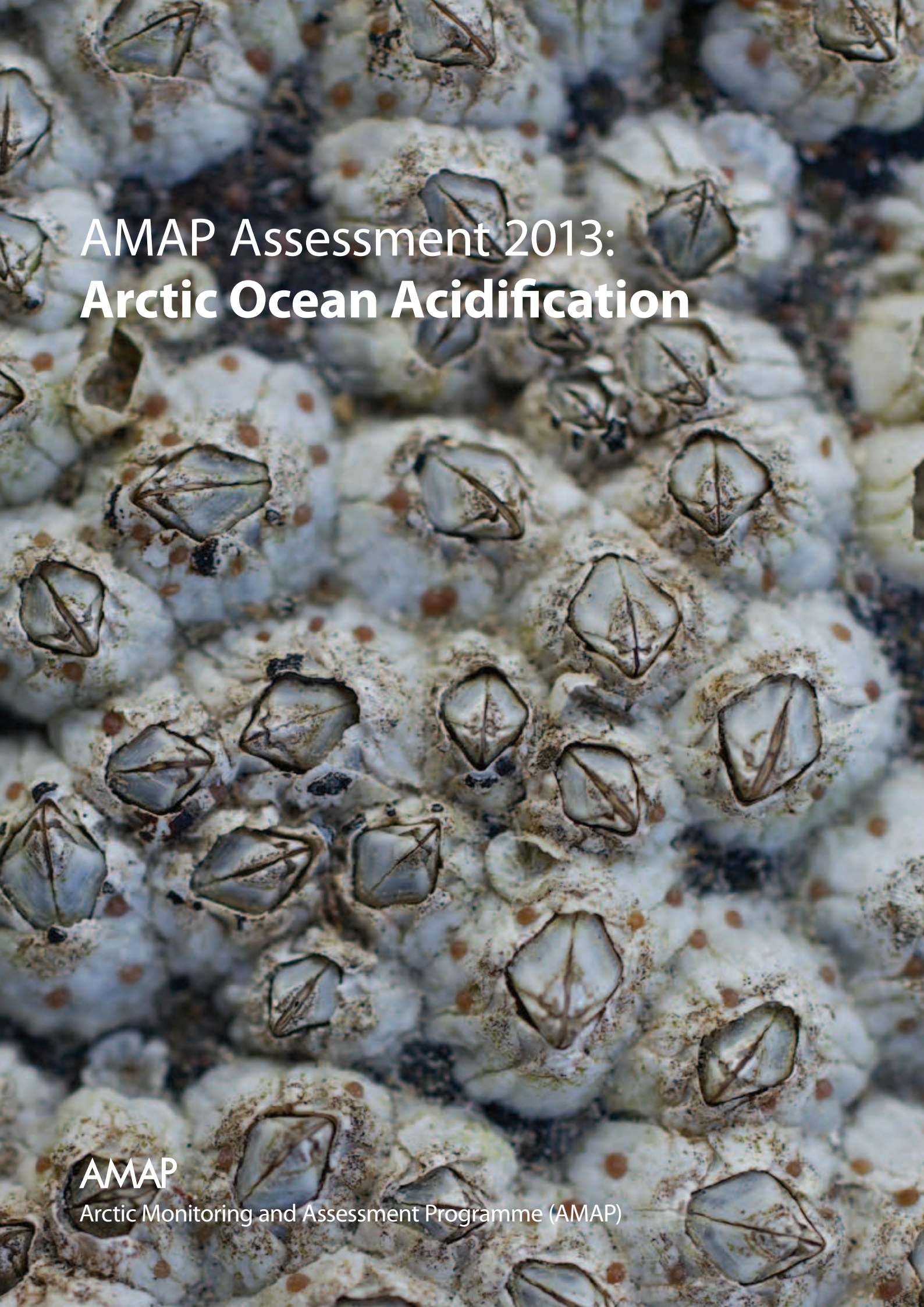


A close-up photograph of a dense colony of mussels on a rocky surface. The mussels have light-colored, slightly translucent shells with dark, radiating lines. They are attached to a light-colored, textured rock. The background is slightly blurred, showing more mussels and the rock surface.

AMAP Assessment 2013: **Arctic Ocean Acidification**

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Arctic Monitoring and Assessment Programme (AMAP)

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Barnacles (*Semibalanus balanoides*); one of the Arctic species being investigated for ocean acidification effects. Photo: Fredrik Pleijel.

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Preface

This assessment report presents the results of the 2013 AMAP Assessment of Arctic Ocean Acidification (AOA). This is the first such assessment dealing with AOA from an Arctic-wide perspective, and complements several assessments that AMAP has delivered over the past ten years concerning the effects of climate change on Arctic ecosystems and people.

The Arctic Monitoring and Assessment Programme (AMAP) is a group working under the Arctic Council. The Arctic Council Ministers have requested AMAP to:

- produce integrated assessment reports on the status and trends of the conditions of the Arctic ecosystems;
- identify possible causes for the changing conditions;
- detect emerging problems, their possible causes, and the potential risk to Arctic ecosystems including indigenous peoples and other Arctic residents; and to
- recommend actions required to reduce risks to Arctic ecosystems.

This report provides the accessible scientific basis and validation for the statements and recommendations made in the *Arctic Ocean Acidification Assessment Summary for Policy-makers*¹ that was delivered to Arctic Council Ministers at their meeting in Kiruna, Sweden in May 2011 and the related AMAP State of the Arctic Environment report *Arctic Ocean Acidification 2013: An Overview*². It includes extensive background data and references to the scientific literature, and details the sources for figures reproduced in the *overview* report. Whereas the *Summary for Policy-makers* report contains recommendations that focus mainly on policy-relevant actions concerned with addressing the consequences of AOA, the conclusions and recommendations presented in this report also cover issues of a more scientific nature, such as proposals for filling gaps in knowledge, and recommendations relevant to future monitoring and research work.

The AOA assessment was conducted between 2010 and 2013 by an international group of over 60 experts. Lead authors were selected based on an open nomination process coordinated by AMAP. A similar process was used to select international experts who independently reviewed this report.

Information contained in this report is fully referenced and based first and foremost on peer-reviewed and published results of research and monitoring undertaken since 2006. It also incorporates some new (unpublished) information from monitoring and research conducted according to well-established and documented national and international standards and quality assurance/ quality control protocols. Care has been taken to ensure that no critical probability statements are based on non-peer-reviewed materials.

Access to reliable and up-to-date information is essential for the development of science-based decision-making regarding ongoing changes in the Arctic and their global implications. The AOA assessment summary reports^{1,2} and films have therefore been developed specifically for policy-makers, summarizing the main findings of the AOA assessment. The AOA lead authors have confirmed that both this report and its derivative products accurately and fully reflect their scientific assessment. The AOA reports and the films are freely available from the AMAP Secretariat and on the AMAP website: www.amap.no, and their use for educational purposes is encouraged.

AMAP would like to express its appreciation to all experts who have contributed their time, efforts and data, in particular the lead authors who coordinated the production of this report. Thanks are also due to the reviewers who contributed to the AOA peer-review process and provided valuable comments that helped to ensure the quality of the report. A list of the main contributors is included at the start of each chapter. The list is not comprehensive. Specifically, it does not include the many national institutes, laboratories and organizations, and their staff, which have been involved in various countries in AOA-related monitoring and research. Apologies, and no lesser thanks are given to any individuals unintentionally omitted from the list.

The support from the Arctic countries and non-Arctic countries implementing research and monitoring in the Arctic is vital to the success of AMAP. The AMAP work is essentially based on ongoing activities within these countries, and the countries that provide the necessary support for most of the experts involved in the preparation of the AMAP assessments. In particular, AMAP would like to acknowledge Norway for taking the lead-country role in this assessment and thank Canada, Norway, Sweden, USA and the Nordic Council of Ministers for their financial support to the AOA work.

The AMAP Working Group is pleased to present its assessment to the Arctic Council and the international science community.

Richard Bellerby (AOA assessment Chair)

Russel Shearer (AMAP Chair)

Lars-Otto Reiersen (AMAP Executive Secretary)

Oslo, May 2013

¹ AMAP, 2013. AMAP Arctic Ocean Acidification Assessment: Summary for Policy-makers. (www.amap.no/documents/doc/amap-arctic-ocean-acidification-assessment-summary-for-policy-makers/808).

² AMAP, 2013. Arctic Ocean Acidification 2013: An Overview. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway.

1. Introduction

AUTHORS: LARS-OTTO REIERSEN, ROBIE MACDONALD, LEIF ANDERSON, RICHARD BELLERBY, SIMON WILSON

1.1 What is ocean acidification?

Ocean acidification refers to a reduction in the pH of the ocean over an extended period, typically decades or longer, which is caused primarily by uptake of carbon dioxide from the atmosphere, but can also be caused by other chemical additions or subtractions from the ocean. Anthropogenic ocean acidification refers to the component of pH reduction that is caused by human activity. (IPCC, 2011)

As a consequence of the higher amounts of carbon dioxide (CO_2) in the atmosphere, the upper ocean has been forced to take up more CO_2 through gas exchange (Figure 1.1) such that it now holds approximately one quarter of the human-generated CO_2 load. This uptake of CO_2 occurs because the surface ocean

attempts to match its dissolved CO_2 content to the partial pressure of atmospheric CO_2 , which has risen from about 280 parts per million, prior to the Industrial Revolution (ca. 1850), to the present 395 parts per million. As CO_2 in the atmosphere continues to increase with further burning of fossil fuels, so too will the amount of CO_2 dissolved in the ocean. Combined with water, dissolved CO_2 forms carbonic acid (H_2CO_3), a weak acid, which then partially dissociates to release H^+ ions (Figure 1.1) thereby increasing the acidity of the ocean. Because the concentration of H^+ ions ($[\text{H}^+]$) in aqueous solutions can vary through many orders of magnitude, chemists use the term pH to describe the acidity of water (see also Box 1.1), where pH is defined as minus the logarithm of $[\text{H}^+]$ (i.e., $\text{pH} = -\log_{10} [\text{H}^+]$).

Box 1.1 Seawater pH

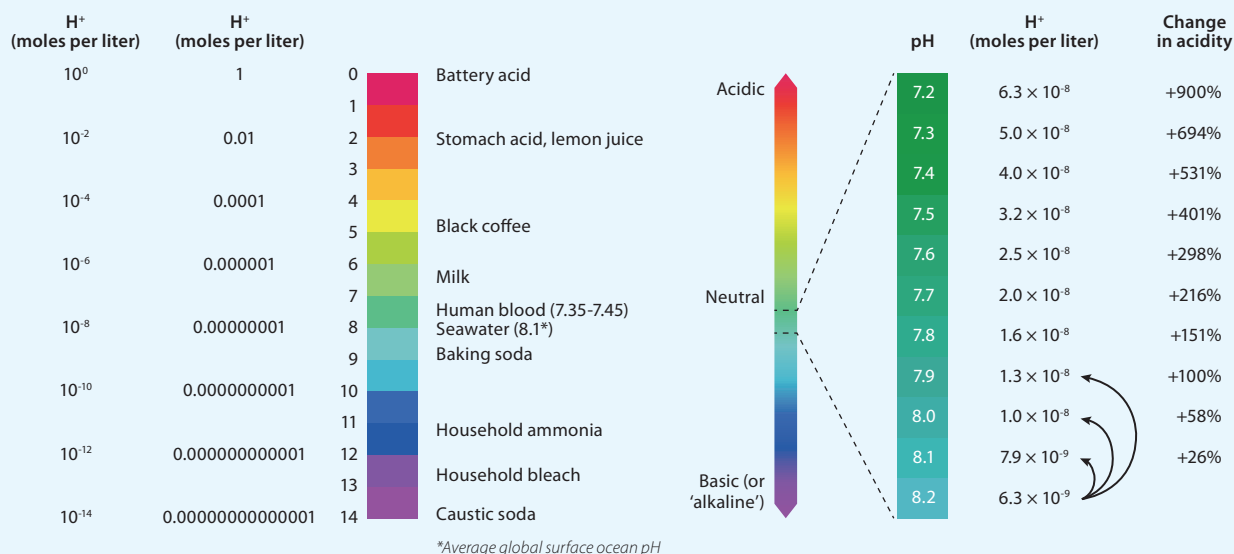
Seawater pH, at the heart of discussions concerning ocean acidification, is a confusing and poorly understood concept. The hydrogen ion concentration ($[\text{H}^+]$) cannot be directly measured and can only be estimated using operationally defined scales, which are based on the nature of the waters being analyzed and the chemistry of the buffers used to calibrate them. Therefore, different disciplines use different pH scales, and there is no unifying agreement on a single, appropriate scale to use.

Nevertheless, independent of the chosen scale, pH represents the *acidity* or concentration of hydrogen ions in a solution. Expressed on a log scale, the pH range between 0 and 14 approximately represents hydrogen ion concentrations between 1 and 10^{-14} moles per liter. Thus, a ten-fold change in the hydrogen ion concentration results in a pH change of 1. The solution is said to be acidic if the pH is below 7, to be alkaline if above 7 and to have a neutral pH at $\text{pH}=7$ (see graphic for examples of common solutions and their pH values). Importantly, a solution can increase in acidity (i.e.,

the pH goes down) without becoming acidic, and an alkaline solution does not have to have a high alkalinity.

Ocean acidification is the ongoing reduction in seawater pH predominantly due to the uptake of CO_2 from the atmosphere. As CO_2 increases, the acidity increases and pH decreases. From a mean global pH of about 8.2 at the beginning of the Industrial Revolution pH has decreased by about 0.1 and with continuing combustion of fossil fuels may fall another 0.25 units by the end of the century (note that these are global averages and many regions will experience greater and lesser pH reductions). These changes represent about a 30% and 125% increase, respectively, in hydrogen ion concentration since 1860 (see right-hand part of graphic for the percentage change in ocean acidity relative to a starting point of pH 8.2 – the value at the start of the industrial era).

Ocean acidification will not, however, lead to an acidic ocean – there is not enough fossil fuel carbon to burn to result in a seawater pH below 7.



Source: Modified from National Oceanic and Atmospheric Administration (NOAA) Pacific Marine Environmental Laboratory (PMEL).

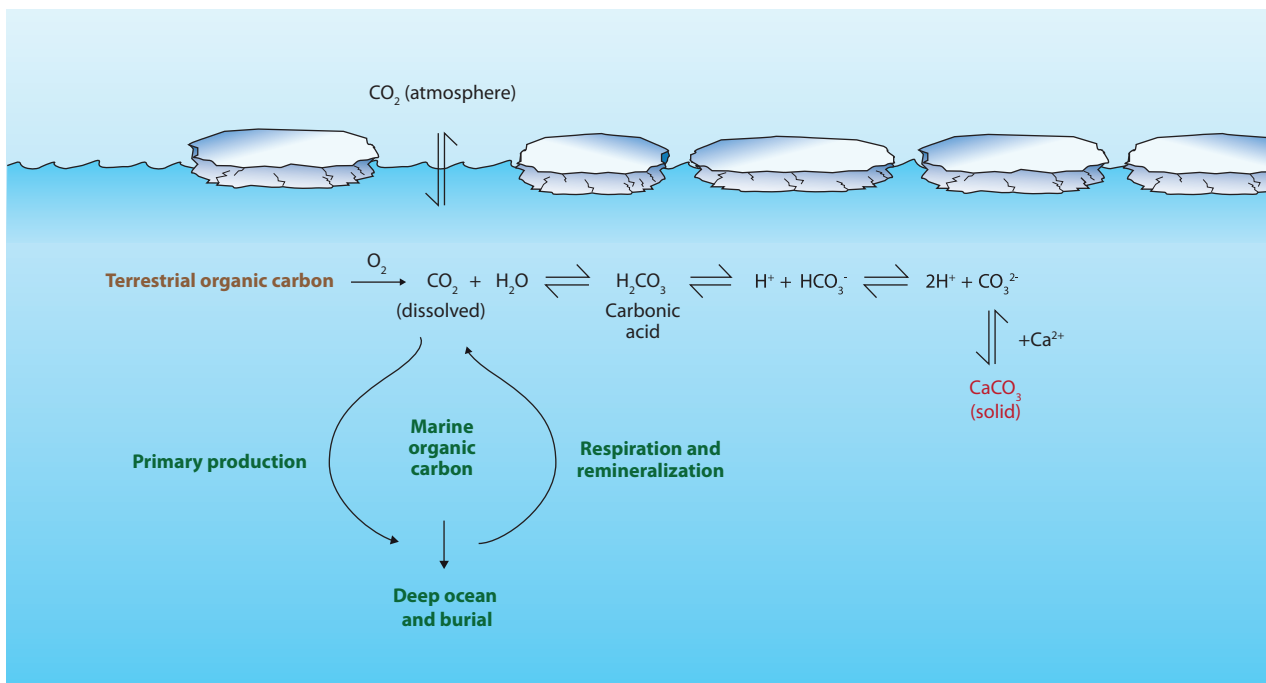


Figure 1.1. A schematic illustration of the inorganic carbon system in the Arctic Ocean. Black lettering shows the equilibria between inorganic carbon components in water; brown lettering shows the potential for terrestrial organic carbon to contribute carbon dioxide (CO_2) through oxidation; green lettering shows the potential for the marine organic carbon cycle to remove CO_2 through primary production or add CO_2 through oxidation of organic carbon, and to transfer CO_2 to the deep ocean through the rain of particulate organic carbon; red lettering shows the potential to remove carbonate ions (CO_3^{2-}) by precipitation of solid carbonate or to add CO_3^{2-} by dissolving solid carbonate. A non-intuitive consequence of this equilibrium system is that the addition of CO_2 at the left side of the equation, either through uptake from the atmosphere or oxidation of organic carbon, promotes the dissolution of solid carbonate at the right side of the equation.

Processes other than atmospheric gas exchange can produce CO_2 or remove it from the ocean and thus affect ocean pH. As is evident in Figure 1.1, carbon dioxide concentration in the ocean ($[\text{CO}_2]_{\text{aq}}$) may also be strongly affected by the organic carbon cycle. Terrestrial organic carbon from rivers and coastal erosion enters the ocean where a proportion of it oxidizes through photolytic or microbial oxidation, producing CO_2 (left-hand side, Figure 1.1). The addition of $[\text{CO}_2]_{\text{aq}}$ by this process will lead to higher $[\text{H}^+]$ and a decline in pH in exactly the same way that CO_2 invasion from the atmosphere does. Within the ocean itself, CO_2 may be removed through primary production during which phytoplankton convert CO_2 to organic carbon. This removal process then leads to an *increase* in pH. Much of the organic carbon produced by phytoplankton becomes oxidized back into CO_2 through grazing by zooplankton, metabolism and respiration and by heterotrophic microorganisms (Figure 1.1, green lettering). However, a small proportion of the organic carbon produced by phytoplankton ultimately enters the deep ocean or becomes buried in sediments and therefore contributes a net loss of CO_2 from the upper ocean.

1.2 Ocean acidification in the global system

During the past decade, ocean acidification has emerged as a new challenge to oceans around the world. Although it has long been understood that the addition of CO_2 to water leads to acidification, it was only in 2004, following an international symposium entitled *The Ocean in a High- CO_2 World* and a report by the Royal Society (The Royal Society, 2005) that

acidification became an urgent issue in ocean research. This ‘other CO_2 problem’ (Turley and Blackford, 2005; Doney et al., 2009) is a direct consequence of the increase in atmospheric CO_2 during the past two centuries due primarily to human use of fossil fuels like coal, oil and gas (Sabine et al., 2004; Forster et al., 2007; IPCC, 2007).

Given the number of processes in the oceans that impact $[\text{CO}_2]_{\text{aq}}$, and thus also pH, there is large variability with time (diurnally, annually) and space, especially near the sea surface.

Within the large seasonal and spatial variability in pH, the consequence of fossil fuel use can be seen in the Pacific Ocean, where a time series collected since 1989 in surface waters near Hawaii, shows a slow, relentless decline in average pH that mirrors the increase in atmospheric CO_2 (Figure 1.2). Since the beginning of the Industrial Revolution, the CO_2 accumulation in ocean surface waters has led to an increase in $[\text{H}^+]$ of ~30%, which corresponds to an average decrease in pH by 0.1 (Caldeira and Wickett, 2003; Doney et al., 2009).

A pH decline in the ocean is of concern because it has the potential to exert far-reaching effects on biological and geochemical systems (e.g., Orr et al., 2005; Guinotte and Fabry, 2008; Hester et al., 2008; Cooley and Doney, 2009; Dore et al., 2009).

Acidification may affect biological systems in a number of ways, these include:

- Directly, through for example interference in the calcification process required by many organisms to build hard-body structure (see also Box 1.2). The list of marine taxa relying on structural carbonate is large and varied, including for example, plankton, mollusks, echinoderms and corals.

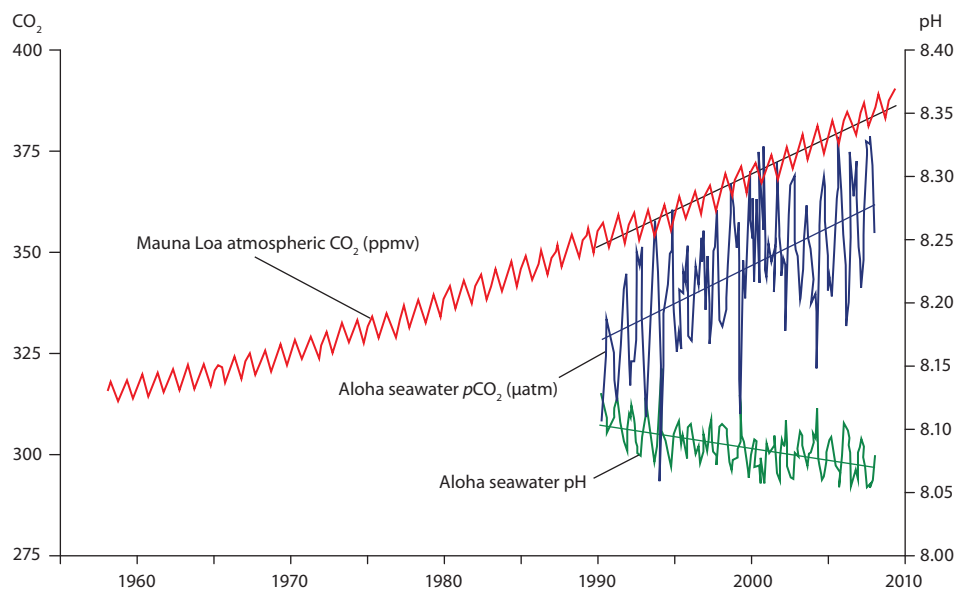


Figure 1.2. Time series of atmospheric CO_2 at station Mauna Loa, and surface water $p\text{CO}_2$ and pH at station ALOHA in the subtropical North Pacific Ocean. Source: Modified after Doney et al. (2009).

- Directly, through physiological impacts at various life-stages, impacts on health through, for example, compromised immune systems, changes to behavior, competition and resource partitioning.
- Indirectly, through alteration of food webs, which could result from loss of carbonate species, and interference with olfaction, respiration and metabolism, and impairment of reproductive success (Gattuso and Hansson, 2009; Williamson and Turley, 2012). On the other hand, some species may thrive in a higher CO_2 world, for example sea-grasses (Hall-Spencer et al., 2008), while others may adapt (Langer et al., 2006).

Box 1.2 Interference in calcification

Interference with the calcification process as a consequence of ocean acidification is one of the more well-known biological responses to ocean acidification. However, this response is complex and cannot be understood by reference to pH by itself. The precipitation of calcium carbonate (CaCO_3), or its dissolution, depends on the product of the concentrations of carbonate and calcium ions (i.e., $[\text{CO}_3^{2-}] \times [\text{Ca}^{2+}]$) (Figure 1.1, right side). Although $[\text{CO}_3^{2-}]$ is related directly to pH through the ocean's carbonate system as depicted in Figure 1.1, $[\text{Ca}^{2+}]$ may be affected by other processes, for example by dilution with river water or sea-ice melt containing lower concentrations of dissolved calcium, and these processes must be factored into the calculations before any inference can be made about the stability of solid CaCO_3 . Finally, CaCO_3 manifests a number of different crystalline structures: in the ocean, the two predominant biological forms are aragonite and calcite with the former tending to dissolve first as pH is lowered. These issues are discussed in more detail in Chapter 2, section 2.2.

1.3 Why assess ocean acidification in the Arctic?

1.3.1 The sensitivity of the Arctic Ocean to acidification

With respect to ocean acidification, conditions in the Arctic Ocean are different from temperate oceans in several important respects. For example, primary production has a smaller diurnal signal at high latitudes, also reflected in pH, because the light conditions do not vary as much throughout the day. On the other hand, the surface water annual pH cycle may be substantial. For example, a $\text{pH}_{\text{in situ}}^{\text{tot}}$ increase in the surface waters of the Barents Sea of between 0.1 in the south to 0.25 in the north was observed from March to May 1998 (Kaltin, et al., 2002). The spatial variability can be even greater, with $\text{pH}_{\text{in situ}}^{\text{tot}}$ values as low as 7.5 in the top 10 m close to the coast and up to about 8.3 in the surface waters of the deep basin. This regional variation may be attributed to oxidation of terrestrial organic matter near the coast.

Commencing in 1998, a sequence of AMAP assessments has shown, without exception, that the Arctic is especially sensitive to human activities at the global scale (AMAP, 1998, 2011a,b; ACIA, 2005; McGuire et al., 2010). Indeed, in a prescient note, Walsh (1991) suggested that ice cover in the Arctic might provide a bellwether for global change. All oceans face acidification due to higher amounts of CO_2 in the atmosphere, but based on experience, and knowing that the organic carbon cycle in the Arctic contains a number of feedbacks that provide opportunities for surprise (Bates and Mathis, 2009; McGuire et al., 2010) it seems prudent to anticipate that the Arctic Ocean and its marginal seas will in some way be especially sensitive to CO_2 – that is, the Arctic Ocean and its marginal seas are also likely to provide a bellwether for ocean acidification (Bellerby et al., 2005; Fabry et al., 2009; Steinacher et al., 2009; Turley et al., 2010).

A number of points of Arctic Ocean sensitivity to acidification can be anticipated. Seasonal under-saturation for aragonite in surface and shallow subsurface waters of the northern polar

seas has already been observed (Yamamoto-Kawai et al., 2009, 2011; Bates et al., 2009), and this ocean is projected through models to be persistently under-saturated by the mid-21st century (Steinacher et al., 2009; Denman et al., 2011). Even if acidification does not lead to local or regional extinction of sensitive species that rely on aragonite for structure, it may set the stage for invasive species to displace such species (e.g., Vermeij and Roopnarine, 2008), which can no longer compete due to stress from acidification.

The recent extensive loss of summer sea ice in the Arctic Ocean has accelerated the invasion of anthropogenic CO₂ into the ocean while at the same time providing a widespread source of brackish water that is impoverished in Ca²⁺. Sea-ice melt is augmented by a very large cumulative inflow of river water, also low in [Ca²⁺], further leading toward under-saturation of aragonite. It may be speculated as to whether or not the northern polar ocean has crossed a sea-ice tipping point (Serreze, 2011; Wadhams, 2012), but it seems clear that we are heading for the aragonite tipping point.

The Arctic shelves have several points of vulnerability. They are well supplied with dissolved and particulate organic carbon (DOC and POC, respectively) from rivers and coastal erosion (estimated at ~11 Mt/y for POC alone; Stein and Macdonald, 2004a). Recently, Vonk et al. (2012) suggested that this terrigenous organic carbon supply may have been seriously underestimated and that as much as 44 ± 10 Mt/y is released to the East Siberian shelf seas alone by the Siberian ice complex, with two-thirds becoming oxidized to CO₂ and the remainder buried in shelf sediments. Whether or not this enormous organic carbon release is a consequence of recent permafrost thawing, if it becomes metabolized in water or sediments beneath the ice, this terrigenous organic carbon will provide a large source of CO₂ (Figure 1.1) that may not be easily evaded to the atmosphere. A particularly sensitive location, in this regard, is likely to be the shallow, nearshore waters that are seasonally covered by continuous landfast ice, thus shutting down CO₂ evasion while still permitting metabolism of terrigenous and marine organic carbon (Garneau et al., 2006). The Arctic shelves tend to have higher primary productivity than the interior ocean, especially the Chukchi and eastern East Siberian Seas, which exhibit some of the highest productivities observed in the world ocean (Grebmeier et al., 2006; Anderson et al., 2011a). The downward flux of organic-rich particulate matter associated with this production then supplies a powerful metabolic engine that releases CO₂ and thus contributes low pH (Bates et al., 2009). Upwelling of CO₂-rich water onto shelves is an effective pathway to place CaCO₃-corrosive water near the surface (Feely et al., 2008). With the loss of sea ice, upwelling has been projected to increase in the Arctic (Carmack and Chapman, 2003), and in the western Arctic Ocean upwelling is likely to access CO₂-rich halocline water, whose origin is the Pacific Ocean via the Chukchi Shelf.

Global warming has the potential to destabilize the large amounts of methane hydrates stored in sediments along the continental margins, releasing methane (CH₄) into the water column and possibly the atmosphere, with the Arctic particularly vulnerable in this respect. Release of CH₄ from melting hydrates in these areas could enhance ocean acidification and oxygen depletion in the water column (Biastoch et al., 2011). Recently, large amounts of CH₄ have been observed to seep out of bottom

sediments in the Siberian seas (Shakhova et al., 2010). This phenomenon may be widespread (Damm et al., 2007; McGuire et al., 2010) over Arctic shelves and offer the possibility of another sort of tipping point (Archer et al., 2009b). In the context of ocean acidification, the metabolism of CH₄ would provide another pathway to contribute CO₂ to bottom waters.

1.3.2 The sensitivity of Arctic marine ecosystems to acidification

Arctic Ocean acidification has a number of potential biological and ecological consequences, including biogeochemical feedbacks. Arctic ecosystems are characterized by low biodiversity and simple food webs. The large dataset of global responses to ocean acidification contrasts with very limited and scarce data concerning responses of Arctic species and ecosystems, however parallels imply that Arctic ecosystems are likely to be at risk from the effects of ocean acidification.

1.3.3 The socio-economic value of the Arctic – and the potential cost of Arctic Ocean acidification

Arctic fisheries are important both regionally and globally. In 2002, the total catch of wild fish in the Arctic amounted to 7.26 million tonnes, around 10% of the world catch of fish. Shrimp and crabs, and farmed fish contributed a further 0.36 and 0.1 million tonnes, respectively (Statistics Norway, 2006). Commercial fisheries also provide an important component in the economy of the Arctic region. Fishing and fish processing accounted for almost 2% of the Arctic regional economies of Alaska, Iceland, Greenland and the Faroe Islands and the Arctic regions of Canada, Finland, Norway, Russia and Sweden in 2005 (Statistics Norway, 2009). The industry is particularly important in the Faroe Islands, Greenland, Iceland, and Arctic Norway, contributing approximately 20%, 12%, 7% and 7% to the regional economies of these four Arctic countries/regions.

Climate change, by itself, is expected to alter northern fisheries, both through changes in productivity (which is generally expected to increase with warming and reduction of sea ice – although this is not certain) and changes in species composition and food-web structure (e.g., as new species move into the Arctic). Arctic Ocean acidification adds another dimension of change, targeting species in a very different way. Marine resource utilization is central to the cultures and lifestyle of northern communities, in particular coastal communities.

People have been living in and adapting to changing conditions in the Arctic for thousands of years. The Arctic is home to around four million residents of which about 10% are indigenous peoples, spread over many communities in the Arctic (AMAP, 1998). The proportion of the population that is indigenous varies widely. In Nunavut, Canada about 90% of the population is Inuit; Inuit also make up most of the population of Greenland, whereas the Saami account for only about 2.5% of the population in northern Scandinavia. Arctic indigenous peoples have survived by using the natural resources available to them. Traditional food use is culturally specific and varies widely between the different communities and regions of the Arctic. People living along the coast mainly rely

on marine foods, including both marine mammals and fish, while people living inland eat mainly reindeer/caribou/muskox and freshwater fish. These traditional foods are rich in nutrients and energy, and thus permitted the first migrations into the region and have continued to support life there ever since.

Over the past three decades AMAP has documented the contamination of important traditional food items by persistent organic pollutants, mercury and radionuclides as a result of long-range transported and local contamination, (AMAP, 1997, 2002, 2009, 2011b). This aspect of food security is a major concern for Arctic indigenous peoples. In cooperation with national governments and responsible agencies, AMAP has promoted actions at both the international level (for example through the Stockholm Convention on Persistent Organic Pollutants and the negotiation of a global agreement on mercury under UNEP) and local level (such as through food consumption advice) to reduce human exposure to these contaminants.

Some parts of the Arctic are experiencing increasing immigration of people from outside the area due to the employment opportunities provided by oil and gas resource development, mining and other industries. One consequence of this, and of the introduction in the Arctic of modern communications and associated media and advertising, has been an increasing introduction of western foods resulting in dietary shifts that are both more expensive and less healthy.

The identification of ocean acidification as a new factor in the Arctic food security debate has led some indigenous peoples (reliant on marine foods) to express concern about what may happen to marine life if the Arctic Ocean becomes more acidic, and in this connection its potential effect on their marine foods

and their traditional culture. This assessment is an attempt to clarify the situation regarding the future consequences of increasing Arctic Ocean acidification also in this regard.

Ocean acidification does not act alone; it is occurring along with other global stressors that are now defining the anthropocene (Steffen et al., 2011) including climate change (e.g., warming, altered hydrology), change in the carbon and nitrogen cycles, alteration of marine foodwebs, and contamination by industrial chemicals. The present assessment rests on a foundation comprising a sequence of assessments dealing comprehensively with these sorts of stressors as they relate to the Arctic (AMAP, 1998, 2011a; ACIA, 2005; McGuire et al., 2010).

1.4 The geographical context of the Arctic Ocean acidification assessment

1.4.1 What are the Arctic Ocean and its marginal seas?

The geographical delineation of the Arctic Ocean and its marginal seas used in this assessment follows previous boundaries defined by AMAP (AMAP, 1998, 2011a). Specifically, the ocean regions considered include the Arctic Ocean, the Bering Sea, the Greenland-Iceland-Norwegian Seas, the Labrador Sea, the Canadian Arctic Archipelago and Hudson Bay (Figure 1.3). This northern Arctic region includes deep basins (Eurasian and Canada Basins, Baffin Bay, Nordic Seas), broad shelf seas (Barents, Kara, Laptev, East Siberian, Chukchi, Bering, Beaufort) and Canadian inland seas (Canadian Arctic Archipelago, Hudson Bay).

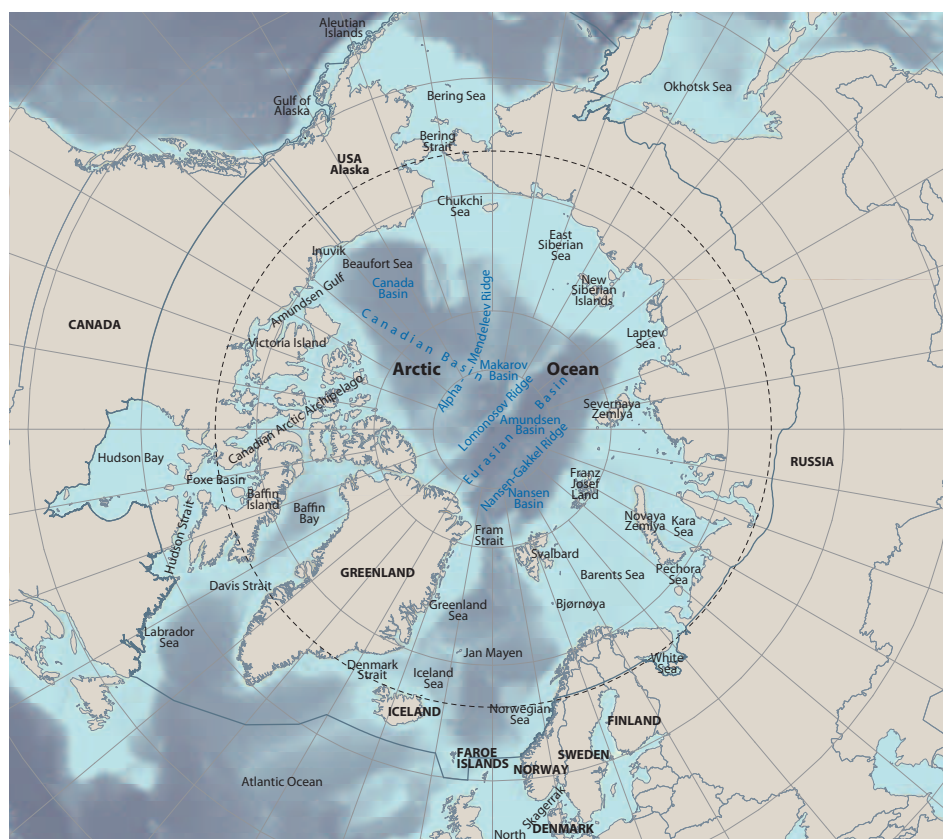


Figure 1.3. The Arctic Ocean and its marginal seas.

1.4.2 The functioning of the Arctic Ocean in the context of acidification

The oceanography of the Arctic Ocean has been well reviewed in previous assessments (ACIA, 2005), and is discussed further in Chapter 2 mainly in the context of features that are crucial for understanding the Arctic's response to ocean acidification. The Arctic Ocean receives its salt water from the Atlantic and Pacific Oceans (Figure 1.4). The Atlantic water enters partly over the Barents Shelf, where it is strongly modified by cooling and ice formation, and partly through Fram Strait. This latter passage is deep, and provides access for the exchange of all the deep water in the Arctic Ocean.

Water from the Pacific Ocean enters the Arctic Ocean via Bering Strait, where it must pass over the broad Chukchi Shelf. Because the Bering Strait sill is shallow (~50 m) and the Pacific water is fresher than the Atlantic water, the Pacific inflow rides above the Atlantic layer within the Arctic, supplying most of the surface water throughout the Canada Basin (e.g., see Ekwurzel et al., 2001). The disposition of Pacific water in the Arctic Ocean is subject to large decadal-scale variation subject to atmospheric pressure fields which vary with the Arctic Oscillation (McLaughlin et al., 1996). The Pacific water entering the Arctic supplies most of the water exiting through the Canadian Arctic Archipelago (McLaughlin et al., 2006) and thence through Hudson Bay and into Baffin Bay (Jones et al., 2003) (Figure 1.4). Because the North Pacific Ocean lies at the end of the global thermohaline circulation system (Schmitz, 1995), its deep water contains high accumulated CO_2 concentrations due to regeneration of organic matter without ventilation to release the CO_2 during the thousand or more years taken to arrive in the North Pacific Ocean. Accordingly,

this water is among the most corrosive in the world oceans to CaCO_3 (Feely et al., 2004, 2008; Sabine et al., 2004).

More than $3300 \text{ km}^3/\text{y}$ of runoff (Serreze et al., 2006) together with net precipitation and the relatively fresh Pacific water ensures strong, pervasive stratification near the surface of the Arctic Ocean (Figure 1.5). This strong layering, which has long been recognized as the defining feature of the Arctic Ocean's water column (Treshnikov, 1959), led McClelland et al. (2012) to liken this ocean to a large, complex estuary. The stratification of the Arctic Ocean inhibits exchange between shallow (~50–100 m) and deep ocean waters. Stratification thus has the important role of limiting deep ventilation and atmospheric CO_2 exchange in the interior ocean, and predominantly, these processes must occur at or near the Arctic Ocean's margins, with recently ventilated water then transporting into the interior Arctic Ocean horizontally (Figure 1.5). An important feature of riverine water and precipitation with respect to ocean acidification is that these freshwaters have a lower capacity to neutralize acid than seawater (Yamamoto-Kawai et al., 2005). The accompanying lower Ca^{2+} concentrations, therefore, lead to under-saturation with respect to aragonite more easily than found in seawater (see Figure 1.1).

Melting during spring and summer converts the 1–2 m layer of floating sea ice into brackish water, which mixes into the surface ocean, further enhancing stratification. Even more important insofar as acidification is concerned, ice melt contains very low concentrations of ions like Ca^{2+} , which therefore means that these waters have even greater sensitivity than river water toward CaCO_3 dissolution when acidified by CO_2 (Yamamoto-Kawai et al., 2011). When sea ice forms in winter it rejects brine into the water column, thus promoting mixing and convection, and under favorable circumstances, deep convection, which can

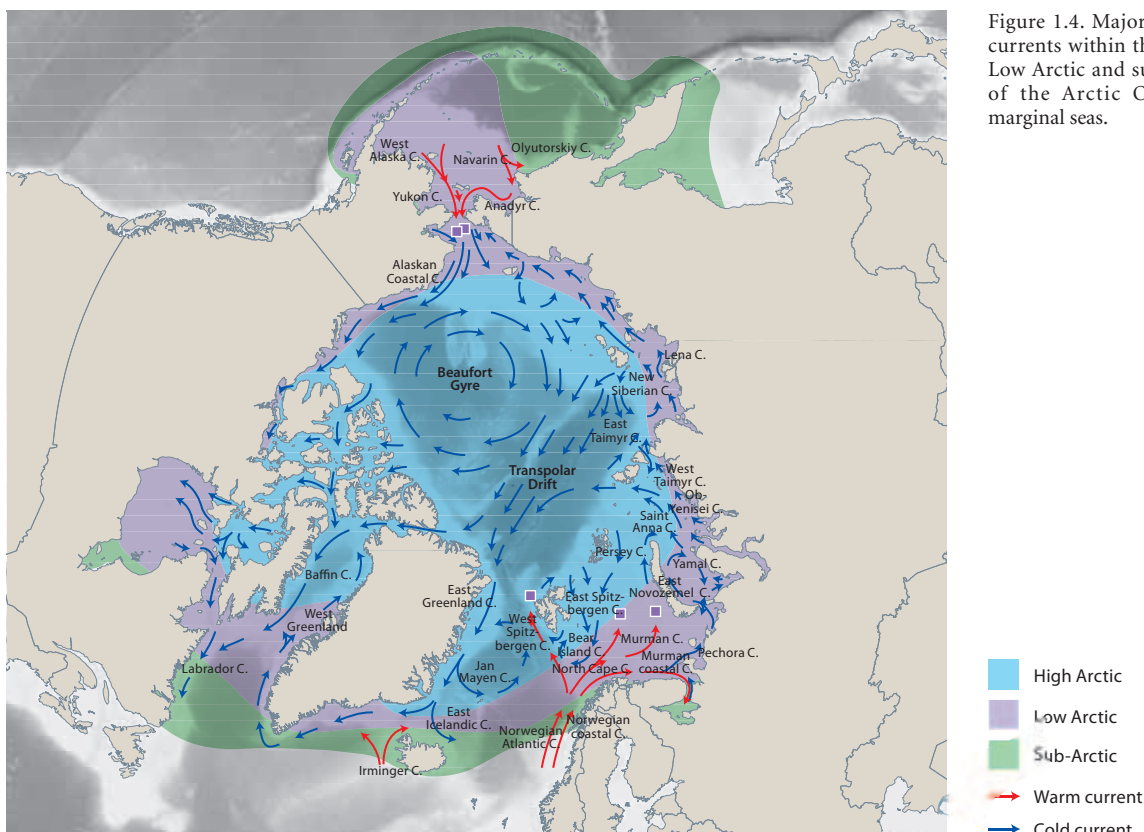


Figure 1.4. Major surface ocean currents within the High Arctic, Low Arctic and sub-Arctic areas of the Arctic Ocean and its marginal seas.

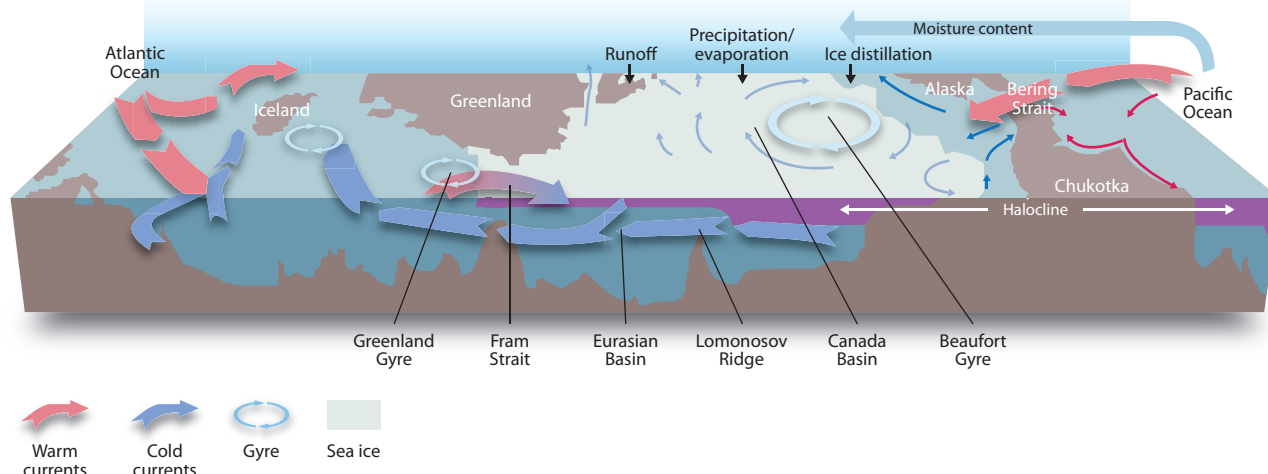


Figure 1.5. Stratification of the Arctic Ocean due to freshwater inputs. Low salinity waters are added to the surface and halocline layers via precipitation and runoff, Pacific inflow via the Bering Strait, and the sea-ice distillation process. Low salinity waters and sea ice are subsequently advected through Fram Strait and the Canadian Archipelago into the convective regions of the North Atlantic. Stratification, and the addition of poorly-buffered freshwater are two important factors that enhance the Arctic Ocean's sensitivity to ocean acidification.

sequester CO_2 to depth in the ocean (Rysgaard et al., 2007). Sea ice cover may also present a partial barrier to exchange of gases between the ocean and atmosphere, but with respect to CO_2 it plays an active role in this exchange through the formation of brine and its subsequent movement within brine channels (Miller et al., 2011). Finally, in regions of the Arctic where sea ice is lost seasonally, the cadence of primary production during open water versus regeneration during ice cover has been proposed as a rectifying mechanism that enhances CO_2 uptake by the surface ocean (Yager et al., 1995).

A special feature of the Arctic Ocean is a pervasive, cold stratified layer occupying the water column from about 150 to 250 m depth. The water in this layer, termed the Arctic halocline (Aagaard et al., 1981), is produced predominantly over the Barents and Chukchi Shelves through cooling and sea-ice formation, which increase the water's density (Jones and Anderson, 1990; Rudels et al., 2004). This water, especially the component produced over the Chukchi shelf, contains elevated concentrations of regeneration products including CO_2 . Like other nutrient-rich waters, when this water is upwelled it delivers to the surface water that is relatively corrosive to CaCO_3 (e.g., see Feely et al., 2008).

