

Parameterization of  
atmosphere–surface  
exchange of CO<sub>2</sub>  
over sea ice

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# Parameterization of atmosphere–surface exchange of CO<sub>2</sub> over sea ice

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## Abstract

We apply a flux parameterisation commonly used over terrestrial areas for calculation of CO<sub>2</sub> fluxes over sea ice surfaces. The parameterisation is based on resistance analogy, and is evaluated and tested on data from seasonal fast sea ice, and the different variables influencing the exchange of CO<sub>2</sub> between the atmosphere and ice are investigated. We found the flux to be small during the late winter with fluxes in both directions. Not surprisingly we find that the resistance across the surface controls the fluxes and detailed knowledge of the brine volume and carbon chemistry within the brines as well as knowledge of snow cover and carbon chemistry in the ice are essential to estimate the partial pressure of pCO<sub>2</sub> and CO<sub>2</sub> flux. Further investigations of surface structure and snow cover and driving parameters like heat flux, radiation, ice temperature and brine processes are required to adequately parameterize the surface resistance.

## 1 Introduction

The Nordic Seas represent an important area for oceanic CO<sub>2</sub> uptake and due to their high productivity their potential uptake rates range among the highest of the world's oceans (Takahashi et al., 2002, 2009). However, these high latitude oceans are partly covered with sea ice, which have been considered to inhibit the gas exchange between the ocean and the atmosphere (Tison et al., 2002). Recent studies show that the formation and melting of sea ice and the chemical processes in the sea ice itself both play an important role for surface partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and thus the oceans capacity for taking up CO<sub>2</sub> in these regions (Papadimitriou et al., 2012; Rysgaard et al., 2007, 2009, 2012, 2013; Søgaard et al. 2013).

In the Arctic, the retreat of sea ice has affected the air–sea gas exchange, but to what extent the Arctic Ocean will remain a future sink for atmospheric CO<sub>2</sub> is debated. In shelf and coastal regions where primary production is high resulting in low surface pCO<sub>2</sub> during the ice free summers, reduced ice cover is expected to increase uptake of

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atmospheric CO<sub>2</sub> (Bates and Mathis, 2009). Studies indicate that the uptake capacity of the Arctic Ocean for atmospheric CO<sub>2</sub> could be limited as a result of surface warming and increased stratification (Cai et al., 2010; Else et al., 2013), while others have shown that chemical processes during ice formation and melting could be an important factor resulting in low surface *p*CO<sub>2</sub> levels during melting of sea ice in summer and that reduced formation of sea ice could result in lowered uptake of CO<sub>2</sub> (Rysgaard et al., 2007, 2012). In addition to these studies regarding drivers of *p*CO<sub>2</sub> in ice free surface water in summer, the understanding of gas fluxes across sea ice is improving. Previously, sea–ice was thought to hinder gas exchange between the ocean and the atmosphere and consequently no carbon cycle models have included CO<sub>2</sub> exchange across sea–ice. However, early studies by Gosink et al. (1976) showed that the sea ice can be permeable to gases including CO<sub>2</sub>, especially at temperatures above  $-7^{\circ}\text{C}$ . Furthermore, recent studies (Nomura et al., 2006, 2010; Papadimitriou et al., 2004) suggest that formation of new ice leads to emission of CO<sub>2</sub> and that ice at higher temperatures is permeable and can take up atmospheric CO<sub>2</sub>. Tank experiments by Nomura et al. (2006) suggest that 0.8% of the TCO<sub>2</sub> 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, studies by Rysgaard et al. (2007) found that only a small amount (0.01%) of CO<sub>2</sub> was released to the atmosphere. These findings suggest that oceans covered by sea ice can act as a source or a sink of atmospheric CO<sub>2</sub> depending on the concentration in the ice, which again is influenced by biogeochemistry, the thickness, the temperature and the permeability of the ice.

Until now only few studies have made an attempt to quantify the CO<sub>2</sub> ice atmosphere flux over a larger area (local to regional scale) (Miller et al., 2011; Nomura, 2010; Papakyriakou and Miller, 2011; Semiletov et al., 2004; Zemmeling et al., 2006). Such assessments await a method for parameterization and up scaling of the CO<sub>2</sub> flux over sea ice as well as more knowledge of the CO<sub>2</sub> fluxes and the processes controlling these in order to estimate the atmospheric CO<sub>2</sub> dynamics in future climate with changing sea ice.

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The objective of this paper is to show that flux parameterisations commonly used over terrestrial areas can be applied to ice surfaces. We present a concept for parameterisation of the CO<sub>2</sub> fluxes over sea ice using properties that can be measured or calculated on a routine basis. The parameterisation is evaluated and tested on data from a seasonal fast ice area and different parameters influencing the exchange of CO<sub>2</sub> between the atmosphere and ice are investigated. This is to our knowledge the first attempt to parameterize air–sea–ice fluxes of CO<sub>2</sub>.

## 2 Theory

The gas transfer between air and ice is in many ways similar to the transfer between terrestrial surfaces and air and to a lesser extent comparable to the transfer over an air–sea interface. The ice surface is not influenced by the atmospheric turbulence and does not change its surface physical characteristics with the wind as water does. However, this does not mean that wind is not an important parameter in driving the flux over ice. Air–surface exchange of gases is a consequence of the same atmospheric exchange mechanisms responsible for the surface fluxes of heat, moisture, and momentum, but is also strongly influenced by a range of surface properties (physical, chemical, and biological).

