ENHANCED AIR-SEA CO_2 FLUX DURING UNSTABLE ATMOSPHERIC STRATIFICATION

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1. Introduction

To understand the effects of anthropogenic emissions of CO_2 it is crucial to understand all parts of the carbon cycle. The ocean is a sink of a large fraction of the anthropogenically produced CO_2. Understanding gas exchange across the air-sea interface is an important component in global climate dynamics. There have been a large number of measurements of oceanic CO_2 during the last decades but the quantification of the total oceanic uptake as well as the regional distribution is still uncertain (Siegenthaler and Sarmiento, 1993; IPCC, 2007; Takahashi et al., 2002). In the global carbon cycle the total exchange at the sea surface is important and presently not very accurately described. This is explained by lack of detailed understanding of the processes controlling air-sea exchange. In Takahashi et al., (2002) global estimates of the total CO_2 uptake by the oceans are increased by 70% using two different formulations of the efficiency of the transfer. For near coastal regions this lack of understanding of the processes has a greater impact due to larger variability of the parameters in the atmosphere and the ocean of possible impact on the transfer.

The exchange of CO_2 between the ocean and the atmosphere is controlled by the air-sea difference in partial pressure of CO_2 (ΔpCO_2) at the surface and of the efficiency of the transfer processes. The partial pressure at the water surface is controlled by biological, chemical and physical processes in the ocean. The efficiency of the transfer processes is determined by the resistance to the transfer in the atmosphere as well as in the ocean. The largest resistance to the CO_2 transfer is by molecular diffusion and turbulent mixing in the aqueous boundary layer. In most investigations the efficiency of the transfer is described by a transfer velocity. Different investigations show different results for the transfer velocity, in part due to uncertainties in measurements, but also because the important processes are not accurately taken into account Fairall et al. (2000).

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The use of the eddy covariance method for estimating the CO_2 transfer velocity has the possibility of increasing our knowledge of the air-sea exchange on shorter timescales and has been used in several experiments (i e, Donelan et al., 2002, McGillis et al., 2004; Iwata et al., 2005; Rutgersson et al., 2008). Micrometeorological marine CO_2 measurements may suffer from problems due to moving platforms or salt contamination at the sensors. By using a stationary platform in a less salty environment we can, however, mainly avoid these problems. In Rutgersson et al. (2008) it was shown that the instrumental uncertainty in the estimation of the transfer velocity was below 20% and mainly due to uncertainty in the high-frequency flux measurement. It was also shown that it is of great importance that the measured pCO_{2w} correctly describes the pCO_{2w} in the foot-print area.

Air-sea exchange of, for example, humidity is strongly dependent on the atmospheric stratification and the present study is focusing possible impact on atmospheric stratification also on the CO_2 transfer velocity. Atmospheric stratification could influence the air sea exchange of CO_2 due to a number of processes. In Erickson (1993) it was shown that the atmospheric stability influences the transfer velocity between 20 and 50 % due to the impact of the atmospheric stratification on the gradients of wind speed and CO_2. Voorrips et al (1994) concludes that the enhanced wave energy during unstable condition means a difference in wave height which does generally not exceed 15% with the higher (and thus steeper waves) during unstable stratification. This implies that possible also the wave breaking could be altered by the atmospheric stratification. Since the wave breaking is thought to have a large impact on air-sea exchange of CO_2 this might also be important.

In the near-surface water, significant temperature gradients may occur due to molecular heat conduction and we get a so called skin effect (warm skin or cool skin). This has previously been shown to have a strong impact on temperature. The cool skin of the ocean is speculated to have a strong impact on the transfer of CO_2 (Robertson and Watson, 1992; van Scoy et al., 1995). Using data from the GasEx-2001 McGillis et al (2004) showed that the flux of CO_2 had a strong diurnal cycle and relatively large values of the transfer velocity at high winds; this was mainly explained by convection in the aquatic boundary layer. In Zülicke (2005) a theoretical framework for this stratification impact of gas transfer due to molecular heat conduction was formulated. The impact was estimated to have a significant effect only below 1-2 m/s with an increase in transfer velocity for unstable and a decrease for stable atmospheric stratification.

2. Measurements

2.1 Site and instrumentation

The measurements used in this study are taken at the Östergarnsholm site in the Baltic Sea. The location of this station is (57º27'N, 18º59'E) (see Figure 1). The measuring site at Östergarnsholm has been running since 1995. It is a land-based 30 m tower situated on the southern tip of a very small, flat island in the Baltic Sea.

