Carbon Dynamics in Northern Marginal Seas

Sofia Hjalmarsson

GÖTEBORGS UNIVERSITET

Abstract

The marginal seas have, despite their relatively small area, an important role in the global carbon cycle. They are largely influenced by carbon and nutrient fluxes from land and a large part of the biological production occurs in the marginal seas.

The carbon dynamic in two shelf areas – The Baltic Sea System (the Baltic Sea, the Kattegat and the Skagerrak) and the Siberian Shelf Seas (the Laptev Sea, the East Siberian Sea and the Chukchi Sea) has been studied in this thesis.

Results from a study using historical data on Total Alkalinity (TA) from the Baltic Sea shows that there has been a change in the riverine TA concentrations. TA has increased in rivers draining areas where limestone dominates the bedrock while there has been a decrease in TA concentrations in granite dominated areas. We give two explanations to this change; acid precipitation and increased concentrations of CO_2 from decay of organic matter.

The Baltic Sea has high DIC concentration relative to its salinity (also due to river input) and as the surface water leaves the Baltic Sea also the DIC is exported and will in the end add to the North Sea carbon budget. We estimated the net carbon export from the Baltic Sea to 5.5 ± 0.3 Tg C year^{-1}. Furthermore, the carbon dynamics in the Skagerrak during 2006 has been studied and we found it to be a sink of carbon with a sea-air flux of $1.3 \cdot 10^{12}$ mol m^{-2} year^{-1}. We also found Skagerrak to be a reasonable source of carbon to the North Sea by a continental shelf pump.

In the Arctic and especially in the Laptev Sea, the large amounts of organic carbon transported by the major Russian rivers as well as from coastal erosion will decay in the shelf seas. This will result in a net efflux of CO_2 to the atmosphere. However, in the eastern part of the East Siberian Sea and in the Chukchi Sea, the river discharge is much less and the biological activity is high. This will instead cause under-saturated surface waters in respect to CO_2. The particulate organic carbon produced in the surface will sediment and starts to decay in the bottom water. As the water flows off the shelf and in to the Arctic Ocean this will result in surface waters under-saturated in pCO_2 and subsurface waters over-saturated in pCO_2.

The marginal seas investigated in the thesis are located in the northern hemisphere and there are fundamental differences in temperature and population density along the coasts. Nevertheless, both areas are influenced by the properties and the carbon content in the entering river water and both areas appear to export carbon to the open ocean trough a continental shelf pump.

KEYWORDS: dissolved inorganic carbon, total alkalinity, continental shelf pump, marginal seas, Baltic Sea, Skagerrak, Laptev Sea, East Siberian Sea, Chukchi Sea

Part B

Research Papers

Papers included in the thesis, referred to in the text by their Roman numerals:

I   Hjalmarsson, S., Wesslander, K., Anderson, L.G., Omstedt, A., Perttilä, M., Mintrop, L., 2008. Distribution, long-term development and mass balance calculation of total alkalinity in the Baltic Sea, *Continental Shelf Research,* vol. 28, 593-601, doi: 10.1016/j.csr.2007.11.010

II   Hjalmarsson, S., Anderson, L.G., She, J., The exchange of dissolved inorganic carbon between the Baltic Sea and the North Sea in 2006 based on measured data and water transport estimates from a 3D model, resubmitted after revision to *Marine Chemistry*

III   Hjalmarsson, S., Chierici, M., Anderson, L.G., Carbon dynamics in a productive coastal region – Skagerrak, submitted to *Journal of Marine Systems*

IV   Anderson, L.G., Jutterström, S., Hjalmarsson, S., Wåhlström, I., Semiletov, I., 2009, Outgassing of CO_2 from Siberian Shelf seas by terrestrial organic matter composition, *Geophysical Research Letters,* vol. 36, L20601, doi: 10.1029/2009GL040046

V   Anderson, L.G., Tanhua, T., Björk, G., Hjalmarsson, S., Jones, E.P., Jutterström, S., Rudels, B., Swift, J.H., Wåhlström, I., Arctic Ocean Shelf – basin interaction, an active continental shelf CO_2 pump and its impact on degree of calcium carbonate solubility, submitted to *Deep Sea Research*

Contribution report:

I   Was responsible for the regressions and the calculations that used the historical alkalinity data and was responsible for the writing of the manuscript.

II   Was responsible for and performed half of the sample and data analysis, did the calculations based on the data from the model provided by DMI, was responsible for writing of the manuscript.

III   Was responsible for and performed half of the sample and data analysis, calculations and was responsible for writing of the manuscript

IV   Contributed to sample and data analysis, involved in writing of the manuscript.

V   Contributed to sample and data analysis, involved in writing of the manuscript.

Populärvetenskaplig sammanfattning

Kusthaven upptar endast en liten del av jordens yta och de utgör gränsen mellan land och öppet hav. Kolsystemet i två olika geografiska områden är undersökta i denna avhandling, dels i Östersjön, Kattegat, Skagerrak och dels i kusthaven norr om Sibirien som består av Laptevhavet, ÖstSibiriska havet och Tjuktjerhavet. De två områdena skiljer sig markant i avseende på klimat och befolkningstäthet längs kusterna. Gemensamt för dem är att de får ta emot stora volymer flodvatten som innehåller organiskt kol och närsalter (framförallt kväve), där det förstnämnda bryts ner i floderna och ute i kusthaven. När det organiska kolet bryts ner i flodernas dräneringsområden bildas koldioxid (CO_2) som kan vittra berggrunden i kalkstensrika områden. När kalksten vittrar bildas bikarbonatjoner som höjer alkaliniteten (ett mått på buffertförmåga) i flodvattnet och vi har funnit att detta skett i floder i södra östersjön medan alkaliniteten i floder från norra Skandinavien har minskat. En bidragande orsak till vittringen och förändringarna i alkalinitet kan även vara den sura nederbörden som var kraftigast främst under 1960 och 70 talen. Vi har även studerat kolsystemet i Skagerrak och funnit att Skagerrak tar upp CO_2 från atmosfären under vintern som binds in till organiskt kol (växtplankton) vid fotosyntesen under våren. Kolet begravs sedan i sedimentet eller exporteras vidare ut i Nordsjön.

Arktis och framförallt Laptevhavet tar emot stora mängder flodvatten från stora ryska floder, den största av dem är floden Lena. Floderna tar med sig stora mängder organiskt kol från tundran och när detta kol bryts ned ute i kusthavet sker en urgasning av CO_2 till atmosfären. Tjuktjerhavet är däremot väldigt påverkat av ytvatten som kommer in från Stilla havet via Berings sund. Stilla havsvattnet innehåller höga koncentrationer närsalter som gör att produktionen av växtplankton är mycket större i detta område. Detta leder till att ytvattnet får en låg koncentration av CO_2 (undermättat). När ytvattnet strömmar ut i den istäckta Arktiska oceanen kommer denna undermättnad att bevaras under isen eftersom kontakt med atmosfären hindras.

Temperaturen i Arktis har ökat under de senaste årtiondena, troligtvis beroende på den ökande halten av CO_2 i atmosfären från förbränning av fossila bränslen. Detta har lett till att mängden is under sommaren har minskat. Med ett minskande istäcke ökar exponeringen av undermättat vatten i Arktis och detta kan leda till ett ökat upptag av CO_2 från atmosfären. Dock kan temperaturökningen även få till följd att permafrosten tinar. Stora mängder organiskt kol är idag bundet i permafrost och om detta frisgörs och följer med floderna ut i kusthavet kommer urgasningen av CO_2 i dessa hav att öka.

Introduction

We humans love the ocean, we swim in it, we sing about it, we fish in it, and above all, we live by it. Around half of the world's population live within 200 km of the coastline and this area represents only 10 % of the earth's total land surface. This imbalance will of course influence the oceans closest to us; the marginal seas. Human activities like agriculture and industrialism introduces pollutants to the marginal seas by river discharge and airborne deposition. Depending on the nature and concentration of the pollutant, processes in the marginal seas can be either stimulated or inhibited. Eutrophication is one of the consequences, when the excess of nutrients from agriculture stimulate the growth of algae in the coastal seas.

Beyond this form of anthropogenic stress there is also the threat of global warming due to emissions of greenhouse gases and among them; carbon dioxide (CO_2). In the Arctic, there are not many people living along the Siberian coast. However, this region is believed to be especially sensitive to a future global warming. A changing climate will not only lead to decreasing sea-ice cover during summer, also thawing of the permafrost and increased river runoff due to increased precipitation are processes that will affect the Arctic environment.