Surface exchange rates of trace gases can be measured by micrometeorological methods. The conservation equation provides the basic framework for measuring and interpreting micrometeorological flux measurements. In concept, the conservation equations state that the time rate of change of the mixing ratio of a gas at a fixed point in space is balanced by the mean horizontal and vertical advection (I), by the mean horizontal and vertical divergence or convergence of the turbulent flux (II), by molecular diffusion (III) and by any source or sink (*S*). The conservation equation is expressed

as:

$$\frac{\partial \bar{c}}{\partial t} = \underbrace{-\bar{u}_i \frac{\partial \bar{c}}{\partial x_i}}_{\text{I}} - \underbrace{\frac{\partial \overline{u'_i c'}}{\partial x_i}}_{\text{II}} + \underbrace{D \frac{\partial^2 \bar{c}}{\partial x_i^2}}_{\text{III}} + S \quad (1)$$

where  $c$  is the concentration;  $u_i$  is the wind velocity where  $i$  denotes the velocity components in the lateral ( $x, y$ ) and vertical ( $z$ ) directions;  $D$  is the molecular diffusion coefficient of the quantity  $c$  in air;  $S$  is a source (positive) or sink (negative) term and overbar and prime denote the time-averaged and fluctuating quantities, respectively. Assuming the surface is uniform and level, no sink or source term exists in the atmosphere above the surface and the concentration of the gas does not vary significantly with time over the measurement period, Eq. (1) reduces to:

$$\frac{\partial \overline{w'c'}}{\partial z} = -D \frac{\partial^2 \bar{c}}{\partial x_i^2} \quad (2)$$

where  $w$  is the vertical wind velocity. Molecular diffusion results from the motion of the molecules due to random thermal motion. In the atmosphere this term is usually negligible in comparison to turbulent transfer, and thus integration of Eq. (2) with respect to height yields (Baldochi et al., 1988),

$$\overline{w'c'} = -D \frac{\partial \bar{c}}{\partial z} \quad (3)$$

implying that the turbulent flux is constant with height within the atmospheric surface boundary layer and equals the molecular gradient-diffusion flux at the surface. This also implies that fluxes measured using micrometeorological techniques (Businger, 1986; Businger and Delany, 1990; Fowler and Duyzer, 1990) at heights above the ground and fluxes measured by the enclosure techniques at the surface (Fowler et al., 2001)

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should be comparable. However, there are measurement issues that apply to all enclosure methods. Modification of the environment within the enclosure introduces many potential differences between the measured flux and that existing prior to the use of the enclosure. According to (Fowler et al., 2001), these differences may result from changes in:

- i. The radiation balance (both short and long wave),
- ii. Temperature differences in air, and surface (here ice),
- iii. Turbulence, wind speed and vertical profile,
- iv. Pressure, inside-outside difference,
- v. Ice-atmosphere gradient in concentration of the trace gas.

One of the largest uncertainties introduced using an enclosure, even assuming that the effect of the enclosure on the environment and hence flux is negligible, is that of spatial variability in the flux. While chamber enclosures usually only integrate the signal over a few hundred cm<sup>2</sup>, exchange processes may be governed by controls that vary on scales of several hundred m<sup>2</sup> (i.e. thickness and wetness of the snow cover, melting ponds, under-ice hydrology).

### 2.1 Surface exchange parameterization

The gas exchange between the surface and the atmosphere can be parameterized and evaluated in terms of resistances, which is understood as the resistance or limitation to the vertical transport between the atmosphere and the surface. The resistance accounts for the chemical, biological and physical processes that inhibit the transport. The resistance analogy has been used in deposition models since the 1980s (Hicks et al., 1987) and is analogous to electrical current resistance. This model has three major resistance components (Hicks et al., 1987; Seinfeld and Pandis, 2012): (1) an aerodynamic resistance (Ra) that is wholly determined by physically atmospheric properties

(predominantly turbulent exchange), (2) a quasi-laminar boundary layer resistance ( $R_b$ ) that accounts for the fact that gas transfer in the vicinity of the surface interface is affected by the molecular diffusivity, and (3) a surface resistance ( $R_c$ ) that combines the consequences of all uptake processes involving individual elements of the surface into a single number that is characteristic for the gas in question and the surface at the site under consideration. The total resistance to transfer from the atmosphere is then  $R = R_a + R_b + R_c$  and the flux  $F$  can be calculated as:

$$\overline{w'c'} = F = (c - c_0) \frac{1}{R_a + R_b + R_c} \quad (4)$$

The resistances and the different layers are illustrated in Fig. 1.

The electrical analogy illustrated in Fig. 1 provides a useful conceptual model. The aerodynamic resistance,  $R_a$ , is derived from the flux–gradient relationship. The vertical flux of trace gases above the surface can be expressed as the product of the eddy diffusivity ( $K$ ) and the vertical concentration gradient  $\partial c / \partial z$  based on the gradient transport theory ( $K$  theory). In practice, the concentration (and wind) profiles in the atmosphere are nearly log-linear (see Fig. 1) when the temperature gradient over the layer does not diverge from the adiabatic lapse rate (neutral stratification). The deviation from this shape is due to the effects of thermal stratification of the air close to the surface. These effects of the temperature structure of the boundary layer increase the rates of turbulent transfer in unstable conditions (temperature decreasing with increasing height) and decrease  $K$  when the surface is cooler than the air (usually nocturnal or winter conditions); stable conditions. The following parameterization for  $K$  is used for neutral surface layer:

$$K = u_* \kappa z \quad (5)$$

where  $u_*$  is the friction velocity, and  $\kappa$  is the von Karman constant ( $\approx 0.4$ ). For the non-neutral surface layers (Hogstrom, 1996) a stability function  $\varphi$  is introduced (Businger

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et al., 1971) i.e.,

$$K = \frac{u_* \kappa z}{\varphi\left(\frac{z}{L}\right)} \quad (6)$$

where  $\varphi(z/L)$  is the stability-dependent dimensionless concentration gradient. Following convention, stability is quantified in terms of  $z$  and the Obukhov length scale  $L$  (Stull, 1988). Consider the flux of  $\text{CO}_2$  with the local concentration gradient  $\partial c/\partial z$  and following the methods of micrometeorology described above, the flux can be expressed in terms of the local vertical gradient of  $c$  as:

$$F = -(u_* \kappa z) \frac{\partial c}{\partial z} \frac{1}{\varphi(z/L)} \quad (7)$$

