Carbon dioxide flux techniques performed during GasEx-98

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Received 9 January 2001; received in revised form 14 May 2001; accepted 14 May 2001

Abstract

A comprehensive study of air–sea interactions focused on improving the quantification of CO 2 fluxes and gas transfer velocities was performed within a large open ocean CO 2 sink region in the North Atlantic. This study, GasEx-98, included shipboard measurements of direct covariance CO fluxes, atmospheric CO 2 profiles, atmospheric DMS profiles, water column mass balances of CO 2, and measurements of deliberate SF 6−3 He tracers, along with air–sea momentum, heat, and water vapor fluxes. The large air–sea differences in partial pressure of CO 2 caused by a springtime algal bloom provided high signals for accurate CO 2 flux measurements. Measurements were performed over a wind speed range of 1–16 m s −1 during the three-week process study. This first comparison between the novel air-side and more conventional water column measurements of air–sea gas transfer show a general agreement between independent air–sea gas flux techniques. These new advances in open ocean air–sea gas flux measurements demonstrate the progress in the ability to quantify air–sea CO 2 fluxes on short time scales. This capability will help improve the understanding of processes controlling the air–sea fluxes, which in turn will improve our ability to make regional and global CO 2 flux estimates. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Air–sea CO 2 fluxes; Direct covariance; Profile method; Deliberate tracers; CO 2 sink; Air–sea interactions; GasEx-98

1. Introduction

The large uncertainties in the estimation of the CO 2 flux between the atmosphere and ocean have limited our ability to predict future atmospheric CO 2 levels. Since approximately 30–40% of anthropogenically produced CO 2 is taken up by the ocean, CO 2 exchange across the ocean–air interface is an extremely important component in global carbon dynamics. However, the kinetics of the ocean–air CO 2 transfer are not well understood, particularly due to the large spatial and temporal variability of the many different mechanisms and properties that control the air–sea flux of CO 2, and because of our inability to measure the gas fluxes on short time scales in nature. For example, surface pCO 2 varies in response to temperature, salinity, bubble entrainment, and biological productivity, while the gas transfer rate depends upon the properties of the gas, wind speed, atmospheric stability, sea-state, and surfactants.

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PII: S0304-4203(01)00042-1
Current estimates of the air–sea flux of CO$_2$ rely on gas exchange models that relate the flux to the air–sea concentration difference using a parameterized transfer velocity. Open ocean CO$_2$ transfer velocities have been derived from the inventories of natural and bomb-produced $^{14}$C in the ocean, radon deficiencies in the surface layer, and the dual-tracer technique. These methods represent integrations over large spatial and temporal scales averaging the variability of $p$CO$_2$ and surface forcing, and causing biases in the derived fluxes due to the nonlinear flux relationship between surface forcing and $p$CO$_2$.

Determining CO$_2$ fluxes from direct air-side measurements has been a controversial subject (e.g., see Broecker et al., 1986). For example, the indirect but well-validated methods such as radiocarbon, radon, and radioisotopic methods give transfer velocities ranging from 12–24 cm h$^{-1}$ (Broecker and Peng, 1982; Jähne, 1985; Peng et al., 1979). Most previous estimates of the transfer velocity using direct covariance flux estimates are an order of magnitude larger (e.g., Jones and Smith, 1977; Wesely et al., 1982; Smith and Jones, 1985) and are at odds with global mass balance constraints of CO$_2$ uptake. While these latter authors have provided a number of possible explanations for their findings, the actual cause for the discrepancies remains a debated topic.

An important problem that remains is to determine how certain environmental parameters influence the transfer velocity of CO$_2$ and the CO$_2$ gas flux. Many wind tunnel experiments have shown that the CO$_2$ transfer velocity is a function of wind speed (Broecker et al., 1982; Jähne, 1985; Wanninkhof and Bliven, 1991). However, the application of these results to the open ocean environment is questionable, given the limited fetch and other possible artifacts in tank experiments. This is particularly true at high wind speeds that are rarely sustained long enough in nature to match the integration time required by the indirect methods. If the relationship between the transfer velocity and mean wind speed is nonlinear, large uncertainties are obtained for moderate to high wind speeds. These uncertainties have resulted in the use of various transfer velocities in different climate models, ultimately producing a wide variety of long-term climate forecasts. The use of a single, accurate parameterization for the CO$_2$ transfer velocity in all climate models would remove one major source of uncertainty in long-term global climate forecasts.

