DIRECT MEASUREMENTS OF CO_2 FLUX IN THE GREENLAND SEA

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ABSTRACT

In summer 2006 eddy correlation CO_2 fluxes were measured in the Greenland Sea. A novel system set-up with two shrouded LICOR-7500 detectors was used. One detector was used exclusively to determine, and allow the removal of, the bias on CO_2 fluxes due to sensor motion. A recently published correction method for the CO_2-H_2O cross-correlation [*Prytherch et al.*, 2010a] was applied to the data set. We show that even with shrouded sensors the data require significant correction due to this cross-correlation. This correction adjusts the average CO_2 flux by an order of magnitude from -6.7×10^{-2} mol m^{-2} day^{-1} to -0.61×10^{-2} mol m^{-2} day^{-1}, making the corrected fluxes comparable to those calculated using the *Wanninkhof* [1992] parameterization for transfer velocity.

INTRODUCTION

Because the atmospheric CO_2 concentration is rising due to the burning of fossil fuels, land use change, and cement production it is important to accurately quantify the size of the total ocean carbon sink and its variations with time. For this we need to know the air-sea CO_2 flux. Because it is difficult to measure the global air-sea CO_2 flux, estimates rely mostly on calculations on the form

$$F_{CO2} = k\ S\ \Delta fCO_2 \qquad (1)$$

where ΔfCO_2 is the difference between the fugacity of CO_2 (fCO_2) in the sea and in the air, S is the gas solubility, and k is an estimate of the gas transfer velocity usually parameterized as a function of wind speed (U_{10N}). The most widely used parameterizations of k have been derived using tracer release experiments [*Ho et al.*, 2006; *Liss and Merlivat*, 1986; *Nightingale et al.*, 2000], wind-wave tank experiments [*Liss and Merlivat*, 1986], and radiocarbon invasion [*Naegler et al.*, 2006; *Sweeney et al.*, 2007; *Wanninkhof*, 1992]. Yet, none of these capture the complete range of processes relevant to air-sea gas exchange, nor are they consistent at high wind speeds. To resolve these issues we need direct measurements of the air-sea CO_2 flux (F_{CO2}).

Direct measurements of the F_{CO2} can be carried out using the eddy correlation (EC) method [*McGillis et al.*, 2001a; *McGillis et al.*, 2004; *Wanninkhof and McGillis*, 1999], but after a decade of significant technical advances several difficulties with the EC method still remain. First among these is that the observed EC F_{CO2} tend to be considerably larger than bulk parameterization or tracer derived fluxes [*Broecker et al., 1986; Kondo and Tsukamoto*, 2007; *Prytherch et al.*, 2010a], which have led to few data sets of F_{CO2} from EC experiments being published. Recent research suggest that the measurements are too high due to a cross-correlation between CO_2 and H_2O stemming from contamination of the exposed sensor optical surfaces by hygroscopic particles [*Prytherch et al.*, 2010a].

In this paper we will present the first data set of EC F_{CO2} measured in the Greenland Sea featuring unique environmental conditions and using a novel instrument set-up. We have used this data set to test whether the PKT correction method [*Prytherch et al.*, 2010a] is suitable for data sets measured in such environmental conditions and with this instrument set-up.

EXPERIMENT AND METHODS

The data were obtained on the Greenland Sea cruise 58GS20060721 [*Olsen and Omar*, 2007], carried out onboard the research vessel *G.O. Sars* between July 21 and August 3, 2006. The cruise started in Akureyri, Iceland and ended in Tromsø, Norway. The flux measurement system was set up on a mast located directly above the bow of the ship ~14.5 m above the sea surface. Two open path LICOR-7500 non-dispersive infrared (NDIR) detectors, a 3D Gill Sonic anemometer, a Motionpak, and a compass were collocated on top of the ship mast. The NDIR detectors were mounted ~1 m from the sonic anemometer and motion system, and both were shrouded in rigid plastic housing. The shrouds prevent loss of data due to severe weather conditions and icing, leading to a more robust data set. The instrument set-up is schematically shown in Fig. 1. Air entered the first sensor, hereafter referred to as 'sample', at 570 l min^{-1} and passed through a mixing chamber connected to a high volume pump; the intake of the second sensor, hereafter referred to as 'null', is taken from the mixing chamber using a second (low volume) flow path at 200 ml min^{-1}. The sensors were mounted next to each other with the long axes aligned vertically so that they experienced the same motion, and the rigid fit in the shroud prevented flexing of the support structures of the detectors. We calculate that the null sensor measurement fluctuations are reduced by 97 % using this set up [*Bariteau et al.*, 2010] such that the remaining signal is due to the motion artifact only. Motion contamination was first described by *Fairall et al.* [2000] and correction methods based on covariance with a calibration gas [*McGillis et al.*, 2001], a second identical null sensor with a sealed input [*McGillis et al.*, 2004], or correlation with measured ship motion variables [*Yelland et al.*, 2009; *Miller et al.*, 2010] have been used previously. The LICOR-7500 has much less motion contamination than their closed-path systems, however [*Miller et al.* 2009]. We assume that the motion artifact is the same for both sensors and subtract this from the sample signal on a point-by-point basis.

