

---

---

# Fluxes and transformation of carbon in the Siberian shelf seas under changing environment

---

---

**Iréne Wählström**



UNIVERSITY OF GOTHENBURG

## AKADEMISK AVHANDLING

för filosofie doktorsexamen i naturvetenskap, inriktning kemi, som med tillstånd från Naturvetenskapliga fakulteten kommer att offentligt försvaras fredagen den 8 juni 2012 kl. 10.00 i föreläsningssal KB, Institutionen för kemi och molekylärbiologi, Campus Johanneberg, Göteborg.

Fakultetsopponent:

Doctor Dorothee Bakker, University of East Anglia,  
Norwich, United Kingdom

Department of Chemistry and Molecular Biology,  
University of Gothenburg  
2012

Fluxes and transformation of carbon in the Siberian shelf seas under changing environment

© Iréne Wählström, 2012

Department of Chemistry and Molecular Biology  
University of Gothenburg  
SE-412 96 Gothenburg, Sweden

ISBN 978-91-628-8473-4

E-publication: <http://hdl.handle.net/2077/28865>

Printed by Ineko

*Erfarenhet är inte vad som händer oss,  
utan vad vi gör av det som händer oss.*

Aldous Huxley



## Abstract

The Arctic is especially vulnerable to the increased air temperature caused by emissions of greenhouse gases to the atmosphere, carbon dioxide being one of them. In this thesis, both fieldwork and modelling of the East Siberian Arctic Shelf (the Laptev Sea and the East Siberian Sea) have been carried out to investigate the carbon system in this region.

Fieldwork in 2008 revealed two distinct hydrological regimes in the East Siberian Sea, one in the western area and one in the eastern area. The western area is dominated by freshwater from rivers flowing into the East Siberian Sea but also from the Lena River plume coming from the Laptev Sea. Nearly all waters in this area are supersaturated with respect to carbon dioxide compared to the atmosphere due to mineralization of substantial amounts of terrestrial organic matter coming from thawing permafrost and coastal erosion. This excess carbon dioxide may be a potential source to the atmosphere and thus increase the atmospheric greenhouse gas content, a positive feedback mechanism. The eastern area is dominated by inflow of Pacific-derived waters that are clear, salty and nutrient rich and therefore favour primary productivity. Phytoplankton consumes carbon dioxide that lowers its partial pressure ( $p\text{CO}_2$ ) making it undersaturated compared to the atmosphere and the Eastern East Siberian Sea becomes a sink for atmospheric carbon dioxide. In addition, the Laptev Sea had supersaturated  $p\text{CO}_2$  equal to an excess of dissolved inorganic carbon of around  $\sim 5 \times 10^{12}$  gC, which is in the same order as for the Western East Siberian Sea. This excess is also a potential source of carbon dioxide to the atmosphere that could enhance climate change.

Modelling work with a one-dimensional, time dependent coupled physical biogeochemical model confirms this conclusion for the late summer when the  $p\text{CO}_2$  in the seawater increases due to mineralization and water mixing. Model simulations for the Laptev Sea were utilized to investigate the net annual sea-air flux caused by different forcings; doubled atmospheric partial pressure of carbon dioxide; 4°C air temperature increase; doubling the concentration in the runoff of dissolved organic carbon or nutrients; increasing the river discharge by 25 %; increasing the wind speed by 10 % or a combination of these forcings. The result revealed decreasing uptake of carbon dioxide when changing the river properties except for the increase of nutrients when the uptake of carbon dioxide increased. The uptake also increased with the changed forcings in air temperature, wind speed and atmospheric partial pressure of carbon dioxide, separately and in combination.

**KEY WORDS:** Carbon system, Carbon dioxide, Arctic Ocean, Siberian shelf seas, Climate change

# Part A

## Table of Contents

1. Introduction .....	1
2. The marine inorganic carbonate system .....	5
2.1 Definition of the carbonate system .....	5
2.2 Transformation of carbon .....	7
2.2.1 Soft parts .....	7
2.2.2 Hard parts .....	8
2.3 Sea-air exchange of CO <sub>2</sub> .....	9
2.4 Analytical methods .....	9
2.4.1 Determination of dissolved inorganic carbon .....	10
2.4.2 Determination of total alkalinity .....	10
2.4.3 Determination of pH .....	11
2.4.4 Calculation of CO <sub>2</sub> flux .....	11
3. Model description .....	13
3.1 Mathematical background .....	13
3.2 Physical part .....	14
3.3 Biogeochemical part .....	15
4. The Arctic system .....	17
4.1 Circulation .....	17
4.2 Vertical distribution .....	18
4.3 Flaw lead polynya .....	19
4.4 Atmospheric pressure field .....	19
4.5 Permafrost .....	20
4.6 Biogeochemistry .....	21
5. The carbon system of the Siberian shelf seas .....	23
5.1 The Laptev Sea .....	23
5.2 The East Siberian Sea .....	27
6. Summary and Conclusions .....	31
7. Outlook for the future .....	33
Acknowledgment .....	34
References .....	36

## Part B

### Research paper:

Papers included in this thesis, referred to in the text by Roman numbers:

- Paper I:** Wählström, I., Omstedt, A., Björk, G., Anderson, L.G., Modelling the CO<sub>2</sub> dynamics in the Laptev Sea, Arctic Ocean: Part I , *J. Mar. Syst.*, accepted 2012.
- Paper II:** Wählström, I., Omstedt, A., Björk, G., Anderson, L.G., Modelling the CO<sub>2</sub> dynamics in the Laptev Sea, Arctic Ocean: Part II Sensitivity of fluxes to changes in the forcing, *J. Mar. Syst.*, submitted, April 2012.
- Paper III:** Anderson, L.G., Jutterström, S., Hjalmarsson, S., Wählström, I., and Semiletov, I.P., Out-gassing of CO<sub>2</sub> from Siberian Shelf Seas by terrestrial organic matter decomposition, *Geophys. Res. Lett.*, 36, L20601, doi:10.1029/2009GL040046, 2009.
- Paper IV:** Anderson, L.G., Björk, G., Jutterström, S., Pipko, I., Shakhova, N., Semiletov, I.P., and Wählström, I., East Siberian Sea, an Arctic region of very high biogeochemical activity, *Biogeosciences*, 8, 1745–1754, doi:10.5194/bg-8-1745-2011, 2011.
- Paper V:** Pipko, I.I., Semiletov, I.P., Pugach, S.P., Wählström, I., and Anderson, L.G., Interannual variability of air-sea CO<sub>2</sub> fluxes and carbonate system parameters in the East Siberian Sea, *Biogeosciences*, 8, 1987-2007. doi: 10.5194/bg-8-1987-2011, 2011

### Contribution report:

- I** Responsible for the development of the model, the calculations and the data analyses as well as writing the manuscript.
- II** Responsible for the modelling, the calculations and the data analyses as well as writing the manuscript.
- III** Contributed to sample analysis, data interpretation and partly in writing the manuscript.
- IV** Contributed to sample analysis, data interpretation and partly in writing the manuscript.
- V** Contributed to sample analysis and somewhat in writing the manuscript

## ***Populärvetenskaplig sammanfattning***

Jordens klimatförändringar anses av de flesta forskare bero på den ökande mängd växthusgaser som människan släpper ut från exempelvis förbränning av fossila bränslen. Växthusgaserna är flera, varav koldioxid är en av dem. Fram till 1994 är det uppskattat att ungefär hälften av människans utsläpp av koldioxid (antropogent) togs upp av haven men upptaget har nu minskat pga. att havens förmåga att ta upp koldioxid minskar ju mer det finns i haven. Växthusgaserna höjer jordens medeltemperatur och denna temperaturökning är speciellt uttalad i Arktis och framför allt över Sibirien och dess grunda kusthav.

Temperaturökningen påverkar miljön i kusthaven genom att t.ex. flodtillförseln ökar, permafrosten tinar samt kusterosionen ökar. En effekt blir att mer organiskt kol (från levande organismer) som är lagrat i jorden tillförs havet. Den mest synbara effekten av temperaturökningen är minskningen av havsistäcket i Arktis. Dessa miljöförändringar påverkar ett flertal processer som orsakar att havets kolinnehåll antingen kan öka eller minska vilket har stor betydelse för hur mycket koldioxid havet kan ta upp. Vi har undersökt två av kusthaven utanför Sibirien, Laptev havet och Östsibiriska havet, dels genom en fartygsexpedition och dels med hjälp av en matematisk modell för Laptev havet. Målsättningen var att studera hur olika processer påverkar koldioxidflödet mellan atmosfären och havet.

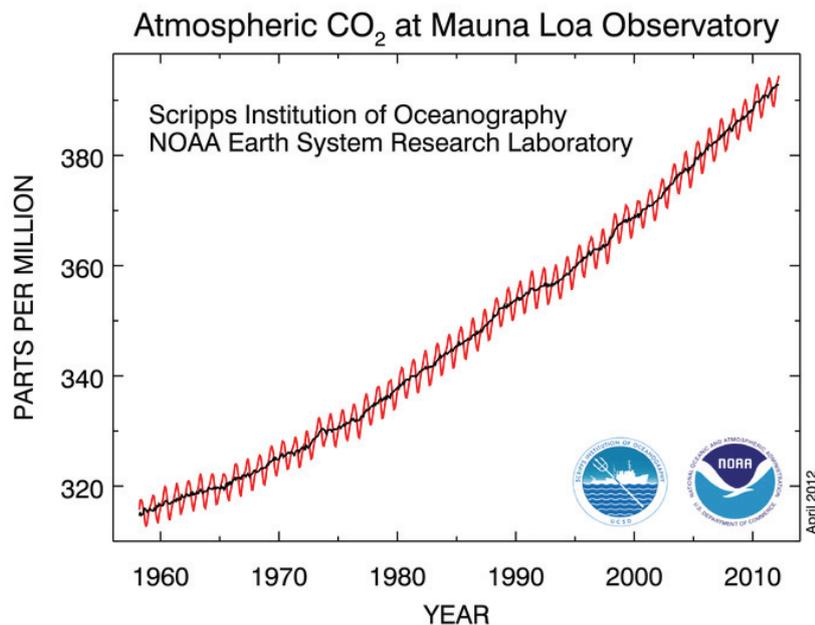
Östsibiriska havet kan delas upp i två områden, nämligen västra respektive östra delen. Denna uppdelning bestäms framför allt av vindarna. Den östra delen påverkas till största delen av Stilla havsvatten som flödar in genom Berings sund och vidare in i Östsibiriska havet. I detta vatten sker mycket fotosyntes under sommaren, vilket konsumerar koldioxid. Detta leder till en lägre halt i havet än i luften och därför tar havet upp koldioxid från luften. I den västra delen tillförs flodvatten dels från floder i Östsibiriska havet men också från det angränsande Laptev havet. I flodvattnet finns mycket organiskt kol som delvis bryts ner till koldioxid i havet och halten av denna ökar då. Detta leder till en högre halt i havet än i luften och därmed flödar koldioxid ur havet till luften och späder på klimatförändringen.

Laptev havet hade ett överskott av koldioxid i samma storleksordning som Östsibiriska havet under sensommarens expedition 2008, troligen också ett resultat av nedbrytning av organiskt material. Modellresultaten visar också ett överskott av kol på sensommaren då nedbrytning sker av organiskt material som bildats under sommarens fotosyntes. Koldioxid konsumeras under fotosyntesen och därför sker ett flöde från luften till havet under denna process. Modellen användes för att simulera hur det årliga nettoflödet av koldioxid mellan hav och luft påverkas av olika klimatrelaterade förändringar. Resultatet visade att en ändring av flodernas egenskaper (ökat utflöde eller innehåll av löst organiskt kol och/eller koldioxid) minskade det årliga upptaget medan en ökning av atmosfärens temperatur, starkare vind eller mer koldioxid i atmosfären ökade havets förmåga att ta upp koldioxid.

Sammanfattningsvis kommer flödet av koldioxid till atmosfären troligtvis att öka med en ökad lufttemperatur, framför allt om den stora reservoar av organiskt kol som finns lagrat i Arktis tundra tinar och tillförs havet.

# 1. Introduction

In recent decades, a debate has been conducted regarding climate change and its coupling to greenhouse gases, such as water vapour, methane and carbon dioxide (CO<sub>2</sub>) where the latter are part of the carbonate system. In pre-industrial times (before mid-eighteenth century) the atmospheric carbon dioxide level was constant at around 280 ppm but has now risen to over 390 ppm (Figure 1). The rise in CO<sub>2</sub> is an ongoing process due to combustion of fossil fuels, land use change and cement production. This enhanced CO<sub>2</sub> concentration in the atmosphere would have been even higher if the ocean and land had not taken up part of the anthropogenic emission of CO<sub>2</sub>.



**Figure 1.** The atmospheric CO<sub>2</sub> record at the Mauna Loa Observatory on Hawaii (<http://cdiac.ornl.gov/trends/co2/>). Units in atmospheric carbon dioxide dry air mole fractions.

