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Air-sea exchange of O_2 and CO_2

Processes controlling the transfer efficiency

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Abstract
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World oceans cover more than 70% of the earth surface and constitutes a major sink of atmospheric CO_2. Two of the most important gases in the marine carbon cycling are O_2 and CO_2 and hence accurate descriptions of the air-sea gas exchange of these gases are crucial. Still there is a lack of knowledge of the relative importance of processes controlling the efficiency of the air-sea gas transfer. This is especially true for Arctic and high latitude seas were studies on air-sea gas exchange are few. By studying processes causing water-side turbulence, using gases of different solubility and various measurement techniques, more knowledge on the governing processes can be obtained.

Here we present the very first air-sea fluxes of O_2 using atmospheric eddy covariance measurements and investigate the dependence between the gas transfer velocity of O_2 and turbulence generated by the mean wind. The instrument was found to suffer from the limited precision and time response, causing significant corrections on the O_2 flux. After correcting for this, the O_2 fluxes displays an anti-correlation with the air-sea fluxes of CO_2 in agreement with the measured air-sea gradient of O_2. The transfer velocities for O_2 indicates a stronger wind dependence than other commonly used parameterizations of the transfer velocity for CO_2 and O_2, this especially for wind speeds > 5 m s^{-1} where the typical onset of wave breaking occur.

During two winter months eddy covariance measurements were taken over a high Arctic fjord. The data revealed a significant enhancement of the gas transfer velocity for CO_2 from water-side convection, generated by cooling of surface waters. The dependence between water-side convection and gas transfer velocity were found for winds as high as 9 m s^{-1}, but were strongest for wind speeds< 7 m s^{-1}. The data also showed on enhanced air-sea gas transfer of CO_2 when conditions were unstable very close to neutral. This enhanced transfer were associated to increased contribution to the CO_2 flux from downdraft of air with higher concentrations of CO_2. The combined effect of water-side convection and turbulence generated by wind results in a very effective transfer, thus the air-sea gas exchange at these latitudes may be significantly underestimated.

Keywords: air-sea flux, oxygen, transfer velocity, water-side convection, Arctic, UVCN

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Akademisk avhandling som för avläggande av filosofie doktorsexamen i meteorologi vid Uppsala Universitet kommer att offentligen försvaras i Hambergsalen, Villavägen 16, Uppsala, fredagen den 17 mars 2017, klockan 10:00. Fackultetsopponent: Dr. Brian Ward (National University of Ireland, Galway). Disputationen sker på engelska.

Referat:

Andersson, A. 2017. Gasutbyte av O_2 och CO_2 mellan hav och atmosfär: Processer som påverkar utbyteshastigheten.

Världshaven täcker mer än 70 % av jordens totala yta och utgör en av de viktigaste sänkorna för atmosfäriskt CO_2. Två av de viktigaste gaserna i den marina kolcykeln är O_2 och CO_2. Att korrekt kunna beskriva de faktorer som påverkar effektiviteten av gasutbytet mellan hav och atmosfär av dessa blir därför central. Även om de dominerande processerna är kända saknas det fortfarande kunskap om till vilken grad de olika processerna påverkar utbytet. Detta gäller särskilt gasutbytet vid Arktis och över hav vid höga latituder, där endast ett fåtal studier av gasutbytet har publicerats. Genom att studera de faktorer som ger upphov till turbulens i vattnet och använda mätningar av gaser med olika löslighet kan en ökad kunskap om de processer som påverkar gasutbytet öka.

I denna avhandling presenteras de första direkta mätningarna av syreflöden mellan hav och atmosfär gjorda med eddy-kovarians metoden. Den begränsade precisionen och responstiden för syreinstrumentet visar sig medföra en underskattning av storleken på syreflödena därtill kommer en betydande densitetskorrektion. Efter att dessa korrektioner genomförts uppvisar syreflödena en negativ korrelation med CO_2 flödet och en riktning på flödet som motsvarar gradienten av O_2 mellan hav och atmosfär. Resultaten visar på ett starkare samband mellan utbyteshastigheten för O_2 och vinden än tidigare mätningar av utbyteshastighetens vindberoende. Detta gäller särskilt för vindhastigheter > 5 m s^{-1}, vilket sammanfaller med uppkomsten av brytande vågor.

Under närmare två månaders tid studerades utbytet av CO_2 över en fjord i Arktis. Data visade på ett tydligt samband mellan utbyteshastigheten för CO_2 och konvektionen i vattnet. Sambandet var som starkast för vindar < 7 m s^{-1} men kunde ses för vindar så höga som 9 m s^{-1}. Data från fjorden visade också på ökade utbyteshastigheter i samband med instabila nära neutrala förhållanden. Denna ökning av utbytet kunde kopplas till en nedåtriktad transport av luft med högre koncentration av CO_2 från lager högre upp i gränsskiktet. Den kombinerade effekten av dessa två processer resulterade i en betydligt effektivare transport av gaser mellan hav och atmosfär än den beskrivning av gasutbytet som vanligen används i modeller för den här regionen.

Nyckelord: atmosfär-hav flöde, syre, utbyteshastigheten, konvektion i vattnet, koldioxid, Arktis, UVCN.

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Dedicated to Teodor and Alva

List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Andersson, A., Rutgersson, A. and Sahlée, E. (2014). Using a high frequency fluorescent oxygen probe in atmospheric eddy-covariance applications. *J. Atmos. Oceanic Technol.*, 31(1): 2498-2511.

II Andersson, A., Rutgersson, A. and Sahlée, E. (2015). Using eddy covariance to estimate air-sea gas transfer velocity for oxygen. *J. Mar. Syst.*, 159, 67-75.

III Andersson, A., Falck, E., Sjöblom, A., Kljun, N., Sahlée, E., Omar, A.M. and Rutgersson, A. (2017). Air-sea gas transfer in high Arctic fjords, *Geophys. Res. Lett.*, DOI: 10.1002 /2016GL072373.

IV Andersson, A., Sjöblom, A. Sahlée, E., Falck, E. and Rutgersson, A. (2017). Enhanced air-sea exchange of CO_2 over a high Arctic fjord during unstable very close to neutral conditions. Manuscript.

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The ideas for **Papers I** and **II** were developed in collaboration with co-authors. For **Papers III** and **IV** the author had the main responsibility for developing the project. The author was responsible for performing the measurements, most of the data analysis and had the main responsibility for the writing of **Papers I**, **II**, **III**, **and IV**.

Contents

1. Introduction

1.1 Background

Today we know that a significant part of the present global warming is addressed to the human activity and the burning of fossil fuels. During more than 400 000 years pre-industrial the CO_2 concentration in atmosphere was found below 300 ppm. But during the last 100 years the global CO_2 concentration has increased rapidly up to today's level of 404 ppm. In the fifth and latest assessment report from Intergovernmental Panel on Climate Change [IPCC, 2013] it was concluded that the oceans has absorbed about 30% of the anthropogenic emitted CO_2. In order to understand and predict the oceans response to the increased emissions of greenhouse gases, accurate parameterization of the processes controlling the air-sea gas exchange is crucial. Even though the large marine sources and sinks of atmospheric CO_2 are known the relative importance and regional distribution of the processes controlling efficiency of the gas transfer is not fully understood [Garbe et al., 2013]. This is especially true for Arctic, where qualitative studies on air-sea gas exchange are few and continuous long term measurements on marine CO_2 hardly exists. Except from ebullition and bubble invasion the gas transfer take place at the air-water interface by diffusion. The magnitude and direction of the diffusive flux (F) of a slightly soluble non-reactive gas such as O_2 or CO_2 can be described by the bulk flux formula:

$$F = k(C_W - \alpha C_a) \tag{1}$$

where α denotes the Ostwald solubility constant, C_w and C_a are the concentration of the gas in the bulk water and overlying air respectively, and k denotes the gas transfer velocity. The transfer velocity describes the efficiency of the gas transfer across the air-water interface and the most robust single parameter to parameterize the k in models is by using wind speed. From the first parametrization by Liss and Merlivat [1986], both square and cubic dependence for the gas transfer velocity on 10 m wind speed (U_{10}) have been suggested. For marine applications one of today's most frequently used parametrization for the gas transfer velocity is from Wanninkhof et al. [2009]:

$$k = 3 + 0.1U_{10} + 0.064U_{10}^2 + 0.0011U_{10}^3 \tag{2}$$

Apart from the forcing by wind shear, this parameterization also includes the effect of breaking waves and bubbles and is used in many models to parametrize the gas flux. In the last few years however, studies both in the laboratory [Woolf et al., 2007], and in field of; DMS [Heubert et al., 2010; Marandino et al., 2007], O_2 [Kihm and Körzinger, 2008; **Paper II**] and acetone [Yang et al., 2014] indicates a solubility dependence of the relation between k and U_{10}. The combined results of these studies suggests that the relation between k and U_{10} increases in strength with decreasing gas solubility. The start of the observed difference in wind speed dependence between gases of different solubility was found to coincide with the onset of breaking waves. This different behavior of gases within the high wind speed regime were suggested to be linked to the theoretical work by Woolf and others [Woolf, 1993; Woolf et al., 1997; 2007]. The concept of the theory is that the transfer efficiency between submerged bubbles (from wave breaking) and the surrounding water increases with decreasing gas solubility.