The Arctic Ocean contains enormous shelf areas, fully half of the ocean's area. Accordingly, processes over the shelves are extremely important to the functioning of this ocean, and these regions are also most important to the inhabitants of the Arctic in terms of travel and access to food. And yet, these regions are also among the most sensitive to climate change (ACIA, 2005).

A last consideration for the Arctic Ocean is the question of how quickly water masses can respond to change in surface-water CO_2 content due to the ongoing loading by anthropogenic CO_2 . Anderson et al. (1998) pointed out that, in terms of inorganic carbon budgets, the Arctic Ocean is playing catch-up with the atmosphere in a process where the outflow at Fram Strait exports old water equilibrated with a former atmosphere, containing less anthropogenic CO_2 , to be replaced by recently ventilated inflowing waters reflecting the present atmospheric CO_2 concentration. For the surface

layer (top ~50 to 100 m) in the Arctic Ocean, the residence times are relatively short (<10 y) suggesting that these waters are influenced more directly by the atmosphere and they can respond faster to changing atmospheric CO_2 increases. Although sea ice may impede exchange with atmospheric CO_2 in this layer, the recent demise of permanent ice cover over an extensive area of the Arctic Ocean (Stroeve et al., 2007; Schiermeier, 2012) suggests that exchange now occurs with much less impediment from the ice (Bates et al., 2006). Deeper in the water column, the Atlantic layer pervades the Arctic Ocean. Circulation occurs more rapidly along the boundaries, with exchange into the interior ocean occurring more slowly such that the ventilation age in this water is approximately 30 years, or more and then more slowly into the interior regions of the ocean, taking approximately 30 years to transit the interior ocean. This time frame suggests that CO_2 concentration in the Atlantic layer waters will lag that in the atmosphere by up to three decades. Finally, the basin waters have been out of contact with the surface for a century or more, suggesting that these will reflect periods well before the recent rise in atmospheric CO_2 .

1.5 Aim of the present assessment

The objectives of the present assessment are to provide the Arctic Council with timely, up-to-date, and synthesized scientific knowledge about the present status, processes, trends, and future consequences of changes in Arctic Ocean acidification.

This assessment complements previous AMAP assessments of climate change in the Arctic, including the Arctic Climate Impact Assessment (ACIA, 2005) and the Snow, Water, Ice and Permafrost in the Arctic (SWIPA) assessment (AMAP, 2011a).

1.6 Reader's guide to this assessment

This scientific report presents the findings of the Arctic Ocean acidification assessment as developed by the report authors, produced under their responsibility. A separate

overview report and summary for policymakers were produced under the responsibility of the AMAP Working Group. The summary for policy-makers was developed for presentation to the Arctic Council Ministers at their meeting 14-15 May, 2013 in Kiruna, Sweden, and includes policy-relevant scientific recommendations. The scientific report (the present report) provides the validated scientific basis for all statements made in the overview report and the summary for policymakers, as confirmed by the lead authors of the scientific assessment.

This report contains five chapters.

Chapter 1 sets the stage for the assessment and describes its scope.

Chapter 2 presents an introduction to the carbon biogeochemical system in the Arctic Ocean: processes that influence the carbon system; processes sensitive to ocean acidification; present sources and sinks of carbon in the Arctic Ocean; current features of ocean acidification in the different Arctic seas; and a discussion of future scenarios.

Chapter 3 provides a description of the biological responses to ocean acidification: impacts on calcification rate, on polymorph mineralogy and elemental partitioning in hard parts like skeletons and shells; viral effects on marine organisms including fish and mammals; effects observed within the Arctic area and in other relevant areas including sub-Arctic waters and Antarctic waters; and interactions between multiple stressors.

Chapter 4 presents analyses of how changes in ocean acidification may affect the economics of marine fisheries in regions of the Arctic and on food security and cultural issues for coastal Arctic indigenous communities.

Chapter 5 presents an overall summary of the major findings and gaps in knowledge on Arctic Ocean acidification. The summary is based on the logical consequences of and conclusions stemming from the scientific findings presented in the preceding chapters.

2. Acidification in the Arctic Ocean

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2.1 Introduction

A consequence of the persistent release of carbon dioxide (CO_2) to the atmosphere following fossil fuel combustion and changes in land use is that there is an increasing net air-to-sea transport of CO_2 . Although this oceanic uptake will reduce the potential for greenhouse warming that would have arisen had the gas remained in the atmosphere, it will also result in major changes in ocean chemistry. The most obvious signal in this respect is the fall in ocean pH and the change in the speciation of the marine carbonate system. The Arctic Ocean is one of the regions where ocean acidification is occurring fastest. From a baseline where the seawater is already poorly buffered and thus small changes in CO_2 content have large changes in pH, there are a multitude of stressors that act on the Arctic Ocean amplifying the acidification.

This chapter summarizes carbonate chemistry in seawater (Section 2.2) and reviews the major processes influencing the Arctic Ocean carbonate system (Section 2.3). The chapter also describes some of the biogeochemical processes sensitive to ocean acidification (Section 2.4). Section 2.5 addresses the major sources and sinks of carbon to the Arctic Ocean, and presents a regional breakdown of contemporary rates of ocean acidification. Finally, simulations from earth system models and regional models are analyzed to project potential changes to the Arctic Ocean carbonate system (Section 2.6).

2.2 Carbonate system in seawater

Carbon dioxide acidifies seawater, because CO_2 is one of a number of compounds (including sulfur and nitrogen dioxides) that hydrolyze water in solution. That is, when CO_2 is added to water, it splits the water molecule, releasing protons (acid):



In seawater and other solutions with high concentrations of carbonate (as well as other compounds participating in acid-base

reactions, such as borate, phosphate, silicate, etc.), the relatively simple equilibria in Equation 1 lead to complex acid-base buffering relationships. In the modern ocean, the net result of all these acid-base equilibria is that most of the carbonate is in the form of bicarbonate ions (HCO_3^-) and the pH is about 8 (Figure 2.1).

The precise relative concentrations of the carbonate system species, as well as the pH, in seawater are related through the conditional equilibrium constants:

$$K'_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad \text{Eqn. 2}$$

$$K'_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}, \quad \text{Eqn. 3}$$

where, K'_1 and K'_2 are defined empirically, based on experiments in sodium chloride and real and artificial seawater solutions (e.g., Hansson, 1973; Mehrbach et al., 1973; Dickson and Millero, 1987; Roy et al., 1993; Lueker et al., 2000). When K'_1 and K'_2 are coupled with the definitions of the directly measurable variables pH, total alkalinity (A_T), total inorganic carbon concentration (C_T), and CO_2 fugacity (f_{CO_2} ; closely related to partial pressure),

$$\text{pH} = -\log [\text{H}^+] \quad \text{Eqn. 4}$$

$$A_T \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] \quad \text{Eqn. 5}$$

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad \text{Eqn. 6}$$

$$f_{\text{CO}_2} = \frac{[\text{H}_2\text{CO}_3]}{K'_0} \quad \text{Eqn. 7}$$

(where K'_0 represents the CO_2 solubility in seawater; Weiss, 1974), it becomes possible to fully define the carbonate system with measurements of only two variables (e.g., pH and alkalinity can be calculated from measurements of C_T and f_{CO_2}).

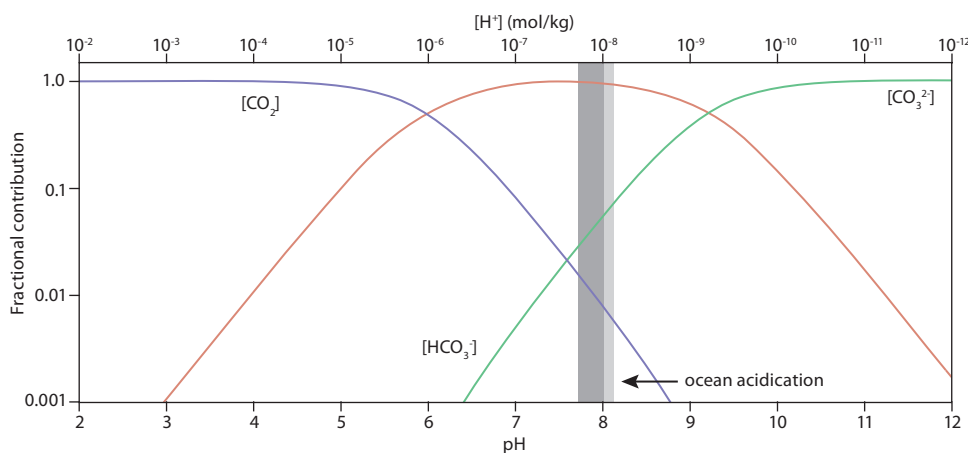
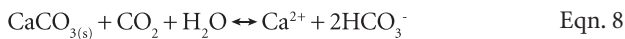


Figure 2.1. Changes in carbonate species concentration with changes in seawater pH. The light grey band indicates the decline in surface seawater pH since the Industrial Revolution and the dark grey band represents the projected change to the end of the century.

Dickson et al. (2007) presented full details of these calculations, including pitfalls to avoid. Certain pairs of variables are preferable for calculating the others, due to their superior analytical precision (e.g., Dickson and Riley, 1978). As analytical methodologies and instrumentation have evolved and as reference materials have become available, the two best variables to measure have not only changed over the years, but also differ between laboratories, depending on resources available. This complicates efforts to compare results from different studies, particularly those from more than 15 years ago.

Although the carbonate system in seawater is more complicated than implied by Equation 1, and therefore less intuitive, adding C_T to a seawater solution of otherwise fixed composition, does simply decrease the pH (Figure 2.2). An important effect of the high total alkalinity and the accompanying complicated chemistry in seawater is to buffer the solution; not only is the pH of seawater higher than in freshwaters, despite the higher C_T concentrations in seawater, but the ocean also resists more strongly further decreases in pH as more C_T is added (Table 2.1). As the table shows, the freshwater influences in the Arctic (i.e., river inflows and sea-ice melt) serve to decrease the pH and reduce the buffering capacity, at least in surface waters.

One of the primary geochemical impacts of seawater acidification is to increase the solubility of calcium carbonate (CaCO_3) minerals. Thus, somewhat counter-intuitively, adding CO_2 to seawater causes CaCO_3 to dissolve:



The saturation state of a CaCO_3 mineral (i.e., its tendency to resist dissolution) in a specific solution is represented by the saturation state:

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K'_{\text{sp}}} \quad \text{Eqn. 9}$$

where K'_{sp} is the equilibrium solubility product (which depends on salinity, temperature, pressure, etc.):

$$K'_{\text{sp}} = [\text{Ca}^{2+}]_{\text{sat}} [\text{CO}_3^{2-}]_{\text{sat}} \quad \text{Eqn. 10}$$

The saturation state for a specific mineral is generally indicated with a subscript: Ω_{Ar} represents the saturation state for aragonite and Ω_{Ca} that for calcite.

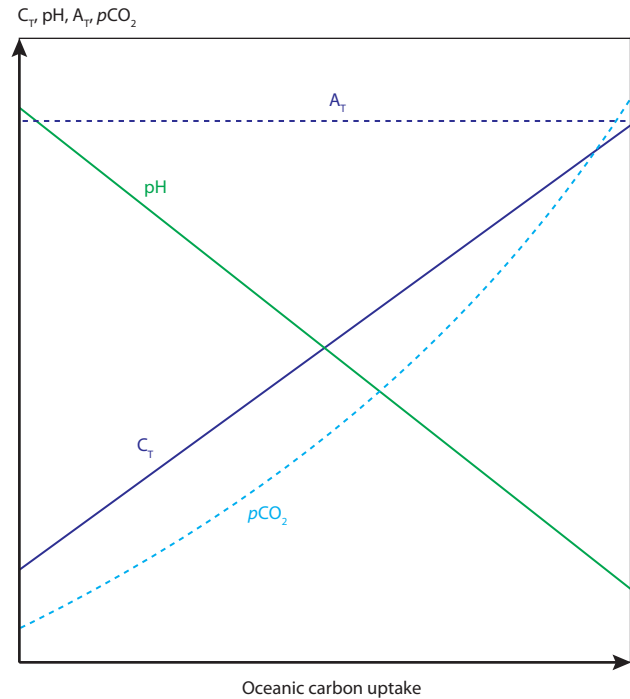


Figure 2.2. Changes in total inorganic carbon (C_T), pH and the partial pressure of carbon dioxide in seawater with increasing ocean carbon uptake and constant total alkalinity (A_T).

In general, if Ω is greater than 1, the mineral is stable, but if Ω is less than 1, the mineral is vulnerable to dissolution. Each specific mineral has a different solubility product; for example, of the two most common biogenic CaCO_3 minerals in the oceans – aragonite and calcite – aragonite has a higher solubility product than calcite (Mucci, 1983). This means that aragonite dissolves more readily than calcite, becoming unstable even in waters at relatively high pH values (see Riebesell et al., 2010 for a more detailed discussion). However, calcite minerals in which some Ca^{2+} ions are replaced by Mg^{2+} ions, called hereafter Mg-calcite, are even more soluble than aragonite. With lower initial surface water Ω and strong freshwater inputs (thus lower Ca^{2+} concentrations), CaCO_3 minerals in the Arctic Ocean are particularly susceptible to dissolution. Depths at which $\Omega = 1$ are often referred to as the ‘saturation horizon’. In the Arctic Ocean, not only is the pH decrease from anthropogenic CO_2 causing the dissolution of CaCO_3 , but increasing river run-off and the pulse of sea-ice melt are further diluting the seawater, causing additional dissolution. (See Section 2.3.5 for further details on this topic.)

Table 2.1. pH and the buffering capacity of different surface water types.

Surface water type	C_T , $\mu\text{mol/kg}$	A_T , $\mu\text{mol/kg}$	pH_T	pH change with +1 $\mu\text{mol/kg}$ C_T
Arctic seawater	2140 ^a	2290 ^a	8.12	-0.003
Tropical seawater	2040 ^a	2390 ^a	8.18	-0.002
High-alkalinity river (e.g., Yukon)	1700 ^a	1710 ^a	7.84	-0.005
Low-alkalinity river (e.g., Kolyma)	600 ^a	500 ^a	7.28	-0.004
Sea-ice melt	400 ^a	400 ^a	7.97	-0.026
Pure water	0	0	7	-0.992

^a Typical values used solely for comparison purposes.

2.3 Influences on the marine carbonate system in the Arctic Ocean

2.3.1 Sea ice

Characteristic of polar oceans, sea ice can substantially affect air-sea CO_2 exchange and, thereby, the acidification state of Arctic waters. In the simplistic view, the presence of a solid sea-ice cover has been thought to inhibit both primary production and direct air-sea CO_2 transfer, however, a number of sea-ice associated processes also act to enhance gas exchange, counteracting and possibly even superseding this inhibition effect.

Although sea ice reduces light transmission to the underlying phytoplankton community, these communities appear to be well-adapted to low-light conditions, and observations of extensive under-ice phytoplankton blooms (e.g., Fortier et al., 2002; Mundy et al., 2009; Arrigo et al., 2012) indicate that at least first-year sea ice may not limit surface water primary production as much as has been assumed. In fact, sea-ice algal communities are important contributors to Arctic primary production, both within the sea ice and as possible seed populations for under-ice blooms (e.g., Arrigo et al., 2010). In addition, the timing of sea-ice retreat and formation can apparently have dramatic impacts on water-column primary production, depending on geographical and meteorological conditions, because in the absence of ice, upwelling events and wind-induced mixing can break down surface stratification and thus foster blooms (Brugel et al., 2009; Tremblay et al., 2011).

Contrary to the long-standing assumption that sea ice is a barrier to gas transport, it is now clear that gases, including CO_2 , are able to move within and through sea ice (Gosink et al., 1976; Semiletov et al., 2004; Zemmelink et al., 2006; Nedashkovsky and Makshtas, 2010; Nomura et al., 2010a,b; Miller et al., 2011; Papakyriakou and Miller, 2011). In the presence of a solid, cold ice cover, the fluxes appear to be small, with upward fluxes from the ice to the atmosphere in winter switching to downward fluxes from the atmosphere to the ice as spring progresses (Nomura et al., 2010a; Miller et al., 2011; Papakyriakou and Miller, 2011). These fluxes are clearly between the atmosphere and the ice, not the underlying water; that is, the ice is not a passive conduit between the surface waters and the atmosphere but constitutes a distinct carbon pool which exchanges with both the atmosphere and the ocean. While sea ice contains less inorganic carbon than an equal volume of the underlying seawater (Rysgaard et al., 2009; Miller et al., 2011), the opposite may be the case for organic carbon for which concentrations can be much higher in sea ice than seawater (e.g., Thomas et al., 2010), and $p\text{CO}_2$ can be very high in sea-ice brines, particularly under very cold conditions (e.g., Loose et al., 2011).

Direct flux measurements (Else et al., 2012) have confirmed the hypothesis developed from water-column data (Anderson et al., 2004; Omar et al., 2005; Loose and Schlosser, 2011) that in the presence of an incomplete or broken ice cover, CO_2 fluxes can be much higher than in open, ice-free waters. Two possible mechanisms may be responsible: boundary-layer turbulence enhancement in both the air and water caused by the presence of sea ice and its formation (e.g., McPhee and Stanton, 1996), and small-scale disruption of the sea-surface microlayer by

frazil ice during ice formation (as suggested by Anderson et al., 2004). High CO_2 fluxes in the presence of a broken and mobile ice cover have profound implications for the net annual air-sea CO_2 budget in an Arctic Ocean covered by first-year, instead of multi-year, sea ice. Winter data are still sparse, but if Arctic surface waters remain undersaturated in CO_2 throughout most of the winter (Miller et al., 2011; Else et al., 2012), high air-sea fluxes in the presence of a broken ice cover would increase the net Arctic CO_2 sink substantially. On the other hand, in areas where surface waters become supersaturated during winter (e.g., Kelley, 1968; Miller et al., 2002), new understanding of the potential for winter gas exchange indicates that outgassing could completely cancel out all summer CO_2 drawdown in those regions. Steiner et al. (2013) tested the implications of enhanced flux in ice-covered areas in an earth system model application. They found that *enhancing* the flux in ice-covered areas of the Arctic alters the seasonal cycle by extending the maximum CO_2 uptake in autumn and reducing uptake in summer. The reduced uptake in summer is likely to be due to earlier ocean $p\text{CO}_2$ equilibration with enhanced flux during autumn and winter, but also hints at a limited uptake capacity of Arctic surface waters as discussed by Cai et al. (2010). Results by Steiner et al. (2013) also show the relative change due to the enhanced flux parameterization in the annual mean to be small if integrated over the whole Arctic region (below 2–3% for the area north of 68°N) but to be significantly higher for the predominantly ice-covered central Arctic (up to 21% north of 80°N). With respect to acidification, they confirmed accelerated ocean acidification with enhanced fluxes. They found that enhancing the CO_2 flux by about 20% increases the surface $p\text{CO}_2$ and decreases the aragonite saturation by over 50% relative to what would be expected if sea ice did not inhibit the flux at all (a 10% enhancement allows for more than a third of the $p\text{CO}_2$ increase / aragonite saturation decrease). The authors concluded that the enhanced uptake could account for a one to two decade difference in the projection of when aragonite undersaturation is reached in certain areas.

A ‘sea ice pump’ may also help export CO_2 to depth (Loose et al., 2011; Rysgaard et al., 2011). When sea ice forms, the salts in the seawater, including carbonates, are not included in the ice lattice but are concentrated in brines. When the brines drain into the underlying seawater, they carry substantial quantities of inorganic carbon. Data indicating that sea-ice brine drainage can indeed inject dissolved inorganic carbon into the surface waters below the ice have been reported by Miller et al. (2011) and Chierici et al. (2011). Because brines rejected from sea ice are important contributors to deep-water formation, the C_T in ice brines may be a significant component of the solubility pump (see Section 2.3.3). In addition, CaCO_3 can precipitate from the concentrated sea-ice brines within the ice as it freezes, and while this only consumes a small fraction of the C_T in the brines, it is responsible for a proportionally greater decrease in A_T (when 1 unit of CaCO_3 precipitates, C_T in the remaining solution is decreased by 1 unit, while A_T is decreased by 2 units). If the solid CaCO_3 remains behind in the ice when the brine drains away, enriching the ice in alkalinity over C_p , and if those CaCO_3 salts dissolve when the ice melts in the following spring and summer, the resulting excess A_T in the surface waters would encourage atmospheric CO_2 absorption, which could then feed

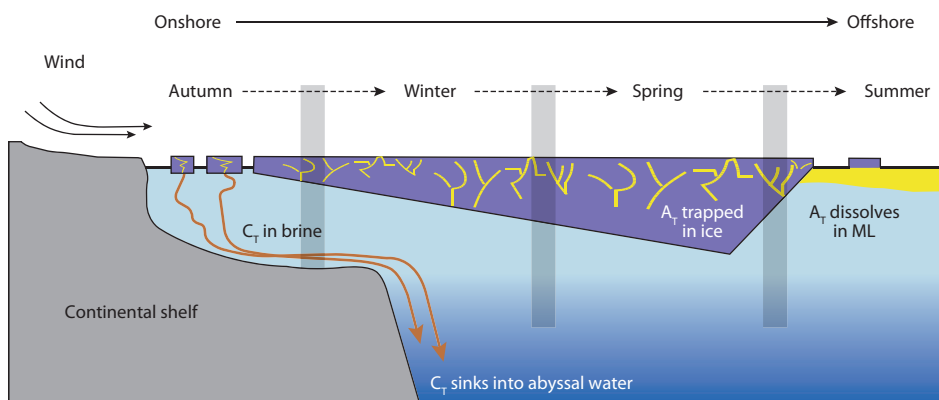
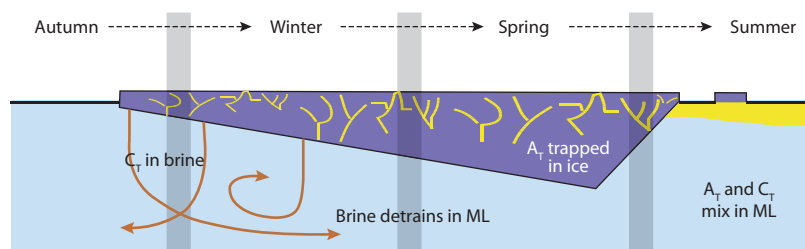
C_T Pump Scenario**Zero Sum Change Scenario**

Figure 2.3. Potential mechanism by which sea ice growth and retreat may enhance atmospheric CO₂ drawdown. Source: modified after Loose et al. (2011).

Schematic of the total inorganic carbon (C_T) pump. In the upper panel, the scenario depicts abyssal water formation in polynyas and the offshore transport of sea ice so that freeze and melt occur in different regions of the ocean. Under such a scenario, if carbonate alkalinity (A_T) remains trapped in the ice as salt crystals and dissolved inorganic carbon (C_T) drains with the brine, then a 'C_T pump' might result in a net transport of inorganic carbon to the deep ocean. The lower panel depicts a scenario where ice forms and melts over a water column with a homogeneous mixed layer (ML). In this case, brine from sea ice is likely to detrain in the mixed layer and subsequently recombine with carbonate alkalinity in the ice. This scenario depicts a zero-sum change in the mixed layer inorganic carbon budget.

further carbon export with sinking brines when the surface waters refreeze the following winter (Figure 2.3). However, this proposed pumping mechanism is still speculative, and the few data available on the A_T:C_T ratio in sea ice are variable and ambiguous.

Estimates of the impact of these various sea-ice processes on the net atmospheric CO₂ drawdown for the Arctic range from 3 to 36 TgC/y (Omar et al., 2005; Nedashkovsky and Shvetsova, 2010; Rysgaard et al., 2011). Bates et al. (2009) also estimated that if summer sea-ice loss increases the exposure of cold, CO₂-undersaturated surface water to the atmosphere, the melt-season CO₂ drawdown could increase by 2 TgC/y, although such an increase in the summer drawdown would also require a substantial increase in wind-mixing to break down melt-induced stratification. Nevertheless, in terms of the physical processes through which sea-ice directly impacts air-sea CO₂ exchange over the annual cycle, the increase in seasonal sea-ice extent at the expense of the multi-year pack currently taking place in the Arctic (AMAP, 2012) is expected to increase the seaward flux of CO₂ over the coming decades.

2.3.2 Freshwater

In the Arctic Ocean, the input of freshwater is one of the most important factors controlling biological and geochemical processes. In particular, the Arctic Ocean receives ~11% of the global river discharge, but contains only 1% of the global ocean volume, and 2.8% of the area. The resultant widespread stratification of the top few hundred meters of the water column due to this freshwater input strongly affects other processes, such as the penetration of atmospheric CO₂ to the depths, and the return to the surface of dissolved inorganic carbon (C_T) and nutrient-rich water from below the surface mixed layer. Approximately 3300 km³/y of freshwater enters the Arctic

Ocean directly via rivers (Serreze et al., 2006), four of which (Yenisey, Lena, Ob, Mackenzie) are among world's largest. This inflow, which exhibits a strong Arctic-wide freshet in May-June, is dominated by snow melt, although significant flow is maintained throughout the year in the larger rivers. Runoff also enters the Arctic Ocean indirectly, carried by the Pacific Inflow through Bering Strait (2500 km³/y) and by the Atlantic Inflow in the Norwegian Coastal Current and Fram Strait (750 km³/y) (Serreze et al., 2006). Runoff, which is distributed unevenly over shelves and basins because it enters from the sides of the ocean, is augmented by a more evenly distributed net input of ~1300 km³/y directly onto the ocean through precipitation (Serreze et al., 2006). The addition of all this freshwater has led to the view that the Arctic Ocean should be considered somewhat like a grand estuary (McClelland et al., 2012).

A residence time of about ten years for surface water in the Arctic Ocean means that there is a considerable storage of the runoff after it enters the ocean (Aagaard and Carmack, 1989), which magnifies the effect on stratification. Climate change and variability are known to affect the runoff component of the freshwater balance in at least two ways. First, there has been an increase in runoff (1964-2000) of ~120 km³/y, unevenly distributed among rivers (McClelland et al., 2006); part of this increase is likely to have been contributed by permanent snows and glaciers, now in retreat due to warming (Olsen et al., 2011; Sharp et al., 2011). One may anticipate that, likewise, with the projected intensification of the hydrological cycle, net direct precipitation onto the ocean is also increasing (e.g., see White et al., 2007). Second, the storage of freshwater can be strongly affected by decadal variation in circulation, for example forced by the Arctic Oscillation (McPhee et al., 2009; Giles et al., 2013; McClelland et al., 2012).

The formation and melting of sea ice provides another, very different, source of freshwater to the Arctic Ocean. In winter,

~2 m of sea ice forms from seawater, rejecting most of the brine to the surface ocean (first-year sea ice has a salinity of ~5–8 compared to the surface ocean at ~33–35). This rejected brine facilitates water-column mixing, which leads to the formation of the polar-mixed layer (PML: 40–50 m), and therefore also helps to redistribute freshwater from runoff into this same layer. During spring and summer, the process reverses; the sea ice melts and 1–2 m of brackish water is added to the ocean surface. The sea-ice component of freshwater is also subject to climate change. The recent replacement of large regions of thick, multi-year ice by first-year ice means that these regions now completely melt their ice cover by the end of summer (e.g., Stroeve et al., 2012a). Furthermore, the saltiness of first-year ice produces an ice phase that is physically and chemically very different from multi-year ice (which has lost almost all of its salt), or freshwater ice.

Aside from controlling the physics and chemistry of the upper ocean, the addition of freshwater from runoff, precipitation and sea-ice melt have a direct effect on the sensitivity of the surface water to added CO_2 . Specifically, these waters are more poorly buffered and contain a lower $[\text{Ca}^{2+}]$, with the result that the mixed water exhibits a greater decline in pH with added CO_2 (Table 2.1), and crosses mineral solubility thresholds sooner. Indeed, it appears that brackish surface water impacted by both runoff and sea-ice melt is already sufficiently corrosive to dissolve aragonite (Bates et al., 2009; Yamamoto-Kawai et al., 2011). In summary, all freshwater additions (precipitation, sea-ice melt, runoff) lead to greater decreases in pH and Ω at the surface of the ocean to an extent depending on the source of freshwater (Table 2.1) and the mixing ratio with seawater (Figure 2.4; Azetsu-Scott et al., 2010).

2.3.3 Solubility pump

Atmospheric gases, including CO_2 , all dissolve in seawater. The same process occurs in the Labrador Sea, where deep convections produce the Labrador Sea Water with high anthropogenic CO_2 content. Their solubilities are different but all increase as water temperature decreases. The air-sea gas flux is governed by Henry's Law by which equilibrium is reached when the partial pressure of the gas is the same in both the air and surface seawater. This is the foundation of the solubility pump. Envisage the North Atlantic with 25 °C Gulf Stream water and the North Atlantic Drift flowing toward high latitudes. In this progress the seawater gives off heat to the atmosphere and, as the temperature decreases, the CO_2 solubility of the surface water increases by as much as 100% (Figure 2.5). The surface seawater becomes undersaturated and by Henry's Law the CO_2 gas transfers from the atmosphere into the sea. As the North Atlantic Drift reaches the Nordic Seas, the seawater has dropped in temperature by 20 °C but still retains a relatively high salinity. In winter, further cooling leads to a density increase with consequent deep vertical convection and formation of Arctic Intermediate- and Arctic Bottom-Water. This process is termed Deep Water Formation. The dense water masses fill the deeps of the Nordic Seas north of the Greenland-Iceland-Faroe-Scotland Ridge and only escape by flowing southward over the submarine ridges in the Denmark Strait, the Faroe Channel and between Iceland and the Faroe Islands.

These deep currents initiate the Thermohaline Circulation which extends through the depths of the Atlantic, Indian and Pacific

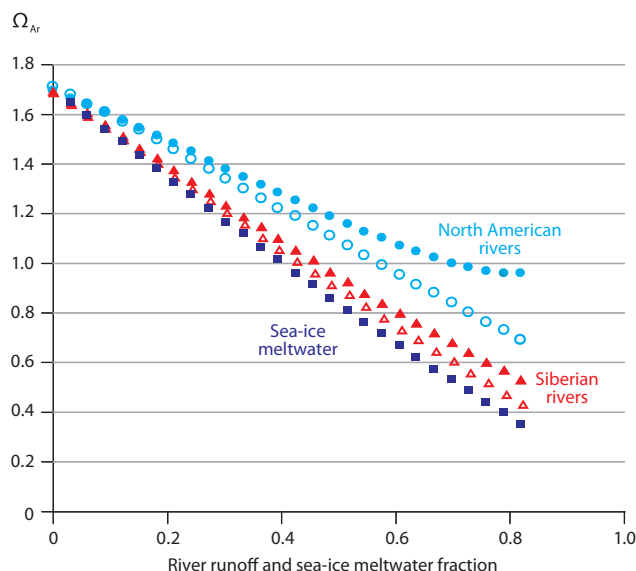


Figure 2.4. Effect of dilution by different freshwater sources on the saturation state for aragonite (Ω_{Ar}). Solid symbols are results that include a $[\text{Ca}^{2+}]$ contribution from the rivers assuming a conservative mixing between freshwater and seawater end members. Open symbols are results using $[\text{Ca}^{2+}]$ calculated from the relationship $[\text{Ca}^{2+}] = 10.28 \times (\text{salinity}/35)$. Source: after Azetsu-Scott et al. (2010).

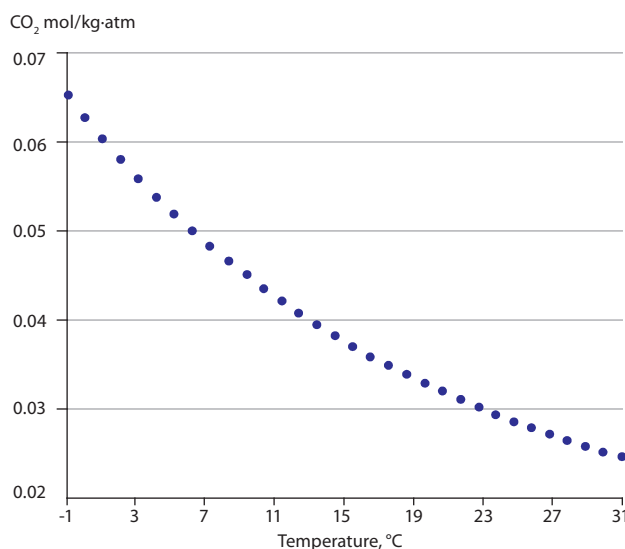


Figure 2.5. The solubility of carbon dioxide in seawater increases as the seawater cools. Shown for a salinity of 35.

Oceans. The solubility pump in this way transfers CO_2 from the atmosphere to the ocean depths to be stored there for centuries. The solubility pump is most intense in the sub-Arctic region of the North Atlantic (Takahashi et al., 2002) where the ocean heat loss to the atmosphere is high, but it also operates to a smaller extent within the Arctic basin, where dense waters formed on the shelves can sink into the halocline and even deeper, isolating CO_2 from the atmosphere for up to hundreds of years (e.g., Jones et al., 1995; Anderson et al., 2010). The solubility pump is sensitive to climatic variations: it is intimately linked to deep-water formation, which is sensitive to freshening, and will become less effective with increasing sea-water temperature.

The solubility pump, and its transfer of anthropogenic carbon into deep waters, is one of the primary drivers of increasing acidification in the Arctic Ocean.

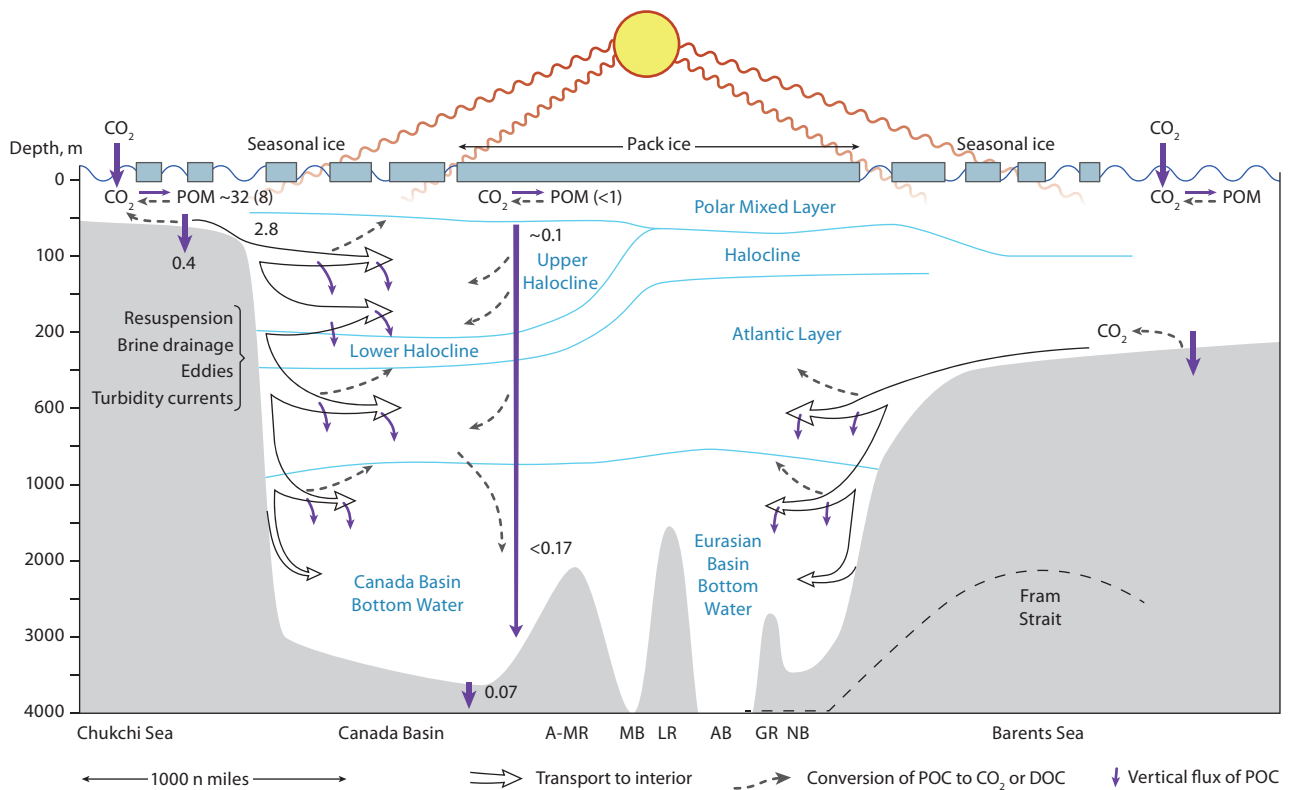


Figure 2.6. A schematic illustration of the biological pump in the Arctic Ocean. Number units are $\text{gC/m}^2/\text{y}$, pro-rated to the area of the receiving environment (total shelf or total basin). For productivity, the rates are given as total production (export production). The flux estimates are derived from: primary production and shelf export to halocline (Sakshaug, 2004), vertical flux (Honjo et al., 2010; O'Brien et al., 2013), and sediment burial rates. Source: Stein and Macdonald, (2004b). Abbreviations: POC, particulate organic carbon; POM, particulate organic matter; DOC, dissolved organic carbon; A-MR, Alpha-Mendelev Ridge; MB, Makarov Basin; LR, Lomonosov Ridge; AB, Amundsen Basin; GR, Gakkel Ridge; NB, Nansen Basin.

2.3.4 Biological pump

The term biological carbon pump describes the suite of biologically driven processes that move carbon from surface waters to depth in the ocean (de la Rocha, 2006). C_T is removed near the surface by conversion to organic matter (OM) during primary production (Figure 2.6). A proportion of that carbon is sequestered at depth in the ocean by the sinking of particulate organic matter (POM) due to gravitational settling, by vertical migration of zooplankton (copepods), or by the advection or mixing of dissolved organic matter (DOM) to depth. The organic particles include phytoplankton, aggregates comprising organic and inorganic detritus, fecal pellets produced by zooplankton, and carcasses of zooplankton or, more rarely, larger animals up to and including whales (e.g., Stockton and DeLaca, 1982; Turner, 2002; Honjo et al., 2008). Because much of this POM is remineralized while sinking (Bishop, 1989), the net effect of the biological pump is to decrease C_T (increase pH) in the upper ocean and increase C_T (lower pH) at depth in the ocean. The biological pump acts on many other elements involved in biological cycles including silicon, phosphorus, nitrogen, metals and metaloids, but from the perspective of ocean acidification the most important component other than POM/DOM is CaCO_3 , which is used by a number of planktonic species (e.g., coccolithophores, pteropods) to form structures. This is discussed in Section 2.3.5.

In the textbook view of ocean productivity, the large areas of the interior ocean basins support more total primary production than the smaller total shelf area, despite higher per-area production rates on the shelves. However, this description does not properly represent the Arctic Ocean. Enormous

shelves, high stratification, and sea-ice cover in the Arctic Ocean combine to create exceptional circumstances where primary production over shelves plays a much larger role than in the global ocean (Figure 2.6). In contrast to the shelves, the oligotrophic interior parts of the Arctic Ocean produce little sinking particulate matter, limiting the efficiency of the biological pump in the central basins (Honjo et al., 2010).

The Arctic Ocean exhibits large spatial heterogeneity: shelf regions supplied externally by nutrients from the Pacific (Chukchi Sea; Lepore et al., 2007) or the Atlantic (Barents Sea; Reigstad et al., 2002) and persistent regions of open water like the Cape Bathurst Polynya (Arrigo and van Dijken, 2004) and the Northwater Polynya (Tremblay et al., 2006) are among the most productive locations in the world ocean, whereas the interior of the Canada Basin has an almost non-existent export production (Hargrave et al., 1994; Honjo et al., 2010; O'Brien et al., 2013). Because of this disparity, the Arctic's biological pump can only be understood by considering the shelf-to-basin OM export. That is, the Arctic Ocean has a strong *continental shelf pump* (Liu et al., 2000; Yool and Fasham, 2001; Anderson et al., 2010), partly due to the contrast in productivity between shelf and interior, and partly due to dense water production over the shelves during winter. This dense water can accumulate OM and metabolic products, including C_T , as the water flows along the shelf bottom thence to be exported to the interior ocean. Aagaard et al. (1981) estimated that as much as $79 \times 10^3 \text{ km}^3/\text{y}$ of brine-enriched water was supplied to the halocline from shelves by this process alone. In the western Arctic Ocean, the upper halocline is a dominant feature that has been enriched with nutrients and C_T and impoverished in dissolved oxygen

during its formation in the Chukchi and East Siberian Seas (e.g., Bates et al., 2005; Mathis et al., 2007; Nishino et al., 2009; Anderson et al., 2010; Griffith et al., 2012). The sequence of high primary production, sinking of POM, partial regeneration to C_T or conversion to DOM near the bottom and then transport of labile OM and regeneration products to the interior ocean produces a widespread nutrient maximum / oxygen minimum within the Arctic Ocean halocline (Figure 2.6). The Barents Sea, likewise, supports the C_T and nutrient enrichment in the Arctic Ocean halocline, albeit to a lesser extent (e.g., see Jones and Anderson, 1986).

A second set of processes, whose importance has only recently been recognized, occurs over the outer shelf in the Arctic. Boundary currents, turbulence and eddies provide the circumstances to re-suspend surface sediment containing OM that has settled there temporarily (e.g., algal mats and other organic detritus from annual production), and then transport this material and accompanying dissolved components along isopycnals into the interior ocean (Schauer et al., 2002; O'Brien et al., 2006, 2011, 2012; Forest et al., 2007; Mathis et al., 2007; Kadko and Aagaard, 2009). During transport to the interior, the POM can sink and become part of the vertical flux, or become metabolized to CO_2 or converted to DOM, both of which remain in the water column (Figure 2.6). Thus, for the Arctic Ocean much of the biological pump operates from the side of the basin, driven by shelf productivity, rather than vertical export of POM produced in the interior. According to this scheme (Figure 2.6) shelf export production, estimated to average $\sim 8 \text{ g C/m}^2/\text{y}$ (Sakshaug, 2004), is delivered to shelf bottom waters with as much as 35% of the export then distributed out into the haloclines or deeper into the Arctic Ocean leading to net CO_2 drawdown in shelf surface water and net increase in CO_2 in shelf bottom water and haloclines.

How might climate change affect the biological pump in the Arctic Ocean? It seems clear that the major factor driving change will be the continued conversion of multi-year sea ice to first-year ice until the Arctic Ocean becomes seasonally clear of sea ice, perhaps within two decades (Schiermeier, 2012). This, by itself, will lead to greater light penetration into the water and a significant warming of surface waters above freezing. Open water will also promote upwelling at the shelf edge, greater mixing by winds, and greater light penetration into the water column, all of which would enhance primary production and lead to an increase in the strength of the biological pump. However, upwelling of nutrients is also accompanied by C_p , thereby limiting carbon sequestration. On the other hand, there is likely also to be an increase in river inflow and greater amounts of sea-ice melt in summer, which would lead to greater stratification, which would generally inhibit nutrient supply to the photic zone. How these various factors might play out in the future is very uncertain, but the response to change is likely to vary widely between shelves, polynyas, and the basins, considering how differently each of these environments function (Carmack et al., 2006; Nishino et al., 2011). Using a sea ice-ocean-biologically coupled 1-D model, Lavoie et al. (2010) simulated the effect of climate change on primary production at the shelf edge of the Beaufort Sea. Their

model projected that by the end of the 21st Century, ice algal production would have declined in relative importance due to the rapid loss of ice early in the year, but export production would have increased by $\sim 16\%$. Slagstad et al. (2011), using a 3-D coupled physical-biological model, found that gross primary production over the Arctic Basin and Eurasian shelves would increase substantially with an 8°C temperature increase (10 to $42 \text{ g C/m}^2/\text{y}$ and 29 to $61 \text{ g C/m}^2/\text{y}$, respectively), but hardly change in the Barents Sea. These disparities suggest that the strength of the biological pump might increase on average, but that the scenario of a relatively strong biological pump over the shelves, a weak pump in the ocean interior, and a large shelf-basin export of particulate organic carbon (POC), DOC and C_T is likely to remain a dominant feature in the future Arctic Ocean.

2.3.5 Carbonate pump

Another biologically mediated carbon pump is associated with the precipitation of $CaCO_3$ from seawater by marine organisms to form, mainly, exoskeletons and shells. This *carbonate pump* is dominated by surface calcification in marine plankton and the subsequent transfer of carbon in the form of $CaCO_3$ from the sun-lit surface into the interior and deep-ocean (Volk and Hoffert, 1985). However, benthic and mesopelagic $CaCO_3$ production also play a significant role.

The carbonate pump has what may be considered a counterintuitive effect on the marine carbonate system (see also Section 2.2). As $CaCO_3$ production partitions carbon from seawater through the reversal of Equation 8 it has the net effect of removing one CO_3^{2-} ion and one Ca^{2+} ion thus reducing A_T and C_T in the proportion 2:1 and increasing pCO_2 and reducing pH (Equation 1). The stability of the $CaCO_3$ will depend on the organic matrix of the skeleton or shell and how effective the organism is at protecting the shell or skeleton. However, in geochemical terms, exposed or unprotected $CaCO_3$ will become thermodynamically unstable if Ω goes below 1 (Equation 9) and will dissolve. Each specific mineral has a different solubility product; for example, of the two most common biogenic $CaCO_3$ minerals in the oceans, aragonite has a higher solubility product than calcite (Mucci, 1983), and thus aragonite dissolves more readily than calcite. However, calcite minerals in which some Ca^{2+} ions are replaced with Mg^{2+} , called hereafter Mg-calcite, are even more soluble than aragonite.

