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Preface

This report is based on several studies of air sea exchange of CO₂ in the coastal area of Greenland. The studies are carried out over 5 years starting in 2009 and ending in 2013. Some of the studies are based on sampling from boats and some are based on measurements at the coast or on sea ice. Bjarne Jensen, Aarhus University, Ivali Lennert, Greenland Institute of Natural Resources and Søren William Lund, Technical University of Denmark, provided technical assistance during field work. The studies were primarily financial supported by Nordic Council of Ministers, by the Nordic Centre of Excellence DEFROST, which is funded by the Nordic Top-level Research Initiative and by The Arctic Research Centre, Aarhus University.

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Summary

The uptake rates of atmospheric CO₂ in the Nordic Seas, and particularly the shelf waters around Greenland, are among the highest in the world's oceans; our study indicate the coastal area including fjords of Greenland take up approximately 1/20 of the CO₂ taken up by the world's coastal area.

The driving factors behind the air-sea exchange of CO₂ in open waters are the difference between the partial pressure of CO₂ (pCO₂) in the atmosphere and the surface waters, leading to an uptake in areas where the pCO₂ of surface waters is lower.

Precipitation of brine and CO₂ from the sea ice, leading to under saturation of the pCO₂ in surface water, is suggested to be an important process related to ice formation. Also the emission of CO₂ to the atmosphere during sea ice formation is estimated to be of high importance.

The estimates we find in this study are based on only few measurements of pCO₂, thus being highly uncertain. Furthermore, the level of pCO₂ is likely to vary over the season as a result of the melting and formation of sea ice, and therefore, the flux estimate depends on the time of year the data has been collected.

Because the coastal area of Greenland is very sensitive to climate change, and because it takes up more CO₂ relative to other marine areas, a realistic estimate of the exchange rates is crucial in order to obtain reliable assessments of the CO₂ uptake by the Greenlandic coastal area. Our calculations reveal the importance of a diminishing sea ice cover; and it is clear that the wind climate is essential to the surface exchange.

Introduction

In the last 150 years, anthropogenic activities have increased atmospheric levels of CO₂ with consequences for the global climate. Next to water vapour, CO₂ is the most important greenhouse gas (GHG) causing atmospheric temperature to increase, due to the absorption of longwave (LW) radiation of CO₂. An increasing CO₂ concentration combined with a decline of sea ice in the Arctic, the latter leading to a decrease in albedo and an increase in LW radiation, is likely to accelerate the heating of the Arctic atmosphere further. However, approximately 25% of the anthropogenic CO₂ emissions are estimated to have been absorbed by the world's oceans (Ciais *et al.*, 2013, Takahashi *et al.*, 2009, Sabine *et al.*, 2004), and the annual global ocean uptake is estimated at 2 Pg C yr⁻¹ with an uncertainty of 0.6 Pg C yr⁻¹ (Wanninkhof *et al.*, 2013). The oceans, covering 71% of the earth, thus play an important role in buffering the effects of human CO₂ emissions, and knowledge of factors influencing the air-sea exchange of CO₂ is crucial in order to predict future climate with any level of confidence.

Estimates of the global ocean CO₂ flux carried out by Takahashi *et al.* 2002, Takahashi *et al.* 2009 and Wanninkhof *et al.* 2013 do not take into account the CO₂ uptake from the circumpolar fjord systems because they exclude coastal data from their estimate. Therefore, the Greenlandic fjords and the coastal area of Greenland are not part of current estimates for global oceanic CO₂ uptake. However, a recent paper by Chen *et al.*, (2013) does report air-sea exchange of CO₂ over the world's coastal seas. This study estimates a total uptake of 0.3 Pg C yr⁻¹ (= 300 Tg C yr⁻¹) by the world's coastal seas but only few measurements from the Greenlandic coastal area were included (Rysgaard *et al.*, 2012; Ruiz-Halpern *et al.*, 2010). A recent compilation of data on CO₂ in coastal areas underlines two points: 1) that the Arctic coastal zone is an important area for ocean uptake of CO₂ and 2) that the Arctic coastal zone is particularly understudied (Laruelle *et al.*, 2014)

An important area for ocean CO₂ uptake is the Nordic Seas (Takahashi *et al.*, 2002; 2009) and the shelf waters (Chen *et al.*, 2013). The uptake rates of atmospheric CO₂ in the Nordic Seas, and particularly the shelf waters around Greenland, are among the highest in the world's oceans (Nordic Seas ~ 2.5 mol m⁻² year⁻¹ (Takahashi *et al.*, 2009), and

Greenland Shelf $\sim 6 \text{ mol m}^{-2} \text{ year}^{-1}$ (Chen *et al.*, 2013)). The driving factors behind the air-sea exchange of CO_2 in open waters are the difference between the partial pressure of CO_2 ($p\text{CO}_2$) in the atmosphere and the surface waters, leading to an uptake in areas where the $p\text{CO}_2$ of surface waters is lower. In coastal shelf areas, the $p\text{CO}_2$ level is regulated by the process called *continental shelf pump*, which is a combination of solubility and biological processes. As the solubility of CO_2 is greater in colder waters, the solubility of the waters is increased due to a cooling in the winter. This change in solubility can lower the $p\text{CO}_2$ below the atmospheric saturation level, thus stimulating uptake from the atmosphere. At the same time, colder and denser surface waters will promote downwelling, removing CO_2 from the surface ocean. Together with this solubility pump, summer primary production of organic matter through photosynthesis causes a continued drawdown of CO_2 in shelf regions: the biological pump. The shelf area covers $26 \times 10^6 \text{ km}^2$ and constitutes only about 8% of the ocean surface. According to Chen *et al.*, (2013), the global shelf waters take up approximately 0.4 Pg C yr^{-1} which is 20% of the global ocean uptake (global ocean uptake $\sim 2 \text{ Pg C yr}^{-1}$). Shelf waters in the northern areas have the most effective uptake rates.