Rearranging and integrating over the turbulent layer between  $z$  and  $z_0$ , which is the familiar roughness length associated with momentum transfer estimated as the height where the logarithmic wind profile in theory becomes zero, leads to the form:

$$c - c_0 = -\frac{F}{\kappa u_*} \left[ \ln \frac{z}{z_0} - \psi\left(\frac{z}{L}\right) \right] \quad (8)$$

where  $\psi(z/L)$  is an integral form of the departure from neutral of the dimensionless concentration gradient and  $c_0$  is the concentration at the roughness height  $z_0$ . The aerodynamic resistance  $R_a$  is given by:

$$R_a(z) = \frac{1}{\kappa u_*} \left[ \ln \frac{z}{z_0} - \psi\left(\frac{z}{L}\right) \right] \quad (9)$$

The second atmospheric resistance describes the resistance over the molecular turbulent sub-layer, which is the layer between  $z_0$  and the height  $z_{0c}$  where the concentration

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yields the equilibrium concentration with the surface ( $c_s$ ). This resistance can thus be written in terms of  $z_0$  and  $z_{0c}$ :

$$Rb = \frac{1}{\kappa U_*} \left[ \ln \frac{z_0}{z_{0c}} \right] \quad (10)$$

Modelling studies and wind-tunnel investigations confirm that Rb is strongly influenced by the diffusivity of the material being transferred. Effects associated with molecular or Brownian diffusivity lie outside the scope of the micrometeorological treatments leading to Eqs. (7)–(9). However, specialized surface transfer models are available to deal with the problem (e.g., Brutsaert, 1975, 1979; Kramm, 1989; Kramm et al., 1991; Kramm and Dlugi, 1994). These models predict a functional dependence of Rb on the Schmidt number, i.e:

$$Rb = \frac{1}{u_*} \left[ \frac{u_{z_0}}{u_*} + B_i^{-1} \right] \quad (11)$$

where  $u_{z_0}$  is a characteristic velocity for the layer  $z_{0c} < z < z_0$  and  $B_i^{-1}$  is the sub-layer Stanton number, which is a function of the roughness Reynolds number and the Schmidt number.

A surface resistance Rc, is introduced to extend the resistance network analogy into the final receptor, corresponding to the assumption that  $c$  tends to reach equilibrium at the surface. The flux for CO<sub>2</sub> can then be described in terms of resistances if Rc and the surface concentration,  $c_s$  is known.

The surface resistance Rc and the quasi-laminar boundary layer resistance Rb over ice surfaces have to our knowledge never been studied. If  $c_s$  and the CO<sub>2</sub> flux can be estimated from measurements, Rc can be found from Eq. (12) assuming Rb can be calculated from Eq. (11):

$$\frac{(c - c_s)}{F} - Ra + Rb = Rc \quad (12)$$

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### 3 Measurement of CO<sub>2</sub> fluxes

Air–ice fluxes of CO<sub>2</sub> were measured over an ice covered Greenlandic fjord close to the town Kapisigdlit (Fig. 2) from 9 to 17 March 2010. The thickness of the ice was 0.5–1 m and 1–7 cm layer of snow covered it (Søgaard et al. 2013). Air temperatures were below 0°C. We used the eddy covariance (EC) technique, which is the basic micrometeorological method for flux estimation. Here, fluxes ( $F_{\gamma}$ ) are derived from the covariance between the vertical velocity,  $w$ , and the concentration of the species of interest,  $\gamma$ , for example potential temperature,  $\theta$ , water vapour or CO<sub>2</sub>:

$$F_{\gamma} = \overline{w \gamma} + \overline{w' \gamma'}, \quad (13)$$

The first part of the flux is the vertical advection and the second term is the eddy correlation flux.

In addition to the EC method, the inertial dissipation (ID) method is also used. The ID method has traditionally been used to reduce the sensitivity to motion and flow distortion (Edson et al., 1991; Fairall and Larsen, 1986; Yelland and Taylor, 1996) for estimation of fluxes measured from moving platforms. However, here we use the method in addition to EC to ensure a higher confidence in the turbulent flux estimate by using two different flux techniques based on different frequency ranges of the turbulence spectrum. Using the ID method, the flux is determined with the aid of the normalized turbulent kinetic energy budget (Edson et al., 1991; Sjoblom and Smedman, 2004) assuming that the production of mechanical turbulence equals the molecular dissipation of the turbulent fluctuation. By using the ID technique, the inertial sub-range of the power spectra is utilized for estimation of the flux. The fluxes are estimated from fast (20 Hz) data of CO<sub>2</sub>, water vapour, temperature and vertical wind speed sampled from a 3.5 m tower on the ice. A small generator powered the equipment.

The EC technique is well known and widely used for atmospheric measurement of CO<sub>2</sub> fluxes (Baldocchi, 2003) over all types of surfaces. The ID technique is less common and rarely used for measurements of CO<sub>2</sub> fluxes, however, it is shown by

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(Sørensen and Larsen, 2010) that it can be applied for CO<sub>2</sub> fluxes over water surfaces and the method showed good agreement with the EC method. The application of the ID technique for CO<sub>2</sub> fluxes is only evaluated for neutral stratified atmospheric boundary layers, which makes the technique less reliable over ice, where the atmospheric stratification is usually very stable due to the cold surface. However, corrections based on scalar stability functions (Businger et al., 1971; Hill, 1989) will at least enable us to assess the magnitude of the CO<sub>2</sub> flux using this approach and thus strengthen the estimate of the flux obtained by the EC technique. To avoid contamination of the measurements from open water, snow scooter exhaust, or generators, we only use data from a limited fetch (wind direction 270–360° and 5–200°), which was not influenced by camp activities. Filtering data, based on equality of the fluxes estimated by the two techniques, and on wind direction left 37% of the original data for further analysis. The fluxes measured using EC are shown in Fig. 3. The measured CO<sub>2</sub> fluxes are in general small varying between  $-34 \mu\text{gCm}^{-2}\text{s}^{-1}$  to  $9 \mu\text{gCm}^{-2}\text{s}^{-1}$  with only a few incidents of upward fluxes but averaged over the sampling period the net flux is downwards ( $-3 \mu\text{gCm}^{-2}\text{s}^{-1}$ ).

