Ship-based measurement of air-sea CO₂ exchange by eddy covariance

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A system for the shipboard measurement of air-sea CO₂ fluxes by eddy covariance was developed and tested. The system was designed to reduce two major sources of experimental uncertainty previously reported. First, the correction for in situ water vapor fluctuations (the “Webb” correction) was reduced by 97% by drying the air sample stream. Second, motion sensitivity of the gas analyzer was reduced by using an open-path type sensor that was converted to a closed-path configuration to facilitate drying of the air stream. High-quality CO₂ fluxes were obtained during 429 14 min flux intervals during two cruises in the North Atlantic. The results suggest that the gas analyzer resolved atmospheric CO₂ fluctuations well below its RMS noise level. This noise was uncorrelated with the vertical wind and therefore filtered out by the flux calculation. Using climatological data, we estimate that the techniques reported here could enable high-quality measurements of air-sea CO₂ flux over much of the world oceans.


1. Introduction

The exchange of carbon dioxide across the air-sea interface is an important component of the atmospheric CO₂ budget. Understanding how future changes in climate will affect oceanic uptake and release of CO₂ requires a process-oriented understanding of the factors controlling the air-sea CO₂ flux, Fc. The flux is typically expressed as

\[ F_c = \frac{k}{\alpha} \left( C_w - C_a \right), \]  

where \( C_w \) and \( C_a \) are the bulk seawater and air concentrations, \( \alpha \) is the dimensionless solubility, and \( k \) is the piston velocity or gas transfer coefficient. The piston velocity in equation (1) is typically parameterized on the basis of geochemical tracers such as dual tracer experiments or \(^{14}\)C \([\text{Nightingale et al.}, 2000; \text{Wanninkhof}, 1992]\). Flux measurements using the micrometeorological technique eddy covariance (EC) have also been used to provide a direct measurement of the piston velocity. EC resolves fluxes at spatial (1–10 km) and temporal (1 h) scales well matched to the atmospheric and oceanic forcing of gas exchange. However, few EC-based air-sea CO₂ flux studies have been published due to the difficulty in making these measurements from ships at sea \([\text{McGillis et al.}, 2001, 2004; \text{Kondo and Tsukamoto}, 2007]\). Improvements in the methodology for air-sea CO₂ flux measurements are necessary to reduce uncertainties in air-sea fluxes and to expand the global flux database.

The EC approach involves the measurement of the turbulent CO₂ flux as \( F_c = \rho_a \overline{w} \overline{c} \), where \( \rho_a \) is the dry air density, \( \overline{w} \) is the vertical component of wind velocity, and \( \overline{c} \) is the dry air mixing ratio of CO₂. The primes denote fluctuations about the mean value, sampled fast enough (typically 10 Hz) to capture the smallest flux-carrying atmospheric eddies, and the averaging interval for the covariance is long enough (typically 15–60 min) to include the large-scale atmospheric eddies contributing to the turbulent flux \([\text{Kaimal and Finnigan}, 1994]\). Early EC measurements of air-sea CO₂ flux in coastal environments yielded fluxes that were unrealistically high relative to estimates based on the global \(^{14}\)C budget or deliberate tracer experiments \([\text{Smith and Jones}, 1985, 1986; \text{Broecker et al.}, 1986]\). Subsequently, McGillis et al. \([2001]\) reported ship-based EC CO₂ fluxes in general agreement with tracer techniques. Their methodology overcame many of the challenges in making EC measurements at sea, including motion effects on the wind vector \([\text{Edson et al.}, 1998]\).

McGillis et al. \([2001]\) also quantified two major sources of uncertainty in the measurement of CO₂ fluxes over the ocean. In situ water vapor fluctuations (the “Webb” correction \([\text{Webb et al.}, 1980]\)) required a correction that averaged 45% of the true CO₂ flux, and motion sensitivity of the CO₂ signal from a commercially available closed-path InfraRed Gas Analyzer (IRGA, LI6262, LiCor Inc.) required a correction that averaged 30% of the true CO₂ flux.

This paper describes the design and operational characteristics of a system for shipboard measurements of air-sea CO₂ flux by eddy covariance. An effort was made to minimize the two major sources of uncertainty identified by McGillis et al. \([2001]\). CO₂ flux data from two cruises in the North Atlantic are presented to demonstrate system performance under field conditions. We then combine our results with climatological data to estimate the fraction of the global ocean that is amenable to direct air-sea CO₂ flux measurements.
measurements using these techniques. Comparison of piston velocities for CO₂ and dimethylsulfide measured in situ during these cruises were reported in a previous paper [Miller et al., 2009].

2. Methods

The measurements were made during two cruises on the research vessel R/V Knorr in the summer of 2007. The first cruise (Knorr-07a) was from Bridgetown, Barbados (13°06′N, 59°37′W) to Reykjavik, Iceland (64°10′N, 21°57′W) and lasted 14 days (29 May to 9 June). The second cruise (Knorr-07b) was from Reykjavik to Woods Hole, MA (41.52°N, −70.66°W) and lasted 10 days (17–26 July).

