Coastal Ocean Air-Sea CO_2 Flux Measurements from an Autonomous Research Vessel

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1.0 Abstract
During my summer 2007 internship, I set up NASA's autonomous Ocean-Atmosphere Sensor Integration System (OASIS) platform with plug-and-play instrumentation for studying the physical controls on continental shelf air-sea CO_2 fluxes. Here, I (a) summarize methods utilized in a field study of continental shelf waters of the Mid-Atlantic Bight, and (b) describe observations of CO_2, air-sea CO_2 flux, wind, water velocity and surface water turbulence. We will continue to make these measurements during planned bi-monthly cross-shelf transects of the MAB into 2008. The ongoing goal is to seek funding to use multiple OASIS vessels and satellite data for a larger- scale study that covers multiple shelf provinces and more firmly quantifies the global role of continental shelves in the carbon cycle.

2.0 Introduction
Recent studies have suggested that the coastal ocean may play a large role in the global carbon cycle, in spite of its small surface area (Thomas et al., 2004; Cai et al., 2006). A "shelf-sea CO_2 pump" has been observed to function in stratified regions, where primary productivity in an upper layer and respiration in the bottom layer are effectively decoupled due to particle settling. Stratification limits vertical mixing and promotes horizontal export of dissolved inorganic carbon produced in the lower layer to the open ocean (Tsunogai et al., 1999; Thomas et al., 2004). In spite of high spatial and temporal variability, the current estimates of CO_2 air-sea fluxes suggest that the shelf-sea pump is only effective in reducing atmospheric CO_2 in temperate and sub-polar waters, and tropical shelves are typically sources of CO_2 to the atmosphere (Cai et al., 2006).

Several limitations of prior studies must be addressed before we can accurately incorporate continental shelves into global CO_2 budgets, however. Shelf CO_2 air-sea flux can have high spatial and temporal variability (Cai et al, 2006), but the expense of ship time and personnel has limited our ability to adequately sample across this variability. In prior studies, estimates of coastal ocean air-water CO_2 fluxes have relied on highly simplified parameterizations of the gas transfer process, indirect tracer methods (e.g. Ho et al., 2002) or the floating dome technique (e.g. Borges et al., 2004). When parameterized, gas exchange is modeled as a function of wind speed, not actually measured (Cai et al., 2003; Borges, 2005). However, this parameterization often fails in the coastal ocean because it neglects other important influences (e.g. surface films, currents; McGillis et al., 2001; Zappa et al., 2003). The tracer approach has the benefit that it can provide spatially and temporally integrated flux estimates of several km^2 and days to weeks, useful for some studies. However, this is also the main drawback of this approach – poor temporal and spatial resolution limits the understanding of how localized processes influence the fluxes. The floating dome method has the advantage of simplicity and capability to observe rapid changes over short timescales. However, the drawbacks of this method are that the dome blocks the wind and distorts water flow below, which are problematic considering that gas transfer has been shown to rely strongly either on wind speed (Wanninkhof and McGillis, 1999) or water currents (Zappa et al., 2003), depending on the local environment.

Two additional approaches for estimating air-sea fluxes of trace gases such as CO_2 are the direct eddy covariance and gradient flux techniques (McGillis et al., 2001a; Zappa et al., 2003). These methods are innovative and will greatly improve our ability to accurately estimate these fluxes and also understand the driving physical mechanisms. The eddy covariance method is ideal because it is the direct measurement of the flux, and may be used to examine processes that occur at fine temporal and spatial scales (minutes and 10s of meters) that are only limited by sensor noise. However, this method is complicated to apply with data from a pitching vessel at sea, because corrections must be applied to the wind velocity data to remove motion contamination (McGillis et al., 2001). The gradient flux method relies on several simplifying assumptions (summarized in **Section 5**), but also has relatively fine temporal and spatial scales (hours and kilometers). In both cases, one assumes that the flux through the water surface is the same as the turbulent flux within meters above the water surface, which is reasonable because the lower part of the atmospheric surface-boundary layer (ASL) is known as the constant flux layer. The data is being collected in this project to apply both techniques, but at this early stage we have only focused on the latter, which is significantly simpler to apply.

