

Air–sea CO₂ exchange and ocean acidification in UK seas and adjacent waters

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EXECUTIVE SUMMARY

Ongoing anthropogenic emissions of carbon dioxide (CO₂) into the atmosphere are driving a net flux of CO₂ into the ocean globally, resulting in a decline in pH called ‘ocean acidification’. Here, we discuss the consequences of this for the seas surrounding the UK from a chemical perspective, focussing on studies published since the previous MCCIP review of ocean acidification research (Williamson *et al.*, 2017). In this reporting cycle, the biological, ecological, and socio-economic impacts of ocean acidification are considered in more detail in separate accompanying MCCIP reviews.

The atmospheric CO₂ concentration continues to increase due to human activities (Le Quéré *et al.*, 2018), increasing the net flux of CO₂ into the global ocean, including the North Atlantic and UK continental shelf seas. Such CO₂ uptake has the desirable effect of reducing the rate of climate change, but the undesirable result of ocean acidification. Our understanding of the factors that drive high spatial and temporal variability in air-sea CO₂ fluxes and seawater pH in UK waters has continued to improve, thanks to observational campaigns both across the entire North-West European continental shelf sea and at specific time–series sites. Key challenges for the future include sustaining time–series observations of near-surface marine carbonate system variables, and of the auxiliary parameters required for their interpretation (e.g. temperature, salinity, and nutrients); developing and deploying new sensor technology for full water-column profiles and pore waters in seafloor

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sediments; and increasing the spatial and temporal resolution of models sufficiently to capture the complex processes that dominate the marine carbonate system in coastal and shelf sea environments, along with improving how those processes are themselves simulated.

1. WHAT IS ALREADY HAPPENING

Processes and drivers

CO₂ uptake and acidification

The average atmospheric carbon dioxide (CO₂) concentration now exceeds 400 parts per million (ppm), with an increase of about 2.3 ppm each year over the past decade (Blunden and Arndt, 2017; WMO, 2018). This ongoing growth is primarily due to CO₂ release by fossil fuel combustion, land-use change and industrial activities (IPCC, 2013). About a quarter of this annual anthropogenic CO₂ emission dissolves into the Earth's oceans each year (Le Quéré *et al.*, 2018). Once dissolved, the CO₂ no longer influences the Earth's heat budget, so this oceanic uptake mitigates human-driven climate change. However, dissolved (or aqueous) CO₂ undergoes a chemical reaction that releases hydrogen ions (H⁺), thereby decreasing the seawater's pH (decreasing basicity). As pH declines, so too does the carbonate ion concentration ([CO₃²⁻]; Figure 1). The [CO₃²⁻] controls the saturation states (Ω) of calcium carbonate (CaCO₃) minerals such as aragonite and calcite; a reduction in [CO₃²⁻] lowers the Ω values, making these minerals more prone to dissolution, and requiring more energy to construct them. These chemical changes are known as 'ocean acidification'. Ocean acidification has negative impacts on many marine species, in particular those that build their skeletons from CaCO₃ such as corals, shellfish, and several important groups of plankton (Doney *et al.*, 2009; CBD, 2014), with adverse consequences for ecosystems and the services they provide (Hoegh-Guldberg *et al.*, 2017; Hurd *et al.*, 2018). Furthermore, ocean acidification reduces the chemical capacity of seawater to take up further CO₂ in the future.

Drivers of air-sea CO₂ fluxes

Overlying the long-term global trend of net oceanic CO₂ uptake, the direction and magnitude of air–sea CO₂ exchange vary geographically and seasonally (Takahashi *et al.*, 2014). The flux direction is controlled by the seawater's CO₂ 'fugacity' (*f*CO₂) relative to that of the atmosphere. Net transport of CO₂ from air to the surface ocean is favoured by processes that reduce seawater *f*CO₂, such as cold temperatures, which increase CO₂ solubility, and biological production (photosynthesis), which converts DIC into organic matter, thus 'creating space' for further CO₂ uptake from the atmosphere (Humphreys *et al.*, 2018). Outgassing of CO₂ (i.e. net sea-to-air transfer) also occurs in several ocean regions, and is favoured by processes that increase seawater *f*CO₂, such as: warming temperatures, upwelling of CO₂-rich deep waters into the surface ocean, and biological respiration and decomposition of organic matter.

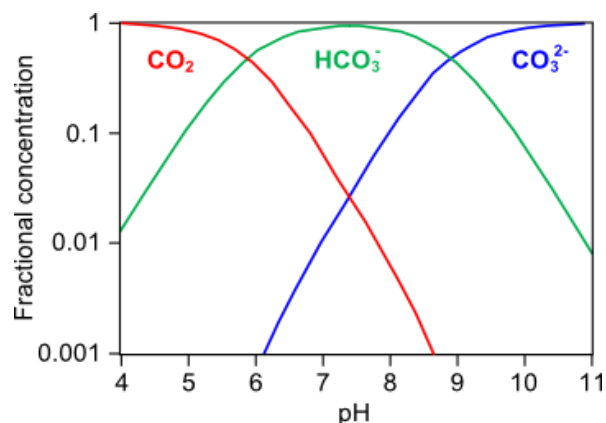


Figure 1.: Relationship between seawater pH and the relative concentrations of the constituents of Dissolved Inorganic Carbon (DIC): aqueous CO₂, bicarbonate ions (HCO₃⁻) and carbonate ions (CO₃²⁻). At typical seawater pH, a little over 8, about 90% of DIC is in the bicarbonate form, ~10% is carbonate, and <1% is aqueous CO₂. Adding more CO₂ increases its relative concentration, shifting the system to lower pH, and thus decreases the abundance of carbonate ions. (Redrawn from Raven *et al.*, 2005.)

Biological processes are the dominant control on seasonal cycles of air-sea CO₂ exchange in temperate and polar regions, leading to CO₂ uptake in the productive spring and summer months, and outgassing or equilibrium with the atmosphere during the winter. Temperature is a more-important control in the tropics and subtropics, leading to a roughly opposite seasonal pattern for seawater *f*CO₂ there (high in summer, lower in winter), with a smaller amplitude (Takahashi *et al.*, 2009; Fay and McKinley, 2017).

The rate-limiting step for oceanic CO₂ uptake overall is transfer from the surface ocean into the deep interior. Equilibration of CO₂ between the atmosphere and surface mixed layer occurs on timescales of the order of a year (Jones *et al.*, 2014). Mixing the CO₂ deeper into the ocean takes orders of magnitude longer, and is facilitated by carbon ‘pumps’ (Volk and Hoffert, 1985): these include the solubility pump, where CO₂ is taken up in cold, high-latitude waters and transferred into the interior through the thermohaline circulation; and the biological pump, where organic matter – formed in the surface ocean – sinks, and is converted back into DIC at depth (Giering and Humphreys, 2018).