Using single wind speed dependence for k, can for many regions also be question on other aspects. This since we know that other factors can have a great influence on the magnitude of the gas flux such as; rain [Ho et al., 1997, 2004; Zappa et al., 2009; Takagaki and Komori, 2007], water-side convection [MacIntyre et al., 2002; Rutgersson and Smedman, 2010; Rutgersson et al., 2011], surfactants/surface films [Broecker et al., 1978; Frew, 1997; Salter et al., 2012] and sea ice [Loose and Schlosser, 2011; Else et al., 2011; Delille et al., 2014]. In wintertime at high latitudes, one typically find unstable stratification and outgoing long wave radiation causing convection both in air and in the water. On a temporal scale the temperature difference between the air and the water can be as high as 10-20°C, causing large heat fluxes. These factors together have shown to cause water-side convection, enhancing the gas transfer velocity, even for conditions with much more moderate heat fluxes than found over the Arctic Ocean.

1.2 Aim of the thesis

In order to gain more knowledge of the relative importance of the processes controlling the transfer efficiency we introduce the first air-sea atmospheric EC measurements of O_2. We also investigate factors that could potentially be important for the gas exchange of CO_2 in Arctic. The specific aims of this thesis were:

- Investigate if the oxygen instrument Microx TX3 could be used to measure air-sea fluxes of O_2 in an eddy covariance (EC) system.
- Study the relation between the air-sea gas transfer velocity and wind speed and hopefully get more knowledge on the importance of solubility for the gas transfer at high wind speeds.

- Study the importance of water-side convection for the air-sea exchange of CO_2 in Arctic and high latitude seas.

2. Air-sea gas exchange

2.1 Gas transfer

Apart from surface disturbances e.g. ice formation and surfactants, the magnitude of k is governed by the rate of turbulence in the water and in the air. The two layer film model [Liss and Slater, 1974] describes the total transfer efficiency as the sum of the air resistance (R_a) and water resistance (R_w) to transfer, where k is inversely proportional to the total resistance (R).

$$k = (R_a)^{-1} + (R_w)^{-1} = (k_a / \alpha) + (\varepsilon k_w) \tag{3}$$

Here ε denotes a chemical enhancement factor and subscripts a and w denotes air and water respectively. For gases of low solubility such as O_2 (α=0.025) and CO_2 (α=0.727) the transfer resistance is almost exclusively found in aqueous sublayer, while for a more soluble gas like DMS with α=12.7 approximately 10% of R is air-phased controlled. This concept allows R_w to be expressed as the sum of the independent resistances, each contributing to the total water-phase resistance, $1/R_w = 1/R_1 + 1/R_2 + ..$, where subscript 1 and 2 refers to independent resistance (e.g. wind, rain, water-side convection or surfactants). In this way a circuit can be formed describing the efficiency of the gas transfer, where the individual resistance can have different significance to R_w depending on the site specific environmental conditions. For measurements of transfer efficiency it´s however more convenient to use k rather than R. In mathematical terms water-side turbulence is described by the water friction velocity u_{*w}. For a smooth surface without waves k can be set as a function of u_{*w} according to:

$$k_w = u_{*w} \beta Sc^N \tag{4}$$

where β and N are surface dependent coefficients, and where Sc denotes the Schmidt number. The Schmidt number (defined as Sc=ν/D) describes the order of diffusion across the air-water interface, with the ratio of kinematic viscosity of water (ν) to the molecular diffusion (D). The relationship between D and k are fundamental in order to convert measurements of one gas into the gas of interest. The majority of models gives that k will be proportional to D^N where $1/2 < N < 2/3$. For a liquid interface with waves most models predict k

to be proportional to $D^{1/2}$ such that the relation between the transfer velocities for two different gases (gas 1 and 2) can be expressed as:

$$\frac{k_1}{k_2} = \left(\frac{Sc_1}{Sc_2} \right)^{-N} \tag{5}$$

This allows us to compare transfer velocities calculated from measurements of different gases at different locations with variations in water temperature and salinity. For air-sea exchange applications of gases with low solubility ($k \approx k_w$), k is usually normalized to its corresponding counterpart for CO_2 at 20°C in seawater (k_{660}).

$$k_{660} = k\left(Sc / 660\right)^{-1/2} \tag{6}$$

If k is driven solely by wind and normalized this way, the measured transfer velocities for CO_2, O_2 and Methane (CH_4) should all fall on the same line when shown against U. As mentioned earlier newer studies on the gas transfer velocity showing the potential importance of bubble-mediate transfer using various gases has questioned the validity of this assumption.

2.2 Eddy covariance method

The eddy covariance method is a technique where the turbulent fluxes are directly measured. Although the EC method was developed already in the late 1800s, the lack of high frequency instruments delayed the use of the EC method until middle of 1900s. Since the first momentum and heat fluxes there have been a rapid technological development and today measurements of vertical turbulent fluxes of constituents such as: H_2O, CO_2, CH_4 are common. The EC method uses the covariance between two simultaneously measured high frequency signals. In order to successfully use the EC method there are certain criteria's that needs to be fulfilled: (*i*) no advection of scalar flux, (*ii*) wind and scalar concentrations are in steady state, (*iii*) flat and horizontally homogenous underlying surface. With these criteria's met Reynold decomposition can be applied [e.g.Aubinet et al., 2012], where the vertical scalar flux F_c becomes constant with height within the surface layer and can be expressed as:

$$F_c = \overline{w'x'} + \overline{wx} \tag{7}$$

where x denotes scalar concentration and w is the vertical wind and the primes represent deviation from mean value (overbar). The first term is the covariance

of the scalar and the vertical wind deviation and represents the turbulent vertical flux. The mean vertical wind becomes zero after a double rotation, aligning *u* in the mean wind direction (tilt correction), thus the second term could theoretically be neglected. For open path concentration measurements (typical for scalar) density variations as a result of variations of temperature, humidity or pressure will appear as false variations of the scalar concentration and thereby affecting the scalar flux. This since the concentration measurements are made within a certain detection volume. This can be corrected for either on the raw signal by converting into mixing ratios [Sahlée et al., 2008b] or in the post processing [Webb et al., 1980] using the following equation.

$$F_{O_2} = \overline{w'\rho_O'} + \mu(\overline{\rho_O} / \overline{\rho_a})\overline{w'\rho_v'} + (1+\mu\sigma)(\overline{\rho_O} / \overline{T})\overline{w'T'} \quad (8)$$

The $\overline{w'\rho_O'}$ term is the measured density flux, the second term on the right hand side $\mu(\rho_O / \rho_a)w'\rho_v'$ account for the contribution from the latent heat flux and the third term $(1+\mu\sigma)(\rho_O / T)w'T'$ is the contribution from the sensible heat flux. Here σ is the ratio of water vapour density to the density of ambient air (ρ_O / ρ_a), μ is the ratio M_d / M_v where M is the molar mass (kg mol^{-1}) where subscript *d, a* and *v* refers to dry air, ambient air and water vapor respectively. The magnitude of the correction will depend upon the relation in magnitude between the heat flux and the scalar flux. This correction also becomes more important for gases with small turbulent fluxes in relation to their mean concentration. This is the case for oxygen, where the WPL-correction has the potential of not only changing the magnitude of the flux but also the direction. Fluxes measured at a certain height represent the average surface flux from a specific area upwind of the instrument. Here it is important to ensure that the conditions within the flux footprint fulfills the criteria's (*i-iii*) and corresponds to an area representative for the study.

3. Sites and measurements

3.1 Östergarnsholm

In **Papers I** and **II** gas fluxes were measured at a site located on the southern tip of the island Östergarnsholm in the Baltic Sea (Figure 1). At the site measurements are performed with both high frequency EC instruments at three levels and slow response instruments for profiles at 5 levels in a 30 m tower. One kilometer south-east of the tower a buoy is situated, equipped with mooring instruments measuring pO_2, pCO_2, salinity and conductivity at 4 m depth and profiles of temperature at 5 levels down to 20 m. The site has been running since 1995 and have been used for several studies of different aspects on air-sea interaction [e.g. Smedman et al. 1999; Rutgersson et al., 2011]. Eddy covariance fluxes of momentum, sensible and latent heat are shown to represent open sea conditions for wind directions (WD) 80°<WD<210° [Högström et al., 2008], while for fluxes of CO_2 data with wind from the sector (80°<WD<160°) are preferable used [Rutgersson et al., 2008]. In **Papers I** and **II** the fast response oxygen sensor Microx TX3 [PreSens, 2006] was used in an EC system together with one sonic anemometer and a gas analyzer, LI-7500 (LI-COR Inc., Lincoln, NE, USA.). In May 2013 the Gill sonic were replaced by a CSAT3 (Campbell Scientific, North Logan, Utah, USA).