2.1. Wind Vector

Sensors were mounted at the foremost location on the Knorr’s 8 m tall bow mast (Figures 1 and 2). The wind vector was measured using two 3-axis ultrasonic (sonic) anemometers (CSAT3, Campbell Scientific, Logan, UT) approximately 6 m above Knorr’s main deck and 14 m above the mean ocean surface. The two sonic anemometers were located 2 m forward of the bow mast, and separated horizontally by 1 m, one sensor portside of the mast and the other starboard. An inertial motion sensor (MotionPak 2, Systron Donner, Walnut Creek, CA) measured linear accelerations and angular rates along 3 orthogonal axes. The motion sensor was located between and slightly aft of the sonic anemometers, 0.75 m from their measurement volumes, and the orientation of anemometers relative to the motion sensor was fixed. A GPS receiver (GPS 16, Garmin International, Olathe, KS) provided ship speed and heading.

2.2. Atmospheric CO₂ and H₂O

Commercially available IRGAs include “open-path” and “closed-path” configurations. The open-path style sensor has its measurement volume exposed to the atmosphere, and is mounted next to the sonic anemometer. Closed-path sensors are located separately from the sonic

Figure 1. R/V Knorr. Anemometers, the motion sensor, GPS, and gas inlets were mounted to the bow mast (inset), approximately 14 m above the ocean surface. Gas analyzers were located in the bosun’s locker, directly below the mast.

Figure 2. Bosun locker layout of the system to measure CO₂ flux, where “MFC” is mass flow controller and “P” is pressure sensor. The CO₂ IRGA was an open-path-style sensor (LI7500, LiCor, Inc.) that was converted to a closed-path sensor. A custom-made aluminum cradle was used for rigidity (inset photo).
anemometer and sample air is drawn by a pump from an air inlet collocated with the sonic anemometer. The flow of the air sample through the tubing results in a time delay between its entrance to the inlet and its sampling by the IRGA, and also to degradation of the turbulent fluctuations due to interactions between the air stream and the walls of the tubing. Many studies have examined these effects [e.g., Leuning and Judd, 1996]. Over the ocean, the main advantage of open-path systems, the absence of tubing-related signal degradation, is overshadowed by the necessity of large corrections for the effects of sensible and latent heat flux (or “Webb” corrections, discussed in detail in section 2.4.1). The Webb correction for water vapor (i.e., latent heat) flux was found by McGillis et al. [2001] to be 45% of the true CO2 flux during their study. More practically, the performance of open-path sensors exposed to the marine atmosphere can degrade quickly (over a period of hours) due to the accumulation of salt spray on the sensor windows.

Closed-path sensors can be configured to minimize the effects of the Webb corrections (discussed in detail in section 2.4.1), and methods exist to correct for signal degradation due to flow through the sample tube [Leuning and Moncrieff, 1990; Massman, 2000]. However, the CO2 signal returned by closed-path sensors has been found to be sensitive to platform motion. McGillis et al. [2001] found that this contamination resulted in a CO2 flux bias that was 30% of the true CO2 flux. The approach used in this study was to combine the advantages of the two sensor styles by converting an open-path sensor (less sensitive to motion errors) to a closed-path configuration (reducing the Webb corrections and data loss due to fouling of sensor windows by sea spray).

Air sampled at the bow mast inlet was analyzed using two fast-response IRGAs plumbed in series (Figure 2) and located in the bosun locker directly below the bow mast (Figures 1 and 2). The “H2O IRGA” (LI7000, LiCor Inc.) was used to calculate the water vapor flux, and the “CO2 IRGA” (LI7500, LiCor, Inc.) was used to calculate the CO2 flux. The H2O IRGA was a closed-path style sensor, while the CO2 IRGA was an open-path style sensor that was converted to a closed-path configuration by inserting a cylindrical glass cell (12.5 cm long, 1.6 cm internal diameter (I.D.), volume 0.025 L) into the optical path. The instrument “head” was rigidly supported by a custom-made aluminum mount (Figure 2). Air was drawn to the IRGAs at 16–18 slpm from a filtered inlet (90 mm diameter, 1 micron) centered between the sonic anemometers. The air was drawn through 14 m of 5.9 mm I.D. polyethylene-lined Dekabon 1300 tubing (Saint Gobain, Garden Grove, CA). The travel time of air in the tubing was approximately 1.2 s, determined empirically both by adding a standard gas step response CO2 concentration change at the inlet and by finding the maximum correlation between sonic anemometer temperature and CO2 concentration in the IRGA cell. The flushing time for the measurement volume of each of the sensors was less than 0.1 s.

2.3. Calculation of Turbulent Fluxes

Turbulent air-sea fluxes of momentum, heat, and CO2 were calculated according to

\[ \tau_x = -\frac{p}{\rho_a} \overline{w'\tau'} \],

\[ H = \frac{p}{\rho_a} cp' \overline{w'T'} \],

\[ L = \frac{p}{\rho_a} L \overline{w'Q'} \],

\[ F_c = \frac{p}{\rho_a} \overline{w'c'} \],

where \( \tau_x \) is the momentum flux in the along-wind (x) direction, \( u \) is the along-wind component of wind velocity, \( H \) is sensible heat flux, \( L \) is latent heat flux, \( cp \) is specific heat capacity of air, \( T \) is dry air temperature, \( L \) is latent heat of vaporization, and \( q \) is specific humidity.