Carbon studies are necessary since carbon in its different forms will have a key role in all of these changes that are affecting our marginal seas.


Figure 1. The Swedish west coast (left) and the Siberian coast (right). Photo from Siberia: Johan Gelting.

The global carbon cycle

Carbon is absolutely essential to life; every organism on Earth needs it either for structure, energy or both. The carbon cycle is the movement of carbon between the atmosphere, the oceans, the biosphere and the geosphere (Figure 2). The carbon cycle is described by pools where carbon is stored, and by fluxes which is the exchange of carbon between the different pools. If more carbon enters a pool then leaves it is called a net carbon sink and the other way around; if more leaves than enters, it is called a net carbon source.

In pre-industrial times the carbon cycle was in balance (steady state). However, today the emissions of fossil fuel and changes in land-use related to food consumption have increased the amount of carbon in the atmosphere which is impacting the most of the fluxes and the pools in the carbon cycle. In figure 2 the red arrows are the fluxes due to anthropogenic carbon emissions, and the black arrows quantify the natural carbon cycle.
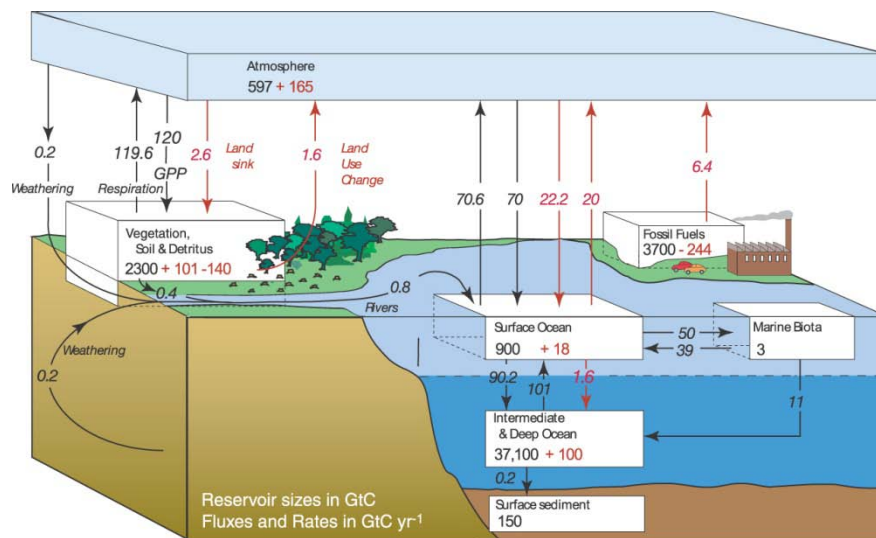

Figure 2. The global carbon cycle boxes are carbon pools and the arrows the fluxes between them. The natural carcon cycle is indicated by black arrows while red arrows show the additional fluxes due to anthropogenic carbon. From IPCC AR 4, ch. 7, references therein.

Global warming or the "greenhouse" effect

In 1897 the Swedish researcher Svante Arrhenius published a paper on how increasing concentrations of CO_2 in the atmosphere would have an effect on the temperature on Earth. From air trapped in Antarctic ice cores the pre-industrial concentration of atmospheric CO_2 has been established to 280 ppm (Petit et al., 1999), today the concentration is around 385 ppm and is still rising (Figure 3). Initially this increase was the result of land-use change (mostly emissions from deforestation) but after about 1900, emissions from fossil fuel started to become significant and since about 1950 it is the dominant source for increasing CO_2 (Schulze et al., 2009).
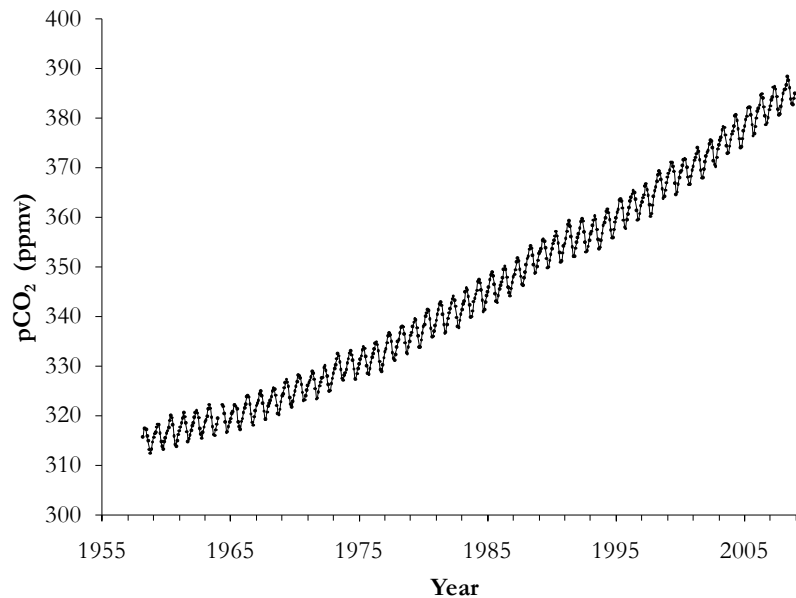
Figure 3. The atmospheric increase of CO_2 measured at Mauna Loa, Hawaii

Not only CO_2 has the property to trap heat in the atmosphere causing this greenhouse effect, also nitrogen oxides, methane and water vapour acts as greenhouse gases. The greenhouse effect is actually a natural occurring process that aids heating the atmosphere and the Earth's surface. Without any greenhouse effect the mean temperature on Earth would be about 30 °C lower than today's 15 °C.

When the energy from the sun passes through the atmosphere, in average only around 50 % of the radiation reaches the surface, the rest is reflected earlier by e.g. clouds and particles (Figure 4). When the surface of the Earth heats, infrared (IR) radiation is sent back towards space and is absorbed by the greenhouse gases which reemit it to the Earth's surface.
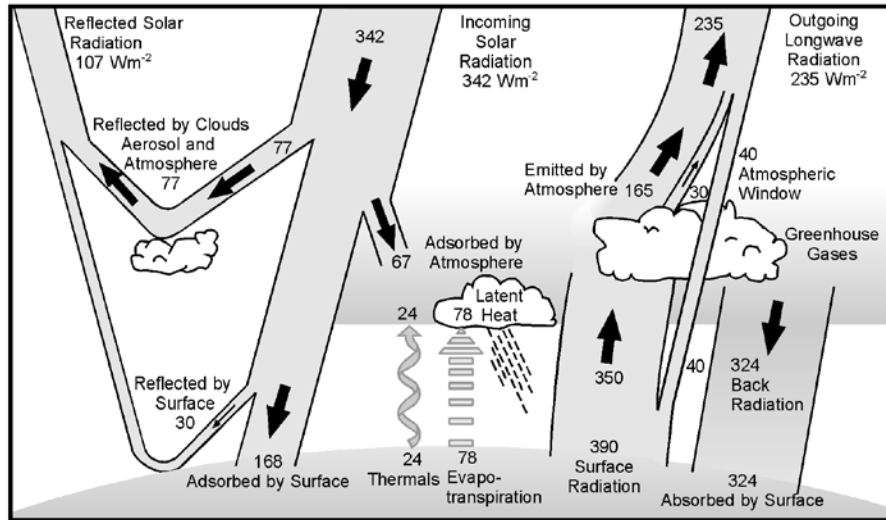
Figure 4. The Earth's radiation balance

The Intergovernmental Panel on Climate Change (IPCC) has since 1990 compiled the existing knowledge on the occurrence of present climate change and the likelihood of future changes. In the 2007 report they predict a global average surface warming of 2 - 4.5 °C with a best estimate of 3 °C if the concentration of CO_2 in the atmosphere is to double (IPCC 2007). They also state that "Most of the observed increase in global average temperatures since the mid-20th century is *very likely* due to the observed increase in anthropogenic greenhouse gas concentrations."