As the organisms die they often sink through the water column into waters that have a lower Ω following respiration of OM (the biological pump, see Section 2.3.4). There are three depths that are commonly used for understanding the distribution of $CaCO_3$ in the water column and on the ocean sediment surface. The first is the saturation horizon (ASH or CSH for aragonite and calcite, respectively) where Ω is unity. As sedimenting calcareous material does not dissolve immediately on passing the saturation horizon, $CaCO_3$ often continues to a depth where a strong gradient in $CaCO_3$ is seen on the ocean floor, termed the lysocline. This depth is rather ambiguous and is termed the lysocline. Below here some $CaCO_3$ will continue its downward journey until a depth where all is dissolved. This demarcation is termed the compensation depth. Dissolution results in an increase in C_T and A_T of the subsurface waters in

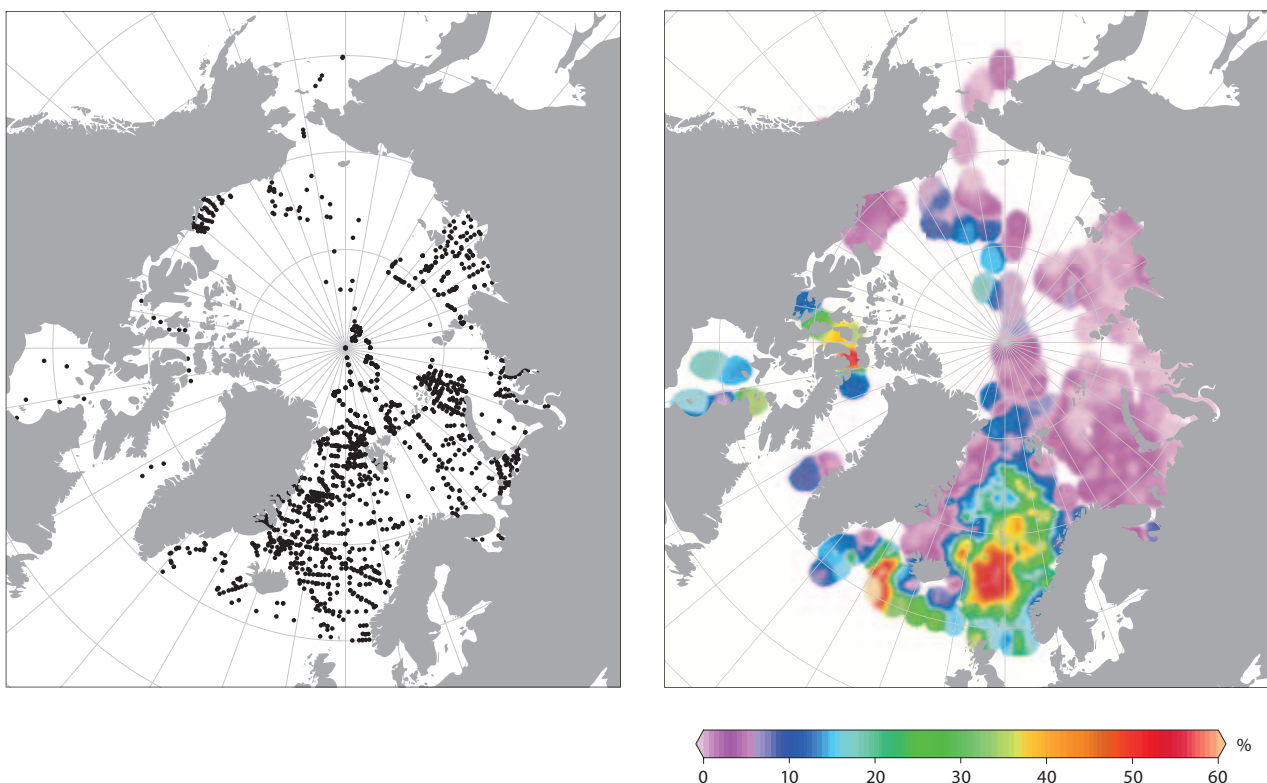


Figure 2.7. Percentage of calcium carbonate in surface sediments in the Arctic Ocean. Core data were extracted from the Pangaea database (www.pangaea.de) and peer-reviewed publications. Left panel shows sampling locations.

tandem with respiration in the biological pump. Dissolution, however, counteracts the pH reduction and $p\text{CO}_2$ increases due to the biological pump.

In most of the surface Arctic Ocean, CaCO_3 is stable as Ω is greater than 1 for both aragonite and calcite. However, with lower initial surface water Ω and strong freshwater inputs (thus lower Ca^{2+} concentrations), CaCO_3 minerals in the Arctic Ocean are particularly susceptible to dissolution following only small additions of CO_2 .

The present-day distribution of CaCO_3 forming planktonic organisms in the Arctic Ocean can be partially inferred from CaCO_3 core top data (Figure 2.7). Highest percentages of CaCO_3 in the sediments are found in the Nordic Seas and this has been linked to the inflow of warm Atlantic Waters (Taylor et al., 2002; Giraudeau et al., 2010). The typical planktonic CaCO_3 forming organisms found in the ice-free regions of the Arctic is the coccolithophorid *Emiliania huxleyi* which synthesizes external CaCO_3 platelets known as coccoliths. In the latter stages of a bloom these coccoliths are released in large numbers giving the water a turquoise-white appearance which is easily detectable both at the surface and from space. Satellite data are now routinely used to map blooms of these organisms using the distinctive brightness and reflectance of the coccoliths (Groom and Holligan, 1987; Moore et al., 2012). Using this approach the distribution of these organisms in the global ocean has been assessed (Brown and Yoder, 1994; Moore et al., 2012). A number of studies have shown large annual blooms of coccolithophorids in the Arctic, most noticeably along the Arctic Front between the Greenland and Iceland seas (Trees et al., 1992), in the vicinity of Iceland (Holligan et al.,

1993), along the Norwegian coast (Findlay et al., 2008; Moore et al., 2012) and in the Barents (Smyth et al., 2004) and Bering Seas (Merico et al., 2003). A comparison between the satellite data showing the occurrence of coccolithophorid blooms and the percentage of CaCO_3 in the sediments is generally best in regions with deeper waters, as in shallower waters the lower carbonate saturation state (see Section 2.2) will lead to greater dissolution of the coccoliths (e.g., Barents Sea). Recent analysis of longer term satellite data suggests that the increased occurrence of coccolithophorid blooms in the Barents Sea (Smyth et al., 2004) may be related to climate change, similarly satellite investigations in the Bering Sea since the 1970s suggest an ecosystem shift toward coccolithophorids driven by climate change (Harada et al., 2012).

2.3.6 Air-sea exchange

The net result of the combined impacts of freshwater and sea-ice distributions in the Arctic Ocean on CO_2 solubility and primary production is that most surface waters within the Arctic Ocean are undersaturated in CO_2 relative to atmospheric values (e.g., Jutterström and Anderson, 2010). To date, in autumn-period studies, sea ice has formed before air-sea exchange has balanced the partial pressures (Miller et al., 2002; Mucci et al., 2010; Else et al., 2012). Consequently, the gas exchange rate largely determines the net air-sea flux, and that rate is heavily dependent on sea-ice conditions, as well as winds. The air-sea flux has been estimated for a number of Arctic Ocean areas (Table 2.2). These estimates are both uncertain and variable and consequently, must be confirmed carefully in this time of changing sea-ice coverage.

Region	Sea-air exchange		Source
	(mmol/m ² /d) ^a	10 ¹² mol/y	
Central Basins	-0.3 to 1		Bates et al., 2006
Barents Sea	-3.7±0.9 ^b	-0.8 -2.4±1 -3.8±1.5 -4.3±0.7 -1.8±1	Fransson et al., 2001 Kaltin et al., 2002 Nakaoka et al., 2006 Omar et al., 2007 Kivimäe et al., 2010
Nordic Seas		-5.8	Jeansson et al., 2011
Kara Sea	-0.1 ^b		Fransson et al., 2001
Laptev Sea	-1.2 to 1.7	-2.1	Nitishinsky et al., 2007 Semiletov et al., 2007
East Siberian Sea	-2 to 10	0.04 to 0.28	Pipko et al., 2011
Chukchi Sea	~ -30 to -90 -15±13 -18 to 3	-2.6 to -3.8 -1.8	Bates, 2006 Pipko et al., 2002 Murata and Takizawa, 2003 Kaltin and Anderson, 2005
Beaufort Sea	-2 -17 to 0 -17 to 3 -25 to -9		Mucci et al., 2010 Murata and Takizawa, 2003 Shadwick et al., 2011 Else et al., 2011
Canadian Archipelago	-7 to 0 -140 to 18		Miller et al., 2002 Fransson et al., 2009
All Arctic Ocean		-2 to ~ -8	McGuire et al., 2009

^a Data are from the summer period with limited ice coverage; ^b annual mean estimate.

Table 2.2. Sea-air exchange in different regions of the Arctic Ocean as reported in the literature. Negative fluxes are from the atmosphere into the ocean.

2.3.7 Geological methane and carbon dioxide seeps

Carbon is added to Arctic waters from the sediment both as C_T and methane, which can be oxidized to CO₂, thereby contributing to ocean acidification (Elliott et al., 2010). Sedimentary processes in the Arctic Ocean have much in common with those in other oceanic regions, with the main difference being the low seawater temperature. Furthermore there are large areas on the Siberian shelves with sub-sea permafrost conditions that contain large deposits of methane hydrates. Since the Holocene transgression, these deposits have been slowly seeping out of the sediment as a result of increasing temperatures. Seeps of methane from hydrate have been observed as gas plumes near West Spitsbergen (Westbrook et al., 2009), on the East Siberian Shelf (Shakhova et al., 2010) and in the Beaufort Sea (Paull et al., 2007). The magnitudes as well as the temporal and spatial variability of the methane fluxes are not well known (Shakhova et al., 2010).

However since the methane concentration within the water column in these seep areas typically reaches a few hundred nM and the oxidation rate has been reported to be very low in cold oxic waters (e.g., Tsurushima et al., 1996), the total CO₂ addition from methane oxidation must be substantially lower than that from decaying organic matter. Although the reported water column methane concentrations in these studies have typically been low, it is possible that destabilization of shelf methane hydrate due to rising seawater temperatures may increase methane release to the water with consequences for ocean pH (Biastoch et al., 2011; AMAP, 2012).

2.3.8 Other ‘acidifying’ compounds

Sulfide oxidation by heterotrophic bacteria ($\text{HS}^- + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+$) and by autotrophic bacteria ($2\text{H}_2\text{S} + \text{CO}_2 \rightarrow \text{CH}_2\text{O} + 2\text{S} + \text{H}_2\text{O}$), and also sulfate reduction ($\text{SO}_4^{2-} + 2\text{CH}_2\text{O} + \text{H}^+ \rightarrow 2\text{CO}_2 + \text{HS}^- + 2\text{H}_2\text{O}$) can change carbon chemistry, including pH. However, no study has yet been done to quantify the effect of these processes on ocean acidification in the Arctic.

Other anthropogenic gases such as sulfur oxides (SO_x), nitrogen oxides (NO_x) and ammonia (NH₃) have the potential to alter ocean pH and carbon chemistry. Doney et al. (2007) assessed the impact of anthropogenic nitrogen and sulfur deposition on ocean acidification using atmospheric and ocean models. Their study found that the global effect of these species on surface water chemistry is only a few percent, at most, of that caused by anthropogenic CO₂. They also concluded that these substances may cause substantial impacts in coastal waters. Hunter et al. (2011) investigated impacts of SO_x, NO_x and NH₃ on ocean acidification in coastal waters and shipping lanes. Their analysis showed that the pH reduction caused by these pollutants is almost completely cancelled out by buffering reactions, but at the expense of a significant decrease in the uptake of atmospheric CO₂ in the same region. More shipping traffic is expected in the Arctic coastal area due to the possibility of an ice-free Northwest Passage and Northern Sea Route and increased resource exploration (AMAP, 2012), so the input of these anthropogenic gases needs to be evaluated.

2.3.9 Terrestrial organic carbon

The Arctic Ocean receives exceptional quantities of organic carbon from land via rivers or coastal erosion (McGuire

et al., 2009). Stein and Macdonald (2004a) estimated that 11 Mt/y of POC was supplied to the Arctic's shelves in this manner, of which ~4 Mt/y was metabolized, forming CO_2 . Decay of terrestrial OM, most likely occurring at the sediment surface, has been shown to greatly decrease pH, producing large regions of both aragonite and calcite undersaturation (Anderson et al., 2011b). Bottom waters of the shelf seas are clearly most vulnerable to this process, especially for the large Siberian seas (e.g., Guo et al., 2004; Vonk et al., 2010; Alling et al., 2012). In this latter context, recent measurements for the East Siberian Sea by Vonk et al. (2012) suggest that the release of old particulate carbon by coastal erosion and subsea permafrost may have been grossly underestimated, or has recently been undergoing a large increase. In that paper, the authors suggested that 44 ± 10 Mt/y of terrigenous POC is presently released, ~66% of which is metabolized. Clearly, warming and thawing of permafrost leading to accelerated release of stored POC (e.g., deConto et al., 2012), could be of immense importance to future acidification of shelf bottom waters in the Arctic.

2.4 Ocean processes sensitive to acidification

2.4.1 Macronutrients

2.4.1.1 Nitrogen species

Ocean acidification should not alter the speciation of the majority of inorganic nitrogen species (N_2 , NO_3^- and NO_2^-). The exception is NH_3 which is a weak base ($\text{pK}_a \sim 9.2$) in equilibrium with its conjugate acid ammonium (NH_4^+) (Clegg and Whitfield, 1995). Ocean acidification will push the equilibrium toward an increase in the relative abundance of NH_4^+ and lead to a possible reduction in the air-sea gas exchange of NH_3 .

Nitrification

Recent work from the tropics indicates that a decrease in the pH of seawater leads to a reduction in oceanic nitrification rates (Beman et al., 2011). This arises as both ammonia-oxidizing bacteria and ammonia-oxidizing archaea utilize NH_3 as a substrate (Martens-Habbenha et al., 2009). The abundance of ammonia-oxidizing bacteria and ammonia-oxidizing archaea in the Beaufort and Chukchi Seas has recently been reported over a seasonal cycle and is strongly related to NH_4^+ concentrations (Christman et al., 2011). Decreasing surface water pH in the Arctic could lead to slower nitrification rates in the water column resulting in increased NH_4^+ concentrations and decreased nitrate (NO_3^-) levels which may cause shifts in the phytoplankton community toward smaller organisms that are more competitive for NH_4^+ . Organisms that are specialists for NO_3^- uptake, such as large diatoms, may be disadvantaged under these conditions, leading to potential changes in the oceanic food web (Beman et al., 2011).

Some archaea in the water column in the Arctic also possess a urease gene providing them with the potential use of urea to fuel nitrification (Alonso-Saez et al., 2012). Earlier studies have shown that urea is frequently found throughout the water column in

parts of the Arctic at concentrations above that of NH_3 (Harrison et al., 1985). This suggests that the biological decomposition of urea may be a significant nitrification pathway in the Arctic.

Denitrification

Sedimentary denitrification occurs predominantly on continental margins (Christensen et al., 1987) and thus the Arctic may be an important contributor to global marine sedimentary denitrification. Sedimentary denitrification rates in the Arctic generally decrease with increasing water depth and correspond to differences in the overlying primary productivity and organic matter flux (Koike and Hattori, 1979; Devol et al., 1997; Chang and Devol, 2009). Denitrification has also been found to occur in Arctic sea ice (Rysgaard et al., 2008), yet water column denitrification overall appears to be a minor process compared to sedimentary denitrification (Kaltin and Anderson, 2005; Lehmann et al., 2005). Denitrification does not appear to be influenced directly by ocean acidification, but modeling studies predict increases in denitrification (Schmittner et al., 2008) due to global increases in the volume of suboxic waters.

Nitrogen fixation

Nitrogen-fixing cyanobacteria from the tropical ocean have been found to increase their fixation rates under high CO_2 conditions (Hutchins et al., 2007). Nitrogen fixation is currently not thought to be an important part of the nitrogen cycle in the Arctic although the distribution of diazotrophs is more widespread in the Arctic than previously thought (Blais et al., 2012).

Anammox

Anammox has recently been detected in the melt waters of Arctic sea ice (Rysgaard et al., 2008) and also appears to be a small contributor to nitrogen cycling in the sediments of an Arctic fjord (Gihring et al., 2010). As the anammox process, which converts NH_4^+ and NO_2^- to N_2 and H_2O , may also be pH dependent, as organisms utilize NH_3 as the substrate for hydrazine hydrolase (HH), the first enzyme involved in anammox (Kuenen, 2008; Karlsson et al., 2009). The final enzymatic step in anammox, converting hydroxylamine to N_2 via hydroxylamine oxidoreductase (HAO), has been reported to be strongly pH dependent (Zou et al., 2011). Currently there are, however, no data on the overall pH sensitivity of anammox in the marine environment, or on whether under climate change anammox will become more or less important in the Arctic.

2.4.1.2 Phosphate speciation

There will be minimal changes in the distribution of phosphate species with ocean acidification as the HPO_4^{2-} species strongly predominates throughout the pH range 7.5–8.1. There are no reports of ocean acidification affecting the uptake of inorganic phosphate by organisms. The hydrolysis of dissolved organic phosphorus (DOP) compounds is, however, pH dependent (Price and Morel, 1990), as are many other enzymatic processes (Yamada and Suzumura, 2010). Indeed the activity of the zinc-centered enzyme alkaline phosphatase decreases with decreasing pH (Kuenzler and Perras, 1965). While DOP can exist in the Arctic in significant concentrations (Simpson et al., 2008) there is currently no evidence to suggest that ocean acidification will

significantly influence the uptake of either dissolved inorganic phosphorus (DIP) or DOP by phytoplankton or bacteria.

The Arctic has been identified as an important mediator between regions of denitrification (the Bering and Chukchi Seas and the North Pacific) and of nitrogen fixation (the Atlantic) through excess phosphate, relative to nitrogen, transported east through the Arctic Ocean (Yamamoto-Kawai et al., 2006). Thus ocean acidification impacts on denitrification (see Section 2.4.1.1) may impact the excess P:N in the Arctic throughflow, with implications for N_2 fixation in the North Atlantic.

2.4.1.3 Silicate species

Under ocean acidification the speciation of silicate will change only slightly as it is dominated by the $Si(OH)_4$ species. As expected, studies investigating the uptake rate of silicate by diatoms find that it is not influenced by pH (Milligan et al., 2004). This has also been seen in identical silicate utilization rates in mesocosms under different pCO_2 regimes (Bellerby et al., 2008). However lower Si:C ratios have been found in culture experiments at low pH due to higher Si efflux from the cell (Milligan et al., 2004). Ocean acidification has also been found to enhance the silica dissolution rate of empty diatom frustules (Milligan et al., 2004). This may have an influence on the ballasting of particulate material, leading to faster rates of remineralization and the nutricline shifting toward the surface. This could lead to a decrease in biological pump efficiency, and a reduction in material reaching benthic communities, as has been suggested for the $CaCO_3$ component of particulate matter under ocean acidification conditions (de Jesus Mendes and Thomsen, 2012). However floating sediment trap studies in the Arctic (Honjo et al., 2010) indicate that there is already an absence of ballast particles in this environment for sinking fine, lightweight POC to depth (see also Section 2.3.4), so the existing condition may be reinforced under ocean acidification with implications for the cycling of some trace metals and organic pollutants.

2.4.2 Trace metals

2.4.2.1 Inorganic speciation and reactivity

On first principles, ocean acidification will directly influence any chemical reaction that depends on either H^+ or OH^- . Thus the chemical speciation of elements that undergo hydrolysis will be altered by changes in pH. Similarly, enzymatic reactions that depend on substrates that are influenced by pH will also be affected.

There have been a number of studies examining the changes in trace metal distributions in the Arctic (see Appendix, Table A1), particularly in the estuarine mixing zone on the Arctic shelf (Martin et al., 1993; Garnier et al., 1996; Guieu et al., 1996; Hölemann et al., 2005). More recently, basin-scale elemental budgets have been constructed for manganese and aluminum in the Arctic Ocean through analysis of box core data (Macdonald and Gobeil, 2012). However, there is a distinct lack of trace metal speciation studies from the Arctic (see Appendix, Table A2), with most of the work in the Bering Sea. Substantial information is available on the distributions of radioactive isotopes in the Arctic (see Appendix, Table A3),

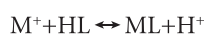
because they have proven to be useful tools for identifying water mass exchange and sources, as well as for studying other processes, including particle fluxes, water-column-sediment interactions, and sea-ice brine rejection.

The inorganic speciation of trace metals in seawater is reasonably well described due to the extensive work performed by physical chemists in simple salt solutions. In more complex media such as seawater, the use of Pitzer equations (Pitzer, 1973) is required, but for many species in seawater the relevant data are still missing. A number of detailed reviews have covered the inorganic speciation of trace metals in natural waters (Turner et al., 1981; Byrne et al., 1988), and recent papers by Byrne (2010) and Millero et al. (2009) have focused on those elements whose inorganic speciation is dominated by hydroxide and/or carbonate species and are therefore particularly sensitive to decreases in pH and increasing CO_2 concentrations.

2.4.2.2 Organic speciation of trace metals

Many of the biologically relevant trace metals are predominantly complexed by organic ligands in seawater; most notably iron (Fe; Gledhill and van den Berg, 1994; Rue and Bruland, 1995), copper (Cu; Coale and Bruland, 1988; Moffett et al., 1990), cobalt (Co; Ellwood and van den Berg, 2001; Saito and Moffett, 2001), nickel (Ni; Nimmo et al., 1989; Saito et al., 2004), cadmium (Cd; Capodaglio et al., 1991; Bruland, 1992) and zinc (Zn; van den Berg, 1985; Bruland, 1989). However very little is known about these metal-organic complexes, although they do appear to be produced by organisms in response to limitation (Reid and Butler, 1991; Wilhelm and Trick, 1994) or metal-induced stress (Moffett and Brand, 1996; Croot et al., 2000). Only a few of these ligands have been isolated and their chemical structures determined (Reid and Butler, 1991; Ahner et al., 1994; Martinez et al., 2001; Vraspir and Butler, 2009).

The relationship between trace metal speciation and bioavailability is an ongoing and evolving field of research, but the impact of ocean acidification on the organic speciation, and hence bioavailability, of trace metals is not straightforward to assess. Little is known regarding the pH dependence of the conditional stability constants of these complexes in seawater. From first principles, the free metal concentration could be expected to increase due to the competition between H^+ and metal for the same ligand (L) complexation sites (see Equation 11).



Eqn. 11

However, in reality this depends on a number of factors; chiefly the acid dissociation constant for the ligand and the conditional stability constant for the metal-ligand complex (which includes other reactions between seawater components and the ligand).

A recent study by Shi et al. (2010) suggested that iron bioavailability decreases with decreasing pH for diatoms grown using media containing the artificial complexing agent EDTA. However these authors also noted that for the natural iron chelator azotochelin there was little change in inorganic iron

as a function of pH within the range anticipated from ocean acidification. Other recent experimental data suggest that the redox potential of the iron complex controls iron uptake by phytoplankton (Maldonado and Price, 2001; Shaked et al., 2004, 2005; Maldonado et al., 2005; Morel et al., 2008). The redox potential for the iron organic complex is also related to its thermodynamic stability and may be subject to pH-induced shifts (Spasojevic et al., 1999; Crumbliss and Harrington, 2009; Harrington and Crumbliss, 2009). However, presently there is little information on the nature of the ligands present in seawater that are responsible for iron binding, and so it is difficult to *a priori* assess the impact of ocean acidification on organic iron complexation or bioavailability.

Similarly, little is known about the pH effects on organic complexation of other elements. One published study directly examined Cu complexation as a function of pH, using natural organic matter isolated from coastal seawater (Louis et al., 2009) and found that over the pH range 7–8 there was little change in the Cu speciation. Recent fieldwork by Xu et al. (2012) indicated that the uptake rates of Cd and Zn are reduced under ocean acidification conditions. These authors suggested that their observations were related to the presence of weak ligands that act to maintain some bioavailable metal at higher pH values.

As the Arctic Ocean is supplied with trace metals predominantly from riverine sources, it is also of interest to examine the influence of high CO₂, low pH on the river systems. Studies in the Baltic examined the role that acidic leaching of trace metals from rivers plays in forming harmful algal blooms (Granéli and Haraldsson, 1993). Changes in the humic content of the rivers have also been suggested to play a role in shifting the species composition from diatoms to dinoflagellates (Granéli and Moreira, 1990).

Ocean acidification and increasing pCO₂ may also impact on the metal requirements of phytoplankton. Recent studies have shown high pCO₂ conditions influence cellular metal quotas; with data for Fe (Milligan et al., 2009), Cd (Cullen et al., 1999; Cullen and Sherrell, 2005) and Zn (Sunda and Huntsman, 2005).

2.4.2.3 Redox speciation – importance of kinetics

For many of the bio-essential trace metals there are major differences in the reactivity, bioavailability and toxicity between redox species. In many cases pH is a critical parameter in the overall kinetics for key redox processes: oxidation of Fe(II) by O₂ (Millero et al., 1987; King, 1998; Santana-Casiano et al., 2005) and H₂O₂ (Millero and Sotolongo, 1989; King and Farlow, 2000; Gonzalez-Davila et al., 2005), and oxidation of Cu(I) by O₂ (Moffett and Zika, 1983; Millero, 1989) and H₂O₂ (Sharma and Millero, 1989; González-Dávila et al., 2009). The overall impact of ocean acidification on the redox processes affecting Fe and Cu will be a shift toward the slower oxidation of the reduced species; Fe(II) and Cu(I). This may result in an increased bioavailability of both elements, particularly in the case of iron, as Fe(II) is significantly more soluble than the oxidized form, Fe(III). Results from a mesocosm experiment have confirmed that a lower pH can result in higher Fe(II) concentrations (Breitbarth et al., 2010).

An important further consideration is that reductions in oxygen concentrations will also be important in maintaining

significant concentrations of thermodynamically unstable redox species in solution. The combined effect of low pH and low O₂ leads to higher fluxes of redox-sensitive metals (e.g., Fe, Mn and Co) and nutrients (e.g., phosphate released from metal oxides) from the sediment to the water column (Ardelan and Steinnes, 2010). Given that the Arctic Ocean contains an extensive area of continental shelf, the potential for increased fluxes from the sediment could be a positive feedback on increased primary productivity in surface waters and reduced O₂ in the bottom waters. This could have implications for regions like the Bering Sea Green Belt – where shelf edge processes are already important to primary productivity (Springer et al., 1996).

2.4.3 Climate-relevant gases

There are few data on the impacts of ocean acidification on the production of other climate relevant gases in general for marine systems and only a few studies of particular relevance to the Arctic.

2.4.3.1 Halocarbons (natural production)

Halocarbons (e.g., iodo-organics) are chemical compounds formed between carbon and halogen atoms (fluorine, chlorine, bromine or iodine). In the marine environment the low molecular weight compounds are typically gases and, along with sea spray, are an important source of halogens to the marine boundary layer of the atmosphere (Carpenter et al., 2012). Sea-air exchange of gaseous organic iodine is the major source of iodine to the atmosphere and is believed to be a major source of new particles in the atmosphere as the iodocarbons are rapidly oxidized to iodine oxide (IO) (O'Dowd et al., 2004; Seitz et al., 2009). Iodine- and bromine-containing halogen species are also believed to have a significant global effect on the concentration and lifetimes of other climatically active gases. This includes catalytic reactions with ozone and modifying the cycling of NO_x and hydrogen oxides (HO_x) in the atmosphere (Carpenter et al., 2012).

Two CO₂ treatments were used during a mesocosm CO₂ perturbation experiment in a Norwegian fjord (present day: 380 ppmv and year 2100: 750 ppmv), and phytoplankton blooms were stimulated by the addition of nutrients (Hopkins et al., 2010). Seawater trace gas concentrations were monitored over the growth and decline of the blooms, revealing that concentrations of methyl iodide were significantly reduced under high CO₂ conditions. Additionally, large reductions in concentrations of other iodocarbons were observed. The response of bromocarbons to high CO₂ was less clear cut. More recent mesocosm experiments in Svalbard performed over a wider range of pCO₂ concentrations showed that in general the response of halocarbons was either very subtle or undetectable (Hopkins et al., 2012). Only the air-sea flux of diiodomethane (CH₂I₂) showed a significant positive response to pCO₂. Iodoform (CH₃I) was strongly associated with biological parameters suggesting a biological source and active turnover. Losses of bromoform (CH₃Br) correlated with total bacteria, suggesting biological consumption of this compound. Thus, based on the studies conducted so far, the direct effects of ocean acidification on halocarbons appear to be marginal, although no long-term studies have been made as yet.

2.4.3.2 Dimethylsulfide

The biogenic gas dimethylsulfide (DMS; CH_3SCH_3) has been implicated in atmospheric aerosol formation (Charlson et al., 1987), a role that is still vigorously debated (Levasseur, 2011; Quinn and Bates, 2011), and its precursor compound DMSP (dimethylsulfoniopropionate) which is used by phytoplankton as an osmolyte, for regulating the internal pressure of the cell, and potentially as a cryoprotectant in ice algae (Kasamatsu et al., 2004) and as an anti-oxidant (Carpenter et al., 2012). The flux of DMS from the ocean to the atmosphere is important because DMS is oxidized in the atmosphere to sulfate aerosols, which in turn act as cloud condensation nuclei resulting in an increased cloud albedo. The potential negative feedback between DMS, algal production and irradiance is the central thesis of the CLAW hypothesis (Charlson et al., 1987).

Ocean acidification should not alter DMS speciation in seawater directly. However, there may be changes in the production and decomposition pathways of DMS from DMSP as, for example, the lyases for DMSP in many organisms are strongly pH sensitive (de Souza and Yoch, 1995; Stefels and Dijkhuizen, 1996). However, the abiotic oxidation of DMS to dimethylsulfoxide (DMSO) by H_2O_2 is not pH dependent under ocean acidification conditions (Amels et al., 1997).

Mesocosm studies simulating ocean acidification have given conflicting results, with claims of increased DMS under conditions of higher CO_2 (Wingenter et al., 2007), while another group reported that when integrated over the entire experiment, neither DMS levels nor DMSP-lyase activity were different between the CO_2 treatments (Vogt et al., 2008). Other mesocosm studies (Hopkins et al., 2010; Avgoustidi et al., 2012) found that DMS and DMSP concentrations were reduced under high CO_2 conditions. Part of the difference observed in the mesocosms may be related to grazing activity, as a further study suggested that DMS will increase due to CO_2 -induced grazing (Kim et al., 2010). Global modeling results suggest that DMS production will increase at high latitudes (Cameron-Smith et al., 2011), although the model was not tuned correctly and exhibited a cold bias in the Arctic with unrealistic sea-ice extent and persistence. More recent work from a pelagic mesocosm experiment off Spitsbergen (Archer et al., 2012) found that DMS concentrations were inversely related to acidity. Contrastingly, the precursor compound DMSP was elevated with increasing acidity due to elevated rates of DMSP synthesis in parallel with increased rates of inorganic carbon fixation. The elevated DMSP production under ocean acidification conditions was suggested to arise from the increased dinoflagellate abundance under these conditions, again indicating that changes in the phytoplankton community speciation and grazing pressure induced by ocean acidification are more important than any direct ocean acidification effects on DMS production and release.

2.5 Current Arctic Ocean acidification

The complex variety of processes occurring in the Arctic and their interactions (Section 2.3) result in wide ranges of pH and CaCO_3 saturation state, with dramatic variations observed both geographically (Table 2.3) and seasonally. Most importantly, the Arctic does not behave in a single, consistent manner, but different

Table 2.3. Observed pH and aragonite saturation states in Arctic seas.

Region	pH	Ω_{Ar}	Source
Nordic seas			
Surface	8.1-8.4	1.5-3.5	Olsen et al., 2009
Bottom	7.9-8.3	0.7-2.2	Olsen et al., 2009
Bering Sea			
Surface	7.9-8.3	0.7-2.9	Winn and Millero, 1993; Mathis et al., 2011a
Bottom	7.0-7.7	0.1-2.0	Winn and Millero, 1993; Mathis et al., 2011a
Siberian shelves			
Surface ^a	7.5-8.1	0.2-2.5	Anderson et al., 2011b
Bottom	7.4-7.9	0.2-1.4	Anderson et al., 2011b
Chukchi & Beaufort shelves			
Surface	7.9-8.4	0.8-2.0	Mucci et al., 2010; Shadwick et al., 2011; Bates et al., 2009
Bottom	7.8-8.1	0.8-2.0	Shadwick et al., 2011; Bates et al., 2009
Canadian Archipelago			
Surface	8.0-8.3	0.8-2.2	Chierici and Fransson, 2009; Azetsu-Scott et al., 2010
Bottom	7.6-8.1	0.6-1.4	Azetsu-Scott et al., 2010
Central Arctic			
Surface	8.0-8.2	1.3-1.8	Jutterström and Anderson, 2005
Deep ^b	8.1±0.02	0.6-1.0	Jutterström and Anderson, 2005

^a Includes data from close to river mouths; ^b >2000 m.

processes dominate in different regions, resulting in a complex mosaic of acidification states and vulnerabilities. The following sections summarize current understanding of regional acidification processes in the Arctic, emphasizing the most important processes in each region and the interactions between them.

2.5.1 Inflow seas

2.5.1.1 Nordic Seas

The Nordic Seas (i.e., the Greenland, Iceland, and Norwegian Seas) are situated north of the Greenland-Scotland Ridge and export dense, cold overflow water into the North Atlantic (e.g., Hansen and Østerhus, 2000). Deep waters formed in the Nordic Seas are an important source for the global thermohaline circulation, and the surface waters entering the Nordic Seas from the North Atlantic Ocean are a vital source of dissolved carbon entering the Arctic Ocean. Approximately one third of that Atlantic carbon in the Nordic Seas enters the Arctic Ocean with the Atlantic Water inflow via the Barents Sea and through Fram Strait (Jeansson et al., 2011).

Vertical mixing, both of the Atlantic Water in the Norwegian Sea and within the convective gyres of the Greenland and

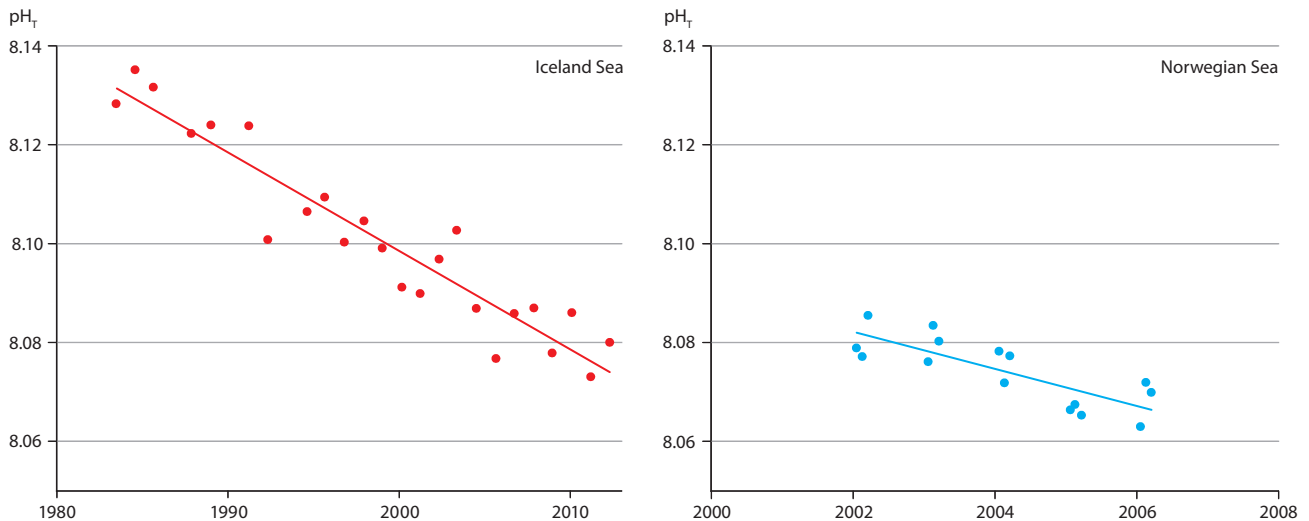


Figure 2.8. Recent changes in surface pH in the Iceland Sea and the Norwegian Sea. Source: after Olafsson et al. (2009).

Iceland Seas, transports dissolved carbon from the surface to deeper water masses (see Section 2.3.3, Olsen et al., 2006, 2010). This deep convection also serves as a conduit transporting anthropogenic CO_2 (C_{ant}) to the intermediate and deep waters of the Nordic Seas, decreasing the pH and shoaling the aragonite saturation horizon.

In the Iceland Sea, water column measurements between 1985 and 2011 show that pH and the carbonate saturation states are indeed decreasing rapidly (Olafsson et al., 2009). The cold waters, with a mean winter temperature of -0.3°C , show clear trends in both pH ($-0.0024/\text{y}$) and Ω_{Ar} and Ω_{Ca} , which have decreased over the observation period by $-0.0117/\text{y}$ and $-0.00721/\text{y}$, respectively (Figure 2.8). In the deep waters ($>1500\text{ m}$), pH has fallen $0.0006/\text{y}$, about four times slower than at the surface, while at the same time, the aragonite saturation horizon ($\Omega_{\text{Ar}} = 1$) has shoaled slightly, to about 1700 m , and the saturation state has decreased by $0.0009/\text{y}$. As a result, substantial sea-floor areas are in transition from supersaturated to undersaturated conditions.

In the Norwegian Sea, surface ocean $p\text{CO}_2$ increased between 2002 and 2006 at a rate of $2.6 \pm 1.2\ \mu\text{atm}/\text{y}$ (Skjelvan et al., 2008). This has resulted in an even stronger decrease in pH ($-0.0038/\text{y}$; Figure 2.8) than seen in the Iceland Sea. The pH evolution in the Greenland Sea surface water has not been evaluated thoroughly, but the CARINA data product (e.g., Key et al., 2009) reveals a large variability with no obvious trend.

There are two major reasons for the rapid acidification of the Nordic Seas. First, the buffer capacity of cold Arctic waters is less than that of subtropical waters. Thus, for the same amount of CO_2 added to seawater, the reduction in pH is greater in the Nordic Seas than at lower latitudes. Second, the Nordic Seas surface waters are undersaturated with respect to atmospheric CO_2 throughout the year due to low temperatures and intense biological utilization (e.g., Skjelvan et al., 1999). This results in an air-to-sea CO_2 flux throughout the year.

Figure 2.9 shows estimates of the total changes in surface Ω_{Ar} in the Nordic Seas since the pre-industrial period. This is based on the estimates of C_{ant} in the Nordic Seas prepared by Olsen et al. (2010). The greatest changes have occurred in

the Atlantic water; a consequence of the fact that this water mass carries the largest concentrations of C_{ant} . Nonetheless, the most vulnerable surface waters appear to be in the Iceland Sea, where Ω_{Ar} at 200 m is already $1.2\text{--}1.4$. This vulnerability is largely because aragonite saturation was already quite low in the pre-industrial period.

The Barents Sea serves as a gateway between the Nordic Seas and the Arctic Basin, including the Laptev and East Siberian Seas (Section 2.5.2.1). Although apparently no or very little C_{ant} uptake takes place within the Barents Sea (Anderson and Olsen, 2002; Omar et al., 2003; Jeansson et al., 2011), the anthropogenic carbon signal is likely to be very strong in this area. Autumn data for 1967 indicate that over the subsequent three decades, pH may have dropped by $0.0019/\text{y}$ and Ω_{Ar} by $0.0081/\text{y}$. Calcium carbonate undersaturation has not yet been observed in the Barents Sea (Jutterström et al., 2010), but Ω_{Ar} approaches 1 in some of the bottom waters. With further anthropogenic acidification and possible increases in primary production, organic matter export, and remineralization in the bottom waters and sediments, parts of this biologically and economically important area could be tipped into aragonite undersaturation in the near future.

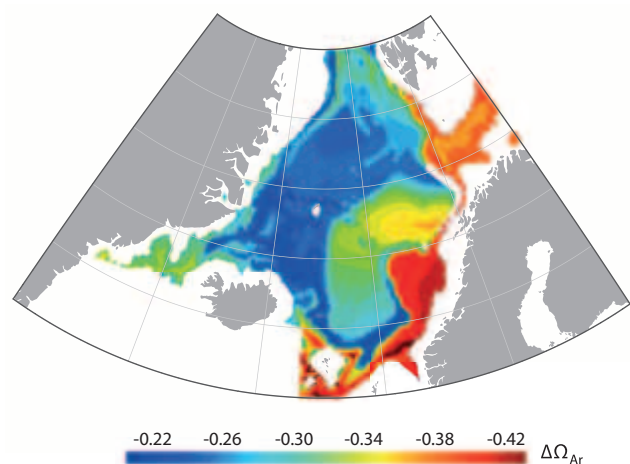


Figure 2.9. Estimated changes in surface aragonite saturation in the Nordic Seas between 1860 and 2004, based on anthropogenic CO_2 concentrations derived by Olsen et al. (2010).

2.5.1.2 Bering Sea

Despite its shallow sill depth, the Bering Sea is an important source of corrosive waters to the Arctic Ocean (Figure 2.10), because of the generally high CO_2 content of aged Pacific waters. However, to date, few carbonate system data are available for the Bering Sea, and most are from the eastern side, off Alaska, although those data span nearly 40 years, back to 1970.

While extremely low pH and CaCO_3 saturation states occur in the deep bottom waters of the central Bering Sea ($\text{pH} = 7.0$ and $\Omega_{\text{Ar}} = 0.1$), even at the depth of the Bering Strait overflow (about 50 m), pH values as low as 7.6 and Ω_{Ar} down to 0.7 have been observed (Winn and Millero, 1993). Seasonal physical and biological processes influencing the carbonate chemistry of the Pacific inflow as it crosses the Bering Sea (Figure 2.10), result in wide spatial, seasonal and interannual variability in pH and CaCO_3 saturation states (Table 2.3).

A few studies have recognized that upwelling frequently brings high- CO_2 waters to the surface, particularly in the southern Bering Sea, along the Aleutian Islands (Kelley et al., 1971; Fransson et al., 2006), but also south of the Chukchi Peninsula (Chierici and Fransson, 2009). However, most studies have focused on the dramatic spring and summer biological CO_2 consumption observed on the eastern Bering Sea Shelf (Codispoti et al., 1986; Kaltin and Anderson, 2005; Mathis et al., 2011a), which mitigates acidification in the surface waters while exacerbating acidification in bottom waters. Across the Bering Sea shelf, primary production rates average $330 \text{ mg C/m}^2/\text{d}$, making it one of the most productive regions in the global ocean (Sambrotto et al., 2008; Mathis et al., 2011a) and generating strong CaCO_3 supersaturations in the surface waters, at least during spring and summer (Mathis et al., 2011a). Much of the organic matter produced during the spring phytoplankton bloom is exported vertically out of the surface mixed layer, introducing a mid-summer pulse of low CaCO_3 saturation into subsurface waters as shallow as 50 m (Mathis et al., 2011a).

Large interannual variability of the marine carbonate system in the Bering Sea coupled with the intermittent frequency of the research to date precludes any concrete, quantitative conclusions about acidification trends in this area. Nonetheless, addition of anthropogenic CO_2 to this system certainly augments the large natural seasonal interactions between ocean biology and seawater carbonate chemistry, additionally lowering both pH and CaCO_3 saturation states.

2.5.2 Shelf seas

2.5.2.1 Siberian Shelf

The Siberian shelf seas encompass the Kara, Laptev, and East Siberian Seas, although to date, carbonate system data are only available for the Laptev and East Siberian Seas. These seas receive oceanic waters from the Atlantic in the west and the Pacific in the east and are highly biogeochemically active (e.g., Semiletov et al., 2005). In these shallow shelf seas, river runoff decreases the salinity and calcium ion concentrations to extremely low values, particularly close to the river mouths. In addition, the substantial quantities of organic matter (both dissolved and particulate; e.g., Semiletov et al., 2011, 2012) brought into the coastal waters by river runoff and coastal erosion are subject to microbial decay that produces CO_2 (Pipko et al., 2008, 2009) and thus, lowers pH. In combination, dilution by freshwater and acidification by respiratory CO_2 increase CaCO_3 solubility (Anderson et al., 2011b). While these are natural processes, to at least some extent, climate change is increasing both river flow and organic matter release, as permafrost thaws.

On the other hand, substantial primary production takes place within the Siberian shelf seas, consuming CO_2 and thus, increasing pH. One effect of these two counteracting processes is that pH spans a very large range in surface waters (Table 2.3). For instance, values from 7.5 to 8.1 were observed in summer 2008 in the East Siberian and Laptev Seas (Anderson et al., 2011b).

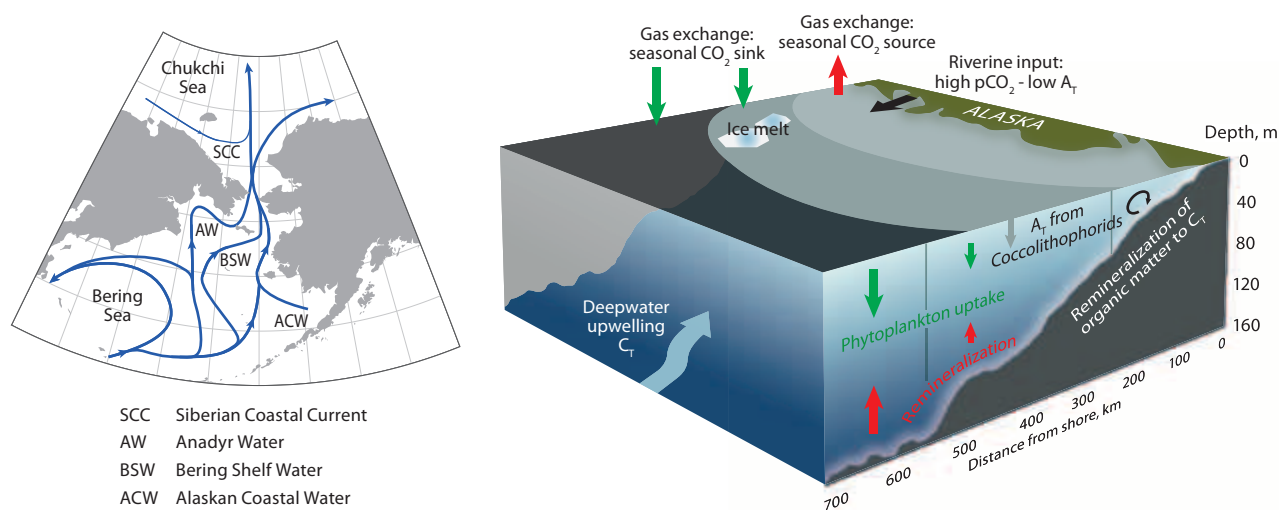


Figure 2.10. Arctic inflow into the Bering Sea (left; Kaltin and Anderson, 2005) and a generalized description of the processes affecting the carbonate chemistry of the eastern Bering Sea shelf (right; Mathis et al., 2011b). River runoff and upwelling create seasonal sources of CO_2 to the atmosphere while reducing carbonate mineral saturation states. Seasonally high rates of primary production lead to a rapid CO_2 drawdown at the surface, creating a strong seasonal atmospheric CO_2 sink and raising surface CaCO_3 saturation states. Organic matter export contributes to remineralization at depth, which lowers saturation states.

