

Ocean acidification

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KEY HEADLINES

- Global-scale patterns and processes of ocean acidification are superimposed on other factors influencing seawater chemistry over local to regional space scales, and hourly to seasonal time scales.
- Future ocean conditions will depend on future CO₂ emissions; there is now international agreement that these should be reduced to net zero, thereby reducing the consequences of both climate change and ocean acidification.
- Assessments of ocean acidification by the Intergovernmental Panel on Climate Change (IPCC) gave high or very high confidence to chemical aspects, but a much wider range of confidence levels to projected biological and biogeochemical impacts. Biotic impacts will depend on species-specific responses, interactions with other stressors and food-web effects.
- Previous MCCIP statements are considered to still be valid, with increased confidence for some aspects.
- Observed pH decreases in the North Sea (over 30 years) and at coastal UK sites (over 6 years) seem more rapid than in the North Atlantic as a whole. However, shelf sea and coastal data sets show high variability over a range of timescales, and factors affecting that variability need to be much better understood.
- UK research on ocean acidification has been productive and influential. There is no shortage of important and interesting topic areas that would improve scientific knowledge and deliver societally-important outcomes.

1. INTRODUCTION

The global-scale changes in seawater chemistry known as ocean acidification have potentially serious consequences for organisms, ecosystems and society. Ocean acidification is not strictly a climate change impact, but does have a crucial commonality with other large-scale perturbations that are occurring in the ocean, such as warming of the waters around the UK and Europe, and changes in North Atlantic circulation. All these processes share the same global driver: the continued atmospheric build-up of the main greenhouse gas, carbon dioxide (CO₂), resulting from human activities.

Atmospheric levels of CO₂ have increased from pre-industrial values of 280-300 ppm to average values now exceeding 400 ppm (Betts *et al.*, 2016). If future emissions are unconstrained, CO₂ levels are projected to reach ~1000 ppm by 2100; however, ~450 ppm is considered the upper limit to achieve the goals of the Paris Agreement (UNFCCC, 2015), thereby keeping the global temperature increase to “well below 2°C” and avoiding dangerous climate change. Current national pledges for reductions in greenhouse gas emissions are estimated to result in atmospheric CO₂ levels around mid-way between those two projected values; their global-scale implications for ocean acidification are shown in Figure 1, in terms of average pH change at the sea surface.

The climate change targets of the Paris Agreement are challenging, yet would be even harder to achieve if the ocean

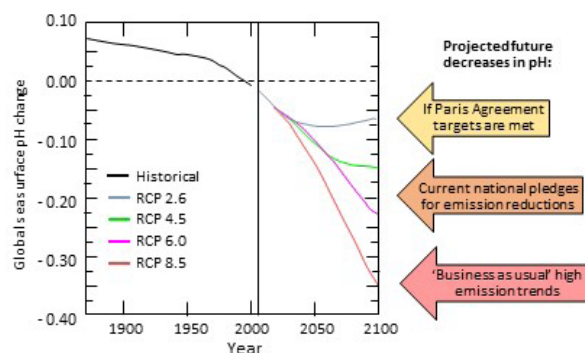


Figure 1: Model-based hindcasts and projections of global average sea surface pH change over 1870-2100, with projections based on IPCC Representative Concentration Pathways (RCPs) and related to outcomes of the Paris Agreement. All changes are relative to 1990-1999. Adapted from Bopp *et al.* (2013).

was not absorbing anthropogenic CO₂ – removing 25-30% of the CO₂ added to the atmosphere, and hence greatly slowing global warming. But ocean uptake of CO₂ is also the cause of ocean acidification: dissolved CO₂ produces carbonic acid, increasing the concentration of hydrogen ions (H⁺). This change is quantified on the logarithmic pH scale, with seawater pH values decreasing as H⁺ increases. Several other chemical changes are driven by dissolved CO₂ and increased

H⁺, including a decrease in the concentration of carbonate ions, and an associated decrease in carbonate saturation state (Ω). When Ω values are less than 1.0, unprotected calcium carbonate dissolves.

Concerns were raised more than 50 years ago regarding the likelihood of such CO₂-driven changes in ocean chemistry (e.g. Bolin and Eriksson, 1959). However, it was not until much more recently that it was demonstrated that such changes were underway, and likely to greatly intensify in future with wide-ranging implications (Royal Society, 2005). Discussion of ocean acidification in the first MCCIP Annual Report Card (2006) was still relatively limited: there were then only a handful of published UK studies, and a hundred or so worldwide.

Since 2006, very many more observations, experiments and model-based investigations of ocean acidification have been carried out, now resulting in a global total of several thousand scientific publications. The UK Ocean Acidification (UKOA, co-funded by NERC, Defra and DECC) research programme and other national initiatives have made a major contribution to that increase in knowledge, closely linked with international research effort. Our understanding of the processes of ocean acidification, and its linkage to climate change, is therefore now much more mature.

There has also been increased policy attention to ocean acidification, particularly at the intergovernmental level. Thus the need for improved monitoring of ocean acidification has been recognised by the Intergovernmental Oceanographic Commission (IOC, of UNESCO) and the Convention on Biological Diversity (CBD), with formal inclusion in UN Sustainable Development Goals (Target 14.3; UN Department of Economic & Social Affairs, 2015). In the context of the EU Marine Strategy Framework Directive (MSFD) and associated targets for Good Environmental Status, ocean acidification is a 'prevailing condition', for which it is important to have both measurements and understanding. Such science-policy work has been supported by inter alia the Ocean Acidification International Coordination Centre (OA-ICC, of IAEA); the OSPAR-ICES Study Group (ICES, 2014); and the development of the Global Ocean Acidification Observing Network (Newton *et al.*, 2015). All these activities have had strong UK involvement.

This overview includes information on the international assessment of ocean acidification carried out by the Intergovernmental Panel on Climate Change (IPCC), also the observed recent changes in the ocean carbonate system in the North Atlantic, European shelf seas and UK waters. More detailed discussion of biological impacts, palaeoclimate studies and socio-economic aspects is given in the 2013 MCCIP 'backing paper' review on ocean acidification (Williamson *et al.*, 2013) and elsewhere (e.g. CBD, 2014).

2. TOPIC UPDATE

Ocean acidification and its impacts were considered in MCCIP Report Cards (and associated reviews) in 2006, 2007-08, 2010-11 and 2013; also in 2015 in the context of implications for marine protected areas. In 2006, there was high confidence that ocean pH is changing and will continue to change for as long as atmospheric CO₂ continues to increase, whilst also noting that the full impacts on marine ecosystems and foodwebs remained largely unknown.

In the 2013 MCCIP review, a similar distinction was made between high confidence in 'what is already happening', considering ocean acidification from a physico-chemical perspective, and medium confidence in 'what could happen', including impacts on ecosystem services and their socio-economic implications. Additional assessments were based on 22 statements on ocean acidification and its impacts,

with quantified confidences based on international expert judgements (Gattuso *et al.*, 2013).

