Direct measurements of CO_2 flux in the Greenland Sea

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[1] During summer 2006 eddy correlation CO_2 fluxes were measured in the Greenland Sea using a novel system set-up with two shrouded LICOR-7500 detectors. 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 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 established parameterizations for transfer velocity.

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1. Introduction

[2] Because the atmospheric CO_2 concentration is rising due to the burning of fossil fuels, land use changes, 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 air-sea CO_2 flux (F_{CO2}) directly, global estimates mostly rely on calculations of the form

$$F_{CO2} = kS\Delta fCO_2 \tag{1}$$

where ΔfCO_2 is the difference between the fugacity of CO_2 in the sea (fCO_2^{sea}) and in the air (fCO_2^{air}). S is the gas solubility, and k is an estimate of the gas transfer velocity usually parameterized as a function of wind speed at a mean height of 10 m above the water surface for neutral atmospheric stability (U_{10N}). We define F_{CO2} to be negative into the ocean. 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 rates [*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. To resolve these issues we need direct measurements of the air-sea CO_2 flux.

[3] Direct measurements of the F_{CO2} can be obtained using the eddy correlation (EC) method [*McGillis et al.*, 2001a, 2004; *Wanninkhof and McGillis*, 1999], but several difficulties with the EC method still exist after a decade of significant technical advances. First among these is the considerable greater magnitude of observed EC F_{CO2} compared to bulk parameterization or tracer derived fluxes [*Broecker et al.*, 1986; *Kondo and Tsukamoto*, 2007; *Prytherch et al.*, 2010], resulting in few published data sets of F_{CO2} from EC experiments. Recent research suggests that the measurements are too high due to a strong contamination of the CO_2 signal by water vapor, in addition to sensor motion contamination and dilution effects.

[4] 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 also use this data set to test the suitability of the PKT correction method [*Prytherch et al.*, 2010] for data sets measured in such environmental conditions and with this instrument set-up.

2. Experiment and Methods

[5] 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 installed at the bow of the ship ~14.5 m above the sea surface. Two LICOR-7500 open path 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 housings. 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 Figure 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 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 thus reducing the motion artifact. On subsequent

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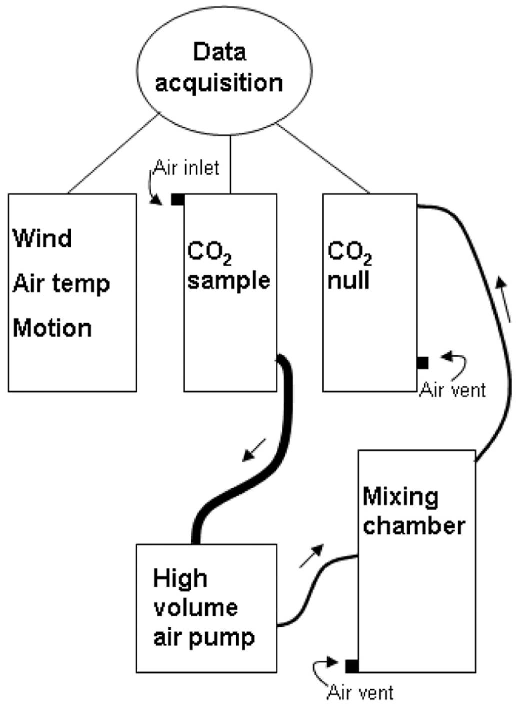

Figure 1. Schematic of the instrument set-up onboard R/V *G.O. Sars* July 21 – August 3, 2006.

deployments it has been found that the mixing chamber acts like a low pass filter with a time constant of 300 s, and by using Equation 11 of *Horst* [1997] we calculate that using this set up the null sensor measurement fluctuations are reduced by ~97%. The remaining signal is thus essentially due to the motion alone. Motion contamination was first described by *Fairall et al.* [2000] and previously correction methods for close-path systems based on covariance with a calibration gas [*McGillis et al.*, 2001b] and a second identical null sensor with a sealed input [*McGillis et al.*, 2004] have been used, and correlation with measured ship motion variables [*Yelland et al.*, 2009; *Miller et al.*, 2010] for open-path systems which need less correction. 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.

[6] The ship was equipped with an underway fCO_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 Earth System Research Laboratory (NOAA/ESRL). Navigation data were retrieved from the ship's measurement system.

[7] Collected data were processed in 10-minute blocks and fluxes were obtained by correlating the motion-corrected vertical velocity with the fast fluctuations of interest (CO_2, temperature, H_2O). The short averaging time does not present a problem since the portions of fluxes not resolved at low frequency represent only a small contribution to the total covariance. For details concerning how the high frequency wind speed measurements were corrected for the ship's movement see *Edson et al.* [1998]. Only data with relative wind vectors ±90° to bow-on were used. Data blocks where the standard deviation of ship speed and ship heading were greater than 0.2 m s^{-1} and 5° respectively were removed, as were data with large motion corrections. The flow tilt calculated from the sonic anemometer was also used to roughly account for flow distortion effects [*Fairall et al.*, 1997]. Because of problems with the NDIR 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 ~7°W. Out of the total 1896 10-minute averages, 652 passed all quality controls.