Sabine et al. (2004) estimated that nearly half of the CO<sub>2</sub> emitted to the atmosphere from combustion of fossil fuels between 1800 and 1994 was taken up by the oceans. From the 1990's to 2006, the growth rate of the global fossil fuel emissions CO<sub>2</sub> has increased from 1.3 to 3.3 % y<sup>-1</sup> which has decreased the oceans' storage from about 50 to ~41 % (Canadell et al., 2007). The acceleration of the emissions has different explanations such as larger demand for energy globally,

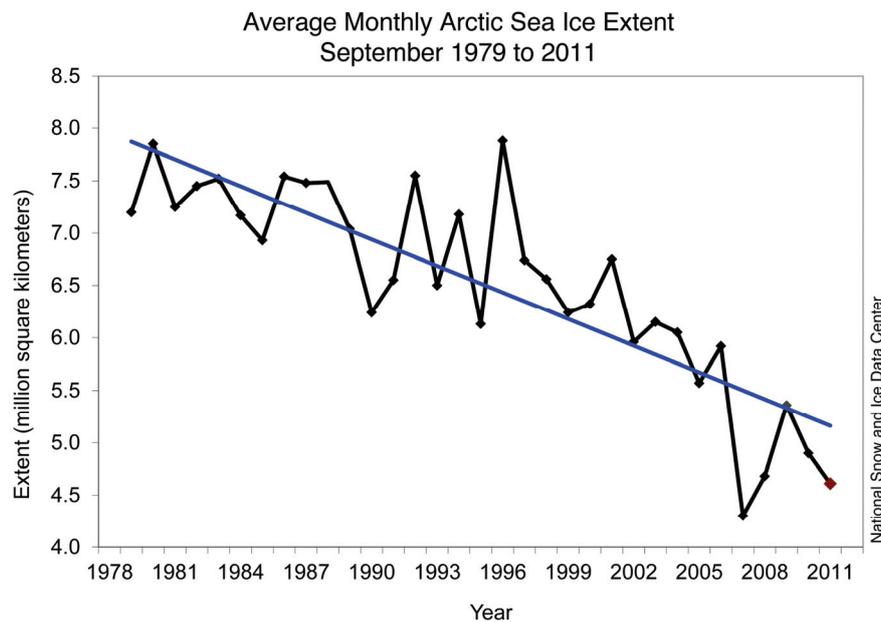
increased energy per capita and population growth. The decreasing uptake proportion depends on the oceans' decrease in pH with increasing CO<sub>2</sub> concentration that lowers the buffer capacity (Bindoff et al., 2007; Sabine and Tanhua, 2010).

A large number of climate models are used today in an attempt to make projections of the impact of the increased greenhouse gases on the Earth's system. The results of these models are assessed by the IPCC, Intergovernmental Panel on Climate Change. In their fourth assessment report (2007) they project that a doubling of CO<sub>2</sub> (to 800 ppm) from the present level in the atmosphere would increase the global mean air temperature by 2.4 °C (B2 scenario) and by 3.4 °C if the CO<sub>2</sub> in the atmosphere were raised to 1250 ppm (A2 scenario) by the end of the 21<sup>st</sup> century.

In the Arctic Ocean, climate change caused by the increased concentration of greenhouse gases in the atmosphere is pronounced and the warming is on average twice that of the global mean (Serreze et al., 2009; Serreze and Francis, 2006). The warming of the Arctic region is assumed to be enhanced and accelerated compared to the rest of the Earth owing to the albedo feedbacks and interactions involving the sea ice and snow cover, the Arctic amplification. Models included in the Arctic Climate Impact Assessment (ACIA) have projected an air temperature increase of 5°C (B2 scenario) and 7 °C (A2 scenario) north of 60 °N by the end of the 21<sup>st</sup> century. For the Canadian Archipelago and the Russian Arctic an increase of 5 °C for the same period is suggested and for Scandinavia a 3 °C increase (B2 scenario). The greatest increase is modelled over the central Arctic Ocean in autumn and winter (B2 scenario) where the air temperature would increase by 9 °C due to its response to ice cover and thickness. In contrast, summer temperature increases over the Arctic Ocean are projected to remain below 1 °C throughout the 21<sup>st</sup> century. The air temperature rise is not the only modelled effect of climate change due to increasing greenhouse gases. These also include sea level rise, precipitation increase and the decrease in snow cover.

However, the most noticeable effect of the increased air temperature is the reduced sea ice cover (Figure 2), which results in a longer period of open water during summer. This is most pronounced on the shallow seas (the shelf seas) surrounding the Arctic Ocean where seasonal sea ice formation and melting occurs.

More open water reduces the water surface albedo, from about 0.85 for snow-covered sea ice to 0.65 for bare ice and down to 0.07 for open water (Stroeve et al., 2012). With lower albedo, surface water absorbs more solar radiation, which warms the surface water and delays the ice formation in the following autumns. This results in a thinner spring ice cover that melts earlier and more rapidly and even more open water is formed the following summer and so on. This is the positive ice-albedo feedback mechanism (Serreze et al., 2007).



**Figure 2.** Sea ice extent in September from 1979 to 2011. From National Snow and Ice Data Centre, University of Colorado, Boulder.

A consequence of longer summer time is the prolonged time-period for the interaction between the ocean and the atmosphere, including the extended light input. This expands the time for primary production but also allows for more gas exchange, e.g. for CO<sub>2</sub> and oxygen. Gas fluxes are further enhanced by the lack of ice cover that hampers sea-air exchange. Another result of open water is more windy conditions, a result from enhanced cyclonic activity by increased evaporation. Stronger wind amplifies the exchange of gases between the atmosphere and ocean through the increase in transfer velocity.

Since the mid 1960's, there has been an increased cyclone activity (low-pressure system) north of Siberia that favours stronger and more frequently warm,

southerly winds (Maslanik et al., 1996; Serreze et al., 2000) leading to amplification of the wind-driven forcing. Strong winds increase wave activity which causes coastal erosion, an effect that can be extensive in the autumn when storms are frequent, especially if no land-fast ice has been formed. A retreat of land of 2-40 m yr<sup>-1</sup> has been reported (Semiletov, 1999) that brings old, terrestrial organic matter into the seawater that at least partly oxidizes to carbon dioxide (Semiletov, 1999; Semiletov et al., 2011).

The terrestrial biosphere will also be affected by greenhouse gas induced air temperature rise, resulting in increasing river discharge and permafrost degradation, including a reduction of its extent. Peterson et al. (2002) found a positive relationship between air temperature and river discharge for the Eurasian rivers, i.e. increased air temperature increases the discharge. This enhanced discharge has been suggested to increase the export of dissolved organic carbon (DOC) as well as phosphate (PO<sub>4</sub><sup>3-</sup>) and dissolved silicate to the Western Siberian shelves. This is due to thawing of the upper active layer in the permafrost of the drainage basins and the mineral weathering in soil waters (Frey and McClelland, 2009). Whether the thawing of permafrost will have any effect on the nitrate (NO<sub>3</sub><sup>-</sup>) is still uncertain (Frey et al., 2007).

The permafrost in the Arctic stores large amount of carbon, both on land but also in the seafloor of the shelves seas. Zimov et al. (2006) estimated the carbon reservoir in the Arctic permafrost to be between 950-970×10<sup>15</sup> gC. This can be compared with the second and third largest carbon reservoir globally; the soil (1500×10<sup>15</sup> gC) and vegetation (650×10<sup>15</sup> gC), the largest being the ocean (40 000×10<sup>15</sup> gC). With increasing air temperature, thawing of the permafrost will probably occur and large amounts of carbon will be released to the atmosphere, this is considered to represent a positive feedback in the context of global change.

The changing climate has profound consequences for the Arctic region environment and it is therefore essential to increase the knowledge of relevant processes and their response to the changing conditions. This thesis is a contribution to the understanding of the carbon system of the Arctic Ocean; both through fieldworks that add to our understanding of how the system works and through modelling that examine the sensitivity of the system to changes in forcings.

## 2. The marine inorganic carbonate system

In the marine system, carbon exists in organic and inorganic forms, both dissolved and particulate. The organic carbon in seawater originates from the terrestrial biosphere via river runoff, as well as from coastal erosion. Another source of organic carbon is within seawater through primary production where photosynthetic organisms produce organic carbon by utilizing light, trace elements, nutrients and inorganic carbon. Dissolved inorganic carbon (DIC) is present in seawater as the chemical species carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ), carbonate ( $\text{CO}_3^{2-}$ ) and dissolved carbon dioxide ( $\text{CO}_2$ ); together these constitute the carbonate system.

### 2.1 Definition of the carbonate system

When  $\text{CO}_2$  dissolves in seawater, the following reactions occur:



When  $\text{CO}_2(\text{g})$  is added to water it dissolves as  $\text{CO}_2(\text{aq})$ , which reacts with water to carbonic acid ( $\text{H}_2\text{CO}_3$ ) that dissociates into bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) ions. In seawater, where pH is around 8 the carbonate system is dominated by  $\text{HCO}_3^-$  (~90 %) followed by  $\text{CO}_3^{2-}$  (~9 %). The remaining 1% is the sum of  $\text{CO}_2(\text{aq})$  and  $\text{H}_2\text{CO}_3$ , which are often added together as it is difficult to analytically distinguish between these two chemical species. Therefore, they are often referred to as  $\text{H}_2\text{CO}_3^*$  (see equation 5).

To describe the carbonate system four measurable parameters can be used; DIC, total alkalinity (TA), pH and the partial pressure of carbon dioxide ( $p\text{CO}_2$ ). If two of the carbonate system parameters are known the other two can be calculated, using for instance the computer program CO2SYS (Lewis and Wallace, 1998). If three of the parameters are determined, CO2SYS can be used to estimate the internal consistency by comparing the calculated values with the measured.

The concentration of DIC is defined as the sum of the inorganic species:

$$\text{DIC} = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (5)$$

Total alkalinity is a measure of the seawater buffer capacity, i.e. the concentration of bases (negative charge) with  $\text{pK} > 4.5$  (at  $25^\circ\text{C}$ ) that will react with added  $\text{H}^+$  (Dickson, 1981). TA is defined as follows:

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{HS}^-] + 2[\text{S}^{2-}] + [\text{NH}_3] - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] \quad (6)$$

pH is defined as the negative logarithm of hydrogen ion activity, where the activity is related to concentration by the activity coefficient. The activity coefficient takes into account the interactions between the hydrogen ion and other dissolved species. The activity coefficient equals one in the standard state, which traditionally was set to a solution with zero ionic strength. In seawater, with high ionic strength, the activity coefficient would thus be less than one because of the interaction with other ions. As it is not possible to exactly determine the activity coefficient for seawater it was decided to adopt a seawater pH scale using seawater as the standard state, i.e. setting the activity coefficient to one in seawater. This by definition means that the activity and concentration are identical. Three different pH scales have been defined in seawater; the free scale, the total scale and the seawater scale. In this thesis, pH is defined on the total hydrogen ion concentration scale,  $\text{pH}_T$ , which includes hydrogen sulphate ions ( $\text{HSO}_4^-$ ) but not hydrogen fluoride (HF) (Hansson, 1973). For  $\text{pH}_T$ :

$$a_{\text{H}^+}(\text{T}) = [\text{H}^+] + [\text{HSO}_4^-] \quad (7)$$

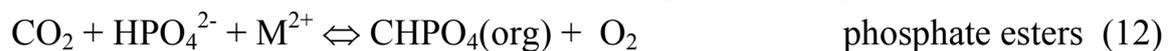
$$\text{pH}_T = -\log_{10} a_{\text{H}^+}(\text{T}) \quad (8)$$

For an ideal gas in equilibrium with seawater, the partial pressure is defined as the product of the mole fraction and the total pressure. Carbon dioxide is not an ideal gas therefore the fugacity of  $\text{CO}_2$  ( $f\text{CO}_2$ ) is used instead that take into account the non-ideal gas behaviour. The ratio between  $p\text{CO}_2$  and  $f\text{CO}_2$  ranges from 0.995 to 0.997 in the temperature interval of  $-2^\circ\text{C}$  to  $25^\circ\text{C}$ .

## 2.2 Transformation of carbon

### 2.2.1 Soft parts

Photosynthetic organisms utilize light as an energy source to convert inorganic carbon (CO<sub>2</sub>), nutrients and trace elements into particulate organic matter (POM) and oxygen (O<sub>2</sub>). The organic matter consists of different forms such as carbohydrates, lipids, proteins and phosphate ester groups. The production of these different forms occurs simultaneously and can be illustrated by the following simplified reactions:



From the four reactions above it is seen that CO<sub>2</sub> is consumed during photosynthesis, which decreases the *p*CO<sub>2</sub> as well as DIC and increases pH. The decrease in the surface water *p*CO<sub>2</sub> has a potential to increase the uptake of atmospheric CO<sub>2</sub>. TA is not affected by the loss of CO<sub>2</sub> but is increased by the production of proteins through the uptake of hydrogen ions and decreased by the production of phosphate esters when hydrogen phosphate (HPO<sub>4</sub><sup>2-</sup>) is used.

Redfield et al. (1963) suggested that organic matter in phytoplankton are built up by a specific relationship between carbon, nutrients (NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>) and oxygen. This is called RKR-ratio after Redfield-Ketchum-Richards that is used in this thesis and is given as:

$$\text{P: N: C: O}_2 = 1: 16: 106: -138 \quad (13)$$

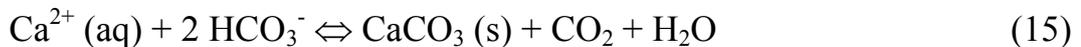
This ratio has been questioned since later investigations have found deviation from the classical RKR depending on depth and location (Anderson and Sarmiento, 1994; Takahashi et al., 1985; Thomas, 2002).

The organic matter produced has different fates; it is consumed by zooplankton, it is mineralized back into its original chemical species; it sinks and mineralizes on its way to deeper water or ends up in the sediment where it could be buried or mineralized with a flux of the decay products back to the bottom water. Mineralization occurs through bacterial degradation, the reverse of reaction (9-12),

i.e. CO<sub>2</sub> as well as nutrients are released and oxygen is consumed. This leads to an increase in *p*CO<sub>2</sub> and DIC and decrease in pH. If the organic matter is mineralized in the photic zone the released constituents can be utilized by the primary producers again or stay as dissolved species in the water. However, if the decay occurs in deeper parts of the water column the carbon is removed from contact with the primary producers and from coming into contact with the atmosphere. This can take hundreds of years depending on the depth and location as well as the circulation and mixing of the water parcel before it is up in the surface again. If the organic matter reaches the sediment it is stored and buried there for a longer period of time but the mineralization continues.

