur on the millimetre to centimetre scale. The sediment profiles shown in figure 3.14 were collected using a microelectrode to measure box core sub cores during research cruises in the North Sea in the summer of 2011 and January 2012. There was a consistent feature of a 0.5 to 1 unit decrease in pH in the upper 1 cm (muddy sands/sandy muds) recorded, which can be seen in plot 3.14b (Parker *et al.*, 2012; Greenwood *et al.*, 2012). The above data illustrate the range of pH values that organisms that live either on or in the seafloor experience on a regular basis. The former include many invertebrates (molluscs, polychaetes and crustacea, as well as cold-water corals) that provide either food or habitat for benthic fish. Whist it is possible that most/all seafloor organisms are genetically adapted to such conditions, there may also be the risk that physiological thresholds (e.g. relating to saturation state) may be crossed as a consequence of future water chemistry changes. To date, experimental studies would seem to have given insufficient attention to the range of conditions naturally experienced.

3.2.4 Future estimates

Take-home messages

3.9 A coupled forecast model estimates the decrease in pH trend within the North Sea to be -0.0036±0.00034 pH units per year, under a high greenhouse gas emissions scenario (RCP 8.5) ■

3.10 Seasonal estimates from the forecast model demonstrate areas of the North Sea that are particularly vulnerable to aragonite undersaturation ■

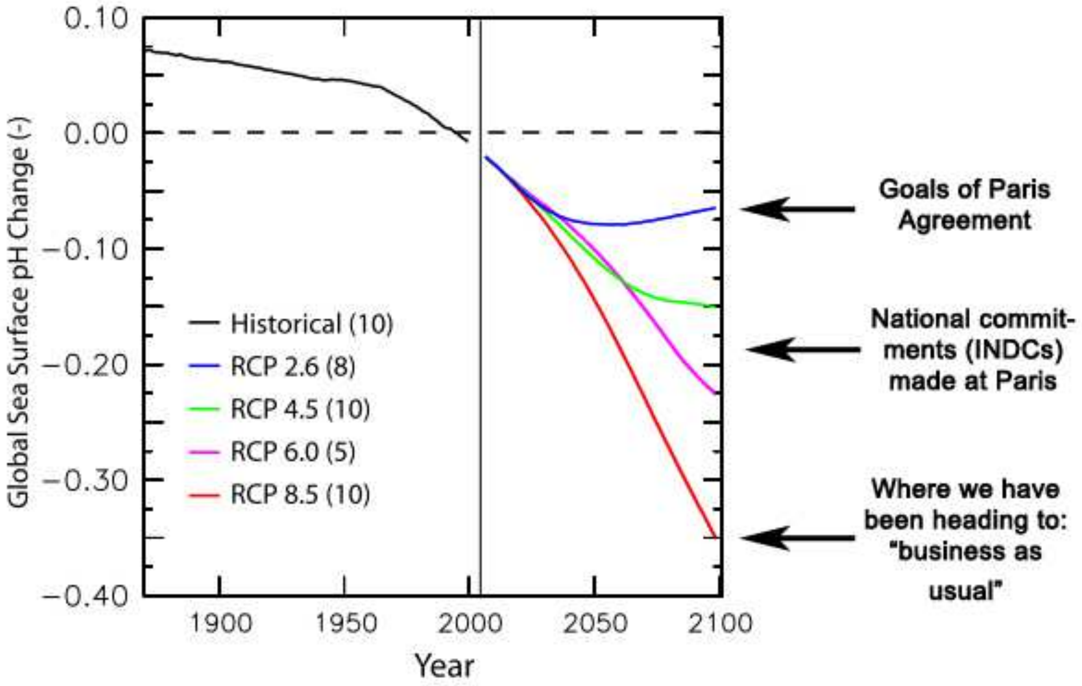


Figure 3.15: Historical and projected changes in global surface ocean pH from 1870 - 2100 for the for IPCC AR5 RCP scenarios, annotated with information from the December 2015 Paris Agreement. INDC = Indicative Nationally Determined Contribution. Adapted from Bopp *et al.* (2013).

