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Air-sea gas exchange of \( \text{CO}_2 \) and DMS in the North Atlantic by eddy covariance

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[1] We report the first simultaneous eddy covariance flux measurements of \( \text{CO}_2 \) and dimethylsulfide (DMS) over the open ocean for two North Atlantic cruises. After normalization for Schmidt number, the two gases give essentially identical gas transfer coefficients and wind speed dependencies for the wind speed range 2–10 ms\(^{-1}\). The data indicate a linear relationship between the gas transfer coefficient and mean wind speed, with measured gas transfer coefficients slightly above the Wanninkhof (1992) parameterization, particularly at low wind speeds. Citation: Miller, S., C. Marandino, W. de Bruyn, and E. S. Saltzman (2009), Air-sea gas exchange of \( \text{CO}_2 \) and DMS in the North Atlantic by eddy covariance, Geophys. Res. Lett., 36, L15816, doi:10.1029/2009GL038907.

1. Introduction

[2] Most current parameterizations of air-sea gas exchange utilize a coefficient \( k \) (the piston velocity) to relate the gas flux to the air-sea concentration difference. This coefficient incorporates all the physical factors controlling gas transport through both sides of the air-sea interface. For different gases, the effect of molecular diffusivity on \( k \) is accounted for by normalizing to a common Schmidt number \((Sc = \nu/D)\), where \( \nu \) is the seawater kinematic viscosity and \( D \) is the diffusivity of the gas in seawater) via \( kSc^{1/2} = \text{const.} \)

Tracer release studies [Ho et al., 2006; Liss and Merlivat, 1986; Nightingale et al., 2000; Wanninkhof et al., 1985] and wind-wave tank experiments [Broecker and Siems, 1984; Jahne and Haußesser, 1998] showed that \( k \) increases with wind speed, though constraining the functional form of this dependence in the oceans has proven challenging due to the long averaging time of tracer studies, and processes affecting gas exchange that are not correlated to wind speed. Theory, laboratory and modeling studies suggest that gas solubility also affects air-sea gas transfer when whitecaps are present due to bubble-mediated transport [Woolf, 1997].

[3] During the past decade, the eddy covariance (EC) technique has been used from ships at sea to measure \( \text{CO}_2 \) and DMS fluxes and piston velocities on shorter temporal and spatial scales. These data show a wide range of wind speed dependencies for \( k \). For low-moderate wind speed, the Gas Ex 2001 experiment (Gas Ex-2001) [McGillis et al., 2004] showed a very weak relationship for \( k \), while four DMS eddy covariance studies exhibited an approximately linear dependence of \( k \) on wind speed [Marandino et al., 2007, 2008a; Huebert et al., 2004; Blomquist et al., 2006]. For higher wind speeds, up to 16 ms\(^{-1}\), the Gas Ex 1998 experiment (Gas Ex-1998) [McGillis et al., 2001] showed a strong (quadratic to cubic) relationship of \( k \) versus wind speed. Some of the differences between \( k \) during Gas Ex-1998 and Gas Ex-2001 were hypothesized to reflect differences in physical forcing of gas exchange in different environments [Hare et al., 2004], while differences between \( k_{\text{CO}_2} \) and \( k_{\text{DMS}} \) measured during different cruises have been hypothesized to reflect the different solubilities of these two gases and the importance of bubble-mediated transport [Blomquist et al., 2006].

[4] Here we present EC-based \( \text{CO}_2 \) and DMS fluxes and piston velocities measured in the North Atlantic during summer 2007. We examine the relationship between the piston velocity and wind speed, and use the gas transfer coefficients of \( \text{CO}_2 \) and DMS measured on the same cruise to provide insight into the sensitivity of gas exchange to gas solubility during low to moderate wind conditions.