### 2.2.2 Hard parts

Some organisms form hard shells or skeletons parallel to the soft parts described above. These consist of biogenic silica (e.g. diatoms) or carbonates of calcium or magnesium, (e.g. coccolithohorids) and are formed according to the reactions:



The effect on the carbonate system of the formation and dissolution of silica (reaction 14) is of minor importance. (SiO(OH)<sub>3</sub><sup>-</sup>) is included in the definition of TA and in oceanic seawater where pH ~8, the concentration of silicic acid (Si(OH)<sub>4</sub>) will be a factor ~40 higher than SiO(OH)<sub>3</sub><sup>-</sup>.

The formation of calcium carbonates (reaction 15) decreases DIC and TA, the latter twice as much as the DIC since two HCO<sub>3</sub><sup>-</sup> are consumed and one CO<sub>2</sub> is produced. The production of CO<sub>2</sub> increases *p*CO<sub>2</sub> and decreases pH in contrast to the production of soft parts. Dissolution of hard parts results in a reverse of reaction (15). However, hard parts are only formed together with soft parts (reaction 9-12) and the latter contains more carbon than the hard parts so the net effect is a consumption of CO<sub>2</sub>. Organic matter with hard parts has a higher density, which makes it heavier and therefore sinks at a higher rate and hence is a more efficient sink for carbon.

## 2.3 Sea-air exchange of CO<sub>2</sub>

Flux of CO<sub>2</sub> is driven by the difference in  $p\text{CO}_2$  between the ocean and atmosphere; if the ocean's  $p\text{CO}_2$  is lower than the atmospheric  $p\text{CO}_2$  uptake by the ocean occurs and vice versa. The atmospheric  $p\text{CO}_2$  is relatively constant and the exchange depends mostly on the ocean's  $p\text{CO}_2$ . The ocean's potential to take up CO<sub>2</sub> depends on the solubility of the gas, which depends on the water temperature, salinity and pressure. The lower the temperature and salinity the higher the solubility and the solubility also increases with higher pressure. At what rate the exchange of CO<sub>2</sub> occurs depends on many different factors such as wind speed, bubble formation, surface film thickness and breaking waves. For the carbonate system, the uptake of CO<sub>2</sub> increases the DIC, lowers pH but does not affect TA.

## 2.4 Analytical methods

For the study of the marine carbon system, several parameters are typically determined, including salinity, temperature, oxygen, nutrients, pH, DIC and TA. The seawater sampled at sea was collected at different depths in bottles mounted on a rosette connected to a CTD (Conductivity-Temperature-Depth). The CTD measures conductivity (giving the salinity), temperature and depth continuously and the bottles are closed at chosen depths. When the rosette-sampler was back on deck the constituents most sensitive to contamination by the atmosphere were sampled first; usually oxygen followed by pH, DIC, TA and nutrients.



**Figure 3.** The CTD-rosette coming out of the Laptev Sea followed by water sampling

The carbonate parameters determined during the field activities that are the basis of most studies in this thesis are TA, DIC and pH. The last two were sampled first since they are the most sensitive to contamination by exchange with atmospheric CO<sub>2</sub>. CO<sub>2</sub> contamination is not a problem for TA since it does not change with addition of CO<sub>2</sub>. However, the samples for all three parameters should be analysed as soon as possible after collection since they are all sensitive to biological activity occurring in the water sample.

#### 2.4.1 Determination of dissolved inorganic carbon

Coulometric titration (Johnson et al., 1985; 1987) was used to determine DIC (**paper III and IV**). A known volume of seawater was acidified with phosphoric acid, which drives the equilibrium reactions so that all DIC was in the form of CO<sub>2</sub>(g). The CO<sub>2</sub>(g) generated was extracted from the sample by an inert gas and carried into an electrochemical cell that contains a solution of ethanolamine which reacts with CO<sub>2</sub> causing a colour-change in the thymolphthalein indicator (blue to transparent) due to the lowering of pH. At the platinum cathode hydroxide ions are produced to bring the solution back to the initial colour. The amount of electrons given off corresponds to the amount of CO<sub>2</sub> in the sample and can be converted to concentration by dividing with the known volume and converted to mass by the measured temperature and salinity. The precision was determined with duplicate samples and the accuracy was determined by calibration against certified reference material (CRM), supplied by A. Dickson, Scripps Institution of Oceanography (USA).

#### 2.4.2 Determination of total alkalinity

Total alkalinity in seawater was analysed using open cell potentiometric titration with a pH sensitive electrode (**paper III, IV** and year 2008 in **paper V**). Hydrochloric acid was added to the sample until all bases have been titrated, after which the change in the potential was directly related to the amount of added acid (Haraldsson et al., 1997). At every addition of acid the potential was recorded and the equivalence point was evaluated by using a Gran function (Gran, 1952). The accuracy and precision of TA was determined in the same way as for DIC. For the determination of TA for 2003 and 2004 another method was used, see **paper V**.

### 2.4.3 Determination of pH

pH was determined by a spectrophotometric method according to Clayton and Byrne (1993) (**paper III and IV**). A pH sensitive indicator (m-cresol purple) was added to the sample and the absorbance was measured at two wavelengths, where the protonated ( $\text{HI}$ ) and the unprotonated ( $\text{I}$ ) have their respective absorbance maxima. In solutions with pH typical for seawater, the third form of the indicator ( $\text{H}_2\text{I}$ ) was insignificant. Perturbation of the seawater pH can occur by adding the indicator to the sample but this can be corrected for (Chierici et al., 1999). The precision for pH was determined on duplicate samples and the accuracy was set by the equilibrium constant for the indicator. pH in 2003 and 2004 was determined potentiometrically, see **paper V**.

### 2.4.4 Calculation of $\text{CO}_2$ flux

To calculate the  $\text{CO}_2$  flux, different formulations have been developed (Wanninkhof, 1992; Wanninkhof et al., 2009; Wanninkhof and McGillis, 1999). The rate and direction of the flux is driven by the  $p\text{CO}_2$  difference between the atmosphere and the surface water as well as by the transfer velocity. The oceanic  $p\text{CO}_2$  for field measurements in this thesis were calculated using pH and TA (**papers III, IV and V**) and from pH and DIC in the model papers (**I and II**). For **papers I, II, III and IV** the carbonate dissociation constants used were those of Roy (1993) as they showed the best internal consistency in the cold waters of the Arctic Ocean. In **paper V** those of Mehrbach (1973) as refitted by Dickson and Millero (1987) were used. The atmospheric  $p\text{CO}_2$  on the cruises in 2003 and 2004 (**paper V**) was determined using a non-dispersive infrared LI-820  $\text{CO}_2$  analyzer ([www.licior.com](http://www.licior.com)) and for the cruise in 2008 (**papers III, IV and V**) an open-cell Licor7500 were used ([www.licior.com](http://www.licior.com)). In the model papers (**I and II**) the atmospheric  $p\text{CO}_2$  were data from Point Barrow, Alaska, downloaded from the National Oceanic and Atmospheric Administration (NOAA) (Thoning et al., 2010).

The sea-air flux of CO<sub>2</sub> was calculated as:

$$F_{CO_2} = k_{CO_2} K_0 (pCO_2^{sea} - pCO_2^{air}) \quad (16)$$

where  $K_0$  (mol kg<sup>-1</sup>atm<sup>-1</sup>) is the gas solubility of carbon dioxide (Weiss, 1974),  $pCO_2^{sea}$  and  $pCO_2^{air}$  (atm) are the partial pressure of carbon dioxide in the surface water and the air, respectively.  $k_{CO_2}$  (cm h<sup>-1</sup>) is the transfer velocity for CO<sub>2</sub>. Different equations have been used in this thesis to calculate transfer velocity. In the model paper (**I and II**)  $k_{CO_2}$  is defined according to (Wanninkhof et al., 2009):

$$k_{CO_2} = k_{660} \sqrt{\frac{660}{Sc}} \quad (17)$$

where  $k_{660}$  is the gas transfer velocity (cm h<sup>-1</sup>) normalized to a  $Sc$  number of 660 (Wanninkhof et al., 2009) and  $Sc$  (non-dimensional) is the Schmidt number (Wanninkhof, 1992) according to:

$$k_{660} = 3 + 0.1 W + 0.064 W^2 + 0.011 W^3 \quad (18)$$

$$Sc = 2073.1 - 125.62 T + 3.6276 T^2 - 0.043219 T^3 \quad (19)$$

Here,  $T$  is temperature and  $W$  the wind speed calculated from the horizontal wind components  $u$  and  $v$  (x and y direction) downloaded from NOAA/OAR/ESRL PSD (see 3.2 for more information)

$$W = \sqrt{(u^2 + v^2)} \quad (20)$$

In **paper V**, the transfer velocity used was in the cubic form according to Wanninkhof and McGillis (1999):

$$k = 0.0283u^3 \sqrt{\frac{660}{Sc}} \quad (21)$$

Where  $u$  is the 10 m wind speed (m s<sup>-1</sup>), where daily average values measured onboard each cruise were used in the calculation.  $Sc$  is defined as above.

### 3. Model description

In the harsh and inaccessible Arctic Ocean, few field studies have been conducted previously and most of the measurements have been done during summertime, which has resulted in limited temporal and spatial understanding of the system. To try to circumvent this scarcity, a biogeochemical model has been developed for one of the Siberian shelf seas, the Laptev Sea (**paper I**). The model is a parameterization but is indeed a useful tool for understanding the system and for carrying out sensitivity studies to test the system's response to different forcings (**paper II**), such as increased air temperature caused by the greenhouse gas effect. Other versions of the model have been applied for simulations in different areas; the Mackenzie estuary (Omstedt et al., 1994), the Baltic Sea (Omstedt et al., 2009) and the Eastern Mediterranean Basin (Shaltout and Omstedt, 2012).

#### 3.1 Mathematical background

In this thesis a fully coupled physical-biogeochemical one-dimensional model has been applied, the PROBE-Laptev model, that uses the equation solver PROBE (PROgram for Boundary layers in the Environment) (Omstedt, 2011). The model is based on state variables ( $\phi$ ), which are solved by the following conservation equation:

$$\frac{\partial \phi}{\partial t} + V \frac{\partial \phi}{\partial z} = \frac{\partial}{\partial z} \left( \Gamma_{\phi} \frac{\partial \phi}{\partial z} \right) + S_{\phi} \quad (22)$$

with

$$V(z) = \frac{Q_{in}(z) - Q_{out}(z)}{A(z)} \quad (23 \text{ a,b})$$
$$\Gamma_{\phi} = \frac{\nu_T}{\sigma_{\phi}}$$

The first term to the left in equation (22) is the change in time for the dependent variable and the second term is vertical advection. The first term to the right represents vertical turbulent diffusion and the second represents source and

sink terms for the dependent variable. The vertical velocity,  $V$  ( $\text{m s}^{-1}$ ), depends on the horizontal area,  $A$  ( $\text{m}^2$ ), as well as on the inflows and outflows of water,  $Q_{in}$ ,  $Q_{out}$  ( $\text{m}^3 \text{ s}^{-1}$ ), at a particular depth,  $z$ .  $\Gamma_\phi$  ( $\text{m}^2 \text{ s}^{-1}$ ) is the diffusion coefficient which depends on the kinematic turbulent viscosity,  $\nu_T$  ( $\text{m}^2 \text{ s}^{-1}$ ) and the Prandtl-Schmidt number,  $\sigma_\phi$  for  $\phi$ .

Boundary conditions for the different state variables couple the diffusion term to fluxes associated with model forcing:

$$\left( \Gamma_\phi \frac{\partial \phi}{\partial z} \right)^{sur,bot} = F_\phi^{sur,bot} \quad (24)$$

$F_\phi^{sur, bot}$  represents the exchange of variable  $\phi$  at the air-water (*sur*) and water-sediment (*bot*) interfaces, respectively.

### 3.2 Physical part

In a one-dimensional model, the basin is assumed to be horizontally homogeneous and in this version the vertical resolution is of the order of one metre with a total depth of 50 m. The physics in the model includes six state variables, which are summarized in Table 1.

**Table 1.** State variables in the physical compartment of the PROBE-Laptev model

Notation	Description	Unit
$\rho U$	Momentum in x-direction	$\text{kg m}^{-2} \text{s}^{-1}$
$\rho V$	Momentum in y-direction	$\text{kg m}^{-2} \text{s}^{-1}$
$H$	Heat content	$\text{J m}^{-3}$
$S$	Salinity	-
$k$	Turbulent kinetic energy	$\text{m}^2 \text{ s}^{-2}$
$\varepsilon$	Dissipation of turbulent kinetic energy	$\text{m}^2 \text{ s}^{-3}$

Boundary conditions for the state variables must be defined and they are largely dependent on the meteorological forcings (air temperature, horizontal wind components ( $u$  and  $v$ ), total cloudiness and relative humidity). These data are downloaded for every sixth hour at  $77.5^\circ\text{N}$ ,  $125^\circ\text{E}$  and were provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their website at

<http://www.esrl.noaa.gov/psd> (Kalnay et al., 1996). The model's circulation is estuarine, which is driven by river discharge taken from the Lena River in the Laptev Sea and inflow of saline water along the bottom from the central deep Arctic Ocean.