The high CO_2 uptake by the Nordic seas has been ascribed mainly to a strong biological drawdown, but chemical processes in the sea ice have also been suggested to play a role (Rysgaard *et al.* 2007, 2009). Furthermore, the summer of 2012 showed that record low sea ice extent is becoming more and more commonplace in an Arctic that is progressing towards a seasonally sea ice-free state; therefore, it is essential to understand the consequences of lower sea ice cover on greenhouse gas exchange at high latitudes. Another possible pump mechanism driving uptake of CO_2 in the coastal sea around Greenland is the inflow of melt water from land and the Greenland ice sheet. Because of the non-conservative behaviour of CO_2 in water, the mixing of meltwater and sea water will result in strongly under saturated surface water with respect to CO_2 (Meire *et al.*, 2014).

In the marine environment, it seems that CO_2 uptake has increased as a response to the recent retreat of the sea ice (Bates *et al.*, 2006), but it is uncertain if this enhanced uptake will continue over the long term (Bates *et al.*, 2011). According to Parmentier *et al.* (2013), the sea ice affects not only the marine uptake of CO_2 but also the terrestrial uptake of CO_2 and CH_4 ; thus, the carbon balance in the Arctic is substantially influenced by changes in sea ice extent. Processes related to the freezing and melting of sea ice constitute large unknowns to the exchange of CO_2 (Garbe *et al.*, 2014), leading to poor descriptions in models today of the

size and direction of CO₂ fluxes over coastal Arctic regions. It is therefore difficult to assess the consequences of the changing climate and sea ice.

Because the coastal area of Greenland is very sensitive to climate change, and because it takes up more CO₂ relative to other marine areas, a realistic estimate of the exchange rates is crucial in order to obtain reliable assessments of the CO₂ uptake by the Greenlandic coastal area.

1. Logistics and methods

The air-sea exchange (flux) of CO₂ is driven by the difference between the partial pressures of CO₂ (pCO₂) in the atmosphere and the ocean, and the rate of the flux is determined by the air-sea gas exchange velocity. In the current study, we have measured CO₂ fluxes, surface pCO₂ and estimated exchange velocities for coastal areas and fjord systems in different Arctic regions.

We have applied a “comparative experimental” approach and conducted measurements at two sites in Greenland that represent a strong gradient in factors important for CO₂ exchange. The two sites (Nuuk (64N) and Daneborg/Zackenbergl (74N) constitute a climatic gradient with differences in climate and hence temperature, vegetation, sea ice cover, freshwater input etc.

Figure 1. Map showing the 6 Arctic regions we use for calculation. The blue dots are the High Arctic settlements

In order to take the different climatic conditions in Greenland into account for our analysis of the CO₂ uptake, the coastal area of Greenland is divided into three High Arctic and three Low Arctic regions, characterized by differences in sea ice cover and wind climate. The analysis is based on data from the coastal towns and settlements in these regions. The towns and the settlements are: High Arctic 1 (Hall Land, Kap Morris Jesup and Station Nord), High Arctic 2 (Pituffik and Danmarkshavn), High Arctic 3 (Daneborg, Illoqqortoormiut and Aputiteeq), Low Arctic 1 (Upernavik, Aasiaat, Sisimiut), Low Arctic 2 (Nuuk, Paamiut, Qaqortoq, Maniitsoq) and Low Arctic 3 (Tasiilaq and Ikermiarsuk).

1.1 Measurements of air – surface exchange

There are methods and equipment which can be used to measure directly the air-sea exchange of CO₂. Eddy covariance is one method, and it has been employed for many years in the Arctic in terrestrial (e.g. Vourlitis *et al.*, 1999; Soegaard *et al.*, 2000; Corradi *et al.*, 2005) and limnic systems (Eugster *et al.* 2003). The eddy covariance can be used for continuous measurements; however, the continuous operation is logistically demanding with respect to electrical power and general maintenance requirements. In NE Greenland, the eddy covariance technique has been used for a decade to estimate exchange of CO₂ by the heath and fen ecosystems and the atmosphere (Groendahl *et al.*, 2007). Recently, a new flux measurement site near Nuuk, W Greenland, has been established. Direct flux measurements over marine surfaces are more difficult than over terrestrial surfaces, due to the much smaller exchange rates. However, techniques to accomplish this have been tested by Sørensen and Larsen (2010), and these spectral methods (Dissipation technique and Cospectral Peak Method) are applied in the study presented here. Additionally, a different spectral analysis method for estimation of fluxes over areas with small surface fluxes has been tested and used for estimation of fluxes over sea ice.

1.1.1 Eddy covariance method

The air-sea exchange of CO₂ is proportional to the mean covariance between fluctuations of vertical velocity (w') and CO₂ (CO_2') around their mean values. This is the basis for the eddy covariance method, with the covariance producing a direct measure of net CO₂ surface exchange (e.g., Swinbank, 1951). Rapid response (<0.1sec) detectors are required for

both wind velocity and CO₂. The vertical wind velocity and the CO₂ concentration are measured simultaneously by instruments installed at a tower or mast 2–10 meters above the surface.