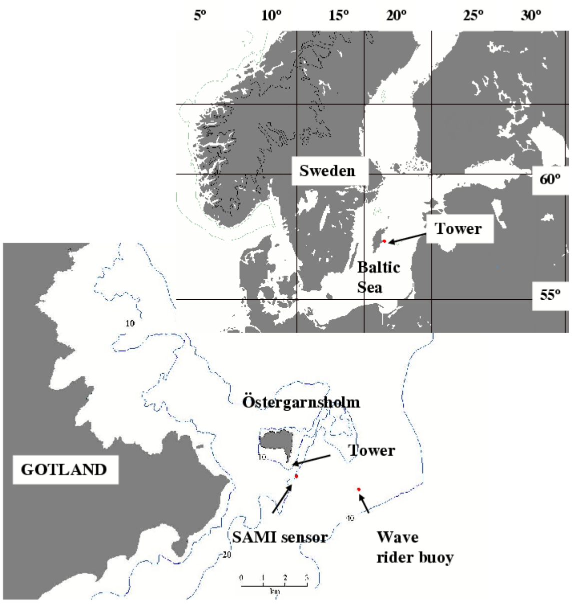

Figure 1. *The Baltic Sea and the Östergarnsholm field station. The positions of the tower, the SAMI sensor and the DWR (Wave rider buoy) are shown by arrows in the lower figure.*

Data from this site have been used in a large number of air-sea interaction investigations. The slope of the bottom topography near the island gives a minor impact of the limited water depth on the wave field (Smedman et al., 1999). For the wind directions (80º<WD<210º), the data has been shown to represent open sea conditions in the sense that the wave field is mainly undisturbed and the atmospheric turbulence as well as the fluxes of momentum, sensible and latent heat are not influenced by the limited water depth or the coast (Högström et al., 2008). The flux of some quantity measured at a certain height is influenced by the surface conditions at a certain distance upwind; this area of influence is called the flux footprint. The relative role of upwind areas can be estimated by applying expressions originally developed for atmospheric dispersion. The flux footprint is highly dependent on atmospheric stability. In Högström et al. (2008) it was estimated that for very stable conditions 60% of the fluxes measured at 10 m origin at an area between 1.7 to 22 km from the tower and for very unstable conditions 60% of the fluxes measured at 10 m origin at an area between 75 to 300 m from the tower. It is the sea surface partial pressure of CO_2 (pCO_{2w}) in this area that is of importance for the flux measured in the tower. In Rutgersson et al. (2008) it was shown that for wind directions from the sector 80º<WD<160º the foot-print represents the tower and that other directions should be used with care (at least during summer). In the present investigation ony data when the winds are from the sector 80º<WD<160º is used.

The tower is instrumented with high-frequency instrumentation for the turbulence data as well as slow response sensors for profile measurements. In May 2005 we deployed a so called SAMI-sensor (submersible autonomous moored instrument, Sunburst Sensors, Missoula, Montana, USA) at about 4 m depth, 1 km SE of the tower (see Figure 1). The instrument is designed for continuous measurements of CO_2-partial pressure in the water (pCO_{2w}). The measurements and instrumentation are further described in Rutgersson et al. (2008).

2.1 Environmental conditions

The CO_2-system has been running semi-continuously since 2005, due to instrumental problems and power failure extended periods are missing. In this study data from 2005 to 2007 has been used. Figure 2 shows three annual cycles of pCO_{2a} (partial pressure in the atmosphere) and pCO_{2w}. The area is a sink or a source region of atmospheric CO_2 depending on the season. pCO_{2w} shows a significant seasonal cycle with values as low as 150 µatm during summer and as high as 800 µatm during winter. A significantly smaller seasonal cycle is seen in the atmosphere with peak-to-peak amplitude of 17 µatm (Rutgersson et al., 2008b). The air-sea difference in partial pressure ΔpCO_2 (where $\Delta pCO_2 = pCO_{2a} - pCO_{2w}$) is relatively large (of the order of 50 to 200 µatm) and positive for all of the data used in this study.

3. Theory

3.1 Eddy correlation fluxes

The CO_2 air-sea flux at the tower is directly measured with the eddy correlation technique, a widely used technique for the exchange of momentum, heat and humidity.