Previous MCCIP reviews

The oceanic uptake of CO₂, and associated process and impacts of ocean acidification, were described in MCCIP reports in 2006, 2007–2008, 2010–2011, and 2013. A decadal overview (Williamson *et al.*, 2017) included synthesis information from the Intergovernmental Panel on Climate Change 5th Assessment Reports (IPCC, 2013, 2014a, b). New developments since those reviews are covered here, with focus on the drivers and progression of ocean acidification, and changing air–sea CO₂ fluxes, in the waters surrounding the UK. For the current MCCIP reporting cycle, the biological

impacts of ocean acidification are considered in detail in separate background papers.

Open ocean

Regardless of where it is emitted, anthropogenic CO₂ is mixed throughout the Earth's atmosphere by wind and weather. The increasing CO₂ uptake by the oceans, and, corresponding pH decline, are therefore global phenomena (McKinley *et al.*, 2017). Landschützer *et al.* (2016) mapped global surface ocean *f*CO₂ from 1982 to 2011 using a neural network approach. They found that the annual global net oceanic CO₂ sink was variable on decadal timescales, with a range from about 0.8 to 2.0 Gt of carbon per year (1 Gt = one thousand million tonnes). Changing patterns of sea surface temperature, themselves likely to be a consequence of climate change, were shown to drive an important component of this variability. Over a similar time period, the magnitude of the seasonal cycle of sea surface *f*CO₂ also increased, driven by stronger seasonal cycles in *f*CO₂ drivers (e.g. temperature), and augmented by the lower chemical buffer capacity of seawater at higher *f*CO₂ due to ocean acidification (Landschützer *et al.*, 2018). In the Atlantic Ocean, surface ocean measurements from Atlantic Meridional Transect (AMT) cruises between 1995 and 2013 revealed a pH decline at a rate of $0.0013 \pm 0.0009 \text{ yr}^{-1}$, corresponding to a growth in seawater *f*CO₂ of $1.44 \pm 0.84 \mu\text{atm yr}^{-1}$, (Kitidis *et al.*, 2017a). These changes are consistent with the atmospheric CO₂ increase, indicating that there was no major change in the net CO₂ sink for the Atlantic as a whole during the observation period, integrated over the variety of different marine environments sampled.

The North Atlantic contains more anthropogenic CO₂ than any other ocean basin, due to the deep-water formation there that effectively transfers CO₂ from the surface into the ocean interior (Sabine *et al.*, 2004; Khatiwala *et al.*, 2013). This result has been independently confirmed by recent studies (Eide *et al.*, 2017; Clement and Gruber, 2018), which have also improved the accuracy of our calculations of the total inventory of anthropogenic CO₂ in the global ocean, and provided a better understanding of the uncertainty in these estimates. Focussing on the north-eastern subpolar North Atlantic, as sampled by the Extended Ellett Line transect between Scotland and Iceland (Holliday and Cunningham, 2013), changes in water mass distributions – driven ultimately by atmospheric variability (Pérez *et al.*, 2010) – have increased the DIC inventory three times faster than expected from the atmospheric CO₂ increase (Humphreys *et al.*, 2016). If sustained, these changes could reduce the amount of anthropogenic CO₂ that can be taken up by the north-east North Atlantic in the future, whilst also accelerating regional ocean acidification.

While North Atlantic deep-water formation is climatically beneficial in terms of exporting CO₂ from the surface into the interior ocean, Perez *et al.* (2018) showed that it also causes ocean acidification at depth. Furthermore,

increasing vertical stratification in response to global climate change has also been shown to decrease deep water pH in some regions (Chen *et al.*, 2017). The consequences of ocean acidification are therefore no longer restricted to the surface ocean, but are also beginning to impact marine species and ecosystems at greater depths, such as cold-water coral reefs (CBD, 2014; Hoegh-Guldberg *et al.*, 2017).

High resolution, autonomous seawater $f\text{CO}_2$ measurements from a UK mooring at the Porcupine Abyssal Plain Sustained Observatory (PAP-SO) in the North-East Atlantic (49°N, 16.5°W) have confirmed that the net air–sea CO₂ flux is controlled by a combination of interacting physical and biological processes (Hartman *et al.*, 2015). Vertical profiles collected at PAP-SO show a typical pattern of lower pH at greater depths (Figure 2). This emphasises how changes in ocean circulation, such as vertical mixing events, could bring high-carbon, low-pH deep waters into the surface layer, thus lowering its pH and reducing the net oceanic CO₂ uptake. These low-pH deep waters also have relatively low Ω values, so their addition to the surface ocean could also hinder calcification and enhance CaCO₃ dissolution.

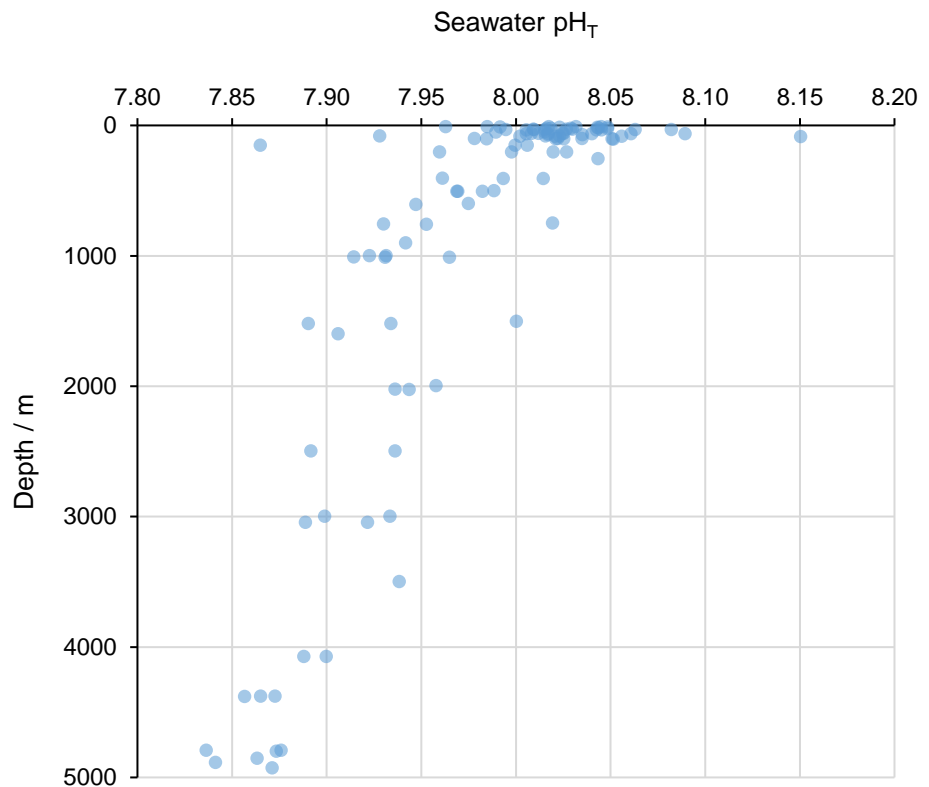


Figure 2: The vertical pH (Total scale) profile at the Porcupine Abyssal Plain Sustained Observatory (PAP-SO) in the North-East Atlantic (49°N, 16.5°W) in April 2016 (S. Hartman, unpublished data) shows the typical pattern of decreasing pH with depth.