Whilst there are many global-scale models of ocean acidification in the upper ocean, full-depth modelling for regional seas – including coastal components, terrestrial inputs and seafloor exchanges – is not so well developed. In the Regional Ocean Acidification Modelling (ROAM) project of UKOA, a coupled physical-ecosystem model was used to project the future pH values and saturation state of the North Western European Shelf. The circulation model used was the Nucleus for European Modelling of the Ocean (NEMO; Madec (2008)) and it included a wide range of processes considered important in the shelf environment (e.g. tidal currents, variable sea surface height). The ecosystem model implemented is the European Regional Sea Ecosystem Model (ERSEM; Blackford *et al.* (2004); Butenschön *et al.* (2016)) that has been widely used to study ecosystem dynamics and impact of climate change and Ocean Acidification in the area (e.g. Holt *et al.* (2012); Artioli *et al.* (2014); Wakelin *et al.* (2015)). The ERSEM carbonate system module has been intensively validated against observational data for this domain (Artioli *et al.*, 2012). To date, the model has been forced with data representative of the IPCC AR5 RCP 8.5 (RCP=Representative Concentration Pathway), as simulated by the UKMO HADGEM model. RCP 8.5 describes a possible climate scenario based on continued high greenhouse gas emissions, as shown as the red line in figure 3.15.

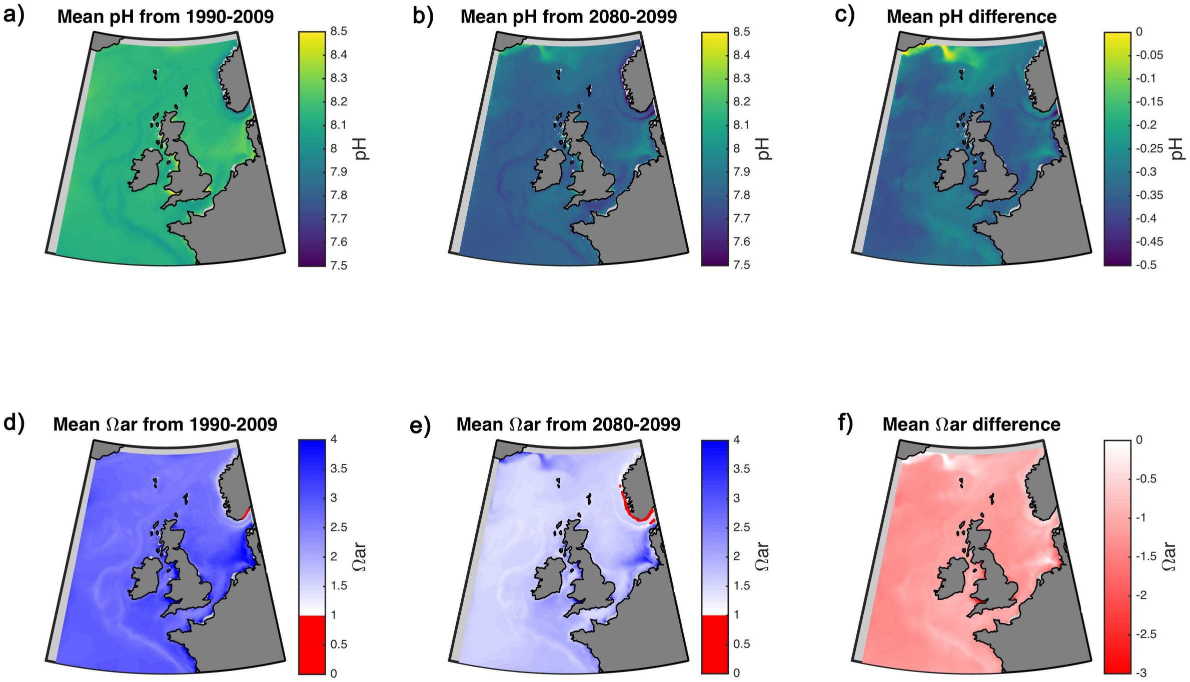


Figure 3.16: Top panel = Mean surface water pH from **a)** 1990 to 2009, **b)** 2080 to 2099 and the **c)** difference between these two periods. Bottom panel = Mean surface water aragonite saturation state (Ωar) from **d)** 1990 to 2009, **e)** 2080 to 2099 and the **f)** difference between these two periods. These projections are modelled based on IPCC AR5 RCP 8.5. Note: The model projects an increase in pH and Ωar close to Iceland, but this is an artefact due to boundary conditions within the model.