2. Methods

[5] The measurements were made from the research vessel RV Knorr during cruises in summer 2007 from Bridgetown, Barbados to Reykjavik, Iceland (Knorr-07a, 29 May-9 Jun), and from Reykjavik to Woods Hole, MA (Knorr-07b, 17–26 Jul). Gas transfer coefficients were determined according to \( F = k(C_w - C_a) \), where \( F \) is the turbulent air-sea species flux, \( C_w \) and \( C_a \) are the bulk seawater and air concentrations, and \( \alpha \) is the dimensionless solubility. \( \text{CO}_2 \) and DMS fluxes were measured using eddy covariance as \( F = \rho_a w \frac{x}{\alpha} \), where \( w \) is the vertical component of wind velocity, \( x \) is \( \text{CO}_2 \) or DMS mixing ratio, \( \rho_a \) is dry air density, primes denote fluctuations about the mean value, and the overbar denotes the covariance over the averaging interval [Kaimal and Finnigan, 1994].

[6] Two ultrasonic anemometers (CSAT3, Campbell Scientific) separated horizontally by 1 m were mounted on the Knorr’s meteorological mast, 2 m forward of the bow and 14 m above the mean sea surface. Gas inlets and a motion sensor (MotionPak2, Systron Donner) were centered between and slightly aft of the sonic anemometer measurement volumes. \( \text{CO}_2 \) concentrations in air and seawater were measured using 5 InfraRed Gas Analyzers (IRGAs, LiCor, Inc.). The methods used to measure the \( \text{CO}_2 \) fluxes and piston velocities are described briefly below, and in further detail by S. Miller et al. (Ship-based measurement of air-sea \( \text{CO}_2 \) exchange by eddy covariance, submitted to Journal of Geophysical Research, 2009).
DMS concentrations and air-sea fluxes were measured using two atmospheric pressure chemical ionization mass spectrometers described by Marandino et al. [2007].

The mean atmospheric and seawater CO2 concentrations were measured continuously in the ship laboratory. Air was drawn from an inlet on the bow mast at 1 slpm through 80 m of 3.9 mm ID tubing to a closed-path IRGA (LI7000). Two additional IRGAs measured the CO2 concentration of closed-loop air streams equilibrated with the ship’s uncontaminated seawater supply: one (LI7000) using a membrane contactor (LiquiCell X40, Knorr-07a and b) and the other (LI820) using a showerhead-type equilibrator (Knorr-07b only). The two systems showed excellent agreement.

Two IRGAs located in the bosun locker directly below the bow mast were used to measure turbulent CO2 fluctuations (CO2 IRGA) and H2O fluctuations (H2O IRGA). Air was drawn to these IRGAs at 16–18 slpm through an inlet filter near the sonic anemometer and 14 m of 5.9 mm ID tubing, with a travel time of approximately 1 second. Water vapor fluctuations and the associated Webb correction were significantly reduced by drying the airstream using a Nafion drier (PD-200T, PermaPure). This reduced the apparent latent heat flux measured by the downstram CO2 IRGA by >90%. Laboratory tests indicated that temperature fluctuations (and the associated Webb correction) were negligible due to heat exchange in the sample tube. The CO2 IRGA was an open-path style sensor (LI7500) converted to a closed-path sensor by inserting a cylindrical cell into the optical path (12.5 cm long, 1.6 cm I.D., volume 0.025 L, flush time less than 0.1 s). This instrument has considerably less motion sensitivity than closed-path sensors (LI7000 and LI6262) previously used for eddy covariance at sea [McGillis et al., 2001]. Fast-response water vapor fluctuations used to calculate latent heat flux were measured by the H2O IRGA (LI7000), installed upstream of the Nafion drier.