Continental shelf seas

The seawater chemistry in shallow (< 200 m) continental shelf seas like those surrounding the UK is generally more variable in space and time than in the open ocean, as it is driven by a more complex set of processes (including terrestrial influences) operating on smaller scales. This requires observations to be carried out closer together and more frequently in order to characterise the magnitude of natural variability and determine long-term trends with the same level of confidence as for the deep open ocean. Efforts to interpolate continuous maps of surface seawater $f\text{CO}_2$ from sparse observations have therefore only recently begun to include continental shelf seas, for example using machine-learning techniques to construct computer-based ‘neural networks’ that can infer the surface ocean carbonate chemistry (Laruelle *et al.*, 2017), or using multi-linear regressions with variables expected to covary with seawater $f\text{CO}_2$ (Marrec *et al.*, 2015). These and other similar studies have shown that globally, continental shelf seas – similar to the open ocean (Landschützer *et al.*, 2016) – absorb a variable, but increasing, amount of CO₂ from the atmosphere (Laruelle *et al.*, 2018).

The Surface Ocean CO₂ Atlas (SOCAT; Bakker *et al.*, 2014) of surface seawater $f\text{CO}_2$ measurements has formed the basis of many air–sea CO₂ exchange studies (e.g. Laruelle *et al.*, 2017, 2018; Landschützer *et al.*, 2018). The SOCAT dataset for the seas surrounding the UK has also continued to expand in recent years (Figure 3). Although there are inevitably gaps in the coverage, different seasonal cycles can be identified in different regions. For example, strong depletion of $f\text{CO}_2$ is observed in the Celtic Sea (south of Ireland) during the spring and summer months (Figure 3b, c), as biological activity transfers CO₂ from the stratified surface layer into deeper waters. However, the southern bight of the North Sea (to the east of the southern UK) retains relatively high $f\text{CO}_2$ values throughout the year, since the water column in this relatively shallow (< 50 m) area does not stratify (Thomas *et al.*, 2004).

The UK Ocean Acidification research programme (UKOA) expanded our marine carbonate system data coverage around the UK and in adjacent waters. The additional data coverage helped to understand the equilibrium chemistry of dissolved CO₂ in this region (Ribas-Ribas *et al.*, 2014). Following from UKOA, the UK Shelf Sea Biogeochemistry research programme (SSB) has further added to the carbonate chemistry dataset available for this region (Figure 4; Hartman *et al.*, 2019; Humphreys *et al.*, 2019). As a result, we are now able to more accurately constrain air–sea CO₂ fluxes across the North-West European shelf and the associated changes in seawater pH and other carbonate chemistry parameters, building on previous knowledge summarised by Ostle *et al.* (2016). Detailed assessments of how physical and biological processes combine to enable CO₂ uptake in the North Sea (Clargo *et al.*, 2015) can therefore now be extended to other parts of the shelf, particularly the Celtic Sea. The SSB programme also investigated how seafloor sediments modify the carbonate chemistry in their pore waters and

exchange this with the overlying water column, further modulating changes in the marine carbonate system driven by atmospheric exchange (Kitidis *et al.*, 2017b; Silburn *et al.*, 2017).

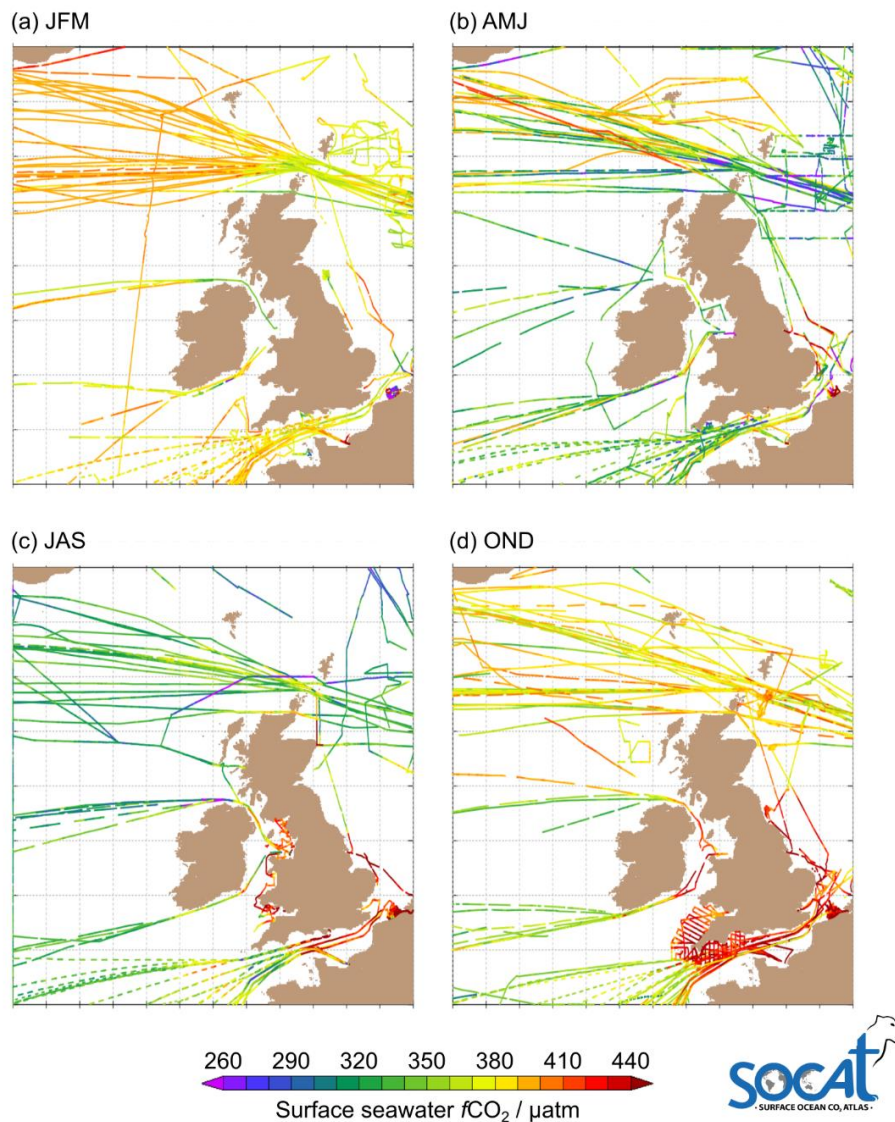


Figure 3: Seasonal measurements of surface seawater $f\text{CO}_2$ near the UK from 2010 to 2016 in the SOCAT version 5 dataset (Bakker *et al.*, 2016): (a) January to March (JFM), (b) April to June (AMJ), (c) July to September (JAS), and (d) October to December (OND).