Figure 3.16 shows the mean pH and aragonite saturation state (Ωar) in surface waters around the UK using the ROAM model and the RCP 8.5 scenario. The model projects an increase in pH and Ωar close to Iceland, but this is an artefact due to boundary conditions within the model. There is a clear decrease in both pH and Ωar between the two periods with areas around the south coast of Norway showing the strongest decrease, and becoming undersaturated in aragonite (red area in figure 3.16e). The model estimates that surface waters will start to become occasionally undersaturated gradually from around 2030 and more rapidly from 2080. By the end of the century the model estimates that an area of surface water of ∼300,000 km^2 could become undersaturated for at least a month. The pH trends estimated from this model output for **OSPAR regions** II (Greater North Sea) and III (Celtic Seas) were -0.0036±0.00034 and -0.0033±0.00019 pH units per year, respectively. These trends are within the standard deviation of each other, and are closely similar to the recent trend (∼0.0035 pH units per year) calculated from the **ICES** pH data in section 3.2.1.

ⓘ A free, simple to use, interactive app for looking at different CO_2 scenarios and consequent changes in temperature, sea level rise and pH can be found here **www.co2modeller.info**.

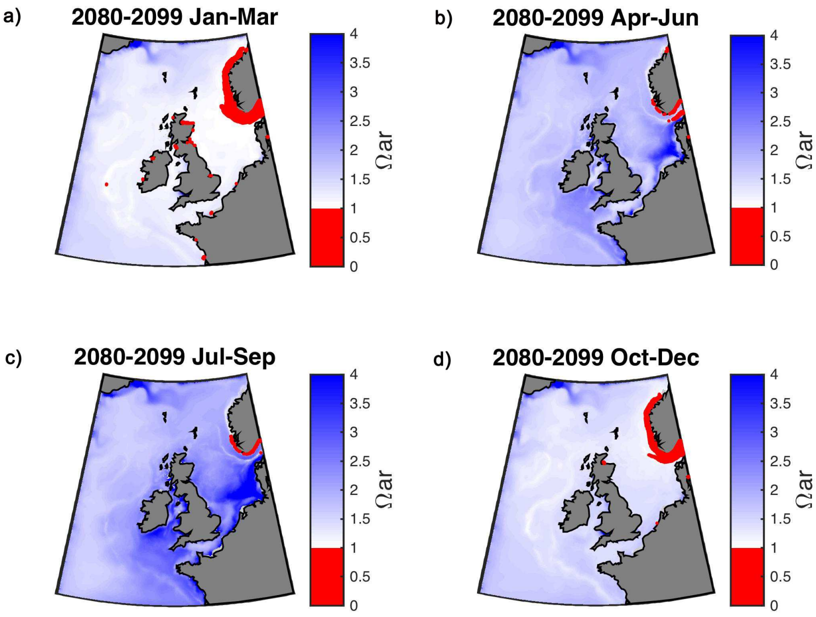


Figure 3.17: Seasonal mean surface water aragonite saturation state (Ωar) between 2080 to 2099 for **a)** January to March **b)** April to June **c)** July to September **d)** October to December. The red area highlights regions of undersaturation (< 1) of aragonite. These projections are modelled based on IPCC AR5 RCP 8.5.