[8] 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 using Equation 8 of *Schotanus et al.* [1983]. We use the bulk algorithm because the sonic anemometer produce more reliable timeseries than fast humidity sensors and because using the bulk algorithm eliminates any effect of spatial separation of the humidity sensor and the sonic anemometer. 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 gas law and the high frequency temperature measurements and air pressure (which is of minor importance). The shroud on the sample sensor acts like a low pass filter with a time constant of 0.3 s which using Equation 11 of *Horst* [1997] gives a signal attenuation of ~5%. This error in the temperature dilution correction due to our set up is within acceptable boundaries. The shrouded set-up is designed to reduce the sensor contamination from rain and heavy sea spray, but the intake is not filtered. As a consequence a larger than expected CO_2–H_2O cross-correlation, which is most likely due to hygroscopic particles on the optical surfaces, was observed also after correcting for the dilution effect. Additional correction was therefore made using the PKT method [*Prytherch et al.*, 2010]. Consistent with subsequent deployments we see an increase in the magnitude of the correction with time, suggesting that contamination is the reason behind the cross-correlation.

3. Results and Discussion

[9] The average EC F_{CO2} calculated from the pre-PKT data is -6.7×10^{-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 (>95%) negative correlation with latent heat flux (F_{H2O}, Figure 2a) which indicates that the PKT correction is warranted. The average post-PKT F_{CO2} is -0.61×10^{-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 *Wanninkhof*'s [1992] k-U_{10N} parameterization (-0.56×10^{-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 (Figure 2b). The post-PKT F_{CO2} is small (Figure 2b), but this is not unexpected given the calm wind conditions (Figure 3). The "flux" measured by the null sensor is on average -8.8×10^{-4} mol m^{-2} day^{-1} with a standard deviation of 0.018 mol m^{-2} day^{-1} (Figure 2c). Removing the null "flux" removes scatter from the sample flux data reducing the standard deviation from 0.23 to 0.11. The difference between flux data before and after removing the null "flux"

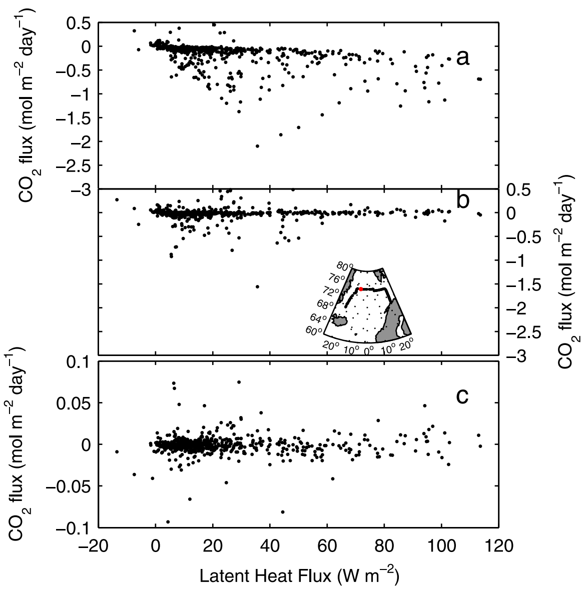

Figure 2. Eddy correlation CO_2 flux as a function of latent heat flux before and after the PKT correction. Two outliers are not shown on plot a (1.7 and −6.3 mol m^{-2} day^{-1}) and one on plot b (−4.8 mol m^{-2} day^{-1}) to avoid the variability appearing smaller. (a) CO_2 flux from the sample LICOR 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 where the red dot indicates 7°W (c) "flux" from the null LICOR. Note that this subplot has a different scale on the y-axis.

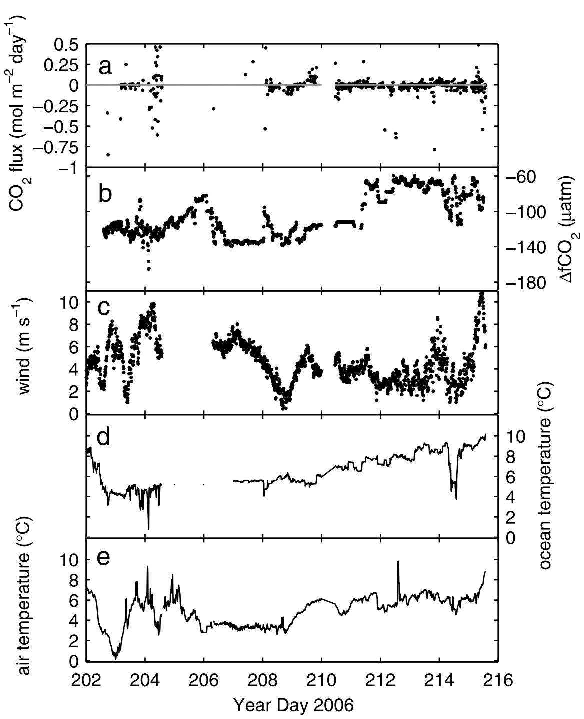

Figure 3. (a) The temporal CO_2 flux with the zero line indicated in grey, (b) the undersaturation (ΔfCO_2), (c) the sonic wind speed, (d) the surface ocean temperature, and (e) the air temperature during the cruise.

