Arctic Ocean carbon biogeochemistry under climate change and ocean acidification

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Scientific environment

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Abstract

Human-induced CO_2 emissions to the atmosphere cause climate change and ocean acidification. The strongest indicators of climate change and ocean acidification are expected to be found in the Arctic Ocean (AO). The AO area is small compared to the world ocean, but the global influence of its carbon biogeochemical system with large spatial and temporal variability is considerable and complex. The AO carbon biogeochemical system is also expected to experience feedback in regard to climate change, and to influence the energy flow throughout the Arctic food web. This thesis investigates the carbon biogeochemical system in the AO: present variability; coupling with processes at the low trophic level; and response to future climate and CO_2 scenarios. The study combines differing methodological approaches: (i) in-situ observations, (ii) field perturbation experiments, and (iii) ecosystem modeling. The thesis is based on four separate papers. **Paper I** describes the natural variability of particulate organic carbon and particulate organic nitrogen in a composition of seston and estimates the carbon to nitrogen (C:N) ratio in the AO seston. The paper is based on 3672 in-situ measurements gathered from sources both published and unpublished. The overall C:N ratio in seston was 7.4, which is significantly higher than the classical Redfield ratio of 6.6. A great regional variability in the seston C:N ratio was found. **Paper II** introduces the inorganic carbonate system around the Svalbard archipelago in the AO, at present and under future climate and CO_2 scenarios. This paper is based on results from a coupled physical-biogeochemical ecosystem model forced by SRES A1B scenario, as well as on results of a CO_2 perturbation study on the natural community conducted in an Arctic fjord. The results presented in this paper suggest that seawater pCO_2 in the area around Svalbard at the end of the 21st century will be 300 μatm higher than at present in the Atlantic influenced region, and 400 μatm higher than at present in the Arctic influenced region. As a result, the waters in the Arctic-influenced region will be undersaturated with respect to aragonite, and waters in the Atlantic-influenced region will be close to the undersaturation state. The modeled summer decrease in seawater pCO_2, and the increase in pH and aragonite saturation state are all steeper in the future. This was

also observed during an experiment on ocean acidification in natural phytoplankton assemblage, which was perturbed with the projected high levels of seawater pCO_2. **Paper III** is based on results from two model simulations, performed with the coupled physical-biogeochemical ecosystem model forced by SRES A1B scenario, parameterized with the constant C:N ratio and with the pCO_2 sensitive C:N ratio. The paper demonstrates that more inorganic carbon could be fixed by autotrophs in the future surface Arctic waters if annual primary production increases in response to the pCO_2 sensitive C:N ratio. As a result of higher primary production, and consequently higher export production in case of pCO_2 sensitive C:N ratio, more carbon is released below the euphotic zone, which leads to lower pH and aragonite saturation states than in case with the constant C:N ratio. **Paper IV** is based on the results of the large-scale CO_2 perturbation experiment, revealing enhanced carbon fixation by autotrophs at high levels of pCO_2 when the phytoplankton assemblage was dominated by a small-sized phytoplankton group. The results of the paper suggest that net community production could enhance if small-sized phytoplankton thrives in the future Arctic Ocean.

The introduction to the thesis provides a comprehensive overview of the carbonate system and processes controlling it. The AO carbon biogeochemistry is introduced, with its uniqueness and importance for the earth climate system. The findings of the four papers are summarized and future prospects for carbon biogeochemistry research in the AO are discussed.

List of papers

Paper I

Frigstad, H., Andersen, T., Bellerby, R. G. J., **Silyakova, A**., & Hessen, D.O.: Variation in the seston C:N ratio of the Arctic Ocean and pan-Arctic shelves. *To be submitted to Journal of Marine Systems.*

Paper II

Bellerby, R. G. J., **Silyakova, A**., Nondal, G., Slagstad, D., Czerny, J., de Lange, T., and Ludwig, A.: Marine carbonate system evolution during the EPOCA Arctic pelagic ecosystem experiment in the context of simulated future Arctic ocean acidification. *Biogeosciences Discussions, 9, 15541-15565, 2012. Manuscript in open discussion, final response.*

Paper III

Silyakova, A., Bellerby, R.G.J., Frigstad, H., Jeansson, E., Nondal, G., & Slagstad, D.: The effect of increasing pCO_2 and C:N stoichiometry on primary production and ocean acidification in the future Arctic Ocean. *Manuscript in preparation.*

Paper IV

Silyakova, A., Bellerby, R.G.J., Czerny, J., Schulz, K.G., Nondal, G., Tanaka, T., Engel, A., De Lange, T., Riebesell, U.: Effect of ocean acidification on net community production and stoichiometry of nutrient consumption during a mesocosm experiment in an Arctic fjord. *Biogeosciences Discussions 9, 11705-11737. Resubmitted manuscript is under review for Biogeosciences.*

Contents

1. Background

1.1 Emissions of carbon dioxide

The main cause of human-induced climate change is the emission of carbon dioxide (CO_2) into the atmosphere (Doney et al., 2009). CO_2 is a greenhouse gas and is released during the burning of fossil fuels, cement production and land-use changes (GCP[1] report No. 7, 2010; GCB[2], 2012). As the atmospheric CO_2 concentration rises, the atmospheric partial pressure of CO_2 ($pCO_{2(atm)}$) increases. The longest record of $pCO_{2(atm)}$ is at the Mauna Loa station (Hawaii, Pacific Ocean), from 1958. It reveals an increase in $pCO_{2(atm)}$ of 70 parts per million (ppm) between 1960 and 2010 (Fig. 1). The observed increase in $pCO_{2(atm)}$ is estimated to be three-to-four times larger, and is taking place 70 times faster than in the last 20-30 million years (Zeebe, 2012). Political efforts have been made to reduce CO_2 emissions to the atmosphere (e.g. the Kyoto protocol in 1997). However, observations of atmospheric CO_2 show that the concentration is rising steadily by approximately ~0.5% $year^{-1}$ (Forster et al., 2007), as CO_2 emissions to the atmosphere are increasing by approximately 3% every year (Le Quere et al., 2009; Olivier et al., 2011).

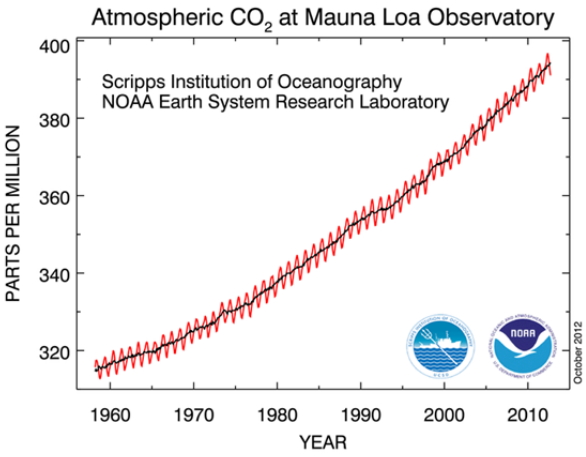

Figure 1. Curve at Mauna Loa of the partial pressure of atmospheric CO2 (http://www.esrl.noaa.gov/gmd/ccgg/trends/)

[1] Global Carbon Project

[2] Global Carbon Budget

Future atmospheric $pCO_{2(atm)}$ scenarios are developed and summarized by the IPCC[3]. The atmospheric CO_2 scenarios SRES[4] A2 and SRES A1B of the IPCC Assessment Report 4 (AR4) have been widely used as input to the earth system carbon-climate and biogeochemical models in recent years (e.g. Fung et al., 2005; Oschlies et al., 2008; Steinacher et al., 2009) (Fig. 2). For IPCC AR5, a new generation of atmospheric CO_2 scenarios has been developed. The purpose of the new RCP[5] CO_2 scenarios is to include a better combination of economic, technological, demographic, policy and institutional factors, as well as global developments and technological improvements. New scenarios provide better estimates of carbon sources and sinks within the global carbon cycle (Fig. 2).