It is well established that a ‘continental shelf pump’ for CO₂ operates in the North Sea (Thomas *et al.*, 2004); this means that the relatively high biological productivity there imparts extra CO₂ to Atlantic waters circulating through the area, thus aiding overall oceanic uptake of CO₂ from the atmosphere. One aim of the SSB research programme (Figures 4–5) was to assess whether a similar mechanism operates in other parts of the shelf, such as the Celtic Sea.

This would be expected given observed annual net CO₂ uptake across the air-sea interface (Marrec *et al.*, 2015). The presence of a continental shelf pump mechanism also raises the question of nutrient supply: we would expect a net flux of CO₂ off the shelf to be accompanied by additional nutrient loss, which cannot be replenished through atmospheric interactions. SSB observations over the course of a full annual cycle showed that the Celtic Sea CO₂ and nutrient cycles were not in steady state over this period, with different total inventories from one winter to the next (Humphreys *et al.*, 2019). Consequently, a full understanding of how the nutrient supply is sustained may require several years of observations, particularly during winter months when the shelf waters are well mixed, such that this interannual variability can be resolved.

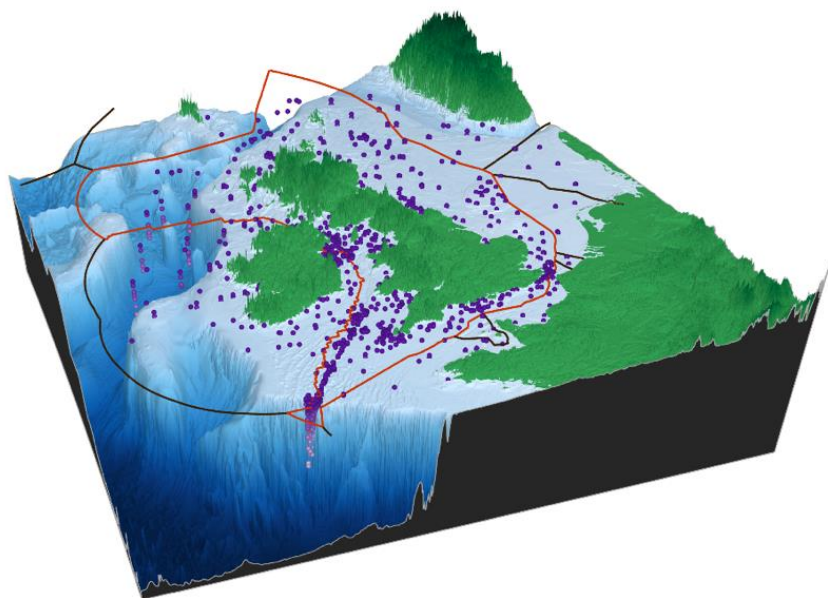


Figure 4: Purple dots show the extensive new observations of seawater CO₂ chemistry collected during the UK Shelf Sea Biogeochemistry research programme. The lines show major national maritime boundaries, with that of the UK highlighted in red.

Data from observational programmes like UKOA and SSB cover a wide spatial area but are relatively restricted in time. They can therefore be augmented by repeated observations at single-point time-series sites. For example, measurements from the L4 time-series site near Plymouth (Cummings *et al.*, 2015) have indicated an almost doubling of the amplitude of the pH seasonal cycle from 2009 to 2014 (Figure 5d). This dataset does not go back far enough for a detailed analysis of the causes of this effect, nor its implications for marine ecosystems; nevertheless, it does match the global increase in seawater *f*CO₂ seasonality reported by Landschützer *et al.* (2018). While an increase in the seasonal amplitude of variables like pH is typically considered to be of concern to the local marine biota, as they will be exposed and forced to adapt to a greater range of chemical conditions, it is important

to recognise that changes in the seasonal cycling of different components of the marine carbonate system (e.g. pH, hydrogen ion concentration, and CaCO₃ mineral saturation states) may vary from each other (Kwiatkowski and Orr, 2018). It is therefore essential to determine exactly which variable directly drives any biological responses to ocean acidification if we are to accurately project its future impacts.

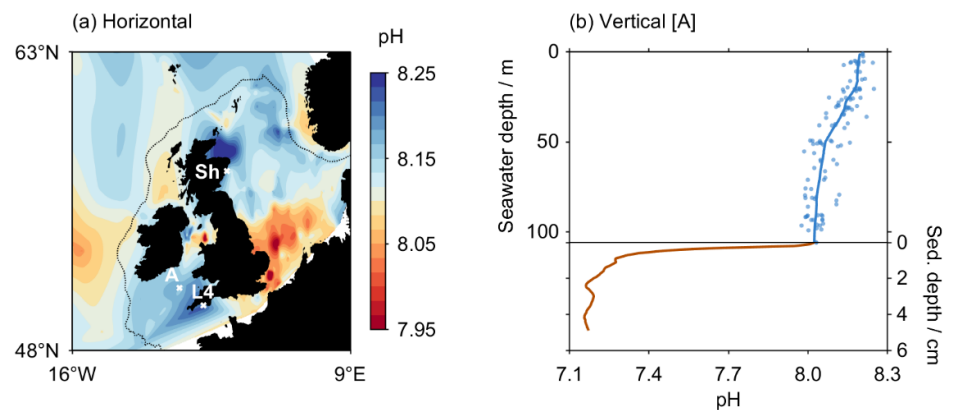


Figure 5: Recent observations of pH (Total scale, derived from DIC and TA using CO₂Sys version 1.1) and its variability in the northwest European continental shelf sea. (a) July–August data, showing strong horizontal gradients in surface layer pH. The dashed black contour (at 200 m depth) marks the edge of the shelf sea. Locations of sampling sites A, L4 and Stonehaven (Sh) are labelled. Data from the Shelf Sea Biogeochemistry (SSB) research programme (Hartman et al., 2019; Humphreys et al., 2019) and the GLODAPv2 data compilation (Olsen et al., 2016). (b) Site A in summer in the Celtic Sea shows vertical changes in pH in the water column and underlying sediment. Data from SSB (Silburn et al., 2017).

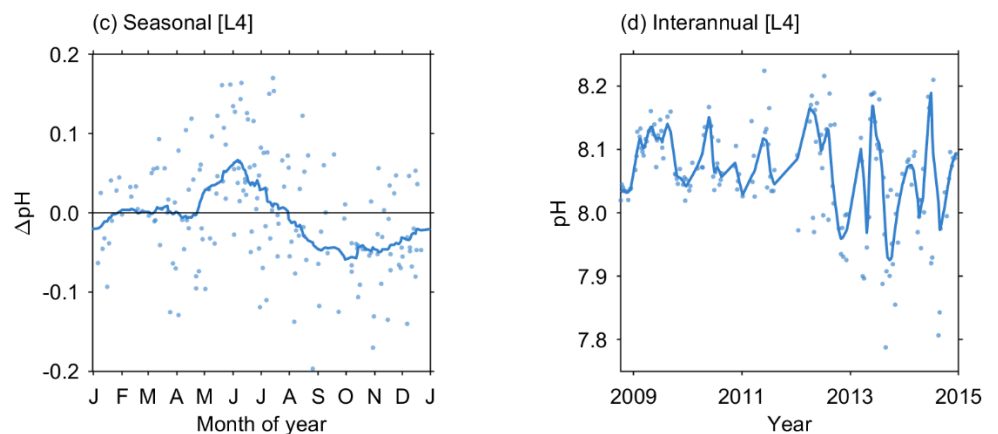


Figure 5 – contd. (c) Time-series observations at site L4 off Plymouth reveal a strong seasonal cycle in surface layer pH. All data from 2009 to 2015 are shown, normalised to each year's annual mean pH (Cummings et al., 2015). (d) The strength of the seasonal cycle in surface layer pH at L4 appears to have increased over the period measured, and the seasonal pattern varies from year to year. The mean pH has decreased over the same time period.