The ship was equipped with an underway pCO_2 system [*Pierrot et al.*, 2009] used to measure the fCO_2 in both the surface ocean and the atmosphere, the sea surface temperature (SST) and the sea surface salinity (SSS). This system is calibrated every 3-4 hours using three referenced standard gases obtained from the National Oceanographic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL). Other meteorological variables, such as air temperature, air pressure, and relative humidity, as well as navigation data were retrieved from the ship's measurement system.

Collected data were processed in ten-minute blocks and fluxes were obtained by correlating the motion-corrected vertical velocity with the fast fluctuations of interest. For details concerning how the high frequency wind speed measurements were corrected for the ship's movement see *Edson et al.* [1998] and *Miller et al.* [2008]. Only data with suitable wind vectors and with reasonable limits on ship maneuvers and ship motion correction were selected. The flow tilt calculated from the sonic anemometer was also used to account for flow distortion effects [*Fairall et al.*, 1997]. Because of problems with the infrared sensors and the ship compass during the first half of the cruise, the results of this study are mostly based on the last half of the cruise, east of ~7ºW. Out of the total 1896 10 minute averages 652 passed all quality controls.

Both latent heat and CO_2 fluxes were computed from the sample NDIR sensor, while the sensible heat flux was computed from vertical velocity–sonic temperature covariance. The humidity contribution to sonic temperature was removed using the bulk latent heat flux. The effects of humidity and temperature on the CO_2 measurements were removed prior to calculating the flux by converting the measured molar densities into mixing ratios using the high frequency temperature and air pressure measurements. This is equivalent to the traditional WPL correction [*e.g. Prytherch et al.*, 2010b]. Using *Bariteau et al.* [2010] we calculate that our set-up gives a ~5 % error in the temperature dilution correction, which is acceptable. The shrouded set-up is designed to reduce the sensor contamination from rain and heavy sea spray, but theintake is not filtered. As a consequence a CO_2–H_2O cross-correlation, which is most likely due to hygroscopic particles, was observed and additional correction for this was made using the PKT method [*Prytherch et al.*, 2010a].

RESULTS AND DISCUSSION

The average EC F_{CO2} calculated from the pre-PKT data is -6.7x10^{-2} mol m^{-2} day^{-1}, with a standard deviation of 0.27 mol m^{-2} day^{-1}. The raw CO_2 flux has considerable scatter, but there is a statistically significant (α<0.05) negative correlation with latent heat flux (F_{H2O}, Fig. 2a) which shows that the data needs further correction. The average post-PKT F_{CO2} is -0.61x10^{-2} mol m^{-2} day^{-1}, with a standard deviation of 0.11 mol m^{-2} day^{-1}. This is comparable to the CO_2 flux calculated using the *Wanninkhof* [1992] k-U_{10N} parameterization (-0.56x10^{-2} mol m^{-2} day^{-1}). The post-PKT F_{CO2} still have considerable scatter, especially when the F_{H2O} is low, but there is no longer a negative correlation (Fig. 2b). It seems that when the F_{H2O} is very small the PKT method overcorrects and adds scatter to the data, leading to a relatively large standard deviation in the corrected F_{CO2}. The added scatter could be due to the dependence of the PKT method on accuracy of F_{H2O} measurements [*Prytherch et al.*, 2010a], and while further tests using data with very low F_{H2O} are necessary, it might be that the PKT method needs to be modified to account for this. The post-PKT F_{CO2} is small (Fig. 2b), but this is not unexpected given the cold ocean and calm conditions (Fig. 3). The "flux" measured by the null sensor is not significantly different from zero (Fig. 2c). The standard deviation in this "flux" is an order of magnitude smaller than that of the post-PKT F_{CO2}. Removing the null "flux" removes scatter from the sample flux data, and the difference is statistically significant with greater than 90 % confidence. This shows that even under very calm ocean conditions having a null sensor to remove the bias from motion is valuable.