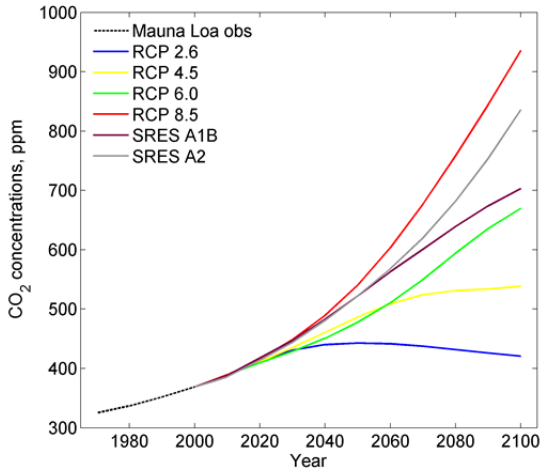

Figure 2. Atmospheric CO_2 concentrations as observed at Mauna Loa from 1958 to 2008 (black dashed line), four projected RCP scenarios from the IPCC AR5 (data available at http://www.iiasa.ac.at/web-apps/tnt/RcpDb/dsd?Action=htmlpage&page=download), and two projected SRES scenarios from IPCC AR4 (data available at http://www.ipcc-data.org/ancilliary/tar-bern.txt)

The atmospheric CO_2 concentration is greatly mitigated by the net absorption of CO_2 by land and ocean, so that the anthropogenic CO_2 emissions are not directly mirrored in the proportion of CO_2 in the atmosphere. The land and ocean combined has taken up 55% of all anthropogenic CO_2 emissions since 1959 (Ballantyne et al., 2012). Approximately 25-30% of annual anthropogenic CO_2 emissions are currently taken up by the ocean (GCP, 2010). The ocean has a great capacity to take up atmospheric CO_2 and once there it exerts a great influence on the carbonate system of the ocean.

[3] Intergovernmental Panel on Climate Change

[4] Special Report on Emission Scenarios

[5] Representative Concentration Pathways

1.2 Contemporary carbonate system of the ocean

The characteristics of the oceanic carbonate system arise from a synergy between the solubility pump and the two biological pumps – the organic carbon pump (or soft-tissue carbon pump) and the calcium carbonate ($CaCO_3$) counter pump (or hard tissue pump) (Fig. 3).

The solubility pump is driven by two simultaneous processes:

- solubility of CO_2 in seawater
- thermohaline circulation

The solubility of CO_2 in water follows Henry's law for gases so that the pCO_2 in the air-sea interface (just above the sea surface) is proportional to the CO_2 concentration in the sea surface layer provided that these layers are in thermodynamic equilibrium. Disequilibrium is due to a gradient between pCO_2 in the air-sea interface ($pCO_{2(atm)}$) and in the sea surface layer ($pCO_{2(sw)}$); this gives rise to a CO_2 flux (FCO_2) as follows:

$$FCO_2 = \alpha k(pCO_{2(sw)} - pCO_{2(atm)}) \quad \text{(Eq. 1)}$$

where, α is the solubility of CO_2 in μmol m^{-3} atm^{-1} and k is a gas transfer velocity in cm hr^{-1}. The solubility depends on temperature and salinity, and the transfer velocity depends on processes such as wind, tides, organic films on the surface and rain.

In cold and fresh water, CO_2 is readily soluble, with the molecules of gaseous CO_2 reacting with molecules of water to form carbonic acid (Eq. 2). Carbonic acid dissociates further to bicarbonate ion and hydrogen ion. Hydrogen ion reacts further with a carbonate ion, which is present in seawater, to form another bicarbonate ion:

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \xleftrightarrow{K_1} HCO_3^- + H^+ \xleftrightarrow{K_2} CO_3^{2-} + 2H^+ \quad \text{(Eq. 2)}$$

where K_1 and K_2 respectively denote the first and second dissociation constants of carbonic acid.

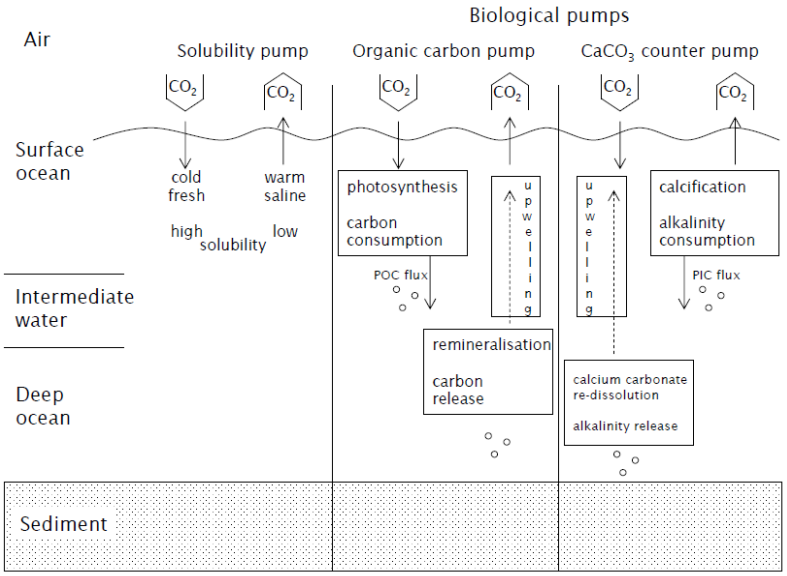

Figure 3. Schematic of the three pathways of atmospheric CO_2 to the ocean (after Heinze et al, 1991)

In warm and saline waters CO_2 is much less soluble, and more molecules of CO_2 remain in seawater in gaseous form.

CO_2 in seawater travels with thermohaline circulation along the global conveyor belt. Regions with cold surface water and regions of deep-water formation normally act as a CO_2 sink. Regions with warm surface waters and upwelling regions (where deep waters are brought up) may act as CO_2 sources.

In general, $pCO_{2(sw)}$ is greater in the deep ocean than near the surface. This is because of photosynthesis in the surface ocean and respiration of organic matter in the deep ocean. The processes of photosynthesis and respiration (Eq. 3, Redfield et al., 1963) partly represent the biological soft-tissue carbon pump of CO_2,

$$106CO_2+16NO_3+HPO_4+122H_2O+18H+E\leftrightarrow\{C_{106}H_{263}O_{110}N_{16}P_1\}+138O_2 \qquad \text{(Eq. 3)}$$

Photosynthesis in the ocean occurs in the upper sunlit layer, known as the euphotic zone. At optimal light and temperature conditions and in the presence of nutrients, autotrophic organisms (phytoplankton) fix inorganic carbon (C), nitrogen (N), phosphorus (P), water and hydrogen ions to form organic matter, also releasing oxygen. As Equation (3) indicates, C, N, and P are bound in the ratio 106:16:1. The same ratio is applicable for the C:N:P composition of organic matter on the right-

hand side of Equation (3). This ratio of 106:16:1 for C, N and P is known as the classical Redfield ratio, and was derived empirically from a dataset of thousands of measurements of C and micronutrient composition of particulate matter (Redfield et al., 1963). The Redfield ratio has become fundamental in understanding biogeochemical cycles and biological processes in the ocean. It is widely applied in ecosystem modeling (e.g. Fasham et al., 1990) to parameterize conversions between nutrients and carbon, and to estimate the production of autotrophs from measurements of (for example) nitrogen (Dugdale and Goering, 1967).