Stonehaven

The Scottish coastal observatory site at Stonehaven in the north-west North Sea (57.0°N, 2.1°W) is about 5 km offshore from north-east Scotland in a water depth of *c.* 50 m. Hydrographic observations at Stonehaven from 1997 onwards were more recently augmented by carbonate system and auxiliary measurements carried out from 2009 to 2013 inclusive (León *et al.*, 2018). These measurements revealed an overall decline in annual mean seawater pH of up to 0.1 during this period. This pH decrease was observed consistently across the entire depth of the water column (Figure 6). The changes were more pronounced during from March to August, with pH values more consistent from year to year from September to February.

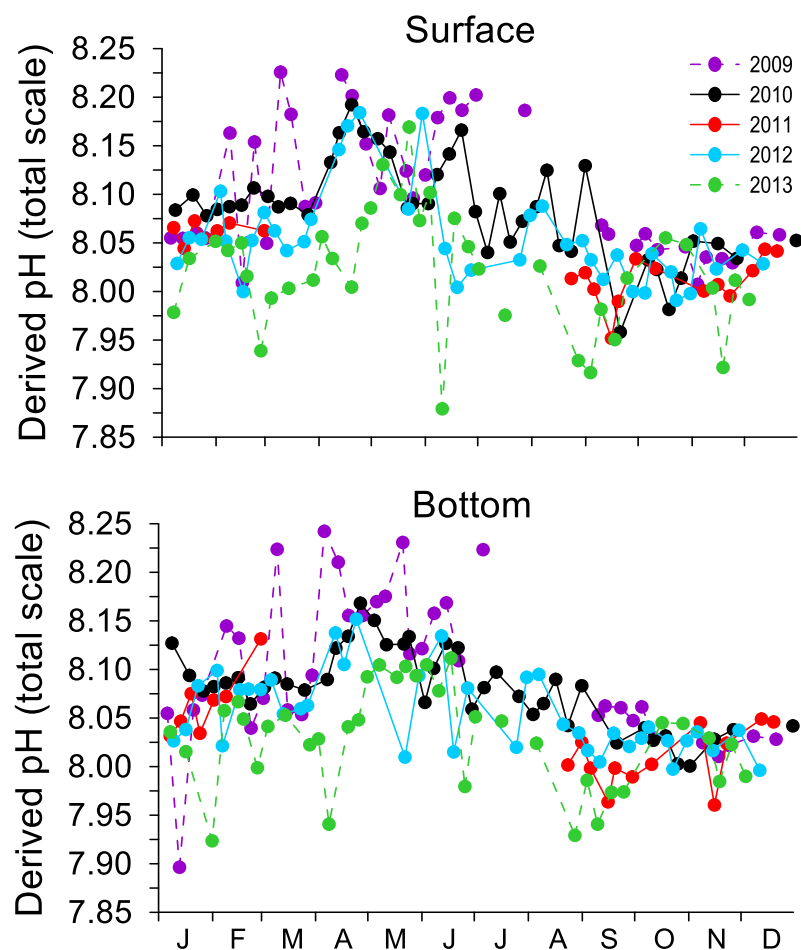


Figure 6: Calculated seawater pH (Total scale, derived from DIC and TA using CO2SYS XLS version 2.1) at Stonehaven (57.0°N, 2.1°W) from 2009 to 2013 (León *et al.*, 2018). The surface layer (1 m depth) and bottom (45 m depth) measurements are shown in the top and bottom panels respectively. The top panel (surface) shows the same dataset as Figure 7c. Horizontal axis shows month of year.

The measurements at Stonehaven were of sufficient temporal resolution (i.e. weekly) to reveal seasonality in pH and its chemical drivers (Figure 7). The long-term change in the annual mean pH (*c.* 0.02 / yr) is superimposed upon

seasonal variability with a range as high as 0.3 within each individual year. The pH increase from April to June (Figure 7c) was primarily driven by a corresponding decline in DIC (Figure 7a), itself caused by biological CO₂ uptake during the spring phytoplankton bloom. The modest increase in Total Alkalinity (TA) from February to May could also be responsible for part of the increase in pH, as increased TA improves the ability of seawater to chemically buffer CO₂-driven pH changes (Egleston *et al.*, 2010; Humphreys *et al.*, 2018). Temperature can also act as an important control on seawater pH, with warming during the summer months leading to elevated pH values (Humphreys, 2017).

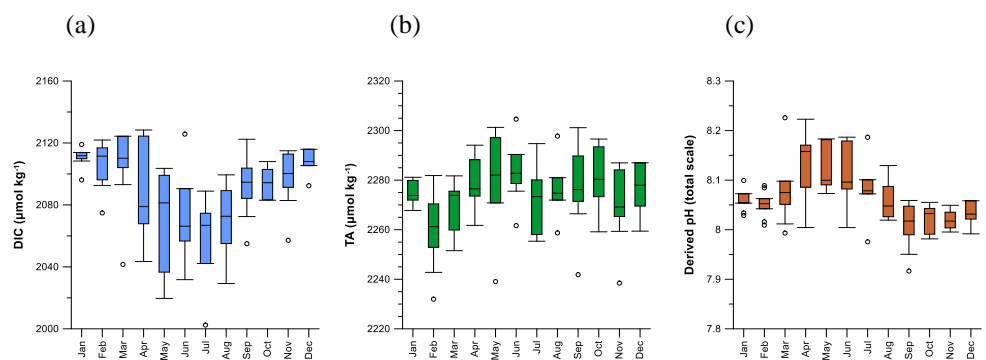


Figure 7: Box plots showing the seasonal cycles of (a) measured dissolved inorganic carbon (DIC), (b) measured total alkalinity (TA) and (c) calculated pH (Total scale), all at 1 m depth at Stonehaven (57.0°N, 2.1°W) from 2009 to 2013 (León *et al.*, 2018). Panel (c) shows the same dataset as the top panel in Figure 6.