The main research findings from the UK Ocean Acidification research programme have been summarised in six online synopses (UKOA, 2015). These cover variability and trends in ocean pH; regional and global modelling; ocean acidification impacts in the upper ocean; impacts on seabed organisms; impacts on fisheries, foodwebs and ecosystem services; and ocean acidification in the geological past. More recent national work has included the project Placing Ocean Acidification in a wider Fisheries Context (PLACID, Defra-funded at Cefas), and a UKOA Synthesis Study, bringing together CO₂ and ocean acidification data for UK shelf seas. Both these projects have recently ended, with publications in preparation; data in the next section of this review includes information from the latter (Ostle *et al.*, 2016).

Relatively-recent international assessments of ocean acidification have included those by the Intergovernmental Panel on Climate Change (IPCC, 2013; 2014a, b) and the Convention on Biological Diversity (CBD, 2014); also policy-directed syntheses by Howes *et al.* (2015) and Gattuso *et al.* (2015) that included consideration of other climate change stressors. Since the IPCC 5th Assessment Report (AR5) includes confidence levels comparable to those used by MCCIP, summary IPCC information is given in Table 1. The grouping of statements is based on their confidence levels (see first asterisked footnote to Table 1), together with comments on research updates and/or UK context. Colour shading distinguishes statements on chemical from biogeochemical/biological aspects of ocean acidification; whilst the colour coding differs from that used in Table 3 of Williamson *et al.* (2013), the outcome is closely similar – with highest confidence in chemical aspects, as found in all previous MCCIP assessments and reviews of ocean acidification.

Based on the above syntheses, and other recent scientific papers, one change in confidence level (from 'medium' to 'high') is considered necessary to the statements on ocean acidification given in Williamson *et al.* (2013) and one change (from 'high' to 'low') for the statements given as Headlines in the MCCIP 2013 Report Card; see Table 2. Two additional statements are proposed in that Table, below, complementing 2013 statements. Colour shading in Table 2 distinguishes 'what is already happening' from 'what could happen', under different climate change projections.

2.1 How our understanding has developed over the past decade

Ocean acidification observations over a range of temporal and spatial scales

In the MCCIP 2006 Report Card, there was 'high confidence' that ocean pH was changing in response to increasing atmospheric CO₂, with that assessment based both on models and time-series data from Hawaii and Bermuda. Such evidence is now even more robust – being of longer duration, and based on a wider range of measurements, with greater geographic coverage. Observations and analyses have also benefited from several linked initiatives to improve knowledge of the global carbon cycle and ocean CO₂ fluxes; e.g. the Global Ocean Data Analysis Project (GLODAP) and the Surface Carbon CO₂ Atlas (SOCAT), also from initiatives that specifically focus on ocean acidification data-gathering, e.g. the Global Ocean Acidification Observing Network (GOA-ON).

Data with high accuracy, precision, and known statistical uncertainties, are needed to reliably detect long-term pH trends. Although the quality of pH sensors is improving rapidly, they are generally insufficiently accurate for such purposes. Thus it is more usual to calculate pH from measurements of other

Table 1. Main statements relating to ocean acidification in the 5th Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC, 2013; 2014a, b). Closely similar statements made in different parts of AR5 are combined below where confidence levels* are the same, but are kept separate if they differ. Colour shading: blue, chemistry; orange, biogeochemistry and biology

* The IPCC confidence scale has 5 values (very high, high, medium, low and very low), based on level of agreement (low, medium and high) and quality/quantity of evidence (limited, medium, robust) (IPCC, 2013). Whilst structurally similar to MCCIP confidence assessments, different combinations of agreement and evidence produce different confidence levels. For example, IPCC's 'very high' and 'high' are technically equivalent to MCCIP's 'high' and 'medium', whilst an IPCC 'medium' could be either an MCCIP 'low' or 'medium'. However, IPCC recognises that "there is flexibility in the relationship" [between evidence, agreement and confidence], and actual usage seems much more comparable.

** WG I = IPCC (2013); WG II (A) = IPCC (2014a), Part A, Chapter 6; WG II (B) = IPCC (2014a), Part B, Chapter 30; Synthesis = IPCC (2014b).

IPCC confidence level	Statement	AR5 source**	Comments, update notes and UK context
Very high	We know the chemical response to increased CO ₂ dissolving in the ocean from the atmosphere.	WG II (B)	
High	The pH of surface waters has decreased by 0.1 since the preindustrial era as a result of ocean uptake of anthropogenic CO ₂ from the atmosphere. Further increases in atmospheric CO ₂ will further decrease ocean pH.	WG I WG II (B) Synthesis	The quoted pH decrease is a global average; observed recent changes are greatest in high latitudes and in sub-surface waters. Recent North Sea decrease in pH is apparently more rapid than in North Atlantic.
	The current rate of ocean acidification is unprecedented within the last 65 million years.	WG II (B)	'Medium' confidence given by WG II to the rate being unprecedented for 300 million yr. However, higher rates did probably occur 66 million years ago, due to asteroid impact (Tyrrell <i>et al.</i> , 2015).
	Rising CO ₂ levels will increasingly affect marine biota and interfere with ecological and biogeochemical processes. Impacts will be irreversible in medium term, affecting marine ecosystems for centuries.	WG II (A) & (B)	Very long duration of impacts (thousands of years) confirmed by new modelling studies simulating future CO ₂ removal from the atmosphere.
	Ecological impacts of ocean acidification will be exacerbated by raising temperature extremes, also by de-oxygenation and local changes (e.g. pollution, eutrophication).	Synthesis	Increasing recent importance given to interactions with other stressors.
	Experiments and field observations show a wide range of sensitivities and responses within and between taxonomic groups.	WG II (A)	Biological variability confirmed by many additional studies
	Mesocosm studies and natural analogues [CO ₂ vents] show that high CO ₂ /low pH causes losses in diversity, biomass and trophic complexity of benthic communities	WG II (A)	Additional CO ₂ vent studies have confirmed such effects. However, most community-scale mesocosm studies have been pelagic rather than benthic.
	Warm-water corals, echinoderms, benthic molluscs and calcifying algae are vulnerable to ocean acidification at RCP 8.5 (high emissions scenario). Warm-water coral structures are at risk of dissolution.	WG II (A)	Vulnerability considered 'medium' by WG II at RCP 6.0 (medium emissions). Statement on dissolution risk for warm-water corals is based on sediment dissolution; bio-erosion may also be enhanced.
	Coastal shifts in upwelling CO ₂ rich waters of NE Pacific have caused larval oyster mortalities in aquaculture.	WG II (A)	Increasing atmospheric CO ₂ now regarded as main factor (rather than 'coastal shifts'). Equivalent effects not observed in UK or European seas.
	Most non-calcifying plants (fleshy seaweeds and seagrasses) and micro-algae respond positively to elevated CO ₂ levels by increasing photosynthesis and growth.	WG II (A)	Meta-analysis by Kroeker <i>et al.</i> (2013) did not show significantly increased photosynthesis by either fleshy seaweeds or seagrasses, but the former did show increased growth.
Medium to high	Coral reefs and polar ecosystems are at greatest risk from ocean acidification	Synthesis	
	Future impacts of ocean acidification range from changes in organismal physiology and behaviour to population dynamics.	WG II (A)	