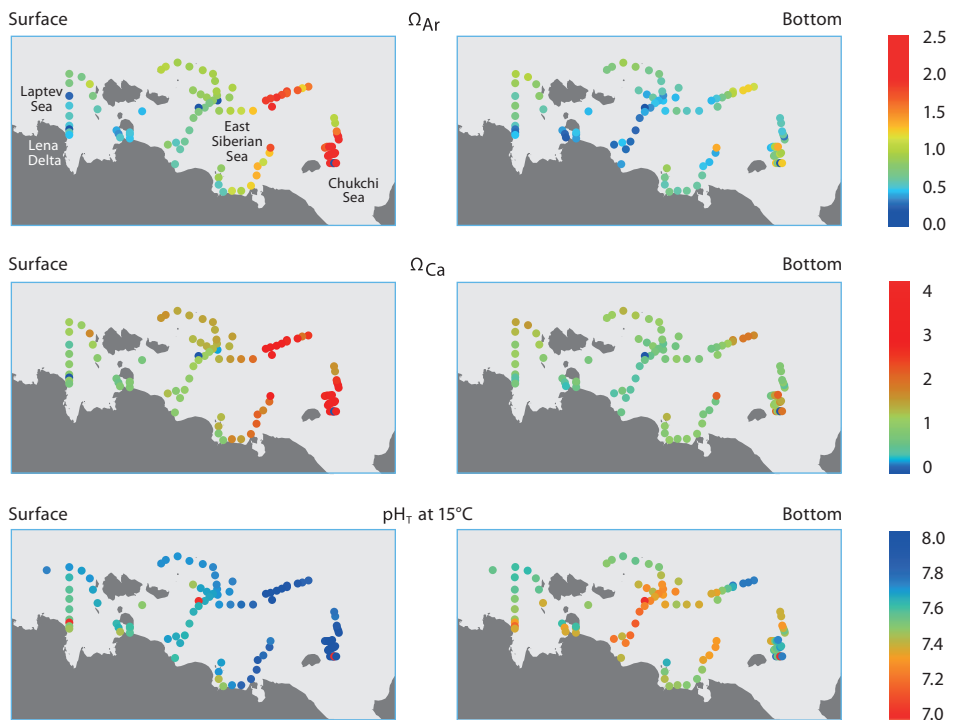


Figure 2.11. Saturation states for aragonite and calcite and pH in the Laptev, East Siberian and western Chukchi Seas in August-September 2008 for surface water (left) and bottom water (right). Source: after Anderson et al. (2011b).

The marine primary production cycle dominates the carbonate system in the eastern East Siberian Sea, where the Pacific is the dominant seawater source. This is reflected in CaCO_3 supersaturations ($\Omega_{\text{Ar}} > 1$) in the surface waters (Figure 2.11). In contrast, the western East Siberian and Laptev Seas are heavily affected by river runoff, and the saturation states in surface waters are less than 1. The bottom waters are undersaturated with respect to both aragonite and calcite in all regions, except for some stations in the Herald Valley and at the continental slope; indeed, the lowest saturation states observed anywhere in the Arctic seas are seen in the bottom waters on the Siberian shelf.

The marine climate in this large shallow region is rapidly changing, with summer sea-ice extent in the East Siberian Sea declining from more than 50% some ten years ago to less than 10% today (Cavalieri et al., 1996 and updated annually). This has many effects: light conditions improve for primary production in areas where terrestrial runoff impact is low; more terrestrial particulate and dissolved organic matter is added to the sea and degraded to CO_2 ; and cyclone frequency and strength will increase, adding to more vertical mixing of the water column. The dominating effect of these processes is to amplify ocean acidification in surface waters.

2.5.2.2 Western Arctic shelves: Chukchi and Beaufort Seas

The shelf waters of both the Chukchi and Beaufort seas are strongly influenced by the Pacific inflow, which introduces naturally low-pH waters into the Arctic (Section 2.5.1.2). Local, seasonal processes act on the Pacific inflow to further reduce pH and CaCO_3 saturation states, and thus, this area is vulnerable to acidification, even without anthropogenic perturbation. Although different definitions are used for the boundaries of these seas, this report considers the shelf areas, out to depths of about 250 m (Figure 2.12).

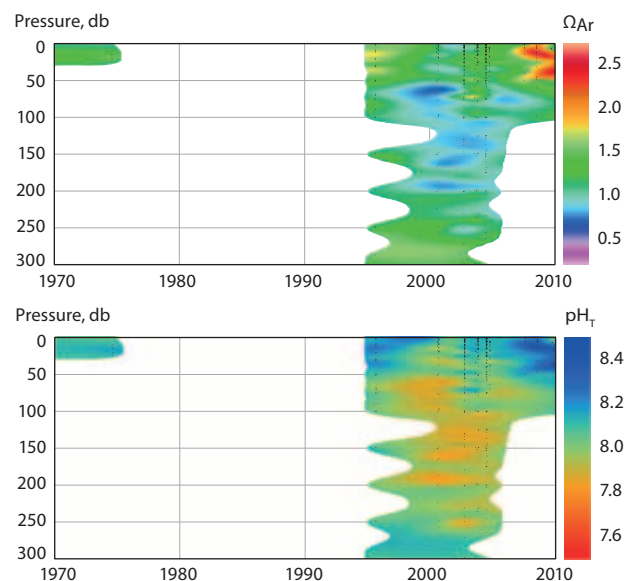


Figure 2.12. Surface currents and sampling points on the Chukchi and Beaufort shelves (upper) and aragonite saturation state (middle) and pH (lower) along the Beaufort Shelf between 1975 and 2010. Source: after Giesbrecht et al. (2013).

Potentially corrosive waters are found in subsurface waters on both the Chukchi (Bates et al., 2009) and Beaufort (Shadwick et al., 2011) shelves, and can readily come to the surface with upwelling (Chierici and Fransson, 2009; Mucci et al., 2010; Mathis et al., 2012). In both areas, summertime phytoplankton primary production increases surface pH and CaCO_3 saturation states (Murata and Takizawa, 2003; Bates et al., 2009; Mucci et al., 2010). Sufficient quantities of the resulting organic matter are apparently exported into deeper waters and remineralized back to CO_2 to generate seasonal decreases in pH and saturation state in subsurface waters (Bates et al., 2009). The converse wintertime process, with decreasing pH and saturation states at the surface due to excess respiration and mixed-layer deepening with sea-ice brine rejection has not been observed consistently (Shadwick et al., 2011; Lansard et al., 2012), and is likely to be dependent on inter-annually variable processes such as ice formation rates and autumn water-column preconditioning (e.g., Melling and Moore, 1995). Thus, interannual variability in the carbonate system of this area is large (Figure 2.12; Murata and Takizawa, 2003; Shadwick et al., 2011; Lansard et al., 2012), although seasonal processes are more likely to tip the system into dangerously low pH and saturation state values as inventories of anthropogenic carbon increase.

2.5.2.3 Canadian Arctic Archipelago to the Labrador Sea

Observed changes in CaCO_3 saturation states in the Arctic surface waters propagate downstream from the Beaufort Sea through the Canadian Arctic Archipelago southward through the Labrador Sea to the Middle Atlantic Bight (Figure 2.13). Along this transect, the CaCO_3 saturation state of Pacific water that was already relatively low in pH decreases further through the addition of sea-ice meltwater and fluvial input, as well as organic matter respiration. Waters undersaturated in aragonite have already been observed at the surface in Coronation Gulf (Chierici and Fransson, 2009), and at only 50 m depth in Hudson Bay (Azetsu-Scott et al., 2008).

A core of undersaturated water at about 150 m observed in profiles in the middle of the Archipelago indicates that the Beaufort Sea and Canada Basin are the source of these waters (Azetsu-Scott et al., 2010), and that a subsurface core of low-saturation state waters can be traced through the archipelago and Baffin Bay to Davis Strait (Figure 2.13). To date, the Amundsen Gulf is the only entrance area to the archipelago in which the carbonate system has been studied in detail (Chierici et al., 2011), although because of a shallow sill depth in Victoria Strait, other entrances appear to carry larger proportions of the total through-flow. While the outflow through Hudson Strait and local mixing in the northern Labrador Sea modifies the

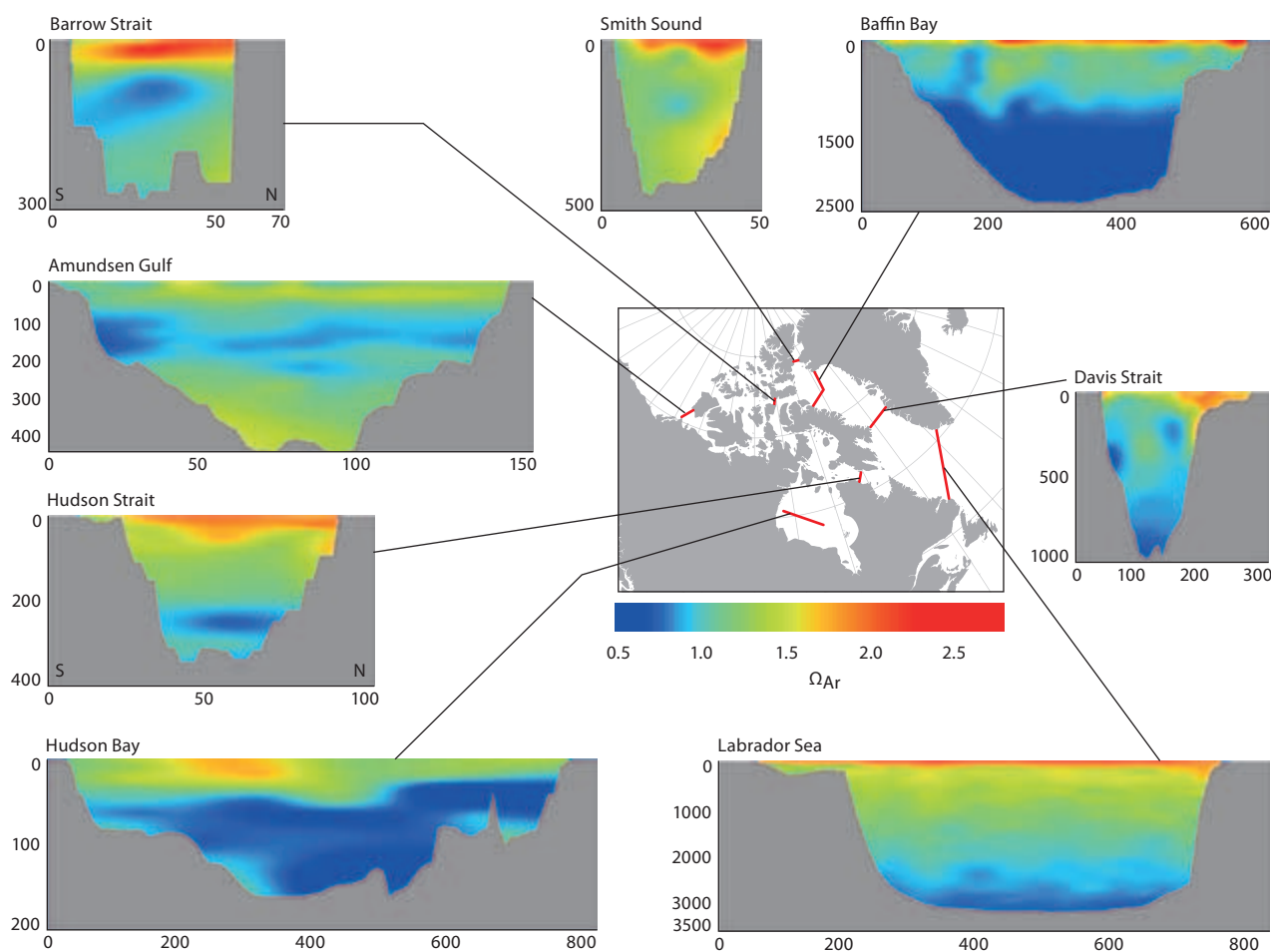


Figure 2.13. Aragonite saturation states across critical gateways in the Canadian Arctic Archipelago. Source: after Azetsu-Scott et al. (2008, 2010), Lansard et al. (2012), Giesbrecht et al. (2013).

low- Ω Arctic outflow, low saturation states can still be identified over the Labrador Shelf, at least as far south as Hamilton Bank. Within the Labrador Sea, the position of the saturation horizon is depressed by local deep convection and mixing with the intermediate and deep water masses of the North Atlantic.

2.5.3 Central Arctic Ocean

The source of the surface waters of the central Arctic Ocean is mainly the surrounding shelf areas, with a small direct contribution from the inflow of Atlantic and Pacific water through the Fram and Bering Straits, respectively. These source waters have high CO_2 solubility, because of their low temperature and relatively high alkalinity, resulting in pH_T values in the range 8.0–8.2. The deep waters of the central Arctic have a smaller range, with the *in situ* pH_T averaging 8.1 below 2000 m (Table 2.3, Figure 2.14). These deep waters are also much less impacted by anthropogenic CO_2 than the surface waters. Aragonite saturation states below 1 occur deeper than about 2500 m, although Ω_{Ca} is still above 1 throughout the water column (Jutterström and Anderson, 2005).

In the Beaufort Gyre freshwater is trapped, and surface salinity can be as low as 30 or even lower, which causes a substantial lowering of the CaCO_3 solubility. Furthermore, the recent unprecedented summer melting of sea ice has substantially lowered Ca^{2+} concentrations and thus also CaCO_3 saturation state, and this area is one of the first where aragonite undersaturated waters have been observed at the surface (Yamamoto-Kawai et al., 2009). Summer sea-ice melting also exposes the surface waters to the atmosphere, and as the surface waters have to date been largely undersaturated in CO_2 (Jutterström and Anderson, 2010), the surface water could be expected to absorb more atmospheric CO_2 , which would further decrease pH and CaCO_3 saturation state. However, increasing stratification, resulting in shallower surface mixed layers, may limit the depth to which CO_2 from air-sea gas exchange can penetrate to subsurface waters.

The halocline water of the Canada Basin has a strong signal of organic matter oxidation, a result of bottom water outflow from the highly productive Chukchi and East Siberian shelves. This water has high nutrient concentrations, high pCO_2 values, and low O_2 and pH. Consequently, the halocline is also undersaturated with respect to aragonite (e.g., Jutterström and Anderson, 2005; Bates and Mathis, 2009). In the past, when the central Arctic Ocean was mostly ice covered in summer as well as winter, this undersaturated water was isolated from the photic zone. However, with less sea ice, the energy for vertical mixing has increased and this water has started to penetrate the lower levels of the photic zone in recent years (Shimada et al., 2006).

2.6 Future scenarios

2.6.1 Introduction

Climate models project a significant retreat in sea-ice cover (e.g., Holland et al., 2006; Solomon et al., 2007; Stroeve et al., 2012a) as well as a shift from multi-year ice to thinner seasonal ice, suggesting a continuation of the trends already being observed (e.g., Maslanik et al., 2007; Giles et al., 2008; Kwok et al., 2009; Stroeve et al., 2012b). Models also suggest a loosening of the ice pack (Zhang et al., 2012) associated with the observed changes in ice conditions. Rampal et al. (2009) found an increase in sea-ice mean speed and deformation rate suggesting an increase in the number of cracks and small leads. All of these changes affect the CO_2 exchange between the atmosphere and ocean either directly (via changes in open water areas) or indirectly (e.g., via changes in biological uptake or changes in sea ice). As discussed in earlier sections, ocean acidification is intensified by increased atmospheric CO_2 and consequent ocean uptake as well as increased freshwater inflow from river runoff, ice melt and low-pH Pacific water, which makes Arctic waters especially vulnerable to a declining saturation state of CaCO_3 minerals such as aragonite and calcite

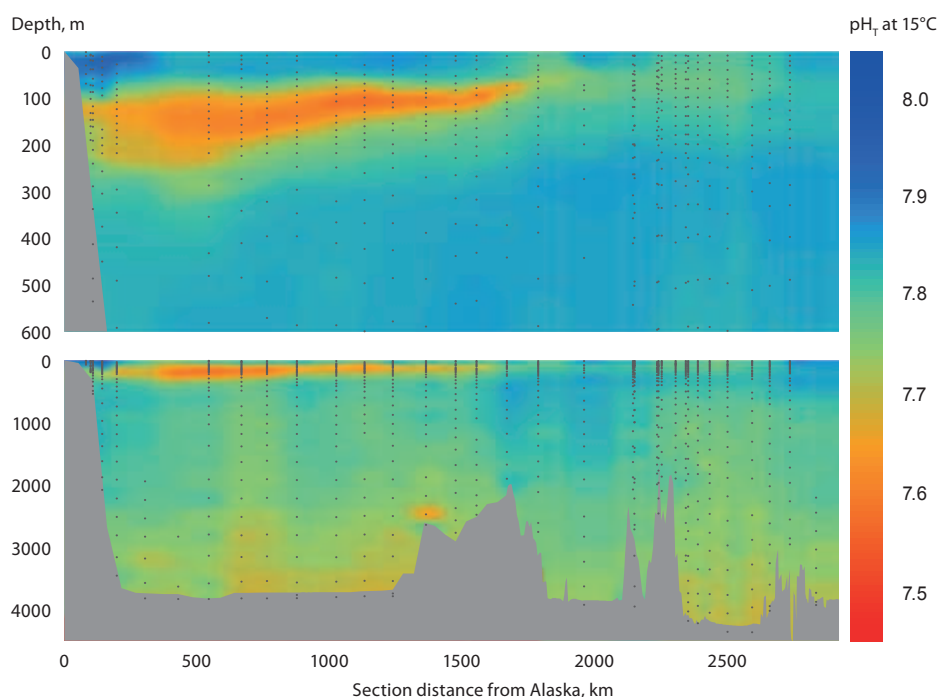
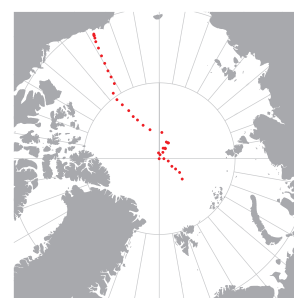


Figure 2.14. Section of pH_T (15 °C) from Alaska to the Gakkel ridge (lower panel) collected during the 2005 *Beringia* cruise. The upper panel shows the detail in the top 600 m. The insert shows station locations.



(e.g., Bates and Mathis, 2009; Yamamoto-Kawai et al., 2009, 2011; Denman et al., 2011).

The observed trend over the past two decades suggests continued ocean acidification on a basin-wide scale with further increase in atmospheric CO_2 . The pattern and timing of future ocean acidification, however, will be a result of the interplay between many factors including excess CO_2 uptake, changes in ocean circulation, land-ocean exchanges, biological productivity and respiration, freshwater contributions and sea-ice dynamics. To develop scenarios of future change requires approximations of these mechanisms through informed process understanding incorporated into mathematical models. So far, model simulations of future Arctic Ocean acidification are largely limited to global earth system models (ESMs) which have limited resolution as well as limited skill in the Arctic region (e.g., Schneider et al., 2008; Steinacher et al., 2010), although both resolution and biogeochemical parameterizations have been improved in the latest suite of ESMs. Published results of ESM simulations generally show enhanced ocean acidification in polar regions (e.g., Orr et al., 2005; Steinacher et al., 2009; Denman et al., 2011; Joos et al., 2011; Steiner et al., 2013) and by now it is widely accepted that the Arctic will exhibit the greatest global reductions in pH (see also McNeil and Matear, 2007; Gangstø et al., 2008; Christian et al., 2010) and the earliest undersaturation in Ω_{Ar} (Figure 2.15). Concurrent with these greatest reductions in saturation state are the greatest percentage losses in CaCO_3 production (Gangstø et al., 2008).

Although the direction of change is understood, the rate, cyclicity and regional distribution of anticipated Arctic Ocean acidification is complicated by the non-linear responses of a plethora of drivers and compensatory mechanisms. For example, increases in CO_2 concentration lower pH and warming of the seawater further enhances this decline. However, the decrease in saturation state (Ω) that follows CO_2 uptake may be, partially, compensated for by ocean warming. On a global basis, temperature increases

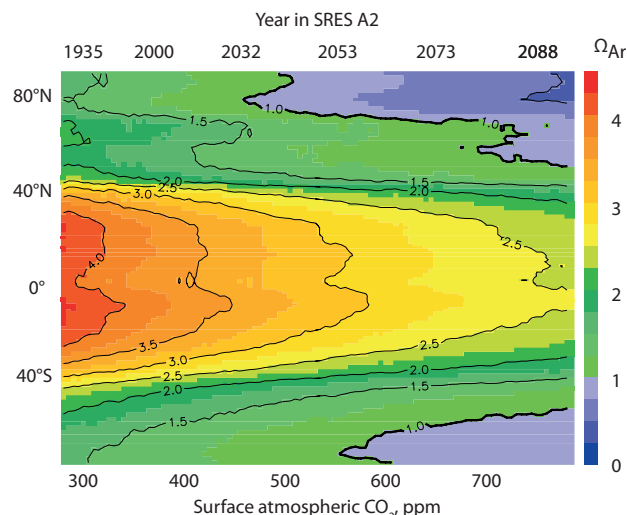


Figure 2.15. Global aragonite saturation state for the surface ocean under the Intergovernmental Panel on Climate Change SRES A2 greenhouse gas emissions scenario. Graphic shows latitudinal means. Source: after Steinacher et al. (2009).

will be the dominant climate change feedback on saturation state (Orr et al., 2005; McNeil and Matear, 2007) but will have little effect on pH (McNeil and Matear, 2007).

2.6.2 Ocean acidification changes projected over the 21st century

Steinacher et al. (2009), using the Climate System Model (CSM) 1.4-Carbon of the US National Center for Atmospheric Research (NCAR), and Denman et al. (2011), using the Canadian ESM CanESM1, report model projections of aragonite and calcite saturation, carbonate concentration, and pH, based on SRES scenarios; all project significant acidification in the Arctic Ocean over the course of the 21st century (see Figures 2.15 and 2.16). CMIP5 results are now publicly available, allowing for a more thorough analysis; however published results are limited

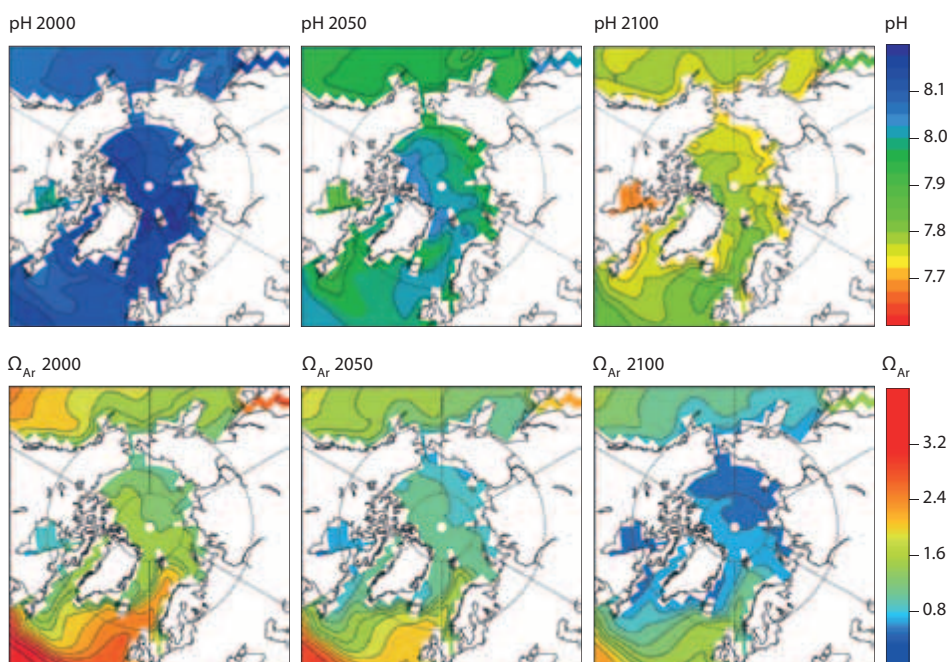


Figure 2.16. Projected change in pH and aragonite saturation through the 21st century using the CanESM-1.0 model. Source: after Denman et al. (2011).

so far. Deal et al. (2013) reported results for the Pacific Arctic (Bering and Chukchi Seas) with the CanESM1.5, a precursor of the Canadian CMIP5 contribution CanESM2, which has already increased resolution in the ocean. They project surface pH for RCP8.5 forcing to further decrease to about 7.9 by mid-century and below 7.7 by the end of the century, which corresponds with the results reported by Steinacher et al. (2009). Projections of Ω_{Ar} and Ω_{Ca} , which also depend on salinity and are significantly affected by increased freshwater contributions from river inflow, precipitation, and ice melt (Yamamoto-Kawai et al., 2009; Denman et al., 2011), are hence affected by how these processes are represented in models. For the end of the 21st century, CanESM1.5 projects Ω_{Ar} to change by about 0.8–1.0 across most of the Pacific Arctic region with somewhat smaller changes north and northeast of the Bering Strait, where surface waters have already become undersaturated in current times (Deal et al., 2013).

Increases in primary production, which act to increase Ω_{Ar} (and Ω_{Ca}) in the surface layer, might counteract a reduction in saturation states in certain areas at certain times. However, projections of Arctic primary production are highly variable. Steinacher et al. (2010) discussed discrepancies between results from empirical approaches and process-based ESMs and pointed out the importance of a realistic representation of nutrient cycling and distribution in order to project changes in primary production. Vancoppenolle et al. (2013) in a recent assessment of projected primary production, nutrient and sea-ice concentrations in 11 CMIP5 ESMs found that the mean model simulates Arctic-integrated primary production for

1998–2005 well, but that models neither agree on what limits primary production today, nor on the sign of future change. A balance of a decrease in available nutrients due to increased stratification and increased light availability due to a reduced sea-ice cover operates in all models; however, it depends on the particular model as to whether the decrease in available nitrate is sufficient to overcome or not the benefits of the light increase. Vancoppenolle et al. (2013) suggested that the main cause for the large inter-model spread was poorly constrained Arctic nitrate concentrations. In view of their results it is not clear whether future changes in Arctic primary production will accelerate or decelerate ocean acidification.

A multi-model comparison including the CanESM2 (Canada, e.g., Arora et al., 2011), IPSL-CM5A-LR (France, e.g., Dufresne et al., 2013), MPI-ESM-LR (Germany, e.g., Ilyina et al., 2013), GFDL-ESM2M (U.S.A., e.g., Dunne et al., 2012, 2013) and HadGEM2-ES (U.K., e.g., Collins et al., 2011) models shows the regionally and 20-year averaged annual mean surface pH to decrease from 8.11 in 1986–2005 to 8.00 in 2026–2045 and further to 7.92 in 2066–2085 for RCP8.5 (Figures 2.17 and 2.18). However, locally, pH values are projected to become even lower. Figure 2.17 shows an example of bi-decadally averaged Arctic Ocean pH in September, with pH below 7.7 in some areas. The very low values in the Hudson Bay for some models are likely to be unrealistic.

CMIP5 model results for the above-mentioned time periods (also including the MIROC-ESM, Japan, e.g., Watanabe, 2011) project Ω_{Ar} and Ω_{Ca} in the Arctic to reduce by about

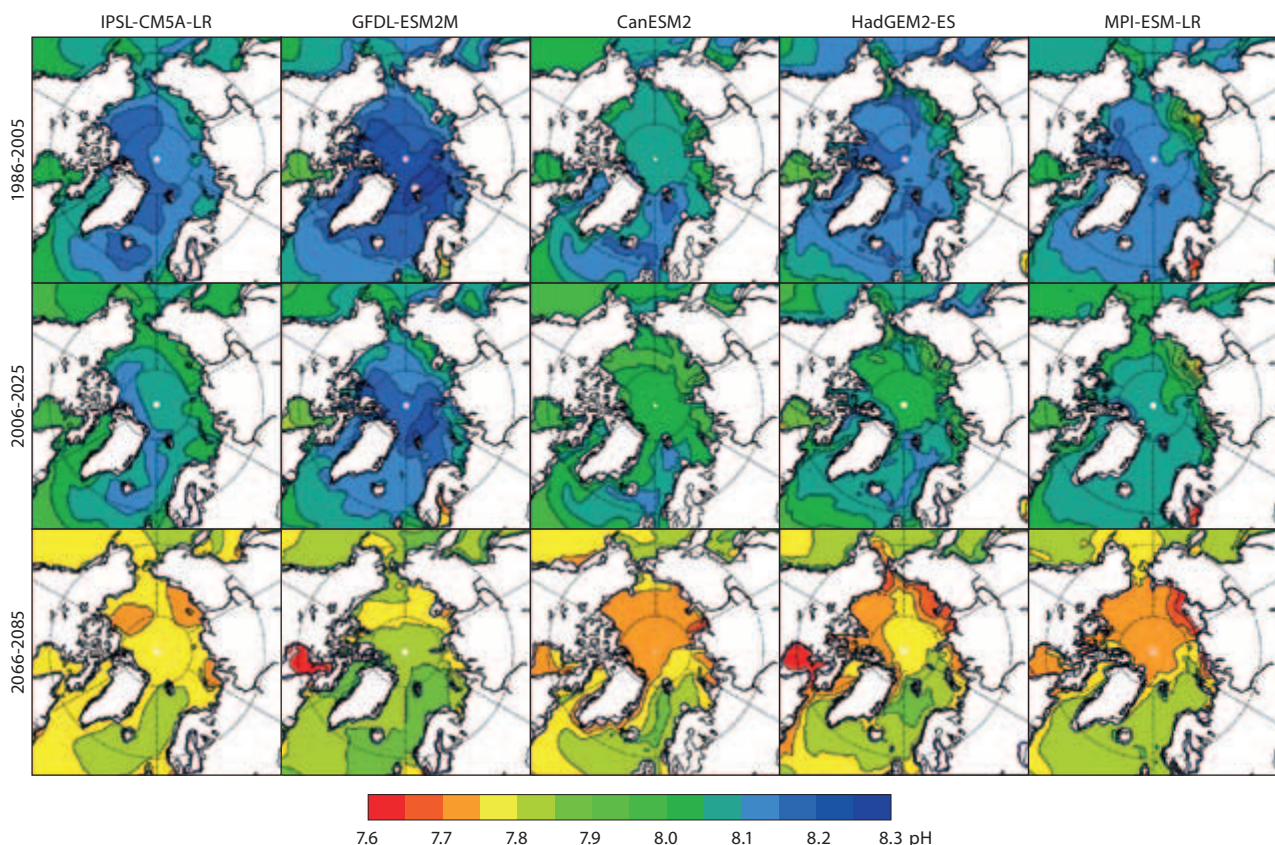


Figure 2.17. Bi-decadal mean pH for September as projected by the CanESM2, IPSL-CM5A-LR, MPI-ESM-LR, GFDL-ESM2M and HadGEM2-ES models. Time periods shown are 1986–2005 (top), 2006–2025 (middle) and 2066–2085 (bottom). Latitude circles indicate 60° and 80° N.

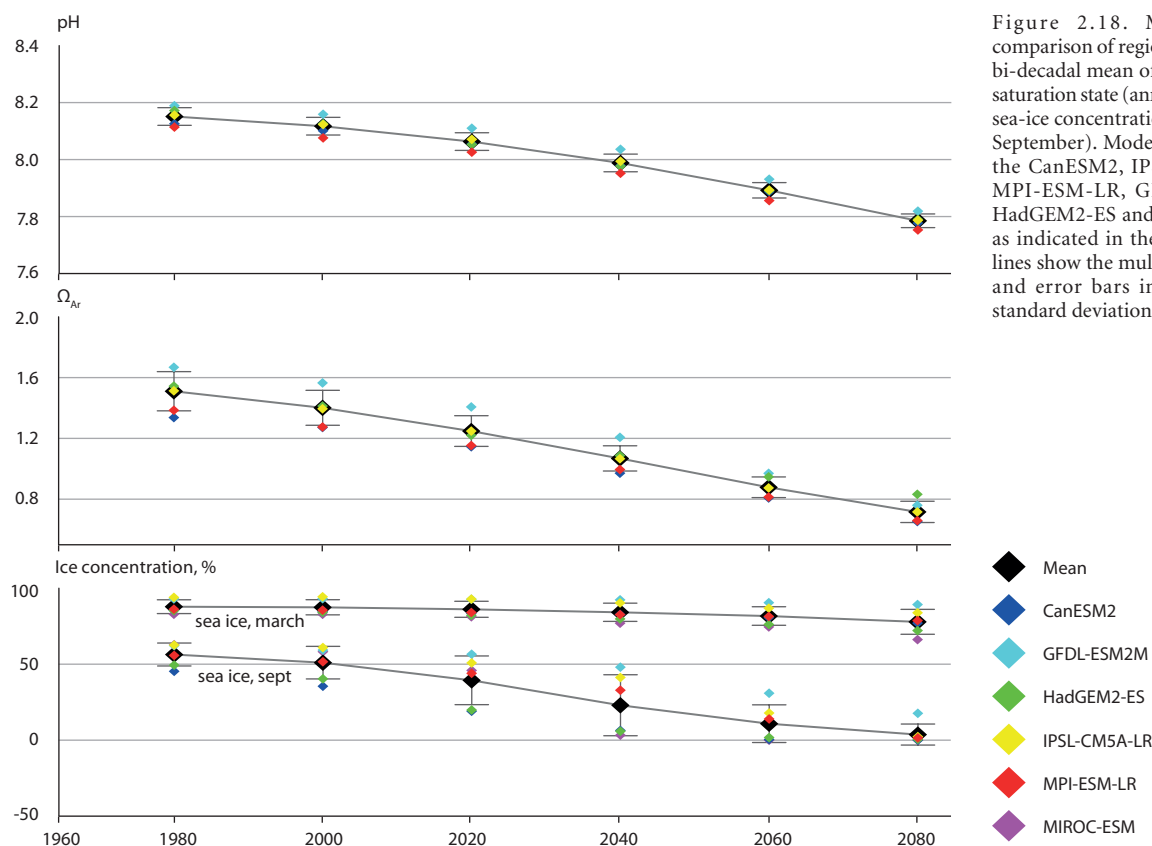


Figure 2.18. Multi-model comparison of regionally averaged bi-decadal mean of pH, aragonite saturation state (annual mean) and sea-ice concentration (March and September). Models included are the CanESM2, IPSL-CM5A-LR, MPI-ESM-LR, GFDL-ESM2M, HadGEM2-ES and MIROC-ESM as indicated in the legend. Solid lines show the multi-model mean and error bars indicate model standard deviations.

0.7–1.0 in correspondence with reductions in summer sea-ice concentrations (Figure 2.18).

Furthermore, as anthropogenic CO_2 penetrates deeper into the oceans, the seawater saturation horizons with respect to various carbonate mineral phases, the layer where Ω equals 1.0, will become shallower (Feely et al., 2004). Consequently, the maximum depth at which deep water corals and other calcifying organisms are found will shoal (Guinotte et al., 2006, Turley et al., 2007). The saturation horizons generally are already comparatively shallower in high latitude temperate and Arctic waters than at lower latitudes (Broecker and Peng, 1982).

Simulated global time series of the zonal mean saturation horizon show a continuous shoaling from pre-industrial times to 2100 for all latitude bands with the exception of the Arctic (not shown). In the Arctic, in addition to a continuous shoaling of the deep saturation horizon, a shallow saturation horizon starts to form close to the surface. This is caused by the combination of increased CO_2 uptake and freshwater contributions at the surface which in a large part of the Arctic Ocean basins leads to surface and possibly subsurface undersaturation. This formation of multiple layers of undersaturation is a special characteristic of the Arctic Ocean. The models vary within the range of about 1.0 in the Ω_{Ar} of deeper layers (below 200 m) and the deep saturation horizon varies between ~2000 m to ~4000 m for the individual models. Waters in the European Basin follow the pattern seen in the major oceans with a rising saturation horizon from bottom to top and surface waters becoming undersaturated much later than the rest of the Arctic.

In addition to long-term changes in Arctic Ocean acidification, changes in the physical environment, specifically sea-ice cover,

might alter the seasonal carbon cycling, affecting seasonal minima in pH and saturation states. In a sensitivity study with CanESM2, Steiner et al. (2013) found that retreating sea ice in the future leads to a shift in the seasonal cycle with an increase in CO_2 uptake in autumn and winter, a more continuous equilibration and hence a reduced uptake in summer. The reduction in summer suggests a limited CO_2 -uptake capacity of Arctic surface waters, which has also been suggested by Cai et al. (2010) and Jutterström and Anderson (2010).

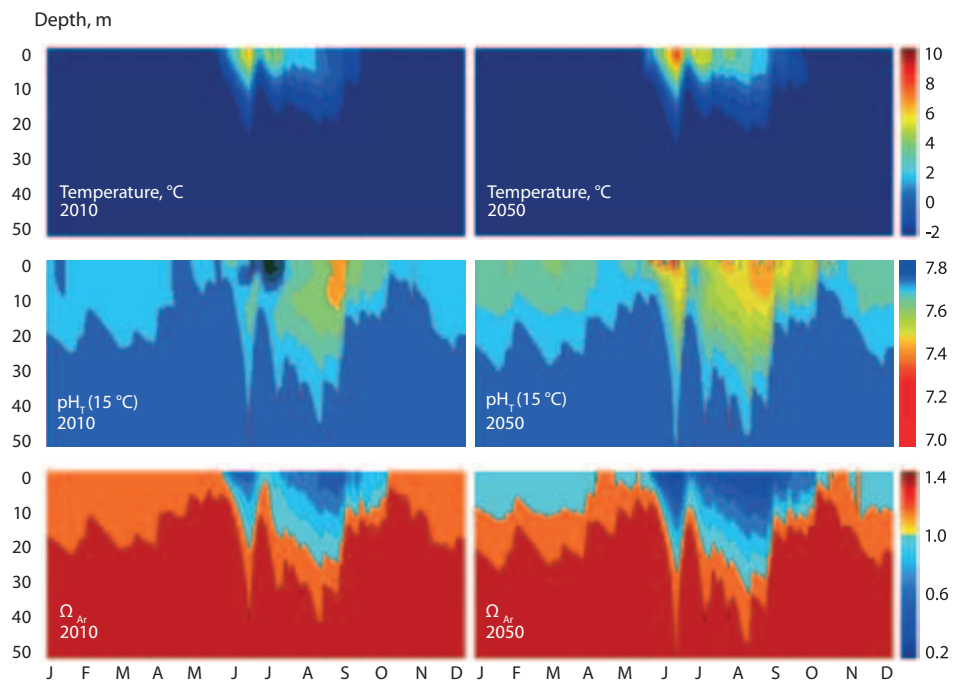
2.6.3 Regional modeling studies

While global model simulations provide consistent projections of reduced pH and first estimates for the timing of when aragonite and calcite undersaturation may be reached in the Arctic, coarse vertical and horizontal resolution and crude (or no) representations of passages and through-flows limit the applicability at local scales. To address the question of specific regional effects, regional models need to be developed and run for future scenarios. AMAP has co-funded two case studies under this reporting project.

2.6.3.1 A 1-D model study for the Laptev Sea

To investigate the combined effect of changes in several forcings on carbon transformation and fluxes, a physical-biogeochemical 1-D model was developed specifically for the Laptev Sea (Wählström et al., 2012, 2013). The model was constructed for a location in the central Laptev Sea and driven by atmospheric forcing, seawater influx from the central Arctic Ocean, and river runoff. The model was further developed to follow the evolution of the carbon system during the 21st century, applying an increase of atmospheric $p\text{CO}_2$ to 900 μatm

Figure 2.19. Change in temperature (upper), pH_T (middle) and aragonite saturation state (lower) in the central Laptev Sea for 2010 and 2050. Note that the plots for 2010 and 2050 have the same scales.



in 2100 (SRES-B1) and a resulting atmospheric temperature increase of 4 °C until 2100. The latter directly affects the temperature of the surface water (Figure 2.19) and thus also the length of the sea-ice period.

One result of the increased atmospheric pCO_2 is elevated CO_2 uptake by the surface seawater, which results in a pH decrease (Figure 2.19). The modeled maximum pH around June–July is due to CO_2 fixation by primary production. Reduced sea-ice cover positively affects this primary production; however, limited nutrient supply ultimately limits the annual new production. The net result is that the drawdown of CO_2 by primary production cannot compensate during the rest of the year for the increased pCO_2 from the atmospheric increase (Figure 2.19). However, one somewhat less significant effect of the increased primary production is the increase in organic matter sedimentation with subsequent remineralization all through the water column.

The effect on pH is directly influencing the solubility of calcium carbonates as illustrated by Ω_{Ar} (Figure 2.19). This reduction in saturation state will be amplified by lowered salinities, either from increased sea-ice melt or increased river discharge. Potential release of alkalinity trapped in sea ice (Section 2.3.1) or increased alkalinity in river waters might counteract this reduction in saturation state to a certain extent.

2.6.3.2 Atlantic-Arctic Greenland-Svalbard-Norway gateway

The Barents Sea, Fram Strait and the continental shelf north of Svalbard are productive shelf regions (Slagstad et al., 2011) and are a large contemporary CO_2 sink (Årthun et al., 2011). A considerable shelf pump transfers natural and excess carbon into the surface and intermediate Arctic Ocean (Kivimäe et al., 2010). Located at the frontier between the Atlantic and the polar waters, this region is very sensitive to changes in water temperature, ice cover and thus air-sea CO_2 exchange. Simulations with a regional

coupled sea-ice ocean biogeochemical model of modifications to the CO_2 system project large reductions in pH over the course of the 21st century (Bellerby et al., 2005, 2012). The pH reductions (between the means of the years 2006 to 2015 and 2099–2090) are large for the whole region and range from 0.24 to 0.35 (Figure 2.20). The greatest changes are associated with the Arctic waters of the East Greenland Current and to the north of Svalbard. Similarly, reductions in Ω_{Ar} are highest in the Arctic outflow waters (Figure 2.21). The changes are, however, very regional, and the different carbon system variables may respond differently on local scales. Increases in carbon are mostly a consequence of excess carbon transport with the Norwegian Atlantic Current and increased gas exchange promoted by decreased ice cover. Warming is especially prominent north of the present-day maximum extent of the marginal ice zone, and this acts to enhance ocean pH reduction and increase Ω_{Ar} . Freshening due to ice melt and increased run-off will lower both pH and Ω_{Ar} . Deep wintertime mixing acts to dampen ocean acidification by diluting the surface excess carbon signal with waters with a lower C_{ant} .

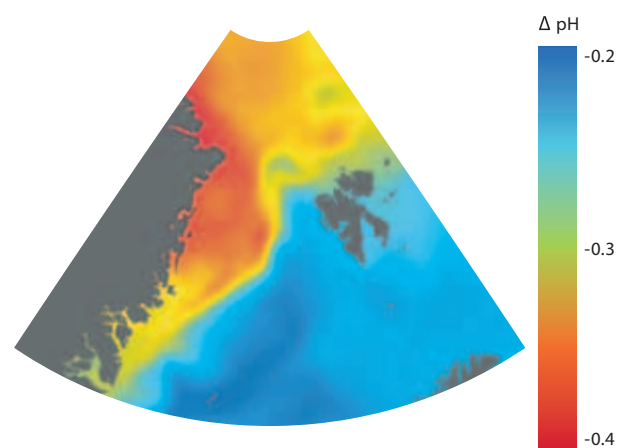


Figure 2.20. Change in surface ocean pH (mean 2006–2015 minus mean 2090–2099) for the Atlantic-Arctic Greenland-Svalbard-Norway gateway region.

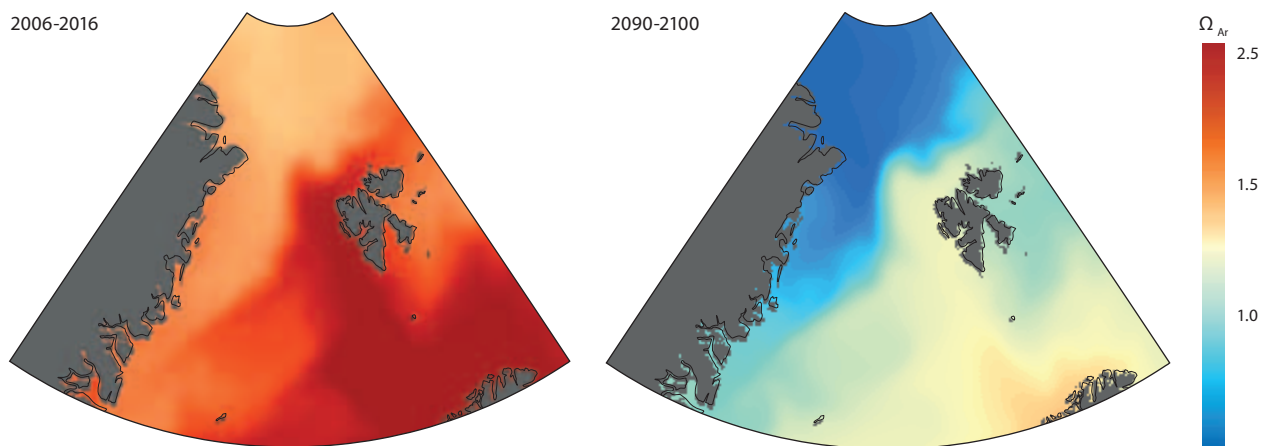


Figure 2.21. Simulated aragonite saturation state through the 21st century (mean 2006–2016 and mean 2090–2100) for the northern Nordic Seas, western Barents Sea and Eurasian continental shelf.

2.6.4 Limitations of future projections

Many of the processes affecting the pace and pattern of Arctic Ocean acidification are inadequately known, such as the changing freshwater distributions within the Arctic Ocean (e.g., Long and Perrie, 2013), the changes in primary production, and the timing and pattern of sea-ice retreat. For example, a model study by Yamamoto et al. (2012) highlighted the importance of the sea-ice reduction rate on acidification, suggesting that future reductions in pH and Ω_{Ar} with an increased pace in sea-ice reduction could be significantly faster than previously projected. Stroeve et al. (2012a) found that while IPCC AR5 models better capture the observed decline in Arctic sea ice than an earlier comparison project (Stroeve et al., 2005), the models exhibit a stronger seasonal cycle in both sea-ice extent and volume, and the inter-model scatter remains, particularly for summer. It is also clear that the spatial variability of ice thickness is not simulated well by the majority of models (Maslowski et al., 2012). The simulated gas flux through small leads and cracks is likely to be underestimated (Steiner et al., 2013) and carbon transport through the sea-ice matrix (e.g., Loose et al., 2011) is not represented in models at all. Another

unknown is the potential release of methane and its subsequent oxidation to CO_2 . Biastoch et al. (2011) showed that the local pH values could be lowered by over 0.25 units if 50% of the methane from hydrates is released over a period of 100 years (Figure 2.22).

The complexity of the ecosystem and carbon modules varies between models (e.g., Vancoppenolle et al., 2013). In many cases, the ecosystem structure is not sufficient to resolve the foodweb structure in the Arctic or to adequately represent complex processes and interactions. Other models might include higher complexities, but applied parameterizations might be inadequate, either due to limited understanding in general or, especially in the case of global models, because global parameterizations might not be suitable for Arctic-specific processes.