During the GasEx-98 study, comparisons of a number of techniques designed to compute the CO$_2$ transfer velocity were performed. The study included strategies that were difficult to implement, such as the direct covariance and profile techniques, and the more commonly used deliberate dual-tracer technique. For the first time, this experiment allowed a comparison of the direct covariance and profile-derived fluxes over the open ocean with the more conventional flux estimates using a mass balance approach computed over the same region and time period.

2. Study site

GasEx-98 was a multi-agency, interdisciplinary air–sea gas exchange experiment conducted aboard the National Oceanic and Atmospheric Administration (NOAA) ship Ronald H. Brown (RHB) from May through June of 1998. This experimental effort was designed as a feasibility study with the long-term goal of quantifying CO$_2$ transfer velocities on regional time scales using remote sensing instrumentation, such that when combined with regional estimates of $p$CO$_2$ in the air and surface water, the global air–sea CO$_2$ fluxes can be determined. One of the short-term objectives of this experiment was to evaluate the feasibility of computing the CO$_2$ flux from an open ocean research vessel using the direct covariance and profile methods. The experiment was designed to allow comparison of the fluxes measured with conventional methods to those obtained from a mass balance approach and computed over the same region and time period.

To facilitate the comparison between the direct and indirect flux measurements, a contained water mass with a large air–sea $p$CO$_2$ difference was located in a warm core eddy near 46°N, 21.5°W using altimeter imagery (Fig. 1). Initial surveying of the water mass revealed relatively stable salinities, surface $p$CO$_2$ values near 285 μ atm (yielding an 85 μ atm CO$_2$ sink) with 20 m mixed layer depths. The near-zero surface nutrient concentrations and high chlorophyll values suggested that the region had passed the peak of the algal bloom.
Fig. 1. Altimeter data for YD149 at the start of the GasEx-98 process study (provided by Gustavo Goni at NOAA/AOML). The GasEx-98 study site selection was based on this altimeter data. Surface water properties in the coherent warm core eddy near 46°N, 21.5°W were surveyed prior to the start of the process study. High, spatially homogeneous air–sea $\Delta pCO_2$ values were measured throughout the eddy.

A SF$_6$–He tracer mixture was injected on May 28 (YD149) in a 3.5-km streak and two $pCO_2$ CARIOCA buoys (Merlivat and Brault, 1995) and a GPS drifter buoy were deployed. Subsequent surveys showed that the buoy trajectories and tracer patch completed a clockwise circle of about 30 km radius during the first 10 days after deployment, confirming the eddy structure. This warm core eddy had a sea
surface temperature of 0.2–0.3 °C lower than the surrounding waters. The SF6 concentrations decreased rapidly over time through downward mixing, gas exchange and dispersion with concentration levels decreasing by nearly a factor of 2 every day. The SF6 patch remained coherent within the eddy, allowing for a successful deliberate tracer experiment.

RHB was instrumented with a comprehensive micrometeorological system to measure air–sea fluxes of momentum, sensible and latent heat, CO2, and DMS. Located on the bow was a scaffold housing the CO2, H2O, and DMS gas detectors. Forward of the scaffold was the jack staff, which held an ultrasonic anemometer/thermometer, platform-motion measurement system, and a fast-response open-path H2O/CO2 sensor.

Profiles of CO2, H2O, and DMS concentrations in the atmosphere were measured from an Atmospheric Profiling Boom (APB) extending off the port side of the ship just aft of the bow (shown in Fig. 3). The CO2, H2O, and DMS APB extended 7 m from the port side gunnel, placing it approximately 10 m from the bow to diminish air flow distortion caused by the ship.