Turbulence data from the sonic anemometer, motion sensor, and CO2 and H2O IRGAs in the bosun locker were sampled at 10 Hz, and measured winds were corrected for platform motion [Miller et al., 2008]. Fluxes were calculated using a 13.7-minute averaging period (8192 10 Hz samples). Similar to previous air-sea gas flux studies, flow distortion was addressed by rejecting flux intervals when the mean relative wind direction over the flux interval was >90° from forward (>60° for the quadrant with the adjacent sonic). The turbulent sensible heat and CO2 fluxes were considered to be stationary when the difference between the 13.7-minute fluxes and the average of the 4 2048 sample (3.4 min) subintervals was less than 30% [Foken and Wichura, 1996]. The loss of high-frequency contributions to CO2 and H2O flux due to tubing attenuation was corrected using the ogive analysis described by Marandino et al. [2007]. The average CO2 (H2O) flux loss was 10% (40%) for unstable and 25% (80%) for stable atmospheric conditions. Here, we present kCO2 data collected only during unstable atmospheric conditions. The measured turbulent fluxes and air-water concentration differences were used to calculate piston velocities for CO2 on the Knorr-07a cruise, and for CO2 and DMS on the Knorr-07b cruise. The three data sets were combined after normalizing the piston velocities to Schmidt number of 660, assuming an Sc−0.5 dependence.

3. Results and Discussion

3.1. Overview of Cruises

The cruise tracks and MODIS chlorophyll map for the study region are provided in the auxiliary material. A broad range of chlorophyll concentrations was measured (0.2–3.8, mean 0.8 mg m−3, Figure 1b). Chlorophyll generally increased with latitude. Sea surface temperatures (SST) decreased with latitude and were lowest during the more eastward Knorr-07a cruise (Figure 1a). SST was much warmer than the air temperature south of 52°N during Knorr-07a with ocean to atmosphere (positive) heat flux, slightly warmer than air temperature between 50–65°N with small net upward heat fluxes, and colder than air temperature south of 50°N during Knorr-07b with net downward heat fluxes. Wind speeds were low to moderate throughout both cruises, with wind at 10-m height range of 1–12 ms−1 (Figure 1a).

Data were collected for 326 hours (1304 flux intervals) during Knorr-07a and 200 hours (800 flux intervals) during Knorr-07b. Intervals were rejected based on the following criteria: air-water pCO2 difference less than 35 ppm (73% of Knorr-07a intervals, 25% of Knorr-07b), instrument spikes (27% Knorr-07a, 32% Knorr-07b), poor wind direction (35% Knorr-07a, 2% Knorr-07b), instability of the turbulent CO2 flux (74% Knorr-07a, 75% Knorr-07b), and stable atmospheric conditions (25% Knorr-07a, 65% Knorr-07b). The resulting high-quality dataset for kCO2 included 88 intervals for Knorr-07a intervals and 126 intervals for Knorr-07b. DMS fluxes are reported here during 128 hours during Knorr-07b. Simultaneous high-quality kCO2 (40 flux intervals) and kDMS (34 flux intervals) data were obtained between 50°N–54°N latitude (Figure 1d). DMS concentrations and fluxes in the high-chlorophyll region north of 54°N were anomalously high and are not included in our analysis [see Marandino et al., 2008b].

3.2. Air-Sea Concentrations and Fluxes

Atmospheric pCO2 was relatively constant during each cruise, 387 ± 4 ppm for Knorr-07a and 377 ± 4 ppm for Knorr-07b. Sea surface pCO2 was undersaturated with respect to the atmosphere, except for the last part of Knorr-07b, when it was supersaturated. 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 (Figure 1b). Surface waters were supersaturated with DMS throughout Knorr-07b, with a mean concentration of 2.5 ± 1.1 nM (Figure 1b) [Marandino et al., 2008b].

The direction of the turbulent fluxes of CO2 and DMS was consistent with their respective water-air partial pressure gradients (Figures 1b and 1c). The average downward CO2 flux was −3.3 ± 0.1 mol CO2 m−2 yr−1 in the ocean sink region, and the average upward flux was 1.7 ± 1 mol CO2 m−2 yr−1 in the source area. DMS fluxes were from ocean to atmosphere, and averaged 5.7 ± 0.4 μmol

1Auxiliary material data sets are available at ftp://ftp.agu.org/apend/gl/2009gl038907. Other auxiliary material files are in the HTML.
3.3. Gas Transfer Coefficients