The fairly coarse resolution in global models does not make it possible to properly resolve the physical processes important for biogeochemical carbon exchange, especially within the Arctic, where shallow shelves and narrow passages are common features. Higher resolution regional models simulating ecosystem and carbon cycle processes will need to be applied to project the impacts of future climates in more detail. However, as seen above, these models are extremely limited, as yet.

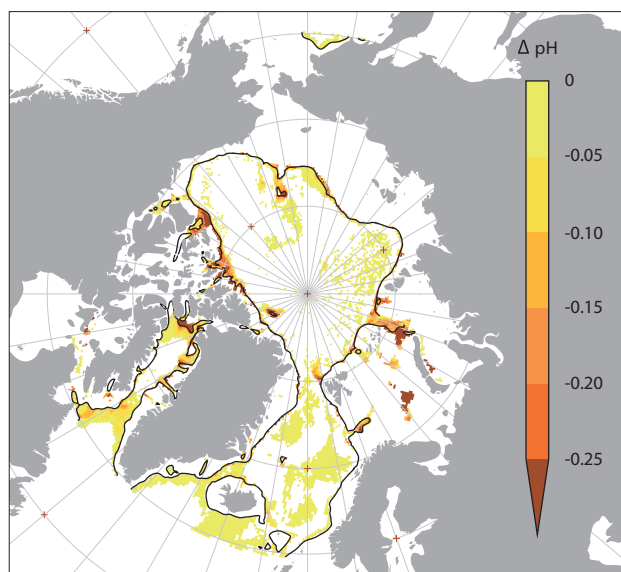


Figure 2.22. Simulated change in pH across the Arctic over a 100-year period due to a 50% methane release. Source: after Biastoch et al. (2011).

2.6.5 Lifetime of ocean acidification

As CO_2 continues to be produced from fossil fuel combustion and other sources, ocean acidification will continue roughly in line with the increasing atmospheric CO_2 concentration. When geological carbon reserves become uneconomic, or legislation is in place and other energy sources are preferred, atmospheric CO_2 will decline, as will surface ocean acidification, as the anthropogenic carbon continues to be mixed into the ocean abyss, increasing deepwater acidification (Caldeira and Wickett, 2003; Archer, 2005) (Figures 2.23 and 2.24). Mixing will be the main moderator of ocean acidification excesses for the next 1000 years. To reduce ocean acidification requires the dissolution of CaCO_3 on the sea floor that will increase the A_T of seawater and therefore increase pH and reduce ocean $p\text{CO}_2$ and then atmospheric CO_2 (Archer, 2005; Ridgwell and Hargreaves, 2007). There is not, unfortunately, enough accessible CaCO_3 to buffer ocean acidification and CaCO_3

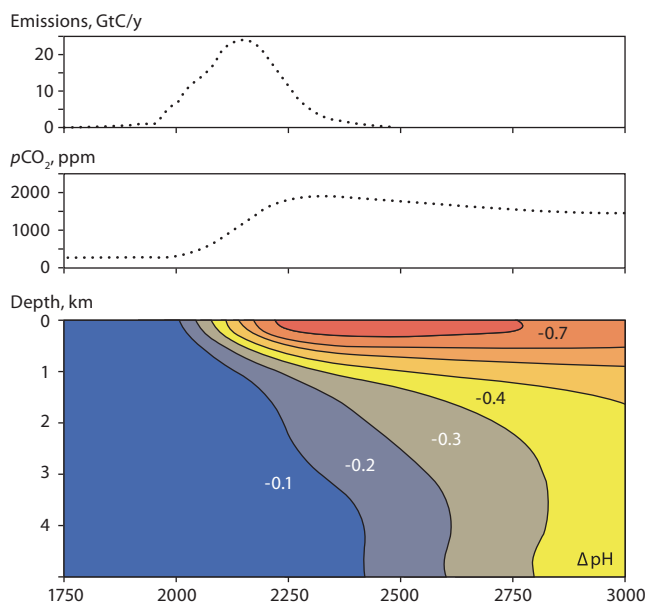


Figure 2.23. Example of mean ocean response to a theoretical carbon emission rate and extent showing the initial surface ocean acidification extreme and then dilution of the surface as carbon penetrates the interior ocean increasing ocean acidification at depth. Source: after Caldeira and Wickett (2003).

compensation will be exhausted over the next centuries. This is when the true geological scaling of ocean acidification will become apparent: the weathering of silicates is required to further neutralize the fossil fuel perturbation. Ultimately, the increasing alkalinity of the ocean will promote calcification and increased sedimentary deposition returning the carbon back into the geological reservoir. However, with a timescale of tens to hundreds of thousands of years (Archer, 2005; Archer et al., 2009a), a return toward pre-perturbation atmospheric CO_2 and ocean pH is of little use in managing ecosystem and societal needs of today.

2.7 Conclusions

There is a building awareness of ocean acidification and the role it has in shaping the chemical matrix of seawater and the effects this may have on ecosystems and biogeochemical cycling in the ocean. There can be no doubt that, as the atmospheric CO_2 concentration rises, the surface ocean pH will drop and there will be a change in the speciation of the carbonate system. The Arctic Ocean is one of the most sensitive ocean regions regarding the ocean acidification response to CO_2 uptake and will be the first ocean to undergo basin-wide acidification, crossing important geochemical thresholds. The seawater in the Arctic is already poorly buffered with low carbonate ion concentrations and a high C_T to A_T ratio which results in large changes in pH with modifications to the CO_2 concentration. Although current knowledge is based on few direct measurements, it is clear that the Arctic Ocean is undergoing rapid acidification. Unique on such a grand scale, in addition to direct anthropogenic CO_2 effects, ocean acidification is also being driven by large-scale freshening and increases in terrestrial carbon fluxes. The Arctic has a rapidly changing freshwater budget through increasing fluvial inputs and in addition a net supply from changes in sea-ice distribution.

Arctic Ocean acidification is being measured throughout the water column with the largest deep-water changes taking place in the Nordic Seas. However, it is in the surface and upper intermediate waters that changes are happening fastest. The bulk of the excess CO_2 is being transported to the Arctic from other ocean basins and is being taken up directly from the atmosphere.

Ocean acidification is changing the geochemistry of the Arctic. Decreases in CO_3^{2-} through CO_2 invasion and reduction in Ca^{2+} from freshwater dilution are reducing the stability of CaCO_3 . Ocean acidification has been shown to influence nutrient cycling and trace element availability. The consequences of these changes on marine organisms and ecosystems are discussed in Chapter 3.

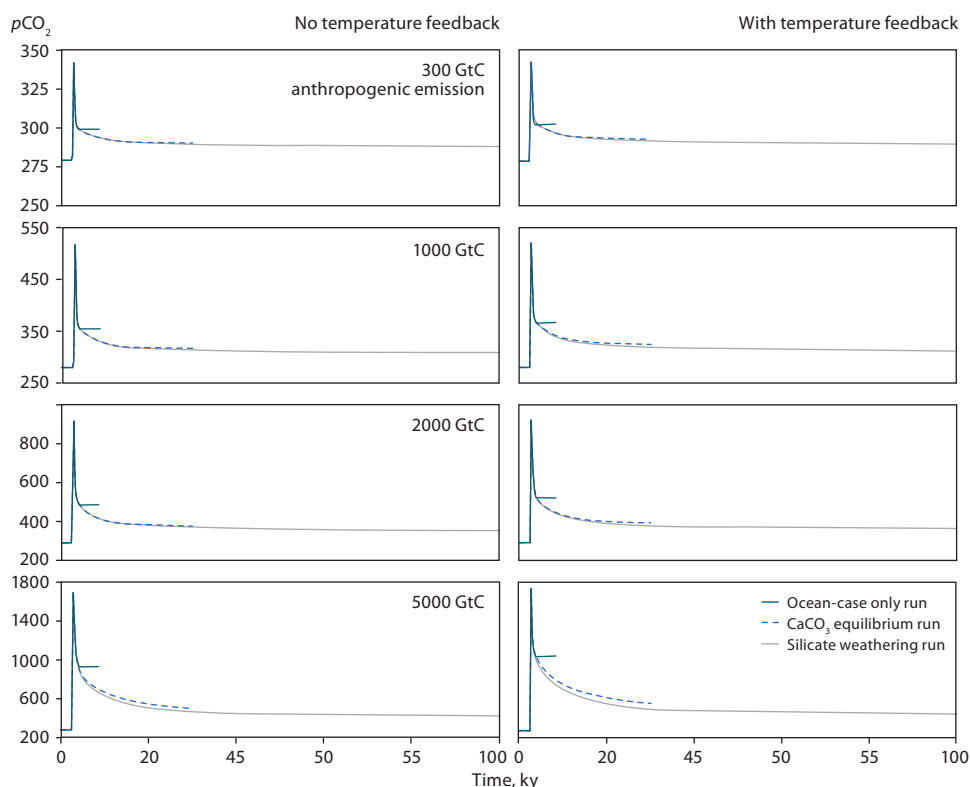


Figure 2.24. Geological lifetime of atmospheric CO_2 . Model results for $p\text{CO}_2$ for different CO_2 emission scenarios and model runs without (left) and with (right) ocean temperature feedback. Source: after Archer (2005).

Ocean acidification, to the first degree, closely follows atmospheric CO_2 concentrations. Ocean acidification is occurring fast in the Arctic such that within decades the entire surface Arctic will be undersaturated with respect to CaCO_3 . Complete undersaturation from the surface to the sea floor in the Arctic Ocean will occur due to the expansion of a deep saturation horizon upward following transport of anthropogenic CO_2 from outside the Arctic and the expansion of a shallow saturation horizon downward due to freshwater addition, enhanced local uptake, mixing, and shelf–ocean interior exchange. Over thousands of years, even when fossil fuel combustion has been reduced, ocean acidification will still be prevalent, although ocean overturning will reduce the surface signal to some extent. Geochemically, removal to marine organisms (corals and other calcifiers) and sedimentary CaCO_3 due to dissolution in the corrosive ocean is the intermediate pathway to buffer ocean acidification. Even if fossil fuel emissions would cease today, the ocean would not return to pre-industrial pH values for tens of thousands of years. However, reductions in emissions will curtail the extent and duration of ocean acidification.

Key points:

- The carbon inventory of the Arctic Ocean is increasing, leading to ocean acidification. *The amount of inorganic carbon in the Arctic Ocean is going up and this is lowering the pH of the seawater and changing the relative amounts of inorganic carbon species.*
- The major driver of increasing ocean acidification is anthropogenic carbon uptake. *The major increase in inorganic carbon is derived from the combustion of fossil fuels.*
- The degree and distribution of Arctic Ocean acidification is further controlled by ice cover, freshening, warming and terrestrial inputs. *In addition to fossil fuel combustion, the other, smaller but significant, contributors to ocean acidification in the Arctic include the changing cryosphere which allows for more air-sea gas exchange, salinity reductions due to ice melt and increasing river run-off, ocean warming and increasing inputs of carbon from land.*
- The carbon dioxide content and pH of seawater has high natural temporal and spatial variability. *High seasonality of the solubility and biological pumps together with the low buffer capacity of Arctic seawater results in high seasonal variability of the marine carbonate system.*
- There will be modifications to some nutrient cycling and trace metal speciation. *Changes in seawater pH can modify the forms of trace elements and nutrients, and thus their bioavailability will be altered.*
- Regions of the Arctic Ocean are, globally, among the first to reach geochemical thresholds of ocean acidification. *Forms of calcium carbonate will become geochemically unstable over the next decades. The Arctic Ocean is the first ocean region where this will become widespread.*
- Ocean acidification will be tenacious. *Geological carbon from fossil fuel combustion will remain in the ocean-atmosphere system for tens of thousands of years. And even after this time, the system will have not recovered to its pre-industrial marine carbonate system state.*

Chapter 2 Appendix: Compilation of published data (1960-2012) on trace elements and their isotopes in the Arctic

Table A1. Trace metal distribution studies in the Arctic.

Element	Region	Source
Aluminum	Lomonosov Ridge Canada and Eurasian Basins Norwegian Sea Amundsen, Makarov and Nansen Basins and the Barents and Laptev Seas	Moore, 1981 Measures, 1999 Hall and Measures, 1998 Middag et al., 2009
Barium	Canada and Eurasian Basins White, Barents, Kara, Laptev and Beaufort Seas Fram and Denmark Straits Canada and Eurasian Basins Canada Basin Makarov Basin Canadian Archipelago	Guay and Falkner, 1997 Guay and Falkner, 1998 Taylor et al., 2003 Alkire et al., 2007 Guay et al., 2009 Abrahamsen et al., 2009 Thomas et al., 2011
Cadmium	Lomonosov Ridge Nansen Basin Barents Sea and Fram Strait Nansen Sound (Ice Island) Fram Strait and Greenland Sea	Moore, 1981 Danielsson and Westerlund, 1983 Mart et al., 1984 Yeats and Westerlund, 1991 Pohl et al., 1993
Cobalt	Nansen Sound (Ice Island)	Yeats and Westerlund, 1991
Copper	Lomonosov Ridge Bering Sea Nansen Basin Barents Sea and Fram Strait Nansen Sound (Ice Island) Fram Strait and Greenland Sea	Moore, 1981 Heggie, 1982 Danielsson and Westerlund, 1983 Mart et al., 1984 Yeats and Westerlund, 1991 Pohl et al., 1993
Iron	Nansen Basin Canada and Eurasian Basins Bering Sea Bering Sea Chukchi Sea Amundsen, Makarov and Nansen Basins and the Barents and Laptev Seas	Danielsson and Westerlund, 1983 Measures, 1999 Aguilar-Islas et al., 2007 Hurst and Bruland, 2007 Nakayama et al., 2011 Klunder et al., 2012a,b
Lead	Barents Sea and Fram Strait Fram Strait and Greenland Sea	Mart et al., 1984 Pohl et al., 1993
Manganese	Nansen Sound (Ice Island) Bering Sea Amundsen, Makarov and Nansen Basins and the Barents and Laptev Seas	Yeats and Westerlund, 1991 Aguilar-Islas et al., 2007 Middag et al., 2011
Nickel	Nansen Basin Nansen Sound (Ice Island)	Danielsson and Westerlund, 1983 Yeats and Westerlund, 1991
Zinc	Lomonosov Ridge Nansen Basin Barents Sea and Fram Strait Nansen Sound (Ice Island) Fram Strait and Greenland Sea	Moore, 1981 Danielsson and Westerlund, 1983 Mart et al., 1984 Yeats and Westerlund, 1991 Pohl et al., 1993

Table A2. Trace metal speciation studies in the Arctic and sub-Arctic.

Element	Region	Source
Copper	Bering Sea	Moffett and Dupont, 2007
Iron	Bering Sea (as tracer) Amundsen, Nansen and Makarov Basins and the Kara Sea	Hurst and Bruland, 2007 Thuróczy et al., 2011
Zinc	Bering Sea (as tracer)	Hurst and Bruland, 2007

Table A3. Natural abundance of trace metal isotopes in the Arctic.

Element	Region	Source
Beryllium	Canada, Amundsen and Nansen Basins and Fram Strait	Frank et al., 2009
Cadmium	Canada and Amundsen Basins	Ripperger et al., 2007
Hafnium	Canada Basin and Central Arctic	Zimmermann et al., 2009
Neodymium	Barents Sea and Fram Strait Canada, Amundsen, and Makarov Basins	Andersson et al., 2008 Porcelli et al., 2009
Lead	Canada Basin Canada and Eurasian Basins	Moore and Smith, 1986 Smith et al., 2003
Radium	Canada Basin Barents Sea, Eurasian Basin Canada and Eurasian Basins Kara and Laptev Seas Chukchi and Beaufort Seas Eurasian and Canadian Basins	Moore and Smith, 1986 Rutgers van der Loeff et al., 1995 Smith et al., 2003 Rutgers van der Loeff et al., 2003 Kadko and Muench, 2005 Kadko and Agaard, 2009
Thorium	Alpha ridge Nansen Basin Norwegian and Denmark Seas Makarov, Amundsen and Nansen basins. Eurasian and Canada Basins Canada Basin Canadian Archipelago Canada, Amundsen, Nansen and Makarov Basins Canada Basin Beaufort Sea Beaufort Sea Chukchi Sea	Bacon et al., 1989 Cochran et al., 1995 Moran et al., 1995 Scholten et al., 1995 Moran et al., 1997 Edmonds et al., 1998 Amiel et al., 2002 Edmonds et al., 2004 Trimble et al., 2004 Lepore and Moran, 2007 Amiel and Cochran, 2008 Yu et al., 2010
Uranium	Canada and Makarov Basins Beaufort Sea	Andersen et al., 2007 Not et al., 2012

3. Biological responses to ocean acidification

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3.1 Introduction

This chapter presents an overview of what is known about the effects of ocean acidification on marine organisms and ecosystems. Information on Arctic species and ecosystem processes is extremely limited owing to the logistical difficulties of working in these environments (remoteness, ice cover, high cost, etc.) and in conducting experiments at very low temperatures (long generation times, working at below freezing temperatures for prolonged periods, etc.). This is clearly illustrated in Figure 3.1 using echinoderms as an example. Where possible, this report presents available data from Arctic and/or polar cases. However, for the reasons just stated, most of the material presented here is from studies on non-Arctic species and ecosystems, accompanied by an attempt to assess what this means in an Arctic context.

This chapter summarizes briefly the natural variability in pH and carbon dioxide (CO_2) in time and space (see Chapter 2 for further details) and presents an overview of the biological and physiological context for assessing the impact of ocean acidification on marine organisms and ecosystems (Section 3.2). This is followed by a description of Arctic ecosystems and food webs (Section 3.3). The chapter then reviews what is known about the effects of ocean acidification on different taxonomic groups; with each sub-section distilling what is known from non-Arctic species and then discussing how that may be relevant to Arctic species and to the key linkages in the Arctic food web (Section 3.4). Ecosystem-wide responses

to ocean acidification are addressed in Section 3.5. There is then a brief discussion of ocean acidification analogs (areas of naturally lower pH and/or high carbon dioxide regions) and their potential for research (Section 3.6). The chapter concludes with some general caveats to this work (Section 3.7), proposals for research priorities (Section 3.8) and a series of conclusions and recommendations (Section 3.9).

3.2 Biogeochemical, biological, and physiological context for assessing the impact of ocean acidification

3.2.1 Natural variability in pH and carbon dioxide in time and space

Uptake of atmospheric CO_2 by the oceans is driving changes in the carbonate chemistry of the Arctic Ocean – this is commonly referred to as ‘ocean acidification’ and is described in detail in Chapter 2. There is high spatio-temporal variability in these changes with, for example, rapid and large fluctuations on the continental shelves and more stable conditions in ancient deep waters that currently contain no anthropogenic carbon. Organisms living in shallow coastal waters may already experience transient changes in pH as great as 7.4–9.2 on a daily basis (e.g., Middelboe and Hansen, 2007). Pelagic organisms will be exposed to less pronounced diel fluctuations, but will encounter seasonal changes in pH of the order of 7.5–9.7



Figure 3.1. Number of published studies investigating the impact of ocean acidification on sea urchins. Source: Sam Dupont, University of Gothenburg.

(Hofmann et al., 2011). The range in pH to which organisms might be exposed is particularly large (7.1–9.7) in eutrophic coastal waters (e.g., Hansen, 2002). In the Arctic, large changes in pH may occur in sea ice, but in open waters pH will typically be in the 7.7–8.3 range. The highest pH values (9.7) have been recorded during algal blooms, whereas the lowest (7.1) occur where respiration lowers the pH, such as below the pycnocline or during winter after prolonged dark periods.

A comprehensive dataset of continuous pH observations spanning polar to tropical ecosystems, and open-ocean to kelp forests and coral reefs, shows that pH in the upper 15 m of the water column can vary by up to 1.43 units (Hofmann et al., 2011). Polar sites (Antarctica) showed low fluctuation (≤ 0.1 pH units), although measurements were only made for two weeks. The most extreme fluctuations were observed in natural CO₂ vent areas (Ischia, Italy), however, kelp-forest, estuarine, and upwelling ecosystems all showed fluctuations of 0.4–0.6 pH units over a period of four weeks (Hofmann et al., 2011). Similar magnitude pH variations have been observed diurnally in tide pools (Wootton et al., 2008; Moulin et al., 2011). In all cases, lower-bound recorded pH values can be below, or well below, those projected for the end of the 21st century for the average surface ocean (IPCC, 2007). This demonstrates that many organisms are already experiencing pH conditions that are lower than previously considered likely. The consequences of fluctuating pH conditions are only just beginning to be investigated. The variability in ocean acidification and Arctic Ocean carbonate chemistry will increase in both space and time as the process of acidification continues. This means that the biological and ecological effects of ocean acidification will vary regionally and with its increase over time. Consequently, as well as a need for more data detailing diurnal/seasonal/annual fluctuations in pH in Arctic habitats, experimental results are also required to consider local scenarios and take into account the effects of fluctuating pH on Arctic species (McElhany and Busch, 2012).

The interpretations and conclusions of the ocean acidification challenge experiments described in this chapter should be set within the context of this natural variability in pH.

3.2.2 General biological responses to lowered pH / elevated CO₂

Marine organisms with external shells made up of calcium carbonate obtain the raw material used to build them from seawater (e.g., Roleda et al., 2012). Therefore, the carbonate chemistry of seawater is an important factor for these organisms as it will, at least in part, affect the shell-building process and, for those organisms whose shells are not protected by a chemically resistant organic layer, also the rate of dissolution (e.g., Lischka et al., 2011). For heterotrophic marine metazoans, pH and the partial pressure of CO₂ ($p\text{CO}_2$) are the main ocean acidification-related variables that impact them: effective respiration requires a diffusion gradient of CO₂ from the extracellular body fluids (blood, haemolymph or coelomic fluid) to the seawater. Typically, $p\text{CO}_2$ in ectothermic marine animal body fluids is about 1000 to 4000 μatm higher than that of seawater (Melzner et al., 2009a). Increases in seawater $p\text{CO}_2$ typically increase body fluid $p\text{CO}_2$ by an equal amount, as

diffusion gradients must be maintained to guarantee constant rates of CO₂ excretion (see Melzner et al., 2013: Fig. 6). These unavoidable changes in body fluid $p\text{CO}_2$ impact physiology primarily through two mechanisms: (1) accumulation of bicarbonate ions in the body fluids in order to stabilize pH at higher levels (e.g., cephalopods, teleost fish, many decapod crustaceans), (2) no bicarbonate accumulation resulting in much larger decreases in pH (Seibel and Walsh, 2003; Melzner et al., 2009a). Both types of reaction can result in pathologies in short- to medium-term experiments (e.g., Melzner et al., 2013).

Many other direct effects of ocean acidification on organisms are possible; for example, sublethal effects on metabolism and energetics, growth rate, condition, reproductive success or behavior (e.g., see Chapters 4–10 in Gattuso and Hansson, 2011). There is also the possibility of indirect impacts through the food web (e.g., Eklof et al., 2012; Rossoll et al., 2012). To complicate matters further, these effects can be very different depending upon the life-history stage being evaluated (although essential, studies that consider the complete life cycle of an organism are rare).

3.2.2.1 Impact on calcification by marine organisms

The calcification rates of a wide range of marine organisms decline when subjected to the seawater pH values projected for the coming centuries due to atmospheric increases in CO₂. Review articles by Kleypas et al. (1999, 2006), Hoegh-Guldberg et al. (2007), Fabry et al. (2008), Doney et al. (2009), Gattuso and Hansson (2011), and Wicks and Roberts (2012) provide excellent summaries of many of the studies conducted to date. Ries et al. (2009) also found highly variable calcification responses of 18 species of benthic marine organisms to $p\text{CO}_2$ treatments of 400, 600, 900, and 2850 ppm. They observed linear negative responses (soft clam, oyster, scallop, periwinkle, whelk, serpulid tubeworm), threshold-negative responses (tropical urchin, temperate coral, conch, hard clam), no response (mussel), parabolic responses (coralline red alga, calcareous green alga, temperate urchin, limpet), a threshold-positive response (lobster), and linear positive responses (crab, shrimp). These disparate responses are attributed to differences in the organisms' ability to regulate pH at their site of calcification, the extent to which their outer shell is covered by an organic layer, the solubility of their biomineral polymorph, and whether they utilize CO₂ directly via photosynthesis. Numerous experimental studies have investigated the effect of CO₂-induced ocean acidification on rates of calcification within marine organisms (see reviews cited above). Far fewer, however, have investigated its effects on other properties of their skeletons (e.g., Cohen and Holcomb, 2009; Dissard et al., 2010), such as polymorph mineralogy, elemental composition, ultrastructure, and biomechanics.

3.2.2.2 Physiological effects

The effect of ocean acidification on phytoplankton and primary production has been one of the main foci of research. Inorganic carbon is one of the essential building blocks of photosynthesis and, therefore, increases in $p\text{CO}_2$ might be expected to increase primary production. This pattern is generally seen in macroalgae

(see Section 3.4.5); however, no consistent pattern of response to ocean acidification has emerged in phytoplankton. This may be related to highly efficient carbon capture systems in many phytoplankton species, however different groups, different species, and even different clones within species show divergent responses to ocean acidification, revealing a highly contextually dependent pattern of photosynthesis, growth, carbon fixation, nutrient usage, and calcification. Phytoplankton blooms are appearing earlier (Kahru et al., 2011) and increased dominance of blooms by picophytoplankton has been attributed to ocean acidification (Newbold et al., 2012) and freshening (Li et al., 2009) of the Arctic Ocean. The extent to which these changes will have flow-on effects in the Arctic food web is unknown but could be substantial. These patterns and their likely consequences are dealt with in more detail in Section 3.4.3. Other work suggests that the harmful algal diatom *pseudo-nitzschia* produces more toxin (domoic acid) under high CO₂ conditions (Sun et al., 2011).

Assessing the sensitivity of Arctic marine animals to ocean acidification must consider the special circumstances and functional characteristics of life in Arctic waters. The Arctic Ocean is an open system in which variability in ambient conditions is driven partly by the influence of waters from the North Atlantic and North Pacific. In these areas, as well as the sub-Arctic, temperatures are low but variable. This contrasts with the more constant temperatures in Antarctic oceans due to its near isolation by the circum-Antarctic current. Understanding the evolution and adaptations of marine polar fauna to changing climate and ocean acidification requires an understanding of the key mechanisms and driving forces involved. The key driving force presently is temperature, although enhanced solubility of CO₂ in cold waters and body fluids may also shape their future sensitivity. High solubility of CO₂ decreases aragonite and calcite saturation states and lowers the pH of the water (see Chapter 2, Section 2.2), which has been hypothesized to threaten calcifying organisms at the poles (Orr et al., 2005; but see Roleda et al., 2012, who argued that calcifying organisms that do not rely on carbonate may not be affected). Multi-year ice melt, increased river input and associated salinity decreases exacerbate the extent of acidification in surface layers of the Arctic Ocean (Denman et al., 2011). The combined effects of warming, acidification, and freshening, on marine ecosystems have not yet been estimated (Ainsworth et al., 2011).

Understanding key physiological and life-history characteristics is critical to estimating the sensitivity of species to climate change. In the Antarctic, such efforts are based on the concept of oxygen- and capacity-limited thermal tolerance (OCLTT; Pörtner, 2006). This concept integrates molecular, cellular, whole organism and ecological characteristics with responses to climate change (Pörtner, 2001, 2002, 2010; Pörtner and Knust, 2007). In general, polar marine ectotherms ('cold-blooded' animals) minimize baseline energy costs in order to maximize growth potential in the cold, especially in the Antarctic. Similar patterns can also be seen in some ectotherms from the High Arctic (e.g., crustaceans, Walther et al., 2010) and sub-Arctic. The temperature variability that characterizes large sections of the sub-Arctic Ocean causes elevated levels of energy turnover in the cold-eurythermal fauna (animals that can tolerate a wide

range of temperatures). This elevation can be seen in species that extend from temperate to Arctic regions (e.g., Atlantic cod, *Gadus morhua*) compared to temperate zone conspecifics (Pörtner and Farrell, 2008). Elevated baseline metabolic costs in cold-adapted eurytherms have been related to their broad thermal tolerance to cold. True polar characteristics as seen in animals from the Antarctic or High Arctic only develop under highly stable, extremely low temperatures around and below 0 °C. Low-energy costs of maintenance at low temperatures are also mirrored in low turnover rates of transmembrane ion exchange and in a lower capacity for acid-base regulation than seen in temperate to warm-water species (Pörtner, 2010). Life-stage and lifestyle dependent capacity for acid-base regulation has been suggested as an over-arching principle that shapes sensitivity to ocean acidification (Pörtner, 2008; Melzner et al., 2009a). Pre-adaptation to climatic regimes will thus influence these patterns, with a decreasing capacity for ion and acid-base regulation in polar species.

Insight into the biochemistry of cold adaptation in Arctic versus Antarctic species confirms these generalizations. Low metabolic rates found in Antarctic marine stenotherms (organisms that only function well within a narrow range of temperatures) contrast with the more costly patterns of metabolic regulation at elevated rates in cold-adapted (sub-Arctic) eurytherms. In light of very limited data, these principles would support the extrapolation that sub-Arctic eurytherms are likely to be more resistant to ocean acidification while Antarctic and High Arctic stenotherms may be more sensitive. Whether calcification processes are also more resistant to ocean acidification in eurythermal Arctic than in stenothermal Antarctic and Arctic species requires further investigation.

Various other environmental factors, such as CO₂ or pollution, have been suggested to constrain aerobic performance and fitness and to thereby narrow the thermal window (Pörtner and Farrell, 2008). They thus act as additional stressors that interact with extreme temperatures. By narrowing the window of aerobic scope, CO₂ elicits passive rather than active tolerance to thermal extremes. The extent to which species are able to acclimate to such challenges over long time scales is as yet unexplored, however recent examples from laboratory and field studies confirm the hypothesis of a reduced thermal window under elevated CO₂ for crustaceans (Metzger et al., 2007; Walther et al., 2009; Findlay et al., 2010b), fishes (Munday et al., 2009a), and corals (via enhanced bleaching; Anthony et al., 2008). Pollutants can also enhance thermal sensitivity (Lannig et al., 2008). These effects, while most likely representing unifying principles, remain to be quantified in Arctic species.

3.3 Arctic marine food webs

The Arctic Ocean is characterized by marine ecosystems in which a small number of taxa channel a large percentage of the energy from zooplankton to vertebrate predators including seabirds, seals, whales, and polar bears (*Ursus maritimus*). As such, the effects of ocean acidification on these ecosystems will depend greatly – and far more so than for ecosystems with a more complex food web – upon the susceptibility of the keystone taxa to ocean acidification and other stressors.

3.3.1 Arctic habitats and biogeography

The Arctic can be broadly divided into High Arctic, Low Arctic, and sub-Arctic (Dunbar, 1968; see also Chapter 1, Figure 1.4). The High Arctic corresponds to areas of the central Arctic Ocean with more or less permanent (multi-year) ice cover and persistently cold water, while the Low Arctic corresponds broadly to the zone with seasonal ice cover on the shelves surrounding the Arctic Ocean basin. The sub-Arctic zone is comprised of the adjacent areas which have little sea ice but relatively low winter temperatures. The Arctic Ocean basins (Canada and Eurasian basins separated by the Lomonosov Ridge) are connected to the deep basins of the Nordic Seas through the deep Fram Strait. The basin of Baffin Bay is separated from the Arctic Ocean by passages through the Canadian Arctic Archipelago with sill depths of about 150 m. The Bering Sea basin is separated from the Arctic Ocean by roughly 1000 km of very shallow areas, mostly <50 m deep.

The Arctic Ocean is in some sense a warm ocean with its deeper waters filled with Atlantic water from about 200–1000 m depths and temperatures of 0–3 °C. However, at the surface, cooling and formation of sea ice lead to seawater at near freezing point under the ice. This cold water may extend to the bottom of shallow shelf areas (100–200 m depths). When the sea ice melts in summer, the lighter meltwater floats as a buoyant upper layer and shields the deeper layer from seasonal warming (also see Chapter 2, Section 2.3.1). Cold Arctic water therefore prevails over shelves as a seasonally persistent layer at depths from about 25 m to 100–150 m. Shallower than this the nearshore waters may be warmed to some degree in summer, while at greater depths warmer water from the intermediate layer in the Arctic Ocean may intrude onto the outer shelf.

Persistently cold waters are found over the deeper slopes and basins of the Arctic Ocean (below about 1000 m) and over relatively shallow shelves surrounding the central Arctic Ocean, which are extensive on the Eurasian side from the northern Barents Sea to the Chukchi Sea, and also in large portions within the Canadian Arctic Archipelago. The Chukchi Sea differs from other Arctic shelf regions by the strong through-flow of Pacific water (Bering slope water) that pushes away the cold water during the summer season.

This temperature regime determines the distribution and biogeography of species. Endemic Arctic species are found mainly in the permanently cold shelf areas and in the deep basins. The number of endemic Arctic species is limited, and the majority of species in the Arctic is comprised of Arctic-boreal species or boreal species with northern ranges that extend into the Arctic. For example, of 242 marine fish species that have been recorded from the ice-covered Arctic, 25% (62 species) were classified as Arctic (or predominantly Arctic), 16% (38 species) as Arctic-boreal, while more than half (53%, 128 species) were boreal or predominantly boreal (Mecklenburg et al., 2011).

Many Arctic species have wide distributions, often circumpolar or near-circumpolar. This is the case for invertebrates as well as for fish, birds, and mammals. For invertebrates and fish, the majority of species is of Atlantic origin. For example, among the 62 species of fish classified as Arctic, 34 species are

found in the Atlantic sector, six in the Pacific sector, and 29 in both. Arctic-boreal species are distributed more evenly, with 15 species in the Atlantic, 13 in the Pacific, and 13 in both sectors. The situation is very different among boreal species of marine fish if the Bering Sea is included as part of the sub-Arctic zone. For this category, the greatest number of species occurs in the Pacific sector with 286 species (out of 375), compared to 85 species in the Atlantic sector. Only four species are identified as amphiboreal (occurring in both Atlantic and Pacific sectors). However, there are many examples of closely related species in the two sectors, for example, twin Atlantic and Pacific species of cod (*Gadus morhua* and *G. macrocephalus*), halibut (*Hippoglossus hippoglossus* and *H. stenolepis*), and herring (*Clupea harengus* and *C. pallasii*) as examples among commercially (and ecologically) important species.

3.3.2 Arctic ecosystems and food webs

Broad species distributions, many closely related species, and similar physical regimes create a large element of commonality in the structure and function of Arctic marine ecosystems. However, marked differences in sea ice, bathymetry, and oceanography also lead to pronounced zonal patterns between the High, Low and sub-Arctic.

Very strong seasonal changes in light and ice conditions between summer and winter are key features that are reflected in the patterns of primary production and its utilization in the food web. The extensive migrations of birds and mammals into the Arctic to breed and feed during the short and hectic Arctic summer benefit from this production: the Arctic provides major breeding – and staging – grounds for most global populations of shorebirds and geese and many populations of ducks (e.g., eiders and scoters) and seabirds (e.g., Arctic tern *Sterna paradisaea*, gulls, and jaegers or skuas). Large populations of many species such as auk and eider migrate between breeding areas in the High or Low Arctic and wintering areas in the sub-Arctic or boreal zones. The three ice-associated whales, bowhead (*Balaena mysticetus*), beluga (*Delphinapterus leucas*), and narwhal (*Monodon monoceros*), also have migratory populations that move into the High Arctic to feed and nurse their calves in summer and back to wintering areas in the southern extent of drift ice. Walrus and seals (e.g., harp seal *Pagophilus groenlandicus* and hooded seal *Cystophora cristata*) undertake similar seasonal migrations. At lower latitudes many species of birds and mammals use sub-Arctic seas for breeding and feeding in summer, while spending the winter at lower latitudes (e.g., northern fur seals *Callorhinus ursinus* and humpback whales *Megaptera novaeangliae*).

Although birds and mammals are not likely to be affected by ocean acidification directly, they might be through the food web if their forage base is affected.

Arctic marine food webs include food chains of different types and lengths, characterized by their basis in the water column, ice, and seabed, respectively. Phytoplankton comprise the dominant primary producers in Arctic marine ecosystems, however ice algae also contribute to production – especially in High Arctic areas with multiannual ice. Benthic macroalgae such as kelp do occur in Arctic waters, but ice scour, suitable substrate, and high turbidity from large Arctic rivers limit their growth.

Primary production spans two orders of magnitude over the Arctic area, with maxima of $> 500 \text{ g C/m}^2/\text{y}$ in the northern Bering Sea and southern Chukchi Sea, and minima of $< 5 \text{ g C/m}^2/\text{y}$ in the central Arctic Ocean under dense pack-ice. The very high production in the northern Bering Sea reflects the northward flow of nutrient-rich North Pacific water in what has been described as a horizontal upwelling system (Sambrotto et al., 1984; Walsh et al., 1989; Springer and McRoy, 1993; Springer et al., 1996). Nutrients are not fully depleted en route through the Bering Strait, and the Pacific water that forms a layer in the upper halocline in the Canada Basin is still nutrient-rich compared to Atlantic water in the Arctic Ocean.

Ice limits light for photosynthesis and thereby limits the length of the season of primary production, although perhaps not as much as previously thought (e.g., Fortier et al., 2002; Mundy et al., 2009; Arrigo et al., 2012). Melting ice forms a surface layer of low salinity water, which effectively restricts the transport of nutrient-rich water from deeper layers, although upwelling events and wind-induced mixing can break down surface stratification and thus foster blooms (Brugel et al., 2009; Tremblay et al., 2011). This leads to a distinct seasonal and vertical pattern in the distribution and production of phytoplankton in ice-covered Arctic seas (Sakshaug and Skjoldal, 1989; Sakshaug, 2004). The annual primary production on the Arctic shelves with seasonal ice cover is typically rather low, in the range of $20\text{--}50 \text{ g C/m}^2$, while production in the sub-Arctic seas in the North Atlantic sector is typically $100\text{--}150 \text{ g C/m}^2$.

The growth of ice algae is strongly light limited: 2 m of sea ice with some snow cover transmits 1% or less of the incoming sunlight to the surface (Bergmann et al., 1991; Cota et al., 1991; Mundy et al., 2005). Ice algae are adapted to low light and start to grow in spring (April) at these low light levels (Michel et al., 1988; Smith et al., 1988; Bergmann et al., 1991). Successive accumulation of algal biomass absorbs more of the transmitted light, limiting further growth of ice algae (and underlying phytoplankton) through self-shading (Smith et al., 1988; Welch and Bergmann, 1989). The onset of melting improves light conditions, but ice algae are also sloughed from the underside of the ice by the meltwater. Extensive studies in the Canadian Arctic have found annual production of ice algae in the range $1\text{--}20 \text{ g C/m}^2$, with a typical mean value of 5 g C/m^2 (Smith et al., 1988; Bergmann et al., 1991; Welch et al., 1992; Michel et al., 2006). After the culmination of the ice-algae bloom, phytoplankton dominate and usually far exceed the ice algae in terms of annual primary production (Welch et al., 1992; Michel et al., 2006).

While heterotrophic and mixotrophic protists, such as ciliates and dinoflagellates, are important grazers in marine Arctic waters (Levinsen et al., 2000), the predominant herbivores in Arctic marine ecosystems are large calanoid copepods. Three species of *Calanus* (*C. finmarchicus*, *C. hyperboreus*, and *C. glacialis*) are important in the Atlantic sector (Conover, 1988; Melle et al., 2004). *Calanus finmarchicus* dominates the sub-Arctic seas (Norwegian and Labrador seas), while *C. hyperboreus* is dominant in Baffin Bay, the Greenland Sea, and the central Arctic Ocean (Østvedt, 1955; Dawson, 1978; Hirche, 1997; Melle and Skjoldal, 1998; Sundby, 2000). *Calanus glacialis* is a shelf species with a circumpolar distribution extending to

the Chukchi and northern Bering seas (Mathisen et al., 1996; Melle and Skjoldal, 1998). *Neocalanus* species (*N. cristatus*, *N. plumchrus*, and *N. flemingeri*) are dominant herbivores in the Bering Sea basin and are advected with the currents up through the Bering Strait region into the Chukchi Sea (Conover, 1988; Springer et al., 1989, 1996; Mathisen et al., 1996). Pteropods also play important roles in Arctic food webs and *Limacina helicina* is a common species in Arctic surface waters after the spring (ice-edge) bloom and is a food source for several species of fish.

The omnivorous euphausiids or krill are important components in sub-Arctic seas and form important prey for fish and whales. *Thysanoessa inermis* and *T. raschii* have amphiboreal distributions and are found both in the Bering Sea and the North Atlantic (Mauchline, 1980). These species are advected into the Low Arctic where they can play important roles in food webs (e.g., for bowhead whales, Lowry et al., 2004; Ashjian et al., 2010). Pelagic amphipods also play important roles in Arctic food webs, feeding on small copepods and other zooplankton prey. *Themisto libellula* can grow to 5–6 cm and is perhaps the single most important link between zooplankton and higher trophic-level consumers including many seabirds and seals (Dunbar, 1946; Welch et al., 1992; Melle et al., 2004).

Several small fish species play a similar linking role to higher trophic levels. Arctic cod (*Arctogadus glacialis*) can be an abundant pelagic species in the central Arctic Ocean (Walters, 1961; Aschan et al., 2009). There is little ecological knowledge about this species, which may fall prey to migratory stocks of beluga (e.g., Suydam et al., 2001, 2005). Polar cod (*Boreogadus saida* – termed ‘Arctic cod’ in North America) has a circumpolar distribution mainly in the Low Arctic. It probably exists with several large migratory (Welch et al., 1992, 1993; Gjosæter, 1998; Benoit et al., 2008) populations. Polar cod is a pillar of Arctic marine ecosystems, where it constitutes a major prey for many piscivores. Capelin (*Mallotus villosus*) has a similar distribution (Stergiou, 1989; Vilhjalmsen, 1994; Gjosæter, 1998; Dodson et al., 2007; Praebel et al., 2008; Mecklenburg et al., 2011).

The extensive pelagic and sea-ice associated food webs of Arctic ecosystems are based upon phytoplankton and herbivorous zooplankton. Large copepods, notably *Calanus hyperboreus* and *C. glacialis*, are major prey for bowhead whales, which also consume other crustaceans such as amphipods and epibenthic mysids. In sub-Arctic waters, krill are an important food for other baleen whales such as fin (*Balaenoptera physalus*), humpback, and minke (*B. acutorostrata*) whales that also eat small fish such as capelin. Beluga and narwhal dive deep and feed mainly on fish and squid. Beluga eats a wide variety of prey (both pelagic and benthic) but probably targets polar cod as its main prey for their seasonal migrations into the Arctic (Bradstreet et al., 1986; Frost and Lowry, 1990; Welch et al., 1992, 1993; O’Corry-Crowe, 2002, 2009). Narwhal also eats polar cod (and Arctic cod) but is considered to be a specialist to feed on deep-water prey including Greenland halibut (*Reinhardtius hippoglossoides*) and the squid *Gonatus fabricii* (Laidre and Heide-Jorgensen, 2005). Narwhal is perhaps the only species of Arctic mammal for which winter feeding is more important than summer feeding: satellite-tracking has revealed that they dive 15–20 times a day to depths of around

1000 m or more, for a duration of 5–6 months during winter (Laidre et al., 2003, 2004a,b; Dietz et al., 2008).

Pelagic crustaceans such as *Themisto libellula*, and small fish (capelin and polar cod) are the primary prey for large stocks of harp seal, and ringed seal (*Pusa hispida*) – the most strongly ice-associated of the seals and the primary prey of polar bears. In contrast, hooded seal dives deep to feed on squid (mainly *Gonatus fabricii*) and various deep-water fish (e.g., *Sebastes* spp. and Greenland halibut). Bearded seal (*Erignathus barbatus*), also an ice-associated seal, mainly feeds on benthic invertebrates, as does the walrus (*Odobenus rosmarus*) that specializes on burrowing bivalves (e.g., *Mya truncata*, *Serripes groenlandicus*, and *Hiattella arctica*). Pacific walrus (subsp. *O. r. divergens*) is the most numerous subspecies (~ 200 000 individuals) and supported by the extensive productive shallow benthic habitats of the Chukchi Sea. Declining summer ice has deprived the walruses of haul-out platforms, forcing them to change to coastal haul-outs, which has reduced their foraging opportunities. Atlantic walrus (subsp. *O. r. rosmarus*) number around 20 000–25 000 individuals. Their lower numbers reflect strong overexploitation in the past as well as less productive and less extensive feeding grounds in the Atlantic sector of the Arctic. Historically, the largest population of Atlantic walrus was probably found in the Gulf of St. Lawrence, where they were exterminated by hunting.

Many seabirds feed on ice, in the water, and in the benthos. The High Arctic Ivory gull (*Pagophila eburnea*) and Ross's gull (*Rhodostethia rosea*) feed on pelagic and ice-associated crustaceans, small fish (notably polar cod), and carcasses, feces, and other remnants of marine mammals including polar bear kills. Glaucous gull (*Larus hyperboreus*) is also a generalist predator and scavenger on a wide range of prey including bird eggs and chicks, polar cod, capelin, fish roe, mussels, sea urchins, and other invertebrates in the Arctic. In the Low- and sub-Arctic, black-legged kittiwake (*Rissa tridactyla*) and northern fulmar (*Fulmarus glacialis*) are two abundant feeders on invertebrates and small fish at or close to the sea surface.

Auks – notably dovekie (or little auk, *Alle alle*) and various species of auklet (least auklet, *Aethia pusilla*, crested auklet, *A. cristatella*, and others) – are common plankton feeders and among the most numerous of all seabirds. Their main prey is large calanoid copepods. The larger common and thick-billed murre (*Uria aalga* and *U. lomvia*) are auks that occur in great numbers at large breeding colonies in Low Arctic and sub-Arctic waters, where there is a combination of cliffs and a rich supply of large zooplankton (krill and amphipods) and small fish (e.g., polar cod and capelin). Murres are conspicuous components of Arctic food webs and have several different subspecies (three to four). In sub-Arctic areas the Atlantic puffin (*Fratercula arctica*) and the Pacific horned puffin (*F. corniculata*) are abundant; breeding where there is an abundant supply of small fish such as herring and capelin. Black guillemot (*Cepphus grylle*) is a dispersed generalist species feeding on a variety of small demersal and pelagic fishes and invertebrates, including polar cod, amphipods, sculpins, blennies, and others. In sub-Arctic and Low Arctic coastal environments eiders are abundant and conspicuous. Common eider (*Somateria mollissima*) and king eider (*S. spectabilis*) have circumpolar distributions, with

the latter being more common in the Arctic whereas several subspecies of common eider occur in boreal and sub-Arctic waters. Spectacled eider (*S. fischeri*) and Steller's eider (*Polysticta stelleri*) are found in the Pacific sector (Steller's eider also breeds in western Siberia). Eiders dive in relatively shallow water (to depths of 30–60 m), where they feed on benthic invertebrates, especially mollusks (for common and spectacled eiders), but also crustaceans and echinoderms. In contrast, Steller's eider specializes on feeding in shallow inshore eelgrass (*Zostera*) or algal beds. Perhaps most remarkably, long-tailed duck (*Clangula hyemalis*), another abundant circumpolar species, is considered to be the deepest diving waterfowl feeding on various benthic invertebrates, predominantly crustaceans and mollusks at depths over 60 m. Less important species such as scoters (black, white-winged, and surf scoters – *Melanitta nigra*, *M. fusca* and *M. perspicillata*) and mergansers (common and red-breasted mergansers – *Mergus merganser* and *M. serrator*), forage mainly in shallow nearshore waters, where scoters eat clams, mussels, periwinkles, and other snails, as well as crabs and shrimps. Mergansers eat mainly small fish in freshwater, estuarine, and coastal habitats.