3. Methods

3.1. Bulk air–sea gas fluxes

The bulk aerodynamic method is used to estimate air–sea momentum and heat fluxes in terms of explicit variables (Fairall et al., 1996). In addition, the bulk technique presents the flux in a mathematical expression that is readily incorporated into numerical models on a variety of scales. The bulk method to determine the flux of a gas relies on the assumption that the transfer across the air–sea interface is governed by the air–sea concentration difference. For example, in the case of carbon dioxide, the expression is

\[ F_{CO_2} = z_{CO_2} k_{CO_2} \Delta p_{CO_2}, \]

where \( k \) is the gas transfer velocity, \( s \) is the solubility of CO2, which is quantified as a function of temperature and salinity, and \( \Delta p_{CO_2} \) is the difference in partial pressure of CO2 between the ocean \( (p_{CO_2o}) \) and the atmosphere \( (p_{CO_2a}) \). The bulk flux estimate requires the gas transfer velocity, surface temperature, salinity, and the air–sea concentration difference. The CO2 transfer velocity depends on a number of environmental factors including wind speed, surface current, atmospheric stability, surface films, bubbles, sea state, and wave age.

Improved parameterization of the gas transfer velocity requires accurate measurement of the flux and concentration difference. The requirement for accurate flux estimates on short time scales was the motivation to measure the CO2 flux using micrometeorological (e.g., direct covariance and profile) methods during the GasEx-98 experiment. However, realizing that the air–sea CO2 flux is difficult to measure directly, other gases and flux techniques were also considered.

3.2. Direct covariance technique

The air–sea gas flux can be measured by direct covariance using gas concentration, \( c \), and vertical wind velocity, \( w \), in the air boundary layer through the expression:

\[ F_i = \overline{c'w'}, \]

where the primes indicate fluctuations about the mean value denoted by the overbar. The shipboard flux system deployed in GasEx-98 was a modification of the direct covariance flux system used to measure momentum and heat fluxes (Edson et al., 1998). With regards to implementing the direct covariance method for gases at sea, the greatest challenges centered around: (1) the presence of adequate signal levels to compute the gas flux using currently available sensors, and (2) the ability to adequately remove the motion contamination and minimize the effect of flow distortion around an ocean-going vessel. The momentum flux is very sensitive to motion contamination because it requires corrections to both the vertical and horizontal velocities, as opposed to the scalar, including gas, fluxes that are mainly influenced by uncertainties in the vertical velocity.

Although the direct covariance technique is commonly used on fixed platforms, it is only recently that routine open ocean applications of this technique have been made for the measurement of turbulent fluxes from research vessels (e.g., Tsukamoto et al., 1990; Bradley et al., 1991; Anctil et al., 1994; Fairall...
On a seagoing research vessel, the measurement of the velocity components necessary to compute covariances becomes significantly more difficult because the motion of the platform contaminates the measured velocity. This motion contamination must therefore be removed before the fluxes can be computed. A detailed explanation of the methodology used to correct for platform motion can be found in Edson et al. (1998).

The resulting corrected wind velocity signals can then be used to compute the direct covariance fluxes using Eq. (2). However, even if the platform motion is removed from the measured velocity signals, the accuracy of direct covariance flux estimates is influenced by flow distortion around the vessel. Edson et al. (1998) provides a comparison of the momentum fluxes computed onboard an ocean-going vessel with those measured from a large spar buoy to quantify vessel flow distortion. The studies by Edson et al. (1998) indicate that the momentum flux should be increased by 15% when using a system such as that deployed on the RHB during GasEx-98. This translates to a bias of roughly 8% in the scalar fluxes, which is used as an estimate of the uncertainty in the CO$_2$ flux estimates due to incomplete motion correction and flow distortion.