1.1.2 Spectral analysis methods

The data obtained from the eddy covariance measurements can also be used for estimating the flux from spectral analysis. Power spectra of vertical wind speed fluctuation and CO₂ fluctuation or co-spectra between vertical wind speed fluctuations and CO₂ fluctuation are calculated, and the flux is estimated from either the amplitude of the cospectra (Cospectral Peak Method), or from the inertial subrange of the power spectra (Dissipation method) (Sørensen and Larsen, 2010; Normann *et al.*, 2012). Recently, a method using modelled and measured ogives (accumulated cospectra) for estimation of CO₂ fluxes was suggested (Sievers *et al.*, 2015a) and applied for measurements over ice and snow surfaces (Sievers *et al.*, 2015b).

1.2 Measurements of marine pCO₂

Estimation of pCO₂ in the water was carried out during field trips by using the air-water equilibrator method (direct and online method) and/or discrete sampling, followed by analysis of total inorganic carbon (TCO₂) in the laboratory. The TCO₂ can be used for calculation of pCO₂ when salinity, temperature and chemical conditions of the water are known (Goyet and Poisson, 1989). To ensure comparable estimates of pCO₂ obtained from the two different methods, intercomparisons of the methods were carried out.

In Godthåbsfjord, we used an equilibrator system consisting of a 10 l glass cylinder in which water was pumped in at the top of the cylinder, and a series of small glass tubes increased the water-air contact surface in order to quickly achieve equilibrium. Air was sampled continuously from the equilibrator into an infrared CO₂ analyzer, and the air flow from the CO₂ monitor was returned to the equilibrator in a circulating flow. The CO₂ monitor, in turn, measured the air sample from the equilibrator system, a calibration gas and the atmospheric air. In this manner, the same instrument was used for determining pCO₂ in the water and in the atmosphere. This equilibrator was constructed in accordance with Dickson and Goyet (1994).

A membrane equilibrator was used for the measurements of pCO₂ in Young Sound. Surface water was pumped through 2 m of Tygon tubing into a membrane equilibrator (Mini Module by LiquiCal, Charlotte, NC, USA) at a rate of approximately 2 l min⁻¹. In the equilibrator, the sea water content of dissolved CO₂ equilibrated with a limited volume of atmospheric air across a gas-permeable membrane. The gas was circulated through a drying column before entering a CO₂ gas analyzer. From the CO₂ gas analyzer, the gas was passed back into the equilibrator, forming a closed circuit containing approximately 200 ml of atmospheric gas at a normal atmospheric pressure.

1.3 Calculation of CO₂ uptake

The surface uptake of CO₂ was calculated using the appropriate exchange velocity, wind climate for Greenland and the surface pCO₂ specific for the region and the season, because pCO₂ depends on temperature and biological activity. The calculation of uptake for the marine ice-free area was based on the Diffusive Boundary Model:

$$F = K_{660} S \Delta pCO_2$$

F is the flux of CO₂, K₆₆₀ is the gas exchange velocity normalized to a temperature of 20 C and a salinity of 35 PSU, S is the CO₂ solubility in seawater, and ΔpCO₂ is the partial pressure difference between the sea surface and the atmosphere. The solubility of CO₂, S, was calculated according to Weiss (1974), using measured water temperature and salinity. The gas exchange velocity was estimated based on empirically derived relationships with wind speeds. We used three different relationships for comparison: 1) the formulation by Nightingale *et al.* (2000), which is developed for coastal areas, $K=0.333U + 0.222U^2$, 2) the formulation by Kuss *et al.*, (2004), which is developed for the Baltic Sea, $K=0.45U^2$ and 3) the formulation by Clark *et al.*, (1995), which is developed for Hudson river, $K=2+0.24U^2$. The two latter have been shown by Mørk *et al.*, 2015 to also be appropriate for shallow fjord systems where U is the wind speed (m s⁻¹) at 10 meter above sea surface.

Table 1. The wind climate (1966–1999) in the 6 different regions; High Arctic 1 (Hall Land, Kap Morris Jesup and Station Nord), High Arctic 2 (Pituffik and Danmarkshavn), High Arctic 3 (Daneborg, Illoqqortoormiut and Aputiteeq), Low Arctic 1 (Upernavik, Aasiaat, Sisimiut), Low Arctic 2 (Nuuk, Paamiut, Qaqortoq, Maniitsoq) and Low Arctic 3 (Tasiilaq and Ikermiuarsuk)

Column1	High Arctic1 (ms ⁻¹)	High Arctic2 (ms ⁻¹)	High Arctic3 (ms ⁻¹)	Low Arctic1 (ms ⁻¹)	Low Arctic2 (ms ⁻¹)	Low Arctic3 (ms ⁻¹)
Jan	4.2	4.6	4.8	3.8	5.6	5.3
Feb	4.1	4.3	4.8	3.3	5.7	5.2
Mar	4.3	4.4	4.6	3.3	5.3	4.4
Apr	4.7	3.8	3.7	3.2	4.7	4.1
May	4.7	3.4	3.2	3.3	4.1	3.7
Jun	4.9	3.4	3.0	3.2	3.9	3.6
Jul	5.0	3.3	2.8	2.9	3.5	3.3
Aug	4.7	3.4	3.1	3.3	3.7	3.4
Sep	4.4	3.9	3.5	3.5	4.1	4.1
Oct	3.9	4.5	4.3	3.9	4.2	4.3
Nov	4.2	4.6	4.4	4.7	4.8	5.3
Dec	4.2	4.5	4.6	4.5	5.4	5.6
Average	4.4	4.0	3.9	3.6	4.6	4.3

1.3.1 Wind effect on the uptake

The wind speed is one of the parameters controlling the gas exchange velocity. Characteristic for Greenland are the many days with dead, calm or light air/slight breeze, in some places at the east coast nearly 60 % of the time. During calm situations a pattern of locally determined winds, such as drainage flows or fall winds from the ice sheet, can be seen. In order to calculate the CO₂ uptake in the different regions the local wind climate is essential.