Anthropogenic carbon in the ocean

The ocean plays an important role since it has the capacity to take up and store anthropogenic CO_2. Averaged over the whole world the ocean will act as a sink, but as the CO_2 concentrations in the atmosphere rises further, the capacity of the ocean to take up CO_2 decreases as the ocean gets more acidic (the buffer capacity decreases). It is difficult to accurately estimate the amount of anthropogenic carbon in the ocean since the anthropogenic signal is small compared to the large background in dissolved inorganic carbon and there are only accurate data from the last approximately 20 years. A number of methods have been developed to calculate the anthropogenic CO_2 content. These methods are based on measured data and corrects for processes (e.g. biology) that also affects the carbon concentration. Examples of these methods are the TroCA (Touratier and Goyet, 2004), the ΔC^* (Gruber et al., 1996), the eMLRs (Friis et al., 2005) and the tracer method; TTD transit time distribution (Waugh et al., 2004; Waugh et al., 2006)

Ocean acidification

Anthropogenic carbon taken up by the ocean will decrease pH, the pH of the surface ocean has decreased 0.01 pH unit since pre-industrial time (Orr et al., 2005). However, although the ocean is acidifying, the pH is still greater than 7, so a more appropriate term is that the ocean is becoming less basic. The most concerning effect is that organisms using calcium carbonate ($CaCO_3$) for their shells or skeletons will have less favourable conditions. Experimental studies has shown changes in reduced calcification at increased CO_2 levels (e.g. (Delille et al., 2005; Engel et al., 2005; Gattuso and Buddemeier, 2000; Riebesell et al., 2000)

Papers

Five papers are presented in this thesis and they are all related to the carbonate system in marginal seas. Three of them (Paper I, II and III) deals with the Baltic Sea System and two of them are based on studies in the Siberian Shelf seas (Paper IV and V). Much of the emphasis is on the influence by the river runoff and on the export of carbon by the continental shelf pump in the two study areas. In Paper I we use historical TA data to evaluate long-term changes in the TA signal of the river runoff entering the Baltic Sea and also, a box-model is evaluated for TA in the different sub-basins of the Baltic Sea. In Paper II we estimate the export of DIC from the Baltic Sea by using water transport values and salinities from a 3D model provided by the Danish Meteorological Institute (DMI) together with measured DIC data from the Kattegat. Paper III describes the carbon dynamic in the Skagerrak, from monthly measurements in 2006 we have also calculated the air-sea flux of CO_2 and assessed the major drivers for the inorganic carbon system. Paper IV is based on data from the ISSS cruise in 2008 and in this paper we show the saturation of pCO_2 along the Siberian coast and in the river mouths of three large rivers. We also calculate the excess of DIC in the surface waters. In Paper V we use data from ISSS together with data from the Beringia cruise in 2005 to show that carbon is exported from the shelf to the Arctic Ocean. We also calculate the uptake capacity of the pCO_2 under-saturated surface water and the excess of DIC in the subsurface water (originating from the bottom water on the shelf). Furthermore, we calculate the under-saturation in respect to $CaCO_3$ in the subsurface water and present a possible evolution for the extent of this under-saturation in the future.

The marine inorganic carbon system

The carbon in the ocean is to the largest degree (97 %) inorganic. In pre-industrial times the inorganic carbon entered the upper ocean trough river input and there was a net flux of CO_2 from the sea to the atmosphere. It is assumed that the ocean at that time was in steady state, i.e. the sources and sinks were equal and the concentration of dissolved inorganic carbon in the ocean did not change with time, at least not since the last glaciations. Nowadays the carbon enters both through rivers and trough uptake from the atmosphere. Some of the inorganic carbon is then transformed into organic carbon by photosynthesis and moves further up the trophic levels. As the organic carbon decays it is remineralised back to dissolved inorganic carbon which can reach the upper ocean trough e.g. upwelling causing out-gassing of CO_2 or it is buried in the sediments. These two processes will remove carbon from the ocean.
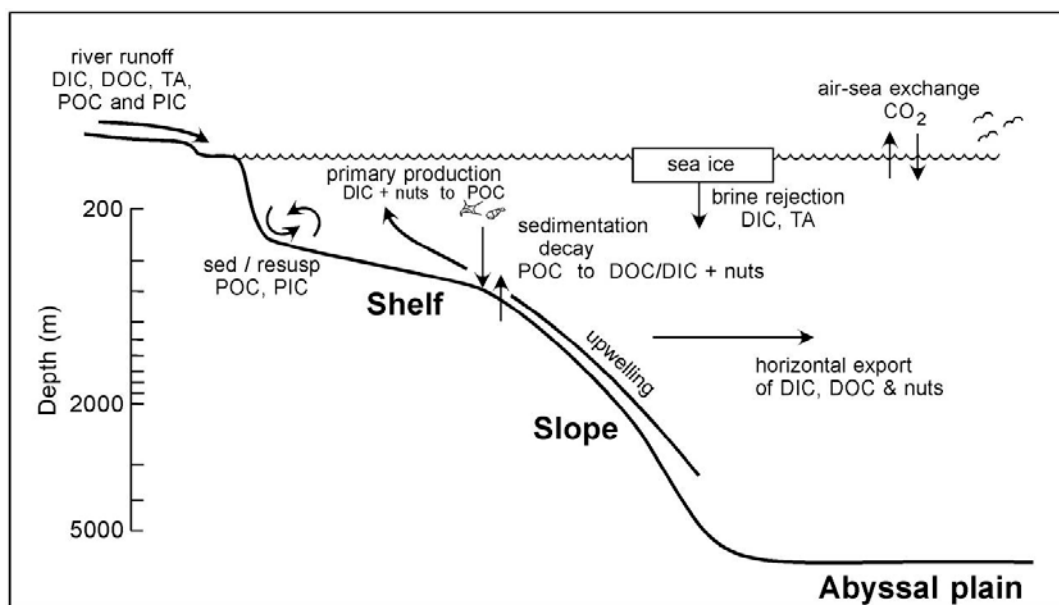
Figure 4. Schematic illustration of some factors that involves transformation and transport of carbon in marginal seas.

When carbon dioxide dissolves in seawater the following reactions occurs:

$$CO_2(g) \leftrightarrows CO_2(aq) \tag{1}$$

$$CO_2(aq) + H_2O \leftrightarrows H_2CO_3(aq) \tag{2}$$

$$H_2CO_3(aq) \leftrightarrows H^+(aq) + HCO_3^-(aq) \tag{3}$$

$$HCO_3^-(aq) \leftrightarrows H^+(aq) + CO_3^{2-}(aq) \tag{4}$$

In *(2)* carbon dioxide is hydrated to form carbonic acid, H_2CO_3. Often *(1)* and *(2))* are combined since dissolved CO_2 and H_2CO_3 are not possible to distinguish analytically. They are then referred to as $H_2CO_3^*$.

Carbonic acid is divalent and can form both hydrogen carbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. The co-existence of these species creates a buffer system and regulates pH in the ocean. At the oceanic pH of around 8, the dissolved inorganic carbon is dominated by HCO_3^- (~90 %), with the concentrations of CO_3^{2-} and $H_2CO_3^*$ comprising about 9 % and 1%, respectively.

Four measurable parameters; dissolved inorganic carbon (DIC), total alkalinity (TA), pH and the partial pressure of CO_2 (pCO_2) are used to describe the carbonate system.

DIC is the sum of the dissolved inorganic carbon species;

$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

TA is defined as the sum of the anions of weak acids (pK $\geq$ 4.5, at 25°C) that will react with added H^+, or in other words; the buffer capacity of seawater. It equals;

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [OH^-] + [NH_3] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] + [HS^-]$$

When working with the marine carbonate system pH can be measured on three scales. Basically pH is defined as the negative logarithm of the hydrogen ion activity $\{a_H\}$;

$$pH = -\log_{10} \{a_H\}$$

The activity is affected by the complexity of seawater as a medium with high ionic strength. In seawater is $[H^+] > \{a_H\}$. This can be illustrated by the change in activity when salt is added to a sample with freshwater. The salt increases the ionic strength in the solution and shields the free ions, hence the activity decreases. In this thesis the total pH scale (pH_T) is used which includes the sulfate ions (HSO_4^-). For pH_T:

$$\{a_H\} = [H^+] + [HSO_4^-]$$

The other two scales are the free scale were $\{a_H\} = [H^+]$ and the seawater scale were $\{a_H\} = [H^+] + [HSO_4^-] + [HF]$.

The partial pressure for an ideal gas in equilibrium with seawater is defined as the product of the mole fraction and the total pressure. However, CO_2 is not an ideal gas and this is accounted for when using the fugacity, fCO_2. The ratio between pCO_2 and fCO_2 at -2 °C to 25 °C ranges from 0.995 to 0.997.

If two out of the four inorganic carbon parameters are determined the other two can be calculated. This can be done using the chemical speciation computer program CO2SYS (Pierrot et al., 2006). For the work in this thesis the equilibrium constants for *(2, 3)* estimated by Mehrbach et al. (1973), refitted by Dickson and Millero (1987) and the constants by Roy et al. (1993) has been used. When more than two parameters are measured CO2SYS can also be used to check the internal consistency

by using two of them to calculate a third which then can be compared to the measured values. Based on this method the constants of Roy et al., (1993) are a proper choice for the cold arctic waters (Mojica and Millero, 2002). Also the salinity range for Roy et al. goes down to 5 while the more commonly used constants of Mehrbach et al.(1973) which in the thesis are used for the Baltic Sea System are determined for salinities over 19. Apart from the equilibrium constants the choice of which pair of parameters to use when calculates the others are important. If only two carbon parameters are to be measured, the pairing of pH and pCO_2 should be avoided since they give the largest uncertainties in the calculated parameters (Anderson et al., 1999; Dickson and Riley, 1978).