The amount of C fixed to the soft tissues of the phytoplankton cells is often referred to as primary production. Oceanic primary production constitutes 50% of global primary production (Longhurst et al., 1995), emphasizing the large amount of carbon delivered to the ocean via the biological soft-tissue carbon pump. This also emphasizes that biological C fixation by oceanic vegetation is significant for the atmospheric pCO_2; this is because, by fixing C in the upper ocean layer, phytoplankton reduces $pCO_{2(sw)}$. A negative gradient occurs between $pCO_{2(sw)}$ and $pCO_{2(atm)}$, which allows for CO_2 flux from the atmosphere to the upper ocean, reducing $pCO_{2(atm)}$. Without the biological soft-tissue C pump, $pCO_{2(atm)}$ would be 100-150 ppm higher (Volk and Hoffert, 1985). Inorganic C, which is fixed by autotrophs in the upper ocean to the particulate organic matter (OM), is either transferred to higher trophic levels due to grazing, or is sequestered to greater depths where it is released to seawater as a result of respiration. In the upper ocean, inorganic C is mostly fixed, and below the euphotic zone inorganic C is mostly released. In addition to the biological soft-tissue carbon pump, there is a $CaCO_3$ counter pump. The fuel for the $CaCO_3$ counter pump is the process of biogenic calcification, in which the $CaCO_3$ is precipitated by diverse marine organisms to form shells and plates. Calcification is described by Equation 4 below, and involves calcium and ions of carbonate or bicarbonate such that $CaCO_3$ is formed with release of CO_2:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad \text{(Eq. 4)}$$

When $CaCO_3$ particles are dissolved in seawater (PIC or particulate inorganic carbon in Fig. 3), CO_2 is consumed. The calcium and carbonate ion concentrations divided by the solubility product ($K_{sp}^{CaCO_3}$) define the saturation state of the waters (Sarmiento and Gruber, 2006):

$$\Omega = \frac{[CO_3^{2-}][Ca^{2+}]}{K_{sp}^{CaCO_3}} \qquad \text{(Eq. 5)}$$

$\Omega > 1$ - water is supersaturated

$\Omega = 1$ - point of equilibrium

$\Omega < 1$ - water is undersaturated

There are two dominant forms of calcium carbonate in the ocean, calcite and aragonite, with differing crystalline structures. In the ocean the saturation state for aragonite is at lower values than for calcite. It follows that organisms which precipitate aragonite may be more sensitive to the carbonate system state.

1.3 Anthropogenic CO_2 perturbation of the ocean carbonate system

As was shown in section 1.1., anthropogenic CO_2 emissions lead to increasing $pCO_{2(atm)}$. As the oceans take up atmospheric CO_2, $pCO_{(sw)}$ increases and more CO_2 molecules react with water to form carbonic acid (Eq. 2).

Due to anthropogenic CO_2 increase, the balance of carbon species in contemporary carbonate system is modified (Doney et al., 2009); this change is called ocean acidification (Caldeira and Wickett, 2003). With ocean acidification the hydrogen ion concentration increases, so that the pH decreases. Since the start of the industrial era, the pH of the surface ocean has dropped globally by 0.1 pH units (Orr et al., 2005), corresponding to a 30% increase in $[H^+]$. According to the IPCC projections of CO_2 emissions (Houghton et al., 2001), the average pH of the surface ocean may drop by another 0.3-0.4 pH units by the end of the 21st century (Caldeira, 2005), which

implies a 100-150% increase in $[H^+]$ (Orr et al., 2005). There is a simultaneous increase in bicarbonate ions, but a decrease in carbonate ion concentration and the saturation state of calcite and aragonite. Because of imbalances in the carbonate system, ocean acidification may affect all three carbon pumps, so that their intensities and directions change. As $pCO_{2(sw)}$ rises, the concentration of carbonate ion reduces. The result is a decrease in the capacity of the ocean to take up atmospheric CO_2, and consequently a weakening of the CO_2 sink (Le Quere et al., 2007).

Ocean acidification may affect the biological carbon pump through the relative amounts of C, N and P consumed by autotrophs. High $pCO_{2(sw)}$ could cause enhanced C fixation relative to nutrient consumption (Riebesell et al., 2007; Bellerby et al., 2008). The consequences for the biological carbon pump would be the increased removal of CO_2 by autotrophs in the upper ocean layer, increased C sequestration and increased CO_2 release below the euphotic zone, due to organic matter degradation (Oschlies et al., 2008).

Ocean acidification may influence the $CaCO_3$ counter pump by altering biogenic calcification. Some experimental studies report reduced calcification in response to ocean acidification (e.g. Delille et al., 2005; Riebesell et al., 2000; Lischka et al., 2011), although some studies find enhanced calcification in response to ocean acidification (e.g. Iglesias-Rodriguez et al., 2008; Lohbeck et al., 2012). These contrasting responses of different calcifying organisms to ocean acidification indicate that the role of biology in the carbon cycle is to some extent unknown.

Changes in the ocean carbonate system and ocean acidification will not occur evenly; there will be regional differences. For example, warm waters at lower latitudes contain high concentrations of the carbonate ion, so that the buffer capacity of these waters is high. Cold waters at high latitudes contain a low concentration of the carbonate ion, and the buffer capacity of these waters is low. This implies that, for a given pCO_2 change, a greater change in carbonate system will be observed in cold waters of high latitudes.

Ocean acidification may significantly alter the natural variability of carbon species in regions of coastal upwelling (Feely et al., 2008; Hauri et al., 2009). Therefore calcifying benthic or pelagic marine organisms abundant in these regions may be affected on seasonal time scales before global mean changes in pH occur.

The Arctic Ocean (AO) is a unique and complex region in the context of inorganic carbon biogeochemistry. The carbonate system of the AO is controlled by numerous factors, including water mass exchange with the Atlantic and the Pacific oceans, local horizontal and vertical circulation of water masses, freshwater runoff from terrestrial systems, the presence of seasonal and multiyear sea ice, primary production and carbon flux from low to high trophic levels. The influence of these factors varies according to region and season, and may alter due to climate change. A broad overview of the AO environment, as well as the influence of surrounding areas, is provided in next chapter. The overview is necessary to give a better understanding of the AO carbon biogeochemical system, and to predict its response to changes.

2. The Arctic Ocean

2.1 Carbonate system of the Arctic Ocean

The AO comprises 4% of the world ocean by area, and is best analyzed via a pan-Arctic approach (Carmack and Wassmann, 2006) that takes into account the surrounding areas with which the AO interacts (Fig. 4). The AO is influenced by the inflow of warm and saline waters from the Atlantic and the Pacific Ocean, as well as by the inflow of freshwater rivers from surrounding land. The surface of the AO is covered with ice, some of which is multiyear ice, and some of which melts in summer and freezes again in winter.