The wind climate which was used for the calculations in the present study was based on mean wind speeds measured in several coastal settlements from 1966–1999 (wind climate tables from www.dmi.dk). Average wind speeds were estimated for 6 regions (3 High Arctic and 3 Low Arctic, see figure 1) and are shown in table 1. According to Eichelberger *et al.*, (2008), the wind speed is expected to increase at the North and High Arctic west coast of Greenland but decrease in the rest of the country.

1.3.2 The coastal surface area

An accurate estimate of CO₂ uptake by the Greenlandic coastal area requires detailed knowledge of the physical and biogeochemical characteristic of the fjords in Low and High Arctic Greenland. According to Hen-

riksen *et al.*, 2009 the area of Greenland's continental shelf underlain by continental crust is estimated to be approximately 825,000 km². A very detailed mapping by Laruelle *et al.* (2013) of coastal waters estimates the surface of estuaries and shelf waters in North and South Greenland to be 638.1 km² and 278.8 km², respectively. In present study we use the area estimated by Laruelle *et al.*, (2013), in order to compare to other studies of CO₂ exchange in coastal waters. The surface area used is shown in table 2.

Table 2. Surface area of marine coastal waters around Greenland

	Watershed Surface 10 ³ Km ²	Estuarine Surface 10 ³ Km ²	Shelf Surface 10 ³ Km ²	Total 10 ³ Km ²
Northern Greenland	373	24.1	614	638.1
Southern Greenland	101	8.8	270	278.8

(Laurelle *et al.*, 2013).

Only few measurements of pCO₂ in Greenlandic fjord systems are reported, and the surface pCO₂ used in present study for calculations of uptake in the Greenlandic coastal area are based on the measurements carried out in our study (Rysgaard *et al.*, 2012 and Sejr *et al.* 2011), representing pCO₂ values for high Arctic fjord systems and low Arctic fjord systems. However the data from Rysgaard *et al.*, 2012 have also been used for upscaling of the fluxes by Chen *et al.*, (2013) and Laruelle *et al.*, (2013), but to our knowledge the comprehensive data set by Sejr *et al.* (2011) and Sejr *et al.* (2014) has not been used for upscaling of CO₂ surface exchange.

Ice cover influences the uptake of CO₂, and obviously, the exchange velocities over water surfaces cannot be used for ice-covered areas. To calculate the air-sea exchange, we have estimated the ice cover in the 6 Arctic regions based on ice cover climate records from the Danish Meteorological Institute (DMI) (www.dmi.dk). The uptake over sea ice was calculated by setting the surface exchange to zero when the water surface was 100% covered by ice. The application of the Resistance Method for flux calculation over sea ice suggested by Sørensen *et al.* (2014) and the controlling parameters found by Sievers *et al.* (2015b) was not feasible due to a lack of knowledge of pCO₂ in snow and ice.

2. Results

The data sampled during field work in Godthåbsfjord (Rysgaard *et al.*, 2012) and in Young Sund, Daneborg (Sejr *et al.*, 2011) formed the basis of our investigation of the exchange of CO₂ between the atmosphere and the marine coastal surface in Greenland during ice-covered and open water periods

2.1 CO₂ air-sea exchange in Greenlandic coastal waters and fjords

In order to estimate the uptake of CO₂ in the coastal area of Greenland, knowledge is needed of surface water pCO₂ and exchange velocities which can be unique for the coastal Arctic region, due to the specific meteorology and oceanographic conditions. Direct measurements of air-sea exchange supplemented with measurements of the pCO₂ in the water and atmosphere are essential for assessing exchange velocities for fjord and coastal Arctic systems.

2.1.1 *pCO₂ in fjord and coastal surface water*

Recent studies (Sejr *et al.*, 2011; Rysgaard *et al.*, 2012, Sejr *et al.*, 2014 and Meire *et al.*, 2014) have shown that the fjords and shelf areas of Greenland have an exceptional high potential for CO₂ uptake.

Measurements of pCO₂ were carried out in July–August from 2006–2009 in the High Arctic fjord, Young Sound by Sejr *et al.*, (2011). The annual mean pCO₂ varied between 250–300 µatm, with an average over the four years of 275 µatm. Measurements in the Low Arctic Godthåbsfjord (Rysgaard *et al.*, 2012) revealed extremely low marine pCO₂ values, ranging from 250 µatm to 90 µatm, with a mean value of 170 µatm.

Rysgaard *et al.* (2012) showed that the production of ikaite (CaCO₃·6H₂O) in the ice during winter, followed by dissolution of ikaite crystals during the melt season, added large amounts of bicarbonate (HCO₃⁻) to the surface waters, thereby reducing surface water pCO₂ (see equation 1).

This depletion of CO₂ can influence the surface water pCO₂ in the month following the ice melt, thus increasing the potential of the surface waters for CO₂ uptake in the month after the melting season.