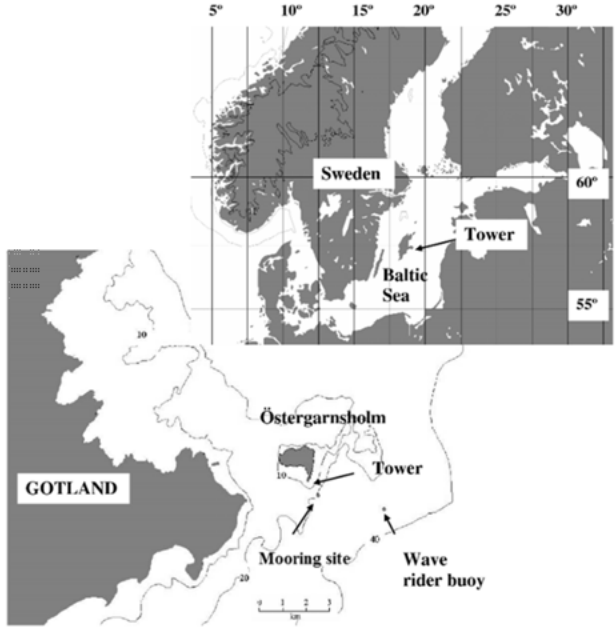

Figure 1. Map of the Östergarnsholm measurements site. Positions of the tower, mooring instruments and wave buoy are indicated by arrows. Thin solid lines represents iso-lines of water depth. (Reprint from **Paper II**)

3.1.1 Microx TX3

The Microx TX3 is a fiber-optic instrument that uses luminescence lifetime of an indicator molecule to determine the partial pressure of oxygen. In the presence of oxygen, the decay time τ_1 (defined as the time between the excited signal and the indicator molecule emitted signal), is shorter compared to the decay time in oxygen free air τ_0. The oxygen-dependent time delay between the excited and the emitted signal is represented by a phase angle ϕ and the Stern-Volmer equation [Stern and Volmer, 1919] is used to determine the partial pressure of oxygen $[O_2]$.

$$1 + K_{sv}[O_2] = \frac{\tau_0}{\tau_1} = \frac{\tan\phi_0}{\tan\phi_1} \tag{9}$$

where K_{sv} is the Stern Volmer constant, subscript 0 and 1 refers to an environment in the absecences and presences of oxygen respectively. The sensor constists of a needle type housing with an oxygen sensitive tip <50 μm and a gas analyzer unit. Together with the fastest sensor (without optical isolation), Microx TX3 attain a response time t_{90}<0.5 s with a resolution of 0.1 % air-

saturation according to the specification [PreSens, 2006]. A thermistor is connected to the Microx TX3 to correct for temperature changes affecting the quenching frequency, this correction is set on a regular interval of 20 s. The output signal unit is selectable between partial pressure (hPa), %-oxygen saturation (0-50%) and % air-saturation (0-250%). The relative unit % air-saturation is an air-water equilibrium unit, where 100% air-saturation corresponds to a water surface in equilibrium with the average volume content of O_2 in air (20.95%) at standard pressure (1013.25 hPa).

3.2 Adventpynten

During nearly two months March to April a field campaign was conducted in the area of Adventfjorden, close to Longyearbyen, Svalbard, Norway. Adventfjorden is a typical high Arctic fjord surrounded by steep mountains and where the valley open out into the water. The fjord is about 7 km long and is a side fjord to the larger Isfjorden. At the site located at the far most point of Adventdalen (Figure 2, right panel red dot) the land is relatively flat and the transition from land to water is smooth. The site consisted of two towers equipped with instruments, one with an EC-system installed at 3 m height above mean sea level, the second tower with slow response measurements of wind, temperature and humidity at two heights (0.5 m and 4 m above ground). The EC system consisted of one Sonic Anemometer CSAT3 (Campbell Scientific, North Logan, Utah, USA) measuring the three wind component and temperature and a LICOR-7500A (LI-COR Inc., Lincoln, NE, USA.) measuring humidity, CO_2 and pressure.

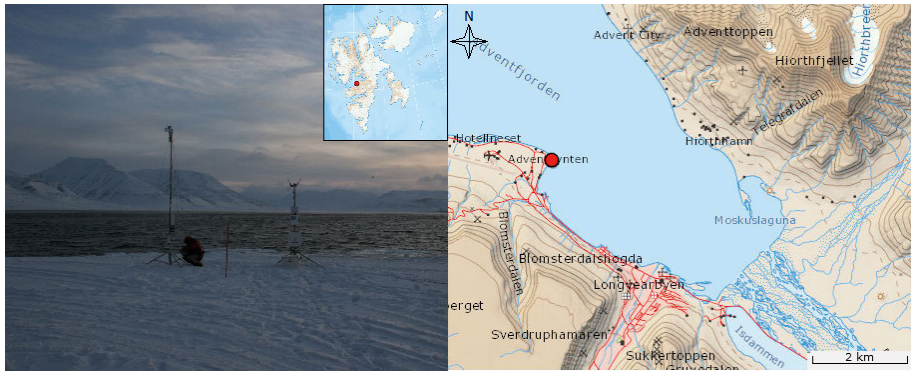

Figure 2. Study area, Adventfjorden with the location of the EC-tower (red dot, right panel). Background map is Toposvalbard (Norwegian Polar Institute, 2016). Left panel, photo of the site with the two towers, EC-tower to the right and profile-tower on the left and with the Adventfjord in the background (from **Paper IV**).

At 5 occasions during the first 3 weeks, measurements were taken of sea surface temperature, pCO_2, salinity in water, and profiles of temperature using a conductivity, temperature and depth sensor (CTD) (SeaBird SBE 19plus V2 SeaCat, Seabird Electronics Inc., Bellevue, Washington, USA). At these occasions a net radiometer (CNR-1, Kipp & Zonen, Delft, The Netherlands) was installed in front of the boat attached to a bar measuring the radiation balance over the water surface.

3.2 Data analysis

Prior flux calculation of the EC data in **Papers I**, **II**, **III**, and **IV** a double rotation were performed on the wind data. Wind vectors were first rotated into the horizontal mean wind direction and then tilt corrected, such that the mean vertical wind becomes zero and wind vector is aligned in the mean wind direction. Data were then despiked and divided into blocks, 60 min block (**Paper II**) and 30 min block (**Papers I, III** and **IV**). For every individual block, data were linearly detrended and corrected for time lag, caused by the separation distance between the sonic and the gas analyzer. To account for density fluctuations caused by heat and moist fluxes, affecting the measured gas flux, data were corrected using (Equation 6) (**Papers I**, **II**, **III** and **IV**). For **Papers III** and **IV** data were screened with a filter using the mean concentrations of humidity and CO_2, also data not fulfilling the criteria of Vickers and Mart (1997) for skewness and flatness were filtered out.

4. Oxygen

4.1 Signal analysis

The Microx TX3 was offered with two types of O_2 sensors, one with optical isolation and one without optical isolation. For atmospheric EC application the sensor without optical isolation is preferably used, due to its faster response time (0.5 s). Immediately after starting measurements a non-physical trend in the oxygen signal was distinguished. This trend was removed by a linear detrend algorithm and its impact on the O_2 fluxes were reduced. More worrying was the limited lifetime of the oxygen sensors, which was found to vary significantly between sensors of the same type, depending on environmental conditions and the quality of the individual sensor. After typically 2-5 days the quality of the signal started to reduce, resulting in unreasonable O_2 fluxes. To estimate the stability and lifetime of the sensor and thereby the amount of useful data, the Monin-Obukhov similarity theory for variances [Monin, 1962] was used

$$\frac{\sigma_x}{x_*} = const \tag{10}$$

where σ_x denotes the variance, $x_* = \frac{-\overline{w'x'}}{u_*}$ denotes the scaling parameters for the scalar, $u_* = \sqrt{-\overline{u'w'}}$ is the friction velocity. For constant atmospheric stability and as long as the O_2 sensor is capable of resolving the true fluctuations of O_2, Equation (10) holds. When resolution decreases this ratio starts to show large deviations. Spectral analysis gives information on an instrument´s potential use in an EC-system, regarding resolution and response time. In figure 3 a mean power spectra for O_2 is showed, averaged over 50 half hour runs measured with the non-optical isolated sensor during near neutral conditions. In accordance with Kolmogorov theory for scalars, the mean O_2-spectra shows a curve slope entering the inertial subrange similar to the expected -2/3, this up to about 1 Hz, with a tendency of a more spiky structure in the range of 0.5-1 Hz. At 1 Hz the detection limit was reached observed as a drastic drop in the frequency response, thus the energy in the range of 2-10 Hz should be considered as noise.

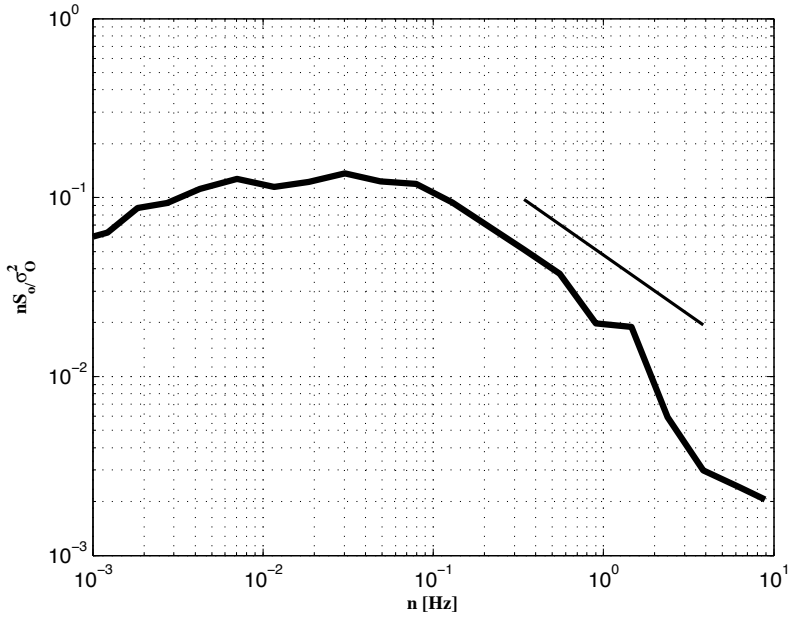

Figure 3. Normalized mean power spectra of O_2 measured with the non-optical isolated O_2 sensor shown against frequency. The spectra is averaged over 50 half hours of data from 29 August to 30 August 2012, at the height of 27 m. Straight solid black line indicates a -2/3 slope (from **Paper I**).