The piston velocities for CO$_2$ and DMS measured on the Knorr-07 cruises were remarkably similar (Figure 2). $k_{CO_2}$ and $k_{DMS}$ increased with wind speed and exhibited scatter typical of air-sea flux measurements. The measured piston velocities were mostly higher than the quadratic relationship of Wanninkhof [1992]. The linear regression of the combined CO$_2$ and DMS data (n = 323) against 10-m wind speed was $k_{CO_2} = 3.0 U_{10} - 2.5$ cm $\cdot$ hr$^{-1}$, $r^2 = 0.57$. Nineteen data points (6% of the data set) were flagged as outliers using the 95% confidence interval of the residuals for the linear fit. The regression slope differed by less than 10% and the $r^2$-statistic decreased to 0.45 when the outlier points were included. The $r^2$-statistic did not improve when a quadratic instead of linear fit was assumed. The $r^2$-statistic was also similar for linear and quadratic regressions calculated independently for CO$_2$ and DMS. To our knowledge, these are the first open-ocean eddy covariance CO$_2$ data suggesting a linear relation between wind speed and piston velocity at low winds. For DMS, the four EC data sets published to date are consistent with a linear $k$ versus $U_{10}$ relationship [Marandino et al., 2008a]. This study, and the previous DMS studies cover a broad range of oceanographic regions and environmental conditions.

Our results are markedly different than those from the GasEx-1998 and GasEx-2001 experiments (Figure 3a).
Wanninkhof and Monahan versus Piston velocity (cm hr$^{-1}$) and DMS EXCHANGE

Thanks to Liz Caporelli, Captains Kent during the Knorr-07 cruises. Theory suggests that breaking waves and bubbles can enhance the transfer of lower solubility gases relative to higher solubility gases [Woolf, 1997]. Gas transfer models that include wind speed and wave state have been developed [Soloviev et al., 2007]. However, measurements of sea state have generally not been reported along with direct gas flux measurements, and wave state effects have been inferred from wind speed measurements alone. For the range of wind speeds measured during the Knorr-07 cruises, the whitecap coverage was expected to be small (0.01–1%) [Monahan and Muircheartaigh, 1980]. The data-based model of Asher and Wanninkhof [1998] predicts only a few percent enhancement of $k_{CO_2}$ relative to $k_{DMS}$ for $U_{10} < 10$ ms$^{-1}$. The data from Knorr-07b show that the measured $k_{CO_2}$ and $k_{DMS}$ were similar over the entire wind speed range (Figure 3b). The similarity between $k_{CO_2}$ and $k_{DMS}$ was found both for the entire Knorr-07b dataset and for the latitude range 50°N–54°N where simultaneous CO$_2$ and DMS data were obtained (Figures 1d and 3b, solid symbols). The data confirm that solubility did not play a major role in gas transfer over the wide range of oceanographic conditions encountered on this cruise.

4. Conclusion

Understanding gas transfer at low-moderate wind speeds is important since winds less than 10 ms$^{-1}$ cover more than 60% of the oceans on average. Eddy covariance piston velocities measured for CO$_2$ and DMS during low-moderate wind speed on two North Atlantic cruises were remarkably similar, exhibiting a linear relationship to wind speed. Wind speed accounted for over half of the variance of the gas transfer coefficient. The wind speed-dependence of these data is quite different than those from earlier CO$_2$-based studies, but similar to prior DMS-based studies. The similarity between the $k$ versus $U_{10}$ relationships for CO$_2$ and DMS suggests that solubility was not a significant factor under these low to moderate wind conditions. The Knorr-07 data set is relatively limited in terms of the overall number of flux measurements, the temporal overlap between the CO$_2$ and DMS flux measurements, and the wind speed range. However, it demonstrates the utility of this approach as a means of improving our understanding of air-sea gas transfer.

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References


Brower, W. S., and W. Siems (1984), The role of bubbles for gas transfer from water to air at higher windspeeds. Experiments in the


Marandino, C. A., W. J. De Bruyn, S. D. Miller, and E. S. Saltzman (2008a), Open ocean DMS air/sea fluxes over the eastern South Pacific Ocean, Atmos. Chem. Phys. Discuss., 8, 12,081–12,114.