With an accurate estimate of the corrected vertical wind velocity, the gas flux was computed by correlating this velocity with atmospheric CO$_2$ concentrations. During the GasEx-98 experiment, a fast-response, closed-path, nondispersive infrared (NDIR) CO$_2$/H$_2$O gas analyzer was used to measure atmospheric gas samples continuously. The air intake line was mounted 0.5 m behind the sonic anemometer sampling volume, and the NDIR detector was located 8 m away from the intake. The sample was drawn through the tube at a constant rate of 10 $\text{l m}^{-1}$, which results in a measurable lag between the gas sample and the sonic anemometer measurement. Pressure and temperature fluctuations were reduced with a pressure reservoir and a thermal equilibrator, respectively.

Estimates of the remaining noise in the flux system were made using the data collected during calibration periods. These calibrations were conducted every 4 h by flushing the analyzer cell with known CO$_2$ concentrations, so that the system measured the calibration gas rather than the atmospheric concentration. In an ideal system, no fluctuations would be measured about the reference level during the calibrations. In the actual system, signals in the CO$_2$ channel of the analyzer caused by pressure fluctuations due to pump noise and ship motion-induced signal changes were observed, caused by gyroscopic motion effects on the analyzer chopper wheel. During the calibration periods, a 10 ppb CO$_2$ detection limit was estimated. The total error in the flux estimates due to this additional noise and incomplete motion correction was estimated by computing the covariances during these periods. An estimation of the uncertainty is calculated to be 2 mol m$^{-2}$ year$^{-1}$ for the direct flux technique (Fairall et al., 2000). Recognizing that the current oceanic CO$_2$ uptake of 2 pg C year$^{-1}$ translates to an average flux of about 0.5 mol m$^{-2}$ year$^{-1}$ illustrates that direct flux measurements are currently limited to large CO$_2$ source or sink regions.

### 3.3. Profile method

Monin–Obukhov (MO) similarity theory can be used to describe turbulent properties in the surface layer (Panofsky and Dutton, 1984). In a surface layer where the flow is driven by mechanical (i.e., shear) and thermal (i.e., buoyancy) forcing, MO similarity states that various turbulence statistics, when normalized by an appropriate set of scaling parameters, are universal functions of the stability function $\xi = z/L$, where $z$ is the height above the surface and $L$ is the MO scaling length. The MO length is defined by

$$L = \frac{T_v}{\kappa g F_{T_v}}$$

where $g$ is the acceleration of gravity, $T_v$ is the virtual temperature, $F_{T_v}$ is the buoyancy flux, $u_*$ is the velocity scaling parameter also known as the friction velocity, and $\kappa$ is the von Kármán constant (assumed equal to 0.4). Note that the MO length represents the ratio of mechanical to thermal forcing, and the height where $z = L$ represents the height at which these two forcing mechanisms are equal. The additional scaling parameters (including the friction...
velocity) required to normalize the equations are given by

$$x_s = -\frac{\omega x'}{u_s} = \frac{F_{sx}}{u_s}, \quad (4)$$

where $F_{sx}$ is the surface flux of the variable $x$, e.g., momentum flux, sensible heat flux, latent heat flux, and other scalar fluxes such as CO$_2$ or DMS.

A pertinent example of MO similarity theory for the profile method is provided using the vertical gradient of some mean quantity $\bar{x}$, where the method predicts that the normalized gradient should be a universal function of $\xi$, such that

$$\kappa \frac{\partial \bar{x}}{x_s \partial z} = \varphi_s(\xi), \quad (5)$$

where $\varphi_s$ is an empirically determined dimensionless gradient function for $x$ (e.g., Paulson, 1970).

Integrating Eq. (5), a logarithmic profile is obtained

$$\bar{x}(z) - \bar{x}(z_{os}) = \frac{x_s}{\kappa} [\ln(z/z_{os}) - \psi_s(\xi)], \quad (6)$$

where $\psi_s$ is the integral form of $\varphi_s$, $\bar{x}(z_{os})$ represents the surface value of $x$, and $z_{os}$ is the surface roughness length for $x$.