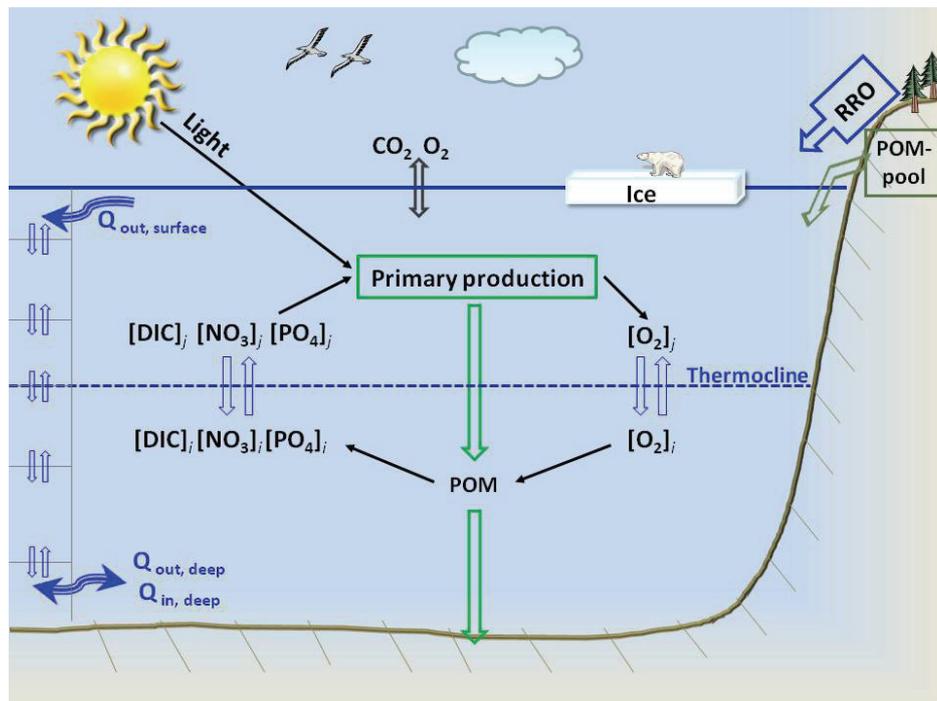
### 3.3 Biogeochemical part

In the model, there are seven state variables included to simulate the biogeochemical system (Table 2), which are coupled to the physical model. The changes in the state variables are written as conservation equations as described by equation (22), with boundary conditions according to equation (24).

**Table 2.** Biogeochemical state variables

Notation	Description	Unit
<i>DIC</i>	Dissolved inorganic carbon	mol C kg <sup>-1</sup>
<i>TA</i>	Total alkalinity	mol C kg <sup>-1</sup>
<i>NO<sub>3</sub><sup>-</sup></i>	Nitrate	mol N kg <sup>-1</sup>
<i>PO<sub>4</sub><sup>3-</sup></i>	Phosphate	mol P kg <sup>-1</sup>
<i>Pl</i>	Plankton	mol P kg <sup>-1</sup>
<i>DOC</i>	Dissolved organic carbon	mol C kg <sup>-1</sup>
<i>O<sub>2</sub></i>	Oxygen	mol O <sub>2</sub> kg <sup>-1</sup>

A schematic illustration of the model's principles is given in Figure 4. The primary production is simplified in the model since it is represented by only one phytoplankton. A sink term for DIC, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> is the primary production; phytoplankton assimilates CO<sub>2</sub>, nutrients and uses light as an energy source to produce POM and O<sub>2</sub>. The POM sinks deeper into the water column and is remineralized back to its origin constituencies, which then becomes a source term for DIC, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> ready to be used again.



**Figure 4.** Schematic illustration of the model components and interactions.

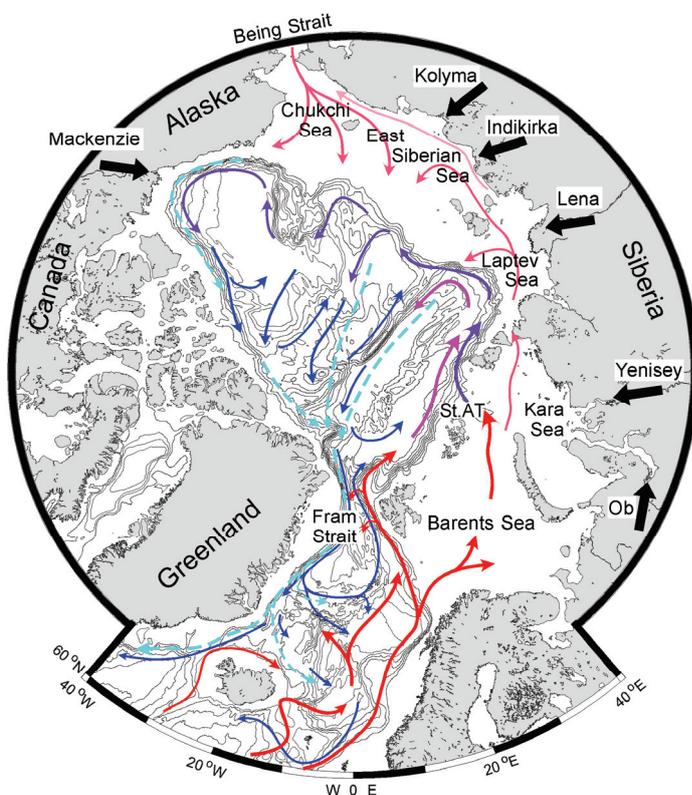
Another source for DIC is the “POM-pool” in Figure 4, comprising the terrestrial particular organic matter that enters the seawater with river runoff (RRO) and coastal erosion. This pool is mineralized back into inorganic constituents, but more slowly than the POM originating from primary production. The DIC is further impacted through the exchange of  $CO_2$  across the sea-air interface, which can act both as a sink and as a source term depending mainly on the  $pCO_2$  in the surface water.

All seven state variables are coupled to the physical part, i.e. they are flowing with the water masses in and out of the model and are also vertically mixed between the different layers in the model. For a more complete description, see Appendix in **paper I**.

## 4. The Arctic system

### 4.1 Circulation

The Arctic Ocean consists of two central basins about 4000 m deep, the Eurasian and Canadian Basins that are separated by the Lomonosov Ridge with a sill depth of about 1600 m. The basins are surrounded by shallow shelf seas which constitute ~50 % of the Arctic Ocean total area (Jakobsson et al., 2003). They are mainly located on the Siberian side with the deepest being the Barents Sea with an average depth of ~200 m.



**Figure 5.** Circulation in the Arctic Ocean, where red and light blue arrows indicate surface currents and dark blue illustrate deep water flow. St AT is the St Anna Trough.

There are two main inflows of seawater into the Arctic Ocean, from the Pacific Ocean and the Atlantic. The Pacific water enters the Arctic Ocean through the Bering Strait and flows into the Chukchi Sea. The Pacific water is divided into different routes through the Chukchi Sea: some flows east, north of Alaska and some flows north into the Arctic Ocean. These waters flow east along the continental margin and exit through the Canada Archipelago and the Western Fram Strait (Jones et al., 1998). There is also a flow of water in a westerly direction into

the East Siberian Sea where it mixes with other waters before it eventually enters the deep central basin.

Warm Atlantic water enters the Arctic Ocean north of Norway with the North Atlantic Current that is an extension of the Gulf Stream. The current is divided into two branches; one enters through the eastern part of the deep Fram Strait (~2600 m depth) between Greenland and Svalbard and one flows into the Barents Sea. The Fram Strait branch follows the continental slope counter clockwise around the Arctic Ocean (Rudels et al., 1994). The Barents Sea branch is modified by cooling through heat loss to the atmosphere and freshened by sea-ice melt water and mixing with the Norwegian coastal current (Gascard et al., 2004). Part of Barents Sea branch enters the Arctic Ocean through the St Anna Trough, where it enters at a depth that corresponds to its density and then follows the same circulation pattern as the Fram Strait branch. The remaining water of the Barents Sea branch enters the Kara Sea, mixes with freshwater from Ob and Yenisey Rivers and continues into the Laptev Sea (Anderson et al., 1994). In the Laptev Sea, the surface water is further mixed with freshwater from river runoff mainly from the Lena River, the river with the second largest discharge into the Arctic Ocean, but is also modified by the formation/melting of sea ice. This modified well-mixed surface water flows both north into the Arctic Ocean and east into the East Siberian Sea where it meets water of Pacific Ocean origin. If the wind is favourable, an alongshore current is formed in the Laptev Sea that flows all through the East Siberian Sea and into the Chukchi Sea, the Siberian Coastal Current (Weingartner et al., 1999).

## 4.2 Vertical distribution

The deep Arctic Ocean is largely ice covered all year long and the shelves are seasonally ice covered. In spring, the melting of ice on the shelves together with a peak of freshwater from the rivers creates a well-mixed surface layer. In autumn, when the seawater freezes about two-thirds of the salt in the water is released when ice crystals are formed. The salt continues to drain out of the ice during ageing through the so-called brine-channels.

The brine-enriched cold and saline water is denser than the adjacent water and therefore sinks to deeper layers. Under the right conditions, it can flow over the shelves into the deep basin and sink while entraining surrounding water until the

density matches that of the ambient water. Some waters can reach the deepest layers of the deep central Arctic Ocean, but the majority enters the halocline where this cold salty water helps maintaining the upper halocline (~50-200 m depth) of the Arctic Ocean (Aagaard et al., 1981). Another source to the halocline is the inflowing Pacific waters entering through the Bering Strait. The halocline shields the cold, less saline well-mixed surface layer (~0-50 m depth) from the warmer Atlantic layer (~200-600 m depth), defined as water temperature above 0°C. This shielding helps protect the perennial sea ice cover leading to a limited melting from below. Under the Atlantic layer there is a fourth layer, the deep layer (>600 m depth) that flows counter clockwise following the hypsography around the basins (Rudels et al., 1994).

### 4.3 Flaw lead polynya

Much of the sea ice in the Arctic Ocean is produced on the shelves seas largely in the polynya (полюнья), a Russian word meaning: “an area of open water surrounded by sea ice” or “råk” in Swedish. A polynya is an area with more or less constant open water between the land fast ice and the drifting ice. It is established when strong offshore winds blow over the sea surface, forcing the ice away from the coast. This results in open seawater that is in contact with the cold atmosphere and new ice is formed. The flaw lead polynya become an ice-factory when intense heat loss from the open seawater to the atmosphere occurs and results in a large ice production, together with brine rejection. The latter can drive deep convection on the shelves seas.

### 4.4 Atmospheric pressure field

The wind pattern in the Arctic Ocean is to a large extent determined by two atmospheric pressure regimes, positive and negative Arctic Oscillation (Proshutinsky and Johnson, 1997). This large-scale atmospheric pattern influences the weather in the Arctic. When the pressure is higher than normal over the Arctic Ocean and lower than normal over the middle latitudes the Arctic Oscillation is in a positive mode (AO<sup>+</sup>). This high-pressure field forms an anticyclonic (clockwise) wind field around the high-pressure. The negative mode (AO<sup>-</sup>) is reverse; the pressure is lower than normal over the Arctic Ocean and higher than normal over

the middle latitudes. This low-pressure field causes a cyclonic (counter clockwise) wind field. In the Arctic Ocean, the wind affects the surface water and determines the circulation of the surface (Dmitrenko et al., 2005) water and thereby also the transport of its constituents.

## 4.5 Permafrost

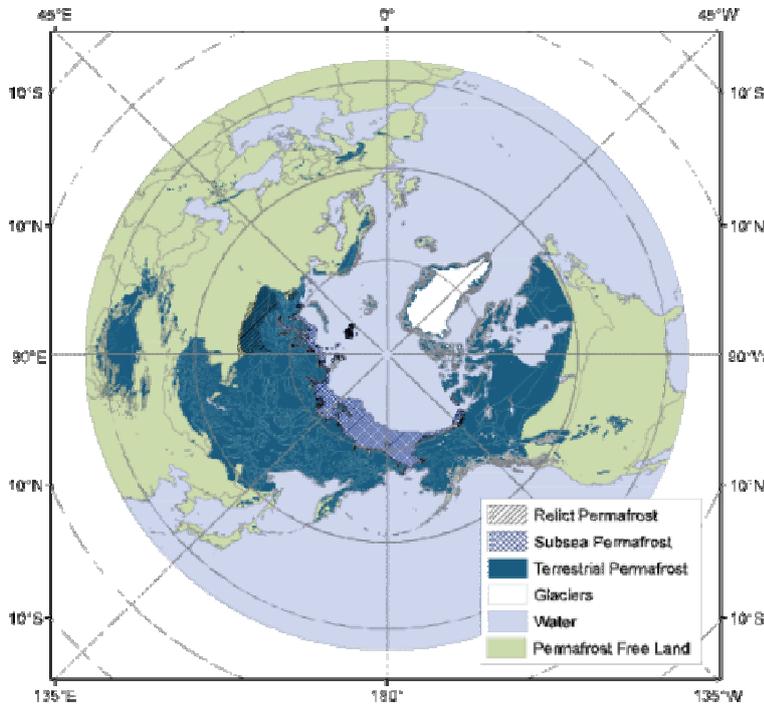
Permafrost is perennially frozen ground (soil, sediment or rock) and is defined solely by temperature. It is defined as: any subsurface material that remains at or below 0 °C for at least two years in a row (Brown et al., 1998). Permafrost is formed under cold glacial periods and is located on both land and below the seafloor (subsea). In the Arctic Ocean, subsea permafrost covers a large area of the shelf seas that was formed during the last glacial period ~12 000 years ago when this area was land and exposed to the cold atmosphere. This cold epoch was succeeded by the warmer Holocene that led to sea level rise and the exposed land became covered with seawater.