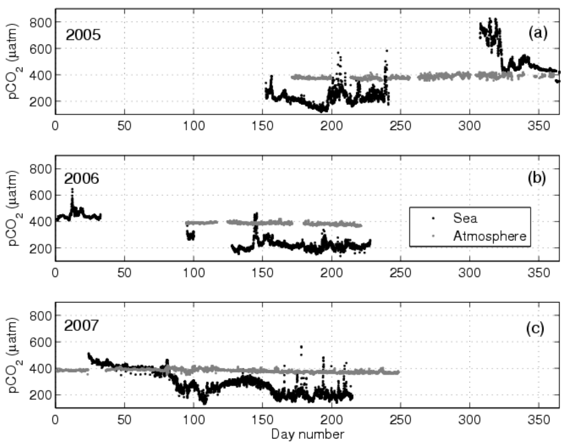

***Figure 2**. Measured pCO_{2a} (grey dots) and pCO_{2w} (black dots) during three consecutive years (2005 to 2007).*

This is a method to directly measure the amount and direction of the flux of CO_2 between the sea and the atmosphere. The idea behind this technique is that high-frequency fluctuations (of the order of 10 to 20 Hz) of vertical wind and the measured parameter (in this case CO_2) are taken simultaneous and are correlated. Applying Reynolds' decomposition on the product between the measurements of vertical velocity, w, and CO_2 concentration, c, the mass flux of CO_2 is:

$$F = w'c' + \overline{w}\overline{c} \quad (1)$$

where overbars represent time averages and primes are deviations from the mean. The last term is usually neglected in eddy correlation measurements since the mean vertical velocity is negligible. However, when measuring the flux of CO_2 this term need to be included since the difference in density between upward and downward moving air result in a non-negligible vertical velocity. This can be done for the calculated fluxes (Webb et al., 1980) or on the high-frequency fluctuations (Sahleé et al., 2008).

3.1 Calculated fluxes

A two layer film model can be used for a flux equation, which is almost universally applied in estimates of air-sea fluxes of trace gases. The exchange of CO_2 between the sea and the atmosphere (F) can be calculated from the air-sea difference in partial pressure of CO_2 at the surface and of the gas transfer velocity (k) using the equation:

$$F_{CO_2} = K_0 k(pCO_{2w} - pCO_{2a}) \quad (2)$$

where K_0 is the salinity and temperature dependent solubility constant. k is the transfer velocity. The transfer velocity is considered to depend mainly on wind speed and on the Schmidt number. The Schmidt number (Sc) is the ratio of the kinematic viscosity of seawater to the diffusion coefficient of the considered gas. Different functions which refer to Sc=660 (CO_2 at 20ºC) have been proposed to describe the Schmidt number normalised transfer coefficient (k_{660}) as a function of wind speed at a reference height of 10 m (U_{10}). Wanninkhof (1992) suggested a quadratic equation:

$$k_{660} = 0.31U_{10}^2 \quad (3)$$

which gives k for any other Sc by

$$k = 0.31U_{10}^2\sqrt{\frac{660}{Sc}} \quad (4)$$

The bulk aerodynamic formula commonly used for transfer of heat and humidity can also be used for air-sea CO_2 flux:

$$F = D_{CO2}U_{10}K_0\Delta pCO_2 \quad (5)$$

where D_{CO2} is the CO_2 Dalton number, it can be related to the transfer velocity as D_{CO2}=k/U_{10}. In the atmosphere gradients of wind, temperature and scalars are dependent on the atmospheric stratification and this influences thus also the transfer coefficients. Neutral stratification is used as the reference state and flux coefficients are then normalised for stratification. Following the derivations summarised in Geernaert (1990) for the transfer coefficient of humidity, the CO_2 Dalton number can be related to the neutral counterpart (D_{CO2N}) using the non-dimensional gradients of wind and the scalar of interest. In this study the expression for the non-dimensional wind gradient from Högström (1996) is used. Edson et al. (2004) estimated the non-dimensional gradient for humidity during unstable conditions; this gradient is suggested by McGillis et al. (2004) to be used also for CO_2. For stable stratification, there is no suggested expression for CO_2, but following the reasoning for unstable stratification we use the temperature gradient developed for stable stratification by Holtslag and DeBruin (1988). Calculating the transfer velocity from D_{CO2N} we would get a stability dependent transfer velocity. Figure 3a shows an example of the transfer velocity for different stabilities for a wind speed of 6 m/s, here the transfer velocity is 20% smaller for z/L=0.5 and 10% larger for z/L=-1 (where L is Monin-Obukohov length and z height above the surface). Figure 3b shows the transfer velocity for three choices of stability (z/L=0.5, 0 and -1 respectively).