2.1.2 Exchange velocities between the water surface and the atmosphere

When applying the exchange velocities suggested by Nigthingale *et al.* (2000), Rysgaard *et al.* (2012) estimated the uptake of carbon by the Godthåbfjord to be approximately 7.5 ton C km⁻² month⁻¹, and Sejr *et al.* (2011) estimated an annual uptake of 32 ton C km⁻² y⁻¹, based on a summer uptake of about 10 ton C km⁻² month⁻¹ and an ice cover of 9 months per year in Young Sound.

These estimates of uptake are highly uncertain due to the lack of knowledge of exchange velocities for fjords and enclosed seas. Furthermore, gas exchange of CO₂ from melt water ponds and polynya areas outside Young Sound has not been considered (Dmitrenko *et al.*, 2015). Knowledge of pCO₂ can be used to show the direction of air-sea exchange and the potential uptake, but knowledge of surface gas exchange velocity is required to calculate actual exchange rates of CO₂ (Liss and Merlivat 1986, Wanninkhof 1992, Nigthingale 2000, Ho 2006). The exchange velocities are usually described as wind speed dependent, and there is large discrepancy between the different studies. Not surprisingly, different exchange velocities, as suggested by different studies, lead to very different estimates of the oceanic CO₂ uptake. Takahashi *et al.* (2002) reported a difference of 70% between flux estimates based on the parameterizations by Wanninkhof (1992) and Wanninkhof and McGillis (2001). A description or parameterization of exchange velocities for the Arctic coastal zone does not exist; thus, most estimates of air-sea exchange in this area are based on parameterizations for oceanic conditions. Estimates of CO₂ uptake based on these exchange velocities, as well as measurements of pCO₂ in the Arctic coastal waters and fjord systems, are thus highly uncertain.

The air-sea transfer velocity of CO₂ for fjord systems was investigated in a shallow estuary in Denmark (Mørk *et al.* 2014, 2015), using measured eddy covariance CO₂ fluxes and air-sea CO₂ partial pressure differences. The data were examined thoroughly, using quality criteria based on both eddy covariance and cospectral peak methods. Mørk *et al.* (2015) found that the transfer velocity for estuaries, such as Roskilde

Fjord, was best estimated based on the parameterization suggested by Clark *et al.* (1995) ($K = 2 + 0.24U^2$) or Kuss *et al.*, (2004) ($K = 0.45U^2$) where U is the wind speed at 10 m. The parameterization by Clark *et al.* (1995) is based on measurements in Hudson River, and the parameterization by Kuss *et al.* (2004) is based on measurements in the Baltic Sea. At low wind speeds, the transfer velocity measured by Mørk *et al.* (2015) was lower than in other coastal waters, and at times even negative. However, a firm transfer velocity parameterization was established for wind velocities above 5 m s^{-1} . It was further concluded by Mørk *et al.* (2014) that turbulence in both air and water influences the transfer velocity. This is an essential finding, suggesting the depth of the fjord to be a key parameter.

The fjords in Greenland are deep, and tides are high; thus, the parameterizations described above might not be appropriate for the estimation of exchanges in a Greenlandic fjord. Measurements of fluxes and $p\text{CO}_2$ have been carried out in Kobbefjord near Nuuk; unfortunately, only few measurements could be obtained from the marine area, due to the wind climate in the fjord, where the prevailing wind direction is south, and only low wind speeds were sampled from a northerly direction (Fig 2).

Figure 2. Location of the measurement station in Kobbefjord, Nuuk, Greenland, where CO_2 flux and wind parameters were measured. The wind rose shows the dominating wind direction and wind speed

The fluxes measured in Kobbefjord over the marine surface in May 2013 were large, ranging from -0.4 to $-1.5 \mu\text{mol m}^{-2} \text{sec}^{-1}$. A preliminary estimate of exchange velocities in Kobbefjord based on discrete measurements of pCO_2 and the few measurements of fluxes revealed exchange rates higher than those found in Roskilde Fjord. This data set is very limited, however, making the estimated exchange rates highly uncertain; thus, the parameterizations by both Clark *et al.* (1995) from a river system and Kuss *et al.* (2004) from a deeper coastal sea are used to estimate the uptake in the coastal region of Greenland, but more measurements of CO_2 air-sea exchange and surface pCO_2 should be carried out in the specific Greenlandic estuaries in order to establish a more accurate parameterization for exchange velocities.

2.2 CO_2 fluxes over ice covered waters

Partial pressure of CO_2 is easily quantified, and about 3 million recorded measurements (Takahashi *et al.* 2009) have been conducted in the world's oceans. Until recently, the ocean CO_2 uptake in the Arctic has primarily been attributed to a cooling of warm Atlantic surface water, combined with the sedimentation of organic carbon from the mixed surface layer (known as the biological pump). Rysgaard *et al.* (2007, 2011 and 2012) show that chemical processes during ice formation and melting could be important factors for lowering surface pCO_2 levels during the melting of sea ice in summer, and likewise, a reduced formation of sea ice could result in a lowered uptake of CO_2 . Preliminary calculations based on measured biogeochemical processes in sea ice suggest that this "sea ice pump" may drive up to 50% of the regional ocean uptake (Rysgaard 2007), thereby potentially being a very important negative feedback mechanism that can accelerate CO_2 accumulation in the atmosphere, as the extent and formation of sea ice diminish. In the present study, we calculate pCO_2 and uptake using current pCO_2 levels which are assumed to be affected by the dissolution of ikaite at the High Arctic. To assess the consequences of less ikaite formation, we also calculate uptake using a slight increase in the surface pCO_2 ($+ 50 \mu\text{atm}$) and a decrease in the sea ice cover during spring and summer.