Low-salinity waters

In near-coastal waters, such as low-salinity estuaries, a number of simplifying assumptions that are made when performing chemical calculations and analyses in ‘normal’ open ocean seawater may no longer apply (Turner *et al.*, 2016). For example, the chemical behaviour of buffer solutions that are used to calibrate pH meters (e.g. tris, *m*-cresol purple) is poorly understood at low and intermediate salinities. The chemical equilibrium constants governing the oceanic CO₂ uptake and magnitude of pH change can also be different in these environments. A more-complex, less empirical approach such as Pitzer modelling is therefore required (Pierrot and Millero, 2017). Laboratory measurements to characterise the chemical behaviour of the pH buffer solutions at low and intermediate salinities are ongoing (Müller *et al.*, 2018; Müller and Rehder, 2018), but more are still required, and the uncertainties in chemical equilibrium constants are not yet well understood.

2. WHAT COULD HAPPEN IN THE FUTURE?

Previous MCCIP report

The many studies on the potential future impacts of continuing CO₂ increases on air-sea exchange and ocean acidification have been assessed by the Intergovernmental Panel on Climate Change (IPCC, 2013; 2014a, b). The IPCC findings were considered in detail by the previous MCCIP report on ocean acidification (Williamson *et al.*, 2017); however, they were not UK-specific.

Modelling results

The following figures and discussion are based on modelling results from the Regional Ocean Acidification Modelling (ROAM) component of the UK Ocean Acidification (UKOA) research programme. ROAM used a coupled physical-ecosystem model to project future pH and aragonite saturation state across the north-west European shelf sea. The circulation model was the Nucleus for European Modelling of the Ocean (NEMO; Madec, 2008), which includes a wide range of processes considered important in the shelf environment (e.g. tidal currents, variable sea surface height). NEMO was coupled to the European Regional Sea Ecosystem Model (ERSEM; Blackford *et al.*, 2004; Butenschön *et al.*, 2016), which has been widely used to study ecosystem dynamics and the impacts of climate change and ocean acidification (e.g. Holt *et al.*, 2012; Artioli *et al.*, 2014; Wakelin *et al.*, 2015). The ERSEM carbonate system module has been validated against observational data for this domain (Artioli *et al.*, 2012). The model was forced with data characteristic of the IPCC AR5 Representative Concentration Pathway (RCP) 8.5, as simulated by the UK Met Office HADGEM model. RCP 8.5 describes a possible climate scenario based on continued high greenhouse gas emissions (Riahi *et al.*, 2011). As such, these results could be considered to represent a ‘worst case’ scenario.

The ROAM model projects pH decreasing at a mean rate of 0.0036 / yr, leading to a drop in mean pH across the shelf of about 0.366 from the present day to the year 2100 (Figure 8). Significant spatial variability in the rate of pH decline is projected, with changes as fast as 0.005 / yr in some coastal areas like the Bristol Channel and the West coast of Denmark, and as slow as 0.002 / yr in the Celtic Sea.

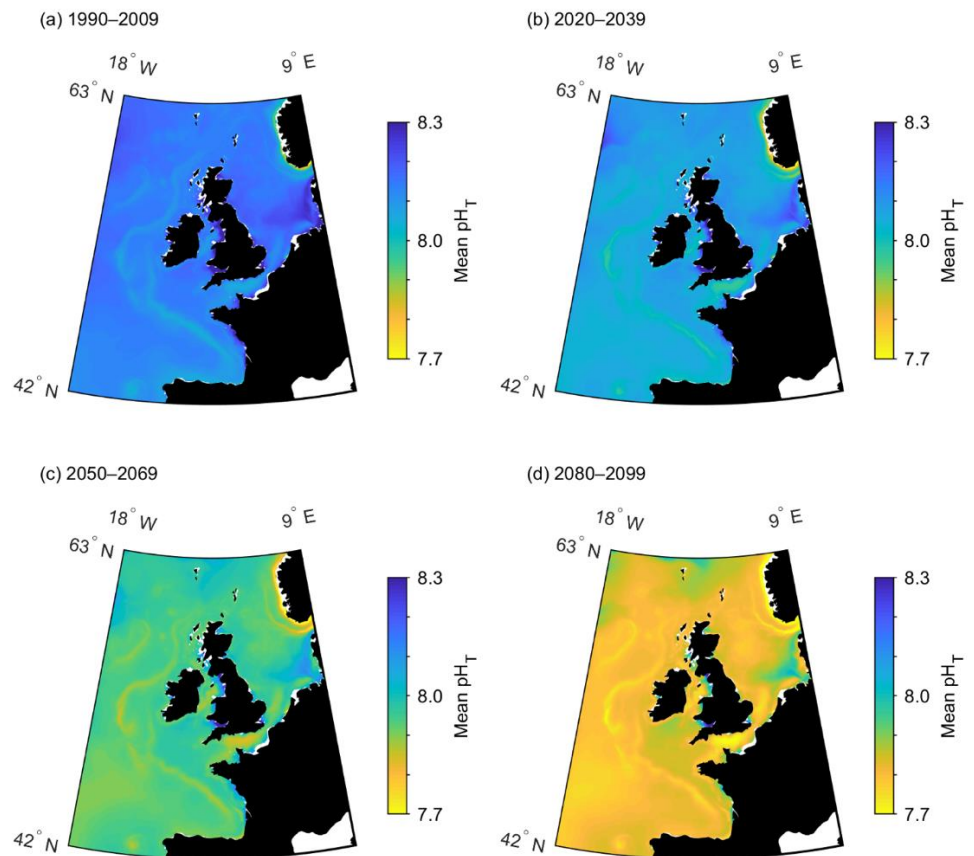


Figure 8: Average surface water pH (Total scale, pH_T) from (a) 1990 to 2009, (b) 2020 to 2039, (c) 2050 to 2069, and (d) 2080 to 2099, modelled for a high CO₂ emissions scenario (RCP 8.5). Unpublished data from ROAM (Y. Artioli and S. Wakelin).

The projected spatial patterns of surface CaCO₃ mineral saturation states matches that for pH (Figure 9). The ROAM model projects aragonite undersaturation of surface waters in the Norwegian Current towards the end of this century. However, the uncertainty in projections for this region is relatively high due to the strong influence of water influxes from the Baltic Sea, which are poorly constrained.