2.4. CO2 Flux Corrections

2.4.1. Density Correction

The CO2 flux is defined in terms of CO2 mixing ratio \( c \) (equation (5)). The IRGAs do not measure CO2 mixing ratio, rather they measure the CO2 molar density \( (\rho_c) \) between the source and detector. In addition to changes in the CO2 mixing ratio, changes in air density due to water vapor, temperature, and pressure will affect the measured molar density. To extract the CO2 fluctuations and flux, this “contamination” requires a correction (the Webb correction) to remove the portion of the measured CO2 molar density caused by the background air density fluctuations. The correction is given by

\[ F_c = \frac{p}{\rho_a} \overline{w'c'} + (1 + \mu \sigma) \frac{p}{T} \overline{w'T'} + \mu \frac{p}{\rho_a} \overline{w'p'c'} + (1 + \mu \sigma) \frac{p}{P} \overline{w'P'}, \]

where \( \rho_c \) is the molar density of H2O, \( \sigma = \rho_c / \rho_a \), \( \mu = M_a / M_o \), \( M \) is molecular weight, subscripts “a” and “w” refer to dry air and water vapor, respectively, and \( P \) is pressure [Webb et al., 1980]. The first term on the right hand side (rhs) of equation (6) is the uncorrected CO2 flux, and the second, third, and fourth terms are the Webb corrections for temperature, water vapor, and pressure fluctuations in the IRGA cell, respectively. For closed-path systems, temperature fluctuations are eliminated by heat exchange as the air sample travels through the inlet tubing, and therefore the second term on rhs of equation (6) is negligible. This was confirmed by laboratory tests using the same tubing and flow configuration as the Knoor-07 cruises (data not shown). Air density fluctuations due to turbulent pressure fluctuations are also routinely assumed to be negligible [Webb et al., 1980]; however, they are retained here to account for
hydrostatic pressure fluctuations due to ship heave (discussed in section 2.4.2).

The Webb correction for water vapor (i.e., latent heat) flux was found by McGillis et al. [2001] to be 45% of the true CO2 flux. In this study, the CO2 flux contamination due to water vapor fluctuations was treated differently than McGillis et al. [2001] in two ways. First, instead of measuring the water vapor flux and making a large correction to the CO2 flux according to equation (6), a Nafion multitube membrane drier (PD-200T, PermaPure) with a dry air counter flow was used to remove water vapor fluctuations in the CO2 IRGA cell (Figure 2). The reduction of the water vapor flux reduced the associated Webb correction, the third term on the rhs of equation (6). The performance of the Nafion tubing was tested in the laboratory, as shown by the time series and spectra of CO2, H2O, and pressure fluctuations in Figure 3. The Nafion had negligible impact on CO2 (Figures 3a and 3d) and pressure (Figures 3c and 3f) fluctuations while dramatically reducing the water vapor fluctuations (Figures 3b and 3e). The elimination of water vapor fluctuations markedly reduced the Webb correction (see section 3). The combination of the Nafion with the elimination of temperature fluctuations in the tubing therefore provides significant advantages relative to open-path sensors or closed-path sensors with an undried air stream.

The second difference in our approach was to apply the Webb correction for residual water vapor and temperature fluctuations on a sample-by-sample (10 Hz) basis, rather than use the averaged fluxes according to equation (6). The advantage of the sample-by-sample correction is that a time series of the CO2 mixing ratio is obtained, which can be used to calculate turbulence statistics and spectra. Because of the Webb contamination, statistics and spectra based on CO2 density (not mixing ratio) are coupled with water vapor and temperature statistics and spectra [Iwata et al., 2005]. The sample-by-sample Webb correction was calculated by applying the Ideal Gas Law according to

\[
c = \left( \frac{\rho_s}{\rho_a} \right) M_a / M_c; \tag{7}\]

\[
\rho_a = P_a / R T; \tag{8}\]

\[
P_a = P - P_v; \tag{9}\]

\[
P_v = \rho_v R T, \tag{10}\]

where the density of CO2 and H2O molecules (\(\rho_c\) and \(\rho_v\)) between the source and detector were measured by the IRGA, \(R\) is the gas constant, and \(P_a\) and \(P_v\) are the partial pressures of dry air and water vapor. Field data have shown the corrected CO2 fluxes using the conventional method (equation (6)) and the sample-by-sample approach (equations (7)–(10)) to be equivalent [Miller et al., 2004].

2.4.2. Ship Heave Effects on CO2 Measurement

Air density fluctuations due to turbulent pressure fluctuations in the IRGA cell are routinely assumed negligible; however, nonturbulent pressure fluctuations can be important on a moving ship. Ship heave motions can induce vertical displacements of order 10 m during high seas, giving rise to pressure fluctuations on the order of 1 mbar. For a background CO2 mixing ratio of 380 ppm, this corresponds to an apparent CO2 fluctuation of 0.4 ppm, which is similar to or larger than the true atmospheric fluctuations in CO2. In this study, pressure in the CO2 IRGA cell was measured with a high resolution (0.03 mbar), fast-response (50 Hz) pressure sensor capable of resolving the hydrostatic fluctuations due to ship heave (Model 6110,
2.4.3. IRGA Motion-Induced Errors

[17] In addition to the effect of pressure on air density, the accelerations caused by ship motion result in spurious CO2 signals in closed-path IRGAs (LI6262 and LI7000, LiCor Inc.). McGillis et al. [2001] found that this contamination resulted in a CO2 flux bias that was 30% of the true CO2 flux. The underlying cause of this motion sensitivity is not known, but the behavior is easily replicated. Laboratory experimentation ruled out some potential causes of this behavior including flexing of the optical bench, variations in detector background due to changes in heat transfer associated with changes in orientation, and inertial changes in the rotational speed of the optical chopper. It thus appears likely that the sensitivity arises in the instrument source, as a flexing of the source filament.