#### 4 Estimation of the surface $p\text{CO}_2$

To estimate the partial pressure of CO<sub>2</sub> in the surface of the ice, measurements of temperature, total inorganic carbon ( $T\text{CO}_2$ ), total alkalinity (TA), and salinity were carried out. Sea ice cores (9 cm diameter) were collected with a MARK II coring system (Kovacs Enterprises, Lebanon, NH). Vertical temperature profiles were measured with a thermometer (Testo, Lenzkirch, Germany, and accuracy 0.1 °C) in the snow cover and in the sea ice at 12 cm intervals at the center of the cores through 3 mm holes drilled immediately after coring. Each sea ice core was then cut into 12 cm sections, and each section transferred to a 1 L polyethylene jar and kept cold (insulated thermo box) until further processing within an hour on board the ship laboratory. In the laboratory, sea ice density was determined by shaping the ice core section into well-defined

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pieces with planar sides and then measuring the volume and weight of each segment. The segments were then cut in two. One half was melted within 2 h and 25 mL collected for salinity measurements. The salinity of the melted sections (bulk salinity) was determined with a sonde (Knick Konduktometer, Germany) calibrated to a PORTASAL salinometer.

The other half of each sea ice section was used to determine TA and  $TCO_2$  concentrations following Søgaard et al. (2013). Routine analysis of Certified Reference Materials (provided by A.G. Dickson, Scripps Institution of Oceanography) verified that the accuracy of the  $TCO_2$  and TA measurements was  $0.5 \mu\text{mol kg}^{-1}$  and  $2 \mu\text{mol kg}^{-1}$ , respectively. Ice samples were melted in gastight enclosures with aliquots of dilution water (artificial seawater) and bulk concentrations of TA and  $TCO_2$  in sea ice ( $C_i$ ) were calculated as described in Rysgaard and Glud (2004);

$$C_i = \frac{C_m W_m - C_a W_a}{W_i} \quad (14)$$

where  $C_m$  is the TA or  $TCO_2$  concentration in the mixture of melt and dilution water,  $W_m$  the weight of the melt water mixture,  $C_a$  the TA or  $TCO_2$  concentration in the artificial seawater,  $W_a$  the weight of the artificial seawater, and  $W_i$  the weight of the sea ice. Average values are given in Table 1.

Temperatures in the ice surface were extracted from sensor array measurements performed at 30 min intervals during the entire campaign. Essentially, custom build thermistors separated by 4 cm distance were fixed on 3 m long strings that were frozen into the ice as described in Jackson et al. (2013). Here, we present the absolute surface values (Fig. 4), while the entire data set on ice, snow and water temperature profiles will be presented elsewhere (McGinnis et al., 2013)

Brine volume (Fig. 4) was calculated based on the temperature measured in the ice ( $T_i$ ), the salinity measured in the ice ( $S_i$ ) and the equation suggested by (Timco and

Weeks, 2010):

$$B_{\text{vol}} = S_i \left( \frac{49.185}{T_i} \right) + 0.532 \quad (15)$$

For the measurement period, the following minimum and maximum values for the sea ice parameters were employed for calculations of  $p\text{CO}_2$  in the ice surface: salinity: 5.3–6.5,  $T\text{CO}_2$ : 264–292  $\mu\text{mol kg}^{-1}$ , TA: 274–350  $\mu\text{mol kg}^{-1}$ . The measured data are shown in Table 1. The partial pressure of  $\text{CO}_2$  in the brine channels was estimated based on algorithms from Lewis and Wallace (1998) using dissociation constants from Goyet and Poisson (1989) (temperature range:  $-1^\circ\text{C}$  to  $40^\circ\text{C}$  and salinity range 1–50) due to low temperature and high salinity of the brine water. We are aware that salinity in the brines can exceed 50 when the brine volume becomes low, which adds uncertainty to the results at low temperatures and low volumes. When the brine volume was below 5%,  $p\text{CO}_2$  was not estimated as the ice is considered to be impermeable at these low brine volumes (Golden et al., 1998).

## 5 Calculation of Ra, Rb and Rc

Using Eq. (12) and observed fluxes we calculate Rc, which, not surprisingly, is several orders of magnitude higher than Ra and Rb. In these very stable boundary layers Ra is large, however, it is clear that the resistance Rc across the surface must be even larger and hence the transport across the surface is dominating and controlling the flux (Fig. 5).

## 6 Flux parameterization and discussion

To estimate the importance of sea ice for the uptake of  $\text{CO}_2$ , a parameterization of the transport coefficients is required and knowledge of the parameters driving their

variation is fundamental. The parameterization of the atmospheric resistances is well known. However, it is also clear from the calculation of  $R_c$  that for this specific site and these specific climatic conditions  $R_c$  is the dominating resistance. Thus, an evaluation of the transfer mechanisms across the surface interface is essential.

## 6.1 Parameters influencing the ice surface $p\text{CO}_2$

The flux magnitude and direction depends on the difference in  $p\text{CO}_2$  between the brines and the overlaying atmosphere. We argue that upward  $\text{CO}_2$  fluxes from ice are associated with refreezing of brine channels leading to a decrease in brine volume, which again increases the brine  $p\text{CO}_2$  levels in the ice surface. This is consistent with the fact that the measured  $\text{CO}_2$  release generally coincided with periods of decreasing ice-temperature (Figs. 3 and 4).

The  $p\text{CO}_2$  on the ice surface varies both spatially and temporally depending on TA,  $T\text{CO}_2$ , brine volume, salinity and temperature of the ice. Therefore high precision TA and  $T\text{CO}_2$  measurements as well as detailed knowledge of variations of temperature, brine volume and salinity are required to obtain a reliable  $p\text{CO}_2$  estimate. Brine volumes were measured at different locations in our study area; however diurnal changes in air temperature, heat fluxes ( $Q$ ) and solar radiation caused the surface temperature of the ice to vary by 1 to 5°C and have to be accounted for to realistically assess variations in  $p\text{CO}_2$  exchange.