4. Results

In Figure 5 the transfer velocity estimated from measurements are shown for different wind speeds intervals.

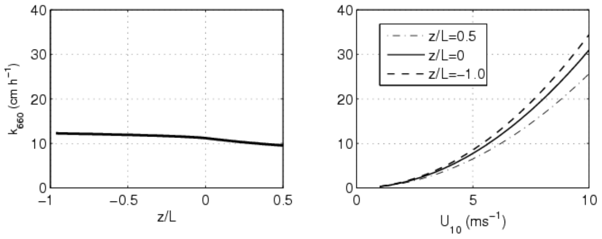

Figure 3*. Transfer velocity, (a) as a function of z/L, for a constant wind speed of 6 m/s and (b) as a function of wind speed for three different stabilities.*

There is relatively large scatter in the data (represented by ± the standard error, defined as one standard deviation divided by the square root of the number of data for each wind speed interval). For wind speeds below 5 m/s the averages of the unstable data is clearly higher than for the stable data. There is also a tendency for the data during higher wind speeds to be larger for unstable data. The stable data is slightly higher than the curve given by Equation 3 the agreement is, however, relatively good.

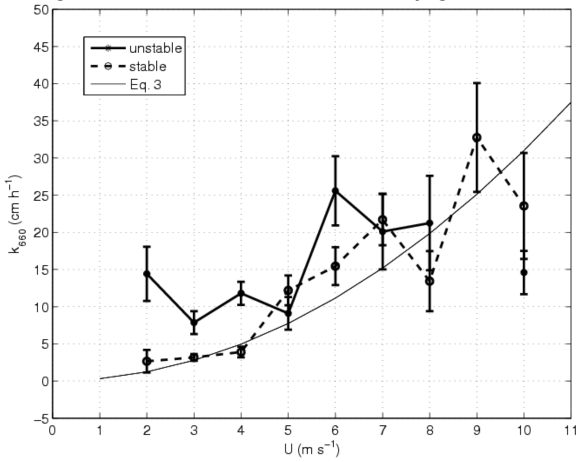

Figure 5*. Transfer velocity for different wind speed ranges for stable and unstable atmospheric stratification.*

The effect of recalculating the transfer velocity to its neutral counterpart is relatively limited (thin gray solid and dashed lines in Figure 6). There is a reduction of the unstable data, up to 20% on the average for wind speeds between 1.5 and 2.5 m/s, for stable data the increase is minor. It is also a reduction in the scatter of the data for unstable stratification, since the standard deviation of the wind speed averages is reduced for the lower wind speeds. However, the stratification impact on the atmospheric gradients (under the assumption that the used non-dimensional gradients are valid) does only explain a very small part of the difference between stable and unstable data.

5. Discussion and conclusions

Eddy-correlation measurements taken at the Östergarnsholm site in the Baltic Sea shows a clearly higher CO_2 transfer velocity for unstable than stable atmospheric stratification. Only a minor part of the enhancement can be explained by stratification effects on the atmospheric gradients. It is more likely that the reason for the enhancement is molecular heat conduction in the aqueous boundary or pCO_2 gradients in the water.

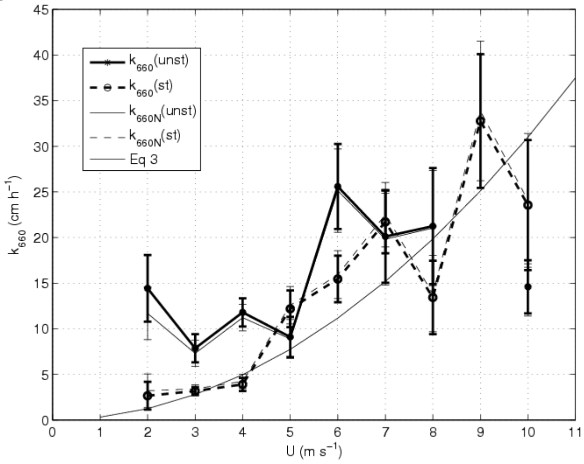

Figure 6. *Transfer velocity for different wind speed ranges for stable and unstable atmospheric stratification (thick lines). Transfer velocities recalculated to its neutral counterparts (thin dashed and solid lines).*

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