Medium to high	Observed shell-thinning in planktonic foraminifera and in Southern Ocean pteropods may be fully or partly attributed to acidification trends	WG II (A)	Shell erosion in pteropods also now observed in low pH waters of NE Pacific, but some attribution aspects still contentious
Medium	[Marine] ecosystems, including cold- and warm-water coral communities, are at increasing risk of being negatively affected by ocean acidification during the next decades.	WG II (A)	Confidence level seems cautious: validity of statement not in doubt (due to increased research).
	Warm-water corals, echinoderms, benthic molluscs and calcifying algae vulnerable to ocean acidification at RCP 6.0 (medium emissions scenario).	WG II (A)	Vulnerability considered to be at 'high' confidence level by WG II at RCP 8.5 (high emissions scenario).
	Cold-water corals are at risk of dissolution under ocean acidification, affecting associated ecosystems.	WG II (A)	Dissolution effects likely to be limited to dead reef structures. Living corals are, however, more fragile under high CO ₂ conditions (Hennige <i>et al.</i> , 2015).
	Limitations in understanding mechanisms of effect and longterm persistence make it difficult to accurately project longterm impacts.	WG II (A)	Confidence level in the statement as written could be considered high (since limitations in mechanistic understanding undoubtedly do make projections difficult).
	Ocean acidification affects energy metabolism; enhanced calcification can sometimes occur at the expense of growth.	WG II (A)	
	Ocean acidification may stimulate global nitrogen fixation	WG II (A)	Confidence level seems higher than supported by IPCC text. Shi <i>et al.</i> (2012) found opposite effect.
Low to medium	[For marine animals] vulnerability decreases with increasing capacity to compensate for elevated internal CO ₂ concentration and falling pH.	WG II (A)	
	Transgenerational or evolutionary adaptation has been shown in some species, reducing impacts of projected scenarios. Adaptation accelerated by high functional variability in offspring (and short generation time).	WG II (A)	Additional evidence from vent studies and experiments make impacts less predictable, but not necessarily of less ecological or societal importance. At vent sites, most benthic calcifiers absent; i.e. unable to adapt.
	Differential sensitivities and associated shifts in performance and distribution will change predator-prey relationships and competitive interactions.	WG II (A)	Confidence level seems cautious; there has been further supporting research. If some species are affected, additional consequences would seem inevitable.
Low	Fish, pelagic molluscs, foraminifera and cold-water corals vulnerable to ocean acidification at RCP 6.0 (medium emissions scenario).	WG II (A)	Vulnerability considered 'medium' at RCP 8.5 (high emissions scenario), except for fish, still at 'low'. Subsequent research on fish has shown range from tolerant to vulnerable.
	Ocean acidification may affect the behaviour of fish larvae and juveniles	WG II (A)	Effects on larval fish behaviour not studied in UKOA, but confirmed elsewhere.
	Early life stages likely to be more sensitive to ocean acidification (as for other environmental stressors), but considered unproven.	WG II (A)	Meta-analysis by Kroeker <i>et al.</i> (2013) confirmed significant life-cycle effects for molluscs; results remain ambiguous for other groups.
	Ocean acidification may stimulate global net primary production.	WG II (A)	High confidence level previously given for statement on photosynthesis and growth by micro-algae, but effect probably modest.
	Ocean acidification may increase grazing on non-calcifying seaweeds and seagrasses due to loss of phenolic deterrent substances.	WG II (A)	
	Enhanced pH reduction and variability in low-salinity waters [e.g. estuaries, brackish seas] may constrain distributions of sensitive species.	WG II (B)	

components of the carbonate system (carbon dioxide partial pressure, $p\text{CO}_2$; total alkalinity, TA; and dissolved inorganic carbon, DIC) together with information on other parameters (temperature, salinity, pressure and nutrients). These additional physico-chemical measurements provide the context for interpretation of ocean acidification trends and variability, complemented by information on biological variables (Newton *et al.*, 2015).

There are now five North Atlantic datasets for the ocean carbonate system of >20 years duration (Figure. 2). These show a consistent pattern of surface-ocean pH decrease although with variability in site-specific values - even for relatively closely-located sites (e.g. -0.0014 pH units per year in Iceland Sea; -0.0026 pH units per year in Irminger Sea) (Bates *et al.*, 2014).

Note that the data presented in Figure. 2 are all 'surface ocean', usually at 5-20 m water depth in the upper mixed layer. There is a natural decrease of pH and saturation state (and increase of $p\text{CO}_2$) with increasing water depth, superimposed on which there is non-uniformity of pH change due to anthropogenic CO_2 . Depth-related changes are shown in Figure. 3, based on a repeat, full-depth transect sampling of the North and South Atlantic over a ~10 year time interval (Woosley *et al.*, 2016).

Data from three other Atlantic transects are analysed by Woosley *et al.* (2016): two in the Western North Atlantic (WOCE sections A20 and A22) and one in the South Atlantic (A10). Taken together, they indicate a surface pH decrease of -0.0021 ± 0.0007 per year over the past decade,

a near-exact match to the mean value of -0.0020 per year from the five North Atlantic time series sites.

There are no UK datasets providing consistently-obtained, quality-controlled information on ocean carbonate system parameters over decadal time-scales. However, long-term data (from different sources, of variable quality and without metadata relating to sensors and methods) are available from the ICES database, and can be grouped according to OSPAR regions. Most observations are for the Greater North Sea, including the English Channel (OSPAR region II), with sufficient pH values ($n = 26,537$) to allow annual means to be calculated for the period 1984-2014. The overall trend for that period is a pH decrease of -0.0035 ± 0.0014 per year, i.e. suggesting more rapid acidification than for the surface Atlantic as a whole; see Figure. 4.

Focusing on the past decade, the ICES North Sea dataset indicates that an increase, rather than decrease, in pH may have recently occurred (Figure. 4). However, that result is not supported by time series surveys between NW Scotland and Iceland (Humphreys *et al.*, 2016; reported in terms of DIC increase); in the Rockall Trough (McGrath *et al.*, 2012); in the Atlantic Meridional Transect surveys (Kitidis *et al.*, 2016), nor in coastal ocean acidification monitoring studies that began in 2008/2009 at L4, off Plymouth, and at Stonehaven, near Aberdeen, supplemented by SmartBuoy sampling. Data for these coastal sites show a marked (and statistically significant, at $P < 0.05$) decline in pH over the period 2008-2015, with strong seasonality superimposed on both year-to-year and short-term variability; see Figures. 5 and 6.