3.0 Instrumentation

OASIS (**Figure 1**) is fitted with physical, chemical and bio-optical sensors for observing air-sea gas fluxes and processes that directly influence these fluxes (e.g. wind speed, water velocity, shear and turbulence). The "Lamont payload" has four main components, described in detail below – (1) an eddy covariance flux system at a height of 2.5 m, (2) a closed path CO_2/H_2O sensor that is fed samples from surface water and the atmosphere at two heights, (3) a rapid-sampling current meter that measures water velocity and turbulence parameters near the sea-surface, and (4) an acoustic Doppler current profiler (ADCP) measuring the profile of water velocity below the vessel. A system is also being developed that performs automated half-hourly vertical profiles of water salinity and temperature using a lightweight winch.

The eddy covariance flux system comprises a Campbell Scientific CSAT 3-D ultrasonic anemometer-thermometer, Licor LI-7500 open path infrared CO_2/H_2O analyzer, and a Systron-Donner MotionPakII inertial sensor with three orthogonal angular rate sensors and linear accelerometers. All sensors are sampled at 10 Hz simultaneously and recorded to a data logger. The eddy flux instruments are mounted on the shorter "mini-mast" on the vessel bow (**Figure 1**), except for the inertial sensor, which is located inside the vessel.

The closed path infrared CO_2/H_2O concentration sensor (Licor, LI-840) receives samples through a gas valve switcher routed in 15-minute increments from six channels: (1) the headspace of an equilibrator that processes surface water from 0.7 m forward of the vessel, with pump intake at 20 cm depth (3 gallons per minute), (2) 1 m height atmosphere, (3) 5 m height atmosphere, (4) 1 m height atmosphere, (5) a tank of N_2, for 0 ppm [CO_2] real-time calibration, and (6) a free channel that is simply taking in air from inside the vessel, but will later also be used for calibration. Concentrations for all samples are measured using the same LI-840 sensor via the switcher, avoiding problems with inter-instrument calibration differences. The gas sample from the headspace of the equilibrator is routed through the LI-840, then back into the water in the equilibrator, forming a closed loop, and allowing equilibration of [CO_2] in the water and headspace air to occur gradually – typically it takes about 5 minutes to achieve a steady concentration estimate.

A 1.75 MHz Modular Acoustic Velocity Sensor, model-3 (Nobska Development Corporation, MAVS-3) is mounted 1.4 m forward of the vessel, sampling ~23 Hz at 50 cm depth. The fast sampling rate allows estimation of the turbulent kinetic energy dissipation rate using the inertial dissipation method (Zappa et al., 2003). A 600 kHz Acoustic Doppler Current Profiler (ADCP; Teledyne-RD Instruments, Workhorse Sentinel) is mounted in a well in the hull below the bow, collecting water velocity profiles from 2.5 to ~50 m depth.

4.0 Field Study: The U.S. Mid-Atlantic Bight

OASIS followed a transect across the Mid-Atlantic Bight on October 17, 2007, as shown by the red line in **Figure 2**. Due to rapid power loss, a conservative approach was used to keep the vessel close to shore, doubling back after traveling some distance offshore – the actual distance covered by the vessel was nearly the length of the full transect (shown in black). The power draw was greater than the solar power generation, even at the period of peak sunlight during the day. At 15:30 h, the Lamont payload was turned off to save power. At night, the batteries quickly lost power, and by 0400h on October 18th, OASIS had too little power to stay on the transect line, and drifted southward. After sunrise, OASIS was able to obtain sufficient power to return to the transect line, but this mission was aborted at this stage.

The Mid-Atlantic Bight (MAB) extends along the United States eastern shoreline from Long Island southward to Cape Hatteras (**Figure 2**). A passive plate margin, the shelf is relatively broad (typically >100 km), as compared with that of Western North America. Relatively steady forcing agents include a coastal current that receives buoyancy from the Labrador Current and typically heads southward along the inner coast (Chapman and Beardsley, 1989), and at the southern end of the MAB, entrainment of relatively warm salty waters from the Gulf Stream (Fennel et al., 2006).