**Figure 6.** Land of peat with permafrost (white regions) and signs of coastal erosion to the right, the Laptev Sea. (Photo Iréne Wählström)

Permafrost on land covers ~80 % of the Arctic drainage basins and can be divided in areal distribution between continuous permafrost (underlying 90-100 % of the landscape); discontinuous permafrost (50-90 %); and sporadic permafrost (10-50 %) or isolated patches (0-10 %). The thickness of the permafrost is variable but ranges from 1500 m in Siberia and 740 m in north of Alaska to less than one metre in the south. Generally, the thickness of the continuous permafrost is 100-800 m; discontinuous 25-100 m and sporadic 10-50 m (Anisimov and Reneva, 2006). At the surface, the permafrost is covered with a seasonally thawed active

layer that varies from centimetres to metres in thickness depending on the local climate and where biological activity occurs.



**Figure 7.** This map of the Northern Hemisphere, looking down at the North Pole, shows different kinds of permafrost. The areas with blue cross-hatching are subsea permafrost, or frozen sea floor. —Credit: Tingjun Zhang National Snow and Ice Data Center, University of Colorado, Boulder.

Model projections of the warming of the Arctic indicate permafrost thawing and degradation. This includes coastal erosion, thickening of the active layer, talik formation (a layer of year-around unfrozen ground within the permafrost), development of thermokarst (depression of land), development or expansion of thaw lakes (thermokarst filled with water), lateral permafrost thawing and a northward migration of the southern permafrost (Zhang et al., 2005).

## 4.6 Biogeochemistry

The biological production of organic matter during photosynthesis affects DIC in the shelf seas. Photosynthetic organisms utilize light as an energy source to convert  $\text{CO}_2$ , nutrients and trace elements to organic matter. This reduces the  $p\text{CO}_2$  and nutrient concentrations while releasing oxygen. Primary production is believed to have a large impact on the removal of marine  $\text{CO}_2$ . The oceans in the northern hemisphere are suggested to be a sink for atmospheric  $\text{CO}_2$  but a source in the areas close to the equator and in upwelling areas (Broecker and Peng, 1992).

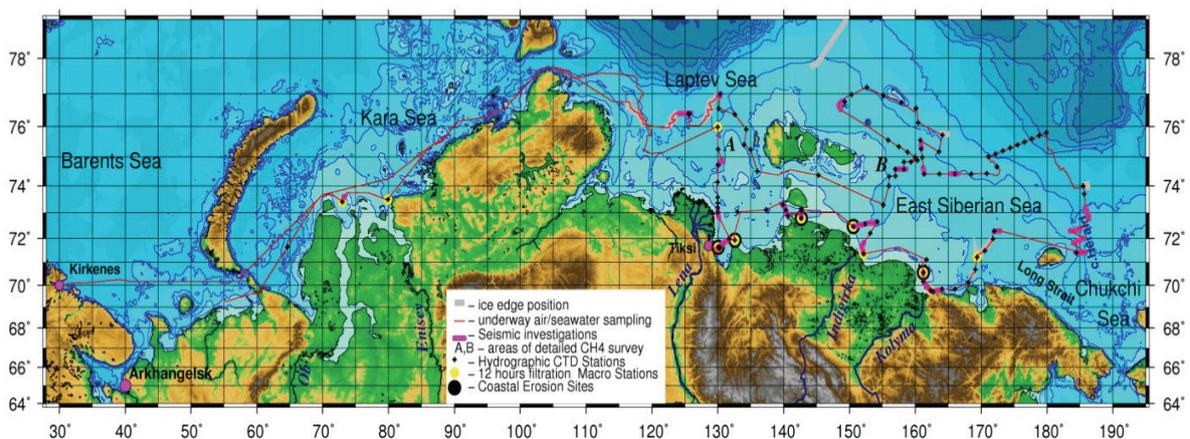
The shelf seas have a variable primary productivity depending on the region. The Barents and Chukchi Seas with inflow of nutrient-rich seawaters from the Atlantic and the Pacific Oceans have the highest productivity of the Arctic shelf seas. Other shelves, mostly impacted by river runoff and upper waters from other shelf areas have lower primary production (Sakshaug, 2004). In addition to the impact from different waters masses the production is also seasonally affected through light conditions (day length and sun radiation angle), sea ice cover, water temperature and depth of the photic zone (Sakshaug and Slagstad, 1991).

The shelf seas are sea ice-covered nine months of the year with land fast ice at the coast, drifting ice to the north and polynya in between. The ice that covers the surface inhibits light penetration into the seawater, which restricts photosynthesis. However, an early phytoplankton bloom can develop in the polynya in spring when the light returns. This bloom utilizes the nutrients supplied to the surface water from the water mixing and runoff during winter. The ice not only restricts the light penetration but also the sea-air exchange of different gases, such as CO<sub>2</sub> and O<sub>2</sub>, and no sea-air equilibrium is established for these gases.

## 5. The carbon system of the Siberian shelf seas

Two shelf seas located north of the Siberian are investigated in this thesis through fieldwork, the Laptev Sea and the East Siberian Sea. These seas, together with Chukchi Sea, were sampled during our summer expedition 2008 (August 15 to September 26), the International Siberian Shelf Study 2008 (ISSS-08). The expedition took place on the Russian vessel Yakow Smirnitskiy together with Russian scientists. At 96 stations (Figure 8), samples from depth profiles of DIC, TA, pH, O<sub>2</sub> and nutrients were collected and analysed on board to investigate the carbon cycle (**papers III, IV and V**).

ISSS-2008



**Figure 8.** Cruise-track of the ISSS-08 expedition, from Norway to Chukchi Sea

Data from the ISSS-08 are also used in the development of a model for the Laptev Sea, with the objective to assess the carbon cycle of the region. At present, models are the only tool available as a limited amount of data is available from this harsh region with very cold winters and a lot of ice (**papers I and II**).

### 5.1 The Laptev Sea

The Laptev Sea, is a shallow shelf sea with an average depth of 48 m, area of 498 000 km<sup>2</sup> and a volume of 24 000 km<sup>3</sup> (Jakobsson, 2002). It is situated between the Kara Sea (to the west) and East Siberian Sea (to the east). Northwards, it deepens to about 100 m before it slopes down to the deep central basin. The region

is the coldest in the Arctic but has experienced an increase in the average annual air temperature of 1 to 3°C since 1954. The models included in ACIA (2004) have projected a further increase of 3 to 5 °C by the late 21<sup>st</sup> century (B2 scenario).

In wintertime, the Laptev Sea is ice-covered nine months each year and the rivers are more or less totally frozen. The exception from the winter ice cover is the more or less constant flaw lead polynya that is located between the land fast ice and the drifting ice in the sea. The flaw lead polynya can be up to 200 km wide and is exposed to cold air temperature as low as –35°C, which continuously freezes the surface water and form dense surface water that sinks towards the bottom. This is the driving force for the hydrography of the Laptev Sea in wintertime. During summer, the shelf hydrography is mainly forced by the freshwater coming with river runoff and spring melting of sea ice that results in a substantial freshening of the surface layer (Dmitrenko et al., 2005; Dmitrenko et al., 2010).

The water transport in the Laptev Sea during summer is mainly forced by wind stress and bottom friction. Low-pressure fields in the atmosphere over the Laptev and East Siberian Seas cause a cyclonic (counter clockwise) wind field and an alongshore current towards the east is formed, which causes the freshwater to flow into the East Siberian Sea, the Siberian Coastal Current. If a high-pressure field is formed over the Laptev and East Siberian Seas, an anticyclonic (clockwise) wind field prevails and a southerly wind forces the Lena River plume offshore and into the Arctic Ocean (Bauch et al., 2009; Dmitrenko et al., 2005; Guay et al., 2001). These patterns are less pronounced in wintertime due to the ice cover.

The Lena River, the second largest river discharge in the Arctic Ocean (the largest is the Yenisei River that flows into the Kara Sea), dominates the freshwater supply to the Laptev Sea. The annual average freshwater discharge from the Lena River is 525 km<sup>3</sup> y<sup>-1</sup> (Gordeev and Sidorov, 1993) of which about 75-95 % occurs in late May or beginning of June owing to the melting of ice and snow in the river and drainage basin. This freshwater supply builds up a 5-10 m deep surface mixed layer (Carmack et al., 2006) that is favourable for and triggers the primary producers (Sorokin and Sorokin, 1996). The rivers are an important link between the land and the ocean since they transport different constituents, such as nutrients and DIC as well as organic matter; recently at an increasing rate as permafrost

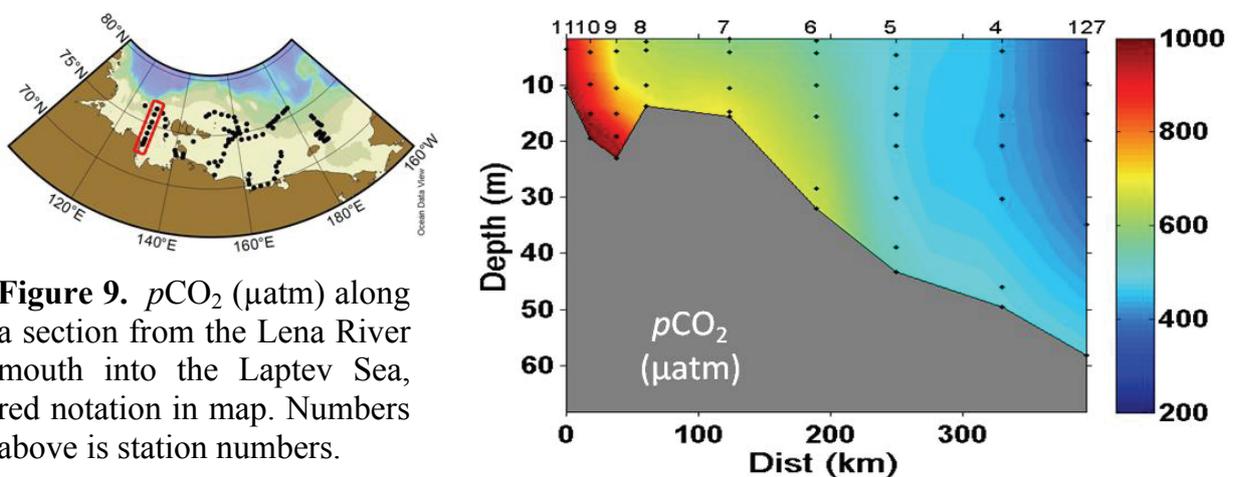
degrades. The spring flood brings large amount of nutrients (Gordeev et al., 1999) and the discharge is supersaturated with respect to CO<sub>2</sub> all year (Semiletov, 1999).

The concentration of DOC in the rivers is suggested to increase when the region is warming due to the greenhouse gases that affect different processes. This increased export of DOC to the sea is due to increased river discharge, thawing and degradation of permafrost. Terrestrial DOC in seawater was previously considered to be refractory, with little effect on the biological cycle or the exchange of CO<sub>2</sub> between the atmosphere and ocean, thus behaving conservatively in a DOC-salinity relation (Dittmar and Kattner, 2003; McGuire et al., 2009). However, Holmes et al. (2008) demonstrated a substantial seasonal variability in lability of the DOC with the most labile DOC occurring during the spring flood and Alling et al. (2010) showed the non-conservative behaviour of DOC with removals of up to 10-20 % in the Lena River estuary. The Lena River is considered to be the major source of DOC to the Arctic Ocean. McClelland et al. (2012) compared the Arctic rivers with other major river around the world and the concentration of DOC in the Lena River is higher than in any other of these (Amazon, Congo, Yangtze and Mississippi). However, due to the low annual runoff the transport is lower than both Amazon and Congo.

Continuous permafrost underlies the Lena River drainage basin with coverage of 78-93 % and a temperature of -2 to -7 °C (Zhang et al., 2005). The active layer is ~1.7 m, which thaws and freezes seasonally due to the air temperature (Zhang et al., 2005). The frozen layer depth in the Lena River delta extends down to 600 m and the subsea permafrost in the Laptev Sea varies between 50 and 200 m depth. The subsea permafrost estimates are mostly based on modelling but some field work has been done showing that this area is a very fragile component of the cryosphere. This is because the average temperature of the upper 100 m subsea sediment layer is around -1 °C temperature (Semiletov et al., 2011), close to the thawing. The subsea is also continuously exposed to waters of temperatures around zero degrees and is thereby not exposed to the strong freezing in winter that the terrestrial permafrost is. Furthermore, pulses of warmer waters of Atlantic origin have been observed to up-well into the Laptev Sea (Dmitrenko et al., 2011; Dmitrenko et al., 2010; Polyakov et al., 2011; Polyakov et al., 2005; Stroeve et al., 2012). This warmer water has the potential to thaw the subsea permafrost resulting

in eroding seafloor and release of methane (Shakhova et al., 2010), an even stronger greenhouse gas than CO<sub>2</sub>.

The thawing of onshore permafrost is expected to increase with warmer air temperatures that will lead to an increased input of terrestrial organic matter to the Laptev Sea. The terrestrial organic matter is added by river runoff, thawing and degradation of permafrost but also by coastal erosion. The supply of terrestrial organic matter will change the carbon budget as well as the biogeochemical cycles; some of the changes are discussed in this thesis. In **paper III**, the results from our expedition to the Siberian coast in the Arctic summer of 2008 are presented. In the Laptev Sea, the low salinity in the surface water supports the river runoff regimes discussed before as the driving force for the shelf hydrography. The distribution of chemical constituents in the surface and the bottom waters reveals some specific features. This water is relatively low in nutrients, supersaturated in  $p\text{CO}_2$  (Figure 9) and has AOU concentrations close to zero ( $\text{AOU} = [\text{O}_2]^{\text{saturated}} - [\text{O}_2]^{\text{measured}}$ ). These features indicate decay of terrestrial organic matter, in combination with uptake of oxygen from the atmosphere. The excess of DIC resulting from the decay of terrestrial organic matter is computed to be  $5 \times 10^{12}$  gC, a potential source of outgasing to the atmosphere. The excess can be compared with reported inputs of annual total organic carbon from river runoff in the Laptev Sea and East Siberian Sea and coastal erosion,  $\sim 9 \times 10^{12}$  gC and  $\sim 2.3 \times 10^{12}$  gC respectively (Sanchez-Garcia et al., 2011).