[18] The open-path IRGA (LI7500) exhibits much less motion sensitivity than the closed-path sensors (Figure 5). For this reason, only data from the open-path sensor (CO2 IRGA) were used to compute air-sea CO2 fluxes. Note that the open-path sensor was converted to a closed-path configuration for this study, as described above. The open-path sensor was not entirely free of motion sensitivity. After correction for the hydrostatic pressure effect described above, a small residual motion-induced signal ($x_{c,mot}$) was found in the converted open-path CO2 channel. This signal was quantified by a linear regression of the CO2 signal against the six components of measured platform motion (3 angle rates and 3 linear accelerations) for each flux interval as

$$x_{c,mot} = B_1 a_x + B_2 a_y + B_3 a_z + B_4 r_x + B_5 r_y + B_6 r_z,$$

where ($a_x, a_y, a_z$) are the 3 linear accelerations and ($r_x, r_y, r_z$) the three angle rates. The motion-related component was...
Temperature and CO2 flux are shown in Figure 6, nor-
subtracted from the CO2 signal. An example of the motion
sensible heat (\(wT\), solid curve) and carbon dioxide (\(wc\),
dashed curve) measured during the Knorr-07b cruise. Each
ogive is the average of 109 13.7 min flux intervals for
unstable and neutrally stable atmospheric conditions that
were subjectively determined to have high-quality flux
cospectra. The line at \(Og_{wc}(f) = 0.5\) (thin solid curve) was
used to calculate a correction for the loss of CO2 fluctuations
(and flux) in the sample tube.

Figure 6. Normalized ogives corresponding to fluxes of
sensible heat (\(wT\), solid curve) and carbon dioxide (\(wc\),
dashed curve) measured during the Knorr-07b cruise. Each
ogive is the average of 109 13.7 min flux intervals for
unstable and neutrally stable atmospheric conditions that
were subjectively determined to have high-quality flux
cospectra. The line at \(Og_{wc}(f) = 0.5\) (thin solid curve) was
used to calculate a correction for the loss of CO2 fluctuations
and flux, which results in a relative shift in flux-carrying
eddies toward lower frequencies. The high-frequency
correction was applied for each flux interval by locating
a cutoff frequency \(f_c\) at which one half of the \(wT\) covariance
was accumulated, \(Og_{wt}(f_c)/wT^2 = 0.5\) (Figure 6), and
assuming that eddies with frequency greater than \(f_c\) made
the same relative contribution (50%) to the CO2 flux. The
corrected CO2 flux was calculated as \(wT^2 corr = 2 Og_{wc}(f_c)\).
The results of this correction procedure were not sensitive to
the selection of the cutoff frequency. The average variation
in the CO2 flux was only 3% when accumulated flux fractions ranging from 0.4 to 0.7 were used.

2.4.4. Loss of High-Frequency Fluctuations

A key challenge associated with the measurement of
air-sea CO2 flux is that the turbulent CO2 fluctuations over
the ocean are small compared to the noise level of commercial
available sensors. Scalar spectral energy densities in the atmospheric surface layer decrease with increasing
frequency, \(f\), according to \(f^{-5/3}\), such that higher-frequency
fluctuations are harder to detect than those at lower frequency.
High-frequency fluctuations are also damped as the sample air passes through the inlet tubing to the gas analyzer [Lenschow and Raupach, 1991]. The turbulent eddies corresponding to these scalar fluctuations may therefore not be represented in the calculated flux covariance, and fluxes are underestimated as a result. Tubing losses can be minimized by using short tubing runs and maintaining turbulent airflow in the sample tube, and methods for correcting for flux loss have been developed [Leuning and Moncrieff, 1990].

We addressed high-frequency losses using an ogive method [Marandino et al., 2007]. Similar to other methods for correcting high-frequency loss [e.g., Moore, 1986], the ogive method assumes similarity between the transport of sensible heat and CO2 in the surface layer. The scalar flux ogives were calculated as \(Og_{wT}(f) = \int_0^L C0_{wT}(f') df'\), where \(C0_{wT}\) is the cospectrum. Average ogives for sonic temperature and CO2 flux are shown in Figure 6, normalized by their respective flux covariances. The normalized ogives reveal the distribution of atmospheric eddies that contributed to the measured covariance or flux. Compared with the \(wT\) ogive, assumed to have no high-frequency loss, the ogive for \(wc\) appeared shifted toward lower frequency in Figure 6. This shift is consistent with the loss of high-frequency CO2 fluctuations and flux, which results in a relative shift in flux-carrying eddies toward lower frequencies. The high-frequency correction was applied for each flux interval by locating a cutoff frequency \(f_c\) at which one half of the \(wT\) covariance was accumulated, \(Og_{wt}(f_c)/wT^2 = 0.5\) (Figure 6), and assuming that eddies with frequency greater than \(f_c\) made the same relative contribution (50%) to the CO2 flux. The corrected CO2 flux was calculated as \(wT^2 corr = 2 Og_{wc}(f_c)\). The results of this correction procedure were not sensitive to the selection of the cutoff frequency. The average variation in the CO2 flux was only 3% when accumulated flux fractions ranging from 0.4 to 0.7 were used.

2.5. Effects of Flow Distortion

There is no generally accepted method for modeling or correcting for the effects of flow distortion. Studies have demonstrated that the effect of flow distortion on scalar fluxes is small compared to the momentum fluxes. Pedreros et al. [2003] found that ‘‘the results for heat flux do not appear to be contaminated by turbulent flow distortion.’’ Since CO2 is a scalar, it is likely that flow distortion effects on the CO2 flux would be similar to the heat flux contamination (very small), rather than the momentum flux contamination. Yelland et al. [2002] modeled flow distortion about the R/V Knorr, and found that effects at the bow mast were relatively small (about 2% acceleration). The resulting uncertainty is small compared with other sources of uncertainty in our measurements.