The upper water column hydrography of the MAB shelf is at times highly variable due to cyclical weather patterns that cause wind reversals and upwelling (Houghton et al., 2004), trapped rotating buoyant discharges from the Hudson River plume (Chant et al., 2006), and Gulf Stream warm-core eddies impinging upon the shelf (Mooers et al., 1979). Spring freshets and storm-related floods can superimpose highly stratified low-salinity pulses of river plume water on top of the coastal current (Houghton et al., 2004). Outflow from the Hudson River varies over a factor of 25 in a typical year, with typical annual flow maxima of ~2000 m^3 s^{-1}, and outflows from the region's other major rivers have similar properties (USGS, 2006).

5.0 Estimating the Air-Water CO_2 Flux

An approach for indirectly estimating the turbulent flux of a trace gas over the ocean is the gradient flux or profile technique (McGillis et al., 2001a; Zappa et al., 2003). Here, vertical gradients in the CO_2 number density, C (molar concentration per unit dry volume of air) are used with common assumptions on turbulent mixing in the ASL to estimate the flux, F_C. The primary benefit of this approach is that it relies on the mean vertical gradient of gas concentration, which is often much easier to measure than turbulent fluctuations. Shortcomings include an assumption that the atmospheric flow and vertical CO_2 fluxes are horizontally uniform, reliance on very small vertical gradients that may be similar to the instrument resolution, and the fact that pitching of vessel may move sensor intake vertically and smear vertical gradients, a problem because gradients are not constant over the atmospheric surface layer. Additional drawbacks depend on the assumptions made regarding ASL turbulent mixing – here, we use a model with an eddy diffusivity, a common simplification:

$$F_C = K_C \frac{\partial \overline{C}}{\partial z} \tag{1}$$

Here, F_C is the CO_2 flux, K_C is the eddy diffusivity for CO_2, $\overline{C}$ is the mean CO_2 number density, and z is the height above the sea surface. Our approach to modeling the eddy diffusivity is to use a simple model for turbulence close to a boundary:

$$K_C = \kappa U_* z \tag{2}$$

Where $\kappa = 0.40$ is von Karman's constant. Utilizing the analytical solution to Equation 1 with $\overline{C}$ data at two heights, and applying estimates of U_* from a quadratic drag law $U_* = C_d^{1/2} U$, observed wind speed U, and an assumed sea surface drag coefficient $C_d = 0.001$ (Large and Pond, 1981), the air-sea flux F_C can then be estimated.

Assumptions underlying the use of Equations 1-2 are that buoyancy effects are negligible, the measurements are in the constant flux layer, which is typically valid in the lower 10% of the unstable atmospheric boundary layer, and measurements are above the wave boundary layer, typically assumed to be 1-2x the significant wave height. The negative implications of violation of the last assumption are stronger for momentum or kinetic energy fluxes, and not as serious for mass fluxes (Edson et al., 2004).

CO_2 measurements are used to compute the vertical gradient in mean C. First, the mole fraction output from the LI-840 is corrected for dilution by water vapor (water vapor concentration is also output from the instrument), then these data are converted to the CO_2 number density, C, using an assumed ambient atmospheric pressure of 101000 Pa and temperature measured with the sonic anemometer.

Measurements of $\overline{C}$ are made from gas sample switcher channels 2, 3, and 4 – low atmospheric (z = 1 m), high atmospheric (z = 5 m), and the replicate low atmospheric samples, respectively. It is important to distinguish between actual vertical gradient in C and the local temporal change over the 15 minutes between channel changes, $\partial C/\partial t$. A first-order correction is computed from the difference between the first and last low atmosphere sample C, then the vertical gradient is computed as the mean of the two gradient estimates (chs. 2 vs 3, and chs. 4 vs 3) – centered on the same time as the temporal change estimate.