Co-spectra of the humidity flux wq, and the flux of CO_2 wCO_2 measured at Östergarnsholm has shown to follow a -4/3 slope in the inertial subrange [Sahlée et al., 2008b]. With the assumption of scalar similarity, co-spectra of oxygen should behave similar to co-spectra of other scalars. In figure 4 normalized mean co-spectra of wO_2, $C_{wO}(n)$ (blue) is compared with co-spectra of wq, $C_{wq}(n)$ (green), and wCO_2, $C_{wC}(n)$ (red). A good agreement were found between $C_{wO}(n)$ and $C_{wq}(n)$ up to a normalized frequency f equal to 0.3. Already at f=0.3 a frequency loss is seen for C_{wO} and C_{wC} compared to $C_{wq}(n)$. This early loss in frequency response for the co-spectra of wO_2 is most likely an effect of the limited resolution of the oxygen sensor, causing an average underestimation of the O_2 flux by 25%. Two common methods to correct for frequency loss are be either using a transfer function based on an idealized shape of the scalar co-spectra $C_{wx}(n)$, or by using a simultaneously measured scalar signal. In **Papers I** and **II** the latter concept was applied, assuming scalar similarity the total O_2-flux was determined from:

$$F_o = \int_{-\infty}^{n_l} C_{wo}(n)dn + \frac{\int_{-\infty}^{n_l} C_{wo}(n)dn}{\int_{-\infty}^{n} C_{wx}(n)dn}\left(\int_{n_l}^{\infty} C_{wx}(n)dn\right) \quad (11)$$

The first term on the right hand side is the oxygen flux up to the loss frequency (n_l), the second term is the relation between the oxygen flux and the flux of the reference signal x, up to n_l multiplied with the part of the reference flux from n_l to infinity. Using this method one needs to be observant for differences in the low frequency part of $C_{wO}(n)$ and $C_{wx}(n)$ and choose a proper start frequency for the ratio in the second term of Equation (11).

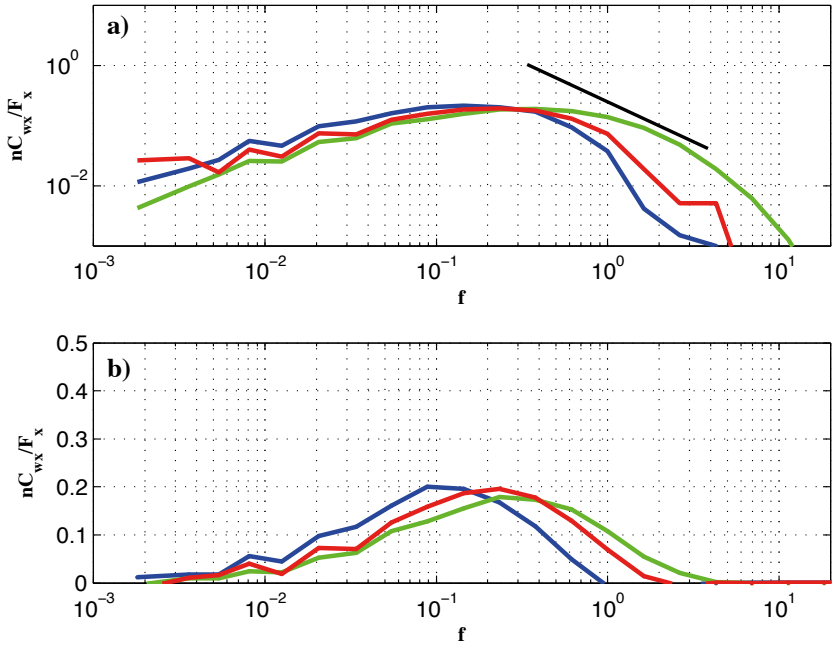

Figure 4. Normalized mean co-spectra nC_{wx}/F_x, of wO_2 (blue), wq (green) and wCO_2 (red) shown against normalized frequency (logarithmic scale), a) real parts of nC_{wx}/F_x is shown along a logarithmic y-axis, b) nC_{wx}/F_x is shown along a linear y-axis. The mean co-spectra contains of 22 half hours of data from 30 August 2012, the solid black line in Fig. 4a indicates a -4/3 slope (from **Paper I**).

4.2 Oxygen flux

A key concept when evaluating gas fluxes is the representatively. For Östergarnsholm CO_2 fluxes data associated to wind from the sector 80<WD<160° are preferable used. Fluxes from this sector represent a fully developed and

undisturbed wave field, also nearshore effects, affecting the horizontal distribution of the vertical CO_2 flux are limited.

During 19-24 of June 2013, EC fluxes of O_2 and CO_2 were measured (Figure 5a), where two periods were found (data within dashed black lines) with wind from the undisturbed sector covering about 12 hours each. The first period showed mostly positive O_2 fluxes (upward directed) in the range 0.6-6.4 µmol $m^{-2}s^{-1}$ in agreement with the measured super-saturation of 5-8% (Figure 5b). As it should the simultaneously measured CO_2 flux were negatively correlated (Figure 2 in **Paper II**) with the O_2 flux and downward directed. After about 24 hours the wind turns to SSW and increases in strength. The O_2 flux changed direction to negative and later on also the CO_2 flux changed direction to positive (upward). From satellite images and measurements of water temperature and pCO_2 (Figure 3 in **Paper II**) the counter-gradient flux for O_2 and CO_2 were found to be associated to a period of upwelling. During this period the flux footprint was no longer situated over the location of the water concentration measurements of O_2. After the upwelling period the winds turns back towards SE and the O_2 flux again changed direction, back to positive (0.35-3.0 µmol $m^{-2}s^{-1}$) in agreement with the measured gradient.

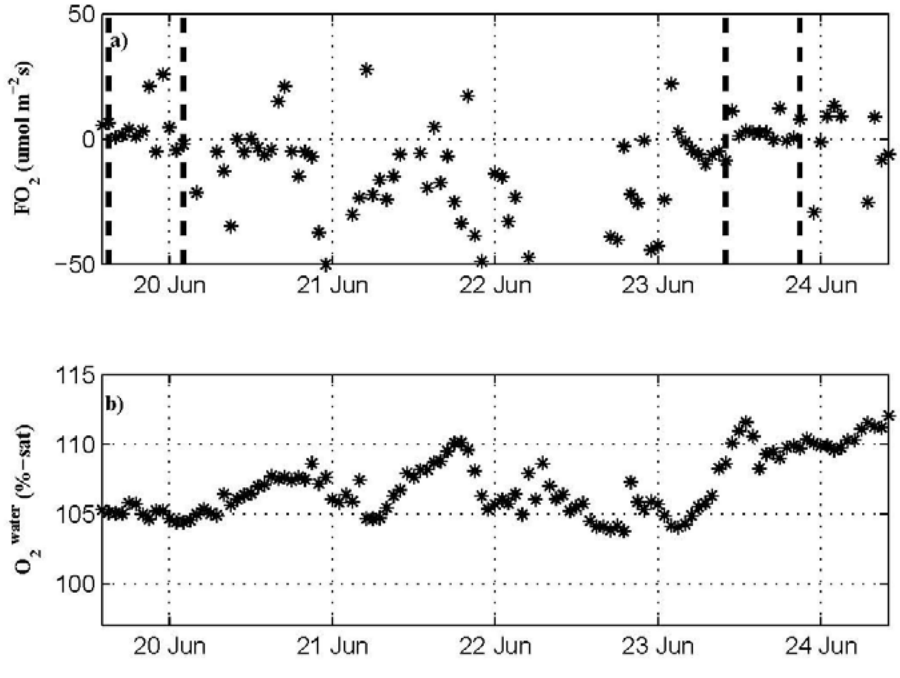

Figure 5. Oxygen flux (a) where positive values corresponds to a flux from water to air, the two selected periods are within the black dashed lines, (b) oxygen saturation in water (from **Paper II**).

5. The gas transfer velocity

5.1 Wind

In **Paper II** we investigated the wind dependence of the gas transfer velocity for O_2 using EC measurements from 3 field campaigns. With conditions considered stationary and wind from the selected sector 80<WD<160, data were evaluated from spectra and co-spectral analysis, resulting in 31 hours of data. The gas transfer velocity was then calculated from the measured O_2 flux and the concentration difference of O_2 between the bulk water and the air, using Equation (1). The relation between the measured normalized gas transfer velocity for O_2 ($k_{660}O_2$) and 10 m wind speed (U_{10}) was studied (Figure 6). For comparison two parameterization are shown, k_{W09} obtained by using Equation (2) (green), and the cubic relation from Kihm and Körtzinger [2010] (k_{KK10}) based on oxygen measurements using a different measurement technique. For winds higher than 5 m s^{-1}, our measured transfer velocities displayed a stronger wind speed dependence than k_{W09} and k_{KK10}. The best fit to the measured gas transfer velocities were given by the curvature of the cubic relation $k_{new}=0.11U^3$ (described by the black line). For a more extended analysis on the behavior of k_{660} for higher winds, we introduced data from the upwelling period 22-23 June 2013. For this data set (as mentioned above), the location of the measurements of oxygen concentration in water at buoy, were not covered in the flux footprint and therefore potentially not representative for the O_2 flux. Nor could the signal of the upwelling be captured in the measured O_2 concentration in the water at buoy. Instead the oxygen concentration in the bulk water within the flux footprint were estimated from the concept of photosynthetic quotient (PQ) (Equation 11 in **Paper II**). By computing k_{660} for CO_2 (Equation 2), using the measured CO_2 flux and the concentrations of O_2 and CO_2 measured at buoy. The gas transfer velocity for O_2 was then calculated from Equation (12) in **Paper II**, using the estimated concentration of O_2 in the bulk water at the location of the footprint area, instead of the O_2 concentration measured at buoy.