**Figure 9.**  $p\text{CO}_2$  (µatm) along a section from the Lena River mouth into the Laptev Sea, red notation in map. Numbers above is station numbers.

In **paper I**, a one-dimensional, time dependent coupled physical and biogeochemical model for the Laptev Sea is presented and shown to reproduce the annual cycle of biogeochemical elements. The model is developed in order to assess the effects of environmental changes on the Arctic marine carbon cycle. The model is utilized in **paper II** to test the response of annual net sea-air fluxes of CO<sub>2</sub> and the primary productivity to changes in forcings, e.g. increasing atmospheric temperature with its consequences for sea ice coverage, river discharge and permafrost thawing as well as wind speed. The Arctic Ocean and the shelf seas are suggested to be a sink for atmospheric CO<sub>2</sub> (Anderson et al., 1998; Bates and Mathis, 2009; Nitishinsky et al., 2007) and the results in **paper II** support this argument but suggest that increasing the river runoff properties (25 % increase of river discharge, increase of the concentration of DOC twofold or of both the concentration of DOC and *p*CO<sub>2</sub> twofold) will decrease the net annual uptake of atmospheric CO<sub>2</sub> in the Laptev Sea. This means that more anthropogenic CO<sub>2</sub> will remain in the atmosphere and enhance climate change.

However, the ocean increases the net annual uptake of atmospheric CO<sub>2</sub> when the air temperature or the wind speed is increased. One explanation for this increased uptake is the acceleration in the primary productivity that consumes CO<sub>2</sub> and decreases the *p*CO<sub>2</sub> in the seawater. The ocean also increases the net annual uptake of atmospheric CO<sub>2</sub> when increasing the atmospheric *p*CO<sub>2</sub>, the nutrients in the river runoff or a combination of all the above forcings. In addition to the net annual uptake of CO<sub>2</sub> calculated in the model, there is also a seasonal variability in the sea-air flux with an uptake in the beginning of the summer due to primary productivity and a more or less pronounced outgasing of CO<sub>2</sub> to the atmosphere in the autumn. This indicates an supersaturation of CO<sub>2</sub> in the autumn and is in agreement with the findings in **paper III**.

## 5.2 The East Siberian Sea

The East Siberian Sea is the broadest Arctic shelf sea and is located east of the Laptev Sea and west of the Chukchi Sea. It has an area of 987 000 km<sup>2</sup>, a volume of 57 000 km<sup>3</sup> and an average depth of 58 m (Jakobsson, 2002) with increasing depth northward to around 100 m before the continental slope and the deep central basin. Since 1954, the regions average annual air temperature has increased by

0.5 °C, which is not as pronounced as in the Laptev Sea. However, the models included in ACIA (2004) have projected an increase of 3 to 4 °C by the end of the 21<sup>st</sup> century (B2 scenario), which is almost as much as in the Laptev Sea (3-5 °C).

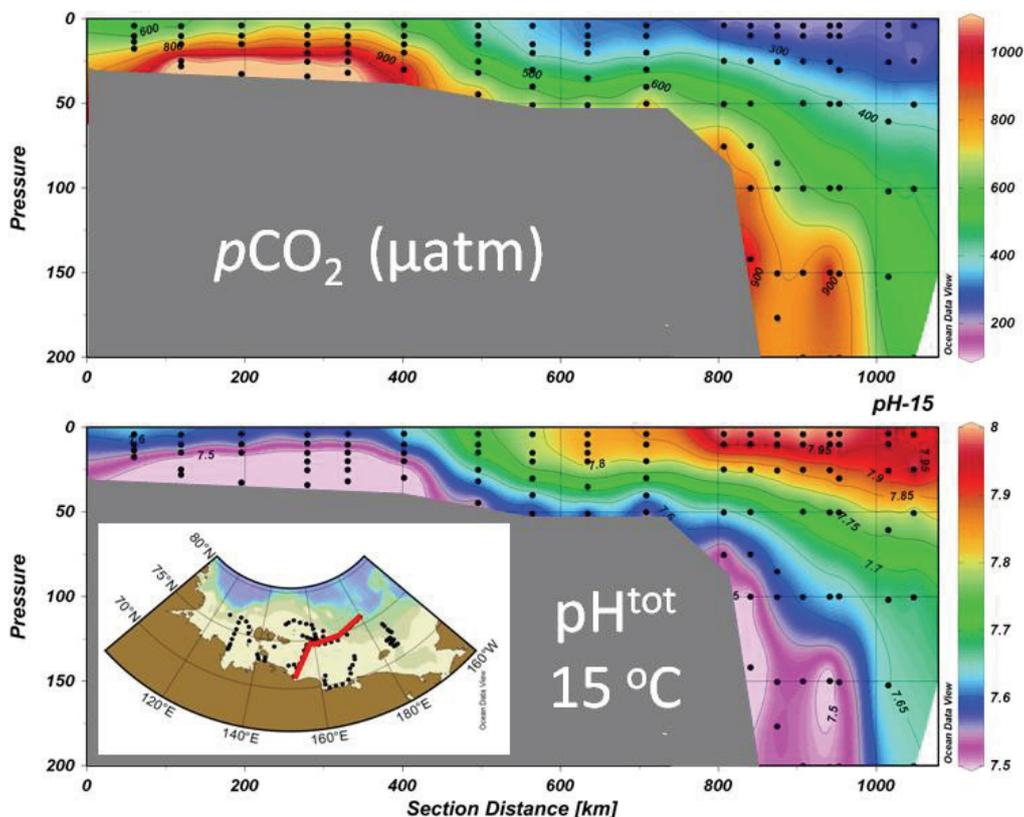
The East Siberian Sea resembles the Laptev Sea regarding the sea ice coverage, including a polynya and frozen rivers in wintertime. The two main rivers entering into the East Siberian Sea are the Indigirka (152 °E) and the Kolyma Rivers (162 °E) with annual freshwater discharge of 54 and 122 km<sup>3</sup> y<sup>-1</sup>, respectively (Rachold et al., 2004). This is substantially less than the Lena River but the annual cycle of discharge has the same pattern with a spring flood occurring in late May or the beginning of June. There is also subsea permafrost and continuous permafrost extent throughout the river drainage basin with the highest rate of coastal erosion occurring between the Lena and Kolyma Rivers (Pipko et al., 2009; Semiletov et al., 2005).

The water transport in the East Siberian Sea during summer is like that in the Laptev Sea mainly driven by the atmospheric pressure field, i.e. a transport mainly in the wind direction. A cyclonic (counter clockwise) wind field over the Laptev and East Siberian Seas produces the Siberian Coastal Current, which forces the Lena River plume to enter into the East Siberian Sea and flow alongshore towards Chukchi Sea. If a high-pressure field is formed, an anticyclonic (clockwise) wind field prevails and an easterly wind forces saline waters from the Chukchi Sea into the East Siberian Sea. The Kolyma and Indigirka river runoff plumes are then forced offshore and westward to the New Siberian Islands, between the Laptev Sea and the East Siberian Sea (Bauch et al., 2009; Dmitrenko et al., 2005; Guay et al., 2001).

The atmospheric pressure pattern significantly influences the internal oceanic circulation and water mass distribution that establish two distinct regimes, the Western and Eastern hydrological area (Semiletov et al., 2005). The Western hydrological area is dominating by inflow of river runoff from the Lena River with substantial amount of terrestrial organic matter. Degradation of the organic matter produces CO<sub>2</sub> that causes an supersaturation, often in the whole water column, relative to the atmosphere that results in outgasing from the sea to the atmosphere. The surface water also has a low transparency from the terrestrial particulate matter that limit the light penetration and by that the primary production.

The Eastern hydrological area is influenced by Pacific-derived water that has been modified in the Chukchi Sea. This water is clear, salty and has a high nutrient content. This favours the primary productivity of the waters in the eastern side of the East Siberian Sea, which lowers the  $p\text{CO}_2$  and an uptake of  $\text{CO}_2$  from the atmosphere therefore occurs.

Decay of organic matter also lowers pH and puts a stress on the marine biota. Both the high  $p\text{CO}_2$  and low pH were very evident in the East Siberian Sea in 2008 (Figure 10), all the way from the coast to the shelf slope. About half way out on the shelf, these signatures were observed all throughout the water column, even if most pronounced in the bottom water. In the outer part and over the shelf slope the surface water had more typical values, i.e. pH close to 8 and  $p\text{CO}_2$  at or below atmospheric levels. This pattern is most likely a result of the larger loading of organic matter in the sediments close to the coast together with the physical mixing in the shallow coastal areas.



**Figure 10.**  $p\text{CO}_2$  ( $\mu\text{atm}$ ) and pH along a section from the coast to the shelf slope of the East Siberian Sea, red line in map.

In **paper V** the interannual and spatial variability between the two regimes were studied for the years 2003 (September), 2004 (September) and 2008 (August-September). These are years with different atmospheric patterns; in 2003 a cyclonic wind field prevailed (counter clockwise), while the low pressure was weaker with an anticyclone formed over the Canadian Arctic Archipelago in 2004. This created a southerly wind that transported the river water northward, towards the Arctic Ocean. In 2008, an anticyclone (clockwise wind field) dominated. The different wind patterns affect the location of the boundary between the Western and Eastern hydrological areas, thus also the magnitude of the CO<sub>2</sub> exchange between the ocean and the atmosphere. The average for all of the investigated years was a slightly positive flux of CO<sub>2</sub>, i.e. an outgasing to the atmosphere. The annual variability ranges from -5.0 mmol m<sup>-2</sup> d<sup>-1</sup> in 2008 to +33.2 mmol m<sup>-2</sup> d<sup>-1</sup> in 2004 when the river water with high organic matter content was distributed throughout the East Siberian Sea.

In **paper IV**, data confirmed the division into two hydrological areas, where decay of terrestrial organic matter dominates in the west and primary production dominates in the east. In the latter region, the undersaturation of CO<sub>2</sub> in the upper 30 m equals a DIC consumption by primary producers of 0.4 (±1)×10<sup>12</sup> mol C y<sup>-1</sup> (~4(±10)×10<sup>12</sup> gC y<sup>-1</sup>). This is half of the estimated primary production (8.2×10<sup>12</sup> gC y<sup>-1</sup>) reported by Vetrov et al. (2009), but considering that the sampling in 2008 was conducted late in the summer when primary production had declined, it is likely to be a low estimate. In **paper III**, the excess of DIC shallower than 50 m in the western region of the East Siberian Sea was calculated to ~5×10<sup>12</sup> gC, which is attributed to the decay of terrestrial organic matter. This excess of DIC drives a sea-air flux but it might not be able to equilibrate before the water flows out into the Arctic Ocean and becomes trapped under the sea ice.

## 6. Summary and Conclusions

The Arctic Ocean is especially sensitive to climate change due to the reduction of sea-ice coverage caused by the increased air temperature. The effects from the increased air temperature and decreased ice coverage are several; e.g. decomposition and thawing of permafrost; increased coastal erosion, wind activity and river discharge; as well as longer time periods for primary production and gas exchange. Some of these effects increase the carbon content in the seawater and some reduce it, but from a climate change perspective it is of interest to examine whether the balance of the sources and sinks will be altered.

The East Siberian Sea is a region of substantial biogeochemical transformation. Two hydrographic regimes exist in the East Siberian Sea, one in the eastern part and one in the western, and their conditions are mainly determined by the atmospheric pressure field. The regime to the west is dominated by an inflow of fresh river water both from the Laptev Sea and from rivers discharging into the East Siberian Sea. These rivers contain large amounts of terrestrial organic matter, both particulate and dissolved. Terrestrial organic matter is partly mineralized in the ocean and makes the water supersaturated in  $p\text{CO}_2$  compared to the atmosphere and thus is a potential source of  $\text{CO}_2$  to the atmosphere. The production of  $\text{CO}_2$  also contributes to ocean acidification, in addition to that caused by uptake of the increasing content of anthropogenic  $\text{CO}_2$  in the atmosphere. The eastern part of East Siberian Sea is dominated by Pacific-derived cold and nutrient rich water that promotes primary production. Hence, the seawater becomes undersaturated in  $\text{CO}_2$  compared to the atmosphere, thus being a potential sink for atmospheric  $\text{CO}_2$ . The position of these two regimes shifts depending on the atmospheric pressure field but the average net flux for three different years (2003, 2004 and 2008) of different pressure fields showed a net outgasing from the ocean to the atmosphere. This indicates that decay of organic matter dominates over primary production during this period and outgasing from the East Siberian Sea will probably increase with more thawing of permafrost and coastal erosion.

The  $p\text{CO}_2$  in the Laptev Sea was also supersaturated in the late summer of 2008 giving an excess of DIC of the same order as that in the Western East Siberian Sea. This is most probably due to mineralization of terrestrial organic

matter resulting in an outgasing of CO<sub>2</sub> from this ocean areas as well. The most probable explanation for the excess of DIC is that the Lena River runoff had high *p*CO<sub>2</sub>, from mineralization of organic matter in the river, as well as a high content of organic matter that is mineralized in the Laptev Sea before sampling. Added to this is the input of organic matter directly into the ocean by coastal erosion that is promoted by thawing of the permafrost.