The undersaturation during the cruise was on average -105±24 μatm, whereas the end of the cruise, where the water is also warmer and more saline, has lower ΔfCO_2 (Fig. 3b). The wind speed during the cruise ranged from 0.5 m s^{-1} to 10.8 m s^{-1} with a mean of 4.5 ± 1.9 m s^{-1} (Fig. 3c). The uncertainty is given as one standard deviation of the mean. 90 % of all wind speed recorded were less than 7 m s^{-1} and 15 % less than 2.5 m s^{-1} so we have a quite large data set of F_{CO2} at very low wind speeds. No previously published EC experiment has reported significant amounts of data at wind speeds less than 2.5 m s^{-1} so the Greenland Sea experiment is in this respect unique.

Transfer velocity (k) was calculated from Eqn. 1 (reference) and bin averaged in 2 m s^{-1} U_{10N} intervals (Fig. 4). The pre-PKT fluxes yield a very strong non-linear relationship in k-U_{10N}, while the corrected fluxes have a k-U_{10N} relationship in the same range as the *Wanninkhof* [1992] parameterization. The dramatic increase in the PKT correction with wind speed was also seen in the flux data from the Southern Ocean Gas Exchange Experiment [*Edson et al.*, 2011], and can be linked to the cubic relationship between CO_2 and H_2O mixing ratios. We presume this is associated with the near-cubic wind-speed dependence of the production of sea-salt aerosols [*Lewis and Schwartz*, 2004]. The variability is quite large, however, and our data set is too small and the wind speed range too narrow to either confirm previous or derive a new k-U_{10N} relationship.

CONCLUSIONS

Application of the PKT correction method to observations of EC CO_2 flux from the Greenland Sea is successful in lowering the flux by an order of magnitude, thus making the corrected fluxes comparable to established k-U_{10N} parameterizations. The data set is too small to confirm previous studies and parameterizations. However, given the magnitude of the correction needed for these data despite using shrouded, and thus somewhat weatherproofed, sensors, it is clear that we need a more dedicated effort to understand the mechanisms causing the large CO_2-H_2O crosstalk. Presented in this study are data at wind speeds less than 2.5 m s^{-1}, and at the overall low wind speeds experienced during this cruise the flux of CO_2 is small and the variability is large. This despite the large ΔfCO_2 which suggests that the potential for carbon uptake is very large, but apparently not utilized in the summer due to low wind speeds. It is thus unlikely to get a robust estimate of the size of the Greenland Sea carbon sink without measurements in fall and winter.

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FIGURES

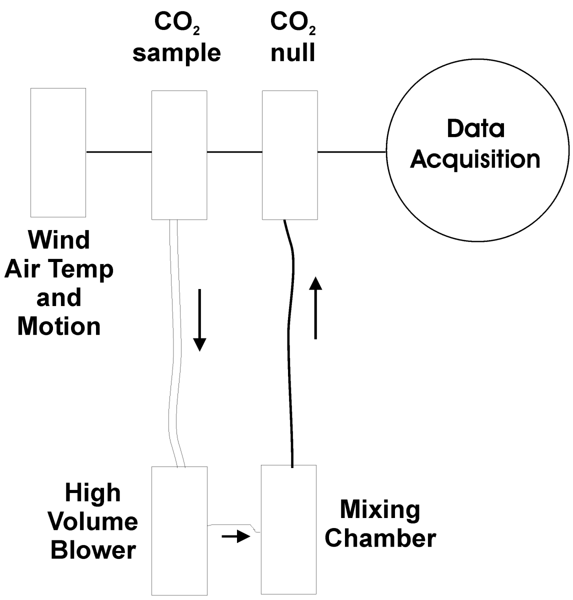

Figure 1. Schematic of the instrument set-up onboard R/V G.O.Sars July 21 – August 3, 2006.