## 6.2 Parameters influencing the surface exchange

As illustrated in Fig. 1 the exchange over the surface is also influenced by the surface wetness and by the layer of snow on the ice surface. Variation in salinity, temperature and  $p\text{CO}_2$  concentration in water or snow on the ice surface will affect the surface resistance. We did not observe water on the ice surface but as mentioned previously the ice was covered by snow. The temperature variation at the snow surface was not measured, however an ice crust on the snow surface was occasionally observed. In-

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formation about the thickness and structure of the snow cover is important in order to properly evaluate the surface resistance,  $R_c$ .

### 6.3 Discussion and parameterization of the surface resistance

At lower temperatures, the salinity,  $TA$ ,  $T_{CO_2}$  in the brine channels become large due to decreasing brine volumes resulting in large calculated  $pCO_2$  values. Furthermore, the measured fluxes are small at low temperatures and the direction of the flux will thus be difficult to estimate. This leads to large uncertainties in the calculated  $R_c$ , which even can become negative. However the magnitude of the calculated  $R_c$  is increasing at colder temperatures due to increase of difference in atmospheric  $pCO_2$  and brine  $pCO_2$ .

We hypothesise that atmospheric heating of the ice surface will result in a decrease of  $pCO_2$  in the brine and an increase of the surface flux leading to a decrease in the surface resistance,  $R_c$ . Radiation was not measured but the magnitude of  $R_c$  aligns reasonably well to the measured heat flux (sensible plus latent) revealing an increase in  $R_c$  with increasing downward heat flux (Fig. 6b). Potentially the correlation between heat flux and  $R_c$  could be confounded by the wind acting on the surface, which will result in a correlation with the friction velocity ( $u_*$ ) and thus indirectly a correlation to the heat flux. However, our data show no correlation between  $u_*$  and  $R_c$  ( $R^2 = 0.04$ ,  $p = 0.16$ ). The relation between  $R_c$  and heat flux is opposite of what was expected, but the downward heat fluxes can be initiated by very low surface temperatures, which gives high surface resistances. The heat flux is dominated by the sensible heat flux, which was primarily downward during the measurement period (mean heat flux =  $-8 \text{ W m}^{-2}$ ). However, this leads to an upward flux of the latent heat (mean heat flux =  $2 \text{ W m}^{-2}$ ), which could explain the formation of an icy crust on the surface possibly causing a high surface resistance. The surface resistance is calculated based on calculated  $pCO_2$  brine values, but the surface exchange will here only be indirectly connected to the brine  $pCO_2$  through the thin snow layer. The vertical and lateral gas transport within the snow layer will control the  $pCO_2$  on the surface (Liptzin et al., 2009; Massman and

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Frank, 2006). An overestimation of  $p\text{CO}_2$  and  $\text{CO}_2$  fluxes near zero, which makes it difficult to estimate the direction of the flux, will lead to large negative values of  $R_c$ .

Despite the large uncertainty in the measured flux and calculation of  $p\text{CO}_2$ , a clear correlation between  $R_c$  and surface temperature was found ( $R^2 = 0.64$ ,  $p < 0.001$ ).

This is expected because calculations of  $R_c$  are linked to  $p\text{CO}_2$  calculations, which are subsequently linked to surface temperatures.

Nomura et al. (2010) found that the flux is dependent not only on the difference in  $p\text{CO}_2$  between the brine and the overlying air but also on the condition of the sea–ice surface and snow cover, especially during the ice-melting season. This indicates that measurements of the air–sea–ice  $\text{CO}_2$  flux should also include detailed observations of the sea–ice surface conditions. The surface resistance is controlled by many parameters as illustrated in Fig. 1b and in order to carry out a thorough test of the relation between heating of the surface and the resistance method, measurements of radiation are required as well as detailed measurements of  $p\text{CO}_2$  and physical-geochemical parameters of the snow cover.

To evaluate the sensitivity in exchange rates toward key variables integrated in  $R_c$  we tested the parameterization of the  $\text{CO}_2$  flux using the relationship, shown in Fig. 6, between the surface temperature ( $T_i$ ) and  $R_c$  ( $R_c = 159.19e^{-2.106T_i}$ ) and between the heat flux ( $Q$ ) and  $R_c$  ( $R_c = 163014e^{-0.301Q}$ ) for parameterization of  $R_c$ . The fluxes were then calculated from Eq. (4) and compared to the measured flux (Fig. 7), which showed an average flux of  $-2.6 \mu\text{g m}^{-2} \text{s}^{-1}$  ranging between  $-34 \mu\text{g m}^{-2} \text{s}^{-1}$  and  $8.7 \mu\text{g m}^{-2} \text{s}^{-1}$ . The calculated  $\text{CO}_2$  flux, where  $R_c$  is based on surface temperature shows only little variation in the flux and the flux is primarily upward with a few cases of large downward fluxes resulting in an average flux of  $-0.55 \mu\text{g m}^{-2} \text{s}^{-1}$  ranging from  $-271 \mu\text{g m}^{-2} \text{s}^{-1}$  to  $5 \mu\text{g m}^{-2} \text{s}^{-1}$ . The  $\text{CO}_2$  flux, where  $R_c$  is based on heat flux shows more variation, but the flux is still mainly upward ranging from  $-65 \mu\text{g m}^{-2} \text{s}^{-1}$  to a few case of fluxes  $> 3000 \mu\text{g m}^{-2} \text{s}^{-1}$  and a mean flux of  $954 \mu\text{g m}^{-2} \text{s}^{-1}$ .

The computed flux is based on a calculated surface  $p\text{CO}_2$  and a deficient  $R_c$ . As previously mentioned, the accuracy of the estimation of the  $p\text{CO}_2$  on the surface is

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crucial, especially to the direction of the flux. Lack of knowledge of the processes in the snow cover can explain differences in the flux sign between the measured and the calculated flux.

