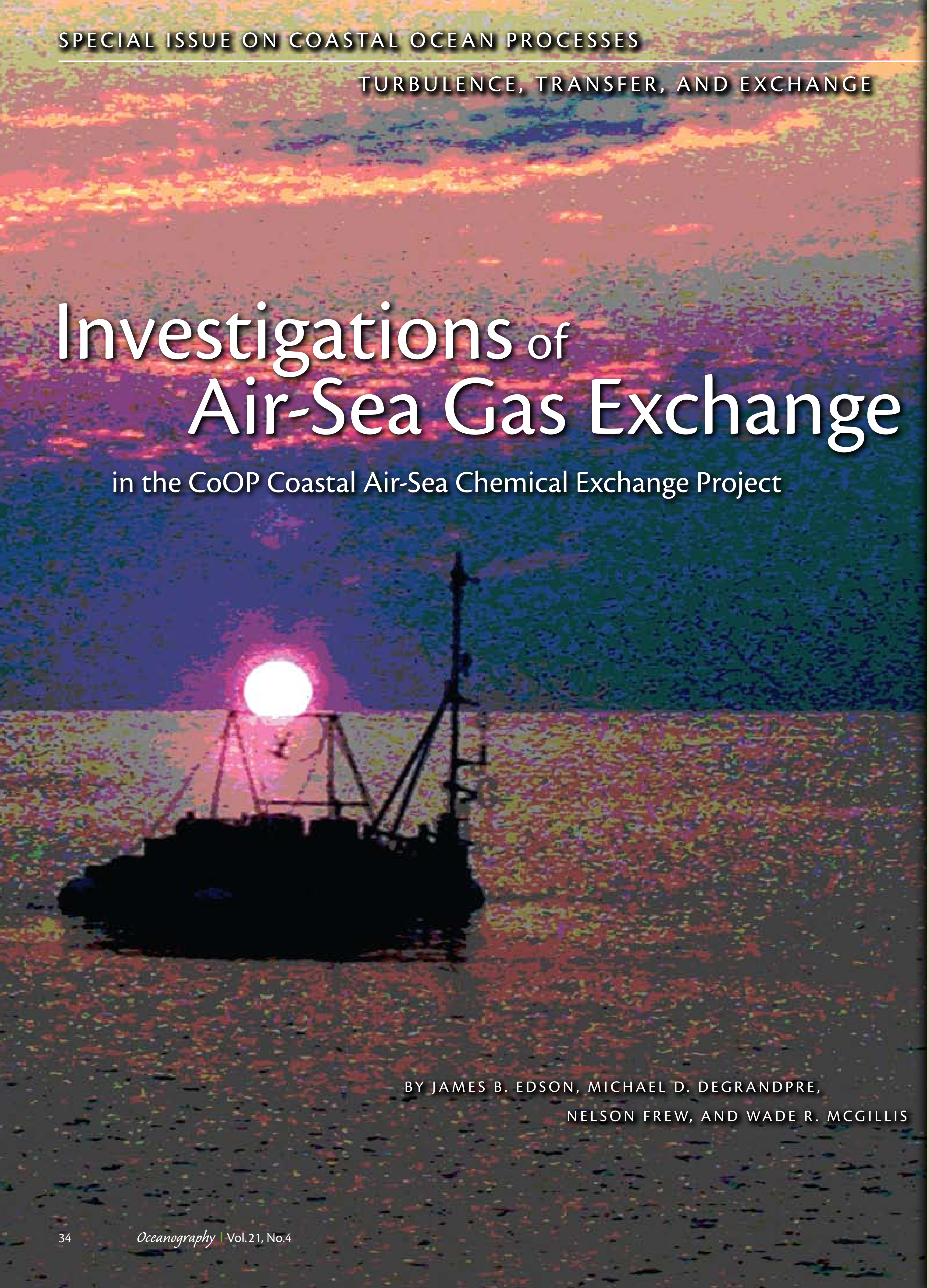
SPECIAL ISSUE ON COASTAL OCEAN PROCESSES