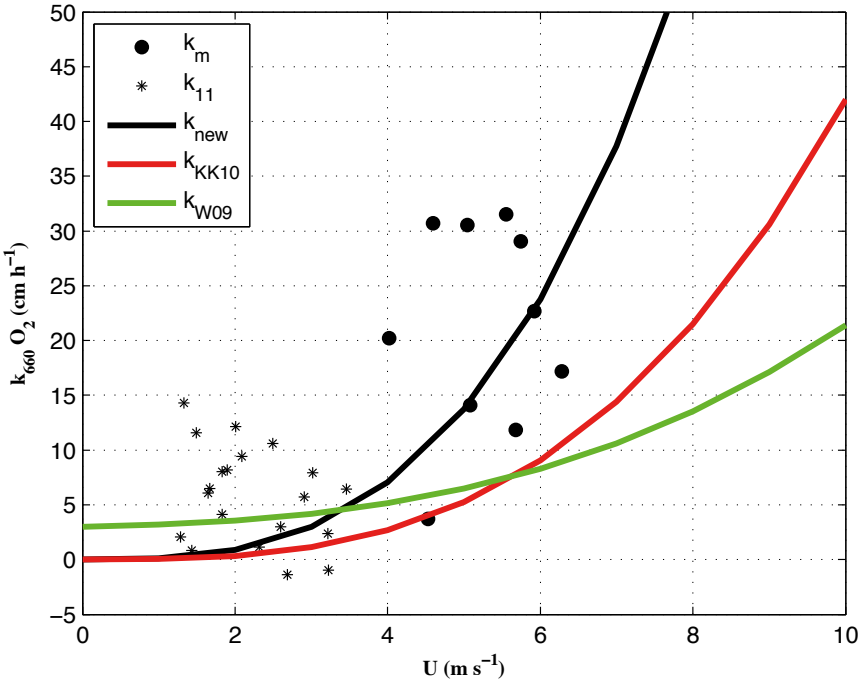

Figure 6. Measured transfer velocities during, summer 2013 and September 2011 (black dots), summer 2011 (stars), normalized to Schmidt number 660 (20°C for CO_2 in seawater) shown against horizontal wind speed (10 m). The black solid line displays the best cubic fit $k_{new} = 0.11U^3(Sc/660)^{-1/2}$ to the measured transfer velocities. For comparison, two prominent parameterizations are included, one based on CO_2 measurements, Wanninkhof et al. [2009] in green, and one based on O_2 measurements, Kihm and Körzinger [2010] in red (from **Paper II**).

Introducing these data the gas transfer velocities are shown against U_{10} (Figure 7) for the directly measured values of k_{660} (k_m) and k_{660} data from the upwelling period using the *PQ* analogue (k_e). The data from the upwelling period supported the stronger wind dependence found for k_m. In the low wind speed regime the k_e were found within the same range as k_m, also following the comparing parameterizations for k_{660}. For higher winds (6-8 m s^{-1}) however, k_e showed a stronger wind speed dependence than k_{W09} and k_{KK10}, rather supporting the stronger wind speed dependence found for k_m. Though the data set are limited, it is interesting to notice that the stronger wind dependence found for k_m and k_e coincides with the visual onset of whitecap formation at winds > 5-6 m s^{-1}. It is possible that processes such as bubble-mediate transfer here acts more effectively for O_2 having lower solubility than CO_2, thereby enhancing the air-sea gas exchange of O_2.

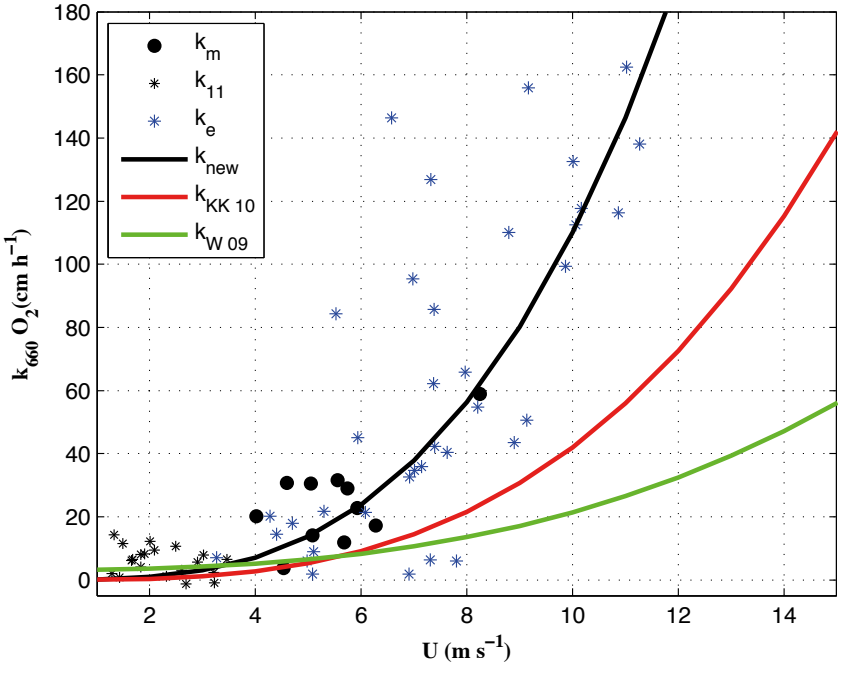

Figure 7. Measured transfer velocities from 3 field campaigns, summer 2013 and September 2011 (black dots), summer 2011 (stars) and estimated transfer velocities during upwelling (blue stars), all normalized to Schmidt number 660 (20°C for CO_2 in seawater) shown against horizontal wind speed (10 m). The black solid line displays the best cubic fit $k_{new} = 0.11U^3(Sc/660)^{-1/2}$ to the measured transfer velocities. For comparison, two prominent parameterizations are included, one based on CO_2 measurements, Wanninkhof [2009]in green, and one based on O_2 measurements, Kihm and Körzinger [2010] in red (from **Paper II**)

Former studies on the slightly unstable boundary layer have shown significant influence from an additional turbulent regime visual in the cospectra of wT and wq as second peak at higher frequencies. In contrast to the normal case where eddies are formed at the surface, eddies at this regime (named the UVCN regime) is created in the shear at the upper part of the surface layer [Hunt and Morison, 2000; Högström et al., 2002]. These detached eddies brings down cold and dry air from layers aloft, enhancing the turbulent fluxes of sensible and latent heat [Smedman et al., 2007a; 2007b; Sahlée et al., 2008a; 2008c].

In **Paper III** and **IV** we investigated the gas transfer over a Svalbard fjord using eddy covariance measurements. When conditions where unstable close to neutral and z/L were found in the range of $-0.15<z/L<0$ the exchange coefficient for sensible heat was found to drastically increase and simultaneously a second peak in the co-spectra of wT started to develop. **In Paper IV** we showed this small scale turbulence also influenced the co-spectra for CO_2 (figure 8). For more unstable stratification (L= -5 m) a single peak at n=0.03 Hz

was observe. But when the boundary layer approaches neutral stratification (-L > 50 m) a second peak started to develop around n=1 Hz and grew in strength as conditions became more neutral. For L= -150 m representing the UVCN regime, the first peak had almost vanished and the second peak dominated the structure of the wCO_2 co-spectra. The fully developed UVCN case (-L>150 m that is -0.02<z/L<0) was however relatively unusual at this site due to the large air-sea difference in temperature which in general was found in the range of 5-20°C. Much more common were data associated to z/L in the range of -0.2 <z/L< -0.02 (37 % of all data), signified by the camel shaped co-spectra. For wT [Smedman et al., 2007a] and wq [Sahlée et al. 2008a] the main driver of the enhanced fluxes were suggested to be related to the different properties of the air aloft (colder and drier), brought down to surface by the detached eddies. Analogously the quadrant analysis of the CO_2 flux (Figure 10, in **Paper IV**) with L= -150 m showed on enhanced contribution from downdrafts of air with higher concentrations of CO_2. As mentioned in section 2.1 the flux of gases with low solubility such as CO_2 are also likely to be enhanced by the potentially increased levels of water-side turbulence related to this regime.