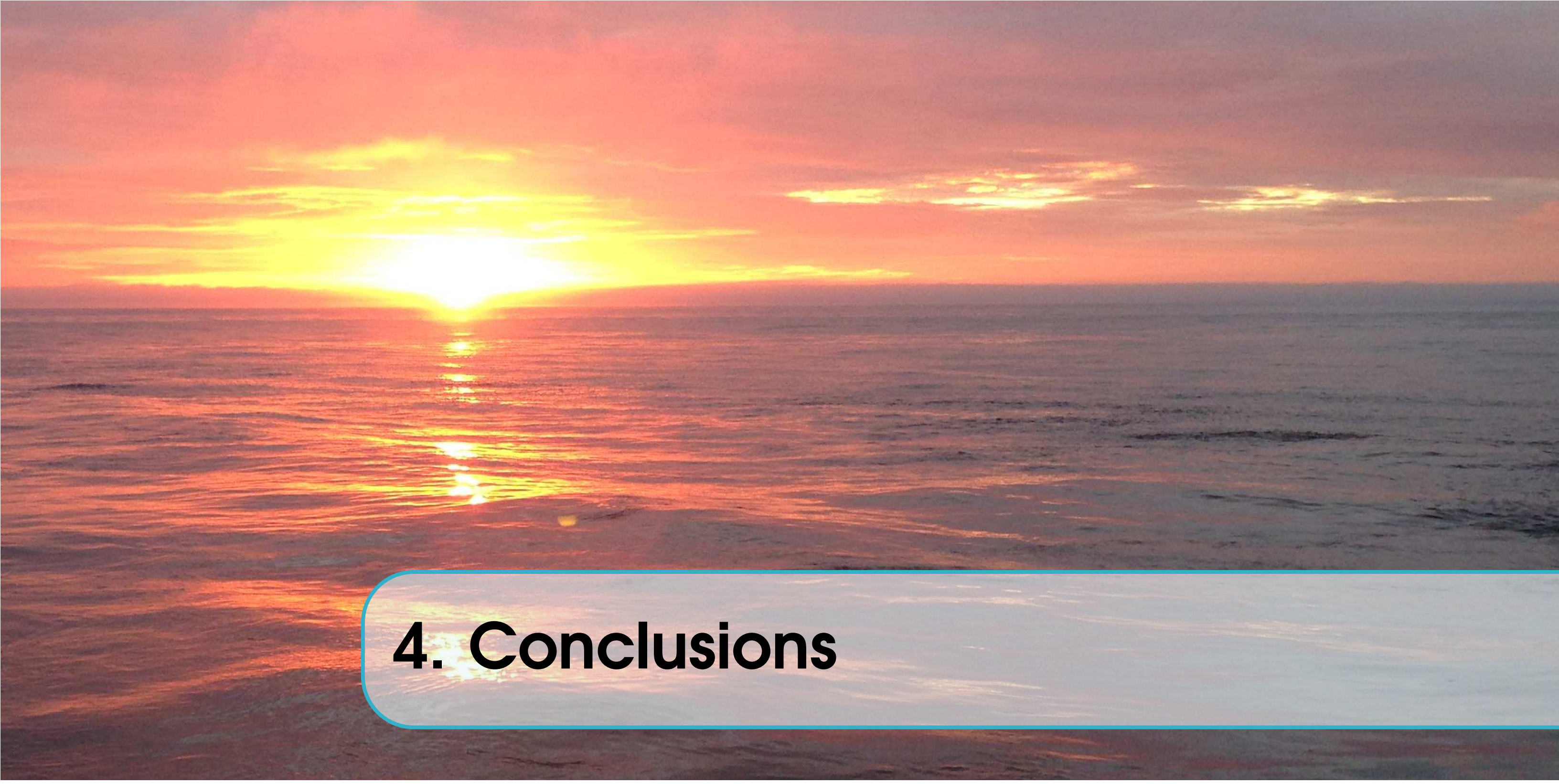
Sasse *et al.* (2015) highlight the importance of accounting for seasonality when looking at saturation states from future scenarios. This is clear in figure 3.17 as the seasonal undersaturation of aragonite (red areas) are larger than when averaging over the whole period from 2080 to 2099. The cooler periods between January - March (figure 3.17a) and October - December figure (3.17d) are when undersaturation in aragonite is greatest, particularly off the Norwegian coast, and many areas are very close to the undersaturation value of 1. There are also some areas around the UK that show undesaturation in aragonite between January - March (figure 3.17a). This seasonality of Ωar in surface waters is in agreement with the observational data shown in section 3.2.2 in figure 3.6, with low values during the winter months.

3.3 Data and products available

Table 3.1: Links and information for the data used within this report.