If the value of the MO length is known from either the direct covariance or bulk fluxes, the scaling parameter ($x_s$) and roughness length ($z_{os}$) can be determined as the slope and intercept, respectively in Eq. (6). Note that the stability parameter can also be determined in an iterative fashion by the profile method alone if the gradients of velocity, temperature, and humidity are also measured. The flux is then calculated by combining this scaling parameter with the friction velocity using Eq. (4).

Since the atmospheric profile method relies on mean gradients in the boundary layer, it offers several advantages in determining air–sea fluxes. Many gases cannot be measured at rates that are fast enough for direct covariance because a wide range of gas measurement techniques rely on slow procedures that can also smear the high frequency response (e.g., water vapor removal, mass spectrometry procedures, gas chromatography). As the gradient of CO$_2$ and other slightly soluble gases are predominantly controlled by the aqueous boundary layer, the profiles can be used to estimate the air–sea flux using Eqs. (4)–(6).

There are several disadvantages to the atmospheric profile technique. MO similarity, which the profile technique requires, is applicable in the marine atmospheric surface layer where the surface momentum and buoyancy fluxes are controlling the flow. The necessary parameterizations have, by and large, been determined over land surfaces, and the parameterizations become invalid when e.g., surface waves and larger scale processes influence the near surface properties. In addition, a number of fundamental assumptions (surface homogeneity, stationarity, turbulent kinetic energy balance) are required for application of MO similarity. Therefore, while there may exist a logarithmic behavior of the profile of gases, the correction for atmospheric stability may not be the same as those used for profiles measured over land. Another disadvantage of using MO similarity arises as a result of the relatively small vertical gradients of trace atmospheric gases because the signal levels may be close to or less than the gas detection noise level. The motion of the ship also creates displacements of the air sampling intake and instruments relative to the sea surface. This is problematic because of the nonlinear nature of the vertical gas gradient. The flow distortion presented by the ship may significantly modify the profile of the gas concentration that is required for the flux computation. Finally, inhomogeneities of the trace gas from the water surface may lead to appreciable advection, which invalidates the application of MO similarity.

The solubility of DMS is larger than CO$_2$ resulting in a greater influence of the atmospheric boundary layer. To estimate the water-side controlled gas transfer velocity of DMS, the measured DMS gas transfer velocity must be corrected for an air-side effect with the following expression:

$$k_{DMS, w} = \frac{k_{DMS}}{1 - \gamma_s}, \quad (7)$$

where $\gamma_s$ is the air-side gradient fraction (McGillis et al., 2000). The water-side controlled CO$_2$ gas transfer velocity is calculated from $k_{DMS, w}$ using a Sc number correction:

$$k_{CO_2} = k_{DMS, w} \left( \frac{Sc_{CO_2}}{Sc_{DMS}} \right)^n, \quad (8)$$
where $Sc_{DMS}$ is the Schmidt number for DMS under the environmental conditions of the observation. In this way, some of the effects of variations in the mass diffusivity are removed. The $Sc$ for DMS is approximately 1.5 times greater than the $Sc$ for CO$_2$. Depending on the environmental conditions, $\gamma_s$ varied from 0.02 to 0.15 during GasEx-98.

For smooth surfaces, experimental and theoretical studies suggest that the air–sea exchange can be modeled as transfer across a smooth wall, with transfer being proportional to the Schmidt number of the gas to the $2/3$ power ($Sc^{-0.66}$) and the friction velocity $u_*$ (Deacon, 1977). With more energetic flows at the interface, gas transfer scales with $u_*$ and $Sc^{-0.5}$. The objective in these regimes is to accurately determine $k$ and $u_*$ in the field. At high winds, when bubble entrainment occurs, other factors such as gas solubility and pressure on the bubbles influence the flux of gases (Keeling, 1993; McGillis et al., 1995; Asher et al., 1995). Exact mechanisms of transfer in this regime are not fully understood or parameterized.