Table 2. Statements relating to ocean acidification in Williamson *et al.* (2013) and the MCCIP 2013 Report Card and their confidence levels on MCCIP criteria; also two additional statements ('this review'). Colour shading: green, what is already happening; yellow, what could happen, based on experiments, observations (e.g. at CO_2 vents) and model projections.

MCCIP confidence level	Statement	Source	Comments
High	Anthropogenic ocean acidification is caused by CO_2 emissions to the atmosphere; it is occurring with measurable chemical consequences, at a faster rate than any equivalent natural change in the past 55 million years.	Williamson <i>et al.</i> (2013)	IPCC WG II included a similar statement, with high confidence for a longer period (65 million years).
	There is growing evidence of the importance of interactions between ocean acidification and other stressors, such as temperature.	MCCIP 2013 Report Card	
	Recent research effort has shown the complexity of the biological effects of ocean acidification, with some species being more tolerant than others.	MCCIP 2013 Report Card	Variability in tolerance can occur intra-specifically, as well as inter-specifically; hence some scope for genetic adaptation.
High (previously medium)	Marine organisms vary in their vulnerability to ocean acidification; some of those that are sensitive may have already been impacted where pH is natural low, e.g. coastal upwelling.	Williamson <i>et al.</i> (2013)	Additional evidence for field impacts (although not in UK or European waters).
Medium	Observed pH decreases in the North Sea (over 30 years) and at coastal UK sites (over 6 years) seem more rapid than in the North Atlantic as a whole. However, shelf sea and coastal datasets show high variability over a range of timescales: seasonal cycles therefore need to be well-characterised in order to determine long-term trends, and local factors influencing carbonate chemistry also need to be monitored and better understood.	This review	

High	The magnitude of future ocean acidification depends on anthropogenic CO ₂ emissions: without rapid and strong mitigation, polar regions will become undersaturated for calcium carbonate within decades, with global average pH in the upper ocean being in the range 7.7-8.0 by 2100. Subsequent recovery would take thousands of years.	Williamson <i>et al.</i> (2013)	Additional modelling of saturation state in Southern Ocean under high emission scenarios show rapid onset of changes, with undersaturation affecting 30% of surface waters by 2060 (Hauri <i>et al.</i> , 2016).
Medium	Future ocean acidification under current trends would have serious impacts on marine biodiversity, ecosystem functions, and biogeochemical processes in UK seas and globally, with potentially significant climatic feedbacks.	Williamson <i>et al.</i> (2013)	'Current trends' assumed to be RCP 8.5, the high emissions scenario. On a global (rather than UK) scale, increase of confidence level to 'high' could be justified for long-term impacts
	Model projections indicate that by 2100 much of the North Sea could be seasonally undersaturated with respect to aragonite. Aragonite is made by many shell-forming organisms.	MCCIP 2013 Report Card	Model projections based on RCP 8.5, the high emissions scenario.
	Around 70% of known cold-water coral locations are estimated to be in waters undersaturated in aragonite by the end of this century.	MCCIP 2013 Report Card	Additional information in MCCIP 2015 Report Card; model projections based on RCP 8.5, the high emissions scenario.
	The overall effect of ocean acidification on marine ecosystems and the services they provide is expected to be deleterious, with risk of substantive reductions in shellfish growth (and harvest) within 50 years. There could be benefits, however, for some micro-algae and seagrass species (due to increased CO ₂ in the sea water).	MCCIP 2013 Report Card	Model projections based on RCP 8.5, the high emissions scenario.
	As ocean acidification continues, it may result in changes in metal toxicity and nutrient availability.	MCCIP 2013 Report Card	Additional studies confirm interactions with copper toxicity (e.g. Campbell <i>et al.</i> , 2014).
	Full implementation of the Paris Agreement would limit further global pH decrease in the upper ocean to ~0.1, greatly reducing impacts.	This review	The "well below 2°C" target may require active removal of CO ₂ from the atmosphere – with potential for acidification impacts
Low	Future ocean acidification under current trends would also have substantive impacts on a range of ecosystem services; however, complex processes and interactions are involved, and the scale of socio-economic impacts is currently uncertain	Williamson <i>et al.</i> (2013)	Socio-economic implications of ocean acidification for UK (e.g. impacts on fisheries) remain uncertain. At global scale, confidence level in such impacts could now be considered 'medium' (even if CO ₂ emissions are much reduced).
Low (previously High)	The current rate of increase in acidity (decrease in surface layer pH) is probably more rapid now than any time in the past 300 million years	MCCIP 2013 Report Card	Change of confidence level based on evidence of asteroid effects 66 million years ago (Tyrrell <i>et al.</i> 2015).

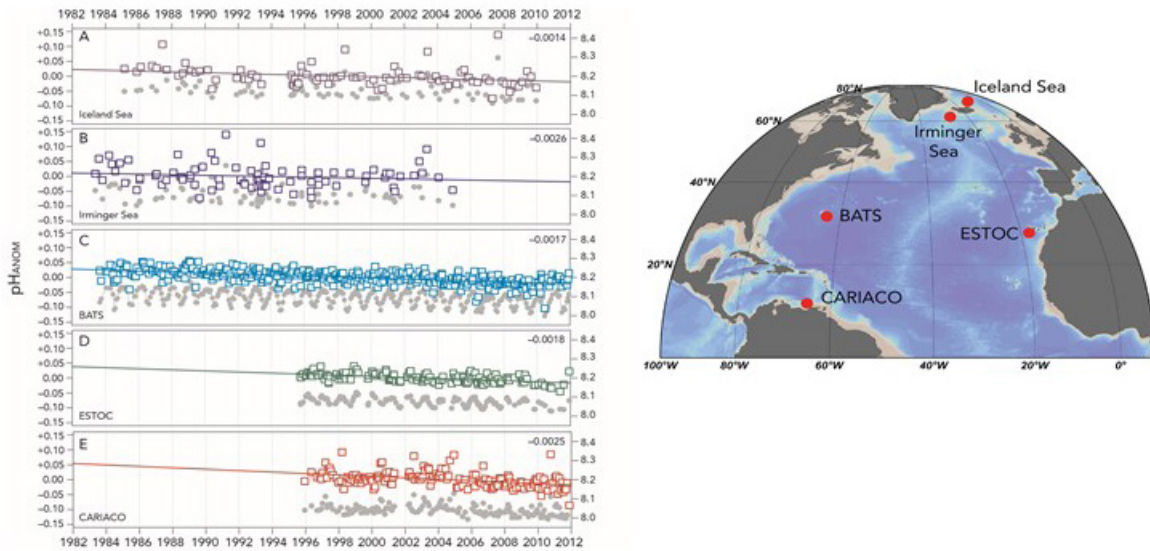


Figure 2. North Atlantic time series showing long-term decrease in surface pH at five sites: Iceland Sea, Irminger Sea, Bermuda (BATS), Canary Islands (ESTOC) and Cariaco Basin, Venezuela (CARIACO). Above: site location map; left: data for each site shown as pH anomalies (coloured symbols, left hand scale) and observed pH (grey symbols, right hand scale), the latter calculated from DIC and TA. From Bates et al. (2014), omitting data from Pacific time series.