6.0 Results and Discussion

Transect data are shown in **Figures 3-5**, including raw CO_2 data, averaged CO_2 mixing ratios (C), and wind speed. Winds were moderate (2-5 m s^{-1}) and from the south all day. The cycle through the gas valve switcher is demonstrated in **Figure 3**, showing raw [CO_2] data. Average CO_2 number densities (C) for the low and high atmospheric gas samples are shown in **Figure 4**. Raw [CO_2] data for switchbox Ch. 2 appears to be biased, when compared with Chs. 3 and 4 – likely from a leaky connection inside the vessel, where there is a high [CO_2]. This is not an uncommon problem, and in subsequent field work at another site the problem appears to have been solved by running a new gas line. As a result, the correction for temporal change between switcher samples was omitted from this analysis; however, [CO_2] in the atmospheric samples (channels #3-4) was not changing rapidly, as shown in **Figure 3**. Therefore, this likely had little negative effect on the accuracy of these results.

The computed air-water flux of CO_2 is shown in **Figure 6** and ranges from 19-32 mmol CO_2 m^{-2} day^{-1}. Comparing our flux estimates with prior studies will be problematic until we have longer temporal coverage because we expect high seasonality for mid-latitude estuarine and coastal ocean fluxes. However, a rapid examination of those prior results suggests that our fluxes are reasonable for a shallow (~20 m) continental shelf location very close to the coastline near the mouth of an estuary. A recent synthesis found that some continental shelves are sources and some sinks of CO_2, with mean flux magnitudes from 0-6 mmol m^{-2} day^{-1} (Cai et al, 2006). A synthesis of estuarine data found higher fluxes, typically from the water to the atmosphere (as in our study), from 0-200 mol C m^{-2} day^{-1} (Borges, 2005). A study of a mid-latitude eddy showed mean fluxes of 12 mmol m^{-2} day^{-1} (McGillis et al., 2001b).

To conclude, we have measured CO_2 concentrations and utilized an innovative method for estimating air-water fluxes across the coastal ocean. The measurements were made aboard an autonomous research vessel that provides the capability to collect similar data year-round at minimal expense. The majority of prior studies estimating coastal ocean air-water CO_2 fluxes have used simplified parameterizations that neglect potentially important driving variables, tracer techniques, or floating domes, which have many drawbacks. The gradient flux method is an improvement because it provides flux estimates on short timescales and relies on few assumptions of what variables drive the gas transfer.

7.0 Future Plans

Deployments are scheduled to occur on a bi-weekly schedule through 2008, which will enable us to study seasonal and cross-shelf variations in CO_2 air-water fluxes. The direct covariance eddy flux measurements that are already being made hold great promise for studying the fluxes and forcing variables at high resolution, and the analysis of these data will be undertaken as part of this ongoing research project. We are adding more batteries and a wind generator to OASIS2 in an attempt to increase power for the next deployment, which will occur November 28-29, weather permitting.

An important improvement to the gradient flux technique will be to use two LI-840 sensors; one for sampling the water [CO_2] through the equilibrator continuously, and the other for only the atmospheric samples. This will allow the atmospheric sampling LI-840 to be calibrated to have much a much narrower dynamic range, improving precision substantially. Perhaps most importantly, this will allow us to use a 1-minute switchbox schedule, dramatically reducing our temporal resolution from 90 to 2 minutes – the reason for the 15-minute switching was purely to support the lengthy time for the equilibration of the water samples.