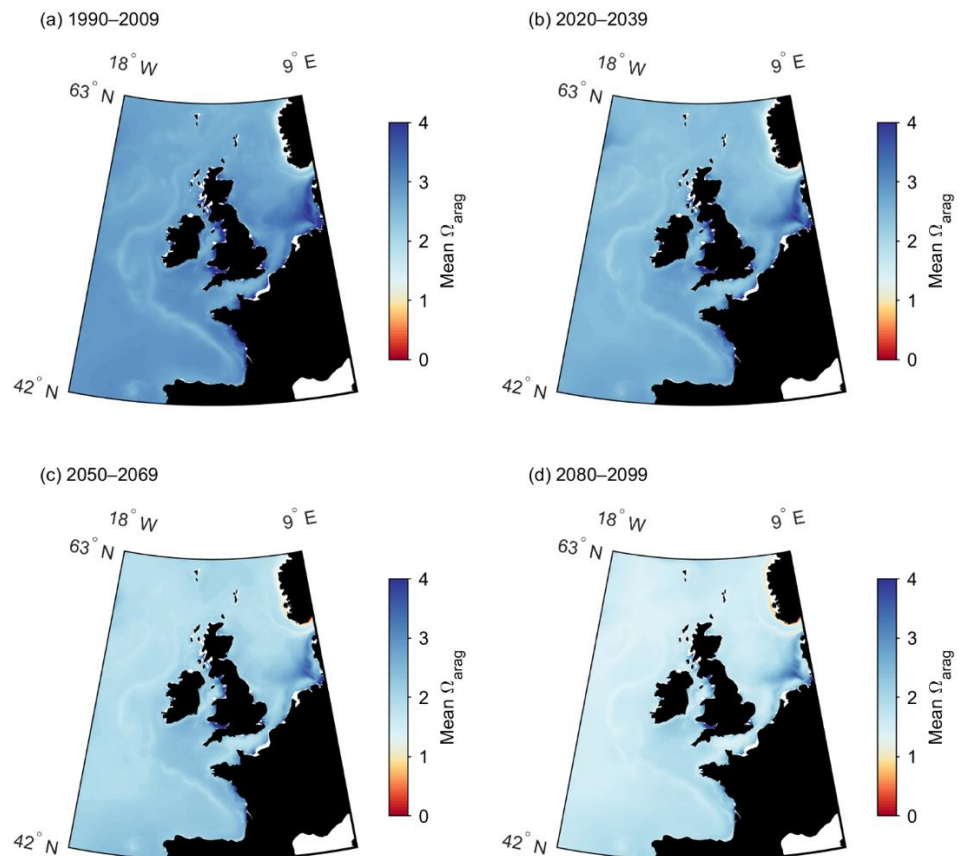


Figure 9: Projected mean surface water aragonite saturation state (Ω_{arag}) from (a) 1990 to 2009, (b) 2020 to 2039, (c) 2050 to 2069, and (d) 2080 to 2099, modelled for a high CO₂ emissions scenario (RCP 8.5). Unpublished data from ROAM (Y. Artioli and S. Wakelin).

Aragonite undersaturation in bottom waters is also projected by 2100 under the RCP 8.5 scenario (Figure 10), particularly during the summer, and in areas with strong seasonal water column stratification, such as the northern North Sea (Artioli *et al.*, 2014). The first episodic undersaturation events are projected to begin by 2030, and to then become a recurrent but spatially restricted feature from the middle of this century. Undersaturation is projected to increase significantly in 2070–2080 to become a widespread phenomenon by the end of the century, when up to 20% of the North-West European Shelf seas may experience undersaturation for at least one month of each year.

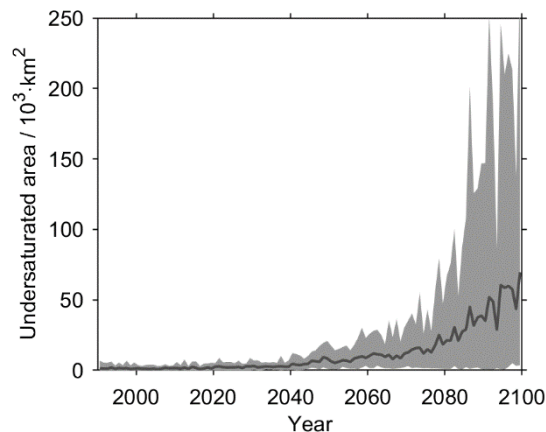


Figure 10: Projected area of the North-West European Shelf seafloor covered by water undersaturated with respect to aragonite, under a high CO₂ emissions scenario (RCP 8.5). The line is at annual resolution, while the shaded area shows the range of monthly mean values. Unpublished data from ROAM (Y. Artioli and S. Wakelin).

The long-term trends in annual mean surface pH and seawater $f\text{CO}_2$ in the shelf seas are projected to be very similar to those for the open ocean (Figure 11). This highlights that the major driver of these changes is the ongoing increase in atmospheric $f\text{CO}_2$. Although the annual mean trends are similar, seasonal biogeochemical variability within the shelf sea is greater than in the open ocean, and the magnitude of this variability is projected to increase due to greater warming on the shelf (Holt *et al.*, 2012). In general, warming of seawater increases pH and carbonate mineral saturation states, whilst CO₂ addition decreases them, with the latter effect being dominant in driving the overall change in seawater chemistry (Humphreys, 2017). On a global scale, a separate model has shown that changes in the seasonal cycling of these marine carbonate system variables may be decoupled from each other, and different in different regions (Kwiatkowski and Orr, 2018).

Overall, the long-term trend in the marine carbonate system variables are projected to be similar in the shelf sea as in the adjacent open ocean (Figures 8 and 9). However, the amplitude of seasonal cycles in pH and other system variables is projected to increase to a greater extent in the European Shelf seas (Figure 11), leading them to experience a wider and more variable range of chemical conditions towards the end of the century.

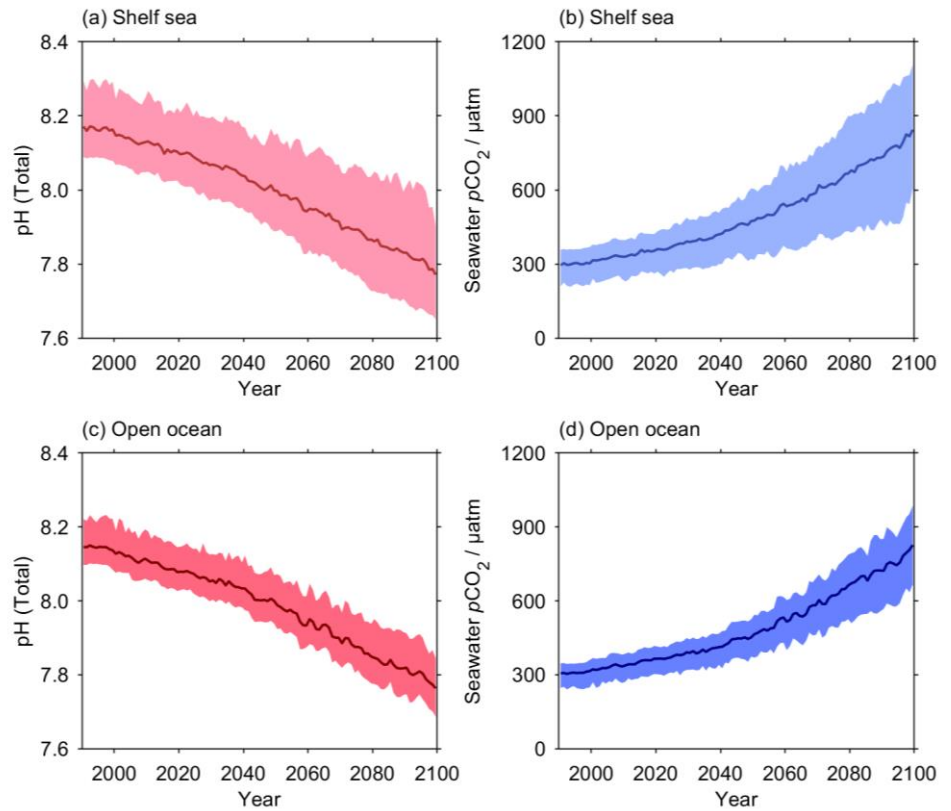
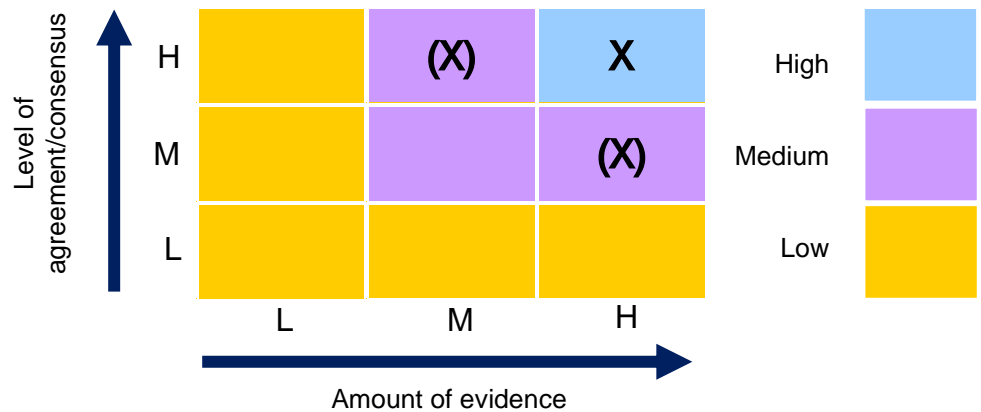