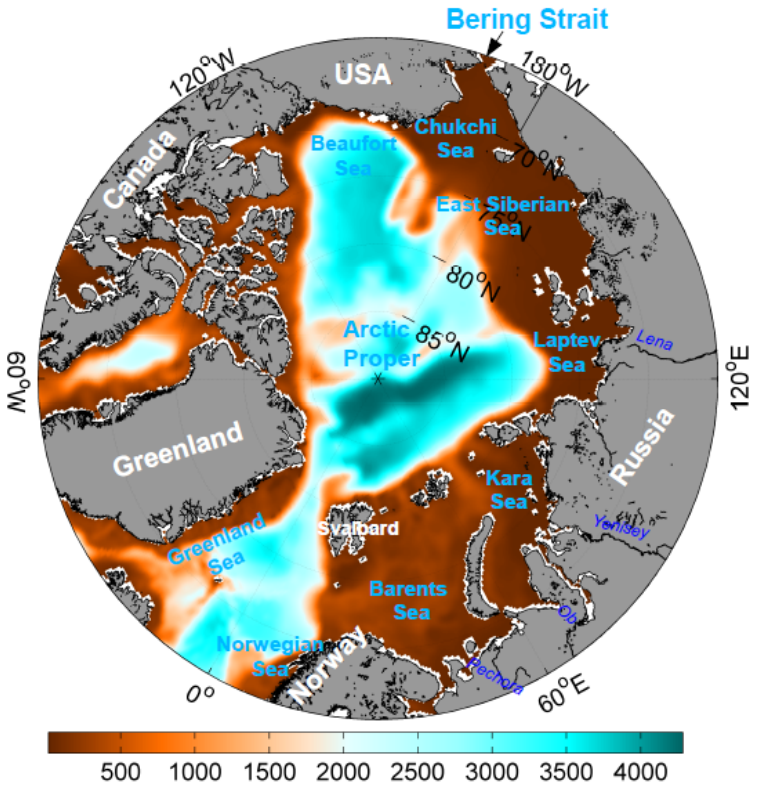

Figure 4. Schematic of the Arctic Ocean. Colors show depth in meters (the topography was adopted from a coupled physical-biogeochemical ecosystem model, SINMOD; see Slagstad and McClimans, 2005).

CO_2 has high solubility in the cold and relatively fresh waters of the AO. The present AO reservoir of inorganic carbon is consequently largely in the form of bicarbonate ions and the concentration of carbonate ion is low. The water temperature increases at

the beginning of summer, reducing the solubility of CO_2. This causes a movement towards more CO_2 dissolved in seawater and $pCO_{2(sw)}$ increases (Fig. 5). Later in summer, during the main phytoplankton bloom, $pCO_{2(sw)}$ decreases because of biological inorganic C fixation. In the fall, and at the beginning of winter, $pCO_{2(sw)}$ increases again, because CO_2 is released to seawater due to OM degradation and sea ice formation. Sea ice in the AO greatly influences carbonate dynamics. Sea ice is a complex system that consists of freshwater crystals and saline seawater fractions. When sea ice forms, salts and gases (including CO_2) are released with the brine rejection, and further CO_2 is released with the formation of calcium carbonate particles, known as ikaite crystals (Dieckmann et al., 2008, 2010; Rysgaard et al., 2012). Melting of sea ice leads to reverse processes, which reduce $pCO_{2(sw)}$. These processes include dilution of surface saline waters with fresh melt water, which contains almost no gases; and dissolution of ikaite crystals which is a source of excess total alkalinity (Rysgaard et al., 2012). The carbonate system of the AO is further influenced by sea ice dynamics and properties. For example, the CO_2 flux could be enhanced through the sea ice, which has high porosity (Loose et al., 2011), and the direction of this flux is defined by the difference between $pCO_{2(sw)}$ and $pCO_{2(atm)}$.

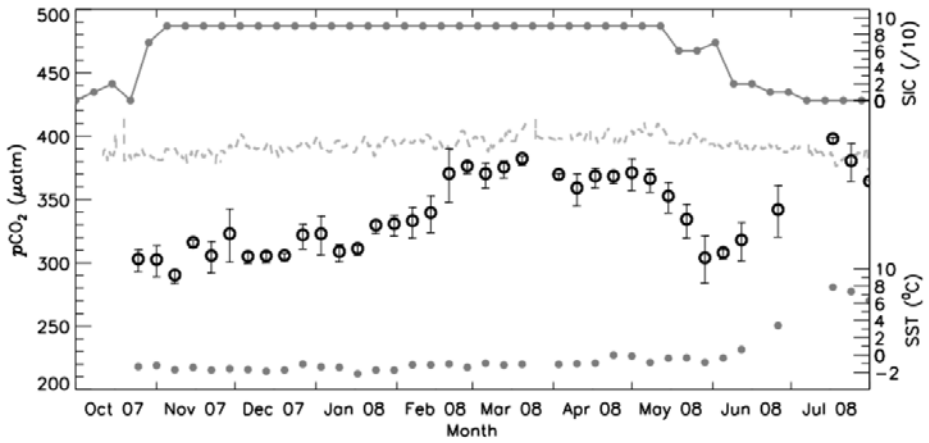

Figure 5. Weekly average $pCO_{2(sw)}$ measurements in Amundsen Gulf (Canadian Arctic) (open circles); error bars are 1 standard deviation. Also shown is the sea surface temperature from the equilibration system (solid grey circles), $pCO_{2(atm)}$ from the meteorological tower (grey dashed line), and sea ice concentration from weekly Canadian Ice Service charts (solid line with grey circles) (from Else et al., 2012).

In coastal regions of the AO, the carbonate system is greatly influenced by the inflow of freshwater rivers, in two ways. First, the rivers have very low concentrations of calcium, so that the saturation state of calcium carbonate in these regions is very low. Second, the rivers that flow into the AO contain the highest reported river concentrations of organic matter in the world (Dittmar and Kattner, 2003). This organic matter respires in the water column, leading to an increase in $pCO_{2(sw)}$, fall in pH, and saturation states of calcium carbonate (Fig. 6). An example of river discharge that leads to an increase in $pCO_{2(sw)}$ is given in the study of Anderson et al., (2009), who investigated surface $pCO_{2(sw)}$ in the Laptev and East Siberian sea. This region is known for the inflow of large Siberian rivers (Fig. 6A). It was found that areas where rivers enter the ocean are always high in $pCO_{2(sw)}$, which can reach levels of 600 – 1400 µatm (Fig. 6B, 6C, 6D).