### 3.4. Deliberate tracer technique

The dual-gaseous tracer technique is based on the injection of a pair of volatile tracer gases, and was first implemented in the North Sea (Watson et al., 1991). The tracers of SF$_6$ and $^3$He have been used exclusively because they can be measured at very low concentrations and their diffusivities are dissimilar. Using the advection–diffusion equation with a first-order decay term for the gas transfer of both tracers and the expressions for the gas transfer velocities of two gases, the relationship for gas transfer across the aqueous boundary layer becomes (Wanninkhof et al., 1993):

$$k = h/\Delta t \ln\left(\frac{R_{t_1}/R_{t_2}}{1 - (Sc_a/Sc_b)^n}\right),$$

where $h$ is the height of the mixed layer, $\Delta t$ is the time interval between samples at $t_1$ and $t_2$, and $R$ is the ratio of gas concentrations (SF$_6$ and $^3$He). The difficulties of using two volatile tracers are that for most gases, the diffusion coefficients, and the Schmidt numbers, differ by only 40%, and that the exponent $n$ changes with interfacial hydrodynamics.

The Schmidt numbers for SF$_6$ and $^3$He differ by a factor of five. Both tracers also have similar low solubilities, such that the exponent $n$ does not change dramatically during bubble entrainment (Asher and Wanninkhof, 1998).

The gas flux estimates over the open ocean using the micrometeorological techniques can be converted to the CO$_2$ transfer velocity through rearrangement of Eq. (1), and compared with the dual-tracer and water column mass balance estimates. This requires accurate measurement of the partial pressure of CO$_2$ in both the ocean and atmosphere to compute the concentration difference, $\Delta p_{CO_2}$. The air-side measurements are readily obtained from the same detector that measures the CO$_2$ fluctuations in the atmosphere for the direct flux measurements, while the water-side measurements are taken from a second detector sampling the headspace gas of an ocean gas equilibrator. The method to equilibrate gas with ocean water is achieved by continuously pumping seawater through a showerhead in an enclosed headspace where the $p_{CO_2}$ in water and headspace reach equilibrium. Gas is then pumped from the headspace of the chamber, through a condenser that removes approximately 90% of the water vapor, and finally a Mg(ClO$_4$)$_2$ drier before being passed through the detector and back to the equilibrator. This system also takes hourly air measurements, such that the $\Delta p_{CO_2}$ can be determined directly as a check and to avoid possible standard biases.

### 4. Results and discussion

Fig. 2 shows both $\Delta p_{CO_2}$ and wind speeds during GasEx-98. This time series shows relatively constant $p_{CO_2}$ levels in the ocean, while the wind speed varied substantially. After a week of moderate winds, a storm hit the study area during the second week of the process study, which greatly changed the conditions in the water and the air. Wind speeds were maintained above 12 m s$^{-1}$ between YD159 and YD161, making it possible to obtain extensive measurements of friction velocity and drag coefficients under these conditions. Water mixed layer depth increased from less than 20 to over 30 m, and
the entrainment also increased the total carbon and decreased the air–water $\Delta p\text{CO}_2$ from $-90$ to $-70 \mu\text{atm}$.

The small CO$_2$ fluctuations found over the open ocean makes any direct measurement of CO$_2$ flux challenging. The study area for GasEx-98 was chosen to optimize the signal-to-noise ratios by locating a region with a relatively large, constant air–sea $p\text{CO}_2$ difference. The CO$_2$ covariance fluxes were computed every half hour, and only those fluxes measured when the relative wind was within $\pm 90^\circ$ of the bow and where the ship made minor course corrections were included. This conditional sampling reduced the errors due to flow distortion and inadequate motion correction.