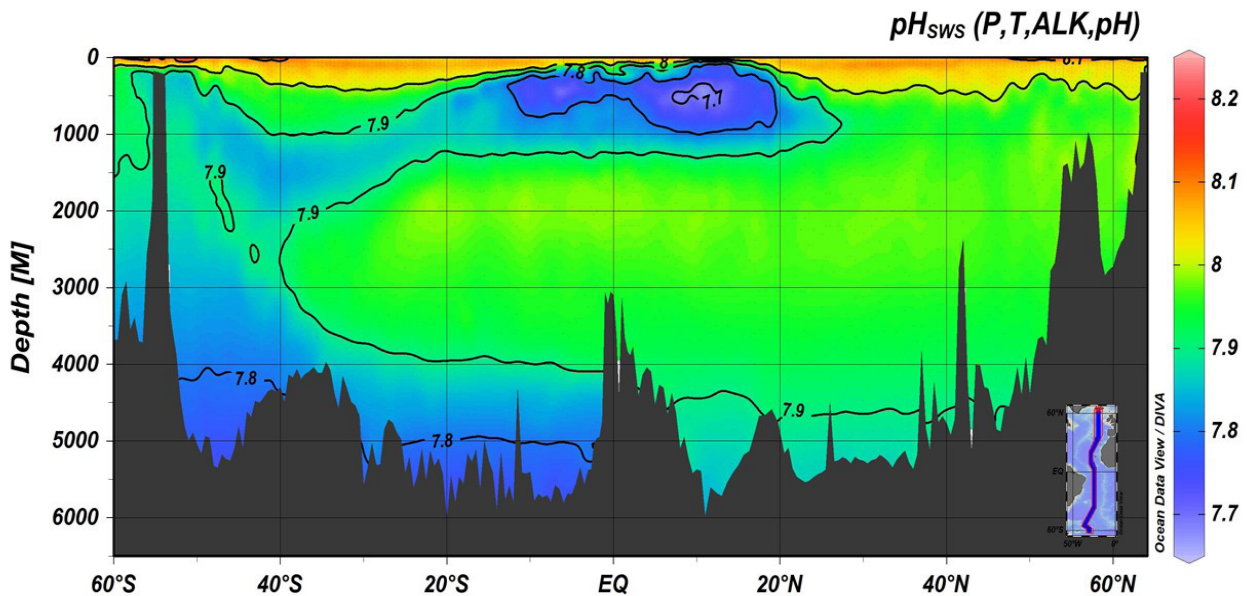


Figure 3. Surface to seafloor pH observations in South and North Atlantic showing depth-related spatial changes, re-calculated for in situ pressure and temperature from GO-SHIP cruises in 2013-14 (WOCE transect A16 from 60°S to 60°N). Credit: R.J. Woosley, F.J. Millero & R. Wanninkhof, unpublished; for additional data, including decadal pH changes, see Woosley et al. (2016).

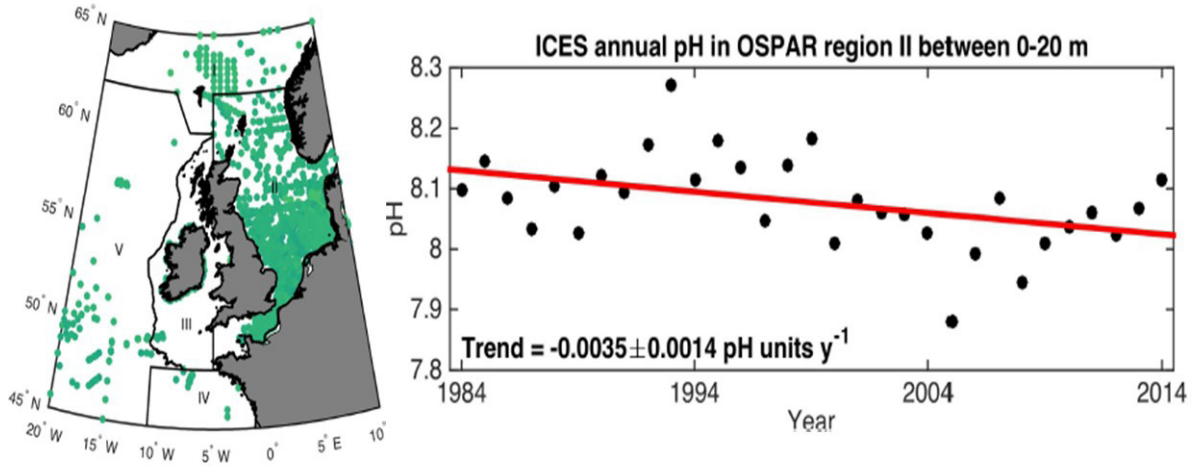


Figure 4. Annual mean values and longterm trend (1984-2014) for pH data in ICES database for Greater North Sea (OSPAR Region II; map on left, with location of sample sites). Note that data quality is uncertain, although the slope does significantly differ from zero ($p < 0.02$). From Ostle *et al.* (2016).