## 7 Conclusions

The exchange of  $\text{CO}_2$  between the atmosphere and the fast sea ice is ultimately driven by the difference of  $p\text{CO}_2$  in the brines and the overlying atmosphere. We found the flux to be small (mean =  $-3 \mu\text{gCm}^{-2}\text{s}^{-1}$ ) during the late winter with fluxes in both directions, and believe this depends on brine volume, surface temperature,  $T\text{CO}_2$ , TA and/or salinity. We show how the air–sea–ice fluxes can be parameterized using the resistance analogy, which is commonly used for terrestrial surfaces. We find that for our measurement site the surface resistance  $R_c$  is the controlling resistance and in order to calculate the fluxes from Eq. (4), a parameterization of  $R_c$  is needed. Such a parameterization requires detailed knowledge of the brine volume, and  $T\text{CO}_2$ , TA and salinity as well as knowledge of snow cover and carbon chemistry in the snow to estimate the accurate surface  $p\text{CO}_2$ . Further investigations of surface structure and snow cover on seasonal sea ice in parallel to measurements of driving parameters like heat flux, radiation, ice temperature and brine processes are required to parameterize  $R_c$  and to thoroughly test the resistance model for calculation of  $p\text{CO}_2$  exchange over the air–sea–ice interface in natural settings.

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**Table 1.** Average concentrations of bulk  $T\text{CO}_2$  and TA and average sea ice bulk salinity. Data points represent

Sea ice depth [cm]	Average bulk $T\text{CO}_2$ [ $\mu\text{mol kg}^{-1}$ ]	Average bulk TA [ $\mu\text{mol kg}^{-1}$ ]	Average bulk salinity [psu]
0	$278 \pm 14$	$312 \pm 38$	$5.9 \pm 0.6$
12	$202 \pm 32$	$240 \pm 68$	$7.6 \pm 0.1$
24	$223 \pm 58$	$265 \pm 69$	$6.0 \pm 0.3$
36	$238 \pm 65$	$273 \pm 98$	$5.9 \pm 0.1$
48	$233 \pm 64$	$331 \pm 35$	$3.7 \pm 0.5$
60	$283 \pm 13$	$319 \pm 20$	$6.3 \pm 0.7$

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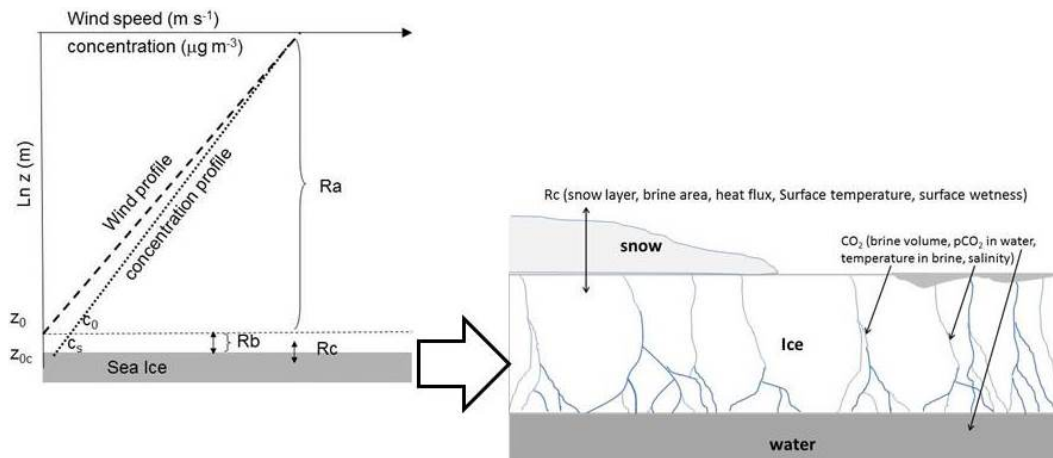
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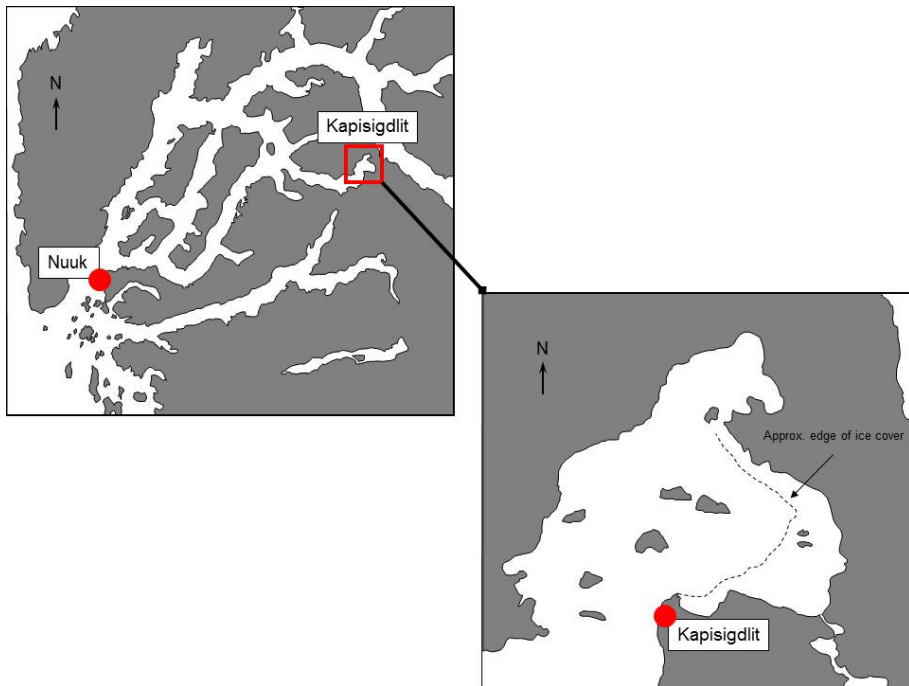
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**Fig. 1.** (a)  $R_a$  is the aerodynamic resistance over the layer dominated by atmospheric turbulence.  $R_b$  is the quasi-laminar boundary layer resistance over the layer, which is influenced by molecular diffusion and turbulence and  $R_c$  is the resistance over the ice/snow–atmosphere interface. The dashed line illustrates the logarithmic wind profile over the surface, which in theory goes to 0 at  $z_0$ . The dotted line illustrates the logarithmic concentration profile, which goes to the surface equilibrium concentration ( $c_s$ ) at  $z_{0c}$ . (b) Sketch showing  $R_c$  and some of the parameters in/at the surface which  $R_c$  is affected by and  $p\text{CO}_2$  in the brine and parameters affecting this.