3.4 Taxon-specific responses to ocean acidification

Information about Arctic species or ecosystem processes is limited. Therefore, the material presented in this section is mainly drawn from non-Arctic studies under the broad assumption that many of these processes will be similar in the Arctic. Each section begins with coverage of what is known from non-Arctic species and is followed by an assessment of what this means for Arctic species.

3.4.1 Effects of ocean acidification on viruses

3.4.1.1 Marine viruses (non-Arctic studies)

There are no studies that definitively show direct effects of ocean acidification on marine viruses. However, since the life cycle and persistence of viruses are directly linked to their hosts, viral processes such as lytic events may be indirectly influenced by ocean acidification. Elevated $p\text{CO}_2$ has been reported to have no effect (Rochelle-Newall et al., 2004), a positive effect, and a negative effect on viral abundance (see review by Danovaro et al., 2011). The effects of ocean acidification on viral infection rates are equally unknown, although several studies indicate that elevated $p\text{CO}_2$ can compromise immune systems of marine invertebrates (e.g., Hernroth et al., 2011; Munari et al., 2012).

3.4.1.2 Polar/Arctic marine viruses: Marine viruses associated with sea ice

Very few data are available on marine viruses associated with sea ice (Maranger et al., 1994; Gowing et al., 2002, 2004; Gowing, 2003; Wells and Deming, 2006). Viral concentrations in sea ice can be 10- to 100-fold greater than concentrations in the underlying water column (Maranger et al., 1994; Gowing et al., 2004), however, the phylogenetic diversity of sea-ice viral communities is unknown at present. Two studies have

isolated bacterial viruses from sea ice, both of which would be considered cosmopolitan in their distribution (Borriss et al., 2003; Wells and Deming, 2006), but data on eukaryotic sea-ice-inhabiting microbes are totally lacking as is their response to ocean acidification.

3.4.2 Effects of ocean acidification on bacteria

3.4.2.1 Bacteria and bacterial processes (non-Arctic studies)

In some studies, bacterial communities responded indirectly to ocean acidification *via* direct effects of acidification on phytoplankton abundance, production, and calcification (McDonald et al., 2009; Liu et al., 2010). Consequently, acidification-induced increases in phytoplankton dissolved organic matter (DOM) production (either by extracellular secretion and/or grazing by protozoa) may enhance biogeochemical activities in some bacterial communities (although it should be noted that phytoplankton responses to elevated $p\text{CO}_2$ are not consistent between studies – see Section 3.4.3).

Although the bacterial community does not appear to be strongly affected by $p\text{CO}_2$, elevated $p\text{CO}_2$ generally increases bacterial productivity (Grossart et al., 2006; Allgaier et al., 2008), whereas bacterial abundance does not change with $p\text{CO}_2$ (Allgaier et al., 2008; Paulino et al., 2008). Variable responses to elevated $p\text{CO}_2$ have been reported for extracellular enzyme activity (Grossart et al., 2006; Piontek et al., 2010; Yamada and Suzumura, 2010) and bacterial diversity (reviewed by Liu et al., 2010).

Some special functions of the microbial food web might be affected by ocean acidification, with potential consequences for ocean biogeochemistry. Note also that the activities in the microbial food web have effects on the pH of seawater through processes such as photosynthetic fixation of CO_2 (increasing pH), microbial degradation of organic material to CO_2 (decreasing pH), and calcite formation (reducing alkalinity). Global-change phenomena occurring in the Arctic that may affect photosynthesis (increased water-column stability, nutrient runoff, improved light conditions due to reduced ice cover, etc.), bacterial activity (increased influx of dissolved organic carbon to the Arctic Ocean from Russian and Canadian rivers, increased denitrification in areas with reduced oxygen content, etc.), or calcification (e.g., changes in the pattern of *Emiliania huxleyi* blooms due to changes in temperature and currents) will therefore, through the associated microbial processes, modify the geographical and temporal patterns in pH variation created by atmospheric CO_2 (see Chapter 2).

The two microbial processes that have received particular attention in relation to changes in $p\text{CO}_2$ and pH are (1) ‘C-overconsumption’, whereby more CO_2 is fixed per nitrogen consumed at high $p\text{CO}_2$, i.e., changing the ‘Redfield ratio’ of C-fixation, and (2) calcification, where a reduced pH lowers the saturation level for calcite and aragonite and, therefore, makes seawater corrosive to calcium carbonate (CaCO_3). The latter process is covered in detail in Chapter 2, Section 2.3.5.

Increased $p\text{CO}_2$ may stimulate carbon fixation and thus potentially increase C:N (e.g., Leonardos and Geider, 2005). The C:N-ratio of material exported from the photic zone is crucial to

the efficiency of the biological C-pump, transferring carbon from the atmosphere to the oceanic interior. Even a small increase in C:N may be important since it could constitute a negative bio-feedback where the efficiency of the biological pump increases as atmospheric CO_2 increases. A C:N = 106:16 = 6.6 (molar) stoichiometric coupling in photosynthesis, as implied by the Redfield ratio, is an average value from which large deviations are observed when examining different phytoplankton species and different growth conditions (Geider and La Roche, 2002), implying a rather loose coupling between the acquisition-incorporation processes for carbon and nitrogen. The most convincing data sets indicating C-overconsumption are from the near-natural systems studied in mesocosms. In a study from Raunefjorden in western Norway, Riebesell et al. (2007) quantified the effect to be an increase in C:N from 6 to 8 as manipulated atmospheric CO_2 increased from 350 to 1050 ppm. How this extra organic carbon is partitioned within the system is not well known, but at least parts seem to be directed to the pool of transparent exopolymeric particles (TEP). Models of the C-overconsumption effect have been constructed that combine an increase in particulate organic carbon (POC) with TEP production (Schartau et al., 2007).

Production of TEP has often been associated with diatom growth, but the primary phytoplankton response to an experimental increase in CO_2 seems to be in the picoplanktonic size fraction with very small cells (< 2 μm) and is consistent with what was observed in a mesocosm experiment in Kongsfjorden, Svalbard, in which the first of a succession of three consecutive blooms exhibited a stimulation of the picoplankton size fraction (Meakin and Wyman, 2011). A phytoplankton-bacteria relationship that has received a lot of attention is the phytoplankton production of the osmolyte DMSP (dimethylsulfoniopropionate) apparently sensitive to acidification, but in a manner variable between species (Spielmeyer and Pohnert, 2012). Mesocosm studies have only revealed small, although statistically significant effects of ocean acidification on DMS (dimethylsulfide) concentration (Vogt et al., 2008). Since bacteria subsequently consume DMSP, probably including the numerically often-dominant SAR11 clade (Reisch et al., 2011), interactions leading to changes in species composition could be possible.

Mesocosm studies in Spitsbergen found few or no substantive effects of elevated $p\text{CO}_2$ on bacterial community composition (Roy et al., 2013).

3.4.2.2 Polar/Arctic bacteria: Bacteria and sea ice

Polar sea ice supports high bacterial productivity and diversity, making this one of the most significant ecosystems in the Arctic and Antarctic (Garrison et al., 1986; Grossmann and Dieckmann, 1994; Amon et al., 2001). Although significant differences in the physics and chemistry of Arctic and Antarctic sea ice cause differences in DOM, particulate organic material (POM), and nutrients, bacterial diversities in Arctic and Antarctic sea ice are similar (Brown and Bowman, 2001; Brinkmeyer et al., 2003; Junge et al., 2004). Bacterial community diversity within sea ice is highly correlated with the diversity in the underlying seawater (Bowman et al., 2012). The response of sea ice bacteria to ocean acidification is unknown.

3.4.3 Effects of ocean acidification on phytoplankton

3.4.3.1 Phytoplankton (non-Arctic studies)

No consistent response to elevated $p\text{CO}_2$ has been observed for marine phytoplankton cell-division rates (Riebesell and Tortell, 2011). For example, ocean acidification has positive effects on division rates in diatoms (e.g., Gervais and Riebesell, 2001), dinoflagellates (Burkhardt et al., 1999), some coccolithophores (Shi et al., 2009; Rickaby et al., 2010), and some cyanobacteria (Barcelos e Ramos et al., 2007; Hutchins et al., 2007); negative (Iglesias-Rodriguez et al., 2008; Langer et al., 2009; Muller et al., 2010) or neutral (Buitenhuis et al., 1999; Zondervan et al., 2002) effects in some coccolithophores; and negative effects in some cyanobacteria (Czerny et al., 2009). Similar variability in response to ocean acidification has been noted in photosynthetic and carbon-fixation rates of marine phytoplankton (Riebesell and Tortell, 2011). Some recent papers concluded that a number of marine phytoplankton are resilient to lowered pH and altered carbonate chemistry (see Hansen et al., 2007; Nielsen et al., 2010, 2011; Riebesell and Tortell, 2011; Renaud et al., 2012). These species would, therefore, be at a competitive advantage over those that are impacted by ocean acidification.

Increasing $p\text{CO}_2$ promotes nitrogen fixation in some cyanobacteria (Barcelos e Ramos et al., 2007; Hutchins et al., 2007; Levitan et al., 2007) and causes a decline in iron availability to phytoplankton (Shi et al., 2010). Ocean acidification can directly influence phytoplankton population community composition (Tortell et al., 2008), and indirectly affect community structure, nutrient utilization, and productivity through nutrient stoichiometry (Blackford, 2010).

Varying responses in calcification in phytoplankton have been a centre of debate in ocean acidification research. Most calcifying phytoplankton show decreased calcification in response to elevated CO_2 / reduced pH. However, some coccolithophores increase their calcification at higher CO_2 whereas others show no response or a non-uniform trend (e.g., Riebesell et al., 2000; Engel et al., 2005; Iglesias-Rodriguez et al., 2008; Barcelos e Ramos et al., 2007; Muller et al., 2010; Fiorini et al., 2011; Raven, 2011).

3.4.3.2 Arctic phytoplankton

Increased $p\text{CO}_2$ has mild negative effects on growth rate in some sea-ice diatoms (Torstensson et al., 2012), however data on other species are lacking. Coccolithophore populations are at risk, although significant gaps exist regarding the contribution of species other than its most abundant and best studied representative, *Emiliania huxleyi*, to polar populations. Non-bloom coccolithophore populations are known to play a major role in carbon export in the subtropics (Sarmiento et al., 2002), but controls on non-bloom populations in polar regions and their contribution to the carbon cycle remain unknown.

More generally, satellite data show that peak phytoplankton blooms now arrive up to 50 days earlier than in 1997 (Kahru et al., 2011). The community composition of these blooms

has also shown measurable trends, with recent shifts toward dominance by smaller phytoplankton. Similar trends toward more picophytoplankton and fewer nanophytoplankton have also been associated with ocean acidification (Newbold et al., 2012), and with a freshening of the Arctic Ocean and reduction in nutrient supply (Li et al., 2009). These shifts may not cause substantial changes in total production but are likely to have broader effects on the food web. For example, the smaller size of primary producers may reduce transfers of carbon up the food chain.

3.4.4 Effects of ocean acidification on foraminifera

3.4.4.1 Foraminifera (non-Arctic studies)

Planktonic foraminifera can contribute up to 50% of the total carbonate in the ocean sediment, playing an important role in the carbonate pump (Schiebel, 2002).

Like most actively calcifying taxa, calcareous foraminifera construct their tests internally (Lowenstam and Weiner, 1989). Increasing $p\text{CO}_2$ generally results in less massive tests for calcareous species (Spero et al., 1997; Kuroyanagi et al., 2009; Dias et al., 2010). Survival of foraminifera around seafloor CO_2 -injection cylinders is generally unaffected by moderate (<0.2 pH units) acidification, but extreme reductions (2.0 pH units) cause calcareous forms to disappear entirely while thecate (organic) and agglutinated forms remain unaffected (Dias et al., 2010). These patterns mirror survivorship changes seen at the Triassic-Jurassic boundary, although why that is so is unclear (Hautmann et al., 2008) and at the Paleocene-Eocene Thermal Maximum (Zachos et al., 2005).

3.4.4.2 Arctic foraminifera

Carbonate sedimentation in the Arctic is highly dependent on the presence of planktonic foraminifera, and they are responsible for the majority of calcite production (Hendry et al., 2009). In particular, a large portion of recent carbonate in the Norwegian–Greenland Sea sediments is produced by *Neoglobobulimina pachyderma* and *Globigerina quinqueloba* the dominant planktonic species (Carstens and Wefer, 1992; Carstens et al., 1997; Pflaumann et al., 1996). Arctic sedimentation rates vary greatly. On the shelves, sedimentation rates over 30 cm/ky (Polyak et al., 2009; Farmer et al., 2010) have been calculated, whereas rates in basins are less than 1 cm/ky. The planktonic:benthic ratios of foraminifera (Stehli and Creath, 1964) in Arctic shelf seas are generally low, but below 200 m can be ≤ 32 (Murray, 1991; Bergsten, 1994). However, Scott et al. (1989) found that the planktonic to benthic ratio was 1:1 in the deep Arctic where there is no organic influx.

Planktonic and benthic foraminifera typically construct tests of calcium carbonate or of agglutinated sediments, although organic- and siliceous-walled forms are found (Sen Gupta, 2002). Planktonic foraminiferal species diversity is extremely low in the Arctic; assemblages are typically dominated by the polar species *Neoglobobulimina pachyderma*, with the subpolar species *Globigerina quinqueloba*, which is also common (Carstens and Wefer, 1992; Carstens et al., 1997). A few other

Globigerinita species are found in small (<2%) proportions (Carstens and Wefer, 1992; Arnold and Parker, 1999). Although *N. pachyderma* and *G. quinqueloba* can be found as deep as 200 m, the highest abundances of these species are in the upper 50 m of the water column in northernmost regions (above 83° N), whereas in southern areas they are found primarily below the pycnocline (Carstens and Wefer, 1992).

Benthic foraminiferal species diversity in the Arctic is low, in part because of its oceanographic isolation. Very small forms (mean test size 79 µm) dominate (Tomanek et al., 2011) in ice-covered regions as well as in some other areas (Michaelidis et al., 2005). Agglutinated foraminifera dominate deeper waters below the calcium carbonate compensation depth (Scott and Vilks, 1991), whereas calcareous species are typically found at shallower depths in cold water. Some calcareous forms, predominately hyaline rotalid foraminiferan tests, can also be found below 1000 m (Lagoe, 1976).

There is currently no evidence that calcite undersaturation impacts recent foraminiferal faunas in eastern and central Arctic bottom waters (Bergsten, 1994) or bathyal Holocene sediments in the Sea of Okhotsk (Barash et al., 2008). However, Gregory et al. (2010) attributed dissolution of near-surface foraminifera to changes in water-column saturation. Moy et al. (2009) also suggested that a 30–35% reduction in shell weight of present-day Southern Ocean *Globigerina bulloides* (relative to pre-industrial Holocene samples) was due to increased $p\text{CO}_2$. Manno et al. (2012a) found no effect of $p\text{CO}_2$ (0.3 pH unit reduction) on survival of *Neogloboquadrina pachyderma*, but shell diameters were significantly smaller under acidification.

Limited evidence indicates that a ~0.2 pH unit decline will have few if any effects on survival of foraminifera, but may influence growth rates. Larger declines in pH are likely to reduce the diversity and survival of calcifying species, and hence, decrease sedimentation of inorganic carbon. The broader ecosystem consequences of increased dominance by non-calcifying species are unknown.

3.4.5 Effects of ocean acidification on macroalgae

3.4.5.1 Macroalgae (non-Arctic studies)

Temperate and tropical non-calcifying macroalgae typically show increases in growth and photosynthesis with high $p\text{CO}_2$ (Borowitzka and Larkum, 1976; Hall-Spencer et al., 2008; Connell and Russell, 2010). Calcifying macroalgae, in contrast, show significant reductions in recruitment and growth under elevated $p\text{CO}_2$ (Hall-Spencer et al., 2008; Kuffner et al., 2008; Martin et al., 2008; Gao and Zheng, 2010) and reductions (Martin and Gattuso, 2009; Ries et al., 2009; Robbins et al., 2009) or non-linear responses (Borowitzka and Larkum, 1976; Anderson et al., 2011a; Price et al., 2011) of net calcification. At the same time, photosynthetic rate of calcifiers typically increases as a function of increasing $p\text{CO}_2$ (Borowitzka and Larkum, 1976; Anderson et al., 2011a; Price et al., 2011). Magnesium content of high-Mg calcite secreted by coralline red algae declined with increasing $p\text{CO}_2$ (Ries, 2010), indicating that coralline red algae may secrete a range

of high-Mg calcites, and that higher-Mg phases preferentially dissolve away under more acidic conditions. The very scant available data indicate growth of calcifying macroalgae may be compromised under future ocean acidification, whereas most non-calcifiers will probably benefit – directly from increased $p\text{CO}_2$ and perhaps indirectly from reduced competition from encrusting calcifying species.

3.4.5.2 Polar/Arctic macroalgae

Studies of polar macroalgae are lacking. Of the few Arctic species that have been studied, non-calcifying red algae (which typically come from habitats with lower natural pH oscillations than green and brown algae) respond positively to higher seawater $p\text{CO}_2$ (Kubler et al., 1999; Gattuso and Hansson, 2011).

Calcified macroalgae may be vulnerable to extreme changes in pH because many polar species are typically weakly calcified. However, data for living Arctic species are lacking. A recent study of temperate and tropical brown macroalgae indicate that in at least in one genus, *Padina*, lower pH conditions may still allow calcification due to increased photosynthesis (Johnson et al., 2012). Studies of post-mortem dissolution rates of the thallus of encrusting Antarctic coralline algae showed that rates were greater under acidification than non-acidification conditions (McClintock et al., 2011).

3.4.6 Effects of ocean acidification on corals

3.4.6.1 Tropical corals

Globally, corals are important calcifiers, and their aragonite skeletons and reefs provide shelter and habitat for a great diversity of other species. Calcification rates of tropical corals are linearly related to Ω_{Ar} of the surrounding seawater (Langdon and Atkinson, 2005). Consequently, CO_2 -induced reductions in Ω_{Ar} are projected to have strong negative effects on corals and coral reefs (Hoegh-Guldberg et al., 2007). Corals calcify internally, and pH within the calcifying polyp varies diurnally by up to 1.8 units (Al-Horani et al., 2003). Nonetheless, acidification to pHs well above daily minima observed within the polyp causes a $\leq 50\%$ reduction in calcification and growth rates (Schneider and Erez, 2006; Kroeker et al., 2010, 2013; Hofmann et al., 2011). Effects of elevated $p\text{CO}_2$ on earlier life stages of corals are less well investigated, but available data indicate negative effects on fertilization, larval metamorphosis, and juvenile growth (Albright et al., 2010; Nakamura et al., 2011). The generally negative responses outlined are not universal, and a few studies show adult corals can calcify at very low Ω_{Ar} levels (reviewed by Hofmann et al., 2010; Form and Riebesell, 2012). This ability may be related to high nutritional status.

3.4.6.2 Polar/Arctic corals

Cold-water coral reef-like structures or mounds (formed by scleractinian corals) and coral gardens (mostly gorgonians) provide important habitats for many organisms including commercially important fish (Kutti and Fosså, 2009). Model

projections suggest that about 70% of cold-water corals, and especially those at higher latitudes, will be in undersaturated ($\Omega_{Ar} < 1$) waters by the year 2100 (e.g., Turley et al., 2007; Chapter 2, Section 2.6.3). Although Dullo et al. (2008) suggested that *Lophelia* may occur in a temperature-salinity niche, very little is known about the distribution of corals in the Arctic, or about possible effects of acidification on cold-water corals. Some data are available for *Lophelia pertusa*, a common reef builder in the sub-Arctic; acidification of ≤ 0.1 pH units reduced calcification rate of *L. pertusa* by $\leq 29\%$ (Maier et al., 2009; Form and Riebesell, 2012). However, longer-term experiments using gradual declines to lower pHs showed calcification was slightly enhanced over initial values, and net growth was sustained even at $\Omega_{Ar} < 1$ (approx. pH ≤ 7.7 ; Form and Riebesell, 2012). This highlights the need for long-term experiments. Importantly, older skeletons of *L. pertusa* and the dead reef mounds themselves are exposed to seawater and are, therefore, likely to experience dissolution at $\Omega_{Ar} < 1$. The ecological consequences of this are not yet known.

Available data indicate that ocean acidification may have limited impacts on live cold-water corals (*Lophelia*), especially if adequate food is available. However, there is currently a complete lack of knowledge about the dispersive early life stages and newly settled juveniles. Effects on dead coral structures – and hence reefs – as well as on non-*Lophelia* species, are unknown. The important role of cold-water corals as habitat for other species means this is a critical gap in knowledge.

3.4.7 Effects of ocean acidification on mollusks

3.4.7.1 Mollusks (non-Arctic studies)

Mollusks are highly diverse with over 20 000 marine species (Chapman, 2009). As calcifiers of tremendous ecological and economic importance, they are one of the key groups studied in ocean acidification research. Data are available for three classes of mollusk: bivalves (especially oysters and mussels), gastropods (notably pteropods), and cephalopods. Mollusks have highly diverse body plans, physiology, calcification mechanisms, and ecology. It is therefore not surprising that a wide range of biological responses to ocean acidification has been described, from an apparent positive effect on fitness-related parameters in a few species (e.g., reduced mortality in a bivalve; Range et al., 2011) to no effects ($\sim 50\%$ of all tested species) or negative effects ($\sim 50\%$ of all tested species). Ocean acidification may impact survival and growth (e.g., Talmage and Gobler, 2009, 2010), calcification (e.g., Ries et al., 2009), physiology (e.g., Melzner et al., 2011), immunology (e.g., Bibby et al., 2008), proteomics (e.g., Tomanek et al., 2011), evolutionary processes (e.g., Sunday et al., 2011), and acclimation (e.g., Parker et al., 2012). In particular, the planktonic pteropods have been relatively well studied due to their ecological importance as a food source, and due to the sensitivity of calcification of a key species, *Limacina helicina*, to elevated pCO_2 (Comeau et al., 2009, 2010; Lischka et al., 2011).

Acute experiments with bivalves show strong reductions in adult calcification under ocean acidification (Gazeau et al., 2007). However, longer-term incubations demonstrate that adults can calcify at $\Omega_{Ar} < 1$ if sufficient food is available

(Michaelidis et al., 2005; Tunnicliffe et al., 2009; Thomsen et al., 2010; Melzner et al., 2011). Clearly, biological control over calcification is possible even where Ω_{Ar} approaches zero, as long as the shell is protected by the organic periostracum and there is sufficient energy to fuel calcification. Early life-history stages tend to be more susceptible (Talmage and Gobler, 2009, 2010; Gazeau et al., 2010; and many others), although successful settlement and dominance of mytilid mussels and other calcifying invertebrates have been observed at seawater pCO_2 values of 700–1000 μatm (Thomsen et al., 2010). Again, this indicates that either local adaptation and/or adequate energy supplies can also allow early life stages to overcome negative impacts of ocean acidification (see Kelly and Hofmann, 2013). Reductions in growth and calcification have typically been observed at much higher pCO_2 , and may be related to elevated metabolic rates and subsequent energy budget re-allocation (Thomsen and Melzner, 2010; Melzner et al., 2011).

The coastal cuttlefish, *Sepia officinalis*, is physiologically robust to 6-week exposure to very high pCO_2 (6000 μatm), although calcification of the cuttlebone increased (Gutowska et al., 2008), which may negatively impact buoyancy regulation. Embryonic *S. officinalis* are more sensitive, showing developmental delay at elevated pCO_2 (> 3500 μatm ; Hu et al., 2011). Open-water species, such as the squid *Dosidicus gigas*, live in less variable pCO_2 environments and are expected to be more sensitive. *D. gigas* shows mild metabolic depression at $pCO_2 = 1000$ μatm (Rosa and Seibel, 2008). No other data for responses of cephalopods to ocean acidification are available.

3.4.7.2 Polar/Arctic mollusks

Bivalves, pteropod gastropods and cephalopods are important components of the Arctic food web (see Section 3.3.2), and consequently impacts of ocean acidification on these species may have broader emergent effects on Arctic ecosystems. The few available studies of polar/Arctic species have reported negative impacts; however, elevated pCO_2 had no impact on survivorship of the Antarctic bivalve *Laternula elliptica* over a longer exposure period of 120 days. Physiological and gene-expression patterns indicated that individuals may not be able to withstand elevated pCO_2 over longer periods (Cummings et al., 2011).

Pteropods can represent as much as 93% of the total zooplankton biomass in high-latitude regions (Hunt et al., 2008) and play a significant role in contributing to carbonate and organic carbon flux and sequestration (Falk-Petersen et al., 2002; Karnovsky et al., 2008; Manno et al., 2010). They play an important role in the food web, and are food resource for many predators such as herring, salmon, whales, and seabirds (e.g., Doney et al., 2009). Models indicate that a 10% reduction of the pteropod population would cause a 20% reduction in mature body weight of pink salmon (*Oncorhynchus gorbuscha*; Feely et al., 2010). Ocean acidification decreases calcification in pteropods (Comeau et al., 2009, 2010; Lischka et al., 2011), increases respiration rates (especially in combination with increased temperature; Comeau et al., 2010) and increases mortality of pre-winter juveniles (Lischka et al., 2011) and adults (Bednarsek et al., 2012; but see Comeau et al., 2012a). Although pteropods can calcify in undersaturated waters, it is possible the extra energy cost necessary to counteract shell

dissolution could seriously affect their energy budget (Lischka et al., 2011; Manno et al., 2012b). Recently, model projections of ocean acidification indicated that in much of the Arctic pteropods would be unable to precipitate calcium carbonate by the end of the 21st century (Comeau et al., 2012b).

Available data indicate that calcifying Arctic mollusks are likely to be negatively impacted by ocean acidification, and especially so at sensitive early life-history stages and/or for thin-shelled planktonic species such as thecosomatous pteropods. The effects of ocean acidification on ecologically important non- (or poorly) calcifying species such as squid are unknown, and data on these species are urgently required.

3.4.8 Effects of ocean acidification on echinoderms

3.4.8.1 Echinoderms (non-Arctic studies)

Most echinoderms calcify as adults and larvae, and consequently echinoderms are one of the primary targets for ocean acidification research (Figure 3.2). The many available studies show that echinoderm responses are generally highly species-, population- and individual-specific, ranging from likely species extinction (9% of studied species; such as the brittlestar *Ophiothrix fragilis*; Dupont et al., 2008), through direct or indirect negative effects (such as delay in development) (52% of studies), to positive effects (6% of studies; e.g., Dupont et al., 2010). It is important, however, to note that most published studies are short term (60% less than two weeks) and focus only on one life stage.

3.4.8.2 Polar/Arctic echinoderms

It has been hypothesized that echinoderms – and especially taxa with high Mg-calcite skeletons – will play the role of the ‘canary in the coal mine’ in polar regions (e.g., McClintock et al., 2011; Sewell and Hofmann, 2011). Available experimental data generally show negative impacts of ocean acidification on a range of processes such as growth. However, these effects do not (as yet) appear to be greater than equivalent responses in temperate and tropical species. For example, some aspects of larval development of the Antarctic sea urchin *Sterechinus neumayeri* are negatively affected by ocean acidification but to a lesser extent than for temperate and tropical species (Clark et al., 2009). Other reported effects of ocean acidification include: increased metabolic rates in the Arctic brittlestar *Ophiocten sericeum* (Wood et al., 2011); reduced ingestion and altered metabolism and immune-system responses in the boreo-Arctic urchin *Strongylocentrotus dreobachiensis* (Dupont and Thorndyke, 2012; Stumpp et al., 2012); developmental delay in the sub-Antarctic urchin *Arbacia dufresni* (Catarino et al., 2012), and reduced fertilization success in the Antarctic urchin *Sterechinus neumayeri* (Sewell and Hofmann, 2011).

While some reports from polar echinoderm species show neutral responses to ocean acidification, the majority of responses reported are negative. Echinoderms are key components of benthic carbon cycling in the Arctic (Renaud et al., 2007) and therefore ocean acidification-induced changes in abundances and performance of Arctic echinoderms are likely to have broader impacts on Arctic benthic ecosystems.

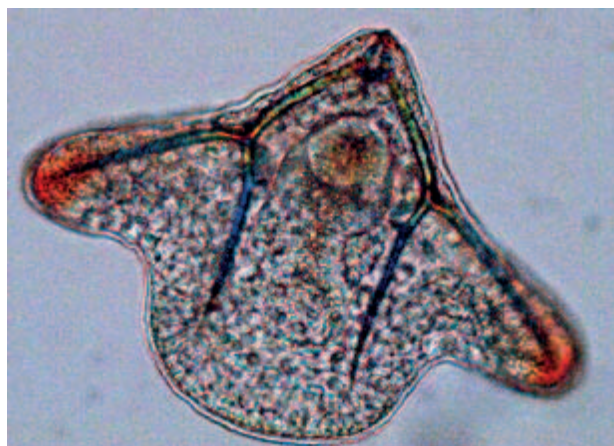
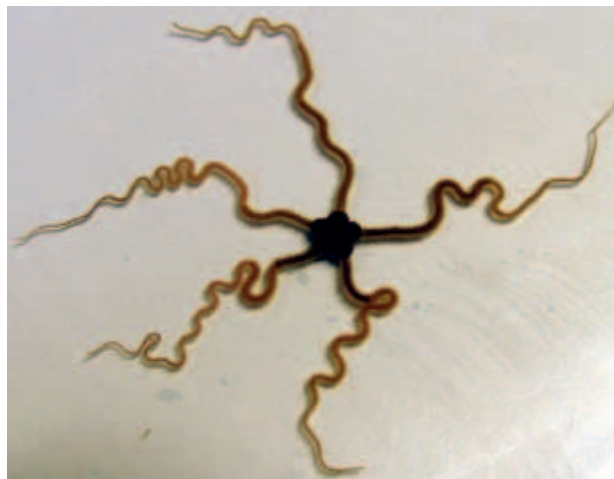


Figure 3.2. Brittlestars (e.g. *Amphiura filiformis*, adult (upper) and larvae (middle)) are particularly sensitive to ocean acidification, while some seastars appear to benefit from ocean acidification (e.g. *Crossaster papposus*, larvae (lower)).

3.4.9 Effects of ocean acidification on crustaceans

3.4.9.1 Crustaceans (non-Arctic studies)

Crustaceans are a highly diverse group of organisms, many of which are highly calcified, and many of which also play key roles in Arctic ecosystems. Perhaps the most ecologically important of these are the pelagic copepods, and yet few studies have investigated effects of ocean acidification on copepods.



Figure 3.3. The effects of ocean acidification have been investigated in several polar/Arctic crustaceans. For example, barnacles such as *Semibalanus balanoides* (upper), copepods such as *Calanus finmarchicus* (middle) and the shore crab, *Carcinus maenas* (lower). Photos: Fredrik Pleijel.

Most work has focused on effects on processes other than calcification (the exoskeleton of pelagic copepods has little, or no, calcium carbonate), and most studies have found no, or only small, responses to ocean acidification. Even exposure to very high $p\text{CO}_2$ levels (pH 7.4) only reduced survival in one species (of four studied), slightly reduced ($\leq 20\%$) egg-hatching success in one species (of three studied), and had no statistically significant effect on egg-production rate (four species) (Kurihara et al., 2004a,b; Kurihara and Ishimatsu, 2008; Mayor et al., 2007). Negative effects on larval (nauplius) survival have been reported but only at extreme levels of $p\text{CO}_2$ (Kurihara et al., 2004a,b). These results indicate that planktonic copepods may not be sensitive to ocean acidification at levels expected to occur within the 21st century. However, an Arctic perspective is lacking.

A number of studies have investigated responses of decapod crustaceans to ocean acidification. The balance of evidence indicates that acidification to levels projected for the year 2100 will influence decapod crustaceans substantially (Whiteley, 2011; Flores et al., 2012). Reported impacts include diverse effects on calcification; negative effects on embryonic development (e.g., Egilisdottir et al., 2009); positive, neutral, and negative effects on larvae (e.g., Arnold and Parker, 1999; Walther et al., 2010, 2011; Flores et al., 2012); and negative effects on growth rates and molting frequencies (Whiteley, 2011). Ocean acidification also affects behavioral patterns in hermit crabs (de la Haye et al., 2011) and penaeid prawns (Dissanayake and Ishimatsu, 2011). At an ecosystem level, abundance and diversity of marine benthic communities decline under ocean acidification, but only at $\text{pH} \leq 7.3$ (Hale et al., 2011).

The effects of ocean acidification on barnacles have been investigated in several species. Results vary, with some species showing reduced shell growth (*Eliminius modestus*) and calcification (*Semibalanus balanoides*), while others showed increased shell growth (*Balanus amphitrite*, *B. improvisus*) and calcification (*B. amphitrite*) (Findlay et al., 2009, 2010a,b; McDonald et al., 2009). Effects on barnacle embryos and larvae also vary: larval condition, cyprid size, larval settlement, and metamorphic success in *B. amphitrite* were all unaffected by very high $p\text{CO}_2$ levels (pH 7.4; McDonald et al., 2009), whereas less extreme levels of ocean acidification had negative effects on *S. balanoides* (Findlay et al., 2009). *Balanus amphitrite* shows changes in gene expression, with negative consequences for energy metabolism and respiration (Wong et al., 2011). Work on multiple stressors produced complex effects, for example, the effects of increasing temperature override those of acidification above a critical threshold (13°C , *S. balanoides*, Findlay et al., 2010b).

3.4.9.2 Polar/Arctic crustaceans

The boreal/Arctic copepod, *Calanus finmarchicus*, is a key species in the sub-Arctic (see Figure 3.3), and although egg-production rates were unaffected by extreme $p\text{CO}_2$ (8000 ppm = pH 6.95), substantial reductions in egg-hatching success were observed (Mayor et al., 2007). The effects of warming-driven northward-range extension of *C. finmarchicus* (Reygondeau and Beaugrand, 2011) in combination with ocean acidification are unknown. Barnacle species in the Arctic are few and are

limited by the extent of sea ice (which scrapes them from the rocks). *Semibalanus balanoides* is common in boreal and ice-free Arctic waters (the larvae tolerate several weeks of freezing in sea ice; Pineda et al., 2005), and the invasive *Balanus improvisus* has also been reported from the Arctic. The responses of these species to elevated $p\text{CO}_2$ (typically $\sim 1000 \mu\text{atm}$, $\text{pH} \approx 7.7$) are mixed, but generally negative, showing small reductions in shell calcification, or compensatory calcification, which incurs increased metabolic costs (Findlay et al., 2011). Data for boreo-Arctic decapod species include the shore crab *Carcinus maenas*, the spider crab *Hias araneus*, and the lobster *Homarus gammarus*. High levels of $p\text{CO}_2$ ($\text{pH} 7.3$) changed gene expression in the gills of the shore crab, although this did not translate into measurable physiological responses (Fehsenfeld et al., 2011). Similar pH drops caused reduced Ca^{2+} uptake by spider crab larvae, especially in populations from Svalbard (the northern margin of the species range; Walther et al., 2011), reduced larval development rate, reduced larval growth and reduced larval condition (Walther et al., 2010), and narrowed the thermal-tolerance window of spider crab adults (Walther et al., 2009). Decreasing pH by 0.3 units had no significant effects on survival, growth (carapace length), and development rates of larvae of the lobster *Homarus gammarus*, but did cause reductions in $\text{Ca}^{2+}/\text{Mg}^{2+}$ content of the larval carapace (Arnold et al., 2009). Interestingly, recent work showed that exposure to pH 7.7 for five months caused reductions in closure strength of the crusher chela (used in feeding and defense against predators) in *C. maenas* (Landes and Zimmer, 2012).

The available data indicate that although crustaceans in general are relatively robust to ocean acidification, polar and Arctic species show significant reductions in function, especially during the larval stages, which is likely to be translated into lower survivorship and reduced population viability.

3.4.10 Effects of ocean acidification on other invertebrates

3.4.10.1 Other invertebrates (non-Arctic studies)

Beyond the cnidarians (corals), mollusks, echinoderms, and crustaceans (see e.g., Doney et al., 2009), there is only direct evidence on the impact of near-future ocean acidification on five other invertebrate phyla: Acoela (positive effect; Dupont and Thorndyke, 2012), Annelida (negative or no effect; Widdicombe and Needham, 2007), Bryozoa (negative or no effect; e.g., Rodolfo-Metalpa et al., 2010), Nematoda (negative effect; Barry et al., 2004), and Nemertea (no effect; Ericson et al., 2010). This illustrates that little research focus (<5% of literature on invertebrates) is currently placed on those taxa that might be less vulnerable to the anticipated changes in ocean chemistry (Melzner et al., 2009a).

3.4.10.2 Polar/Arctic other invertebrates

Only one published paper considers the impact of ocean acidification on a polar (Antarctic) species. Near-future ocean acidification conditions had no significant effect on fertilization and early embryogenesis of the Nemertean *Parborlasia corrugates* (Ericson et al., 2010).

3.4.11 Effects of ocean acidification on fishes

3.4.11.1 Fishes (non-Arctic studies)

Juvenile and adult fishes have sufficient capacity and flexibility in their acid-base regulation systems to cope with the projected changes in environmental CO_2 levels over the 21st century (Pörtner, 2008; Melzner et al., 2009a,b). However, due to their high surface-to-volume ratios and less developed acid-base regulation systems, eggs and early larval stages might be more sensitive to changes in environmental CO_2 levels (Kikkawa et al., 2003; Ishimatsu et al., 2004). Recent experimental work has demonstrated direct, negative effects of high CO_2 on larval growth and survival of some marine fishes (Baumann et al., 2012; Frommel et al., 2012), but not others (Munday et al., 2009a, 2011a). In addition to growth and survival, laboratory experiments have documented effects of elevated CO_2 on other physiological processes. Rearing at elevated CO_2 concentrations ($>1000 \mu\text{atm CO}_2$) resulted in hyper-calcification of the otoliths in larval sea bass *Atractoscion nobilis* (pelagic spawner) (Checkley et al., 2009) and in clownfish (*Amphiprion percula*; benthic spawning species) reared at $\sim 1700 \mu\text{atm CO}_2$ but not at lower CO_2 concentrations more likely to be observed in the ocean within the next 50–100 years (Munday et al., 2011b).

Little is known about the effects that chronic exposure to high $p\text{CO}_2$ might have on fish reproduction. The few preliminary studies available indicate that impacts are small. Sperm motility of some flatfish species is arrested by mild increases in $p\text{CO}_2$ (Inaba et al., 2003), but similar effects were not observed in the Baltic cod, *Gadus morhua* (Frommel et al., 2010), or 11 other species from a range of families (Inaba et al., 2003). Sensitivity of fish eggs to elevated CO_2 varies markedly between species, but species tested to date typically have 24h LC50 (lethal concentration resulting in 50% mortality) values well above $10\,000 \mu\text{atm CO}_2$ (Ishimatsu et al., 2008). Rearing eggs of Atlantic herring in acidified water had no detectable effect on fertilization success, embryonic development, hatch rate, length and weight at hatching, and yolk size (Franke and Clemmesen, 2011). Furthermore, Munday et al. (2009b) did not detect any effect of exposure to $\sim 1000 \mu\text{atm CO}_2$ on the embryonic duration or survival of clownfish eggs. Consequently, the evidence currently indicates that embryos of marine fish are tolerant of increases in oceanic $p\text{CO}_2$ up to the stage of hatching.

Larval stages are predicted to be more sensitive to elevated $p\text{CO}_2$ than adults because they have a larger surface-area-to-volume ratio, and are, therefore, more susceptible to changes in ambient conditions, but also because they might have less developed mechanisms for acid-base balance compensation (Ishimatsu et al., 2008; Melzner et al., 2009a). Although very little is known about the mechanisms and pathways of acid-base regulation in larval fishes, it is clear that they must be capable of acid-base homeostasis, at least in later ontogenetic stages (Brauner, 2008). Larval mortality of the estuarine species *Menidia beryllina* increased when exposed to near-future CO_2 levels (Baumann et al., 2012), and tissue development was disrupted in Atlantic cod reared at high CO_2 (1800 and 4200 $\mu\text{atm CO}_2$) (Frommel et al., 2012). These studies indicate that larval stages of some marine fishes may be sensitive to rising CO_2 levels in the ocean.

However, Miller et al. (2012) found that reduced growth and survival observed in juvenile anemonefishes *Amphiprion melanopus* reared at high CO₂ levels were reversed when the parents experienced the same CO₂ conditions as the juveniles. This indicates that it is premature to conclude that near-future CO₂ levels will have negative effects on the growth, development, or survival of marine fishes until more studies include exposure to high CO₂ during both the parental and offspring generations, as well as for multiple generations.

Concentrations of CO₂ reported to cause mortality in adult fish are generally an order of magnitude or more higher (>10 000 µatm) than the CO₂ levels projected for the atmosphere and shallow ocean by the end of the 21st century (up to ~1000 ppm under a business-as-usual scenario of CO₂ emissions) (Ishimatsu et al., 2008). Therefore, direct effects of rising CO₂ levels on mortality are unlikely for adults. Very high concentrations of CO₂ (>10 000 µatm) are known to affect respiration, circulation, and metabolism of some fishes (Ishimatsu et al., 2005); however, the effects of CO₂ concentrations projected to occur in the shallow ocean this century are largely unknown. One concern is that increased energetic costs of acid-base balance and/or reduced respiratory capacity may limit the scope for aerobic performance as CO₂ levels rise (Pörtner and Farrell, 2008). In one of the few studies conducted to date, aerobic scope in two tropical cardinal fishes (*Ostorhinchus doederleini* and *O. cyanosoma*) declined by >30% when they were exposed to ~1000 µatm CO₂ at the average summer temperature (29 °C) for the study population and at temperatures up to 3 °C above average (Munday et al., 2009a). In contrast, Atlantic cod maintained their standard and active metabolic rates, critical swimming speeds, and aerobic scope after prolonged exposure (four and 12 months) to 3080 and 5800 µatm CO₂ (Melzner et al., 2009b). These contrasting results indicate that sensitivity to elevated CO₂ varies greatly among species and possibly that aerobic performance of cool-water fishes will be more tolerant of rising pCO₂ than in warm-water fishes. Pörtner and Knust (2007) demonstrated that oxygen limitation due to rising water temperature was likely to be responsible for range contractions and population declines of North Sea eel pout (*Zoarces viviparus*), and rising CO₂ levels may compound this problem, although this has not yet been tested. In general, the metabolic performance of species and life stages with high-oxygen demand, such as pelagic species and pelagic larvae, are predicted to be most sensitive to elevated oceanic CO₂ levels.

A potentially serious consequence of rising pCO₂ is that it can affect sensory systems and behavior of some marine fishes (Munday et al., 2009c, 2010; Simpson et al., 2011; Domenici et al., 2012). Larval reef fish exposed to elevated CO₂ lose their ability to discriminate between ecologically important chemical cues, such as odors from different habitat types, kin and non-kin, and the smell of predators (Munday et al., 2009c; Dixon et al., 2010). Recent experiments report that the response to auditory cues is also affected (Simpson et al., 2011) and a range of behavioral problems has been detected, including the loss of behavioral lateralization (Domenici et al., 2012). Whether elevated CO₂ causes similar behavioral impairment in larvae of polar fishes is unknown, but should be a priority area for further research.

Recent experiments have demonstrated that adult reef fish also suffer impaired olfactory ability and altered behavior when

exposed to elevated pCO₂, with potential effects on predator-prey interactions (Cripps et al., 2011; Ferrari et al., 2011) and homing to resting sites (Devine et al., 2012). Given that adult reef fish experience significant daily fluctuation in pH and pCO₂ in coral reef habitat (Ohde and van Woesik, 1999; Kuffner et al., 2008), and thus might be expected to have some tolerance to higher CO₂ levels, it should be expected that behavior of adult fish in other habitats, including polar regions, will also be affected. New research shows that elevated pCO₂ alters fish behavior by interfering with brain neurotransmitter function, specifically GABA-A receptors (Nilsson et al., 2012). Given the ubiquity of GABA-A receptors in the vertebrate brain, there is good reason to expect that polar fishes might be susceptible. The ecosystem effects of impaired sensory behavior, altered predator-prey interactions, and changes in behavioral attributes are unknown, but have the potential to be significant.

Striking differences in the responses to elevated CO₂ have been detected, both within and between species. If this variation has a genetic basis, rapid selection of tolerant individuals might be expected (see Munday et al., 2013). Therefore, an understanding of how individuals respond to elevated CO₂, and the variation in performance within local populations, is needed to make predictions about how species from all habitats and ecosystems will respond to future ocean conditions.

3.4.11.2 Polar/Arctic fishes

The effect of ocean acidification on Arctic fishes is unknown. The most applicable work to date on the direct effects of ocean acidification has focused on two commercially important (and closely related) gadoids, Atlantic cod and walleye pollock (*Theragra chalcogramma*). Consistent with expectations for larger-bodied fishes, experiments on juveniles of these species found that long-term exposure to elevated CO₂ (>2500 µatm) did not significantly impact growth or swimming capacity (Melzner et al., 2009b; Hurst et al., 2013). Conversely, a study rearing larval cod in mesocosms found increased incidence of developmental anomalies at high-CO₂ levels (1800 and 4200 µatm; Frommel et al., 2012). However, the physiological damage incurred by larval Atlantic cod due to high pCO₂ rapidly disappeared with the development of pH regulatory mechanisms (Frommel et al., 2012). Further, fish reared at those high-CO₂ levels (much higher than would be expected under most scenarios) did not exhibit slower overall growth or behavioral changes (Frommel et al., 2012; Maneja et al., 2013). An important caveat is that these experiments have been conducted with animals from more southerly populations at warmer temperatures, reflecting conditions in the more southerly portions of each species range. It is possible that adaptations of Arctic populations to other climate and habitat features increases sensitivity to ocean acidification or that the physiological ability of these fishes to adapt to elevated CO₂ may be compromised at lower temperatures when metabolic rates are constrained. This concern extends to other benthic fishes adapted to the persistently low temperatures of the Arctic (Pane and Barry, 2007). Further, whether the sensory and cognitive disruption at elevated CO₂ levels in coral reef fishes occurs in Arctic species is unknown (but see Maneja et al., 2013), as are the ecological consequences of these effects (but see Ferrari et al., 2011).