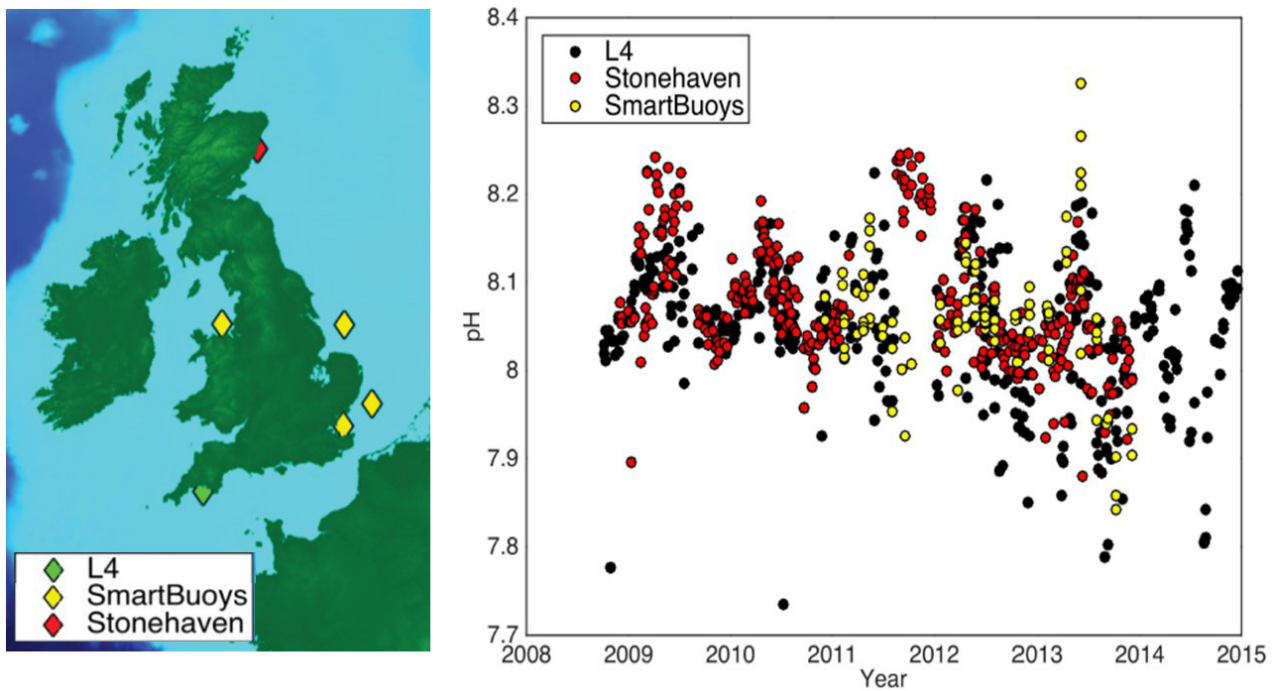


Figure 5. pH observations (calculated from DIC and TA) at the L4 and Stonehaven time series, 2008-2015; also data from three SmartBuoys in the North Sea and one in the Irish Sea. From Ostle *et al.* (2016)

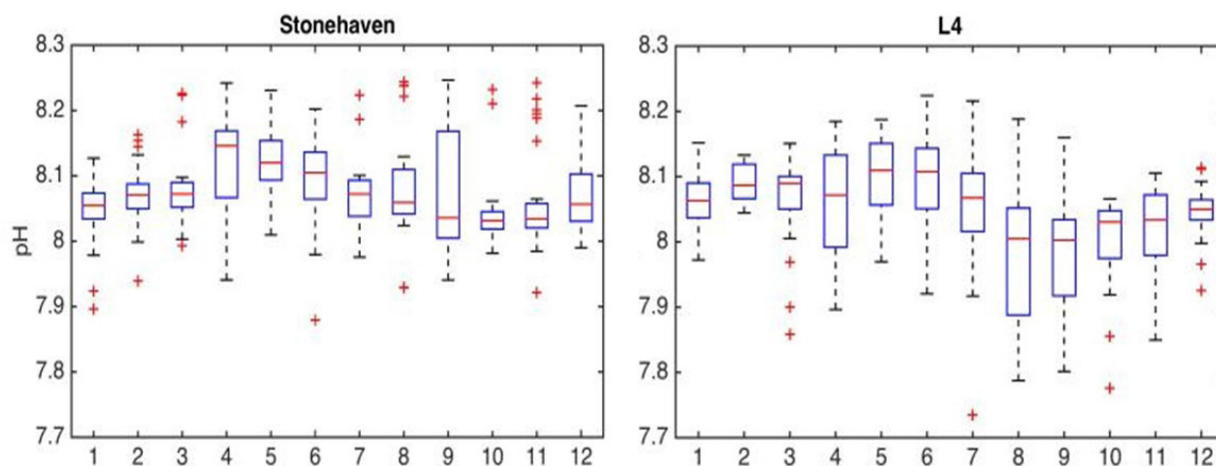


Figure 6. Box and whisker plots of seasonal variability of pH at Stonehaven and L4, combining data for 2008-2015. Red lines indicate monthly median values; boxes cover the 25th-75th percentile range; whiskers show 2.7 x standard deviations; and red crosses are outliers. X axis: months of year, 1 – 12 (January – December). From Ostle *et al.* (2016)

At both L4 and Stonehaven, highest pH values usually occur in spring and early summer (April-June) and lowest in autumn and early winter (Figure. 6); these changes can be related to changes in the balance between photosynthesis (by phytoplankton) and respiration (by zooplankton and bacteria), that respectively remove and add CO₂ to the surface sea water, also mixing effects (establishment and breakdown of stratification). Whilst pH values are closely similar at the two sites, saturation state values for aragonite (a form of calcium carbonate) differ because of temperature dependency effects, with annual maxima and minima occurring around mid-summer and mid-winter. At Stonehaven, monthly mean values for Ω_{arg} range between 1.8 -2.2 (SD range 1.6 – 2.7); at L4, the mean range is 2.1 – 2.5 (SD range 1.8 – 2.9) (Ostle *et al.*, 2016).

Additional spatially- and seasonally-characterised observations for UK and European waters have been provided by: research cruises (e.g. Ribas-Ribas *et al.*, 2014); new SOCAT surface pCO₂ data (Bakker *et al.*, 2014; 2016); and depth-related DIC data collated by GLODAP (Olsen *et al.*, 2016; Lauvset *et al.*, 2016). Relevant features of these datasets are discussed in Ostle *et al.* (2016).

Further analyses of the above datasets should enable a process-based understanding of the factors (in addition to atmospheric CO₂) that affect local pH, saturation state and other carbonate system parameters, whilst also providing much-needed knowledge of the conditions actually experienced by both pelagic and benthic organisms in UK shelf seas. Two further aspects of ocean acidification dynamics warrant attention:

- Seafloor conditions, particularly in the benthic boundary layer, within sediment pore-waters, and for cold-water coral habitats. In the North Sea, local hydrodynamic conditions strongly affect benthic ocean acidification (van Leeuwen *et al.*, 2016) and pH changes of ~0.8 units occur within the top 1-2 cm of sediment (Ostle *et al.*, 2016; Silburn *et al.*, 2017).
- Diel variability, particularly for intertidal habitats. In Californian rockpools, daily ranges of 7.22-9.0 in pH, and 0.4-8.4 in Ω_{arg} have been recorded (Kwiatkowski *et al.*, 2016).

All such factors have implications for future monitoring of ocean acidification, as well as experimental design for biological impact studies. To date, the latter has mostly focused

on laboratory matching of current and projected global atmospheric CO₂ values, with a control of 350-400 ppm and typical treatments of 750-1000 ppm, reducing pH from 8.1 to ~7.7. An alternative approach is to superimpose those perturbations on the *in situ* environment, using mesocosms or free-ocean CO₂ enrichment (FOCE) techniques (Gattuso *et al.*, 2014). Temporal changes in carbonate chemistry will then follow those naturally experienced by organisms, with seasonal variability matching different stages of their life-cycles.