Analytical methods

To be able to assess the carbonate system in the ocean accurate analytical methods are crucial tools, not only for the inorganic carbon parameters but also for ancillary parameters. In general this includes salinity, temperature, oxygen, nutrients and transient tracers. A rosette sampler is normally used to collect the water; this is basically a frame to which a number of sample bottles (12-24) are attached. The rosette sampler is also equipped with a CTD (Conductivity-Temperature-Depth) sensor for the measurement of salinity, temperature and pressure. There can also be other sensors e.g. for chlorophyll, turbidity and oxygen mounted on the rosette sampler. The CTD transmit the data to a computer onboard the ship through the cable and this connection is also used to remotely control the rosette sampler in order to close the bottles at the preferred depths. When the CTD is back on deck the samples that are most sensitive to contamination are taken first, usually the transient tracers and oxygen followed by the inorganic carbon parameters affected by the CO_2 in the atmosphere. Afterwards, the samples for the parameters that are unaffected by the surrounding air are taken e.g. nutrients.
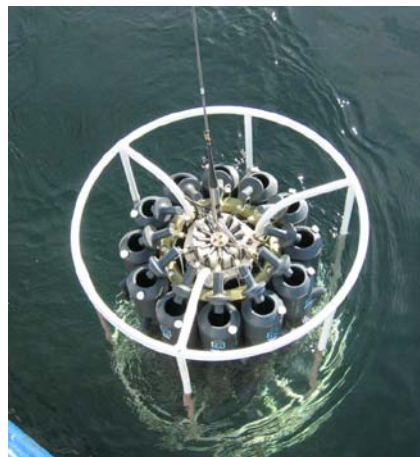
Figure 6. A 12 bottled rosette onboard the RV Skagerak.

The first step for a good analytical work is the sampling procedure. Representative samples have to be taken and contamination has to be avoided. Seawater samples have in this work been collected by a rosette sampler and for the carbon parameters, water for the determination of pH were drawn first, followed by DIC and TA. Care must be taken to avoid air bubbles as well as contact with air when sampling pH and DIC while TA is not contaminated by atmospheric CO_2. The samples should be stored cold and dark and the analysis should be carried out as soon as possible after sampling since all three are sensitive to biological activity, even if TA is less so.
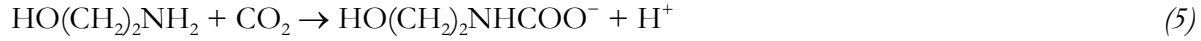
The emphasis of the methods described in this chapter will be on DIC, pH and TA and how they have been measured in the studies that are the basis for the papers presented in this thesis.

Figure 7. A ship lab, from the left: the TA system, the pH system and the DIC system.

DIC is determined using coulometric titration (Johnson et al., 1987). A known volume of the seawater sample is acidified with 10 % phosphoric acid. The addition of a surplus of H^+ by the acid shifts the inorganic carbon species of the equilibrium reactions *1 - 4* into CO_2. The produced CO_2 is then stripped out of the sample by an inert gas, typically nitrogen. The gas is bubbled through a glass cell with a reagent solution containing ethanolamine, which reacts with the carbon dioxide to produce hydroxyethylcarbamic acid *(5)*. The cell solution is coloured but will shift toward transparent when it reacts with CO_2. The pH in the reagent solution is monitored colorimetrically through the indicator thymolphthalein. As the transmission increase, electrons are added by sending a current through the cell electrodes which splits water at the cathode *(6)* while silver is oxidised at the anode *(7)*. The produced H^+ will counter-act the reactions in the solution and the initial colour will return. The current is then stopped and the electrons needed for the titration can be converted to concentration as the sample volume is known.

$$HO(CH_2)_2NH_2 + CO_2 \rightarrow HO(CH_2)_2NHCOO^- + H^+ \tag{5}$$

$$H_2O + e^- \rightarrow \tfrac{1}{2}\,H_2(g) + OH^- \tag{6}$$

$$Ag(s) \rightarrow Ag^+ + e^- \tag{7}$$

When measuring pH, most people would refer to an ion selective pH electrode. This potentiometric method requires calibration with a buffer with the same temperature and ionic strength as the sample if accurate results are required. However even under favourable condition this method only gives an accuracy of about 0.01 pH units, and in the study of the marine carbon system an accuracy of 0.001 pH units is optional. Instead, spectrophotometric determination of pH can be used (Clayton and Byrne, 1993). In this method a pH sensitive indicator such as m-creosol purple is added to the sample and the absorbance is measured at two wavelengths. The best precision is archived when the wavelengths are chosen at the maximum absorbance for the indicators acid and base specie, respectively. From the ratio between them the pH in the sample can be calculated according to;

$$pH_T = log_{10}\,K_{HI}(T) + log_{10}\left(\frac{Q - e_1}{e_2 - Qe_3}\right) \tag{8}$$

where K_{HI} is the equilibrium constant for the indicator equilibrium; $I^{2-} + H^+ \leftrightarrows HI^-$, and

$$Q = \frac{A_2}{A_1} \qquad e_1 = \frac{\varepsilon_2^{HI}}{\varepsilon_1^{HI}} \qquad e_2 = \frac{\varepsilon_2^{I}}{\varepsilon_1^{HI}} \qquad e_3 = \frac{\varepsilon_1^{I}}{\varepsilon_1^{HI}}$$

where $A_{1,2}$ is the absorbance maxima for the indicator species HI^- and I^{2-}, respectively, and ε is the molar absorptivity of HI^- or I^{2-} at the absorbance maxima 1 and 2.

The pH of the indicator may be different from the pH in the sample and this need to be corrected for (Chierici et al., 1999). During later years, optodes for pH measurements have been developed and used in sediments and overlying seawater (e.g. Zhu et al., 2005; Hakonen and Hulth, 2009). This is a promising in-situ tool and can in the future hopefully be deployed together with underway pCO$_2$ system on voluntary observing ships.

In our field studies total alkalinity has been determined using open cell potentiometric titration (Haraldsson et al., 1997). The sample is titrated with hydrochloric acid (HCl) and the pH change is monitored. Acid is added until the bases included in TA are protonized, the equivalence point. At this pH acid is added in volume steps in order to get information to apply a Gran function evaluation (Gran, 1952) after the equivalence point.

In Paper I historical data of TA is used. The reported most common determination technique was the back titration by Wattenberg 1930 and modified by Gripenberg (1936). Since the inorganic

carbon species dominates the TA the overall procedure for this method is to acidify the sample with an excess of H^+ (typically from HCl). The produced CO_2 is then removed by boiling or by bubble the sample with CO_2 free air. The excess of H^+ not taken up by the carbonate system is then titrated with NaOH or an iodometric titration with thiosulfate.

The precision of the modern methods is estimated from the standard deviation of the results from analysing replicates and are typically about $\pm$ 1-2 µmol kg^{-1} for DIC and TA and $\pm$ 0.002 units for pH. The accuracy for DIC and TA is set by analyses of Certified Reference Materials (CRM), supplied by A. Dickson, Scripps Institution of Oceanography (USA). For pH the accuracy is set by the indicator stability constant and is reported to be $\pm$ 0.002 pH units (Dickson, 1993). For the few historical measurements where the analytical accuracy is reported, it corresponds to about $\pm$ 3-5 µmol/L but is probably larger in general.
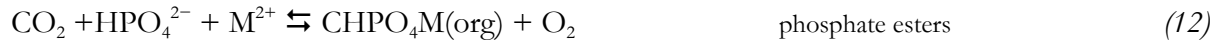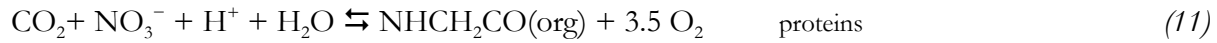
For the study reported in Paper II and III oxygen was determined using a modified Winkler titration with visual endpoint detection described by (Hansen, 1999) and for the study in Paper IV and Paper V and automatic Winkler titration system with precision ~1 µmol kg^{-1} was used. The inorganic nutrients were determined using an automatic spectrophotometric system (SmartChem from Westco Scientific Instruments, Inc.) in the studies of Paper IV and partly for Paper V.