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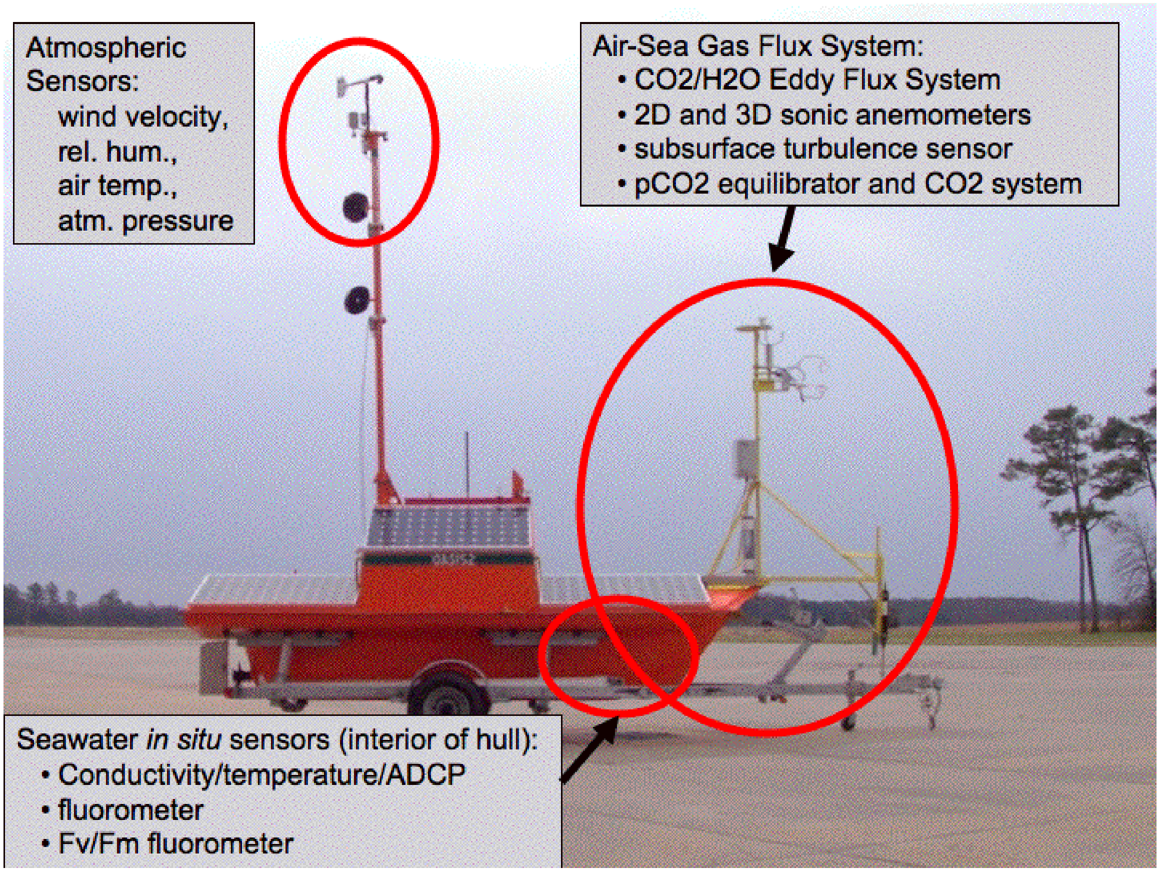

Figure 1: An Ocean Atmosphere Sensor Integration System (OASIS), a solar-powered (battery stored) surface autonomous vessel that can be controlled by satellite communication. This picture shows the system "set up" last year, but much of the summer internship was actually spent doing engineering work, setting up the instrumentation and cabling to be plug-and-play – when power is cycled on the vessel, instruments automatically start sending data to data loggers without any action by NASA scientists or engineers. This will permit OASIS to collect our data during planned year-round transects such as the one described in this report.