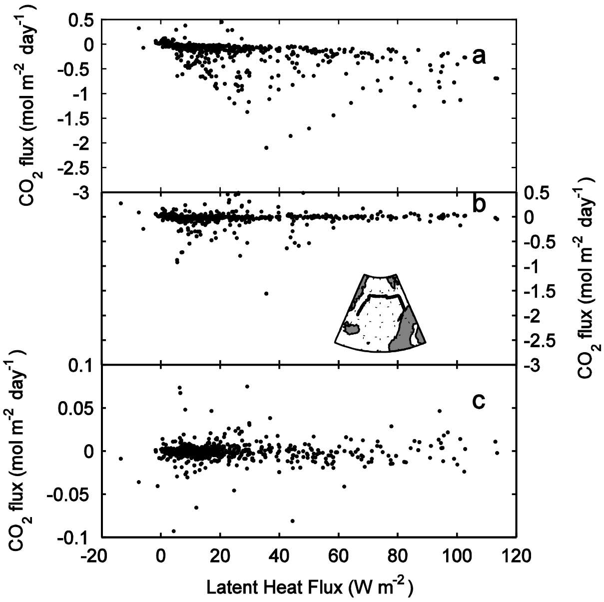

Figure 2. Eddy correlation CO_2 flux as a function of latent heat flux before and after the PKT correction. Two outliers are not shown on plot a (1.7 and -6.3 mol m^{-2} day^{-1}) and one on plot b (-4.8 mol m^{-2} day^{-1}). a) CO_2 flux from the sample LICOR before PKT correction, b) CO_2 flux from the sample LICOR after PKT correction, also shown is a map of the cruise track covered between July 21, 2006 and August 3, 2006 c) “flux” from the null LICOR. Note that this subplot has a different scale on the y-axis.

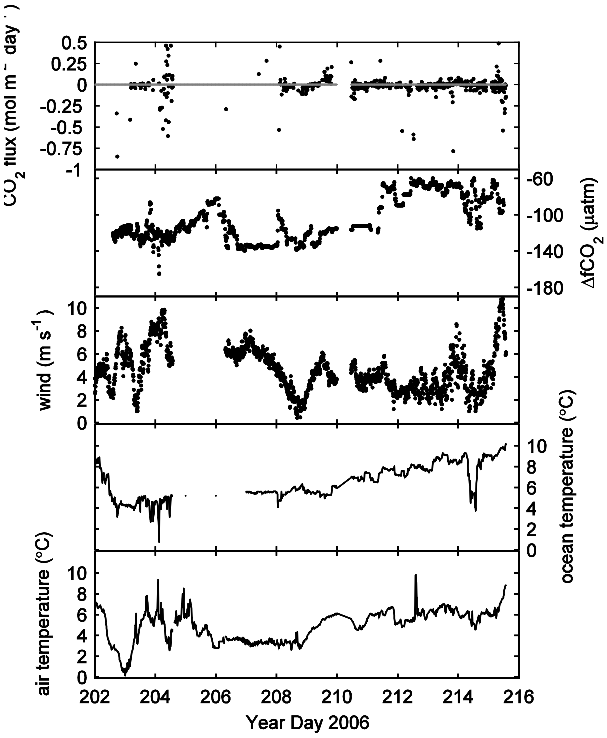

Figure 3. a) The temporal CO_2 flux with the zero line indicated in grey, b) the undersaturation (ΔfCO_2), c) the sonic wind speed, d) the surface ocean temperature, and e) the air temperature during the cruise.

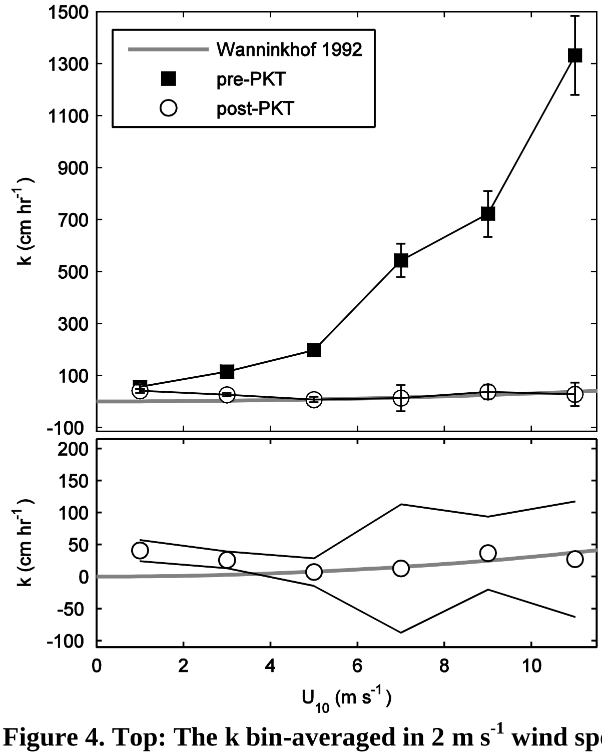

Figure 4. Top: The k bin-averaged in 2 m s^{-1} wind speed intervals plotted against U_{10N}. See the legend for details. The error bars show the standard error of the mean. Bottom: Close-up of the post-PKT k. The thin black lines show the 95 % confidence interval (estimated as plus or minus two times the standard error of the mean). The point at 11 m s^{-1} is based on only seven data points, and should not be given as much weight as the other points.