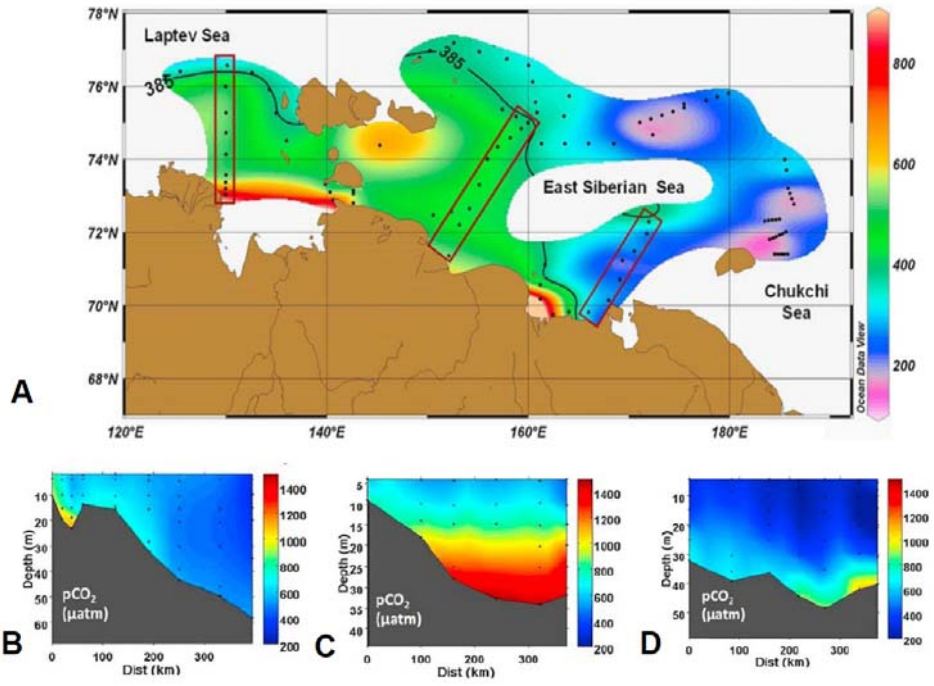

Figure 6. A – The top panel shows the distribution of surface pCO_2 in summer 2008. The lower panel shows sections of pCO_2 in the Laptev Sea (B), western East Siberian Sea (C) and eastern East Siberian Sea (D) (from Anderson et al., 2009).

The factors that control the carbonate system of the AO will be affected by climate change. The observed and potential future responses of the AO carbonate system to a changing climate are discussed in section 2.2.

2.2 Response of the Arctic Ocean carbonate system to climate change

The AO sea ice is reducing drastically in response to climate change, and a new record of minimum sea ice extent was observed in September 2012. This exceptional reduction in the extent of sea ice makes it plausible that the AO surface in the summer season will be ice free in a few years, not decades as projected earlier (Kerr, 2012). Less sea ice in the AO means a decrease in albedo; more solar radiation penetrates the surface waters, and the sea surface temperature rises. Mainly because of the effect of positive albedo feedback (IPCC AR4), the Arctic is warming 2-3 times faster than other areas of the planet; this phenomenon is known as the Arctic amplification (Loeng, 2005, Trenberth and Josey, 2007, Serreze and Barry, 2011).

Sea ice reduction and increasing water temperature cause shifts and changes in the AO system, in a cascade effect (Wassmann et al., 2011). The ice-free surface of the AO is more aerated, and has greater potential for open water gas exchange. The present total CO_2 flux from the atmosphere to the surface Arctic ocean (hereafter air-to-sea CO_2 flux) is estimated to be between 66 and 199 Tg yr^{-1}, which is 5-14% of the global sink (Bates and Mathis, 2009). Observations of CO_2 flux are still regionally and seasonally sparse, but they already show that the regions of the AO with high biological production have much greater air-to-sea CO_2 flux than regions with low biological production. For example, air-to-sea CO_2 flux in the most highly productive Barents Sea is found to be between 44±16 Tg yr^{-1} (Kaltin et al., 2002) and 77±12 Tg yr^{-1} (Omar et al., 2007). The air-to-sea CO_2 flux in another productive region, the Chukchi Sea, is in the range 11 Tg yr^{-1} (Murata and Takizawa, 2003) to 53±14 Tg yr^{-1} (Kaltin and Anderson, 2005). These are contrasted with regions of poor biological production, which have air-to-sea CO_2 flux from 1 Tg yr^{-1} in the Kara Sea (Fransson et al., 2001) to 19 Tg yr^{-1} in the Central Arctic basin (Bates et al., 2006). Future

directions and intensities of the CO_2 flux in the AO will largely be controlled by the rates of biological production in productive regions (Bates and Mathis, 2009).

57% of the AO area is the continental shelf, most of which exhibits intense seasonal phytoplankton blooms (Pabi et al., 2008) due to favorable nutrient and light conditions (Hill and Cota, 2005). The AO shelf accounts for 80% of primary production observed above 65°N (Sagshaug et al., 1994). The wide scatter of areas having intense biological production in the AO contributes to the great regional variability in the properties of the AO carbonate system. Extreme seasonality of biological production in productive areas can be responsible for up to 50% of seasonal variability in carbon biogeochemistry (Chierici et al., 2011).

The mean annual biological production is increasing at present (Fig. 7) (Arrigo et al., 2008; Pabi et al., 2008). This is in response to a greater amount of sun light and longer growing season caused by reduction in summer sea ice and a longer ice melt season (Comiso, 2006; Serreze et al., 2007; Comiso et al., 2008). In addition to the open waters, under-ice biological production is increasing (Arrigo et al., 2012).

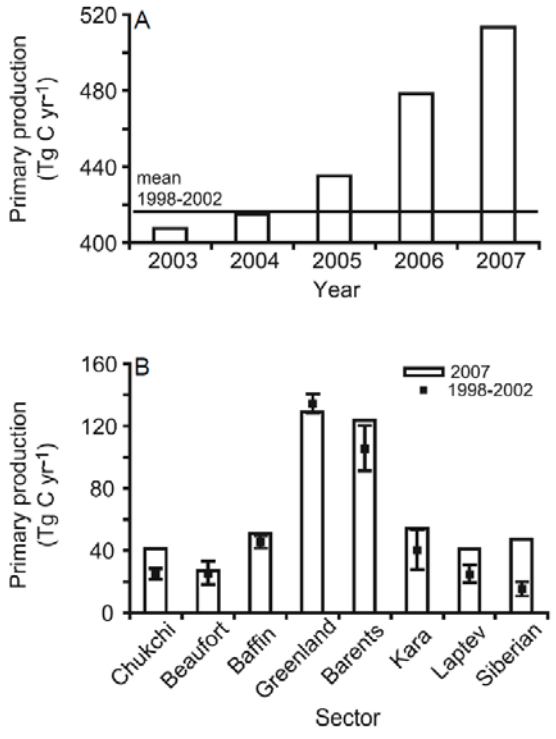

Figure 7. A) Increase in annual primary production in the Arctic (the solid horizontal line represents the mean annual primary production in the Arctic for the years 1998-2002). B) Primary production by geographic sector in 2007 compared to the average values from 1998-2002 (from Arrigo et al., 2008).