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**Fig. 2.** Map showing the Nuuk fjord area in Greenland and the location of the field site near the town Kapisigdlit ( $64^{\circ}26'10''$  N;  $50^{\circ}16'10''$  W).

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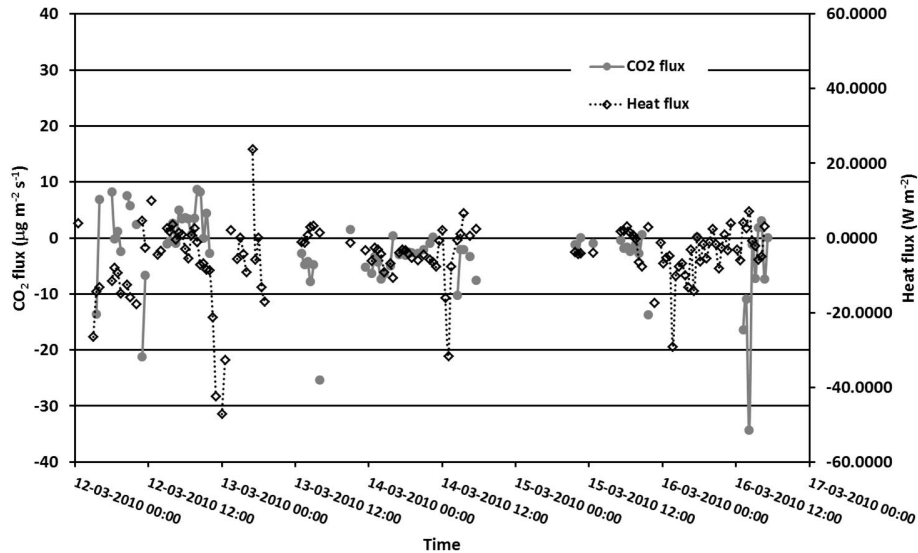
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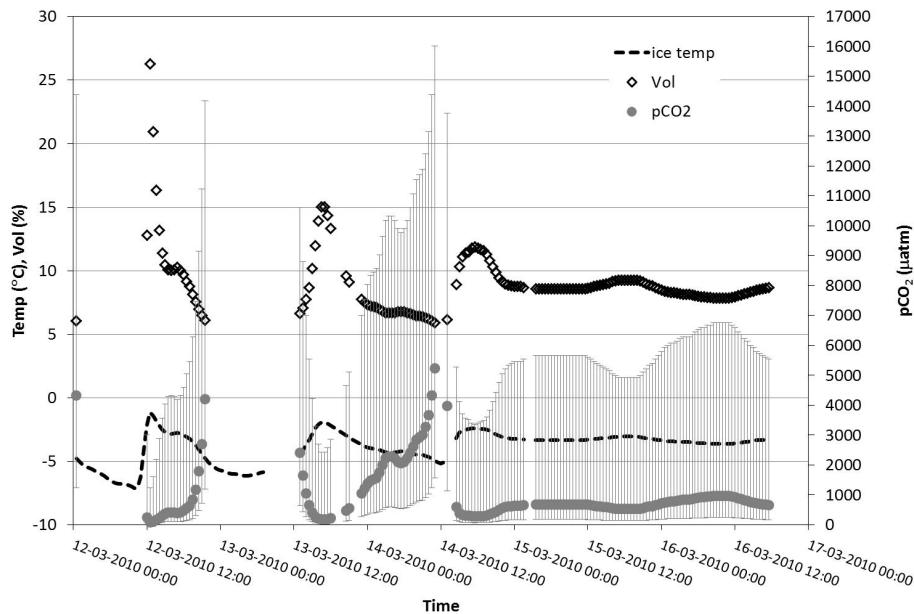


**Fig. 3.** Measured CO<sub>2</sub>, and heat fluxes ( $Q$ ) using the eddy covariance technique over the ice. The measurements are filtered by using the ID analysis method.

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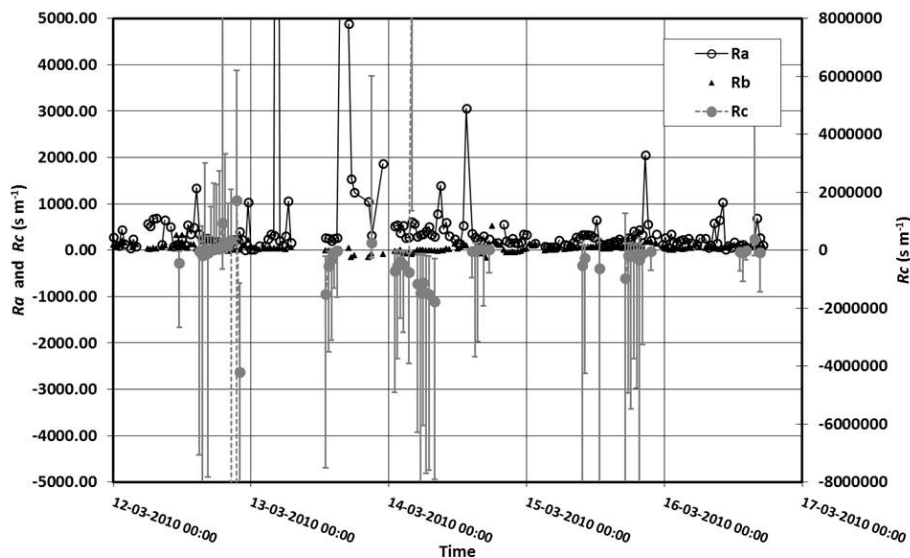


**Fig. 4.** Measured ice surface temperature (°C) and calculated brine volumes (%) and  $p\text{CO}_2$  ( $\mu\text{atm}$ ) in the brine channels from 12 March to 16 March. The error bars around the  $p\text{CO}_2$  are based on maximum and minimum values using the standard deviation on the measured salinity,  $\text{TCO}_2$  and TA (see Table 1).