Processes impacting the inorganic carbon content in Marginal Seas

The marginal seas separate the coastal zone from the open ocean. The main differences between marginal seas and the open ocean are the shallower depth and the proximity to land which makes it more influenced by human activities. Continental margins, if considered to be from the coastline to a depth of 200 m, only cover 7 % of the seafloor and less than 0.5 % of the oceans volume (Chen and Borges, 2009). Despite this the primary production is higher than in the open ocean due to the higher supply of nutrients from rivers and coastal upwelling.

Biology

Biology has a large impact on the carbon system where the dominating processes are photosynthesis and remineralisation affecting organic matter through the following reactions:

$$CO_2 + H_2O \leftrightarrows CH_2O(org) + O_2 \qquad \text{carbohydrates} \qquad (9)$$

$$CO_2 + H_2O \leftrightarrows CH_2(org) + 1.5\ O_2 \qquad \text{lipids} \qquad (10)$$

$$CO_2 + NO_3^- + H^+ + H_2O \leftrightarrows NHCH_2CO(org) + 3.5\ O_2 \qquad \text{proteins} \qquad (11)$$

$$CO_2 + HPO_4^{2-} + M^{2+} \leftrightarrows CHPO_4M(org) + O_2 \qquad \text{phosphate esters} \qquad (12)$$

CO_2 is accordingly taken up during primary production and released during remineralisation. pH will increase during the primary production while TA is only marginally affected.

The photosynthesis is also depending on the sunlight, inorganic nutrients (nitrate, phosphate) and trace elements. Physical processes like river runoff and mixing can influence the primary production. River runoff and vertical mixing can bring nutrients and trace elements to the photic zone which then increases the primary production. This effect is enhanced by the eutrophication where the excess of fertilizers from the agriculture in the drainage areas is either directly or exported by rivers to the oceans. The rivers also bring organic carbon that is remineralised in ocean. This river export of organic carbon has a large impact in the Arctic due to the large content of carbon that is tied up in the permafrost. In Paper IV this issue is further addressed.

The ratio between carbon and nutrients and oxygen during photosynthesis and remineralisation are often referred to as the Redfield ratio. Redfield (1963) suggested the ratio to be 1:16:106:135 for $P:N:C:O_2$. Even though there are deviations from the N:P ratio of 16:1, Arrigo (2005) stated that the ratio can be used as general average for the diverse oceanic phytoplankton assemblages.

Some organisms also form shells of calcium carbonate for which the following reaction applies:

$$Ca^{2+} + CO_3^{2-} \leftrightarrows CaCO_3(s) \qquad (13)$$

If in chemical equilibrium, the solubility product, $K_{sp} = [Ca^{2+}] \cdot [CO_3^{2-}]$, determines the individual concentrations. However, seawater is not in chemical equilibrium and the surface water is

over-saturated. The degree of saturation is often described by omega (Ω; reaction *14*) that equals 1 if in equilibrium, if $\Omega < 1$ the water is under-saturated and if $\Omega > 1$ is oversaturated with respect to $CaCO_3$.

$$\Omega = \left(\frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \right) \tag{14}$$

There are two common polymorphs of $CaCO_3$, calcite and aragonite, of which aragonite is more soluble.

According to reaction *(13)* TA will decrease during formation of the calcium carbonate shells and increase when they dissolve.

If more CO_2 is present in the water the concentration of CO_3^{2-} decreases (at constant DIC) (Figure 8) and the reaction above forming $CaCO_3$ will be less favourable. When organic matter is remineralised CO_2 is produced and the rate of $CaCO_3$ dissolution increases. In shallow coastal waters most remineralisation occurs at the sediment surface and hence the whole water column is normally oversaturated $\Omega > 1$. On the other hand the sediment pore water is often under-saturated only a few mm below the surface leading to dissolution of $CaCO_3$ shells.
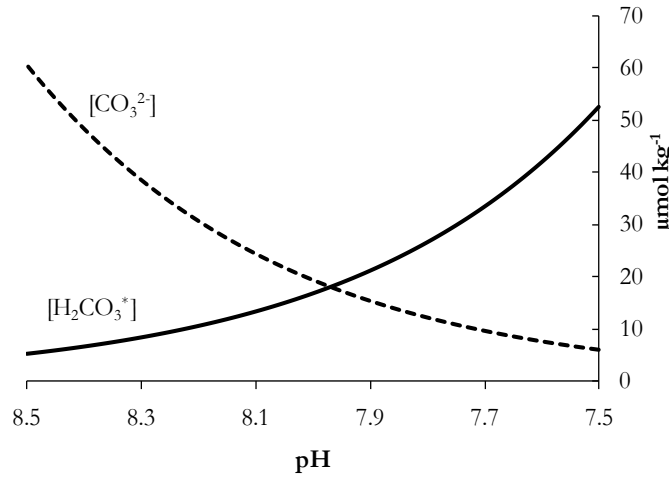
Figure 8. The change in CO_3^{2-} and $H_2CO_3^*$ with changing pH.

DIC, temperature and salinity is constant.

Air-Sea exchange

The air-sea flux of CO_2, F_{CO_2}, is parameterized using the formula:

$$F_{CO_2} = K_0 \, k \, (pCO_2^w - pCO_2^a) \qquad (15)$$

where K_0 is the salinity and temperature dependent solubility of CO_2 which is calculated according to Weiss (1974), k is the gas transfer velocity and pCO_2^w and pCO_2^a are the partial pressure of CO_2 in the water and atmosphere respectively.

The largest uncertainty lies in the parameterization of k. Several studies have been published (e.g. see the review in Liss et al., 2004), where the overall agreement is to express k as a function of wind speed. The following parameterization of Wanninkhof (1992) is among the most commonly used and it has a quadratic dependency on wind speed:

$$k = 0.31u^2 \left(\frac{Sc}{660} \right)^{-\frac{1}{2}} \qquad (16)$$

where u is the wind speed, Sc the Schmidt number; the ratio of the kinematic viscosity of water to the diffusion coefficient of CO_2 and 660 the Schmidt number for CO_2 in seawater at 20 °C used for normalization.

Carbon "pumps"

In ocean biogeochemistry, three ways of transformation and transfer of carbon are often referred to as the biological pump, the continental shelf pump and the solubility pump. The biological pump is a generic term for the biological processes that transport carbon from the euphotic zone to the ocean interior. In most shallow waters, the biological pump is not that effective due to the winter convection which mixes the whole water column. Instead, a modification of the biological pump; the continental shelf pump, was first proposed by (Tsunogai et al., 1999) for the East China Sea. The author's description is that the shallow seas take up CO_2 due to the large biological activity. The CO_2 transformed to organic carbon which sinks and is regenerated especially at the shallow bottom. The coastal bottom water, enriched in dissolved and particulate carbon is by processes like advection and diffusion transported into the subsurface layer of the open ocean. The continental shelf pump has later been applied on the North Sea (Thomas et al., 2004) and more globally discussed by Chen and Borges (2009).

The third pump; the solubility pump is particularly important in high latitudes. This is driven by the relationship between solubility of CO_2 and temperature. As the water flow towards higher latitudes, e.g. the Arctic, it gets cooler and takes up more CO_2. As it gets colder the water also become denser and starts to sink, contributing to the deepwater formation and the thermohaline circulation. The CO_2 can also be exported to the deep water through brine rejection during sea-ice formation.