2.2 Modelled projections of future trends and impacts

The challenge of matching a global-scale driver with local-scale impacts is particularly great for modelling studies of ocean acidification – that (ideally) need to include physical, chemical, biogeochemical, physiological, ecological and socio-economic components. Such complexity provides a paradox: whilst there can be high confidence that unabated ocean acidification will cause ecological disruption (Nagelkerken and Connell, 2015) and associated economic damage, model-based assessments of specific future conditions and societal vulnerabilities remain uncertain (Hilmi *et al.*, 2015).

That situation is also true for other aspects of marine climate change (Payne *et al.*, 2015) with scale of impacts dependent on the scale of future CO₂ emissions (Gattuso *et al.*, 2015; Manqnan *et al.*, 2016) and societal responses (Ekstrom *et al.*, 2015). Nevertheless, for ocean acidification there are additional uncertainties due to interactions with other stressors (Breitburg *et al.* 2015), the potential for some evolutionary adaptation (Sunday *et al.*, 2014), and the wide range of factors affecting carbonate chemistry in the coastal zone (Duarde *et al.*, 2013).

UK modelling effort for ocean acidification has mostly been directed at the development of shelf-sea simulations of carbonate chemistry that include seafloor exchanges, tidal currents, terrestrial inputs and ecosystem processes, at relatively high spatial resolution (~12km). Such models successfully show strong seasonality in pH at the sea surface, in the water column and at the seafloor, with spatial and temporal heterogeneity strongly linked to local hydrodynamics and biological activity (Artioli *et al.*, 2014). Future projections have to date been based on high (A1B and RCP 8.5) emission scenarios: under such conditions, seasonal undersaturation of

aragonite is projected for ~30% of the bottom waters of the North Sea by 2100 (Artioli *et al.*, 2014), with surface undersaturation also occurring in some coastal waters in winter (Figure 7). Based on the RCP 8.5 scenario, the modelled rate of pH change for the greater North Sea region (OSPAR region II) for the period 1990-2099 is -0.0036 ± 0.0003 units per year; i.e. a very close match to the ICES-based estimate previously given in Fig 4.

As noted above, future seafloor conditions are of interest with regard to the implications of carbonate chemistry changes for benthic calcifiers. Jackson *et al.* (2014) compared model-based estimates of the future shoaling of the aragonite saturation horizon (below which unprotected carbonate structures are corroded) to the distribution of the coldwater coral *Lophelia pertusa* along the shelf edge. That was based on global models of ocean acidification at relatively low resolution, with high emission scenarios; there is need for additional, high resolution work that distinguishes the impacts of low to medium emission scenarios, e.g. resulting in global temperature increases of 1.5°C, 2.0°C and 3.0°C.

The potential for ocean acidification to cause changes in phytoplankton community structure (Flynn *et al.*, 2015) and trophic interactions (Fernandes *et al.*, 2013; Morris *et al.*, 2014) are additional considerations that have not yet been included in the biogeochemically-based regional models. More direct effects on commercial fisheries are briefly considered below.

2.3 Ocean acidification and fisheries

A low confidence level was given by the most recent IPCC assessment with regard to the vulnerability of finfish to

ocean acidification for an RCP 6.0 emissions scenario (Table 1). That reflects high inter-specific variability in experimental results, continuing in more recent data. Thus there would seem relative resilience for Atlantic herring and European sea bass (Franke and Clemmeson, 2011; Pope *et al.*, 2014) although other species, e.g. cod, may be more sensitive, at least at high CO₂ levels that can cause increased larval mortality and lower recruitment (Stiasny *et al.*, 2016). For commercially-important crustacea, physiological effects have been documented for the European lobster (Small *et al.*, 2015, 2016); their population-level significance is uncertain. Additional UK studies on lobsters are nearing completion.

A recent modelling study used a multi-species approach (finfish and shellfish) to estimate the ecological and socio-economic impacts of both ocean acidification and warming for high and low emission scenarios (Fernandes *et al.*, 2016). Temperature was considered to be the more important driver, with combined effects for RCP 8.5 resulting in losses in revenue and employment (fisheries and associated industries) of up to 20% by 2050.

3. KNOWLEDGE GAPS AND KEY CHALLENGES

The planning phase (mostly in 2008-09) of the UK Ocean Acidification research programme provided the opportunity to identify – with involvement of policy stakeholders, Defra and DECC – what were then perceived as highest-priority knowledge gaps and research challenges. Most topics related to uncertainties regarding the impacts of future ocean acidification on key components of pelagic and benthic ecosystems, including commercially-important species (fish, crustacea and molluscs) and cold-water corals. Laboratory studies were expected to be of relatively long duration, and to

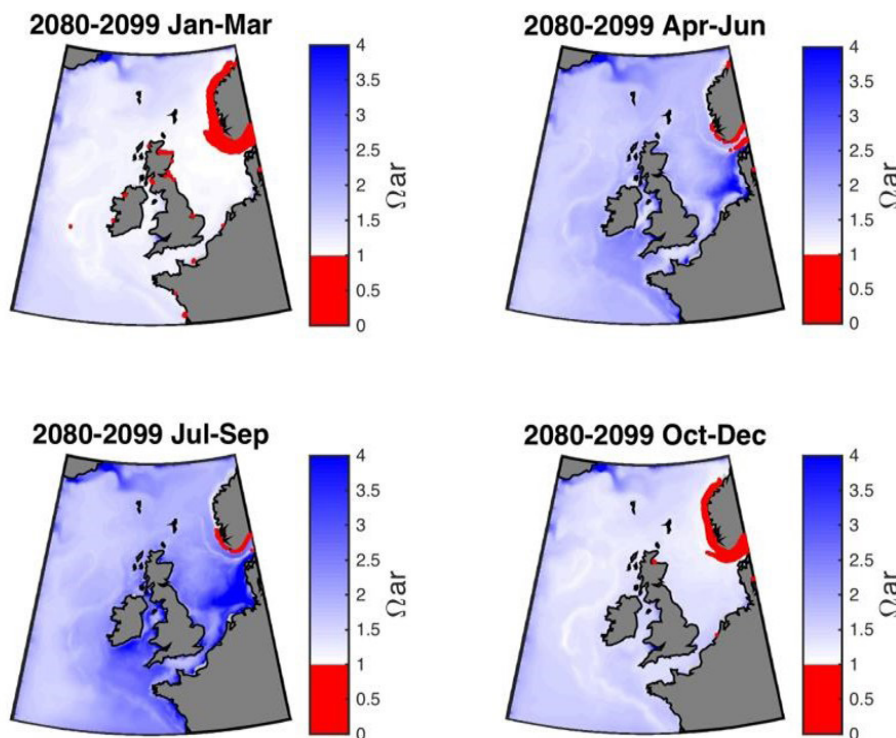


Figure 7. Seasonal changes in projected sea surface aragonite saturation (Ω_{ar}) for 2080-2099 under a high CO₂ emissions scenario (RCP 8.5). Undersaturated water shown in red, affecting parts of UK coast in January-March. (Artioli *et al.*, unpublished; Ostle *et al.* 2016).

take account of potential interactions with temperature increases of 2-4°C. Responses of phytoplankton and microbes to ocean acidification were to be investigated by ship-based, bioassay experiments around the UK and at high latitudes (Arctic and Southern Ocean). In addition, large-scale observational studies would be developed, linking with SOCAT; geological precedents for global ocean chemistry changes would be investigated; and regional and global modelling would provide the framework for theoretical analysis and future projections.