2.2.1 Processes within the ice

As ice forms from seawater, dissolved salts are trapped in liquid brines, and the brine becomes increasingly concentrated as temperature decreases. Solid salts begin to precipitate out of solution, starting with ikaite at -2.2 C. The formation of ikaite results in CO₂ production. The CO₂ formed on surface ice is likely to be released to the atmosphere, resulting in highly alkaline surface pH. The ikaite produced on the sea ice surface will take up an equally large part of CO₂ when sea ice melts and mixes with the marine surface water. Below the ice surface, the brine drainage from sea ice is likely to result in the removal of dissolved CO₂ along with salts. Ikaite crystals may remain trapped within the skeletal layer where they act as a store of HCO₃⁻, becoming a source of excess HCO₃⁻ to the ocean water upon subsequent mineral dissolution during summer melt, as described by equation (1). This lowers partial pressure of CO₂ of surface waters affected by melting sea ice, thus causing an increase in the air-sea exchange of CO₂.

Rysgaard *et al.* (2014) found ikaite in high concentrations in an ice pool study and also in Young Sound (Rysgaard *et al.*, 2013). The effects on the pCO₂ in the surface water, as well as the exchange between the ice surface and the atmosphere, still have to be quantified, especially the exchange with the surface when snow cover is affecting the temperature of the surface (Rysgaard *et al.*, 2014; Sievers *et al.*, 2015b).

2.2.2 Exchange between the ice surface and the atmosphere

Sea ice has been thought to inhibit gas exchange between the ocean and the atmosphere (Tison *et al.*, 2002; Toggweiler *et al.*, 2003); consequently, no carbon cycle models have included CO₂ exchange through sea ice (Toggweiler *et al.*, 2003). Early studies by Gosink *et al.* (1976) showed that sea ice can be permeable to gases, including CO₂, especially at temperatures above -7 C. Recent studies (Nomura *et al.*, 2006; Nomura *et al.*, 2010; Papadimitriou *et al.*, 2004) suggest that the formation of new ice leads to emission of CO₂, and that ice at higher temperatures is permeable and can take up atmospheric CO₂. Based on data from tank experiments, Nomura *et al.* (2006) suggest that 0.8% of the total inorganic carbon (TCO₂) in sea water that becomes sea ice is emitted to the atmosphere during ice formation, resulting in a total emission of 0.04 Gt Carbon per year from ice formation in the Arctic and Antarctic. However, Rysgaard *et al.* (2007) found that only a small amount (0.01%) of CO₂ was released to the atmosphere. These findings suggest that oceans cov-

ered by sea ice can act as a source or a sink of atmospheric CO₂, depending on the concentration in the ice, which again is influenced by the biogeochemistry, the thickness, the temperature and the permeability of the ice. Knowing that the formation of sea ice around Greenland leads to a release of CO₂, we consider release of CO₂ to take place during ice formation in early winter according to the emission rates estimated by Nomura *et al.*, (2006).

2.3 CO₂ uptake by the coastal marine area of Greenland

The present study calculated the CO₂ uptake based on exchange velocities from Clark *et al.* (1995), who derived their parameterization from measurements in Hudson River, as well as those of Kuss *et al.* (2004) and Nightingale *et al.* (2000) from coastal regions. The sea ice was considered to inhibit the exchange of CO₂ between the atmosphere and the water. When using the exchange velocity from Kuss *et al.* (2004), the fluxes range from 1 to 9×10^{-3} g-C m⁻² hr⁻¹, depending on the time of year and the region, and the calculated total uptake for the whole coastal region is 14.5 Tg C y⁻¹. The exchange velocity from Clark *et al.* (1995) results in lower fluxes, ranging from 1 to 7×10^{-3} g-C m⁻² hr⁻¹, suggesting a total uptake of 11.65 Tg C y⁻¹. When the more commonly used exchange velocity from Nightingale *et al.* (2000) is used, fluxes range between 1 and 6×10^{-3} g-C m⁻² hr⁻¹, resulting in a total uptake of 9.74 Tg C y⁻¹. It could be argued that the exchange rate suggested by Kuss *et al.* (2004), based on measurements in the Baltic Sea, is the most suitable for deep fjord systems; in the present study, however, we have selected the parameterization from Clark *et al.* (1995) as the basis for analysis since; 1) this is derived for a river which have similarities to an estuary/fjord and 2) according to Mørk *et al.* (2015), the exchange coefficient suggested by Clark *et al.* (1995), is the best fit to measurements in Roskilde Fjord. Furthermore there are no exchange coefficients estimates available for Arctic coastal areas or fjords.

The coastal marine surface of Greenland is only 0.08% of the total global ocean surface and 1.1% of the global coastal area. However, the uptake of CO₂ is around 0.5% of the global ocean uptake (2000 (±600.0) Tg C y⁻¹ (Wanninkhof *et al.*, 2013)) and 6.1% of the global coastal uptake (190 Tg C y⁻¹ (Laruelle *et al.*, 2014)).

2.3.1 *CO₂ uptake taking sea ice processes into account*

CO₂ is released to the brine and further into the sea water below the ice when sea ice is formed; however, a study by Nomura *et al.* (2006) showed that CO₂ is also emitted to the atmosphere from the surface during sea ice formation. Nomura *et al.* (2006) found that the emission during ice formation ranged between 2×10^{-4} g-C m⁻² hr⁻¹ and 5×10^{-4} g-C m⁻² hr⁻¹. We suspect the reported high values can be attributed to the low atmospheric start concentration in their tank. Furthermore these numbers depend on the pCO₂ in the water.