Study Areas

Two different shelf areas have been investigated for this thesis; the Baltic Sea System and the Siberian shelf (Figure 9). Both areas are located in the northern hemisphere and receives large amounts of river runoff, but there are fundamental differences, the Baltic Sea system is surrounded by industrialised countries while there hardly is anyone living along the Siberian coast. Previously, not much work has been done regarding the carbon dynamics in parts of the Baltic Sea System (the Kattegat and the Skagerrak) and also the knowledge on the processes on the Siberian shelf has been sparse. Moreover, both areas seem to be divided in regions that are sinks or sources of CO_2 depending on the relation between production and input of organic material.
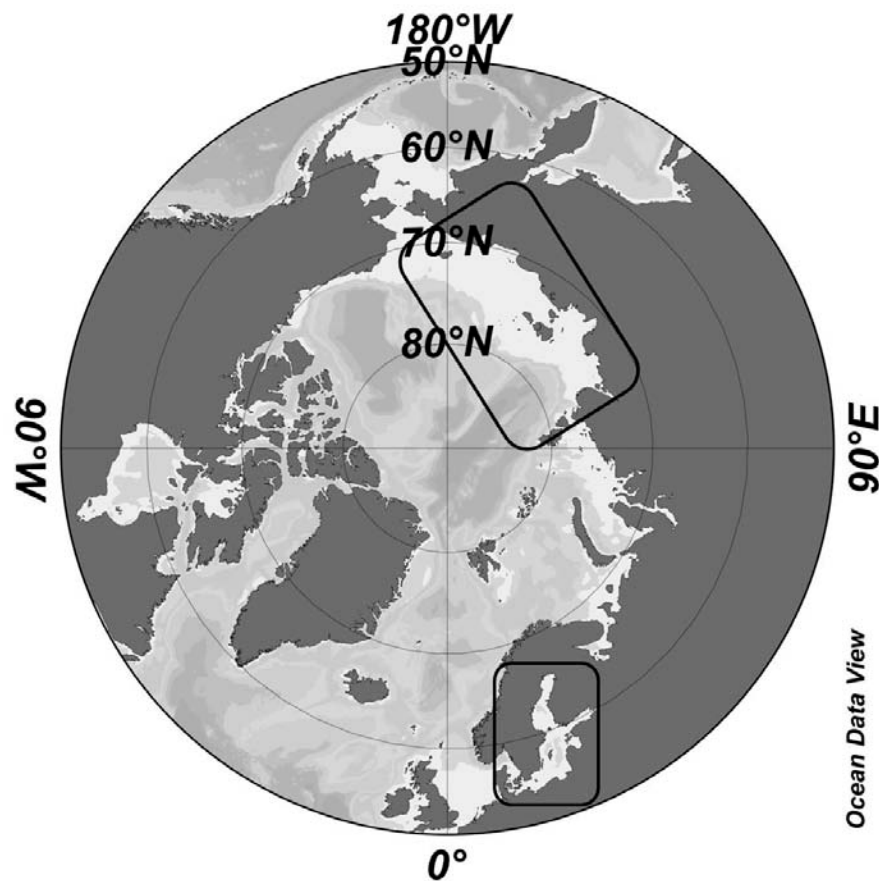
Figure 9. A map of the two study areas; the Siberian Shelf seas and the Baltic Sea System.

The Baltic Sea System

The Baltic Sea System is here considered to consist of the Baltic Sea, the Kattegat and the Skagerrak. (Figure 10) It is connected to the North Sea in the northwest and Skagerrak and Kattegat constitute the transition area to the Baltic Sea. The Baltic Sea is divided in several sub-basins, e.g. the Bothnian Bay, the Bothnian Sea, the Baltic Proper, the Gulf of Finland and the Gulf of Riga (Figure 10). The Baltic Sea receives large amount of river runoff, in average about $14\,000 \text{ m}^3\text{s}^{-1}$ between the years 1921 and 1998 (The BACC Author Team (2008). The freshwater forms a surface current flowing towards the North Sea out of the Baltic Sea following the Swedish coast trough the transition area before leaving Skagerrak along the Norwegian coast. An inflow of high salinity North Sea water to the Baltic Sea occurs but is hampered by the shallow Kattegat and even further by the shallow sounds in the Belt Seas and the Öresund. In Skagerrak, the North Sea water meets the out-flowing Baltic Sea water, creating the cyclonic gyre that dominates the circulation of the area (Rodhe, 1996).
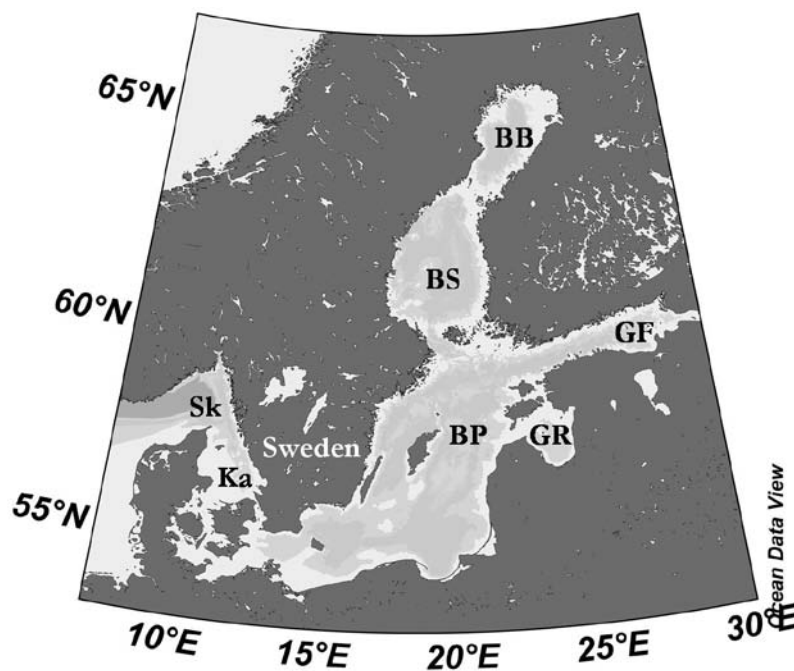
Figure 10. Map of the Baltic Sea System consisting of the Skagerrak (Sk), the Kattegat (Ka) and the Baltic Sea divided in the Bothnian Bay (BB), the Bothnian Sea (BS), the Baltic Proper (BP), the Gulf of Finland (GF) and the Gulf of Riga (GF).

The salinity of the Baltic Sea surface waters increases towards the south. In the Baltic Proper the salinity of the surface water is around 7 and below the stable halocline at ~60 m the salinity is 10-12 (Samuelsson, 1996). In the Kattegat the surface salinity is 20-25 and the Baltic influenced water is spread over the surface area even though the current has weak maxima along the Swedish coast (Gustafsson and Stigebrandt, 1996). The Kattegat deep water is heavily impacted by North Sea water and has a salinity of 32-33. In the Skagerrak the brackish water that is produced by the mixing

of Kattegat water and Baltic Sea water is pushed towards the coast due to the collision with the high saline North Sea water in strong fronts. The salinity in the surface layer is 20-25 close to the Swedish coast and increases to the west, with denser North Sea water (salinity ~35) beneath (Rodhe, 1996).

The Baltic Sea is considered as a sink for CO_2 (Chen and Borges, 2009). However, the northern part – the Bothnian Bay and the Bothnian Sea – is a net source of CO_2 to the atmosphere with a release of 9.7 and 7.1 mmol m^{-2} d^{-1}, respectively (Algesten et al., 2004). The lower value in the Bothnian Sea is due to higher primary production. According to Algesten (2006) the out-gassing in the Bothnian Bay is a result of the input of organic carbon from rivers and export production from the Baltic Proper.

During the last century and in particular during the last 30 years, the production in the Baltic Proper has increased by a factor of 2.5 (Schneider and Kuss, 2004) which the authors suggest is due to increased N_2 fixation. The increase in production can be related to the ongoing eutrophication and even though efforts have been made to reduce the nitrogen input the problem is far from being solved. Due to the high production rates, the Baltic Proper is a sink of CO_2 with an estimated uptake of 0.9 mol m^{-2} $year^{-1}$ (Thomas and Schneider, 1999).

A study by Feuerpfeil et al. (2004) in a eutrophicated part of the southern Baltic Sea showed that the area was a potential source for the organic carbon deposition of the deeper Baltic Sea areas. Schneider (2002) partly confirms this as they investigate the accumulation of CO_2 in the stagnant deep water. They did not only see an increase in the DIC concentration during the time period the water was stagnant, but they also found that only 10 % of the POC on the sediment surface was derived from the overlying water column. The southern Baltic Sea is also a sink for CO_2 with an annual uptake in the Arkona Sea estimated to $1.5 \cdot 10^{12}$ Tg C (Kuss et al., 2006).

In this thesis, Paper I, II and III deal with the Baltic Sea System. In Paper I a box model for TA in the Baltic Sea is developed and it also focuses on the long term changes in TA entering the Baltic Sea through the river runoff. The TA concentration in the runoff depends on the bedrock in the drainage area. In Scandinavia the bedrock is mainly granite, while limestone (calcium carbonate) dominates in the south. The weathering of $CaCO_3$ is enhanced by acid precipitation which peaked during the 1960s and 1970s but is still present. Also, decay of organic matter increases weathering of $CaCO_3$ through the production of CO_2 that hydrates to carbonic acid. The runoff from drainage basins rich in limestone will hence have high TA concentrations. An effect of this is that the Baltic Sea has a high TA concentration relative to its salinity, even if this varies depending on the basin. Furthermore, due to changes in the chemical conditions caused by e.g. atmospheric deposition and land-use in the drainage basins TA has decreased in rivers entering the Bothnian Bay and increased in the Gulf of Finland. As the main contribution to runoff TA is from HCO_3^- the Baltic Sea also contains an excess of DIC relative to its salinity. This excess is impacted by primary production as well as from decaying organic matter. The excess of DIC is exported with the surface water. In Paper II we assess the export of DIC between the Baltic Sea and the North Sea for the year 2006 using water transport values and salinities from the operational model DMI-BSHcmod, a 3D model provided by the Danish Meteorological Institute (DMI) together with measured DIC data from the

Kattegat. We estimated the net carbon export to 5.5 ± 0.3 Tg C year^{-1}, or $0.45 \pm 0.03 \cdot 10^{12}$ mol year^{-1}.