The methodology used in all previous air-sea gas flux measurements has been to limit the range of relative wind directions. In our analysis, we followed this same approach. The relative wind direction criteria used by McGillis et al. [2001] was ±60 degrees of the bow, while Blomquist et al. [2006] used ±120 degrees, and Marandino et al. [2007] used ±60 degrees. We used a 60 degree criterion for the quadrant in which the other sonic anemometer is mounted, and a 90 degree criterion in the quadrant that has no obstruction from other sensors. Our range of wind directions lies within the range of the previous studies.

2.6. Seawater pCO2

The CO2 concentration in seawater was measured continuously in the ship’s wet laboratory using two separate equilibrator systems. In each system, air was equilibrated with seawater from the ship’s uncontaminated seawater supply, and recirculated in a closed loop through an IRGA. The first system used a membrane-based gas/liquid contactor (LiquiCell X40) with an LI7000 closed-path IRGA (LiCor, Inc.). This equilibrator was deployed during both Knorr-07a and Knorr-07b cruises. The second system was a homemade showerhead-type equilibrator and an LI820 closed-path IRGA (LiCor, Inc.). This equilibrator was deployed only during the Knorr-07b cruise. Seawater pCO2 measured by the two systems showed excellent agreement (linear regression slope 1.02, \(r^2 = 0.99\)).

2.7. Data Processing and Quality Control

Turbulence data from the sonic anemometer, motion sensor, and CO2 and H2O IRGAs in the bosun locker were sampled at 10 Hz and archived in 1 h data files. The data processing steps are summarized in Figure 7. The measured...
The wind vector was corrected for platform motion using the motion signals and GPS data following Miller et al. [2008]. The IRGA signals were time shifted to account for the 1.2 s travel time in the sample tube. The first and last 160 s of the 1 h time series were removed to eliminate edge effects of digital filters used for the platform motion corrections. The remaining 55 min time series was divided into four 13.7 min subintervals (8192 10 Hz samples) for calculating fluxes. For each subinterval, the wind vector was rotated into a ‘natural’ coordinate frame, with a nonzero along-wind component and zero-mean cross-wind and vertical velocity components. The corrected winds and scalars were used to calculate the turbulent fluxes according to equations (2)–(5), and the H2O and CO2 fluxes were corrected for high-frequency flux losses as described previously.

3. Results and Discussion

A total of 526 h of data were collected, including 326 h during Knorr-07a and 200 h during Knorr-07b. Since each hour was divided into four subintervals, there were a total of 2104 flux intervals. The results of the quality control tests are summarized in Table 1. For the combined data set, 429 of the intervals (20%) passed objective quality tests related to the turbulent flux measurement (system up and sampling, sufficient pump flow, no instrument spikes, acceptable wind direction, and stationarity), with a high percentage (65%) of the intervals failing the stationarity test. Fewer intervals (9%) passed subjective inspection of the flux cospectra, and only 73 intervals passed both the objective and subjective quality tests. The fact that many intervals failed the stationarity test (Table 1) was surprising.
since the flux interval length of 14 min was relatively short. This was potentially due to small background changes in CO2 concentration (heterogeneity), or due to low-frequency sensor drift.

### 3.1. Meteorology and Heat Fluxes

[28] Wind speed at 10 m height was low to moderate throughout the Knorr-07 cruises, averaging 6 m s⁻¹ for Knorr-07a and 7 m s⁻¹ for Knorr-07b (range of 1–15 m s⁻¹, Figure 8a). During Knorr-07a, south of 45°N, sea surface temperature (SST) was higher than air temperature (Figure 8b), with upward sensible and latent heat fluxes (Figure 8c). For this cruise, the atmosphere was unstable (\(z/L < -0.07\)) for 64% of intervals, stable (\(z/L > 0.07\)) for 4% of intervals, and neutral for 32% of intervals. During Knorr-07b, the average air temperature was warmer than SST, with negative (downward) sensible and latent heat fluxes (average \(-24\) and \(-7\) W m⁻², respectively, Figure 8c). For this cruise, the atmosphere was unstable for 17% of intervals, stable for 40% of intervals, and neutral for 43% of intervals. Fog conditions during stable periods resulted in higher rates of data loss, presumably due to condensation in the sample lines. For each flux interval, the correlation between the sonic temperature and the H₂O IRGA water vapor signal was examined for a range of sample shifts to determine the tubing delay. During unstable conditions the relationship showed a clear maximum which was used as an empirical estimate of the tubing delay. During stable conditions, there was frequently no clear maximum in the correlation, which we believe was due to condensation in the sample lines, as the stable conditions often corresponded to the presence of fog.

### 3.2. Air and Seawater pCO₂

[29] Atmospheric pCO₂ was relatively constant during each cruise, 387 ± 4 ppm for Knorr-07a and 377 ± 4 ppm for Knorr-07b (Figure 8d). Sea surface pCO₂ was mostly undersaturated with respect to the atmosphere. This was presumably a result of biological production, as chlorophyll levels were relatively high (Figure 8d). During the last part of Knorr-07b, along the North American continental shelf, seawater pCO₂ was supersaturated with respect to atmospheric levels (Figure 8d). The mean water-air pCO₂ difference was \(-49 ± 22\) ppm during undersaturated periods north of 39°N, and 43 ± 28 ppm in the supersaturated region. Overall, less than half (46%) of the intervals had an air-sea pCO₂ difference greater than 40 ppm (Table 1).