The Laptev Sea model strengthens this conclusion where the seasonal cycle of *p*CO<sub>2</sub> shows an increase in late summer when the undersaturation of *p*CO<sub>2</sub>, caused by primary production, diminishes. The undersaturation caused by primary production results in uptake of CO<sub>2</sub> from the atmosphere to the ocean but this is partly hampered by the increasing summer temperature that decreases the solubility of CO<sub>2</sub> (increasing *p*CO<sub>2</sub>). The net annual oceanic uptake of CO<sub>2</sub> decreased in a model simulation when increasing the *p*CO<sub>2</sub> and/or DOC in the river runoff or the river discharge, resulting in a positive feedback to the atmospheric CO<sub>2</sub> content.

The net annual oceanic uptake of CO<sub>2</sub> increased when increasing the air temperature, the wind speed, nutrients in the river runoff, the *p*CO<sub>2</sub> in the atmosphere or combining all of these forcings. The consequence is a negative feedback to the atmospheric CO<sub>2</sub> content. More studies have to be done in order to develop a more detailed understanding of how a combination of changes in the different forcings will impact the uptake of CO<sub>2</sub> by the Siberian shelf seas, especially in a situation with a gradual change. However, it is obvious that climate change potentially has a profound impact on the carbon cycle and the sea-air exchange of CO<sub>2</sub> in these waters.

## 7. Outlook for the future

The Arctic Ocean is still an area where limited marine data is available, despite the increased sampling work in recent years. However, to understand all the physical and biogeochemical processes occurring in this harsh region it is essential to accelerate the data collection, both temporally and spatially. Nearly all ship based studies in this region are performed during the Arctic summer when it is open water and possible to access this mostly sea ice covered area. Time series are performed by buoys and moorings that collect continuous data series of some properties, mainly physical. It would be an advantage if these moorings were also equipped with sensors for chemical constituents. For the carbon system they are available for, e.g.  $p\text{CO}_2$  and pH, but their stability and energy requirement is such that they are at present not suitable for Arctic Ocean studies, where service is normally possible only during the summer season. Development of long term stable sensors for carbon system parameters would give us times series, which would be a valuable contribution to understanding how the Arctic Ocean responds to increased amount of greenhouse gases. Since the ice cover is decreasing, the shipping traffic will probably increase and the research community can utilize this through online sensors (e.g. T, S,  $\text{O}_2$ ,  $p\text{CO}_2$ , pH) onboard voluntary ships to measure these constituents underway. For the carbonate system,  $p\text{CO}_2$  sensors have been in use for some years and pH sensors become more frequently used during recent years.

It would be valuable to improve the meteorological forcing in the modelling, e.g. by including the atmospheric pressure field. Furthermore, the inclusion of more processes such as mineralization of organic matter through the whole water column and in the sediment, with a flux of decay products back to the bottom water, would be beneficial. The model will also be improved when more data is available, as the rate of processes can be better constrained, which for the region of the Siberian shelf at present is inadequate.

Some other questions of interest for the future are:

- What is the flux of  $\text{CO}_2$  through snow and ice?
- What will the effect of an increased supply of terrestrial organic matter be on the Arctic Ocean carbon cycle, and what effect will this have on ocean acidification?
- How does the warming of the Atlantic layer affect the subsea permafrost, especially in a shelf sea with less sea ice coverage and thus possibly more upwelling?

## Acknowledgment

Hur klarar man att säga tack till alla som varit med, påverkat och stöttat genom åren? Vet inte, men detta är mitt försök...

Först av allt vill jag tacka min handledare, **Leif Anderson!** Du trodde på mig trots allt och vågade anställa mig (igen). Du har skickat iväg mig till världens ände, mer eller mindre utan mat, men vi har också åkt på trevligare turer där du fått lära dig lite om hur ungdomar betar sig idag. Din dörr har alltid varit öppen för mig och du har stöttat mig genom åren, fått svara på ändlöst många frågor och skrivit om många syftningsfel.

Tack också till mina biträdande handledare **Göran Björk** och **Anders Omstedt**. Anders för att du blev min handledare, försåg mig med en fungerande modell och hjälp med att konvertera den till Laptev havet. Men också din entusiasm och uppmuntran när det gick mindre bra. Göran, för all hjälp med olika frågor, allt från hur man styr CTD'n till MATLAB script och allt däremellan. Vi hade trots allt en god tur 2008, den kommer jag aldrig att glömma!

Sen vill jag tacka hela **Oceanografi gruppen** på GVC, både nuvarande och före detta, för att ni välkomnade mig när jag flyttade upp till er och fick bli en del av er grupp, det betydde mycket för mig då och nu. Men också för att ni aldrig tröttnat på att svara på och diskutera olika frågor.

**Tellus doktorander; Andreas, Azad, Christian, Eva och Lena.** Det har varit skönt att ha några att prata och diskutera med under de här fem åren, eller bara ta en lunch eller öl med. Keep up the good work, it is soon your big day! Och tack **Eva** för läsningen, så där i sista stund.

Tack till den nybildade **Marina gruppen**, nu har vi doktorander inte bara en handledare utan många ☺! Speciellt tack till **David Turner**, för att du trots mycket arbete med att avsluta din tid som dekanus orkade korrekturläsa min kappa. Thanks also to **Misha** and **Dasha** for helping me with the Russian.

Thanks to all at the 4:th floor for nice coffee- and lunch-breaks. Special thanks to the Nano-group and to Caroline that took the time to read my thesis.

Ett stort tack till **Bertil Romanus** för att du trodde på mig och fick mig att våga ta steget att börja plugga efter att ha arbetat under många år. Du är min mentor och jag är för evigt tacksam för att du finns i mitt liv och jag hoppas att det förblir så.

**Inger** och **Jonas**, min syster och svåger, som jag terroriserade med mina frågor under Komvux-tiden när min lärare inte lyckades förklara för mig. Tack för ert tålamod! Utan er hade jag inte stått där jag är idag.

**Catharina**, jaha vad säger man? Ord kan nog inte säga vad vi delat och vad jag känner för dig. Nu är det din tur att nå dina drömmars mål!

**Emma** och **Kjell**, ni är speciella för mig! Ni har stötta mig och funnits där för mig och jag vet att det alltid finns en plats för mig hos er. Ni har också tagit mig/oss till underbara platser och fler ska det bli...

Min **MATS**, du är det bästa som hänt mig. Tack för att du stöttat mig under denna tid! Vad tråkigt livet vore utan dig!

Finally, financial support to conduct the research included in this thesis was received from the Swedish Research Council (contract no 621-2006-3240 and 621-2010-4084); the European Union projects DAMOCLES (contract 018509), CarboOcean (contract no 511176-2), EPOCA (contract 211384) and CarboChange (project reference 264879); and Tellus, the Centre of Earth Systems Science at the University of Gothenburg. Support for the expedition logistics was received from the Knut and Alice Wallenberg Foundation and from the Swedish Polar research Secretariat.

## References

- Aagaard, K., Coachman, L.K., Carmack, E., 1981. On the halocline of the Arctic Ocean. *Deep-Sea Research Part a-Oceanographic Research Papers* 28, 529-545.
- ACIA, 2004. Arctic Climate Impact Assessment. Cambridge University Press, p. 1042 pp.
- Alling, V., Sanchez-Garcia, L., Porcelli, D., Pugach, S., Vonk, J.E., van Dongen, B., Morth, C.M., Anderson, L.G., Sokolov, A., Andersson, P., Humborg, C., Semiletov, I., Gustafsson, O., 2010. Nonconservative behavior of dissolved organic carbon across the Laptev and East Siberian seas. *Global Biogeochemical Cycles* 24, 15.
- Anderson, L.A., Sarmiento, J.L., 1994. Redfield ratios of remineralization determined by nutrient data-analysis. *Global Biogeochemical Cycles* 8, 65-80.
- Anderson, L.G., Bjork, G., Holby, O., Jones, E.P., Kattner, G., Koltermann, K.P., Liljebld, B., Lindegren, R., Rudels, B., Swift, J., 1994. Water masses and circulation in the Eurasian Basin -results from the Oden91 expedition. *J Geophys Res-Oceans* 99, 3273-3283.
- Anderson, L.G., Olsson, K., Chierici, M., 1998. A carbon budget for the Arctic Ocean. *Global Biogeochemical Cycles* 12, 455-465.
- Anisimov, O., Reneva, S., 2006. Permafrost and changing climate: The russian perspective. *Ambio* 35(4), 169-175.
- Bates, N.R., Mathis, J.T., 2009. The Arctic Ocean marine carbon cycle: evaluation of air-sea CO<sub>2</sub> exchanges, ocean acidification impacts and potential feedbacks. *Biogeosciences* 6, 2433-2459.
- Bauch, D., Dmitrenko, I.A., Wegner, C., Holemann, J., Kirillov, S.A., Timokhov, L.A., Kassens, H., 2009. Exchange of Laptev Sea and Arctic Ocean halocline waters in response to atmospheric forcing. *J Geophys Res-Oceans* 114, 8.
- Bindoff, N.L., Willebrand, J., Artale, V., A, C., Gregory, J., Gulev, S., Hanawa, K., Quéré, C.L., Levitus, S., Nojiri, Y., Shum, C.K., Talley, L.D., A. Unnikrishnan, 2007. Observations: Oceanic Climate Change and Sea Level. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Broecker, W.S., Peng, T.H., 1992. Interhemispheric transport of carbon-dioxide by ocean circulation. *Nature* 356, 587-589.
- Brown, J., O.J. Ferriars, J., Heginbottom, J.A., Melnikov, E.S., 1998. Circum-arctic map of permafrost and ground ice conditions. Boulder, CO: National Snow and Ice Data Center/World Data Center for Glaciology.
- Canadell, J.G., Le Quere, C., Raupach, M.R., Field, C.B., Buitenhuis, E.T., Ciais, P., Conway, T.J., Gillett, N.P., Houghton, R.A., Marland, G., 2007. Contributions to accelerating atmospheric CO<sub>2</sub> growth from economic activity, carbon intensity, and efficiency of natural sinks. *Proceedings of the National Academy of Sciences of the United States of America* 104, 18866-18870.
- Carmack, E., Barber, D., Christensen, J., Macdonald, R., Rudels, B., Sakshaug, E., 2006. Climate variability and physical forcing of the food webs and the carbon budget on panarctic shelves. *Progress in Oceanography* 71, 145-181.

- Chierici, M., Fransson, A., Anderson, L.G., 1999. Influence of m-cresol purple indicator additions on the pH of seawater samples: correction factors evaluated from a chemical speciation model. *Mar. Chem.* 65, 281-290.
- Clayton, T.D., Byrne, R.H., 1993. Spectrophotometric seawater pH measurements - total hydrogen-ion concentration scale calibration of m-cresol purple at-sea results. *Deep-Sea Res. Part I-Oceanogr. Res. Pap.* 40, 2115-2129.
- Dickson, A.G., 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep-Sea Research Part a-Oceanographic Research Papers* 28, 609-623.
- Dickson, A.G., Millero, F.J., 1987. A comparison of the equilibrium-constants for the dissociation of carbonic-acid in seawater media. *Deep-Sea Research Part a-Oceanographic Research Papers* 34, 1733-1743.
- Dittmar, T., Kattner, G., 2003. The biogeochemistry of the river and shelf ecosystem of the Arctic Ocean: a review. *Mar. Chem.* 83, 103-120.
- Dmitrenko, I., Kirillov, S., Eicken, H., Markova, N., 2005. Wind-driven summer surface hydrography of the eastern Siberian shelf. *Geophysical Research Letters* 32, 5.
- Dmitrenko, I.A., Ivanov, V.V., Kirillov, S.A., Vinogradova, E.L., Torres-Valdes, S., Bauch, D., 2011. Properties of the Atlantic derived halocline waters over the Laptev Sea continental margin: Evidence from 2002 to 2009. *J Geophys Res-Oceans* 116.
- Dmitrenko, I.A., Kirillov, S.A., Tremblay, L.B., Bauch, D., Holemann, J.A., Krumpfen, T., Kassens, H., Wegner, C., Heinemann, G., Schroder, D., 2010. Impact of the Arctic Ocean Atlantic water layer on Siberian shelf hydrography. *J Geophys Res-Oceans* 115, 17.
- Frey, K.E., McClelland, J.W., 2009. Impacts of permafrost degradation on arctic river biogeochemistry. *Hydrological Processes* 23, 169-182.
- Frey, K.E., McClelland, J.W., Holmes, R.M., Smith, L.C., 2007. Impacts of climate warming and permafrost thaw on the riverine transport of nitrogen and phosphorus to the Kara Sea. *Journal of Geophysical Research-Biogeosciences* 112, 10.
- Gascard, J.C., Raisbeck, G., Sequeira, S., Yiou, F., Mork, K.A., 2004. The Norwegian Atlantic Current in the Lofoten basin inferred from hydrological and tracer data (I-129) and its interaction with the Norwegian Coastal Current (vol 31, art no L01308, 2004). *Geophysical Research Letters* 31, 1.
- Gordeev, V.V., Dgmalov, R.G., Zekcep, I.S., Julidov, W.W., Brizgalo, W.A., 1999. Estimations of inflow of nutrient with river runoff and ground water in Marginal Seas of Russian Arctic. *Water Source* 26 (2), 206-211.
- Gordeev, V.V., Sidorov, I.S., 1993. Concentrations of major elements and their outflow into the Laptev Sea by the Lena river. *Mar. Chem.* 43, 33-45.
- Gran, G., 1952. Determination of the equivalence point in potentiometric titrations. *Analyst* 77, 661-671.
- Guay, C.K.H., Falkner, K.K., Muench, R.D., Mensch, M., Frank, M., Bayer, R., 2001. Wind-driven transport pathways for Eurasian Arctic river discharge. *J Geophys Res-Oceans* 106, 11469-11480.
- Hansson, I., 1973. New set of pH-scales and standard buffers for sea-water. *Deep-Sea Research* 20, 479-491.