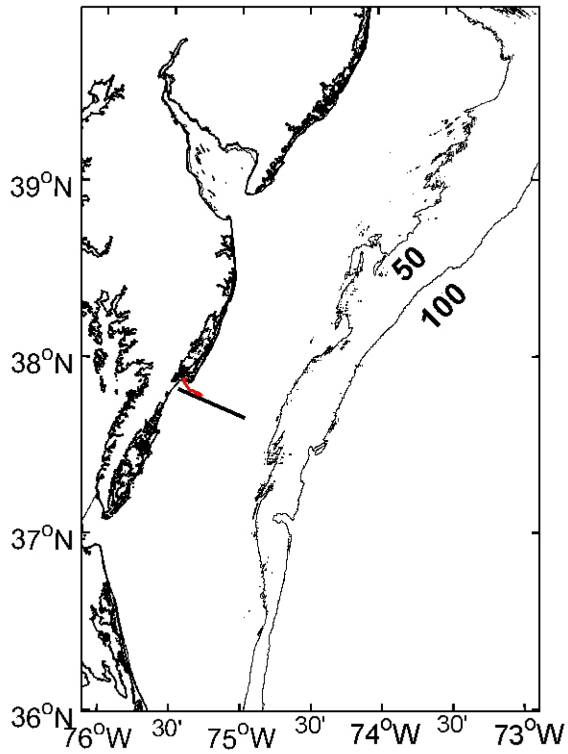

Figure 2: Central region of the Mid-Atlantic Bight, with location of the OASIS transect on October 17, 2007 (red line) and the planned transect (black) – this is the "COBY line", run with an additional vessel that makes bio-optical and hydrographic measurements every two weeks. Only the portion of the red ship track when the Lamont payload was turned on is shown.

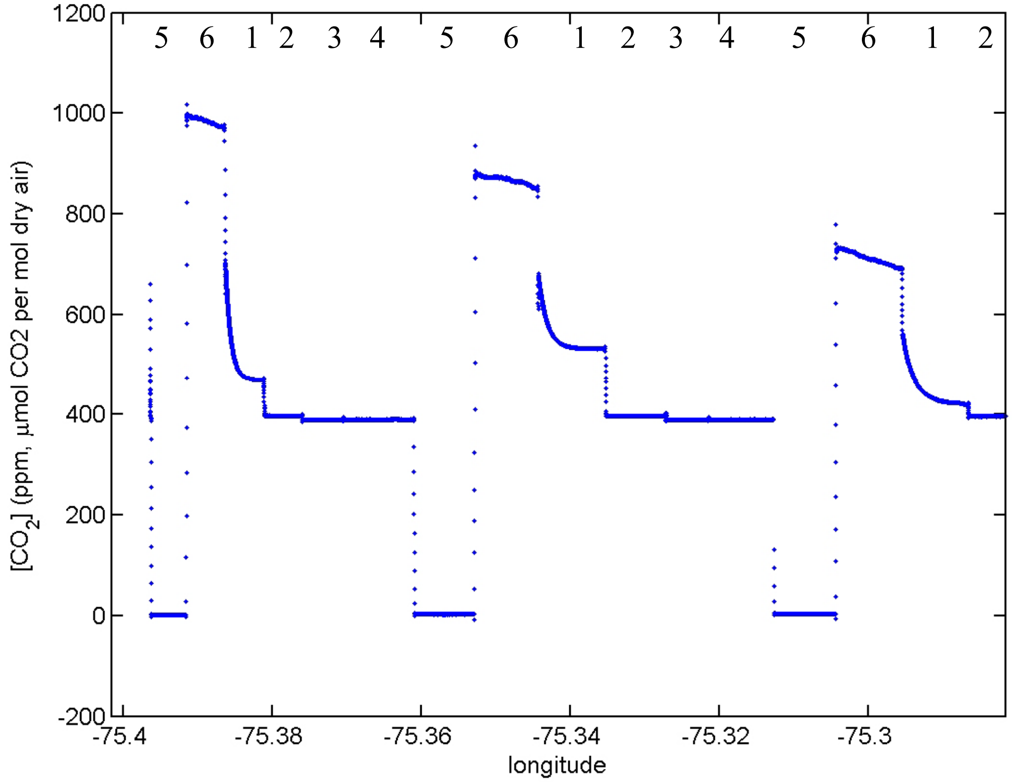

Figure 3: Raw CO_2 along the transect from the LI-840 instrument. Data for Ch. 2 appears likely to be bad, when compared with Chs. 3 and 4 – likely from a leaky connection inside the vessel, where there is a high [CO_2]. The sloping curve during sampling on channel 1 is due to gradual equilibration of the water CO_2 sample in the equilibrator, discussed in **Section 3**.