To assess the importance of CO₂ emission during sea ice formation, we applied the emissions from Nomura *et al.* (2006). The emission area is estimated as the seasonally formed ice, based on sea ice maps from the Danish Meteorological Institute (DMI), and the formation rate is anticipated to be 3 months in early winter. Based on these calculations, we found a somewhat high emission of CO₂ to the atmosphere from the formation of sea ice in the coastal area of Greenland, compared to the uptake by the ice-free water. The total emission ranges between 0.2 Tg C and 0.5 Tg C, depending on the ice area. This is about 2 % of the total coastal uptake although the emission flux from ice formation (ca 3.5×10^{-4} g-C m⁻² hr⁻¹) is 1/10 of the magnitude of marine uptake flux (ca 1 to 7×10^{-3} g-C m⁻² hr⁻¹). We argue that these results can be ascribed to the relatively small area of newly formed sea ice and the relatively short time (100 days) over which it is formed. However, in a changing climate with more seasonal sea ice, these emissions are likely to increase and formation of seasonal sea ice can become a significant CO₂ source.

As mentioned in section 3.1, Rysgaard *et al.* (2011 and 2012) found that the surface waters can be excessively under saturated with respect to pCO₂ when sea ice melts, which can lead to a subsequent increase in the air-sea CO₂ flux.

The under saturation of CO₂ is more important in the spring and early summer, while air-sea exchange processes contribute to the establishment of equilibrium between the atmospheric CO₂ and the CO₂ in the water in summer. However, the equilibrium will not be reached prior to the formation of ice, again due to chemical processes and biological activity in the surface water. To assess the effect of these processes we computed the CO₂ flux, using lower pCO₂ levels in the water during spring and maintaining the annual mean pCO₂, by increasing the levels of pCO₂ in fall. Due to higher wind speeds in the fall, the total uptake of CO₂ decreased slightly from 11.65 Tg C y⁻¹ to 11.5 Tg C y⁻¹. The brine precipitation process has an impact on the total CO₂ flux which is comparable in magnitude to the atmospheric emissions from ice formation,

but it is clear from our calculations that the temporal resolution of wind climate and water chemistry data is important. Thus, in order to assess the effect of ice processes on the surface water $p\text{CO}_2$ and the emissions to the atmosphere, a detailed study of $p\text{CO}_2$ and CO_2 surface exchange during the whole season is needed.

Taking into account known sea ice processes did not change the estimated uptake significantly; however, the $p\text{CO}_2$ data used for all calculations (with or without sea ice processes) are direct $p\text{CO}_2$ measurements from Arctic fjords, and as such, they are influenced by sea ice processes.

Chen *et al.* (2013) estimated the CO_2 uptake of the global estuaries and continental shelf to be 300 Tg C yr^{-1} , implying that the coastal uptake of Greenland constitutes 3–4% of the total global coastal uptake. However, Chen *et al.* (2013) did not take sea ice cover into account. Furthermore, they estimated the uptake by the Greenlandic estuaries and shelf area to be 66 Tg C yr^{-1} . This estimate, however, is based solely on data from Rysgaard *et al.* (2012) whose measurements are from Godthåbsfjord where the $p\text{CO}_2$ levels are much lower than in the higher latitude fjord, Young Sound. Laruelle *et al.* (2014) estimated the uptake by the Greenlandic shelf surface at 16 Tg C yr^{-1} which is comparable to our estimates, depending on the choice of exchange coefficient and the size of the sea ice cover.

We have not included exchange across the ice surface during winter in our estimates because the processes controlling this exchange are still not well described; however, they are suggested to be important (Bates *et al.*, 2011). Sievers *et al.* (2015a) have suggested a radiation-related flux where heating of the ice surface causes the brine to open and also trigger a dissolution of CaCO_3 , leading to an uptake of CO_2 . Since these processes are not yet quantified, however, they are difficult to incorporate in calculations.

3. CO₂ uptake in a future climate

Climate change has a large impact on the Arctic, and the changes will also affect the coastal water uptake of CO₂. Many of the parameters which are influenced by the increased temperature affect the CO₂ uptake in different ways but are often interrelated or seen to interact. In the following section, we have roughly assessed the effect of a changing wind climate and a change sea ice cover on the marine coastal CO₂ uptake.

3.1 Change in wind climate

No detailed estimates on the change in the wind climate for Greenland exist. Regional differences in wind speed changes predicted by different climate models make it difficult to draw meaningful conclusions based on the results from any single model simulation. Eichelberger *et al.* (2008) examined the mean predicted change and the degree of consensus between a large numbers of global circulation models. They showed that on an annual basis, climate change is predicted to cause stronger surface wind speed values across the boreal regions of the Northern Hemisphere, including much of Canada, Siberia and Northern Europe. However, Greenland is expected to experience decreasing wind speed except at the northern coastal area, and the changes in the annual mean are expected to be less than $\pm 0.2 \text{ ms}^{-1}$ in general.

In order to conduct a simple assessment of the effect of the change in wind climate, we have recalculated the flux, using increased wind speeds in the High Arctic (0.2 ms^{-1} as an example) and decreased wind speeds in the Low Arctic area (0.2 ms^{-1}). The analysis reveals a decrease in the CO₂ uptake from $11.65 \text{ Tg C y}^{-1}$ to $11.28 \text{ Tg C y}^{-1}$. The decrease in uptake is small, and it can be attributed to increasing wind in the High Arctic where the ice cover is larger and decreasing wind in the south where there is more open water and larger under saturation with respect to CO₂. However, in a warmer climate, the ice cover in the High Arctic will also change, leading to a larger surface area for the exchange, but the

change in sea ice cover will also affect the level of $p\text{CO}_2$ in the surface water, probably counteracting the effect from the enlarged surface area.