### 3.3. Atmospheric CO₂ Fluctuations

[30] The standard deviation of CO₂ fluctuations (\(\sigma_u\)) measured by the CO₂ IRGA during Knorr-07b was \(~0.13\) ppm, comparable to the manufacturer’s root-mean square (RMS) noise specification of 0.11 ppm for 10 Hz sample rate (Figure 9). However, atmospheric CO₂ fluctuations were expected to be much smaller. An estimate of the expected \(\sigma_u\) was obtained using a simple neutral surface layer scaling, \(F_c = C_1 \sigma_u \sigma_w\) with \(C_1 = 0.4\), analogous to relationships used for other scalers [Stull, 1988]. For this estimate, the CO₂ flux \(F_c\) was calculated according to equation (1), using the parameterization of Wanninkhof [1992] to estimate the piston velocity, and the Knorr-07b measured air-sea pCO₂ difference, wind speed, and standard deviation of vertical wind, \(\sigma_w\) (Figure 9). This calculation suggests much smaller CO₂ fluctuations (\(\sigma_u ~ 0.05\) ppm or less, open circles) than those measured (open squares). The difference between the measured and expected \(\sigma_u\) magnitude and the similarity between the measured \(\sigma_u\) and the manufacturer’s noise specification suggests that the sample-to-sample CO₂ fluctuations mostly reflected the sensor noise and not the true atmospheric CO₂ fluctuations.

[31] The sensor noise levels shown in Figure 9 were also found in the CO₂ power spectra. Measured CO₂ and H₂O power spectral densities (\(Sₜ(f)\)) are shown in Figure 10, along with theoretical-empirical surface-layer relationships (“Kaimal” spectra) calculated as \(fSₜ(f) = \alpha_s^2 \gamma_a \gamma_w (2\pi K)^{2/3} \phi_z^{-1/3} \phi_\alpha(fz/\tilde{U})^{-2/3}\). Here \(f\) is frequency, \(\alpha_s = -w\alpha^3/\mu_a\) is the turbulent CO₂ or H₂O scale, \(\gamma_a\) is a constant (assumed 0.8), \(K\) is the von Karman constant (0.4), \(\phi_z = (1 + 0.5|z/L|^{2/3})^{-3/2}\) and \(\phi_\alpha = (1 + 16|z/L|)^{-1/2}\) are the stability functions for dissipation and heat flux, and \(\tilde{U}\) is the mean wind speed [Kaimal et al., 1972]. The Knorr-07b measurements of \(\tilde{U}, u_w, \tilde{w}_q,\) and \(z/L\) were used to calculate the Kaimal spectra. The turbulent CO₂ scale \(\alpha_s\) was estimated from the CO₂ flux calculated from equation (1). The measured water vapor power spectrum shape and magnitude were similar to the Kaimal spectrum between \(~0.02–0.2\) Hz (Figure 10a). In contrast, the measured CO₂ power spectrum was several times larger than the Kaimal spectrum (Figure 10b). At frequencies larger than 0.1 Hz, the measured CO₂ power spectra increased, whereas the Kaimal spectrum decreased. The behavior of the CO₂ spectrum is consistent with a noise-

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<th>Table 1. CO₂ Flux Quality Control</th>
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<td><strong>Knorr-07a</strong></td>
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<td>Barbados–Iceland</td>
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<td>Days at sea</td>
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<td>13.7 min flux intervals</td>
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<td>Objective quality controls intervals passed</td>
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dominated signal at frequencies above 0.1 Hz. At frequencies less than 0.1 Hz, neither the CO2 nor H2O power spectrum showed inertial range behavior (Figure 10b).

To resolve CO2 fluxes, the IRGA must therefore be capable of measuring CO2 fluctuations much smaller than the sensor’s RMS noise specification. The covariance (cospectra) between CO2 and vertical wind used to calculate fluxes (flux cospectra) served as a noise filter since the CO2 signal noise was uncorrelated with w. This is demonstrated by the wc and wT cospectra (Figure 11). Except for frequencies above 1 Hz where the CO2 flux was attenuated by tubing loss, the wc and wT cospectra were similar. The wc and wT cospectral shapes were also similar to the Kaimal cospectra (note: the Kaimal cospectra in Figure 11 are for neutral stability, and were not frequency-shifted to account for stability effects). These cospectra indicate that the true atmospheric CO2 fluctuations were detected by the CO2 IRGA, even though they were masked by instrumental noise.