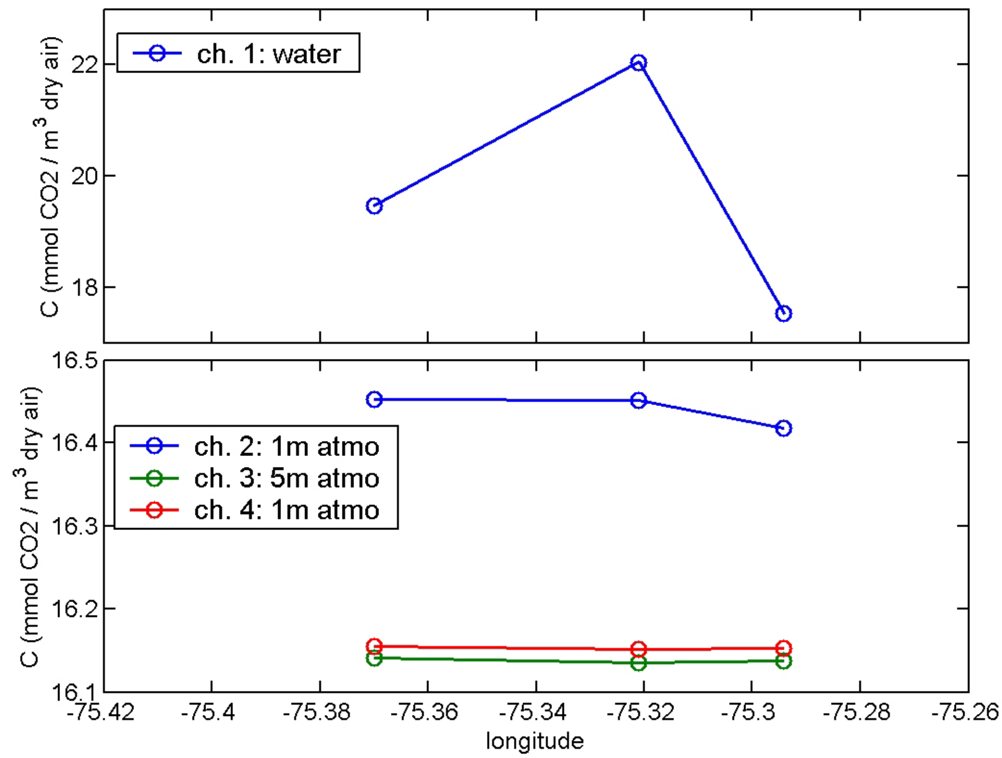

Figure 4: Average CO_2 along the transect, including CO_2 number density (C) data for switcher channels (1) water, (2) 1m atmosphere, (3) 5m atmosphere, and (4) 1m atmosphere. Only data from the last half of each 15-minute period is used in the average.