Biologically fixed inorganic carbon in the upper ocean can be exported to the deep ocean, if the phytoplankton bloom occurred early in the summer when the concentration of zooplankton is low (Hunt et al., 2002). The export of carbon in this situation either couples pelagic and benthic marine ecosystems, providing food from one to another (e.g. Bergmann et al., 2008; Morata and Renaud, 2008); or potentially degrades below the euphotic zone (Francois, 2002), causing an increase in $pCO_{2(sw)}$ in the layers where respiration takes place. Another pathway for biologically fixed inorganic carbon is to be transported to higher trophic levels through grazing by zooplankton. Either way, the amount of biologically fixed C plays an important role in the carbonate system of the whole water column, as well as in the quality of food transported to higher trophic levels. The amount of fixed carbon is usually estimated through the C:N:P ratio of uptake or the C:N:P ratio in the composition of organic matter. The study of C:N:P ratios is usually referred to by the term 'stoichiometry', which has been defined as “the science of measuring the quantitative proportions or mass ratios in which chemical elements stand to one another” (Partington, 1948). C:N:P stoichiometry varies throughout the year (Frigstad et al., 2011) and among regions (Sterner et al., 2008; Sardans et al., 2011). Variability of the C:N:P stoichiometry is still poorly understood, but many studies have found that it is multifactorial. In the Arctic a key factor in regulating C:N:P stoichiometry is the spectral quality of light. It was found that the C:N and C:P ratios increase due to greater C fixation by phytoplankton exposed to high amounts of photosynthetic active radiation (PAR; Hessen and Anderson, 2008). Exposure of phytoplankton to ultraviolet radiation, which is likely to occur in the Arctic because of ozone layer depletion (Manney et al., 2011), diminishes C fixation relative to phosphate uptake (Leu et al., 2006, 2007; Hessen and Anderson, 2008).

Future biological production, and consequently the amount of fixed inorganic carbon in the upper ocean, could be altered by the effects of climate change. If smaller phytoplankton cells dominate the community composition under freshening (Li et al., 2009) and ocean acidification (Brussaard et al., 2012), then inorganic carbon requirements and fixation will be determined by the growth rates (Finkel et al., 2009) and growth strategies of these organisms (Klausmeier et al., 2004; Arrigo, 2005;

Mills and Arrigo, 2010). The rates of biological production and inorganic carbon fixation in the upper ocean could decrease in the long term, because of nutrient limitation due to greater stratification (Toole et al., 2010). Regions with low biological production at the present time, and regions where biological production will be lowered due to the effects of climate change experience a weak air-to-sea CO_2 flux (Cai et al., 2010) and may become sources of CO_2 to the atmosphere. At present the AO is a sink for atmospheric CO_2. As a CO_2 sink the AO contained 2.5 to 3.3 Pg of anthropogenic carbon by 2005, which is ~2% of the global ocean inventory of anthropogenic carbon (Tanhua et al., 2009). Part of this anthropogenic carbon is transported from the North Atlantic, which is also a CO_2 sink region and presently a large inventory of anthropogenic carbon itself (Olsen et al., 2010).

Future weakening of the air-to-sea CO_2 flux may be caused by the $pCO_{2(sw)}$ increase, which could even reaching the level of $pCO_{2(atm)}$. One reason for increasing $pCO_{2(sw)}$ is the increased mean annual temperature of the AO waters. Warmer waters have lower solubility for CO_2, so that $pCO_{2(sw)}$ rises. Further increases in $pCO_{2(sw)}$ are caused by respiration of organic matter (Amon and Meon, 2004; Belanger et al., 2006), of which a large source is currently thawing under the effect of climate change permafrost (Pipko et al., 2011). Larger ice-free areas of the AO surface have a great potential for fetch over longer distances. This could cause increased coastal erosion, which is also a source of organic matter (e.g. Mars and Houseknecht, 2007). The respiration of this organic matter increases $pCO_{2(sw)}$ (Anderson et al., 2009). Intensified storm-induced upwelling in some regions of the AO could bring deep waters, with high $pCO_{2(sw)}$, to the surface. At present, storm-induced upwelling events in the Beaufort Sea occur regularly throughout the year (Pickart et al., 2011), and could cause an increase in the sea surface pCO_2 to more than 500 μatm (Mathis et al., 2012) (Fig. 8, 9a).

Various factors, including air-to-sea sink of anthropogenic CO_2, horizontal transport of anthropogenic CO_2 from the North Atlantic, respiration of terrestrial organic material, and amplified warming of the Arctic, all act to increase $pCO_{2(sw)}$; as a result the AO will undergo greatest acidification in the global ocean (Steinacher et al.,

2009). Models predict undersaturation with respect to aragonite surface waters in most of the AO by 2050 (Anderson et al., 2010). Waters at depth 0-50 meters that are undersaturated with respect to aragonite have already been observed for many summers in a row (Chierici and Fransson, 2009; Chierici et al., 2011; Yamamoto-Kawai et al., 2009; Bates et al., 2012; Mathis et al., 2012 (Fig. 9b)).

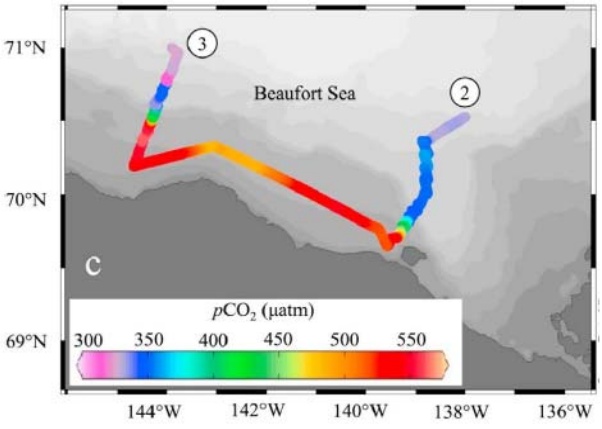

Figure 8. Surface pCO_2 in the Beaufort Sea, October 2011 (From Mathis et al., 2012).

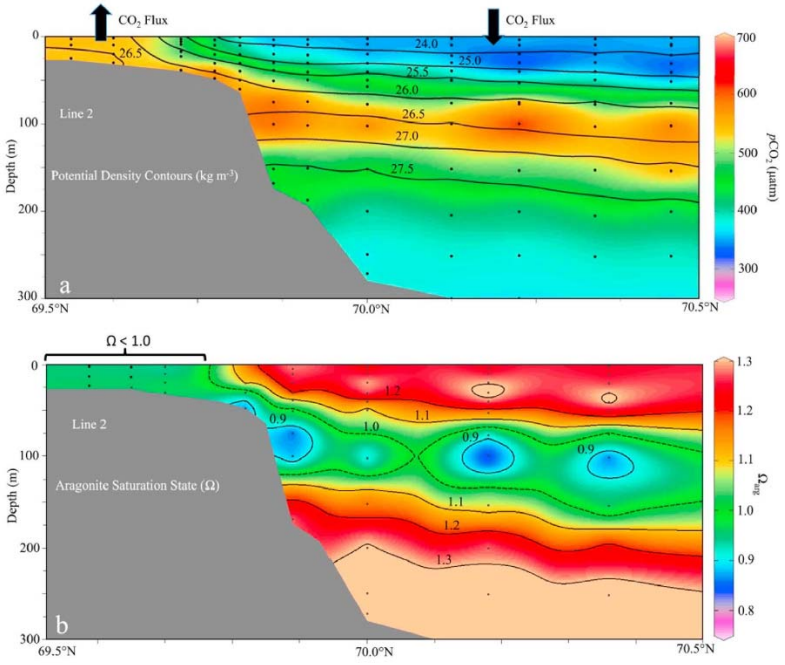

Figure 9. a) Cross-sectional plot of pCO_2 (µatm) with density contours along line 2 on the figure above. Black arrows indicate the direction of the of the CO_2 flux. b) Cross-section plot of the aragonite saturation state, with contour lines along line 2. The dashed line illustrates where the saturation state of aragonite (Ω_{Ar}) = 1 (from Mathis et al., 2012).