3.2 Change of sea ice cover

The sea ice cover will decrease with increasing temperature, and in order to assess the effect of a decreasing ice cover on the CO_2 uptake, we recalculated the CO_2 flux at a sea ice cover reduced by 30%. As expected, this revealed an increase in the total uptake from 11.65 Tg Cy^{-1} to 16.57 Tg Cy^{-1} which is more than a 40% increase. The increase is not linear with the decrease of ice cover because several other parameters, such as wind speeds, are important as well. The decrease of sea ice has a larger effect in the southern part of Greenland where the $p\text{CO}_2$ levels are lower.

The calculations above are based on a simple assumption of sea ice being a passive barrier. However, the decrease of sea ice will probably result in less multiyear ice and more seasonal ice which can act as a pump of CO_2 between the surface and the deeper ocean. The increase in the annual formation of new sea ice will affect the brine precipitation which will have a large impact on the sea surface $p\text{CO}_2$. This precipitation process can add to the increased uptake caused by a decrease in sea ice coverage. On the other hand, the formations of ice can also lead to increased emission of CO_2 .

However, the emission to the atmosphere and the effect of brine precipitation on surface $p\text{CO}_2$ still needs to be quantified to carry out a proper assessment of coastal Arctic CO_2 uptake in a changed climate.

4. Conclusion

The Greenlandic coastal waters are important sinks for CO₂, while they take up about 1/20 of the world's coastal area. These estimates are based on only few measurements of pCO₂, thus being highly uncertain. Furthermore, the level of pCO₂ is likely to vary over the season as a result of the melting and formation of sea ice, and therefore, the flux estimate depends on the time of year the data has been collected. Precipitation of brine and CO₂ from the sea ice, leading to under saturation of the pCO₂ in surface water, is suggested to be an important process related to ice formation. Similarly, our calculations suggest that the emission to the atmosphere during the formation of sea ice can be significant if the emission rates suggested by Nomura *et al.* (2006) are valid.

Our calculation reveals the importance of a diminishing sea ice cover; however, the multiyear sea ice and the seasonal sea ice have different effects, where one mainly serves as a lid and the other as an active pump of CO₂ to the underlying deeper water and the atmosphere above. We need to study further the processes related to the formation and melting of sea ice, as well as the exchange processes at the ice surface during ice formation and melt season in order to estimate the role of the sea ice in the Arctic coastal region in a future climate.

Furthermore, it is clear that the wind climate is essential to the surface exchange, and only very few studies have been conducted on the development of the wind climate and the future wind climate in Greenland at all latitudes.

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Sammenfatning

Optaget af CO_2 i de nordiske have er blandt de højeste CO_2 optag i verdens have og især er optaget i de grønlandske kystområder stort. Vores studie indikerer at det grønlandske kyst område, inklusivt fjorde, optager omkring 1/20 af det CO_2 der er optages af det globale kystområde.

Den styrende faktor bag hav-luft udvekslingen af CO_2 over åbent vand er forskellen i partieltrykket af CO_2 ($p\text{CO}_2$) i luften og i overfladevandet, hvilket betyder at CO_2 optages i områder hvor $p\text{CO}_2$ i overfladevandet er lavere end i luften.

I studiet blev det vurderet at udfældning og nedsynkning af saltvand og CO_2 fra hav-is som forårsager undermætning af $p\text{CO}_2$ i overfladevandet er en vigtig proces der er relateret til dannelse af hav-is. Derudover er CO_2 emissioner til atmosfæren under hav-isens dannelse også anslået til at være vigtig.

Idet det grønlandske kyst område er meget følsomt overfor klimaændringer, og fordi området optager relativt mere CO_2 end andre marine områder, er det vigtigt at have realistiske hastigheder for hav-luftudvekslingen af CO_2 , for dermed at opnå en mere sikker bestemmelse af CO_2 optaget over det grønlandske kystområde. Vores beregninger viser desuden at den mindskende hav-is og et evt. ændret vindklima er af stor betydning for det fremtidige marine CO_2 optag.

Resultaterne i dette studie er baseret på målinger af $p\text{CO}_2$ fra kun to fjord områder, og er derfor behæftet med stor usikkerhed. Desuden vil $p\text{CO}_2$ niveauerne sandsynligvis variere over året som et resultat af smeltning og dannelse af hav-is og derfor vil flux bestemmelserne afhænge af årstiden hvor dataene blev opsamlet.

Coastal marine uptake of CO₂ around Greenland

The uptake rates of atmospheric CO₂ in the Nordic Seas, and particularly the shelf waters around Greenland, are among the highest in the world's oceans. The driving factors behind the air-sea exchange of CO₂ in open waters are the difference between the partial pressure of CO₂ (pCO₂) in the atmosphere and the surface waters, leading to an uptake in areas where the pCO₂ of surface waters is lower. Because the coastal area of Greenland is very sensitive to climate change, and because it takes up more CO₂ relative to other marine areas, a realistic estimate of the exchange rates is crucial in order to obtain reliable assessments of the CO₂ uptake by the Greenlandic coastal area. The results from present study reveal the importance of a diminishing sea ice cover; and it is clear that the wind climate is essential to the surface uptake of CO₂.

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