Polar cod (*Boreogadus saida*), a circumpolar species, channels up to 75% of the energy from zooplankton to vertebrate predators including seabirds, seals, whales, and polar bears (Bradstreet et al., 1986; Welch et al., 1992). This species typically represents the bulk ($\geq 50\%$) of ichthyoplankton occurring in Arctic seas, including the Beaufort and Chukchi Seas (Chiperzak et al., 2003a,b; Parker-Stetter et al., 2011; Rand and Logerwell, 2011; Paulic and Papst, 2013; K. Suzuki, University of Laval, unpublished data). Like most marine fishes, the larvae of polar cod feed almost exclusively on copepod nauplii (Drolet et al., 1991; Michaud et al., 1996) while juveniles feed on copepodites (Renaud et al., 2012). The calanoid species *Calanus* spp. and *Pseudocalanus* spp. comprise the bulk of prey ingested by polar cod at all life-history stages (Dominique Robert and colleagues, Memorial University of Newfoundland, unpublished data). Potential impacts of increasing $p\text{CO}_2$ on copepods have been examined using the temperate and boreal species *Acartia* spp. and *Calanus finmarchicus* (Kurihara, 2008; Whiteley, 2011). While detrimental effects were observed on *C. finmarchicus* at $p\text{CO}_2$ levels much higher than those predicted in nature in the foreseeable future, no study has reported acidification impact on copepods under CO_2 levels projected for the next two centuries. For instance, even exposure to a high- CO_2 concentration of 2380 ppm did not affect the survival, growth, and development of *Acartia tsuensis* at all life stages through two successive generations (Kurihara and Ishimatsu, 2008). Therefore, ocean acidification is unlikely to impact polar cod through decreased prey availability.

3.4.12 Effects of ocean acidification on seabirds and marine mammals

The effect of ocean acidification on seabirds and marine mammals will be through the food chain. For example, those seabirds or mammals that feed upon calcifying forms (e.g., pteropods, bivalves – see Section 3.3) may have to switch to other food sources if these species disappear as a result of ocean acidification.

3.5 Ecosystem-level responses to ocean acidification

The effects of ocean acidification on ecosystems are far more complex than the sum of the individual parts outlined in single-species or single-factor studies. Controlled mesocosm studies (e.g., Riebesell, 2004; Hale et al., 2011; Eklof et al., 2012) provide an approach that has shown that complex emergent results can arise from inter-specific differences in scaling of responses to ocean acidification, often in combination with other stressors. Kordas et al. (2011) gave an excellent example of how climate change effects on a simple predator-prey system (seastars and mussels) can lead to non-intuitive outcomes: increased predation rates by the seastar at higher temperatures outweighed the benefits of increased growth rates of the mussels, so that the overall effect of temperature on the mussel was negative. Equivalent investigations of the effects of ocean acidification on the shore crab *Carcinus maenas* and its prey, the snail *Littorina littorea*, showed that negative effects of acidification on both species (decreased chela strength in the crab, and decreased shell strength in the snail), resulted

in no net change in predation pressure (Landes and Zimmer, 2012; see also Hoegh-Guldberg and Bruno, 2010; Potera, 2010; Griffith et al., 2011, for effects on food webs). Rossoll et al. (2012) also demonstrated that $p\text{CO}_2$ can impact food quality with negative consequences for the next trophic levels (copepods, fish larvae).

Emergent ecosystem responses to ocean acidification will be a result of biotic and abiotic factors operating independently and in combination. At the biotic level, responses will be determined by the relative scaling of responses to ocean acidification in different species that interact. This principle is exemplified by the predator-prey examples above (Kordas et al., 2011; Landes and Zimmer, 2012), but also includes the influence of nutritional status on tolerance to ocean acidification (e.g., Thomsen et al., 2010), as well as how ocean acidification affects relative competitive ability (for which no relevant examples could be found). Abiotic stressors such as temperature, salinity, and pollutants not only affect species directly, but will also mediate the ecological interactions between them by moderating the relative scalings of their responses to ocean acidification. For example, including the effects of ocean warming in investigations of the effects of ocean acidification on the crab *C. maenas* preying on the snail *L. littorea* did not alter the relative scalings. Responses were the same at both temperatures (Landes and Zimmer, 2012), although the capacity for interactions between these variables is clear. To date, there are very few studies that have investigated the combined effects of biotic and abiotic factors on ocean acidification responses in marine waters, including the Arctic (but see Findlay et al., 2010b; Wood et al., 2011, and Eklof et al., 2012). Such studies are urgently needed.

With respect to Arctic food webs, there are as yet no data available. Therefore, there is a pressing need for studies on ecosystem-level responses to ocean acidification, from simple predator-prey interactions to higher-level emergent ecosystem responses.

3.6 Observations in naturally occurring low pH and/or high- CO_2 regions

Observations in areas that have natural gradients of pH, such as CO_2 vents (Hall-Spencer et al., 2008; Fabricius et al., 2011), estuaries, areas with acid soil runoff (Amaral et al., 2011; Mucci et al., 2011), and upwelling areas, provide opportunities to study the effects of a gradient of low pH on ecosystem-level responses in a variety of coastal ecosystems, as well as the adaptation of individual organisms (Wootton et al., 2008; Thomsen et al., 2010; Barry et al., 2011). The acidified waters near tropical and temperate CO_2 vents affect calcification, recruitment, growth, survival, and species interactions (Hall-Spencer et al., 2008; Fabricius et al., 2011). Many species of microalgae, macroalgae, seagrass, foraminifera, corals, polychaetes, crustaceans, mollusks and bryozoans are remarkably tolerant of long-term exposures to high and variable CO_2 levels at the vents (Kroeker et al., 2010, 2013; Johnson et al., 2011). However, a fall in mean pH from 8.1 to 7.8 can have detrimental effects on the recruitment of benthic organisms from the plankton (Cigliano et al., 2010) and many adult communities show dramatic reductions in biodiversity along the gradients of

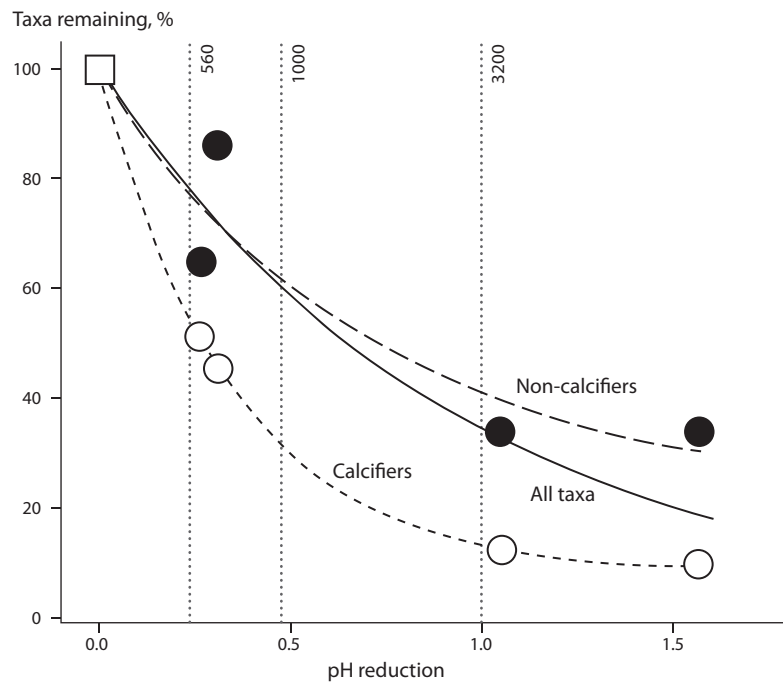


Figure 3.4. Change in Mediterranean coastal biodiversity as a function of declining pH. The biodiversity remaining (percentage of taxa that occurs in areas with no pH reduction [open square]) is shown for calcifying taxa (51 taxa total, white circles) and non-calcifying taxa (71 taxa total, black circles). Atmospheric $p\text{CO}_2$ levels (ppm CO_2) that would be required to cause pH changes in ocean surface waters equivalent to those observed at three locations along a pH gradient are indicated by dotted vertical lines. For calcifiers, non-calcifiers, and all taxa combined, exponential regressions explained 99%, 90%, and 88% of the variance. Fitted regressions indicate a loss of biodiversity of about 40% for non-calcifiers and all taxa, and about 70% for calcifiers, for a pH reduction corresponding to the atmospheric $p\text{CO}_2$ level projected by climate models for 2100. Source: Barry et al. (2011), based on Hall-Spencer et al. (2008).

increasing CO_2 in both temperate and tropical coral systems with around 30% fewer species in adult communities at mean pH 7.8 than in adjacent areas at mean pH 8.1 (Hall-Spencer et al., 2008; Fabricius et al., 2011). Important groups, such as coralline algae, calcified foraminifera, and sea urchins are common outside the vent systems but are absent from areas with mean pH ≤ 7.8 (Figure 3.4). However, these studies also show many more subtle effects such as changes in the architecture and community composition of corals in response to differential tolerances to ocean acidification (Fabricius et al., 2011) that had not been predicted. These natural analogs have the disadvantage of being constrained to a limited area: mobile species and/or life-stages may choose to move away or be advected to non-acidified environments. Similarly, ocean acidification-sensitive early life stages generated in distant, non-acidified, habitats may be able to recruit into acidified areas once they have grown beyond a size- or tolerance-threshold (e.g., Ferrari et al., 2011). Consequently, although natural ocean acidification analogs provide a valuable picture of some ecosystem-level effects this picture is inevitably incomplete.

A key question is how results from acidified areas in temperate and tropical systems might translate to polar waters. For example, the effects of naturally high CO_2 on mussels vary dramatically depending on food availability; populations in the Baltic Sea are able to settle and grow well but are unable to do so in the oligotrophic conditions of the Tyrrhenian Sea (Thomsen et al., 2010; Melzner et al., 2011; Rodolfo-Metalpa et al., 2011). To better understand the effects of low pH / saturation state on Arctic ecosystems, ecological shifts that occur along natural pH / carbonate-saturation gradients such as in upwelling areas or in fjords and in areas affected by tundra soil runoff are important to investigate. Areas of naturally lower pH in Arctic waters may be an important focus of future studies to reveal which types of organisms are resistant to ocean acidification and so provide a glimpse of the future diversity and functioning of marine ecosystems as anthropogenic CO_2 emissions rise.

3.7 Caveats

3.7.1 Time-scales of experiments in the context of acclimation and adaptation

The literature on the impact of ocean acidification is mostly based on short-term perturbation experiments. For example, 66% of all studies exploring the impact of ocean acidification on echinoderms consider exposure times of less than two weeks (data updated from Dupont et al., 2010). However, longer acclimation times (more than ten weeks) to high $p\text{CO}_2$ trigger negative effects on survival on such long-lived adult invertebrates (Pörtner et al., 2004; Shirayama and Thornton, 2005; Kurihara et al., 2008). Moreover, short exposure times are not sufficient to allow (or take into account) potential acclimation to a new environment. For example, the sea urchin *Strongylocentrotus purpuratus* is able to reshape its skeleton and change its behavior in a matter of eight to 20 weeks when exposed to a different habitat structure (Hernández and Russell, 2010). As a consequence, short-term exposure may both over- (no acclimation, no selection, no positive carry-over effects) and underestimate (not enough time to induce lethal effects, no negative carry-over effects) the real impacts of a chronic exposure to high $p\text{CO}_2$. The roles of natural variability and rate of change are other neglected parameters that may lead to over- and underestimation of the real impact of ocean acidification on marine species. For practical reasons, most perturbation experiments published to date used abrupt changes in pH. However, abrupt changes can lead to an overestimate of the real impact on fitness (e.g., $p\text{CO}_2$ changes on terrestrial ecosystems; Klironomos et al., 2005).

One of the critical gaps in knowledge is the lack of information on long-term exposure taking into account phenotypic plasticity and natural selection during multi-generation exposures. In other words: is there enough genetic variability and plasticity for populations to cope with near-

future ocean acidification? Phenotypic plasticity occurs when individual genotypes produce different phenotypes in different environmental conditions. This is an adaptive strategy, but is complicated by the fact that plasticity is itself genetically determined and can be under strong selective pressure. Thus, species and populations experiencing high environmental variability may have higher acclimation potential to additional stressors. Natural selection occurs when some genotypes have higher fitness and, therefore, are selected within a population during environmental changes. These parameters are critical and yet have only been considered in relatively few studies (Dupont and Thorndyke, 2008; Kurihara et al., 2008; Parker et al., 2012; but see Garrard et al., 2013). Evolutionary perspectives are only now starting to be considered. Using different clones of bryozoans, Pistevo et al. (2011) demonstrated the existence of genotype variation, which may sustain populations by natural selection during falling pH. Sunday et al. (2011) showed that the sea urchin *S. franciscanus* has vastly greater levels of phenotypic and genetic variation for larval size in future CO_2 conditions compared to the mussel *Mytilus trossulus*. Further, selectively bred fast-growing oysters were more resilient to ocean acidification (Parker et al., 2012).

In a recent paper, Parker et al. (2012) pre-exposed adult oysters to high $p\text{CO}_2$ (856 μatm) for five weeks during reproductive conditioning and showed a positive carry-over effect on larval growth. On the other hand, exposure to an environmental stressor also can induce negative carry-over effects that persist into later stages. For example, exposure to an environmental stressor during the pelagic phase can reduce juvenile performance and be exacerbated if stressful conditions persist (Emler and Sadro, 2006). Adult sea urchin pre-exposure to elevated $p\text{CO}_2$ had a direct negative impact on subsequent larval settlement success. Five to nine times fewer offspring reached the juvenile stage in cultures using gametes collected from adults previously acclimated to high $p\text{CO}_2$ for four months (Dupont and Thorndyke, 2012). In conclusion, considering impacts on a single life-history stage can also lead to misinterpretation of the impact of high $p\text{CO}_2$ on a given species.

3.7.2 Multiple stressors

In the Arctic Ocean, the main drivers of change in the near-future will be warming and multi-year ice melt, which will drive shifts in geographic range – and hence species composition of ecosystems (e.g., Beaugrand et al., 2008) – as well as changes in physiology. Some cold-water adapted high polar species may be marginalized and lost as their physical niche contracts (as in montane streams, e.g., Sauer et al., 2011), or suffer reduced productivity (e.g., Torstensson et al., 2012). At the same time temperature may favor an increase in general productivity that could benefit other species (e.g., Miller et al., 2012). The combination of temperature changes with ocean acidification has the potential to further constrain benefits (Pörtner and Knust, 2007), although available evidence is as yet limited. In addition to increased $p\text{CO}_2$ (i.e., ocean acidification), the additional influence of ice melt to freshen the water column may also have an effect on organisms, although again, data are lacking. A large meta-analysis of multiple stressors in climate change from non-polar regions showed that effects of a wide range of stressors were additive (26% of cases), synergistic (36% of cases) or antagonistic (38% of cases; Crain et al., 2008). The distributions of additive, synergistic and antagonistic effects were also reflected in studies involving ocean acidification, although the number of studies involved was very low (Crain et al., 2008).

3.8 Research priorities

There is an almost complete lack of information on the effects of ocean acidification (in isolation or in combination with other environmental stressors) on keystone species and processes in the Arctic. Accordingly, there is an urgent need for focused research on the likely impacts of ocean acidification on a range of taxa and processes. Some of these are listed below. Note that these points are not mutually exclusive and should, whenever possible, be combined. Further, notwithstanding logistical difficulties, experiments should be conducted *in situ* whenever possible and/or using pelagic and benthic mesocosms (Figure 3.5).

- In field studies, locate pH and CO_2 sensors in the same places that assessments of biological and ecological responses are being conducted.



Figure 3.5. Two experimental approaches to investigate the impact of ocean acidification on marine species: laboratory-based perturbation experiments (left, Maj Arnborg) and large-scale field-based mesocosms (right, Maike Nicolai).

- Assess responses of key components of Arctic and sub-Arctic food webs to ocean acidification and determine whether their responses are in any way different from those observed in other geographic regions, for example: viral and microbial communities; heterotrophic and mixotrophic protists; planktonic and under-ice microalgae and how seasonal changes in sea-ice coverage influences primary production and carbon transfer through the food web; clarify the relative effects of the acidification-induced changes in proportion of carbon species used in calcification (CO_2 , HCO_3^- , and CO_3^{2-}); foraminiferans (e.g., determine the respective functional roles of calcifying and non-calcifying foraminifera in order to assess the ecosystem consequences of diversity shifts under ocean acidification); corals (e.g., determine the effects of ocean acidification on *Lophelia* and non-*Lophelia* Arctic coral species and the effects of acidification-mediated loss of unprotected coral structure on coral-associated biodiversity); crustaceans, especially the copepods *Calanus finmarchicus*, *C. hyperboreus* and *C. glacialis*, amphipods (*Themisto libellula*), pteropods (mostly *Limacina helicina*) and commercially important crabs; fish, especially Arctic cod (*Arctogadus glacialis*), polar cod (*Boreogadus saida*), and capelin; seabirds and marine mammals (e.g., assess the dietary flexibility of seabirds and marine mammals to, for example, switch to food sources not affected by ocean acidification).
- Adaptive capacity and environmental plasticity of all stages of the life cycle, including possible local adaptations. This could include (but need not be limited to): long-term transgenerational and selective-breeding experiments; long-term studies investigating adaptations and acclimation capacity; long-term studies investigating the potential for effects to 'carry-over' to subsequent life stages and/or generations; address the issue of whether the increased generation time of many Arctic species confers reduced adaptive capacity to near-future climate change (in comparison to temperate and tropical species); multi-population studies to quantify genetic and phenotypic intra-specific variation of key traits influencing fitness; effects of multiple stressors (ocean acidification, carbonate saturation state, temperature, salinity, oxygen, toxins, etc.) on species-level and ecosystem-level processes (including trophic interactions); assess the effects of food limitation / nutritional status on species-level and ecosystem-level processes (e.g., do Arctic species show the same amelioration of ocean acidification impacts under high food / nutrient levels?).

3.9 Conclusions and recommendations

- Based on studies from other oceans, it is highly likely that a significant change will occur in Arctic marine ecosystems due to ocean acidification.
- Presently, too few data are available to determine how vulnerable Arctic ecosystems are to ocean acidification.
- It is likely that some organisms will benefit (e.g., seagrasses, some phytoplankton) from a high- CO_2 world, while others will be disadvantaged (e.g., calcifiers), possibly to the point of local extinction.
- Early life stages and life-stage transitions (e.g., molting) are, in general, more susceptible to ocean acidification.
- There are major knowledge gaps on ecological interactions and on individual species response through acclimation and adaptation.
- Ocean acidification impacts must be assessed in the context of other ecosystem drivers associated with change in the Arctic (e.g., warming, loss of ice cover, freshening of surface waters).

Ocean acidification may cause changes to Arctic marine systems at the organism and ecosystem levels. At the organism level, there will be both direct effects on physiology and behavior and indirect effects *via*, for example, trophic interactions (e.g., food availability and quality). Ocean acidification will affect energy flux through food webs and material flux through changes in the vertical movement of organic and inorganic matter. Pelagic and benthic calcifiers are at greatest risk to ocean acidification. The early life stages of both invertebrates and vertebrates, particularly larval forms with limited autoregulatory capacity, will generally be more susceptible. Sessile benthic organisms will in general be more susceptible to ocean acidification and are likely to be excluded from some regions in which they were previously present. On the other hand, productivity of autotrophs (e.g., dinoflagellates) are likely to increase as may primary productivity (as a result of higher CO_2 and temperature). Organisms inhabiting regions that have always exhibited marked fluctuations in pH and CO_2 may prove highly resilient to ocean acidification. Northward movement of some organisms – driven by warming of the oceans – may be limited by direct or indirect effects of ocean acidification. These potential impacts of ocean acidification on the Arctic are considered in the modeling scenarios presented in Chapter 4.

4. Potential economic and social impacts of ocean acidification on Arctic fisheries

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4.1 Introduction

The objective of this chapter is to review existing knowledge on the impact of ocean acidification on social and economic aspects of Arctic fisheries. A secondary objective is to discuss how change in ocean pH under future scenarios of anthropogenic carbon dioxide emission may present a risk to marine fisheries-based economies, the food security and culture of indigenous communities, and recreational fisheries values in the Arctic. The chapter builds on information presented earlier in the report on the chemistry (Chapter 2) and biological effects (Chapter 3) of ocean acidification in the Arctic. The information presented here shows that ocean acidification is likely to affect the abundance, productivity and distribution of marine species although the magnitude and direction of the changes are uncertain. This, in turn, is likely to affect the price of fish, the cost of fishing, and the fisheries benefits to the indigenous and local populations of the Arctic. The chapter concludes by providing suggestions about ways to manage and counteract the effects of ocean acidification on Arctic fisheries. However, given that the effects of ocean acidification are difficult to isolate from the effects of other anthropogenic impacts, this chapter concludes by stressing the need to strengthen marine management in general.

4.2 People in the Arctic

Estimates of population numbers for the Arctic depend on the geographical boundaries used: varying from between 2 and 4 million people (ACIA, 2005) to 9.9 million people (Duhaime and Caron, 2009). Of these, approximately 2.3 million people live within about 50 km of the coasts of the Arctic Ocean and its marginal seas (see Table 4.1). Estimates of the population of indigenous peoples vary between 400 000 and 1.3 million (AMAP, 2011a), and the proportion of indigenous peoples out of the total population in the various Arctic regions varies greatly (Table 4.1). These include many different ethnic groups. For instance, in the Russian Arctic, there are an estimated 2 million people with native ethnic status (Aslaksen et al., 2009).

In many Arctic regions, non-local and non-indigenous populations are the majority populations. Only in Nunavik and Nunavut in Canada, and in Greenland is more than 80% of the population indigenous or local; in other regions the share is much lower (Table 4.1). The number of local indigenous people in the Arctic increased by approximately 1.5% annually between 1990 and 2010, but their proportion of the total population declined over this period due to immigration (Rasmussen, 2011).

The general demographic trends in the Arctic region show a diminishing number of people in the active workforce, an ageing population with higher education levels, and decreasing household size. The Nordic countries, including the Faroe Islands and Greenland, are experiencing a decline in birth

rates, combined with emigration of young people (in some areas particularly women), which adds to a skewed population distribution. In parts of the Canadian Arctic, birth rates remain high enough to enable populations to grow despite emigration, while in parts of the Russian Arctic low birth rates are leading to declining populations (Rasmussen, 2011).

Many of the indigenous peoples can be characterized by a mixed-economy lifestyle that combines subsistence activities with cash income (ACIA, 2005; Poppel, 2006; Larsen et al., 2010; AMAP, 2011a; Poppel et al., 2011). The Arctic is experiencing major social and environmental changes, while retaining indigenous languages, and engaging in traditional activities (ensuring continuity and a connection to nature) (Aslaksen et al., 2009; Poppel, 2011). Hunting, fishing, herding livestock and gathering other food are important activities for securing daily needs as well as a source of income, and they help maintain cultural identity and social roles (AHDR, 2004; Hovelsrud et al., 2011). Such activities require investment in appropriate equipment, and thus some cash income.

The nature and level of subsistence activities, including fishing and berry picking, and hunting marine mammals, birds or big game, varies among different regions in the Arctic. With the exception of Alaska, these activities are not included in official statistics (Aslaksen et al., 2009). It is therefore difficult to assess their contribution to household economies. However, large structural changes are occurring and agricultural, hunting and fishing communities are experiencing emigration and negative population growth. While many studies uphold the nutritional value of traditional food, the economic and cultural importance of harvesting activities is decreasing (Rasmussen, 2011). Changes in the availability of marine resources due to stressors such as ocean acidification could exacerbate these trends.

4.3 Socio-economic factors

The economy of the circumpolar north (see Chapter 1, Figure 1.3 for a definition of 'circumpolar north') is large in relation to the population size. Gross Domestic Product (GDP) for the region was estimated at USD 225 billion in 2003. This estimate does not include production in the subsistence sector and is therefore an underestimate. Fisheries are relatively important, with the catch in 2002 accounting for over 10% of the world's total catch of wild fish and over 5% of the crustacean catch (Statistics Norway, 2007). The region also has some aquaculture production. However, most of the aquaculture and much of the wild catch is produced in the sub-Arctic regions (see Chapter 1, Figure 1.4 for a definition of 'sub-Arctic regions').

Differences in disposable income per capita across Arctic countries are smaller than differences in gross regional product (GRP) per capita, and the gap between Arctic and non-Arctic

Table 4.1. Basic economic and social conditions, Arctic regions, 2006. Source: modified from Duhaime and Caron (2009).

Region	Total population	Approx. % of population living within ca. 50km of coast of Arctic Ocean and its marginal seas	Share of aboriginal peoples in the total population	Share of women in the total population	Share of children aged 0-14 years in the total population	Life expectancy in years	Infant mortality per thousand live births	Share of tertiary education graduates in the total population	Personal disposable income, USD-PPP	Dependency ratio	Composite index ¹
Alaska	670 053	72	13.1	48.5	21.5	76.7	6.7	24.7	32 811	0.6	9
Labrador	26 364	0	37.8	49.3	20.6	76.1	4.4	9.4	19 044	1.3	6
NWT	41 465	13	49.8	48.8	23.9	79.1	4.2	19.4	30 339	0.7	8
Nunavik	10 815	100	89.2	49.1	36.3	63.5	17.3	9.6	19 532	1.9	4
Nunavut	29 475	100	84.5	48.7	33.9	70.4	10.0	11.9	24 495	1.6	5
Yukon	30 375	<1	25.0	49.7	18.8	76.4	11.0	23.4	29 761	1.0	8
Faroe Islands	48 183	100	0.0	48.1	22.8	78.9	4.4	23.0	15 275	0.7	7
Lapland	184 935	<1	0.8	49.9	16.3	78.6	5.9	20.7	14 000	1.5	7
Oulu	465 018	0		49.7	19.8	79.0	4.2	22.7	13 847	1.4	7
Greenland	56 901	100	88.6	47.0	24.8	68.3	15.4	n.d.	15 237	0.9	5
Iceland	299 891	98	0.0	49.6	21.8	81.2	1.4	23.5	17 957	0.8	8
Finnmark	72 937	93	9.2	49.2	20.5	77.6	4.3	21.4	18 687	1.1	7
Nordland	236 257	100		50.0	19.3	79.4	3.3	19.8	18 700	1.2	7
Troms	153 585	99		49.6	19.7	79.0	3.7	25.1	18 550	1.0	8
Norrbotten	251 886	0	3.6	49.3	15.6	79.5	5.1	13.6	14 721	1.3	6
Västerbotten	257 581	0		50.0	16.1	80.4	3.1	19.4	14 139	1.2	7
Arkhangelsk	1 280 200	29	0.5	53.3	16.3	64.8	10.2	12.1	7 465	1.1	3
Chukchi	50 500	46	20.9	47.9	21.7	58.9	23.2	14.6	19 267	0.3	5
Evenk	17 000	0	19.3	50.0	24.2	59.1	21.3	11.5	9 765	0.5	4
Karelia	693 100	3	0.0	54.2	15.5	63.8	7.6	13.7	6 734	1.0	3
Khanty-Mansii	1 488 300	0	1.4	50.8	19.9	68.8	7.5	15.9	16 851	0.7	6
Komi	974 600	0	1.0	52.5	17.5	64.2	7.0	12.2	10 710	1.1	4
Koryak	22 600	23	34.2	50.0	22.0	56.0	33.0	9.9	12 389	0.6	3
Magadan	168 500	0	8.7	51.6	17.0	63.4	14.2	15.4	10 682	0.8	4
Murmansk	857 000	41	0.2	51.6	15.7	65.2	10.3	15.5	9 853	0.9	5
Nenets	42 000	13	14.3	51.2	22.3	62.2	15.2	9.9	..	0.5	4
Sakha	950 000	2	2.4	51.5	23.6	65.6	10.6	14.6	10 733	1.0	5
Taimyr	38 400	4	19.0	51.8	22.9	63.8	7.4	13.3	11 641	0.7	5
Yamal-Nenets	532 600	2	5.9	50.7	21.3	68.9	13.0	16.8	20 447	0.5	6

¹ This index is based on the six indicators: female proportion, life expectancy, infant mortality, tertiary education rate, personal disposable income, and dependency rate.

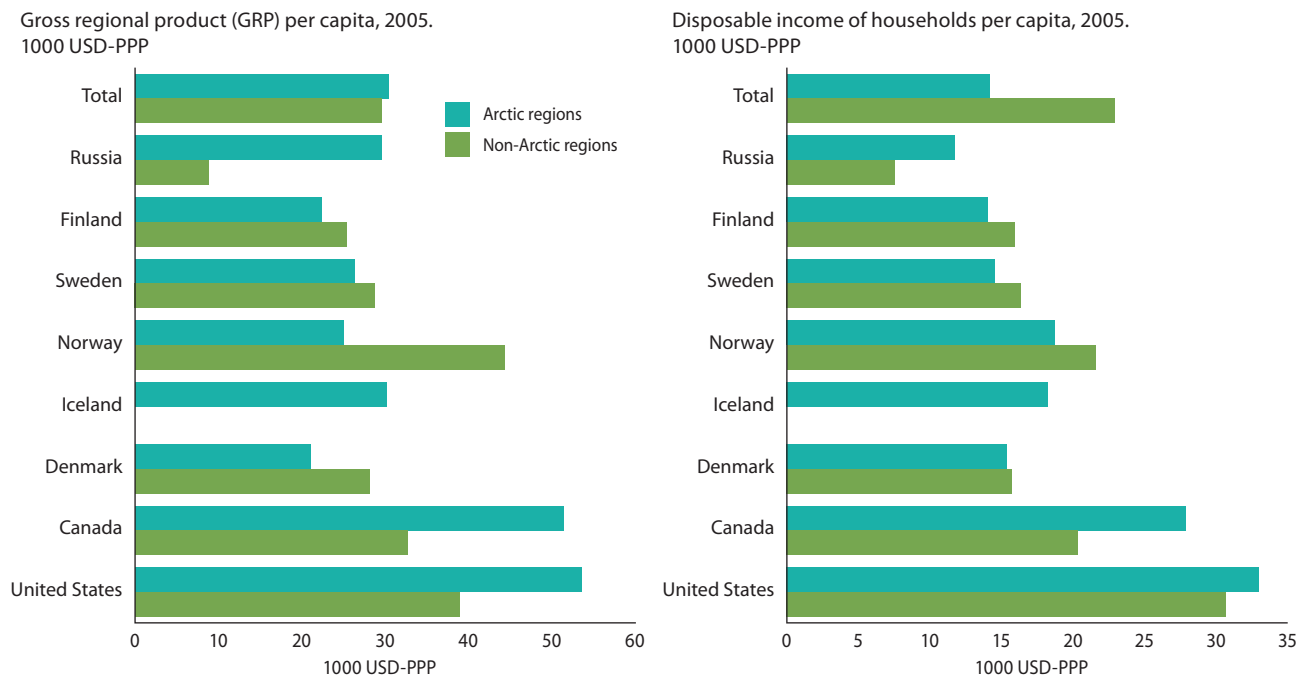


Figure 4.1. Gross regional product per capita and disposal household income per capita. Note: PPP denotes purchasing power parity, which relates the value of the U.S. dollar to what it can actually buy in each country relative to the USA. Source: Duhaime and Caron (2009).

regions is considerably smaller than the difference in GRP per capita (Figure 4.1). This is largely explained by mechanisms of national income redistribution. As shown, disposable income per capita is highest in the United States. A comparison of disposable income per capita between countries only roughly indicates differences in welfare, however¹. Hence, the above figures may overestimate the actual welfare level of Arctic regions when compared with non-Arctic regions. On the other hand, subsistence activities are more widespread in the Arctic regions than elsewhere in these countries and contribute to overall welfare.

For indigenous peoples, marine resources contribute to their economy, livelihoods, nutrition, health and well-being. The contributions from these subsistence activities are not considered in official Arctic GRP assessments, yet their importance in the mixed cash-subsistence economies of the Arctic is well documented (e.g., Hovelsrud, 1999; Rasmussen, 2005; Poppel, 2006; Kruse et al., 2008; Aslaksen et al., 2009; Poppel and Kruse, 2009). For example, locally produced food accounts for more than half of the diet in Inuit households (Poppel et al., 2007). An example illustrating the difficulties with attaching values in GRP accounts is that of whale meat: this can either be distributed among kin in non-monetary exchanges or sold locally (Nuttall, 2002), complicating rigorous assessments of the value gained. This example highlights the potential conflict between traditional indigenous perspectives and modern commercial interests that commonly influences discussions on Arctic natural resources. Arctic regions where traditional subsistence activities play a more dominant role (e.g., Greenland and northern Canada) have a much lower GRP compared to the largest economies in the Arctic (AMAP, 2011a).

4.4 Marine fisheries in the Arctic region

Catch statistics supplied by the UN Food and Agriculture Organization (FAO) represent a primary source for describing the marine fisheries in the Arctic region in more detail. The Arctic marine area extends over five FAO fisheries statistical areas (Figure 4.2), of which only one (FAO Fishing Area 18: Arctic Sea) lies completely within the Arctic region. The other four (FAO Fishing Areas 21: Northwest Atlantic; 27: Northeast Atlantic; 61: Northwest Pacific; 67: Northeast Pacific) extend well beyond the Arctic. However, the Arctic areas of these four regions contain important fisheries.

4.4.1 FAO Fishing Area 18 (Arctic Sea)

Fishing area 18 covers the central Arctic Ocean Basin and the following Arctic shelf seas: the Kara, Laptev, East Siberian and Chukchi Seas, the Beaufort Sea, the Canadian Arctic Archipelago, and Hudson Bay/Hudson Strait (see Figure 4.2). The scope for undertaking commercial fisheries in this area is limited by the presence of sea ice during large parts of the year. This is reflected in catch data reported to FAO; for example, the FAO database only records catches of some 460 and 590 t of cod/haddock/hake by Russia in 2008 and 2010, respectively. However, subsistence fishing by people living along the coasts of these Arctic seas is likely to be extensive. Zeller et al. (2011) attempted 'educated guesses' of the historic catches in the region and suggested catches of around 10 000 t in the mid-2000s (declining from around 24 000 t in 1950). The species involved were mostly salmonids (coregonids, Arctic char, trout and salmon species). About 80% of the reconstructed catch was attributed to Russia, while Alaska and Canada shared the remaining 20% equally.

¹ For better comparability, public expenditures to household services should be added to the disposable incomes, and differences in price levels between Arctic and non-Arctic regions (generally higher in Arctic regions) should be taken into account.

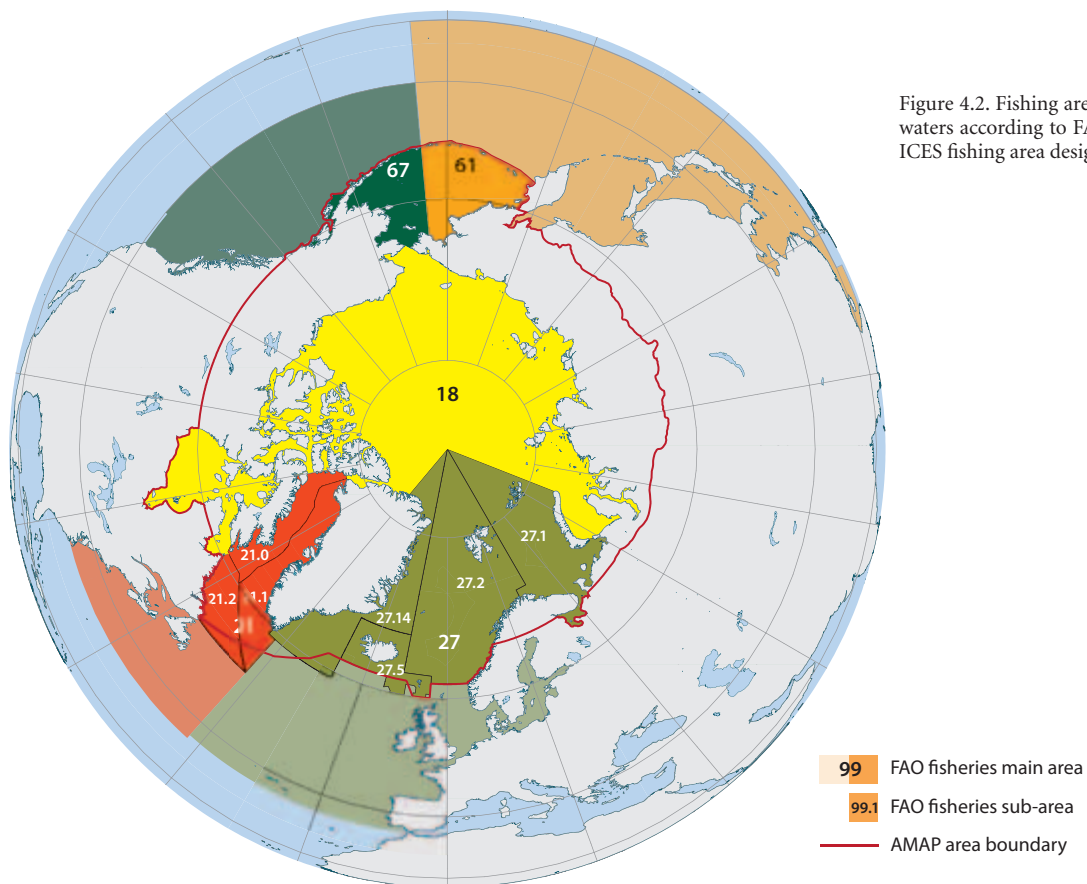


Figure 4.2. Fishing areas in Arctic waters according to FAO/ICNAF/ICES fishing area designations.

With the observed and projected decline in sea ice in response to global warming, the scope for exploiting the fish and shellfish resources in this area will increase, with the inherent danger that unregulated catches may lead to overfishing of stocks.

In 2009, the US North Pacific Fishery Management Council (NPFMC) approved, and the National Marine Fisheries Service (NMFS) implemented a management plan based on a precautionary perspective that covers the Arctic waters of the United States in the Chukchi and Beaufort Seas. This Fishery Management Plan for Fish Resources of the Arctic Management Area (Arctic FMP) prohibits commercial fishing in the Arctic waters of the region that are under US jurisdiction until more information is available to support sustainable fisheries management. Subsistence fishing is not affected.

4.4.2 FAO Fishing Area 21 (Northwest Atlantic)

The International Commission for the Northwest Atlantic Fisheries (ICNAF) maintains catch statistics based on a comprehensive division of FAO Fishing Area 21 into several sub-areas (see Figure 4.2).

For the Arctic areas, catches from the Baffin Bay/Davis Strait areas west of Greenland (sub-areas 0A and 0B, 1A to 1F, and 2G to 2J) are considered to represent fisheries mainly in the Low Arctic. The average total catch (1992–2011) in these areas amounts to 209 000 t. Of the two countries bordering the region, Canada is responsible for 31% of the catch, while Greenland takes 63% (Table 4.2). Table 4.3 lists the main species (groups) landed over the past 20 years and for two ten-year periods separately.

A further 273 000 t is caught in sub-areas 3K–3P, fisheries on the Grand Banks that are located just outside of the AMAP Arctic area. About 65% of this catch is taken by Canada. The remainder is taken by other countries fishing mainly in international waters off Flemish Cap, and thus not contributing to the economy of the Arctic region.

The catches of species fished in Fishing Area 21 (sub-areas 0, 1, and 2) since 1992 are dominated by pandalid shrimp (on average 71% of the total catch) (Figure 4.3), followed by Greenland halibut (16%) and redfish (over 5% in the latter half of the period); other species groups represent smaller fractions. Remarkably, invertebrates (crustaceans, mollusks, echinoderms) represent more than 45% of the total catch also in the 21.3 sub-area.

Table 4.2. Average total annual catch by country in FAO Fishing Area 21 (ICNAF sub-areas 0, 1 and 2) over the past two decades (1992–2011). Source: UN Food and Agricultural Organization (www.fao.org/fishery/topic/3457/en).

FAO Fishing Area 21	Average annual catch, Kt
Total Arctic region (sub-areas 0, 1 and 2)	209
By country	
Canada	65 (31%)
Greenland	131 (63%)
Russia	4 (2%)
Faroe Islands	1 (<1%)
Iceland	1 (<1%)
Other (non-Arctic)	7 (3%)

Table 4.3. Average annual catches by species in the Arctic part of FAO Fishing Area 21 (ICNAF sub-area 0, 1, and 2) over the past two decades (1992–2011). Source: UN Food and Agricultural Organization (www.fao.org/fishery/topic/3457/en).

Fishing Area 21	Average annual catch, t		
	1992–2011	1992–2001	2002–2011
Capelin	88	118	59
Cod	4934	1579	8289
Other gadoids	1201	1747	656
Grenadiers	114	174	54
Wolffish	251	87	414
Lumpfish	3003	1069	4938
Redfish	8256	2758	13755
Greenland halibut	34550	29061	40040
Witch flounder	7	3	12
Halibut	60	95	24
Other flatfish	3	2	3
Salmonids	111	191	30
Other fish	431	663	200
Sharks	19	37	0
Rays and skates	7	7	6
Shrimp	148608	117430	179787
Other crustaceans	6038	7327	4748
Echinoderms	16	21	11
Mollusks	1656	1539	1772
Total	209352	163909	254796

4.4.3 FAO Fishing Area 27 (Northeast Atlantic)

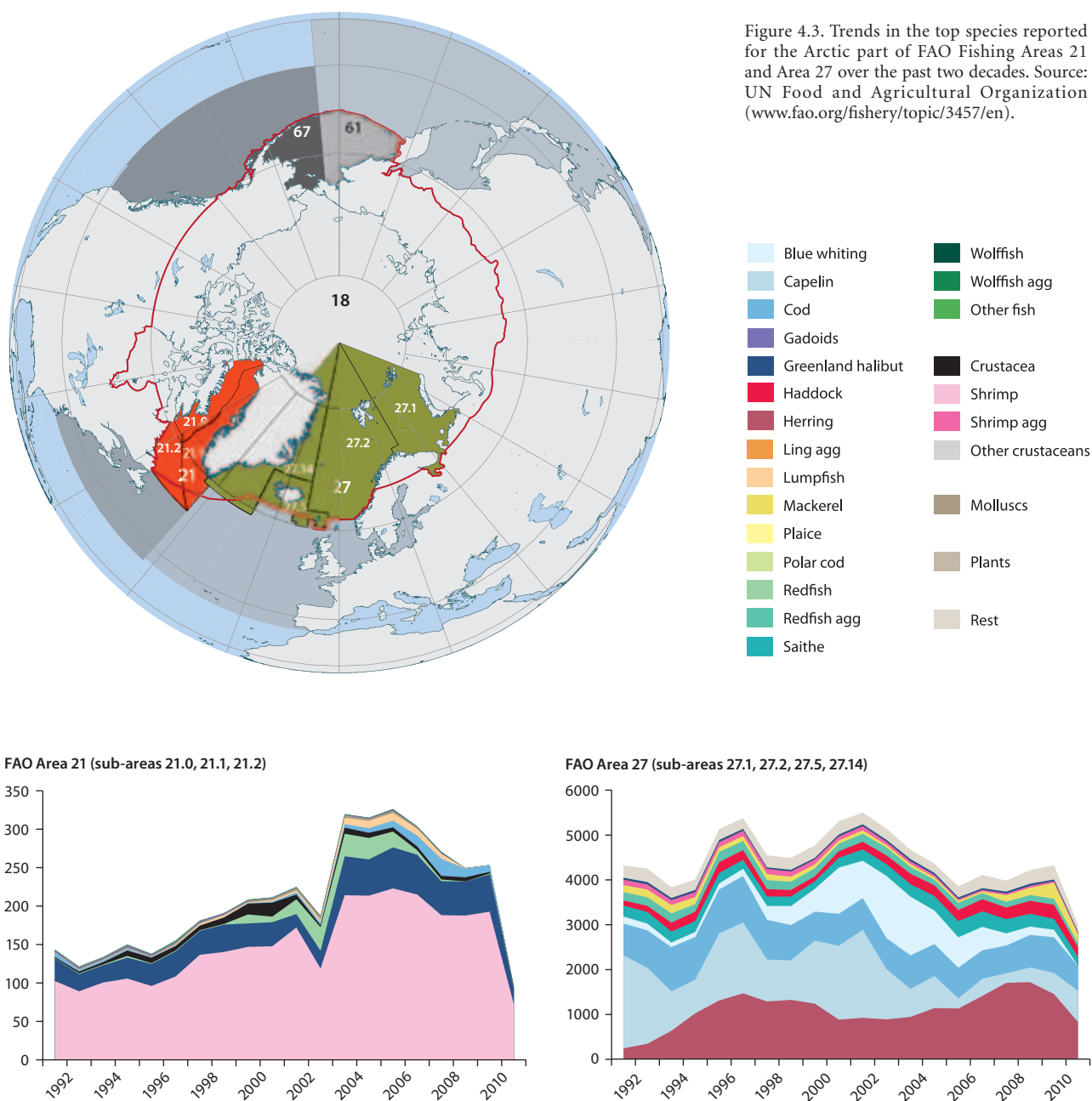
Within FAO Fishing Area 27 (Northeast Atlantic), sub-areas 27.1 and 27.14 can be considered to represent the High/Low Arctic (see Figure 4.2 and Chapter 1, Figure 1.4 for a definition of this area), while sub-areas 27.2 and 27.5 essentially represent the Low/sub-Arctic region (see Figure 4.2). The average total catch (1992–2011) by sub-area (Table 4.4) indicates that the vast majority is taken in the sub-Arctic regions (84%). Iceland and Norway take about equal shares, followed by Russia and the Faroe Islands. Non-Arctic countries fishing in the area together take 4%, while Greenland lands only 1%. Table 4.5 lists the average catches of the most important species (groups) landed over the past 20 years and for two ten-year periods separately. The top ten species (herring, capelin, cod, blue whiting, saithe, haddock, redfish, mackerel, pandalid shrimp, Greenland halibut) account for 91% of the total average catch. Among these, blue whiting and mackerel do not represent separate stocks, but form part of much larger oceanic stocks that have their centre of distribution (and spawn) in more temperate waters. The other species represent (often multiple) stocks that reside and spawn within the Arctic region. Herring and capelin are pelagic species that spawn near the coast (capelin even inshore), but migrate offshore to feed. Cod, saithe and haddock are typical demersal species that remain on the shelf to spawn and feed, although they migrate over large distances. Redfish, Greenland halibut and pandalid shrimp represent deep-water species and their stock structure is less well known. Although there are differences between the two periods, these data do not suggest that there have been large

Table 4.4. Average total annual catch by sub-area and country in FAO Fishing Area 27 over the past two decades (1992–2011). Source: UN Food and Agricultural Organization (www.fao.org/fishery/topic/3457/en).