was analysed using a one-way ANOVA test and found to be statistically significant with >90% confidence. This shows that even under very calm ocean conditions having a null sensor to remove the bias from motion is valuable.

[10] The ΔfCO_2 was large throughout the cruise but there are two distinct regimes: the cold, fresh Polar waters in the west with on average -119.5 ± 13 (1σ) μatm; and the warmer and more saline Atlantic waters in the east with on average -76.5 ± 12 (1σ) μatm (Figure 3b). This implies a large negative flux of CO_2 into the sea. 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 (1σ) m s^{-1} (Figure 3c). 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.

[11] Transfer velocity (k) was calculated using equation (1) and bin averaged in 2 m s^{-1} U_{10N} intervals (Figure 4). The pre-PKT fluxes yield a very strong non-linear relationship in k-U_{10N}, while the corrected fluxes imply a k-U_{10N} relationship in the same range as established parameterizations. There are, however, significantly higher k at very low wind speeds than has been reported previously, and the two first bin averages in Figure 4 are significantly higher than *Wanninkhof*'s [1992] line (grey). The second is biased high due to three outliers in this data subset, while the first have very low F_{H2O} which could lead to the PKT correction not

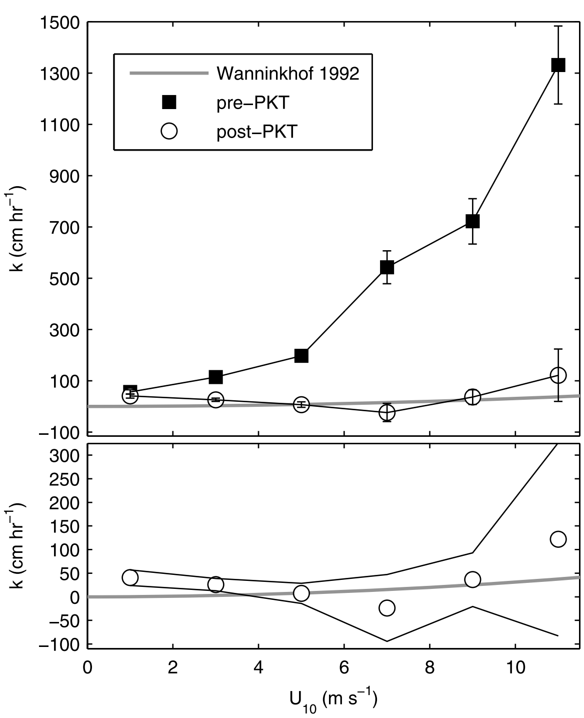

Figure 4. (top) The k bin-averaged in 2 m s^{-1} wind speed intervals plotted against U_{10N}. The number of data points in each bin is 23, 313, 168, 40, 25, and 7 respectively. See the legend for further details. The error bars show the standard error of the mean. (bottom) Close-up of the post-PKT k. The thin black lines show the 95% confidence interval (estimated as plus or minus two times the standard error of the mean).

working optimally [*Prytherch et al.*, 2010]. There is no significant diurnal cycle in the F_{CO2} and the buoyancy fluxes so diurnal processes, like nighttime mixed layer deepening and surface renewal, cannot explain the elevated k at very low wind speeds like it could in the equatorial Pacific [*McGillis et al.*, 2004]. The dramatic increase in the PKT correction with wind speed, which is also seen in unpublished flux data from the Southern Ocean Gas Exchange Experiment, is likely due to there being only a few data points at winds greater than 8 m s^{-1}, which all have significantly higher F_{H2O} than the data at lower winds. This thus leads to the humidity dependent PKT correction being larger. The variability in the corrected data is quite large, 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.

4. Conclusions

[12] Application of the PKT correction method to observations of EC CO_2 flux from the Greenland Sea lowers EC flux data by an order of magnitude, thus making the corrected direct fluxes comparable to bulk fluxes determined using established k-U_{10N} parameterizations, at least within the narrow range of wind speeds we encountered at this cruise. However, the combined high variability and limited range in wind speed means that the results from this data set cannot confirm established 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 cross-correlation. 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. Measurements in fall and winter are obviously needed in order to get a robust estimate of the size of the Greenland Sea carbon sink.

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