The above scientific priorities related to the main programme goal: “to increase understanding of processes and reduce uncertainties in predicting impacts”. That can be considered as having been successfully addressed (UKOA, 2015), with the UK providing a major global contribution to ocean acidification publications (Figure. 8). An additional goal was “to improve policy advice” in the context of wider knowledge exchange; that has also been achieved, benefitting greatly from partnerships with colleagues in Germany, Europe, USA and elsewhere, and strong linkages with intergovernmental bodies (including IOC, CBD and UNFCCC).

There have, however, been new challenges in ocean acidification research over the past decade. Whilst some have been addressed by other projects and initiatives, many questions remain unanswered.

4. EMERGING ISSUES (CURRENT AND FUTURE)

The following topics are examples of ocean acidification research opportunities and needs. Whilst several relate to uncertainties identified in international assessments and reviews (e.g. IPCC, 2014a; CBD, 2014; Laffoley & Baxter, 2016), the list is neither comprehensive nor prescriptive. Many of these topics would benefit from a transdisciplinary approach (Yates *et al.*, 2015) as well as exploiting recent developments in sensor technologies (Martz *et al.*, 2015).

1. The variability observed in carbonate chemistry in UK coastal waters needs to be much better understood, requir-

ing continuation of existing ocean acidification time series, the measurement of other parameters, dedicated effort on data interpretation and the further development of guidelines for cost-effective and integrated biogeochemical monitoring to meet national and international policy needs. The linkage between river water quality, carbonate chemistry in estuaries and coastal ocean acidification is a specific aspect that has been neglected, and warrants further attention

2. The validity and applicability of laboratory-based impact studies need to be re-visited in the context of the observed natural variability in environmental conditions. Free ocean CO₂ enrichment (FOCE) techniques should be developed and used for *in situ* experiments; e.g. on cold-water corals. Studies that raise, rather than lower, pH (i.e. restoring water quality to a more pristine state) are likely to provide novel insights (Albright *et al.*, 2016).

3. Multi-stressor interactions need much more attention, moving beyond the inclusion of temperature as an additional variable. Interactions with toxic metals (such as copper), oxygen and food supply are potentially of crucial importance, requiring attention to fundamental physiological processes as well as smart experimental design.

4. New water treatment techniques make it possible to separately control pH and carbonate saturation state. Whilst different species almost certainly respond differently, and several components of the ‘ocean acidification syndrome’ (CO₂, H⁺, CO₂- or HCO₃⁻) may be responsible for adverse impacts (Walbusser *et al.*, 2015), it has yet to be resolved what matters most in terms of ecosystem impacts.

5. The vulnerability (or resilience) of the UK aquaculture industry to future ocean acidification needs to be better assessed, using emerging results from the PLACID programme and building on those outcomes to strengthen and develop international partnerships (e.g. with the US, Chile, China and India).

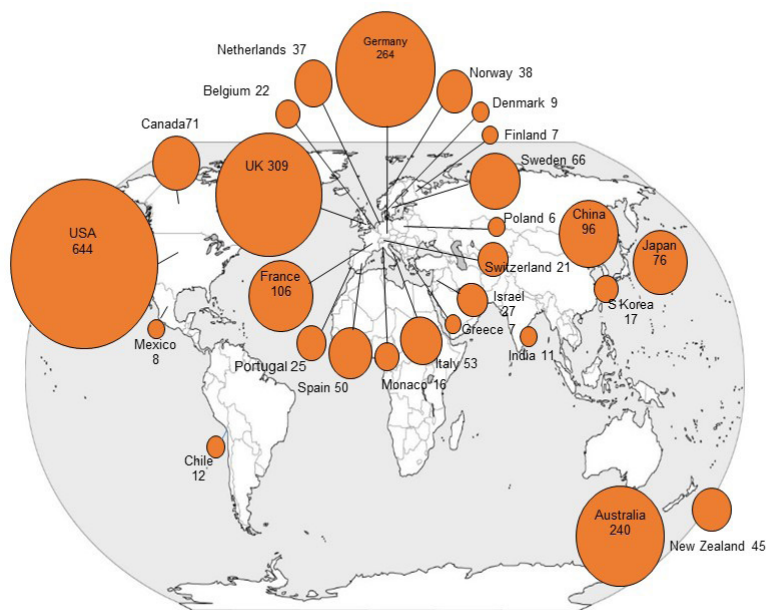


Figure 8: National involvement in ocean acidification research based on first authors' addresses for peer-reviewed papers published 2005-2014 for countries with 5 or more ocean acidification publications. From Mathis *et al.* (2015) based on data from the Ocean Acidification International Coordination Centre.

6. The potential for genetic adaptation to ocean acidification warrants further attention, based on intra-specific variability in responses and the use of CO₂ vent sites to investigate evolutionary processes and their molecular basis.

7. Uncertainties regarding the sensitivity of pteropods to present-day ocean acidification conditions in polar seas and upwelling areas need to be resolved, to assess their suitability for monitoring (as indicator species) and distinguishing the impacts of different climate policy targets, e.g. limiting warming to either 1.5°C, 2.0°C or 3.0°C.

8. The UK's marine stewardship responsibilities are not limited to the UK EEZ but also extend to the 14 British Overseas Territories, covering a very wide geographic range, from polar regions to the tropics, with high marine biodiversity. Relatively little research has been carried out on their vulnerability to ocean acidification, warming and other stressors. A comprehensive assessment would seem timely.

9. The potential impacts, negative or positive, of large-scale removal of carbon dioxide from the atmosphere ("negative emissions") need to be investigated for ocean acidification. Some techniques, e.g. enhanced weathering, are now receiving increased attention on the basis that acidification can be ameliorated (Taylor *et al.*, 2016). Wider issues relating to ocean impacts have been identified (Williamson and Turley, 2012; CBD, 2012), but have yet to be resolved.

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