Figure 8. Summary of Knorr-07 cruises. (left) Latitude increasing: Bridgetown, Barbados, to Reykjavik, Iceland (29 May to 9 June). (right) Latitude decreasing: Reykjavik, Iceland, to Woods Hole, Massachusetts (17–26 July). (a) Wind speed at 10 m height (m s\(^{-1}\)); (b) SST (°C, solid curve) and air temperature (°C, dashed curve); (c) sensible heat flux (solid curve), latent heat flux (dashed curve), and effective latent heat flux measured by the CO2 IRGA downstream of the Nafion drier (dotted curve); (d) air (solid thick curve) and seawater (dashed curve) pCO2 (ppm), and MODIS chlorophyll (mg m\(^{-3}\), solid thin curve) plotted on a reverse axis using (left) the 17 May to 17 June 2007 image and (right) the July 2007 monthly image; and (e) air-sea flux of CO2 (mol CO2 m\(^{-2}\) yr\(^{-1}\), triangles) along with CO2 flux estimated using equation (1) and the parameterization of Wanninkhof [1992] (solid curve). Also shown is the CO2 flux along the cruise track from the climatology of Takahashi et al. [1997] (thick dashed curve).
The wc cospectra provide strong evidence that air-sea CO2 fluxes were resolved in our measurements. The similarity between the wc and wT cospectra was not an artifact of the Webb correction for water vapor since the sample stream was dried and the wq cospectrum of the dried air stream was essentially zero (Figure 11b, dash-dotted curve). Similarly, our laboratory tests (not shown) and similar tests by LiCor (George Burba, personal communication, 2009) indicate that even short runs (2 m) of tubing are sufficient to eliminate temperature fluctuations at the IRGA, provided the tubing walls are conductive (we used aluminum-lined tubing). Furthermore, Figures 3c and 3f show that pressure fluctuations were largely unaffected by the Nafion tubing bundle. The similarity between the wc cospectrum and both the measured wT cospectrum and the theoretical-empirical surface layer cospectrum supports that the true CO2 flux was resolved by the system.

These results suggest that the IRGA was capable of resolving CO2 fluctuations in the atmosphere below its RMS noise level. The CO2 signal quantization associated with the analog-to-digital (A/D) conversion of the detector output provides a lower limit (i.e., best-case scenario) of the IRGA resolution. The sensor uses a 16-bit A/D converter, and the CO2 signal is oversampled and averaged, providing an effective A/D resolution of 19 bits at 10 Hz (G. Burba, personal communication, 2009). For the CO2 absorbance range of the LI7500, this yields a resolution of approximately 0.003 ppm. This limit is indicated in Figures 9 and 10 (horizontal dash-dotted curves). Assuming this limit represents the effective CO2 resolution, Figures 9 and 10
suggest that the IRGA is capable of measuring fluxes over most of the conditions encountered during the Knorr-07 cruises. This reasoning assumes that all sources of sensor noise (due to temperature sensitivity, drift, etc.) are uncorrelated with the vertical wind. The true effective sensor resolution to CO2 fluctuations presumably lies somewhere between the sensor’s RMS noise level and the A/D resolution (i.e., between the dashed and dash-dotted curves in Figures 5 and 6).

3.4. Air-Sea CO2 Flux

[35] The turbulent CO2 fluxes calculated using the portside and starboard side sonic anemometers showed good agreement. A linear regression of the fluxes calculated using the two anemometers was 0.93, and the r² statistic was 0.87. The CO2 flux during the Knorr-07 cruises was generally from the atmosphere to the ocean (negative), consistent with the water-air partial pressure difference (Figures 8d and 8e). The flux magnitude increased with wind speed (Figure 12a), and was in broad agreement with the gas exchange parameterization of Wanninkhof [1992] (Figure 8e). The average air-to-sea CO2 flux of the 429 intervals that passed quality control was $-3.1 \pm 0.1$ mol CO2 m⁻² yr⁻¹. For comparison, the CO2 flux along the Knorr-07 cruise tracks was extracted from the monthly CO2 flux climatology of Takahashi et al. [1997], using the month of June for Knorr-07a and July for Knorr-07b (Figure 8e, dashed curve). For both cruises, the mean CO2 flux from the climatology was $-2.3$ mol CO2 m⁻² yr⁻¹. Some features of the climatology were seen in the measured and calculated fluxes. During Knorr-07a, both the climatology and calculated CO2 flux showed a marked transition from near-zero to higher (negative) fluxes between 38 and 40°N (Figure 8e). During Knorr-07b, the climatology and calculated fluxes showed a change from CO2 uptake to emission as the ship crossed into waters along the North American continental shelf.

[36] The removal of water vapor fluctuations in the CO2 IRGA sample cell with the Nafion drier almost completely eliminated the Webb correction. The average latent heat flux magnitude measured by the H₂O IRGA upstream of the Nafion drier was 48 Wm⁻². In contrast, the average latent heat flux magnitude measured by the CO2 IRGA downstream of the Nafion drier was only 1.2 Wm⁻² (e.g., Figure 8c). The use of the drier therefore resulted in a 97% reduction in both the latent heat flux and the Webb correction for water vapor, which scales linearly with latent heat flux (equation (6) and Figure 12b). The average Webb correction to the CO2 flux for the undried air stream was 13 mol CO2 m⁻² yr⁻¹, more than 4 times the average CO2 flux magnitude. In contrast, the Webb correction for the dried air stream measured by the CO2 IRGA averaged only 0.26 mol CO2 m⁻² yr⁻¹, or 8% of the average CO2 flux.

[37] The correction for the loss of high-frequency flux due to tubing attenuation was small and, as expected, increased the magnitude of the flux (Figure 13). In contrast, the motion contamination of the wind vector and the sensitivity of the IRGA CO2 channel to platform motion were large, and their impacts differed between the two Knorr-07 cruises. The motion contamination of the wind vector resulted in more positive CO2 fluxes for both cruises, and its magnitude was large enough to change the sign of the measured flux during Knorr-07a. The motion sensitivity of the IRGA resulted in a more negative CO2 flux during Knorr-07a and a more positive CO2 flux during Knorr-07b. We did not find a simple relationship between the size and

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**Figure 12.** (a) CO2 flux (mol CO2 m⁻² yr⁻¹) versus 10 m wind speed (m s⁻¹) measured on Knorr-07 cruises. All of the points passed objective quality control tests, and solid circles indicate intervals that also passed subjective inspection of cospectra. (b) Histogram of the Webb correction term (mol CO2 m⁻² yr⁻¹) for CO2 flux due to the latent heat flux for the dried sample air stream (dashed curve), and which would have been necessary if the sample air stream had not been dried (solid curve).