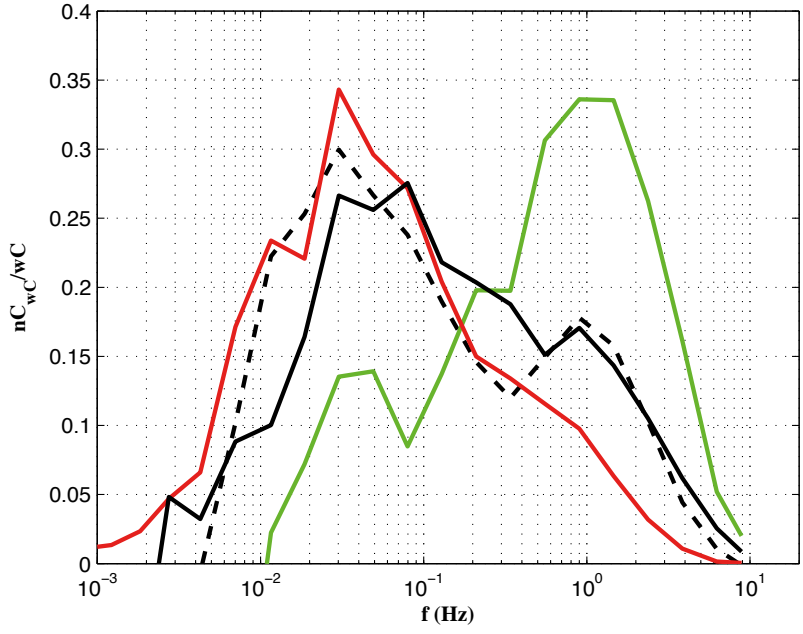

Figure 8. Normalized mean cospectra of wCO_2 shown against frequency for data from sector S_2, associated to L= -150 m (green), L= -100 m (black solid curve), L= -50 m (black dashed curve) and L= -5 m (red curve). Each mean cospectra is based on 2-7 hours of consecutive data (from **Paper IV**).

After removing the influence from the two dominant processes regulating the magnitude of k (shear induce turbulence from mean wind k_{W09} and water-side convection k_c), the impact from the additional small scale turbulence on the gas transfer velocity was studied (Figure 9, grey dots). For more unstable conditions related to low values of u_* data scattered around zero, indicating that the transfer velocity is well described by the two dominant processes. As the thermal forcing weakens and z/L>-0.2, k_{660}-(k_{W09}+k_c) increases as conditions become more neutral, a large scatter is however observed for data in the regime -0.2<z/L>-0.1. For data related to z/L>-0.1 and winds > 6.5 m s^{-1} (red dots), a different characteristic were found. Here 80% of the data were associated to transfer velocities larger than 10 cm h $^{-1}$ and with a mean value of k_{660}-(k_{W09}+k_c) above 14 cm h^{-1}.

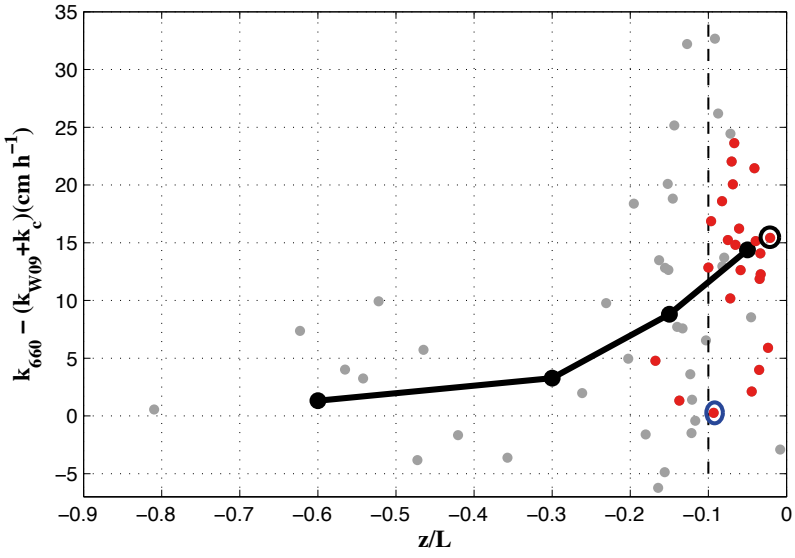

Figure 9. Plot of k_{660}-(k_{W09}+k_c) against stability parameter z/L, with k_c calculated from the relation $k_c = 2300\, w_{*_w} - 17$ and k_{W09} from Equation (2). The black solid curve shows the mean value of k_{660}-(k_{W09}+k_c) for each stability class with center values according to the black dots. Red marker denotes data related to wind speeds > 6.5 m s^{-1} (from **Paper IV**).

5.2 Water-side convection

During situations with strong surface cooling and/or evaporation, buoyant motions are generated in the water column leading to a vertical mixing within the water column. As these convective motions (water-side convection) approach the water surface, turbulence is generated in the sub-surface water and thereby enhancing the gas transfer velocity. Previous studies [e.g. MacIntyre et al., 2002, Rutgersson and Smedman 2010] has showed an enhancement of the air-

sea gas transfer with the presence of water-side convection defined as $w_* = (Bz_{ml})^{1/3}$, with z_{ml} the mixed layer depth and B the buoyancy flux determined from:

$$B = \frac{gaQ_{net}}{c_{pw}\rho_w} + \frac{g\beta_{sal}Q_{lat}}{\lambda\rho_w} \tag{12}$$

The first term on the right hand side describes the effect from surface cooling, where g is gravity, a is the thermal expansion coefficient, Q_{net} is the sum of the sensible- and latent heat flux, the heat to or from the water body by advection, the net long wave radiation and the incoming short wave radiation., c_{pw} denotes the specific heat of water and ρ_w the density of water. The second term describes the contribution from evaporation where β_{sal} is the saline expansion coefficient, Q_{lat} denotes the latent heat flux and λ the latent heat of vaporization. In **Paper III** we explored the importance of water-side convection for the air-sea gas exchange of high latitude waters, using EC measurements of CO_2 measured over a high Arctic fjord. This data set were characterized by large heat fluxes, generally found in the range 50-200 W/m^2 with maximum values as high as 400 W/m^2. In figure 10 the w_{*_w} is shown as function of the gas transfer velocity, with the influence from wind removed according to Equation (2), where the color of each point corresponds to the wind speed measured at 3 m height above mean sea level. The data cover convective velocities in the range of 0.0096 m s^{-1}< w_{*_w} <0.0145 m s^{-1}, where the largest contribution to w_{*_w} comes from the surface cooling term (term 1 in Equation 12). A clear relation between w_{*_w} and k_{660}–k_{W09} was observed, where k_{660}–k_{W09} increases as w_{*_w} increases, this also for winds well exceeding 6 m s^{-1}. It was also found that situations with stronger winds (U_3 > 5 m s^{-1}) in general were associated to water side convection w_{*_w} > 0.012 m s^{-1}. The combination of wind-induced transfer and transfer caused by buoyant motions in the water results in a very efficient air-sea transfer of CO_2 over the fjord.

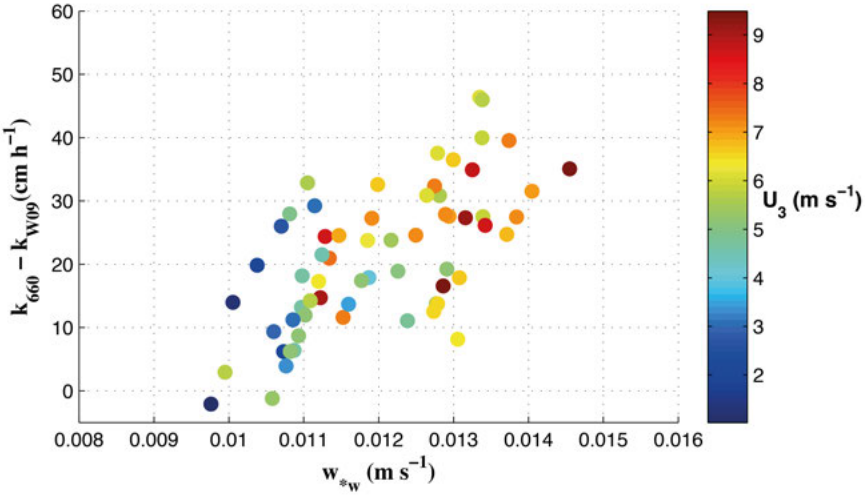

Figure 10. Plot of k_{660}–k_{W09} against the water-side convection velocity (w_{*w}); the colors denote the wind speed at a height of 3 m. From **Paper III**.

For comparison we used data presented in Rutgersson and Smedman [2010] (Figure 11, triangles) measured at the site Östergarnsholm. These data were associated to lower wind speeds (U_{10}< 6.5 m s^{-1}) than the data measured at Adventpynten. Despite the substantial different climatic conditions at these two sites, a good agreement between the two data sets were found regarding the relation between the gas transfer velocity and w_{*w}. The best fit to all data were given by $k_c = 3300 w_{*w} - 24$ (black line, Figure 11), somewhat stronger dependence than the expression from Rutgersson and Smedman [2010] (red line in Figure 11). After correcting for the potential underestimation of the wind induced transfer, due to the higher turbulence over the fjord than normally found over open ocean for the same wind conditions (further investigated in **Paper IV** and shown in 5.1), the best fit to the data were given by $k_c = 2300 w_* - 17$. Still the relative contribution from water-side convection to the calculated total CO_2 flux remained as high as 34%. The strongest relation between k_c and w_{*w} were found for data associated to U_{10}< 7 m s^{-1}, best described by the relation $k_c = 2650 w_{*w} - 19$, which is similar to the expression of Rutgersson and Smedman [2010].Their relation were also based on EC measurements of CO_2 associated to wind speeds lower than 7 m s^{-1}.