Profiles of CO$_2$, H$_2$O, and DMS were measured using the APB that extended approximately 10 m off the port bow (Fig. 3). The CO$_2$ and H$_2$O profiles were measured with two NDIR detectors, while the DMS measurements were made using a micro-GC and pulsed flame detector (Dacey et al., 1999). One of the NDIR detectors was used to profile the CO$_2$ and H$_2$O within the atmospheric surface layer from 3 to 13 m above the mean water surface. The second NDIR detector continuously sampled CO$_2$ and H$_2$O at 13 m. With this configuration, the signal from the
second detector was used to remove any bias between the two detectors at the start of each profile when the sample intakes are at the same height (Fig. 4). This bias removal was critical to the success of the technique due to the typically small gradients of H$_2$O and CO$_2$. Fig. 4 demonstrates that the atmospheric horizontal variability of H$_2$O ($\sigma = 0.278$ g kg$^{-1}$) is greater than the vertical boundary layer.
gradients ($\sigma = 0.085 \text{ g kg}^{-1}$). The atmospheric horizontal variability is a factor of 3 greater than the vertical gradients. By using the difference between two measurements, the atmospheric variability was removed. The precision of the profiles was increased because the same instrument was used to measure concentrations at each height. Therefore, the scaling parameter was computed from

$$\bar{z}(z) - \bar{z}_r = \frac{x_r}{\kappa} \left[ \ln \left( \frac{z}{z_r} \right) - \psi_L \left( \frac{z}{L} \right) + \psi_L \left( \frac{z_r}{L} \right) \right],$$

(10)

where $\bar{z}_r$ was the reference value of CO$_2$ or H$_2$O measured with the second detector, and each sampling profile began at $z = z_r$. Using this referenced sampling strategy, profiles of H$_2$O and CO$_2$ were measured with high precision as shown in Figs. 5 and 6. The data consistently show that the atmospheric profiles were semilogarithmic.

The gradients of CO$_2$ in the atmospheric boundary layer were relatively small, however, DMS has a large air–sea concentration difference with a flux from the ocean into the atmosphere (Fig. 7). DMS is a valuable tracer for air–sea CO$_2$ flux, as detectable fluxes of DMS exist over the entire ocean from which air–sea gas transfer velocities can be determined. The concentration profiles were corrected for the ship motion and the inset on Fig. 7 shows the predicted DMS concentrations in time. The sample port locations move relative to the ocean surface due to waves and ship motion. Because the concentration boundary layer is semilogarithmic, the concentrations near the surface will have a high bias toward lower elevations. The profiles were corrected assuming a semilogarithmic concentration profile and ship motion estimates using the integrated accelerometers.

The transfer velocities computed from the CO$_2$ micrometeorological techniques and the dual-tracer method are shown in Fig. 8. This is the first time that the dual-tracer and the direct covariance techniques have been deployed simultaneously in the open ocean. The uncertainty in the gas transfer velocity derived from the dual-tracer technique is $\pm 25\%$, based on the least square fit of the natural log of the $^3\text{He}/\text{SF}_4$ concentration ratio vs. time (Eq. 9). These transfer velocities derived from the covariance technique are in good agreement with the parameterization developed by Wanninkhof (1992) using indirect estimates of the flux at low to moderate wind speeds.
Fig. 6. Carbon dioxide profile measured from the Atmospheric Profiling Boom. The solid line is the model-fit to the data. The dashed line is the model with a height correction.

Fig. 7. Profile of dimethylsulfide taken from the Atmospheric Profiling Boom. The solid line is the model-fit to the data and the dashed line is the model with a height correction. The inset shows the concentrations varying with height. Because the inlets move with the ship, concentrations in the marine boundary layer change with height. The concentrations at 3 m are higher with greater fluctuations than at 7 and 13 m.
However, the covariance results give higher values for wind speeds above 12 m $s^{-1}$. The fit to the data using a cubic dependence on wind speed is given by:

$$k_{660} = 3.3 + 0.026 U_1^3.$$ 

(11)

A cubic relationship satisfies the global bomb $^{14}\text{C}$ oceanic uptake constraint (Wanninkhof and McGillis, 1999; Wanninkhof et al., 2001) and has good agreement with mass balance measurements in high latitudes (Tsunogai and Tanaka, 1980; Schneider et al., 1999; Signorini et al., 2000). This is also the first study with a significant number of measurements at winds greater than 12 m $s^{-1}$. Flux measurements during high wind speeds are difficult to obtain from a research vessel. This is partly due to the ship motion and flow distortion experienced in high wind speeds, as well as the distribution of wind speeds. In general, the lack of measurements in high winds is a consequence of the low frequency of high wind speeds and the short duration of research vessel expeditions.