- Haraldsson, C., Anderson, L.G., Hasselov, M., Hulth, S., Olsson, K., 1997. Rapid, high-precision potentiometric titration of alkalinity in ocean and sediment pore waters. *Deep-Sea Res. Part I-Oceanogr. Res. Pap.* 44, 2031-2044.
- Holmes, R.M., McClelland, J.W., Raymond, P.A., Frazer, B.B., Peterson, B.J., Stieglitz, M., 2008. Lability of DOC transported by Alaskan rivers to the arctic ocean. *Geophysical Research Letters* 35.
- IPCC, 2007. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Summary for Policymakers, Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp.
- Jakobsson, M., 2002. Hypsometry and volume of the Arctic Ocean and its constituent seas. *Geochemistry Geophysics Geosystems* 3, 18.
- Jakobsson, M., Grantz, A., Kristoffersen, Y., Macnab, R., 2003. Physiographic provinces of the arctic ocean seafloor. *Geological Society of America Bulletin* 115, 1443-1455.
- Johnson, K.M., King, A.E., Sieburth, J.M., 1985. Coulometric TCO<sub>2</sub> analyses for marine studies - and introduction. *Mar. Chem.* 16, 61-82.
- Johnson, K.M., Sieburth, J.M., Williams, P.J.L., Brandstrom, L., 1987. Coulometric total carbon-dioxide analysis for marine studies - automation and calibration. *Mar. Chem.* 21, 117-133.
- Jones, E.P., Anderson, L.G., Swift, J.H., 1998. Distribution of Atlantic and Pacific waters in the upper Arctic Ocean: Implications for circulation. *Geophysical Research Letters* 25, 765-768.
- Kalnay, E., Kanamitsu, M., Kistler, R., Collins, W., Deaven, D., Gandin, L., Iredell, M., Saha, S., White, G., Woollen, J., Zhu, Y., Chelliah, M., Ebisuzaki, W., Higgins, W., Janowiak, J., Mo, K.C., Ropelewski, C., Wang, J., Leetmaa, A., Reynolds, R., Jenne, R., Joseph, D., 1996. The NCEP/NCAR 40-year reanalysis project. *Bulletin of the American Meteorological Society* 77, 437-471.
- Lewis, E., Wallace, D.W.R., 1998. Program developed for CO<sub>2</sub> system calculations, ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee.
- Maslanik, J.A., Serreze, M.C., Barry, R.G., 1996. Recent decreases in Arctic summer ice cover and linkages to atmospheric circulation anomalies. *Geophysical Research Letters* 23, 1677-1680.
- McClelland, J.W., Holmes, R.M., Dunton, K.H., Macdonald, R.W., 2012. The Arctic Ocean Estuary. *Estuaries and Coasts* 35, 353-368.
- McGuire, A.D., Anderson, L.G., Christensen, T.R., Dallimore, S., Guo, L.D., Hayes, D.J., Heimann, M., Lorenson, T.D., Macdonald, R.W., Roulet, N., 2009. Sensitivity of the carbon cycle in the Arctic to climate change. *Ecological Monographs* 79, 523-555.
- Mehrbach, C., Culberso, Ch, Hawley, J.E., Pytkowic, Rm, 1973. Measurement of apparent dissociation-constants of carbonic-acid in seawater at atmospheric-pressure. *Limnology and Oceanography* 18, 897-907.
- Nitishinsky, M., Anderson, L.G., Holemann, J.A., 2007. Inorganic carbon and nutrient fluxes on the Arctic Shelf. *Continental Shelf Research* 27, 1584-1599.
- Omstedt, A., 2011. Guide to process based modelling of lakes and coastal seas, Springer-Praxis books in Geophysical Sciences, Springer-Verlag Berlin Heidelberg.
- Omstedt, A., Carmack, E.C., Macdonald, R.W., 1994. Modeling the seasonal cycle of salinity in the Mackenzie self estuary. *J Geophys Res-Oceans* 99, 10011-10021.

- Omstedt, A., Gustafsson, E., Wesslander, K., 2009. Modelling the uptake and release of carbon dioxide in the Baltic Sea surface water. *Continental Shelf Research* 29, 870-885.
- Peterson, B.J., Holmes, R.M., McClelland, J.W., Vorosmarty, C.J., Lammers, R.B., Shiklomanov, A.I., Shiklomanov, I.A., Rahmstorf, S., 2002. Increasing river discharge to the Arctic Ocean. *Science* 298, 2171-2173.
- Pipko, I., Pugach, S.P., Semiletov, I.P., 2009. The autumn distribution of the CO<sub>2</sub> partial pressure in bottom waters of the East Siberian Sea. *Doklady Earth Sciences* 425, 345-349.
- Polyakov, I.V., Alexeev, V.A., Ashik, I.M., Bacon, S., Beszczynska-Moeller, A., Carmack, E.C., Dmitrenko, I.A., Fortier, L., Gascard, J.-C., Hansen, E., Hoelemann, J., Ivanov, V.V., Kikuchi, T., Kirillov, S., Lenn, Y.-D., McLaughlin, F.A., Piechura, J., Repina, I., Timokhov, L.A., Walczowski, W., Woodgate, R., 2011. Fate of Early 2000s Arctic Warm Water Pulse. *Bulletin of the American Meteorological Society* 92, 561-566.
- Polyakov, I.V., Beszczynska, A., Carmack, E.C., Dmitrenko, I.A., Fahrbach, E., Frolov, I.E., Gerdes, R., Hansen, E., Holfört, J., Ivanov, V.V., Johnson, M.A., Karcher, M., Kauker, F., Morison, J., Orvik, K.A., Schauer, U., Simmons, H.L., Skagseth, O., Sokolov, V.T., Steele, M., Timokhov, L.A., Walsh, D., Walsh, J.E., 2005. One more step toward a warmer Arctic. *Geophysical Research Letters* 32, 4.
- Proshutinsky, A.Y., Johnson, M.A., 1997. Two circulation regimes of the wind driven Arctic Ocean. *J Geophys Res-Oceans* 102, 12493-12514.
- Rachold, V., Eicken, H., Gordeev, V.V., Griggoriev, M.N., Hubberten, H.-W., Lisitzin, A.P., Shevchenko, L., Schirrmeister, L., 2004. Modern Terrigenous Organic Carbon Input to the Arctic Ocean, in: Stein, R., Macdonald, R.W. (Eds.), *The Organic Carbon Cycle in the Arctic Ocean.*, Heidelberg, Germany, pp. 33-55.
- Redfield, A.C., Ketchum, B.H., Richards, F.A., 1963. The influence of organisms on the composition of sea-water, in: Hill, M.N. (Ed.), *The Sea*, Vol. 2, Interscience, New York, pp. 26-77.
- Roy, R.N., Roy, L.N., Vogel, K.M., Porter Moore, C., Pearson, T., Good, C.E., Millero, F.J., Campbell, D.M., 1993. The dissociation-constants of carbon-acid in seawater at salinities 5-45 and temperatures 0-degrees-C to 45\_degrees C. *Mar. Chem.* 44, 249-267.
- Rudels, B., Jones, E.P., Anderson, L.G., 1994. On the intermediate depth waters of the Arctic Ocean., in: Johannessen, O.M., Muench, R.D., Overland, J.E., (Ed.), *The role of the Polar Oceans in Shaping the Global Climate.* Geophysical Monographs vol. 85 American Geophysical Union,, Washington, pp. 33-46.
- Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong, C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J., Peng, T.H., Kozyr, A., Ono, T., Rios, A.F., 2004. The oceanic sink for anthropogenic CO<sub>2</sub>. *Science* 305, 367-371.
- Sabine, C.L., Tanhua, T., 2010. Estimation of Anthropogenic CO<sub>2</sub> Inventories in the Ocean, *Annual Review of Marine Science.* Annual Reviews, Palo Alto, pp. 175-198.
- Sakshaug, E., 2004. Primary and secondary production in the Arctic Seas, in: Stein, R., Macdonald, R.W. (Eds.), *The Organic Carbon Cycle in the Arctic Ocean.*, Heidelberg, Germany, pp. 57-81.
- Sakshaug, E., Slagstad, D., 1991. Light and productivity of phytoplankton in polar marine ecosystems - a physiological view. *Polar Research* 10, 69-85.

- Sanchez-Garcia, L., Alling, V., Pugach, S., Vonk, J., van Dongen, B., Humborg, C., Dudarev, O., Semiletov, I., Gustafsson, O., 2011. Inventories and behavior of particulate organic carbon in the Laptev and East Siberian seas. *Global Biogeochemical Cycles* 25, 13.
- Semiletov, I., Dudarev, O., Luchin, V., Charkin, A., Shin, K.H., Tanaka, N., 2005. The East Siberian sea as a transition zone between Pacific-derived waters and Arctic shelf waters. *Geophysical Research Letters* 32, 5.
- Semiletov, I.P., 1999. Aquatic sources and sinks of CO<sub>2</sub> and CH<sub>4</sub> in the polar regions. *Journal of the Atmospheric Sciences* 56, 286-306.
- Semiletov, I.P., Pipko, I., Shakhova, N.E., Dudarev, O.V., Pugach, S.P., Charkin, A.N., McRoy, C.P., Kosmach, D., Gustafsson, O., 2011. Carbon transport by the Lena River from its headwaters to the Arctic Ocean, with emphasis on fluvial input of terrestrial particulate organic carbon vs. carbon transport by coastal erosion. *Biogeosciences* 8, 2407-2426.
- Serreze, M.C., Barrett, A.P., Stroeve, J.C., Kindig, D.N., Holland, M.M., 2009. The emergence of surface-based Arctic amplification. *Cryosphere* 3, 11-19.
- Serreze, M.C., Francis, J.A., 2006. The arctic amplification debate. *Climatic Change* 76, 241-264.
- Serreze, M.C., Holland, M.M., Stroeve, J., 2007. Perspectives on the Arctic's shrinking sea-ice cover. *Science* 315, 1533-1536.
- Serreze, M.C., Walsh, J.E., Chapin, F.S., Osterkamp, T., Dyrgerov, M., Romanovsky, V., Oechel, W.C., Morison, J., Zhang, T., Barry, R.G., 2000. Observational evidence of recent change in the northern high-latitude environment. *Climatic Change* 46, 159-207.
- Shakhova, N., Semiletov, I., Salyuk, A., Yusupov, V., Kosmach, D., Gustafsson, O., 2010. Extensive Methane Venting to the Atmosphere from Sediments of the East Siberian Arctic Shelf. *Science* 327, 1246-1250.
- Shaltout, M., Omstedt, A., 2012. Calculating the water and heat balances of the Eastern Mediterranean Basin using ocean modelling and available meteorological, hydrological, and ocean data. *Oceanologia*, in press.
- Sorokin, Y.I., Sorokin, P.Y., 1996. Plankton and primary production in the Lena river estuary and in the south-eastern Laptev sea. *Estuarine Coastal and Shelf Science* 43, 399-418.
- Stroeve, J.C., Serreze, M.C., Holland, M.M., Kay, J.E., Malanik, J., Barrett, A.P., 2012. The Arctic's rapidly shrinking sea ice cover: a research synthesis. *Climatic Change* 110, 1005-1027.
- Takahashi, T., Broecker, W.S., Langer, S., 1985. Rdfield ratio based on chemical-data from isopycnal surfaces. *J Geophys Res-Oceans* 90, 6907-6924.
- Thomas, H., 2002. Remineralization ratios of carbon, nutrients, and oxygen in the North Atlantic Ocean: A field databased assessment. *Global Biogeochemical Cycles* 16, 12.
- Thoning, K.W., Kitzis, D.R., Crotwell, A., 2010. Atmospheric Carbon Dioxide Dry Air Mole Fractions from quasi-continuous measurements at Barrow, Alaska; Mauna Loa, Hawaii; American Samoa; and South Pole, 1973-2009, Version: 2010-07-14, Path: <ftp://ftp.cmdl.noaa.gov/ccg/co2/in-situ/> ed.
- Wanninkhof, R., 1992. Relationship between wind-speed and gas-exchange ove the ocean. *J Geophys Res-Oceans* 97, 7373-7382.
- Wanninkhof, R., Asher, W.E., Ho, D.T., Sweeney, C., McGillis, W.R., 2009. Advances in Quantifying Air-Sea Gas Exchange and Environmental Forcing, *Annual Review of Marine Science*. Annual Reviews, Palo Alto, pp. 213-244.

- Wanninkhof, R., McGillis, W.R., 1999. A cubic relationship between air-sea CO<sub>2</sub> exchange and wind speed. *Geophysical Research Letters* 26, 1889-1892.
- Weingartner, T.J., Danielson, S., Sasaki, Y., Pavlov, V., Kulakov, M., 1999. The Siberian Coastal Current: A wind- and buoyancy-forced Arctic coastal current. *J Geophys Res-Oceans* 104, 29697-29713.
- Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2, 203-215.
- Vetrov, A.A., Romankevich, E.A., 2009. Production of phytoplankton in the Arctic Seas and its response on recent warming. *Influence of Climate Change on the Changing Arctic and Sub-Arctic Conditions*, 95-108.
- Zhang, T.J., Frauenfeld, O.W., Serreze, M.C., Etringer, A., Oelke, C., McCreight, J., Barry, R.G., Gilichinsky, D., Yang, D.Q., Ye, H.C., Ling, F., Chudinova, S., 2005. Spatial and temporal variability in active layer thickness over the Russian Arctic drainage basin. *Journal of Geophysical Research-Atmospheres* 110, 14.
- Zimov, S.A., Schuur, E.A.G., Chapin, F.S., 2006. Permafrost and the global carbon budget. *Science* 312, 1612-1613.