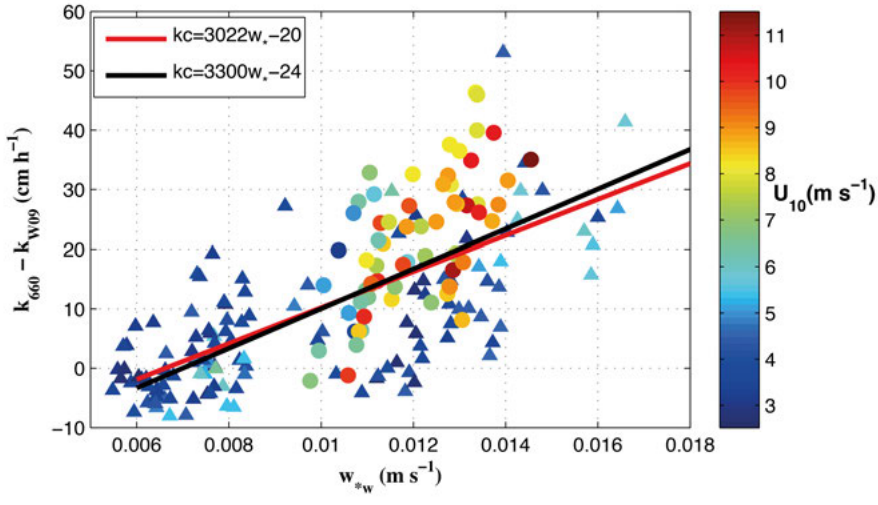

Figure 11. Plot of $k_{660} - k_{W09}$ against the water-side convection velocity (w_{*_w}) for Svalbard data (circles) and those of Rutgersson and Smedman [2010] (triangles). The colors of the symbols denote the wind speed at a height of 10 m (m s^{-1}). The black solid line shows the best linear fit to all data ($k_c = 3300\, w_{*_w} - 24$) and describes the dependence between k_{660} and w_{*_w}. The red line denotes the parametrization $k_c = 3022\, w_{*_w} - 20$ of Rutgersson and Smedman [2010]. From **Paper III.**

6. Summary and conclusions

Accurate descriptions of the processes controlling the air-sea gas exchange are fundamental in order to forecast the climate effect of the increasing emissions of greenhouse gases. For gases of low solubility like O_2 and CO_2 the efficiency of the air-sea transfer is almost exclusively governed by the turbulence generated in the surface water. The main source of water-side turbulence originate from wind stress acting on the water surface. For many areas single wind speed parameterization of the gas transfer velocity are acceptable, however, as showed in this thesis that kind of simple parameterizations are not always sufficient.

In this thesis processes affecting the gas transfer velocity are studied. Introducing the first atmospheric EC measurement of O_2 in **Paper I**, we present air-sea fluxes of O_2 and investigate the dependence between the gas transfer velocity and wind speed in **Paper II**. In **Paper I** we investigate the potential use of the Microx TX3 oxygen micro sensor to serve as an instrument in an eddy covariance system. Spectral analysis shows the signal of O_2 to follow the Kolmogorov theory showing a -2/3 slope entering the inertial subrange. Approaching the inertial subrange, the co-spectra of wO_2 follows a -4/3 slope similar to the curve of wCO_2 when normalized. The instrument does however suffer from the limited resolution and response time visual as a drop off from the expected -4/3 slope when approaching 0.5 Hz. As for all effective open path measurements where the flux are small compared to the average concentration the density correction on the O_2 flux becomes large. Despite several drawbacks we conclude that the instrument can be used in an atmospheric eddy covariance system for short term measurements of the air-sea flux of O_2 when conditions are favorable. Favorable conditions are: large air-sea gradient of O_2, atmospheric stratification close to neutral, temperature above freezing and no precipitation.

In Paper II a time serie of simultaneously measured O_2 and CO_2 fluxes are presented. In agreement with the air-sea gradient of O_2, the measured O_2 fluxes were upward directed and displayed a negative correlation with the CO_2 flux. During the upwelling period the oxygen flux changed direction to downward and the oxygen saturation increased from being 105% to 110%, indicating a potential uptake of O_2. Using data from 3 field campaigns the wind dependence for the air-sea gas transfer velocity of O_2 were investigated in **Paper II**. The data are indeed limited and attributed to corrections, but clearly indicated a stronger wind speed dependence for the gas transfer velocities of O_2

than former EC studies on the gas transfer velocity for CO_2. It is interesting to notice that this stronger wind dependence for the gas transfer velocity of O_2, starting at wind speed > 5 m s^{-1} coincides with the typical onset of whitecap formation within the flux footprint area. The main conclusions in **Paper II** were that the oxygen flux took reasonable values and also showed a negative correlation with the CO_2 flux. The stronger dependence found for the transfer velocities of O_2 compared k_{660} based on measurements of CO_2, could potentially be explained by bubble mediate transfer. The data presented in Paper II are however limited and there is a need for progress concerning the quality of the Microx TX3, before measurements of k_{660} can be performed with such precision that details on its wind dependence can be confirmed. I hope these studies encourage to further instrumental development such that more studies on the gas transfer velocity for O_2 and other gases can be carried out using the eddy covariance technique.

In **Paper III** we studied the importance of water-side convection for the air-sea gas exchange in high Arctic using EC measurements of CO_2. Measurements from the fjord revealed a significant impact from water-side convection, enhancing the gas transfer velocity, this especially for wind speeds < 7 m s^{-1}. The enhanced transfer arises from large fluxes of sensible and latent heat often found over high latitude seas in wintertime. From 3 weeks of measured values of heat fluxes, net-radiation and mixed layer depth the contribution from water-side convection to the total CO_2 flux were calculated. For comparison, we applied our approach to published data collected from Östergarnsholm in the Baltic Sea, which is exposed to very different climatic conditions. The two data sets showed a good agreement in terms of the relation between water-side convection and gas transfer velocity. Former studies have found a dependence of the transfer velocity for low winds. **In Paper III** we conclude that this dependence is also valid for Arctic waters and can be extended to winds as high as 9 m s^{-1} for situations with strong water-side convection. The relative mean contribution from water-side convection to the calculated total CO_2 flux during the 3 weeks of measurements were found as high as 34%.

When condition are unstable very close to neutral ($-0.15<z/L<0$) former studies have shown on influence from an additional turbulence regime (termed the UVCN regime). **In Paper IV** we show that the EC heat flux over the fjord was enhanced when $-0.15<z/L<0$, visual as an increase of the bulk transfer coefficient C_H. Simultaneously a peak started to develop in the high frequency part of the cospectra of wT and wCO_2. This peak grew in strength as conditions became more neutral. Quadrant analysis of the fluxes of wT and wCO_2 showed on increased contributions to the vertical flux from downdrafts of air from layers aloft. In **Paper IV** we showed that the additional turbulence associated to the downdrafts also attains the potential to enhance the air-sea transfer of CO_2. During these conditions ($-0.15<z/L<0$) the transfer velocities were found to increase in magnitude with increasing values of z/L. We conclude that a major part of the increased transfer results from a combination of increased

water-side turbulence generated by the downdrafts, and the higher concentration of CO_2 in the air brought down.

The work of this thesis only cover on a minor part of the processes controlling the efficiency of the air-sea gas transfer. Still it can be concluded that much more work is needed on the processes affecting the gas transfer velocity. Measurements presented in **Paper II** suggests a different dependence of the transfer velocity for O_2 compared to the transfer velocity for CO_2, also observed in other studies of O_2 using different measurement technique. This could be an indication of a more effective bubble-mediate transport for gases of lower solubility and I would like to see more studies on the effect of gas solubility within the high wind speed regime.

In P**aper III** and **Paper IV** we showed on two processes that were found to enhance the air-sea gas transport in Arctic, during winter conditions. The combined effect of water-side turbulence from water-side convection and wind stress resulted in a much more effective gas transport than what is obtained from single wind speed parameterization of the gas transfer velocity. Thus our results highlighted that the air-sea CO_2 uptake in the Arctic and at high latitudes might be significantly underestimated during winter. This can have serious implications for the total carbon uptake in marine Arctic areas and I strongly encourage to long term year round EC measurements of CO_2 in these areas, such that the importance of water-side convection for the total CO_2 transfer can be established.

7. Acknowledgements

Firstly I would like to thank my main supervisor Anna Rutgersson and my co-supervisor Erik Sahlée for giving me the opportunity to become a PhD student. Working with science within meteorology related to the important issue of global warming have been a dream for me ever since I was teenager. Thanks for all good advice and discussions at our meetings giving me the inspiration to develop as a scientist. Thanks Anna for always taking your time with me, and for believing in and supporting my ideas on the measurements in Svalbard. Thanks also for your constructive way of dealing with my sometimes too ambitious plans.

I would also like to thank my co-authors: Anna Sjöblom, Eva Falck, Natscha Kljun, Abdirahman Omar and all people involved in the field campaign on Svalbard 2013 making it a successful pilot project. Also a special thanks to Hans Bergström, Gunnar Bergström, Lillis, Björn, Marcus and all people that are and have been involved in the Östergarnsholm site. I also want to mention Ann-Sofi Smedman who I truly look up to in terms of the work that you have accomplished.

A special thanks to you Eva for all the fun we have had together, discussing data, whiskey and everything in between, also thanks for all the days of hard fieldwork. Especially, thanks for being one of my best friends. You will always have a special place in my heart. Thanks also to my other former roommate Katrin for all interesting discussions related to outdoor life and thanks Monica and Conny for getting to know you.

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Finally I want to thank my family and especially my fiancée Sandra Rosenberg for your tremendous support through life.