In conclusion, the AO is one of the least studied but most likely region to show an amplified and complex response to changing climate. The carbonate system of the AO is likely to be the most dynamic in the world ocean. To shed light on future feedbacks of the AO carbonate system to climate, and to estimate the role of the

carbonate system in future succession and health of the AO ecosystem, better understanding of carbon biogeochemistry is needed.

The aim of this PhD thesis is to provide new information about the contemporary setting of carbon biogeochemistry of the AO, and how it might evolve in the future under a changing climate and ocean acidification. The work focuses on three objectives:

- To better understand the present spatial and temporal variability of the marine carbon biogeochemical system, with emphasis on the pools of particulate organic carbon (Paper I) and inorganic carbon chemistry (Paper II)

- To gain more information about the drivers that control spatial variability and temporal changes of the marine carbon biogeochemical system (Paper I, Paper II)

- To study the synergy between the Arctic marine carbon cycle and pelagic ecosystem in the present and under future climate and CO_2 scenarios, in order to investigate the roles of solubility and biological pumps under future climate change and ocean acidification (Paper III, Paper IV)

3. Methods

3.1 Historical dataset analysis

Paper I is based on the analysis of historical datasets, including data on *in-situ* concentrations of particulate organic carbon (POC) and particulate organic nitrogen (PON) in the Arctic Ocean. Data were obtained from published and unpublished sources involving 10 individual research programs conducted north of 60º between 2001 and 2008. The data were divided into 11 regions, following the seafloor topography analysis by Jakobsson et al., (2003, 2004). Statistical approaches were used to determine the natural variability of the POC:PON ratio (henceforth the seston C:N ratio). The non-parametric Kruskal-Wallis Rank Sum test was used to determine significance in the seston C:N ratio regional variability. The significance of the relationship between the C:N ratio and Chl *a* was tested with linear model on log-transformed data. The constancy of the C:N ratios across the range of seston concentrations was tested by a standardized major axis (SMA) regression.

3.2 Modeling

Papers II and III interpret simulations results from a coupled physical-biogeochemical ecosystem model of the AO - SINMOD (SINtef MODel, sinmod.no). The SINMOD model is a 3D hydrodynamic model based on the primitive Navier-Stokes equations, and is established on a z-grid (Slagstad and McClimans, 2005). Horizontal resolution of the hydrodynamic model is 20 km, and in the vertical z-direction there are 25 levels. The hydrodynamic model is coupled with an ice model similar to that of Hibler (1979), which has two state variables: the average ice thickness, and the ice compactness. On top of the hydrodynamic model is the conceptual ecosystem model (Wassman et al., 2006), which has state variables specifying the low trophic level food web: dissolved organic carbon, nutrients, bacteria, phytoplankton, micro and mezozooplankton, and sinking organic particles. The marine carbonate system is built in the hydrodynamic model and is related to the ecosystem model through the C:N ratio of uptake by phytoplankton. In Papers II and III, SINMOD was forced by SRES A1B climate and CO_2 scenarios from IPCC AR4, so as to gain new information about

the present state of the carbonate system in the AO and its dynamics during the 21st century. For Paper III, SINMOD was parameterized with the pCO_2 sensitive C:N ratio in order to study the role of C:N stoichiometry in coupling between organisms in the low trophic level of the pelagic ecosystem, and the carbonate system of the AO, during the 21st century.

3.3 Mesocosm perturbation experiments

Paper IV, and partly Paper II, are based on the results of a large scale mesocosm experiment. A mesocosm is an observatory and experimentation facility constructed as an enclosure attached to a hard frame or a raft, intended for deployment in open waters (Fig. 10). Mesocosms are applied to study natural aquatic ecosystems while manipulating and controlling various environmental factors. Mesocosms have been used in marine ecology studies since the 1950s, and as a simplified model of nature, mesocosms allow scientists to study the response of biotic and abiotic components of marine ecosystems to environmental changes (Oviatt, 1994).

Figure 10. Structure of the Kiel Off-Shore Mesocosms for future Ocean Simulations (KOSMOS), http://mesoaqua.eu/kiel_kosmos. The sketch on the left-hand side is from Riebesell et al., 2012. The photo on the right-hand side was taken by A. Silyakova during the mesocosm experiment in Kongsfjorden, Svalbard.

For the experiment reported in papers II and IV, mesocosms were deployed in Kongsfjorden, west of Svalbard (78° 56.2′ N, 11° 53.6′ E) (Riebesell et al., 2012).

The experiment was conducted from May to July 2010, and is to date the northernmost large scale experiment conducted on ocean acidification. Nine mesocosms were simultaneously filled with fjord water so that they all had approximately the same natural plankton assemblage. Seven of the nine mesocosms were perturbed with varying pCO_2 levels in the range 270 to 1450 µatm. Two mesocosms were not perturbed with CO_2, and were used as control systems with ambient pCO_2 of 175 µatm. A comprehensive dataset based on 31 days of sampling, and various analyses and incubations taking place during the experiment, facilitated the integrated study of pelagic ecosystem processes under CO_2 perturbation. Measurement of inorganic carbon concentrations and total alkalinity (Paper II), as well as CO_2 gas exchange and concentrations of inorganic nutrients, made it possible to assess the net production and stoichiometry of carbon in relation to nutrient consumption by the pelagic community (Paper IV).

By combining the results of in-situ observations, perturbation experiments and 3D ecosystem modeling it is possible to gain an overview of the present state of the AO organic and inorganic carbon pools, and their response to future climate and CO_2 scenarios.

4. Main results

The aim of **Paper I** was to investigate natural variability of the C:N ratio in the particulate organic matter (seston) in the AO. The average seston C:N ratio was found to be 7.4, which is significantly higher than the classical Redfield ratio of 6.6. In all pan-Arctic shelf seas the seston C:N ratio was significantly higher than the Redfield. This did not apply to the Chukchi and East Siberian Seas, in which the inflow of nutrient rich Pacific waters plays an influential role in the stoichiometry of the organic pool. The Kara and Laptev Seas are those most affected by the terrigenous load of carbon due to river discharge and coastal erosion. These regions had a high seston C:N ratio. The highest seston C:N ratio was found in the regions of the North and the Northeast Water Polynyas (8.9). A large difference in the seston C:N ratio was observed between regions of the Barents Sea, which are influenced by the Arctic and Atlantic water masses. The Norwegian, Greenland Seas and southern part of the Barents Sea, which are influenced mainly by water masses from the Atlantic Ocean, all had similar seston C:N ratios. No strong correlation was found between the seston C:N ratio and day length and latitude. The seston C:N ratio increased with higher concentrations of chlorophyll a, but decreased at higher concentrations of seston. This paper shows that the seston C:N ratio in the AO is higher than the Redfield ratio. Regional variability in the seston C:N ratio is due mainly to regional factors, which define, for example, the concentration of chlorophyll a, the amount of terrigenous material, the concentration of seston, etc. A new relationship to describe overall seston C:N ratio in the AO was proposed as $POC=7.4\ PON^{0.89}$.