Organisation/Project	PI/Ref	Region	Period used	Parameters	info/link/doi
GLODAP V2	Key *et al.* (2015) Olsen *et al.* (2016) Lauvset *et al.* (2016)	Global	2000 - 2013	DIC/TA	Data available from CDIAC
SOCAT V3	Bakker *et al.* (2014, 2016)	Global	2010 - 2014	fCO_2	Data available from SOCAT
ETH SOM FFN	Peter Landschützer Landschützer *et al.* (2015a,b)	Global	2010 - 2014	pCO_2	Data available from CDIAC
PML/WCO	Helen Findlay Cummings *et al.* (2015)	L4 - English Channel	2008 - 2014	DIC/TA	Data available from BODC doi:10/7dj
Cefas	Naomi Greenwood	Warp, West Gabbard, Liverpool Bay (smartbuoys)	2011-2014	DIC/TA	Data available from BODC
Marine Scotland	Pamela Walsham	Stonehaven	2009-2015	DIC/TA	Data available from MSS
UKOA	Toby Tyrrell (Ribas-Ribas *et al.* (2014b) Ribas-Ribas *et al.* (2014a))	UK Seas	2011-2012	DIC/TA/pCO_2/pH	Data available from BODC doi:10/thr doi:10/sbz
Cefas/UKOA/PLACID	Naomi Greenwood	UK Seas	2010-2013	DIC/TA	Data available from BODC
PML/AMT	Andrew Rees, Vassilis Kitidis, Ian Brown	Atlantic	2012	DIC/TA/pCO_2/pH	Data available from BODC
NOCS	Susan Hartman Hartman *et al.* (2016)	North-East Atlantic	2011-2012	DIC/TA	Data available from BODC doi:10/bb89
SAHFOS	Clare Ostle Stevens (2014)	B-route North-East Atlantic	2008-2013	phytoplankton zooplankton	Data available from SAHFOS doi:10.7487/2014.44.1.10
PML/NEMO-ERSEM	Yuri Artioli (Madec (2008), Blackford *et al.* (2004); Butenschön *et al.* (2015))	North Western European Shelf	1990 - 2099	pH/Ωar	Data available form Yuri Artioli
ICES	ICES Historical pH dataset 2015. ICES, Copenhagen	North Western European Shelf	1984 - 2014	pH	Data available from ICES

Pathfinders Ocean Acidification project, lead by Jamie Shutler, provides a useful site for downloadable ocean acidification datasets here **www.pathfinders-oceanacidification.org**.



4. Conclusions

4.1 Concluding remarks

This report identifies many new observations of carbonate chemistry in UK waters, whilst also extending previously-existing time-series. These recent datasets greatly advance our understanding of the dynamic nature of CO_2 exchanges and ocean acidification from a national perspective, improving on the knowledge base available to Charting Progress 2.

The evidence presented for 2010 - 2015 is fully consistent with the global trend for ocean acidification, as driven by atmospheric CO_2. Nevertheless, the variability in conditions is now much better appreciated, both spatially (including with water depth) and temporally. Whilst there is consistent information from three UK time series (for L4, Stonehaven and SmartBuoys), no assumptions can necessarily be made that all UK waters will respond similarly, since other data sources, including from ship-based surveys, indicate significant spatial differences.

Further datasets are known to have been collected, and are currently being analysed. The future continuation of such measurements cannot be assumed, since there is no statutory requirement for such monitoring. Nevertheless, it is highly desirable that relevant, well-focussed data collection continues, not only in the context of OSPAR and MSFD Assessments, as identified, but also to address UN Sustainable Development Goal 14 (with target 14.3 *"to minimise and address the impacts of ocean acidification including through enhanced scientific cooperation at all levels"*) - and to test the effectiveness of the Paris Agreement in minimising such impacts, by slowing (and ideally, halting) future ocean acidification.

Five specific recommendations are made:

1. High-quality observations of ocean acidification should continue to be supported, with adequate resources for data analysis and interpretation, in view of the importance of such datasets in assessing local conditions and long-term changes.
2. Additional, non-UK datasets should be brought together with those presented here, to further improve our understanding of variability and its causes on a European scale, whilst also contributing to the wider global research effort.
3. Additional effort should be made to make seafloor measurements of ocean acidification at seasonally-stratified sites, including at habitats (e.g. coldwater corals) of high conservation value.
4. New sensors and platforms (gliders and profiling floats) currently under development should be further tested, and used to increase the cost-effectiveness and spatial coverage of UK ocean acidification measurements.
5. Future national modelling effort should include sea-floor conditions, and investigate the implications of emission scenarios consistent with the full and partial implementation of the Paris Agreement.

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