Figure 11: Left panels: projected temporal evolution of mean surface water pH (a) in the North-West European continental shelf, and (c) in the open ocean region shown in Figures 8 and 9. Right panels: projected temporal evolution of mean surface seawater pCO₂ (b) on the shelf, and (d) in the open ocean. The lines show annual mean values, while the shaded areas show the ranges of monthly mean values, all under a high CO₂ emissions scenario (RCP 8.5). Unpublished data from ROAM (Y. Artioli and S. Wakelin).

3. CONFIDENCE ASSESSMENT

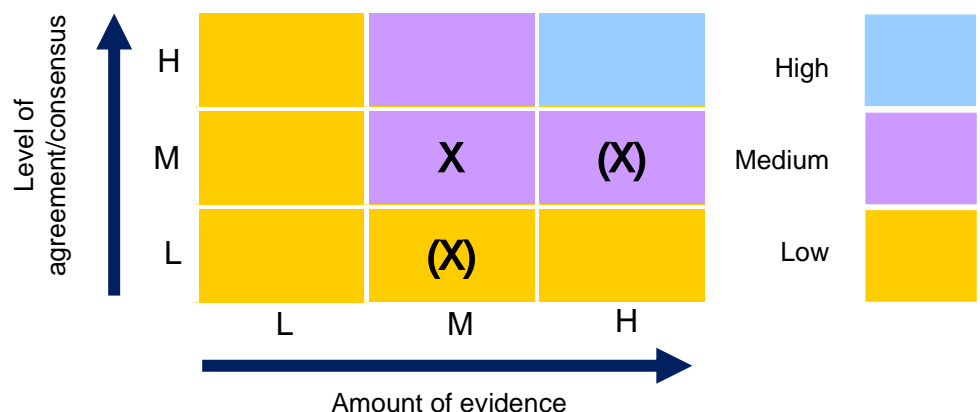
What is already happening?



As shown in the above schematic, it is not easy to give a single confidence value to ‘what is already happening’, since different considerations apply to the different aspects discussed in this review. It is more meaningful for a ‘confidence’ rating to be expressed in relation to a specific statement (e.g. as used by IPCC), than for a relatively wide topic area. The fundamental chemistry underlying air–sea CO₂ exchange and the pH decline that results from anthropogenic CO₂ uptake is very well established. The seasonal cycles and spatial patterns in the ocean regions that relatively easy to access by traditional ship-based expeditions are well-constrained and their main drivers understood, having been investigated by a multitude of independent techniques with concordant results. For those reasons, a high confidence level overall can be justified for ‘Air–sea CO₂ exchange and ocean acidification in UK seas and adjacent waters’, based on both high agreement and high evidence.

However, there are still significant knowledge gaps for shelf sea carbonate chemistry, including many of the factors affecting local and short-term variability. Furthermore, in regions where historically sampling has been more restricted (like the remote, wind-swept and ice-affected Southern Ocean) there are significant differences between ship-based flux maps and new datasets from autonomous platforms. As these occur only in regions where the ship-based flux maps had no real data to work from (and were therefore extrapolating rather than interpolating) this is not a true disagreement but rather it highlights the need to keep developing these autonomous sensing technologies, and running manually or semi-autonomously sampled observational time-series so their datasets can be validated.

What could happen in the future?



As above, it is not easy to give a single confidence value to ‘what could happen in the future’: different considerations apply to different aspects, and there are additional inherent uncertainties relating to societal behaviour. In particular, whether the national greenhouse gas emission reductions already committed under the Paris Agreement will not only be implemented, but

further strengthened – in order to stabilise atmospheric CO₂ at levels that keep global warming ‘well below 2.0°C’.

There is very high confidence in the first order expectation that global mean seawater pH and saturation states of carbonate minerals will decrease in response to increasing atmospheric CO₂. However, specific details of regionally resolved decadal trends and changes in interannual and seasonal variability are less certain, because they are emergent properties of a complex, interactive array of drivers. An important uncertainty in the modelling results presented here is how closely our actual greenhouse gas emissions will follow the trajectory anticipated by different IPCC scenarios. RCP 8.5 is used here as the ‘business as usual’ scenario; RCP 2.6 is arguably now more relevant, but was not explored by the ROAM study. Since there are no other closely similar, high resolution models for UK waters, the overall confidence level is at best ‘medium’, and possibly ‘low’.

The high importance of relatively small-scale processes in near-coastal environments adds uncertainty to model results for these regions that are gradually being reduced by improving the spatial and temporal resolution at which simulations are carried out, as well as further developing the representations of biogeochemical processes that are employed within the models.

4. KEY CHALLENGES AND EMERGING ISSUES

Three of the most important challenges that need to be addressed in order to provide better advice to policy makers are:

1. Sustaining time–series observations of the marine carbonate system at key point sites and transects, and improving high resolution monitoring of the near-coastal marine environment;
2. Developing accurate and stable autonomous observing technologies for pH and related variables, deploying them in difficult-to-sample regions, and linking and analysing their measurements effectively with other data streams;
3. Improving the spatial and temporal resolution of models, along with their descriptions of biogeochemical processes, to capture the relatively small-scale controls on the marine carbonate system in complex coastal and shelf sea environments.

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