8. Sammanfattning på svenska

Gasutbyte av O_2 och CO_2 mellan hav och atmosfär: *Processer som påverkar utbyteshastigheten.*

Idag vet man att en betydande del av den globala uppvärmningen som skett sedan industrialiseringens start har orsakats av mänsklig aktivitet och förbränning av fossila bränslen. Koldioxid är en mycket potent växthusgas och koncentrationen av denna i atmosfären är starkt kopplad till atmosfärens temperatur. Från att ha legat på en nivå under 300 ppm i mer än 400 000 år har koncentrationen av CO_2 stigit till dagens 404 ppm på lite drygt 100 år. Ur ett klimatologiskt perspektiv är 100 år en mycket kort tid, där vi ännu inte sett de fulla konsekvenserna av dagens höga nivå av CO_2 i atmosfären. Vad vi däremot vet är att uppvärmningen i dagsläget sker i rasande fart och att de 10 varmaste åren globalt sett sedan 1880 (då globala temperaturmätningar tog sin start) alla återfinns under 2000-talet och där 2015 utmärker sig som det hittills varmaste året. Tillika har havsisen över Arktis minskat med hela 13 % per årtionde sedan mätningarna av denna startade 1979. Data för det sista halvåret av 2016 är ännu inte sammanställt, men var och en av de första 6 månaderna under 2016 var individuellt sett de varmaste för respektive månad som uppmätts sedan 1880.

Med bakgrund av detta torde det vara enkelt att begripa att något radikalt måste göras för att minimera utsläppen av växthusgaser och därigenom bromsa den pågående uppvärmningen. En utmaning för forskarvärlden ligger däri att övertyga beslutsfattare om de allvarliga klimatologiska konsekvenser som de ökande utsläppen av växthusgaser medför. En del i detta arbete ligger i att kartlägga storleken på källor och sänkor av atmosfäriskt CO_2 och därigenom förbättra beskrivningen av koldioxidutbytet i klimatmodellerna. Genom förbättrade klimatmodeller kan effekterna av de ökande utsläppen av växthusgaser bestämmas med större precision. En av de största sänkorna för atmosfäriskt CO_2 är världshaven och dessa utgör mer än 70 % av jordens totala yta. Två av de absolut viktigaste gaserna i den marina kolcykeln är O_2 och CO_2.

Utbytet mellan hav och atmosfär av icke reaktiva gaser som de två nämnda styrs av skillnaden mellan koncentrationen av gasen i ytvattnet och i den ovanliggande luften, samt hur effektivt gasutbytet sker däremellan. Effektiviteten i gasutbytet brukar benämnas utbyteshastigheten. För gaser med låg löslighet såsom O_2 och CO_2 avgörs storleken på utbyteshastigheten uteslutande av mängden turbulens i ytvattnet. Där mer turbulens genererar större värden på

utbyteshastigheten. Experimentellt kan utbyteshastigheten bestämmas utifrån mätningar av gasflödet och koncentrationsskillnaden av gasen mellan hav och atmosfär. Man känner idag till ett flertal faktorer vilka påverkar utbyteshastigheten däribland: vind, brytande vågor, bubblor, konvektion i vattnet och regn. En väg för att nå ökad kunskap om de processer som påverkar utbyteshastigheten är att från mätningar av gaser med olika löslighet studera de processer som generar turbulens i vattnet. Då med fördel också använda olika mätmetoder.

Det huvudsakliga syftet med den här avhandlingen har varit att genom eddy kovarians mätningar studera de processer som påverkar storleken på utbyteshastigheten. I avhandlingen presenterar vi de första atmosfäriska mätningarna av syreflöden mellan hav och atmosfär gjorda med eddy kovarians metoden. Det ska här också sägas att den korta livstiden på varje sensor som är 2-5 dygn gör att instrumentet inte lämpar sig för långtidsmätningar. Den begränsade upplösningen och tidsresponsen på syreinstrumentet medför korrektioner på syreflödet. Som för liknande mätningar av gasflöden behöver syreflöden också korrigeras för densitetsvariationer orsakade av fluktuationer av temperatur och vattenånga. För syreflödena medför detta en osäkerhet av storleksordningen 20-25%. De korrigerade syreflödena uppvisar en negativ korrelation med samtidiga mätningar av CO_2-flödet och riktningen på det uppmätta O_2-flödet motsvarar den förväntade utifrån den uppmätta gradienten av O_2 mellan hav och atmosfär. Utifrån dessa mätningar beräknar vi sedan utbyteshastigheten för O_2 och undersöker relationen mellan utbyteshastigheten och vinden på 10 m höjd. För låga vindhastigheter uppvisar utbyteshastigheten för O_2 en liknande relation som de vedertagna beskrivningarna för utbyteshastigheten som funktion av vindhastigheten, baserat på mätningar av CO_2 och utbyteshastigheter för O_2 från andra mätmetoder. För starkare vindar och då i synnerhet för vindhastigheter > 5 m s^{-1} visar utbyteshastigheterna för O_2 ett starkare beroende mot vindhastigheten än de vedertagna beskrivningarna. I denna studie gjordes inga mätningar av vågfältet i havet utanför mätplatsen men det är intressant att notera att det är vid 5-6 m s^{-1} som vågorna vanligtvis börjar bryta.

Tidigare studier har visat att vid förhållanden med låga vindhastigheter kan utbyteshastigheten förstärkas betydligt som följd av konvektion i vattnet. Konvektionen bildas genom en avkylning av ytvatten som följd av stora uppåtriktade värmeflöden, det avkylda ytvattnet sjunker då ner mot botten som följd av den högre densiteten. Detta genererar storskaliga turbulenta strukturer i vattenkolumnen. När dessa strukturer närmar sig vattenytan bryts de ner så att turbulensen ökar i ytvattnet vilket förstärker utbyteshastigheten. Konvektionen kan också förstärka exempelvis ett uppåtriktat CO_2 flöde genom att vatten med högre koncentration av CO_2 förs upp till ytan. Kraftig konvektion i både atmosfär och hav som följd av stor temperaturgradient mellan ytvattnet och luften ovan är symptomatiskt för förhållandena över Arktis vintertid. I avhandlingen presenteras mätningar av CO_2 utbytet över en fjord i Arktis.

Mätningarna pågick under närmare två månaders tid och under två veckor i slutet på mars utfördes också samtidiga mätningar av blandningsdjup och partialtrycket av CO_2 i ytvattnet. De mätningarna visade på ett tydligt samband mellan utbyteshastigheten för CO_2 och konvektionen i vattnet där utbyteshastigheten ökade i takt med en starkare konvektion i vattnet. Detta samband var starkast för vindar < 7 m s^{-1} men kunde ses för situationer med vindar upp till 9 m s^{-1} och stark konvektion. En jämförelse med mätningar av utbyteshastigheten gjorda vid den maritima forskningsstationen Östergarnsholm visade på en god överensstämmelse av sambandet mellan utbyteshastigheten och konvektionen i vattnet. Det relativa bidraget från konvektionen i vattnet till flödet av CO_2 mellan hav och atmosfär under fältkampanjen beräknades till hela 34 %.

Data från fjorden visade också på ökade utbyteshastigheter i samband med instabila nära neutrala förhållanden då stabilitetsparametern z/L befann sig i området $-0.15<z/L<0$. Från co-spektra av wCO_2 observerades ett maxima vid frekvensen 1 Hz, kopplad till småskalig turbulens vid förhållanden då $-0.15<z/L<0$. I takt med att de atmosfäriska förhållandena blev alltmer neutrala ökade inflytandet från den småskaliga turbulensen och det maxima vid 1 Hz växte i storlek, samtidigt som inflytandet från turbulensen lokaliserad vid maxima 0.03 Hz minskade. Kvadrantanalys på flödena av CO_2 visar att den småskaliga turbulensen förmodligen härrör från luftskikt högre upp i gränsskiktet innehållande högre koncentration av CO_2. Bidraget till det uppåtriktade CO_2 flödet från nedåtgående luft med högre koncentration av CO_2, ökade i takt med att z/L antog högre värden. Motsvarande signal observerades också i co-spektra av wT och kvadrantanalysen för densamma visade på ökat bidrag till flödet från en nedåtriktad transport av kall luft från högre liggande luftlager. I likhet med vad som presenterades för UVCN regimen [Smedman et al., 2007a] ökade också värdet på utbyteskoefficienten för sensibel värme i takt med att $-L$ ökade, här inom regimen $-0.15<z/L<0$. Den ökade småskaliga turbulensen i atmosfären bidrog sannolikt också till en ökad turbulens i vattnet vilket gav upphov till den observerade ökningen av utbyteshastigheten för CO_2.

Den här avhandlingen berör endast ett fåtal av de processer som kan effektivisera gasutbytet över hav, ändock visar det på komplexiteten i att på ett bra sätt kunna beskriva utbyteshastigheten. Den kombinerade effekten av bidragen från konvektionen i vattnet och turbulens i ytvattnet genererade av vindar resulterar i en betydligt effektivare transport av gaser mellan hav och atmosfär än den beskrivning av gasutbytet som vanligen används i modeller över Arktis. För många områden där värmeflödena över hav är stora däribland Arktis vintertid kan detta innebära att flödet av CO_2 och andra gaser som O_2 tidigare har underskattats i modeller. Vidare har studier under de senaste åren, liksom den presenterad i den här avhandlingen visat på att utbyteshastighetens vindberoende vid höga vindhastigheter mycket väl kan vara beroende av gasens löslighet.

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