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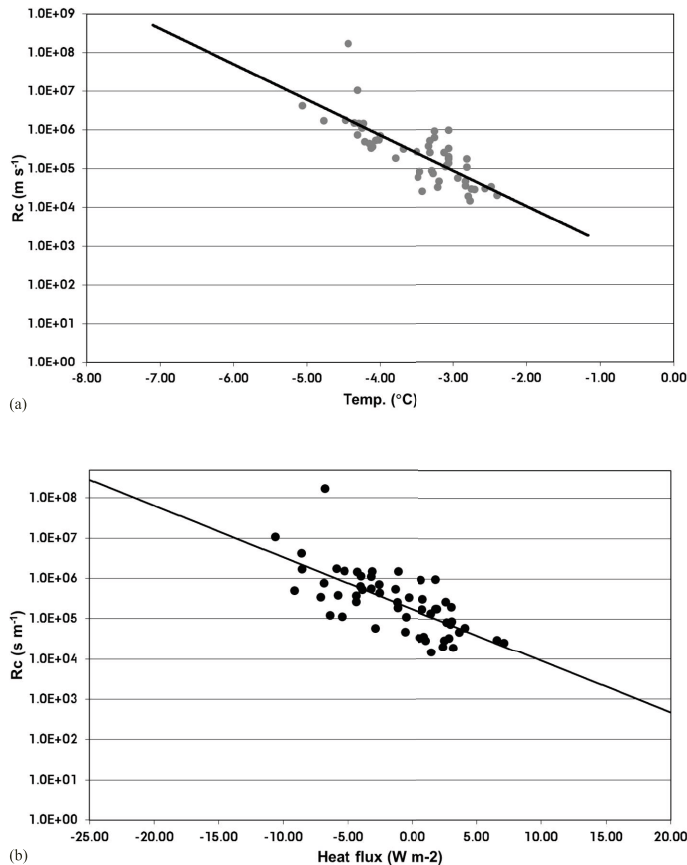


**Fig. 5.** Development of  $R_c$ ,  $R_a$  and  $R_b$  from 12 March to 16 March. The mean  $R_a$  is  $5.24 \times 10^2 \text{ s m}^{-1}$  ranging from  $0.05 \times 10^2 \text{ s m}^{-1}$  to  $236.32 \times 10^2 \text{ s m}^{-1}$  and mean  $R_b$  is  $0.43 \times 10^2 \text{ s m}^{-1}$  ranging between  $5.14 \times 10^2 \text{ s m}^{-1}$  and  $-1.68 \times 10^2 \text{ s m}^{-1}$ . The  $R_c$  (mean  $-1.07 \times 10^7 \text{ s m}^{-1}$  ranging between  $1.1 \times 10^7 \text{ s m}^{-1}$  and  $-17.1 \times 10^7 \text{ s m}^{-1}$ ) is several orders of magnitudes higher than  $R_a$  and  $R_b$ . The error bars around  $R_c$  are based on the calculated maximum and minimum values of  $p\text{CO}_2$  in the surface brines

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**Fig. 6.** (a) The relation between the calculated  $R_c$  and the measured surface temperature. The correlation coefficient  $R^2$  is 0.64. (b) The relation between the calculated  $R_c$  and the measured heat flux. The correlation coefficient  $R^2$  is  $\sim 0.5$ .

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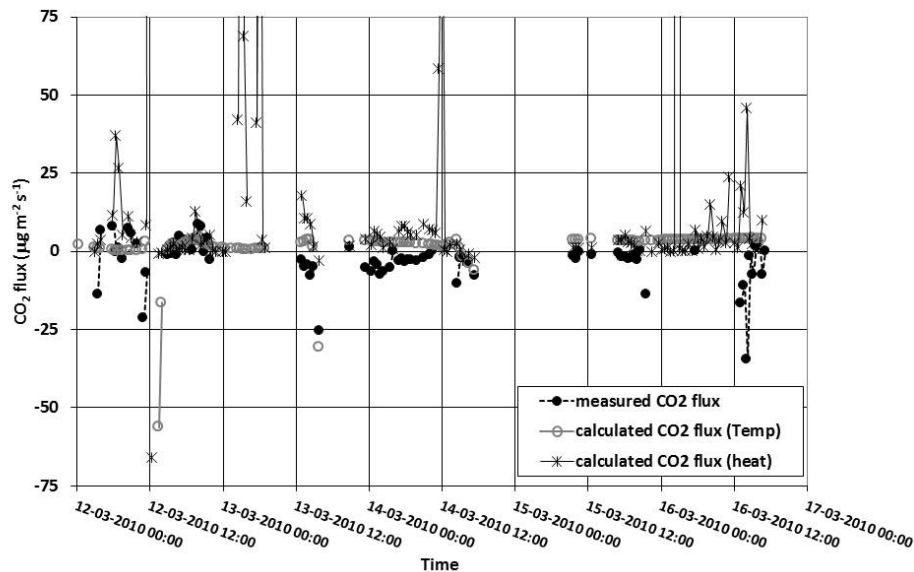
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**Fig. 7.** The measured fluxes and the calculated fluxes using varying concentration based on brine volume calculated from ice temperature and  $R_c$  using the ice temperature parameterization of  $R_c$  (o) as in Fig. 6b and the heat flux parameterization of  $R_c$  (\*) as in Fig. 6a.

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