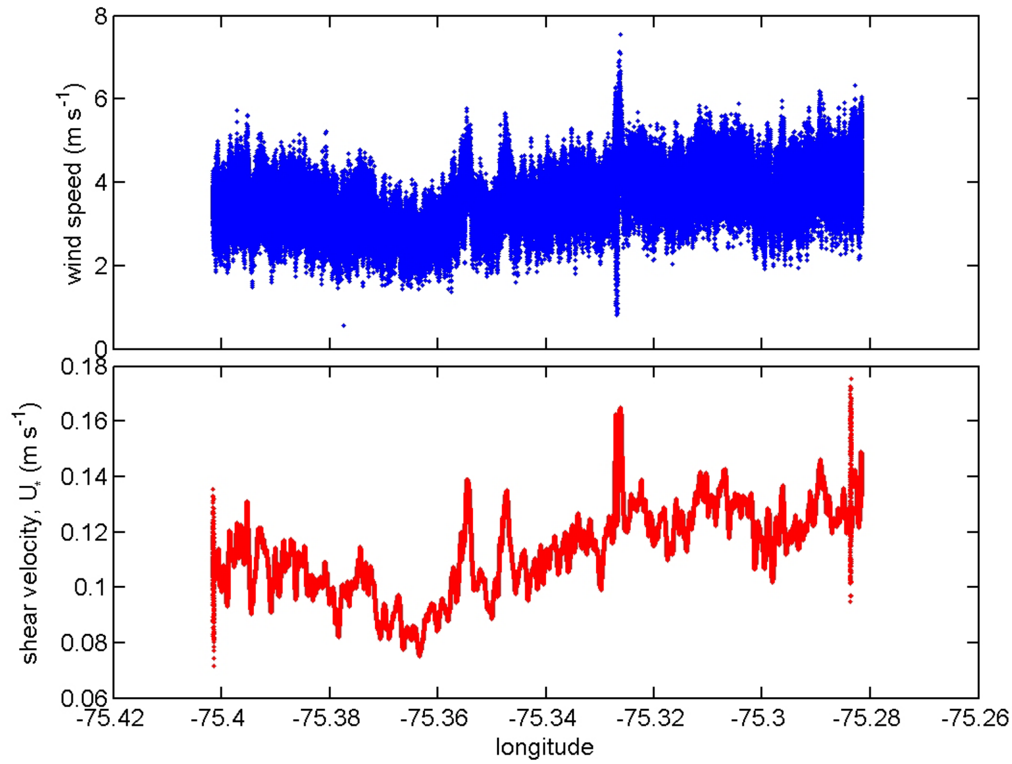

Figure 5: Wind speed data and shear velocity estimates along the OASIS transect. Shear velocity is smoothed with a 1-minute running average.

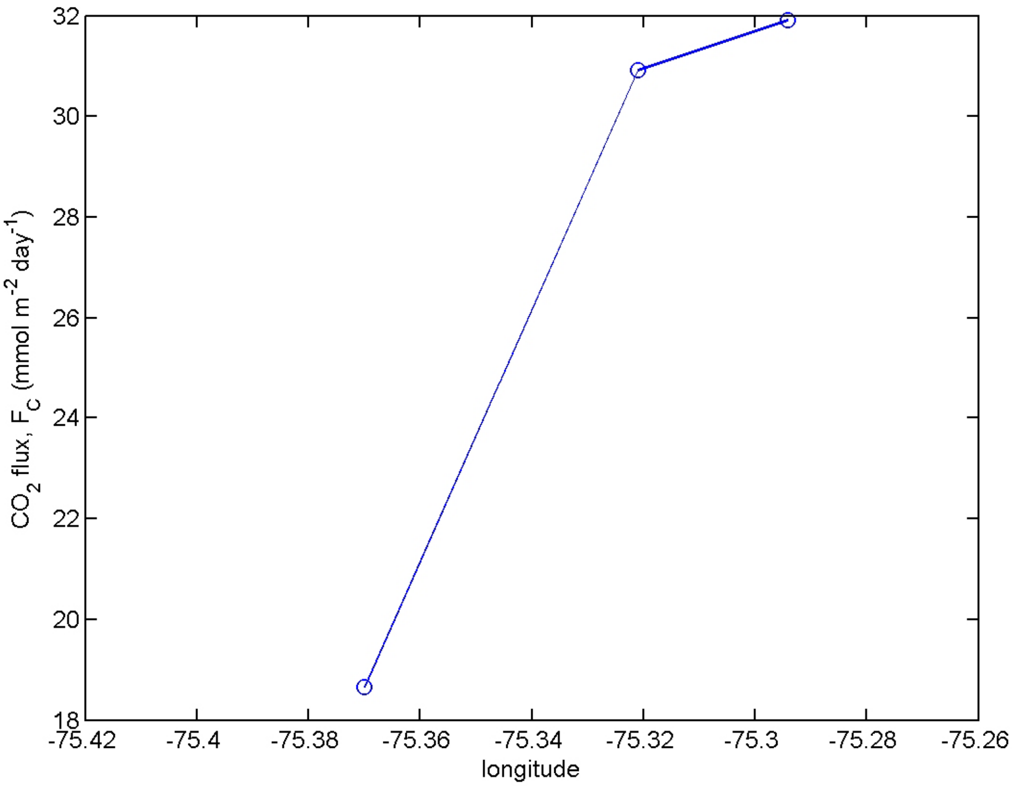

Figure 6: Air-water CO_2 fluxes computed using the gradient flux method.