Skagerrak (Figure 10) is a productive region and in Paper III we evaluate the processes controlling the carbon dynamic in the Skagerrak during 2006. We also investigate the possibility of export through the continental shelf pump to the North Sea. The results from the Skagerrak show that CO_2 from the atmosphere is taken up by the ocean during the first half of the year 2006. The magnitude of this uptake is not compensated by out-gassing later in the year, neither by an accumulation of DIC in the water column. This leads to the conclusion that not all of the CO_2 taken up by primary production is recycled in the Skagerrak, instead it is exported to the North Sea with the bottom water or buried in the sediments.

With our result that Skagerrak is a sink for CO_2, at least during 2006, it can be suggested that the whole Baltic Sea System is a sink for CO_2. Furthermore, even if any regional sea has a limited impact on a global scale it has been suggested that the global continental margins correspond to an additional sink of ~27-30 % of the CO_2 uptake by the open oceans (Chen and Borges, 2009), where the high and mid-high latitudes are the most effective. These kinds of estimates are realistic since they are based on studies in the individual regions which are then added together.

The Siberian Shelf seas

The Arctic Ocean consists of deep basins surrounded by shallow continental shelves. The majority of them are located along the Siberian coast with a width of up to 900 km off the coast, while on the American side the shelf only extends 50-100 km (Bauch and Kassens, 2005). There is also a difference in the annual river runoff volume which is much larger on the Siberian side where the major Russian rivers enter the Arctic Ocean. The most prominent feature of the Arctic shelf seas that makes them so special is of course the severe long and cold winter period with extensive sea ice coverage.

Water from the Pacific Ocean enters the Arctic Ocean via shallow Bering Strait and into the Chukchi Sea, the Beaufort Sea and parts of the East Siberia Sea (Björk, 1989). The surface water and the sea-ice are then transported mainly by the Beaufort gyre and the transpolar drift towards the Fram Strait and the Canadian Arctic Archipelago; where the waters and the sea-ice exit the Arctic Ocean . Surface water is also entering through Fram Strait and the Barents Sea and this contributes to the waters of the Kara, Laptev and East Siberian Sea. In the northern Laptev Sea extensive sea ice production occur in a flaw lead polynia. Sea ice and surface waters from these shelves is mainly transported by the transpolar drift out of the Arctic Ocean by the way of Fram Strait.
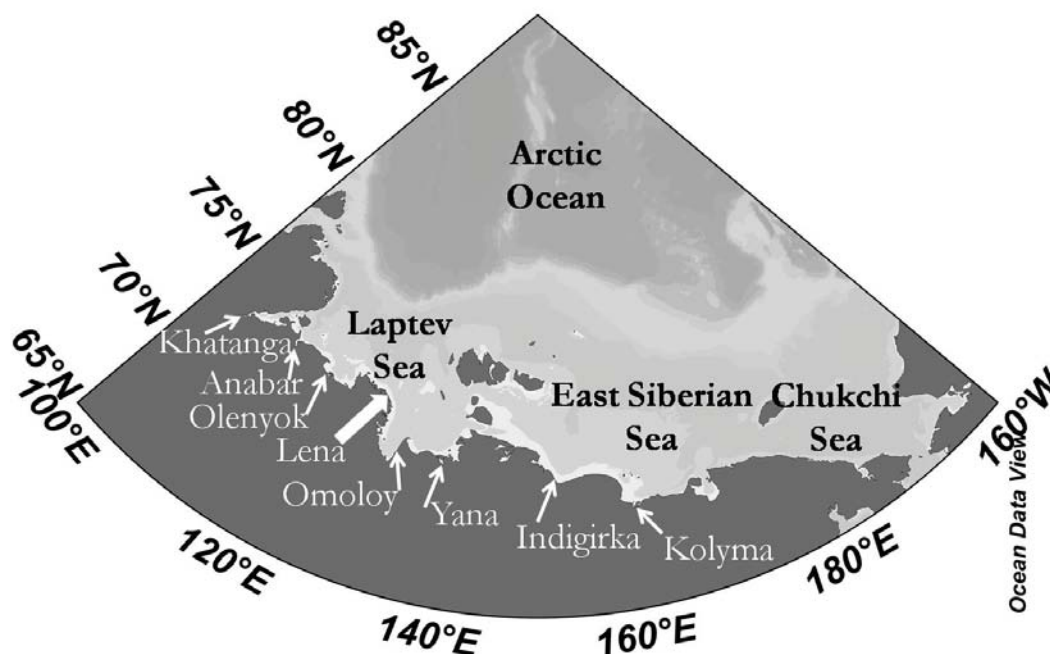
Figure 11. The Siberian Shelf seas, the arrows indicate rivers.

In Paper IV and V the carbon transformation and fluxes within the Siberian Shelf seas - the Laptev, the East Siberian Sea and the Chukchi Sea (Figure 11) - are evaluated. Going east along the Siberian

coast the salinity in the surface water will increase from less than 20 in the Laptev Sea to over 25 in the Chukchi Sea (Bauch and Kassens, 2005). The Laptev Sea and the East Siberian Sea are defined as interior shelf seas (Carmack and Wassmann, 2006) and are characterized by the strong impact of Arctic rivers. Six major rivers (Yana, Omoloy, Lena, Olenyok, Anabar and Khatanga) empty into the Laptev Sea (Stein and Fahl, 2004) and the discharge from Lena is by far the largest. The rivers Kolyma and Indigirka (Figure 11) exits in the East Siberian, however the discharges are much lower. The input of river runoff in the summer causes the surface water to flow off the shelf. This shifts in the winter when ice is formed and the rejected brine instead flows off the shelf close to the bottom (Carmack and Wassmann, 2006).

The Laptev Sea is nearly completely frozen for 9 months each year except for a more or less permanent large polynia, the cold climate causes even larger rivers to freeze solid for several months. In the short summer thawing of the uppermost permafrost leads to erosion and also the spring flood causes erosion along the river paths. This implies that substantial amounts of dissolved and particular matter as well as nutrients are carried out to the shelf seas.

In Paper IV results from the International Siberian Shelf Study (ISSS) along the Siberian coast in the summer of 2008 are presented. It is evident that the rivers heavily influence the study area. Most of the surface waters in the Laptev Sea were over-saturated in respect to atmospheric CO_2 concentrations and we argue that the pCO_2 signal is dominated by decay of terrestrial organic matter added both from rivers and by coastal erosion. The tendency of over-saturated pCO_2 values reduces as we move east trough the East Siberian Sea and towards the Chukchi Sea. In the latter, the surface waters are on the contrary under-saturated relative to atmospheric CO_2 as a result of marine primary production.

Similar results have been reported from earlier nearshore studies by Semiletov et al., (1999; 2004). They observed high pCO_2 concentrations within the Lena river plume (~850 μatm) and in the Kolyma river plume (~500 μatm). Under-saturation of pCO_2 in the Chukchi Sea of the same magnitude (~200 μatm) has also been reported (Fransson et al., 2009).

The inflowing waters from the Pacific Ocean foster the more marine conditions in the most eastern part of the Siberian shelf. The general transport of water is northward across the Chukchi sea shelf with four major outflows into the Canada Basin and the Beaufort Sea through Long Strait, Central Channel, Herald Valley and Barrow Canyon (Woodgate et al., 2005). The inflowing Pacific water is also laden with nutrients resulting in intense biological activity during the summer compared to other Arctic Ocean shelves (Bates et al., 2005). 15 % of the produced carbon in the Chukchi Sea is converted to suspended particulate carbon that gets exported from the shelf (Bates and Mathis, 2009). The effect of this continental shelf pump is evaluated in Paper V. We confirm previous studies (Bates, 2006) that have shown that the Chukchi Sea is a source for the continental shelf pump. Moreover, we show for the first time that also the East Siberian Sea exports a substantial amount of carbon to the Arctic Ocean. The result is surface waters under-saturated in pCO_2 and subsurface waters over-saturated in pCO_2. The under-saturation in the surface water will persist due to the sea-ice cover in the central basins of the Arctic Ocean which hampers further uptake from the

atmosphere. However, with decreasing sea-ice coverage in the future this uptake likely will increase. The other aspect is the pH decrease attributed to decay of organic matter in the subsurface water. We found that the $CaCO_3$ form aragonite was extensively under-saturated and calcite just below the limit for under-saturation at some stations. With the increasing anthropogenic carbon in the Arctic Ocean (Tanhua et al., 2009) the under-saturation in $CaCO_3$ (and high pCO_2) can extend to the surface in the future which instead can result in out-gassing of CO_2.