Fishing Area 27	Average annual catch, Kt
Total Arctic region (sub-areas 1, 2, 5 and 14)	4457
By sub-area	
27.1	507 (11%)
27.2	1990 (45%)
27.5	1739 (39%)
27.14	221 (5%)
By country	
Iceland	1638 (37%)
Norway	1557 (35%)
Russia	752 (17%)
Faroe Islands	292 (7%)
Greenland	25 (1%)
Other (non-Arctic)	192 (4%)

Table 4.5. Average annual catches by species in the Arctic part of FAO Fishing Area 27 (ICES sub-areas 1, 2, 5, and 14) over the past two decades (1992–2011). Source: UN Food and Agricultural Organization (www.fao.org/fishery/topic/3457/en).

Fishing Area 27	Average annual catch, Kt		
	1992–2011	1992–2001	2002–2011
Herring	1092	972	1211
Other clupeoids	1	1	0
Capelin	1004	1334	673
Cod	770	853	687
Blue whiting	460	309	611
Saithe	255	224	287
Haddock	205	167	242
Ling species	23	20	26
Tusk	22	24	20
Polar cod	22	23	20
Other gadoids	19	22	15
Argentines	23	17	29
Wolffish species	36	38	35
Redfish species	166	192	141
Lumpfish	7	8	5
Mackerel	125	129	121
Greenland halibut	42	43	41
Plaice	11	13	8
Other flatfish	15	18	13
Salmonids	1	1	0
Other fish	21	17	25
Sharks	3	4	1
Rays and skates	2	2	2
Nephrops	2	2	2
Shrimp	81	112	49
Other crustaceans	7	2	12
Echinoderms	1	0	1
Bivalves and gastropods	21	30	13
Plants	21	21	21
Total	4456	4600	4313



long-term trends in any of the species. The rank order has mostly been maintained. However, there are major differences in the rank order of the dominant species in the different sub-areas and also large annual fluctuations (Figure 4.4).

In the Barents Sea (sub-area 27.1), the three species dominating the catch are cod, capelin and haddock, with marginal contributions from the others. Cod yields a consistently high catch, while capelin periodically exceeds the cod catch but is virtually zero between these periods. This is a consequence of the management system that only opens the fishery when the stock is predicted to be above some threshold in order to set aside enough food for predators. The cod and haddock in this area migrate to sub-area 27.2 to spawn.

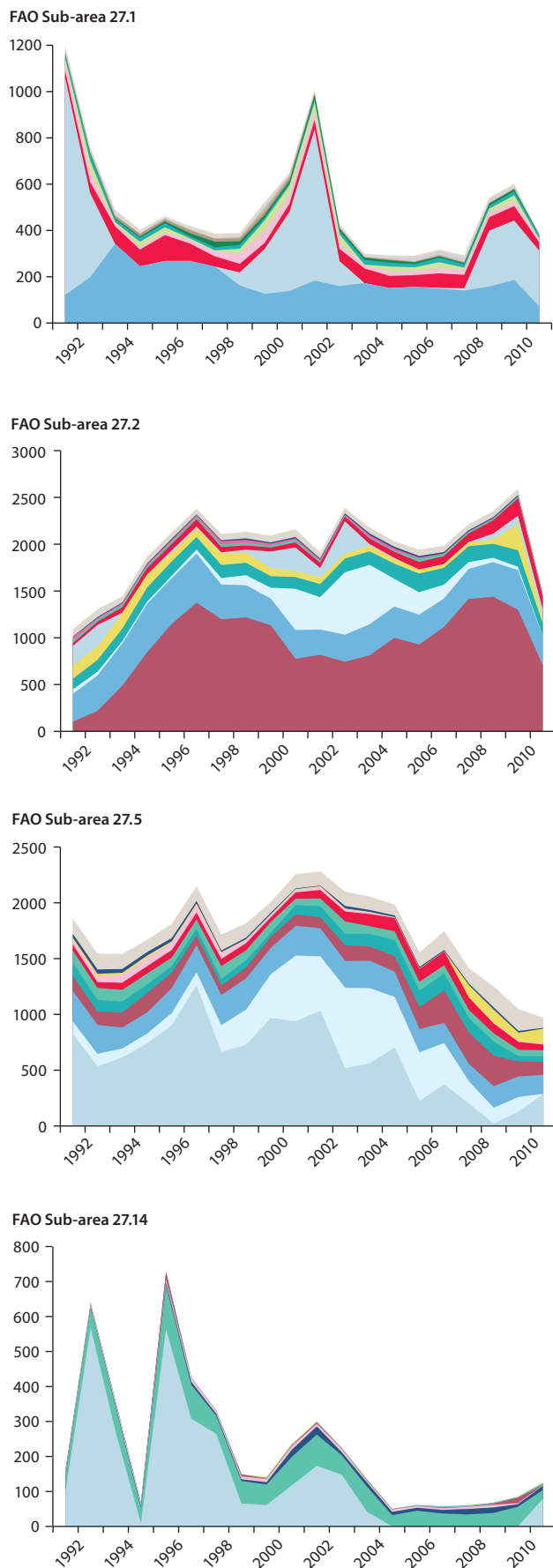
In the Norwegian Sea (sub-area 27.2), the herring stock of spring spawners started to recover in the 1970s, grew through the 1980s due to strict harvest regulations, and since the early

1990s has contributed almost consistently more than 50% of the catch with cod coming second. The third-ranked species is blue whiting, but large catches were restricted to the early 2000s, when these fish apparently penetrated waters farther north than is usually the case.

In Icelandic and Faroese waters (sub-area 27.5), the bulk of the catch consisted of capelin and blue whiting, but their contribution has declined strongly over the past ten years. Recently, the top ten species are more equally distributed in terms of their contribution to the total catch. Also, the rest of the group represents a major component.

In Greenlandic waters (sub-area 27.14), deep-water species (redfish, Greenland halibut, pandalid shrimp) are consistently well represented in the total catch, although capelin is by far the dominant species on average. However, as is the case in sub-area 27.1 capelin yields have fluctuated widely.

Figure 4.4. Trend in the top-ten species reported for the Arctic part of FAO Fishing Area 27 over the past two decades. Source: UN Food and Agricultural Organization (www.fao.org/fishery/topic/3457/en). For key to species see Figure 4.3.



4.4.4 FAO Fishing Areas 61 (Northwest Pacific) and 67 (Northeast Pacific)

The statistical information for FAO Major Fishing Areas 61 (Northwest Pacific) and 67 (Northeast Pacific) does not include detailed information by sub-area that can be used to separate Arctic fisheries from non-Arctic fisheries. Wild fish catches in the eastern and western Bering Sea were 1.84 and 0.52 million t, respectively in 2002 (Statistics Norway, 2007) with an additional 0.01 million t of crustaceans (snow crabs) caught in the eastern Bering Sea. Pollock was the main species caught comprising approximately 80% of the wild fish catch in the eastern Bering Sea and 77% of the catch in the western Bering Sea. Pacific salmon, flatfish and other ground fish species made up most of the remainder of the catches.

4.5 Impacts of ocean acidification on Arctic fisheries

On the basis that ocean acidification is likely to affect the abundance, productivity and distribution of marine species in different ways (see Chapter 3 for further details), the ecosystem services associated with these species will also be affected. However, the magnitude and direction of the changes expected at the ecosystem level are uncertain, because the effects of ocean acidification cannot be seen in isolation (because the effects of other factors (such as temperature rise and ice melt) that evoke responses in individual species with respect to distribution and population dynamics. These factors may strengthen or counteract each other and until more insight is gained regarding such interactions, predicting the effects on ecosystem services must involve much speculation. To date, there has been little research on the economic impacts of ocean acidification on fisheries. Those studies that have been undertaken have been species-specific and have focused on shell-forming species (e.g., Cooley and Doney, 2009; Narita et al., 2012). A comprehensive, broad-based approach for understanding the impact of ocean acidification on marine ecosystems and their services, such as fisheries (including the socio-economic dimensions), is almost non-existent (but see Armstrong et al., 2012; Hilmi et al., 2013).

Global simulation modeling (e.g., Cheung et al., 2010) suggested that climate change may lead to increases in potential fisheries yield in the Arctic, while follow-up studies with a model that accounts for hypothesized physiological effects of ocean acidification suggested that there may be a substantial reduction in potential yield in the North Atlantic if waters become more acidic (Cheung et al., 2011). Predicting the effects of ocean acidification on potential yield is complicated by species interactions and multiple stressors on ecosystems. Using both ecosystem models with explicit trophic linkages (Ecopath with Ecosim) and a Dynamic Bioclimate Envelope model that incorporates ecophysiology and spatial population dynamics of marine species, ocean acidification in combination with hypoxia is projected to reduce maximum catch potential by 2050 relative to 2000 in the North Atlantic under different assumptions regarding future greenhouse gas emissions scenarios (IPCC SRES A1B or A2) (Ainsworth et al., 2011; Cheung et al., 2011). However, these projections are sensitive to the assumed vulnerability to ocean acidification of the modeled

organisms, which is poorly understood (see Chapter 3). Responses of marine species may interact with other human stressors such as overfishing, which might exacerbate the impacts of ocean acidification on yield (e.g., Wootton et al., 2008; Russell et al., 2009; Ainsworth et al., 2011). The estimated changes in quantity, quality and predictability of catches have direct implications for fisheries (Sumaila et al., 2011).

Decreasing pH in ocean surface waters is synergistic with other effects of climate change, such as increases in ocean temperature, changes in salinity, and possible expansion of anoxic zones (Stramma et al., 2010), but the combined effects of these factors in the Arctic are still unknown. Despite the fact that the impact of ocean acidification is still uncertain, further increases in ocean acidity can be expected to add more stress to marine ecosystems and the human communities that depend on them.

Increasing amounts of dissolved carbon dioxide in the ocean is expected to reduce, in particular, the growth of calcifying marine species such as mollusks (see Chapter 3 for further details). A reduction in the productivity of commercially targeted mollusks could have substantial impacts on their fisheries, and hence, on the communities that depend on these for food and income (Cooley and Doney, 2009; Cooley et al., 2009; Narita et al., 2012).

The description of fisheries in the Arctic region (see Section 4.4) clearly indicates large differences in species composition by area, and because ecosystems differ by region, a universal response to ocean acidification would seem unlikely. Most probably, shelf systems cannot be treated in the same manner as oceanic or deep-water systems. Moreover, any effects of ocean acidification on potential yield will be embedded in responses to other factors affecting these systems, specifically global warming. Unless the quantitative effects of each of these factors separately can be evaluated, any prediction of their integrated effects remains speculative.

Nevertheless, a few speculations may be inferred from the previous chapters:

- If ocean acidification is expected to be stronger in areas of melting sea ice (Chapter 3), sub-Arctic regions may suffer less than Low Arctic regions.
- If ocean acidification is expected to be stronger in surface waters than in deep waters, shelf species may be affected more than deep-water species.
- If ocean acidification is expected to be stronger in colder regions, global warming might to some extent compensate for the effects.
- If food webs are less complex in Low Arctic regions than in sub-Arctic regions (as supported by fewer species dominating the total yield), and therefore less resilient to ocean acidification, the negative effects on fisheries in terms of catch composition and total output may be greater.
- If mollusks are more susceptible to effects of ocean acidification, fisheries in the Low Arctic region of the northwestern Atlantic would suffer more than in the northeastern Atlantic, because bivalves and gastropods score higher among the species groups dominating the catches there.

4.5.1 Economic impacts of ocean acidification on Arctic fisheries

Environmental impacts of economic activity are not included in standard GDP, as opposed to ‘green GDP’, and it is therefore a challenge to develop environmental statistics and environmental indicators that can be applied in conjunction with economic indicators (Statistics Norway, 2009).

Kite-Powell (2009) has provided a global perspective on the economics of ocean acidification. Although there is still no detailed study on the economic impact of ocean acidification on global fisheries, Armstrong et al. (2012) suggested that ocean acidification may have negative as well as positive effects on fisheries and aquaculture.

Clearly, more work is needed to help reveal the potential impact of ocean acidification on the fisheries of the Arctic, as well as on marine ecosystems in general. Despite valuable attempts (Hilmi et al., 2013), a comprehensive, broad-based approach for understanding the impact of ocean acidification on the marine ecosystem, fisheries, and eventually the associated socio-economic dimensions, is still lacking. One approach to estimating these impacts is to use ‘Economic Valuation’ based on changes in ex-vessel prices, fishing costs and projected catch under different ocean acidification scenarios. Other than the change in landed value or total revenue, ocean acidification may also affect the cost of fishing by changing the fishing effort (the number of fishing days, travel distance, gear to be employed, etc.) required to catch the same amount of fish, when the distribution and abundance of target species are affected by ocean acidification. The wages earned may also be affected. Because fisheries represent a primary industry (i.e., an industry that relies on basic raw materials and whose product – fish – is used by other sectors of the economy, such as retail), change in catch potential may also indirectly affect other dependent sectors, from boat building to international transport (Dyck and Sumaila, 2010). Thus, it is crucial to take indirect economic activities into account when assessing the full economic impact of ocean acidification on fisheries. It should be noted, however, that this type of analysis is yet to be done. To have a more reliable economic model for estimating impacts of ocean acidification, a better understanding of the biophysical responses of marine species and the ecosystem to ocean acidification in the Arctic is necessary.

4.6 Impacts of ocean acidification on Arctic indigenous peoples and local communities

The indigenous peoples in the Arctic continue, to a large extent, to rely on food harvested locally. This makes them vulnerable to the effects of environmental contaminants that concentrate in Arctic food chains (Huntington et al., 1998), and to reduced harvests due to the consequences of other environmental stressors. These include the consequences of climate change (loss of sea ice) as well as other factors related to human development (pollution from atmospheric transport). Marine ecosystems in the Arctic region involve a small number of key species at each trophic level (Murray et al. 1998) and food webs tend not to be especially complex because

species diversity is relatively low. Most of the species present, however, are important food sources for indigenous peoples (Huntington et al., 1998; Figure 4.5). Adequate management of these resources is crucial, and countries exploiting the resources in the Low Arctic and sub-Arctic regions have developed management procedures that are at least aimed at preventing overfishing. In the High Arctic region (mainly FAO Fishing Area 18), where only subsistence fishing occurs, fish stocks are not under management plans. The exception is Alaska, where a precautionary management plan prohibits commercial fishing until more information has been put in place to support sustainable fisheries management.

Table 4.6 lists the marine fish and shellfish species, marine mammals, and seabirds commonly harvested in the Arctic region (between May and October) for consumption and trade, with an estimate of how likely they are to be affected by ocean acidification either directly (via its effects on life functions of the organism) or indirectly (via its effects on a major prey of the organism). Table 4.6 shows that some indigenous groups depend on marine species that are at the highest risk of impact from ocean acidification, and thus there are potential risks of ocean acidification impacting on their food security (see Turley and Boot, 2011: their figure 13.2; Gattuso et al., 2011).

Table 4.7 summarizes the marine organisms that some Arctic indigenous peoples depend on, and shows the variety between geographical locations (Huntington et al., 1998). Most indigenous

groups harvest a range of organisms and can adapt by shifting their harvest to species not affected by ocean acidification, but there may be distinct seasonal losses or specific cultural losses resulting from changing harvests of some of these organisms. These impacts, combined with rising ocean temperatures and the resulting sea-ice reduction, suggest that the livelihoods of indigenous peoples will be increasingly compromised (Hovelsrud et al., 2011).

Developing an economic assessment of the potential ocean acidification driven losses for indigenous peoples and other local communities could underestimate the multiple values of marine harvests in Arctic cultures. Some peoples view natural resources as economic assets, whereas others view them as sources of cultural identity (Nuttall, 2002). Economically-based forms of accounting often insufficiently acknowledge political, cultural, or social factors and therefore provide limited insight into risk to Arctic peoples. For many Arctic indigenous peoples, the impact of a combination of changes, including climate change and ocean acidification, poses challenges in economic, social, cultural and environmental terms. The availability of and access to resources is fundamental to Arctic cultures and identities and for livelihood activities such as fishing (e.g., Nuttall, 2005; Ford and Furgal, 2009; Hovelsrud et al., 2011; Hoover et al., 2013). As such, ocean acidification represents a potential risk to Arctic food systems, as well as to cultures and livelihoods.

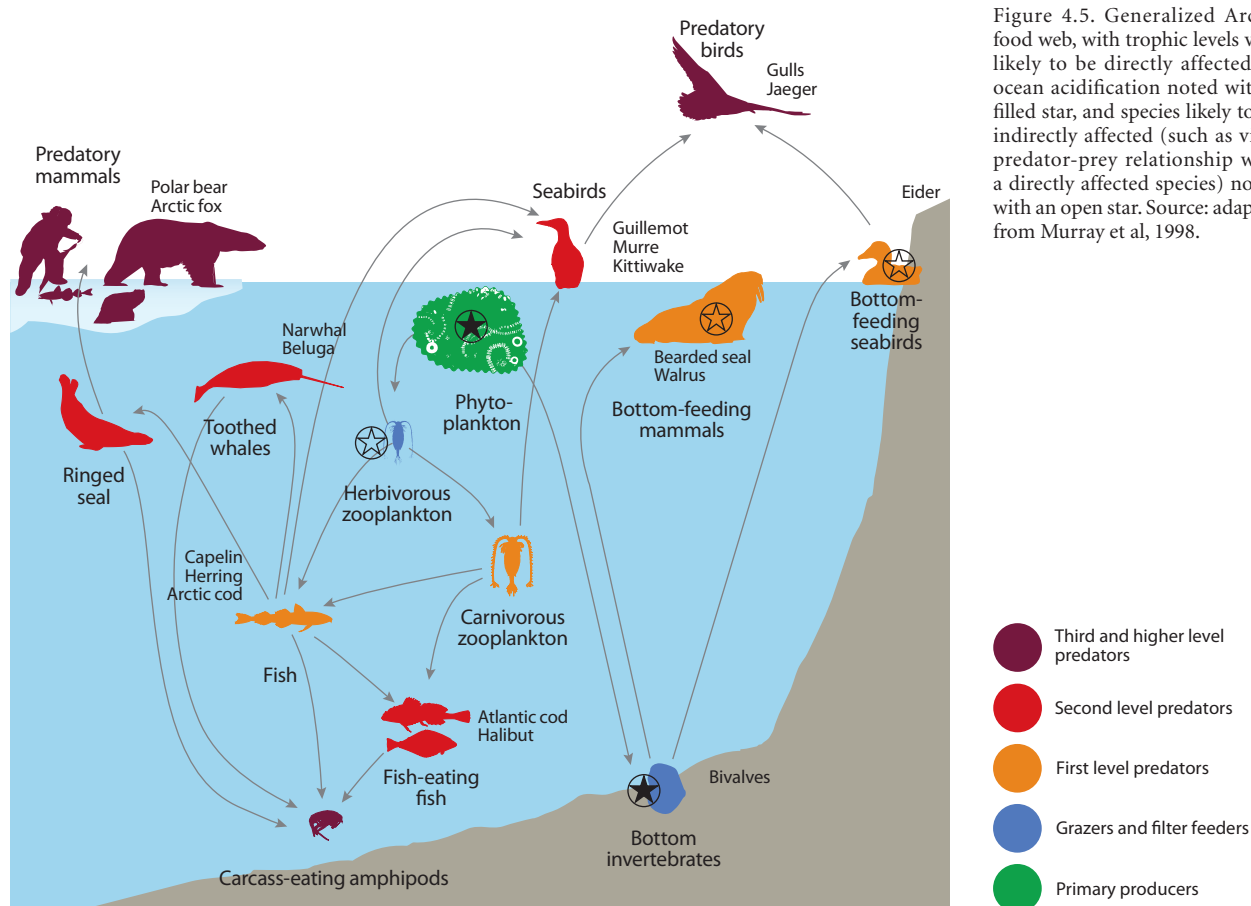


Figure 4.5. Generalized Arctic food web, with trophic levels very likely to be directly affected by ocean acidification noted with a filled star, and species likely to be indirectly affected (such as via a predator-prey relationship with a directly affected species) noted with an open star. Source: adapted from Murray et al., 1998.

Table 4.6. Arctic organisms harvested by indigenous peoples and their risk of effects of ocean acidification. Major prey items which are very likely or extremely likely to experience direct effects of ocean acidification are indicated. Risk of indirect effects from trophic relationships are indicated in the final column of the table: harvested species that prey on many directly impacted species have high risk; species that prey on a mixture of directly impacted species and non-impacted species have medium risk; and species that prey mostly on non-impacted species have low risk. Harvested organisms that are at greatest risk are at the top of each subgroup. Source: adapted from Huntington et al. (1998), Nuttall (2005), and Kroeker et al. (2013).

	Harvested organism	Major prey of harvested organism. Direct effects likely to occur in all entries marked by an 'X'.										Risk of prey-related (i.e. indirect) ocean acidification effects
		Mollusks other than squid ^a	Echinoderms ^a	Crustaceans (shrimp, crab) ^b	Phyto/Zooplankton/Krill ^b	Squid ^b	Smaller fish (incl. juvenile forms)	Invertebrates (benthic, worms, etc.)	Marine mammals	Plants	Insects	
Fish	Atlantic wolffish/ocean catfish	X	X	X								High
	Rough dab	X		X			X	X				Medium
	Redfish	X		X				X				Medium
	Arctic char	X					X				X	Medium
	Haddock		X	X			X					Medium
	Atlantic cod, Greenland halibut, Mackerel			X	X		X					Medium
	Salmon			X	X		X				X	Medium
	Blue whiting, herring			X	X							Medium
	Blue ling			X			X	X				Medium
	Greenland cod			X			X					Low
	Muksun, Siberian sturgeon, tusk			X				X				Medium
	Nelma/inconnu, ling				X		X					Low
	Capelin				X							Medium
	Coalfish, saithe						X					Low
	Greenland shark						X		X			Low
	Plaice							X				Low
Shellfish	Crab ^b	X	X	X				X				Medium
	Clams, scallops ^a				X							Low
	Shrimp ^b				X							Low
	Norway lobster/langoustine ^b						X	X				Low
Marine mammals	Bearded, harbor and hooded seals	X		X			X					Medium
	Walrus	X		X				X				Medium
	Narwhal			X		X	X					Medium
	Beluga whales			X			X	X				Low
	Harp and ringed seals			X			X					Medium
	Bowhead whales				X	X						Medium
	Fin and minke whales				X	X						Low
	Fur seals, pilot whales, sealions					X	X					Medium
	Common seals						X					Low
	Polar bear								X			Low
Seabirds	Arctic tern	X		X			X				X	Medium
	Ducks	X					X			X	X	Medium
	Sea gulls	X					X	X				Medium
	Eider	X						X				Medium
	Dovekie			X	X							Medium
	Thick-billed murre			X		X	X					Medium
	Black guillemot			X			X					Medium
	Kittiwakes				X	X						Low
	Cranes, geese						X			X	X	Low
	Swans									X		Low

^a Evidence exists that these organisms are *extremely likely* to be directly affected by ocean acidification; ^b evidence exists that these organisms are *very likely* to be directly affected by ocean acidification.

Table 4.7. Marine and coastal organisms harvested by Arctic peoples. Omission of a particular relationship in this table indicates lack of data rather than a lack of dependence. Source: adapted from Huntington et al. (1998).

Harvested animal		Aleut, Alutiiq	Athabaskan	Siberian Yupik	Inuit	Kalaallit	Icelanders	Faeroese	Northern Norwegians	Saami	Murmansk Oblast	Nenets and Yamalo-Nenets Autonomous Okrug	Taimyr Autonomous Okrug	Arctic Districts of Sakha Republic
Fish	Arctic char				×	×				×			×	
	Atlantic cod/cod					×	×	×	×	×	×			
	Atlantic wolffish ^a / ocean catfish ^a , capelin					×	×		×					
	Blue ling, blue whiting, coalfish, tusk, ling, mackerel							×	×					
	Greenland cod, saithe, Greenland shark					×								
	Greenland halibut/ halibut					×	×	×	×		×			
	Haddock						×	×	×		×			
	Herring						×	×	×		×		×	
	Muksun, nelma/inconnu												×	
	Plaice, rockfish										×			
	Redfish						×	×	×					
	Rough dab					×								
	Salmon	×	×			×			×	×	×			
	Siberian sturgeon												×	×
Shellfish	Norway lobster/langoustine, scallops						×		×					
	Shrimp					×	×		×					
Marine mammals	Bearded seals												×	
	Beluga whales		×		×	×						×	×	
	Bowhead whales			×										
	Common seals												×	×
	Fin whales, harbour, harp, hooded, seals; minke whales, Narwhal; polar bear					×			×					
	Pilot whales							×						
	Ringed seals					×							×	×
	Sealions													
	Walrus			×		×								
Seabirds	Arctic tern, dovekie, eider, sea gulls					×								
	Black guillemot, thick-billed murre					×					×			
	Cranes													
	Ducks				×							×	×	×
	Geese				×	×				×		×	×	×
	Kittiwakes										×			

^a Most likely to be affected by ocean acidification because of direct effects or a predominance of prey species that will suffer direct effects (see Table 4.6).

4.7 Impact of ocean acidification on the recreational value of Arctic ecosystems

Local people and tourists utilize many parts of the Arctic nature for recreational purposes, and have done so for decades, and even centuries. The tourism industry is one of the fastest growing global industries (Cisneros-Montemayor and Sumaila, 2010), also in the Arctic. In this region, the industry is based both on use values (e.g., fishing and hunting) and non-use values (e.g., whale and landscape watching) that people ascribe to nature. Some consumers are willing to pay a premium to travel from their lower-latitude countries to remote Arctic areas by plane or cruise ship (which contributes to the emission of greenhouse gases) to fish for their preferred trophy fish, though this does not represent the majority of recreational fishermen (Aas, 2008; Borch et al., 2011; NJFF, 2011). For many local people, their appreciation of nature is supplemented by its value as part of their cultural heritage and the fact that it provides a foundation for their commercial livelihoods. Recreational attractions are found on land, in freshwater and at sea.

In 2002, the Earth Summit in Johannesburg focused on sustainable tourism development. The World Tourism Organization defines sustainable tourism as *tourism which leads to management of all resources in such a way that economic, social and aesthetic needs can be fulfilled while maintaining cultural integrity, essential ecological processes, biological diversity and life support systems*. In addition, there is an increasing focus on eco-tourism and responsible tourism. In 2007, the Davos Declaration aimed at increasing knowledge of the links between tourism and climate change. In 2008, the Green Economy Report considered tourism as a main component of the Green Economy Initiative and created the term 'green tourism'. Finally, Rio+20 reinforced the global community's commitment to sustainable development in 2012.

With regard to tourism in the Arctic, there are three categories potentially at risk:

- Land-based tourism in the coastal zone.
- Recreational activities in inshore waters by local people and long-distance foreign tourists.
- Ocean and coastal cruising.

The Arctic marine ecosystem is changing owing to several stressors, including ocean acidification (see Chapters 1, 2 and 3). This will affect lower-trophic (e.g., krill and fish) and higher-trophic (e.g., seabirds and marine mammals) species. Whale watching is a rapidly expanding form of ecotourism that contributes to coastal economies, also in countries with whaling activities, such as Iceland, Norway and the USA (Cisneros-Montemayor and Sumaila, 2010; Cisneros-Montemayor et al., 2010). With the rapidly changing environmental conditions in the Arctic area, whale migration routes may change, thus enabling mixing between populations that was previously inhibited (Heide-Jørgensen et al., 2010). Walrus (*Odobenus rosmarus*) may be affected by ocean acidification (Jay et al., 2011), as well as most cetaceans and pinnipeds, but to what extent is still not known.

Acidification of the ocean may, or may not, have direct and indirect economic and employment effects on tourism activities

in the Arctic region. A major issue is which species are affected, and to what extent, and how these are valued by tourists. To the extent that people ascribe different values to particular species and ecosystems as a whole, the economic effects on the local and national economy may differ. This is due to both natural and social causes, of which the latter includes demographic shifts, income changes, economic structural changes and trade. Recreational fishing has been defined by the FAO as *Fishing of aquatic animals that do not constitute the individual's primary resource to meet nutritional needs and are not generally sold or otherwise traded on export, domestic or black markets* (quoted from Borch et al., 2011). Marine fishing tourism in Norway is an example of a growing industry based on the recreational value of fish resources and other natural amenities. The long and mainly sheltered Norwegian coastline makes recreational salt-water fishing attractive for increasing numbers of people from other European countries. Historically, domestic people, both rural and urban, have used the fish resources not only for commercial purposes, but also for nutritional needs and recreation. Long distance recreational fishers are still quite few.

The mix of fish species caught in recreational fisheries varies across countries and regions (e.g., Aas, 2008). Recreational fishers are attracted by the fish itself and by the natural amenity services at the fishing spot. Well-managed stocks with fish that taste good, look nice, are big, and are strong fighters (trophy fish) are in greatest demand and fishers are willing to pay for the recreational provision of nature (Toivonen et al., 2004; Flaaten, 2011). Vølstad et al. (2011) provided data on catches in Norway's coastal tourist fishery and from this concluded that tourist fishers behave opportunistically by simply catching what is available. Cod and saithe are the dominant species in the north of Norway, while saithe, mackerel and ling are the major species in the south. But the key question that remains is which of these species will be most affected by global warming and ocean acidification?

If ocean acidification mainly affects crustaceans and mollusks at lower trophic levels, the fishing tourism industry and recreational fishing may hardly be affected unless there is some indirect impact via the food web. Recreational fishing of marine crustaceans is not common in the countries bordering the Arctic Ocean, but there are some exceptions, such as lobster (*Homarus gamarus*) and red king crab (*Paralithodes camtschaticus*) in Norway. Note that red king crab in this country is an alien species that many people think should be eradicated.

Tourists and local recreational fishers in the AMAP area appear adaptive and target those species available in their areas. To the extent that ocean acidification will affect some species more than others this may in the future alter the relative composition of recreational catches by tourists and local residents, but it is not likely that people's overall pleasure and welfare will be affected by such a change. Over this long period, commercial harvests of some species have risen and declined (e.g., North Sea cod, *Gadus morhua*), others have fluctuated, but still sustain great fisheries (e.g., Norwegian spring-spawning herring *Clupea harengus*). As a result of human carbon dioxide emissions, the average acidity of surface ocean waters worldwide is now about 30% higher than at the start of the Industrial Revolution (Chapter 1, Section 1.1). It is not known if and to what extent this 30% increase in ocean acidification has contributed to the

decline in some stocks and fluctuations in others or what will be the impacts of future changes in Arctic Ocean acidification.

Fishing is important for recreational activities of tourists and local people in the Arctic. It may therefore be of grave concern if important species are impacted by acidification, directly or indirectly through effects on important prey species as well as on the phytoplankton and zooplankton communities. Increased research into ocean acidification and its implications for specific ecosystems and stocks now takes place in many countries, also in the Arctic (e.g., Cooley et al., 2009; IMR, 2011). A study of economic impacts of global warming on the Barents Sea fisheries indicated that the management system in operation seems to be of greater importance for future fishery performance than possible environmental changes caused by global warming (Eide, 2007).

4.8 Marine management in the face of ocean acidification

Identifying specific management measures to stem the impacts of ocean acidification is virtually impossible because ocean acidification is occurring in combination with many other anthropogenic stressors affecting marine ecosystems. Hence, in addition to mitigating the emissions of greenhouse gases, it is crucial that marine ecosystems are strengthened, for example by not overfishing, to make them sufficiently resilient to withstand the effects of multiple stressors, including ocean acidification. To this end, the following management measures need to be reinforced where they exist or introduced where they do not.

- In 1996, Arctic nations put in place a cooperative framework, embodied in the Arctic Council, where a priority given to scientific research and with less emphasis placed on remedial action. The existing arrangement is voluntary, with few resources for cooperative action. Changes in the Arctic are due to global factors (ACIA, 2005), but the consequences (ecological aspects and development) will occur at the regional level. Arctic nations would have to fight global developments through cooperation and mutual efforts to protect their marine environment and their traditional way of life.
- There is a need to establish and maintain, with appropriate management, marine protected areas to increase resilience of marine habitats to ocean acidification and support fish and shellfish populations for sustainable marine harvests. Marine protected areas need to be designed carefully in order to be successful (Polacheck, 1990; Sumaila et al., 2000; Fernandes et al., 2009; Flaaten and Mjølhus, 2010; Osmond et al., 2010).
- Adaptive management of aquaculture species and methods (e.g., selection of resistant species, and selective breeding and improvement of aquaculture practices) might provide solutions to impacts of ocean acidification on specific seafood sources to enhance future economic and social opportunities.
- Arctic nations need to coordinate their efforts to promote sustainable development of the natural and living resources and of the region's people. New development opportunities and threats will also appear from expanding economic

activities (new shipping routes, oil and gas exploration, new commercial fishing). These create new management challenges that require cooperation between the different Arctic nations and provide a transboundary approach that includes a monitoring system to evaluate the health of ecosystems.

- The initiative for an ecosystem-based management system for the Arctic environment adopted by the Arctic Council needs to be further strengthened.
- The Arctic region needs a sustainable tourism strategy. This is because tourism is predicted to increase at the same time as the impacts of ocean acidification on tourism are predicted to increase.
- It would be beneficial to apply traditional knowledge in marine management systems to tackle ocean acidification and other global change multi-stressors. See Binder and Hanbidge (1993), Joks (2003), Manseau et al. (2005) and Berkes et al. (2007), for discussions of the role of traditional knowledge in the management of marine ecosystems.

4.9 Concluding remarks

Fish stocks would be more resilient to ocean acidification if the combined stresses from overfishing, habitat degradation, pollution runoff, land-use transformation, competing aquatic resource uses and other anthropogenic factors are minimized. People have had to adapt to changes in fish stocks and catches over time owing to other factors, such as seasonal, inter-annual and multi-decadal climate variability. Experience gathered over the years could inform the adaptation strategies needed even though the scale and speed of the expected changes in relation to ocean acidification are much greater than have been observed to date. Possible adaptation strategies in the face of dwindling fish stocks include restricting the use of particular gear types and the implementation of livelihood diversification measures.

Adaptation and mitigation measures can either be carried out in anticipation of future effects, or in response to effects once they have occurred. Some can be implemented via public institutions, others by private individuals. Responses to the direct effects of adverse events on fisheries infrastructure and communities may be more effective if they are anticipatory, as part of a long-term participatory, broad-based approach to fisheries management (Sumaila et al., 2011). Such an integrated approach has the potential to increase ecosystem and community resilience and to provide a valuable framework for dealing with ocean acidification.

Ocean acidification is expected to affect fish stocks, marine ecosystems and the commercial, subsistence, and recreational fisheries of the Arctic. However, many aspects of this issue are still unknown. Interdisciplinary studies that investigate fisheries responses to ocean acidification are needed. This contribution is therefore only a start in the long journey to determine the bio-economic effects of ocean acidification in the Arctic. Ultimately, reducing carbon dioxide emissions is the only way to control increases in ocean acidification. Thus, it is important that while adaptation measures may help to some degree, all with interests in the fisheries of the Arctic sector should strengthen the case for lower carbon dioxide emissions.

5. Conclusions and further work

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5.1 The changing Arctic

In concert with the rising atmospheric concentration of carbon dioxide (CO₂), the ocean inorganic carbon inventory is increasing due to a net air-sea flux of CO₂ at the surface. Atmospheric CO₂ levels are the highest for at least 800 000 years and, generally, global ocean surface CO₂ increases are following the atmospheric change. Consequently, the pH of the ocean is going down and the relative speciation of inorganic carbon is changing at a rate likely to have been unsurpassed over the past 55 million years (Kump et al., 2009). This process has been termed ocean acidification; following the increase in the concentration of hydrogen ions in seawater. The Arctic is inherently susceptible to ocean acidification as it has a low buffer capacity and as such will exhibit greater changes in ocean acidification per unit CO₂ increase. As in most of the world oceans, the major driver of ocean acidification in the Arctic Ocean is directly attributable to the increasing atmospheric carbon load following the combustion of fossil fuels and land use changes. However, rapid ocean warming and ice melt are accelerating ocean acidification over most of the Arctic. Carbonate chemistry responds not only to the trends in atmospheric CO₂ but also to shorter-term ocean climate variability. The solubility and biological pumps exert a huge influence on seasonal changes in carbonate chemistry, where the greatest surface annual changes are associated with the seasonal-ice zone over the Arctic shelves. Ocean acidification will affect some nutrient and micronutrient availability for biological production and may change the bioavailability of some trace metals. The Arctic Ocean has already crossed significant geochemical thresholds following ocean acidification and, without significant reductions in atmospheric CO₂ concentrations, ocean-wide aragonite (one of the two most common biogenic calcium carbonate minerals in the oceans) undersaturation will occur. These changes will be long-lasting with high levels of ocean acidification persisting for many thousands of years unless CO₂ emissions are curtailed. Even if emissions peak today, the system will not return to pre-industrial levels for tens of thousands of years. Ocean acidification is only one of the stressors on the Arctic Ocean system. In concert with ongoing ocean warming and freshening are changes to ocean productivity and heterotrophy which, along with the increasing organic carbon supply are rapidly changing the oxygen distributions in the Arctic. Changing sea-ice cover is changing the light and turbulence regimes and therefore impacting on air-sea fluxes and ocean productivity. All these processes interact with the carbon cycle and thus may either compound or alleviate ocean acidification.

5.2 Experimental direction

There is an almost complete lack of information on the effects of ocean acidification – in isolation or in combination with other environmental stressors such as temperature, salinity, oxygen concentration – on keystone species and processes in the Arctic. Accordingly, there is an urgent need for focused research on

the likely impacts of ocean acidification on a range of taxa and processes. Notwithstanding logistic difficulties, experiments should be conducted *in situ* whenever possible and/or using pelagic and benthic mesocosms. It will also be important to conduct experiments over timescales that are more relevant ecologically than the very short-term experiments typical of this field to date. To increase confidence in the conclusions and interpretations of experiments, multiple biological and ecological end-points should be assessed simultaneously. The responses of key components of Arctic and sub-Arctic food webs to ocean acidification must be assessed and compared with those observed for organisms in other geographic regions. Such studies would need, for example, to consider the following: viral and microbial communities; heterotrophic and mixotrophic protists; planktonic and under-ice microalgae, including how seasonal changes in sea-ice coverage influence primary production and carbon transfer through the food web; the effects of ocean acidification on Arctic coral species and the effects of acidification-mediated loss of unprotected coral structure on coral-associated biodiversity; crustaceans, especially the copepods *Calanus finmarchicus*, *C. hyperboreus* and *C. glacialis*, amphipods (*Themisto libellula*), pteropods (mostly *Limacina helicina*) and commercially important crabs; fish, especially Arctic cod (*Arctogadus glacialis*), polar cod (*Boreogadus saida* – termed ‘Arctic cod’ in North America), and capelin (*Mallotus villosus*); seabirds; and marine mammals (e.g., to assess the dietary flexibility of seabirds and marine mammals in switching to food sources not affected by ocean acidification). Adaptive capacity (over multiple generations) and environmental plasticity of all stages of an organism’s life-cycle must be assessed. This could include (but need not be limited to): long-term transgenerational and selective-breeding experiments; long-term studies investigating adaptations and acclimation capacity; long-term studies investigating the potential for effects to ‘carry-over’ to subsequent life stages and/or generations; the issue of whether the increased generation time of many Arctic species confers reduced adaptive capacity to near-future climate change (in comparison to temperate and tropical species); multi-population studies to quantify genetic and phenotypic intra-specific variation of key traits influencing fitness; effects of multiple stressors (ocean acidification, carbonate saturation state, temperature, salinity, oxygen, toxins...) on species-level and ecosystem-level processes (including trophic interactions); and the effects of food limitation / nutritional status on species-level and ecosystem-level processes (e.g., do Arctic species show the same amelioration of ocean acidification impacts under high food / nutrient levels?).

5.3 Socio-economic advances

A comprehensive assessment of the socio-economic consequences of ocean acidification needs to build upon a solid scientific understanding of the chemical changes and biophysical effects of these changes. As stated at the start of the previous section, “There is [at present] an almost complete

lack of information on the effects of ocean acidification” on the biophysics of the ocean. Given this limitation, the only avenue left to economists and other social scientists is to rely on theoretical and simulation modeling together with scenario building to keep advancing our socio-economic understanding of the potential impacts of ocean acidification.

Based on these approaches, it is concluded that fish stocks will be more resilient to ocean acidification if the combined stresses from overfishing, habitat degradation, pollution runoff, land-use transformation, competing aquatic resource uses and other anthropogenic factors are minimized. People have had to adapt to changes in fish stocks and catches over time resulting from fishing pressure combined with other factors, such as seasonal, inter-annual and multi-decadal climate variability. Experience gathered over the years could inform the adaptation strategies needed; however, the scale and speed of the expected changes in relation to ocean acidification and ongoing climate change are generally much greater than have been encountered to date. Possible adaptation strategies in the face of dwindling fish stocks include restricting the use of particular gear types and the implementation of livelihood diversification measures. Adaptation and mitigation measures can either be carried out in anticipation of future effects, or in response to impacts once they have occurred. Some can be implemented via public institutions, others by private individuals. Responses to the direct effects of adverse events on fisheries infrastructure and communities may be more effective if they are anticipatory, as part of a long-term participatory, broad-based approach to fisheries management. Such an integrated approach has the potential to increase ecosystem and community resilience and to provide a valuable framework for dealing with ocean acidification.

Ocean acidification is expected to affect fish stocks, marine ecosystems and the commercial, subsistence, and recreational fisheries of the Arctic. However, many aspects of this issue are still unknown. Interdisciplinary studies that investigate fisheries responses to ocean acidification are needed. This contribution is therefore only a start in the long journey to determining the bio-economic effects of ocean acidification in the Arctic. Ultimately, reducing CO₂ emissions is the only way to control increases in ocean acidification. While adaptation measures may help to some degree, all with interests in the Arctic fisheries should strengthen the case for lower CO₂ emissions.

5.4 An interdisciplinary approach

The important advances that have come from recent cooperation between many scientific research disciplines and marine resource end-users (including fishers and indigenous peoples groups) illustrate an awareness of the need to collaborate at the science and policy levels in order to understand the extent and consequences of Arctic Ocean acidification. It is apparent that the changes in Arctic Ocean acidification are happening faster than in any other ocean basin. This requires a unique research perspective that challenges the paradigm that ocean carbonate chemistry follows atmospheric CO₂ increases directly. Despite the lack of *in situ* data, current understanding of the marine carbonate system is sufficient to state that ocean CO₂ will increase faster in the Arctic than elsewhere and that critical thresholds for particular geochemical and biological processes will be

reached first in the Arctic. As a consequence, experimentation on organisms and ecosystems and the interpretation of experimental results of biotic response should not be restricted to only following the ‘average state’ or timescales implied by the scenarios of atmospheric CO₂ evolution developed by the Intergovernmental Panel on Climate Change (IPCC). Doing so could result in incomplete or inadequate information to inform the policy debate. Instead, each unique habitat, ecosystem or biome should be studied to determine the potential impacts of future ocean acidification on it. The information on future ocean acidification should dictate the range of conditions that need to be addressed in biological experimentation. This will in-turn furnish relevant information for climate mitigation and socioeconomic policy measures.

5.5 Monitoring networks

The Arctic is one of the least understood regions on the planet and current understanding of the marine components of the Arctic carbon cycle is based largely on very few measurements combined with extrapolation of what is known about the functioning of other ocean systems. It is of paramount importance that long-term, dedicated marine carbonate system observation programs are developed. As the Arctic is undergoing changes in other biogeochemical and ecological stressors, these programs should be integrated within a framework that monitors the changes in the key variables including oxygen, temperature, salinity and nutrients. These programs should be in the form of repeated surveys, *in situ* observational platforms such as moorings, drifting buoys and ocean gliders. New technologies are required to enable measurements under Arctic conditions where the exceptional challenges, including low temperatures and ice cover, require advances in instrument design. It is imperative that the physico-chemical monitoring is coordinated closely with biological observations. Management of platform design, observational logistics and data management should, preferably, be coordinated at the international level.

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Glossary

Ω_{Ar}	Saturation state of aragonite	O ₂	Oxygen
Ω_{Ca}	Saturation state of calcite	OM	Organic matter
A _T	Total carbonate alkalinity	pCO ₂	Partial pressure of carbon dioxide
C	Carbon	pH	Acidity or concentration of hydrogen ions in a solution
Ca ²⁺ / [Ca ²⁺]	Calcium ion / Concentration of calcium ions	POC	Particulate organic carbon
CaCO ₃	Calcium carbonate	POM	Particulate organic matter
C _{ant}	Anthropogenic carbon dioxide	TEP	Transparent exopolymeric particles
Cd	Cadmium	Zn	Zinc
CH ₄	Methane		
CO ₂	Carbon dioxide		
C _T	Total inorganic (dissolved) carbon		
Cu	Copper		
DMS	Dimethylsulfide		
DMSP	Dimethylsulfoniopropionate		
DOC	Dissolved organic carbon		
DOM	Dissolved organic matter		
ESM	Earth system model		
FAO	United Nations Food and Agriculture Organization		
Fe	Iron		
GDP	Gross domestic product		
GRP	Gross regional product		
H ⁺ / [H ⁺]	Hydrogen ion / Concentration of hydrogen ions		
IPCC AR5	Fifth Assessment Report of the Intergovernmental Panel on Climate Change		
Mg ²⁺	Magnesium ion		
N	Nitrogen		
NH ₃	Ammonia		
NH ₄ ⁺	Ammonium		

Arctic Monitoring and Assessment Programme

The Arctic Monitoring and Assessment Programme (AMAP) was established in June 1991 by the eight Arctic countries (Canada, Denmark, Finland, Iceland, Norway, Russia, Sweden and the United States) to implement parts of the Arctic Environmental Protection Strategy (AEPS). AMAP is now one of six working groups of the Arctic Council, members of which include the eight Arctic countries, the six Arctic Council Permanent Participants (indigenous peoples' organizations), together with observing countries and organizations.

AMAP's objective is to provide 'reliable and sufficient information on the status of, and threats to, the Arctic environment, and to provide scientific advice on actions to be taken in order to support Arctic governments in their efforts to take remedial and preventive actions to reduce adverse effects of contaminants and climate change'.

AMAP produces, at regular intervals, assessment reports that address a range of Arctic pollution and climate change issues, including effects on health of Arctic human populations. These are presented to Arctic Council Ministers in 'State of the Arctic Environment' reports that form a basis for necessary steps to be taken to protect the Arctic and its inhabitants.

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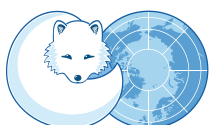
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