Paper II studied the response of the AO carbonate system to future climate and CO_2 scenarios. The paper uses results from the large scale mesocosm experiment on ocean acidification, conducted in Kongsfjorden, West of Svalbard, in 2010, as well as results from the coupled physical-biogeochemical ecosystem model of the AO for the area around Svalbard. A model simulation running 100 years ahead showed 300 µatm of centennial increase in $pCO_{2(sw)}$ in the Atlantic-influenced region, and 400 µatm of centennial increase in $pCO_{2(sw)}$ in the Arctic influenced region. This corresponds to a decrease in pH of 0.25 in the Atlantic influenced region, and of 0.35 in the Arctic

influenced region. Model simulations also showed that, by the end of the 21st century, surface waters in the Atlantic-influenced region will be close to undersaturation with respect to aragonite (Ω_{ar} = 1.4), whereas waters in the Arctic-influenced region will be undersaturated with respect to aragonite (Ω_{ar} = 0.8). Analysis of temporal changes showed that the largest centennial changes of the present century in the carbonate system would occur in waters associated with the Arctic. Seasonal changes in $pCO_{2(sw)}$, pH and Ω_{ar} due to biological production will be more rapid in the future than at present. Therefore, in the period of biomass growth between spring and summer, the curves of $pCO_{2(sw)}$, pH and Ω_{ar} will be steeper in the future than at present. This result is consistent with observations during large scale mesocosm experiments on ocean acidification, which found that changes in $pCO_{2(sw)}$, pH and Ω_{ar} due to biological production was more rapid under high $pCO_{2(sw)}$ conditions, which are predicted for the future AO.

Paper III is a model study of the AO under the future climate and atmospheric CO_2 scenario. The paper focuses on the relationship between primary production, export production and the carbonate system. The model was parameterized with two types of C:N stoichiometry. One simulation had a constant C:N ratio of 7.6, found in the particulate organic matter in the contemporary central Barents Sea (Reigstad et al., 2002). The other had a C:N ratio sensitive to pCO_2; this ratio increased with increasing $pCO_{2(atm)}$, from 7.6 in 2000 to 8.86 by 2100. 100-year simulations of the ecosystem model revealed that mean annual primary and export production, in case with the constant C:N ratio, did not change before 2070, after which both began to decrease. The mean annual primary and export production in the case with the pCO_2 sensitive C:N ratio both increased until 2070, after which both did not change or began to slightly fall. The carbonate system responded to the difference in mean annual primary and export production between two cases. The total amount of carbon fixed in the upper ocean and of carbon released below the euphotic zone during the 100 years of simulation was higher in case with pCO_2 sensitive C:N ratio, which led to lower $pCO_{2(sw)}$ in the upper ocean and higher $pCO_{2(sw)}$ below the euphotic zone in 2099.

Paper IV sought to investigate the net effect of biological carbon fixation and release (net community production, NCP) in the natural fjord system enclosed in 9 mesocosms and perturbed with differing pCO_2 levels ranging from 175 to 1450 µatm. Cumulative changes in nutrient concentrations were also assessed, and net carbon and nutrient consumption were both presented as C:N and C:P uptake ratios. There was a shift in community composition from larger to smaller phytoplankton during the course of the experiment (Brussaard et al., 2012), which made it possible to investigate the species-specific response of NCP and C:N:P uptake ratios at different stages of phytoplankton bloom. When there was a homogeneous phytoplankton composition in all pCO_2 treatments, at the beginning of the experiment, the NCP increased with higher pCO_2. The C:N and C:P ratios were low, but the C:N ratio increased with high pCO_2, whereas the C:P ratio did not show any clear response to pCO_2 perturbation. In the final stage of the experiment the community composition varied among mesocosms; in most mesocosms the community was dominated by relatively small phytoplankton cells. Heterogeneity in the community composition resulted in a time mismatch of the blooming peaks between individual pCO_2 treatments. As a result, high NCP rates followed peaking of the biomass in low pCO_2 treatments. In mesocosms with high pCO_2, the biomass was low and was still growing at the end of the experiment; as a result the NCP in these mesocosms was low. Trends of the NCP, C:N and C:P ratios at the end of the experiment were all negative in response to pCO_2 treatment.

5. Summary and future prospective

The four papers combined in this PhD work show that the carbon biogeochemistry in the AO undergoes great spatial, seasonal and long term temporal variability. Spatial variability of the biogeochemical system in the AO is largely defined by whether the region is influenced by waters from the Atlantic Ocean, the Pacific Ocean and/or by freshwater runoff from ice melt and terrestrial systems. The AO must be studied together with surrounding areas (pan-Arctic), as significant signals of climate change and ocean acidification enter the AO via their effects on surrounding areas.

Spatial variability in the AO biogeochemistry is also specified by whether the region has high or low biological activity. Biological activity of low trophic level organisms plays a large role in the annual and 100-year dynamics of the carbon biogeochemical system. The effects of climate change and ocean acidification on the carbon biogeochemical system might therefore be greatly mitigated by future biological activity.

Paper I shows that the seston C:N ratio in the AO is higher than the Redfield ratio, and its spatial variability is large. In gaining a better understanding of the mechanisms controlling present-day spatial variability of the C:N ratio, as well as the origin of seston material, the seston C:N ratio appears to be a good indicator of a changing environment. By parameterizing the spatial variability of the C:N ratio in terms of the ecosystem models of the AO, better estimates of the primary production would emerge, and consequently of inorganic carbon fixation in the differing types of systems. Better representation of primary production would also be possible by improving the conceptual ecosystem models of the AO by parameterizing sea-ice algae, which give a contribution to the total mean annual primary production of the AO of between 10% (Gradiner, 2009) and 57% (Gosseling et al., 1997). The proposed shift in the marine pelagic ecosystem toward dominance by smaller phytoplankton cells in the AO pelagic ecosystem, due to freshening (Li et al., 2009) and increasing $pCO_{2(sw)}$ (Brussaard et al., 2012), could affect primary productivity and consequently the total primary production of the AO. Parameterization of smaller

phytoplankton groups as a dominant low trophic level group of organisms in the ecosystem models of the AO would generate more information about future productivity of the AO. Further studies of the physiological responses of smaller phytoplankton groups to climate change and ocean acidification would improve our understanding of the future coupling of primary production and the carbonate system in the AO. A better understanding of how calcifying phyto- and zooplankton would function in $CaCO_3$-undersaturated waters would enable estimates of the contribution of these organisms to primary and secondary production in the future AO. It is important to determine the role of competitive interactions within the microbial food web (Thingstad et al., 2008) in the future pelagic ecosystem. Greater stratification may lead to nutrient limitation (Toole et al., 2010; Riebesell et al., 2009), so that competition for nutrients within the microbial food web may increase considerably. In the present AO the microbial loop is very active (Seuthe et al., 2010; Rokkan Iversen and Seuthe, 2010). Modeling of the processes within the microbial loop would assist in defining the role of organic matter respiration in the marine carbonate system under future climate and CO_2 scenarios.

In conclusion, this PhD work has emphasized:

- the importance of looking at AO systems with a pan-Arctic perspective in order to define the causes of spatial variability in carbon biogeochemical settings;

- the value of a multidisciplinary approach, because understanding of the carbon biogeochemical system under future scenarios involves looking at the combined effects of physical, chemical and biological processes;

- the importance of investigating AO carbon biogeochemistry using different methods, including in-situ observations, large scale experiments on the response of the marine pelagic ecosystem to future scenarios, as well as 3D ecosystem modeling. A combination of the results from different methodological approaches is more likely to provide a comprehensive

understanding of how the systems work and their responses to abrupt changes in the AO.

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