**Figure 13.** Bin-averaged CO2 flux (mol CO2 m⁻² yr⁻¹) versus 10 m wind speed (m s⁻¹) showing the impact of different flux corrections for (a) Knorr-07a and (b) Knorr-07b: corrected fluxes (thick solid curve), without high-frequency correction (thin solid curve), without vertical wind correction for platform motion (dotted curve), and without motion regression applied to open-path IRGA (dashed curve). Error bars are standard error.
The CO2 fluxes measured during the Knorr-07 cruises are compared with estimates calculated using equation (1) for different atmospheric stabilities in Figure 14. The difference between the measured and calculated fluxes exhibited atmospheric stability-dependent behavior. During unstable conditions, the measured and calculated fluxes showed good agreement (Figure 14, top). Neutrally stable cases showed good agreement for flux magnitudes less than 5 mol CO2 m⁻² yr⁻¹; but, for higher flux magnitudes, the measured fluxes were less than calculated fluxes (Figure 14, middle). For stable atmospheric conditions, the magnitude of the measured fluxes was lower than the computed fluxes (Figure 14, bottom). During stable conditions and during high winds, the proportion of the turbulent flux at high frequency increases. The underestimation of the measured flux during these conditions could therefore have resulted from high-frequency losses that were not adequately corrected by the procedure described previously. Further measurements are needed to assess the system performance during stable atmospheric conditions.

### 3.5. Piston Velocity

The measured CO2 flux and air-sea pCO2 difference were used to calculate the piston velocity according to equation (1). The CO2 fluxes measured during the Knorr-07 cruises are compared with estimates calculated using equation (1) for different atmospheric stabilities in Figure 14. The difference between the measured and calculated fluxes exhibited atmospheric stability-dependent behavior. During unstable conditions, the measured and calculated fluxes showed good agreement (Figure 14, top). Neutrally stable cases showed good agreement for flux magnitudes less than 5 mol CO2 m⁻² yr⁻¹; but, for higher flux magnitudes, the measured fluxes were less than calculated fluxes (Figure 14, middle). For stable atmospheric conditions, the magnitude of the measured fluxes was lower than the computed fluxes (Figure 14, bottom). During stable conditions and during high winds, the proportion of the turbulent flux at high frequency increases. The underestimation of the measured flux during these conditions could therefore have resulted from high-frequency losses that were not adequately corrected by the procedure described previously. Further measurements are needed to assess the system performance during stable atmospheric conditions.

### 3.6. Global Estimate of the CO2 Flux Measurement Capability by Eddy Covariance

The approach taken in this study, primarily the reduction in Webb correction by drying the air stream, resulted in a significant improvement in the signal-to-noise ratio of the air-sea CO2 flux measurement. This improve-
heat flux climatology, assuming a closed-path CO2 flux correction "climatology" was calculated from the latent resolution and averaged to a monthly time step. A Webb ties. For the undried sample stream, the correction was larger than the climatological CO2 flux for flux due to the uncertainty in the latent heat flux Webb simulated dried air stream (dashed curve). Global CO2 flux climatology is from Takahashi et al. [1997], and latent heat flux climatology is from Saha et al. [2006]. Drying of the air stream was assumed to eliminate 97% of the water vapor fluctuations (and flux; see Figure 8). Uncertainty in the air-sea latent heat flux measurement by eddy covariance systems was assumed to 20%. Ratios greater than one indicate correction uncertainties larger than the actual flux. 

Figure 16. Global estimate of the uncertainty in the air-sea CO2 flux due to the uncertainty in the latent heat flux portion of the Webb correction (i.e., for closed-path eddy covariance systems), plotted as the ratio of the Webb correction uncertainty magnitude to the true air-sea CO2 flux magnitude for an undried (solid curve) and for a simulated dried air stream (dashed curve). Global CO2 flux climatology is from Takahashi et al. [1997], and latent heat flux climatology is from Saha et al. [2006]. Drying of the air stream was assumed to eliminate 97% of the water vapor fluctuations (and flux; see Figure 8). Uncertainty in the air-sea latent heat flux measurement by eddy covariance systems was assumed to 20%. Ratios greater than one indicate correction uncertainties larger than the actual flux.

4. Conclusion

The results from the Knorr-07 cruises suggest that the air-sea flux of CO2 was successfully measured by eddy covariance with the system and signal processing techniques described. Significant improvement in the flux measurement was obtained by reducing the Webb correction associated with latent heat flux. The impact of ship motion was reduced by the use of a converted open-path sensor, and an empirical regression technique. The CO2 sensor used in this study appears to have sufficient sensitivity to resolve the CO2 flux, even though the ambient fluctuations lie below the RMS noise level of the sensor. This is due to the strong noise filter imposed by the covariance of atmospheric CO2 with vertical wind. A significant increase in the signal-to-noise characteristics of the CO2 sensor (i.e., by a factor of 10) would be needed to directly obtain reliable statistics and spectra of atmospheric CO2 fluctuations.

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