Vulnerability and possible future evolution

Marginal seas are more vulnerable to climate change and anthropogenic forcing than the open ocean due to the larger fluxes of organic and inorganic carbon from land. Increased river discharge has already been observed in the Arctic (Peterson et al., 2002) and models predict even larger increase in the future, especially in the Arctic region (Manabe et al., 2004) as a result of increased precipitation in high latitudes with a warmer climate (Manabe and Wetherald, 1985).

Land-use activities such as agriculture, deforestation and urbanization are changing the fluxes to the coastal ocean and rivers will bring more organic carbon, DIC (and TA) and also nutrients to the marginal seas. The nutrients brought by the rivers can increase primary production in the marginal seas which can enhance the continental shelf pump and the uptake of CO_2. This could as well increase the production of N_2O that will add to the greenhouse effect if escaping to the atmosphere, but that is outside the scope of this work.

More precipitation likely promotes weathering in the drainage basins and as a result the concentrations of HCO_3^- in the rivers increase (Cai et al., 2008). Also the CO_2 produced in the rivers when the organic matter decay conduces to the weathering of limestone in the drainage basin as discussed in Paper I. In the Arctic the river water from the Mackenzie River has a high TA concentration for the region but the CO_2 signal from remineralisation is despite this dominating. According to Chierici and Fransson (2009) the "acidic" river water decreases the concentration of CO_3^{2-} in the river plume, and with that the saturation state of $CaCO_3$. However, since saturation of $CaCO_3$ also is dependent on the concentration of Ca^{2+} which is much lower in rivers, the runoff dilutes the Ca^{2+} ions as does the melting of sea-ice and it will hence decrease the saturation of $CaCO_3$ (Yamamoto-Kawai et al., 2009).

In the open ocean the invasion of anthropogenic carbon in the surface waters is by far the most important reason for the ocean acidification with decreasing saturation of $CaCO_3$ as a consequence (Feely et al., 2004). However, in marginal seas there are additional processes that can enhance the acidification. From a mass balance approach (Andersson and Mackenzie, 2004) states that due to the transport and deposition of organic matter the shallow water ocean environment will become increasingly net-heterotrophic (the respiration will exceed the production) resulting in $CaCO_3$ dissolution. But also emissions of sulphur and nitrogen can increase the acidification in marginal seas (Doney et al., 2007) since the majority of acid-deposition occurs close to the primary source. The dissociation products of strong acids as HNO_3 and H_2SO_4 will decrease TA and pH in the surface waters and increase the CO_2 concentration (reaction *3, 2*). The effects of acidification can yet

be modulated by enhanced primary production due to eutrophication (Gypens et al., 2009) or by an increase of the buffering capacity from riverine TA.

The mean air temperatures over the Arctic have increased by ~2- 3 °C in summertime and by ~4 °C in winter since the 1950's (Chapman and Walsh, 2003). The most visible consequence of this is the observed retreat of summer sea ice (Belchansky et al., 2005). A longer ice-free summer season can lengthen the productive period and the productive area; Arrigo (2008) estimated a more than 3-fold increase. Even though nutrient availability, which might limit primary production, was not considered in their work, primary production will increase even though the magnitude still is uncertain. An increase will affect the uptake of CO_2 by the Arctic Ocean. Murata and Takizawa (2003) instead emphasize the solubility pump. They present post-bloom results and suggest that the low temperature is the main reason for the strong under-saturation and the CO_2 uptake in the western Arctic shelf seas. In that case, an increase in temperature due to global warming would decrease the CO_2 uptake.

A longer ice-free season may likely increase the coastal erosion since the ice would no longer protect the coast during fall when heavy storms hit the land. Moreover the permafrost contains a large pool of organic carbon and a warmer Arctic increases the thawing of permafrost and hence the release of carbon. Both increased coastal erosion and the thawing of permafrost will cause increased out-gassing of CO_2 in e.g. the Laptev Sea as discussed in Paper IV.

Summary

Despite their small area, marginal seas are important in a global perspective. They separate the coastal zone from the open ocean and are heavily influenced by land. Both natural and anthropogenic processes on land release organic and inorganic carbon as well as nutrients that are brought to the marginal seas by rivers. Furthermore, increasing emissions from burning of fossil fuels is increasing the concentration of CO_2 in the atmosphere which is a likely cause for the observed climate changes.

The Baltic Sea System and the Siberian Shelf seas are two areas characterized by large amounts of river runoff relative to their respective area. However, due to the large environmental differences they will differ in their responses. The Baltic Sea is surrounded by land and the bedrock changes from being dominated by granite in the northern part to limestone in the southern part. Acid precipitation and CO_2 produced from decay of organic matter will increase the weathering of the limestone adding to the TA of the rivers. In the northern part where the weathering is small the TA will instead decrease. High TA in the southern rivers contributes to the DIC concentration in the Baltic Sea, and together with high biological production rates the Baltic Sea has an excess of DIC relative to its salinity. The Baltic Sea is driven by a general estuarine circulation i.e. the input of freshwater from the river will cause an outflow of Baltic Sea surface water towards the North Sea. Hence, the DIC from the Baltic Sea will also be exported and will in the end add to the North Sea carbon budget. We estimated the net carbon export to 5.5 ± 0.3 Tg C year^{-1}.

Skagerrak is a productive marginal sea that boarders to the North Sea. In the winter when the surface is cooled, Skagerrak will take up CO_2 which is then used during primary production since there is no compensating efflux of CO_2 later in the year. We calculated a net sea- air flux of 1.3 mol m^{-2} year^{-1}. The carbon that was taken up in the surface is exported by a continental shelf pump to the North Sea or is buried in the sediments.

In the Arctic and especially in the Laptev Sea, the large amounts of organic carbon transported by the major Russian rivers and particulate organic matter added by coastal erosion will decay in the shelf seas. The high concentrations of produced pCO_2 will not be compensated for by primary production which also is hampered by the high turbidity in the river plume. Instead, there will be an out-gassing of CO_2 in the Laptev and the western East Siberian Sea. However, in the eastern Siberian Sea and the Chukchi Sea the inflow of Pacific water laden with nutrient favours the conditions for a large primary production and the result is an uptake of CO_2 in this region. The organic matter produced by primary production sinks out of the photic zone and decay at the sediment surface. This will result in a flux with decay products back to the bottom water. As the water flows off the shelf and in to the Arctic Ocean this will result in surface waters under-saturated in pCO_2 and subsurface waters over-saturated in pCO_2. In a future with less sea-ice the result might be an increased uptake of CO_2 from the atmosphere.

Future Outlook

Carbon cycle dynamics in coastal environments can shift rapidly, particularly in response to changes in nutrient and organic matter inputs. Variable river influence and inter-annual changes can for example shift the particular marginal sea from being a source to become a sink for atmospheric CO_2 and vice-versa. Furthermore, the role marginal seas play in the marine ecosystem due to the large primary production makes them vulnerable to ocean acidification. Thus, there is a need for long-term observations.

It is also a challenge to develop appropriate observing systems to get sufficient data coverage i.e. to observe the large temporal and spatial variations of pCO_2. Voluntary observation ships (VOS), moorings, drifters and gliders are useful tools. However, there are no self-evident in-situ techniques for measuring the carbon parameters that can be deployed on this kind of equipment (except pCO_2 system). If developed, this would be a break-through. In the Arctic the largest challenge for year-round observations is the harsh conditions during winter. Hence, high quality unmanned observing systems for the carbon parameters would be a great step forward, to accomplish accurate estimations and predictions for future system changes. Research is also needed to determine constants for calculations of the inorganic carbon system, in particular for low-salinity waters (carbonic acid dissociation constants, etc.).

In addition to measurements, interesting studies includes:

- the effect on marginal seas from CO_2 induced mineral weathering and increased decay of organic carbon
- assess the drivers for surface water acidification in marginal seas
- the CO2 air-sea exchange in marginal seas

Acknowledgement

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