The transfer velocities computed with the profile method are also shown in Fig. 8. While within the range of uncertainty, these estimates are somewhat higher than those obtained from the direct covariance flux measurements. This slight offset between the profile and covariance results could be caused by some of the possible biases discussed. The profile method may be an attractive alternative to compute gas fluxes when the direct covariance method cannot be used due to sensor limitations. This is especially true for fixed towers or spar buoys where the flow distortion and motion correction can be reduced or removed entirely.

5. Conclusions

During the GasEx-98 study in the North Atlantic, results were obtained for measured CO$_2$ fluxes, along with findings on factors controlling variations of pCO$_2$ on short time scales. The CO$_2$ direct covariance flux measurements gave estimates of gas exchange with winds of up to 16 m $s^{-1}$. Measurements of exchange were performed on time scales of less than one week and on spatial scales less than 30 km. The culmination of the air–sea gas transfer velocities reported during GasEx-98 were in general agree-
ment, even with the different uncertainties subject to individual techniques. The CO\textsubscript{2} covariance measurements were in reasonable agreement with the profile method measurements of CO\textsubscript{2} and DMS in the marine boundary layer. There was also good correspondence with gas transfer velocities determined from the water-side measurements using the dual-deliberate tracer technique. The next step is to reduce the uncertainty in the CO\textsubscript{2} flux measurements and explore the variability of CO\textsubscript{2} flux with environmental conditions and biogeochemical processes.

An analysis of the direct covariance data, along with global constraints using bomb \textsuperscript{14}C invasion, supports a cubic relationship with wind speed. If such a relationship holds over most of the ocean, it will sustain a major impact on estimates of carbon dioxide uptake based on air–sea disequilibrium by increasing estimated oceanic CO\textsubscript{2} uptake by approximately 40%. Possible explanations for the enhanced transfer shown by our direct covariance fluxes at high wind speeds are being explored. This includes an investigation of processes associated with enhanced drag and wave breaking. Improved parameterization of the gas transfer is important because a disproportionate amount of the flux occurs at high winds due to the nonlinear relationship between gas exchange and wind speed. Observationally, the problem becomes more complicated in high winds due to the difficulty of obtaining accurate measurements in this regime and because of the limited high wind distribution in nature. While wind speed distributions during GasEx-98 were very close to a global distribution, sustained wind speeds above 20 m s\textsuperscript{-1} were not experienced. The probability of these high winds is relatively low and such data are difficult to obtain on short cruise campaigns. Thus, longer-term observational strategies should be explored for the study of gas transfer under these conditions.

To constrain CO\textsubscript{2} uptake by the ocean on seasonal to interannual time scales, it is essential to quantify the ocean–atmosphere CO\textsubscript{2} flux. To reach the goal of estimating the global CO\textsubscript{2} uptake by the oceans, improved understanding of the processes controlling the CO\textsubscript{2} fluxes over short time and space scales are needed. Once our understanding of the processes is improved, confidence in estimating the flux on a global scale will be greatly enhanced. Significant advances were made in the GasEx-98 study to quantify fluxes and gas transfer velocities, and these measurements have been used to investigate the factors controlling gas transfer. Of particular interest will be the ability to relate these measurements to remotely sensed parameters for global extrapolations.

Acknowledgements

We would like to thank the crew of the NOAA ship Ronald H. Brown for their assistance during the cruise. We would also like to acknowledge Keith Contre, who assisted our efforts to compute direct covariance CO\textsubscript{2} fluxes as a Woods Hole Oceanographic Institution 1996 Summer Student Fellow. This work was supported by the US National Science Foundation Grant OCE-9711218 and NOAA Global Carbon Cycle program, Grant NA96GP0201 and represents Woods Hole Oceanographic Institution Contribution Number 9991.

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