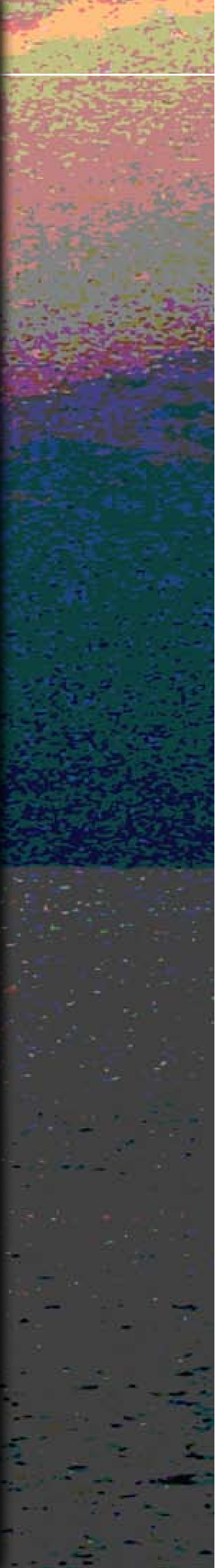
TURBULENCE, TRANSFER, AND EXCHANGE



Investigations of Air-Sea Gas Exchange

in the CoOP Coastal Air-Sea Chemical Exchange Project

BY JAMES B. EDSON, MICHAEL D. DEGRANDPRE, NELSON FREW, AND WADE R. MCGILLIS



ABSTRACT. The exchange of CO_2 and other gases across the ocean-air interface is an extremely important component in global climate dynamics, photosynthesis and respiration, and the absorption of anthropogenically produced CO_2. The many different mechanisms and properties that control the air-sea flux of CO_2 can have large spatial and temporal variability, particularly in the coastal environment. The need for making short-time-scale and small-spatial-scale estimates of gas transfer velocity, along with the physical and chemical parameters that affect it, provided a framework for the field experiments of the Coastal Ocean Processes Program (CoOP) Coastal Air-Sea Chemical Exchange (CASCEX) program. As such, the CASCEX project provided an opportunity to develop some of the first in situ techniques to estimate gas fluxes using micrometeorological and thermal imagery techniques. The results reported from the CASCEX experiments represent the first step toward reconciling the indirect but widely accepted estimates of gas exchange with these more direct, higher-resolution estimates over the coastal ocean. These results and the advances in sensor technology initiated during the CASCEX project have opened up even larger regions of the global ocean to investigation of gas exchange and its role in climate change.

GAS EXCHANGE IN COASTAL ENVIRONMENTS

The exchange of CO_2 and other gases across the ocean-air interface is an extremely important component in global climate dynamics, photosynthesis and respiration, and the absorption of anthropogenically produced CO_2. The many different mechanisms and properties that control the air-sea flux of CO_2 can have large spatial and temporal variability, particularly in the coastal environment. For example, the surface concentration of CO_2 can vary with temperature, salinity, bubble entrainment, physical mixing, and biological productivity. Also, gas transfer rates can vary with sea state and surface chemical enhancement.

Laboratory experiments (e.g., Liss and Merlivat, 1986) show that gas exchange can be reasonably modeled using

$$F_G = K_G\,(G_w - G_a/H) = K_G \Delta G \qquad (1)$$

where F_G is the gas flux, K_G is the gas transfer velocity, G_w and G_a are the gas concentrations in bulk seawater and in the air, and H is the appropriate Henry's law solubility constant (McGillis et al., 2000; Hintsa et al., 2004). This approach is closely related to the bulk flux method (e.g., Fairall et al., 1996, 2003; Hare et al., 2004) in which, $K_G = C_G U_r$ where C_G is a dimensionless transfer coefficient for gas exchange and U_r is the wind speed relative to water. Therefore, we would expect K_G to vary at least linearly with wind speed. Studies also show that K_G varies with oceanic and atmospheric stability, sea state, Schmidt number (a gas-dependent function of temperature and salinity), and a host of surface processes (e.g., Liss, 1983; Liss and Merlivat, 1986; Liss et al., 1988; Brutsaert and Jirka,1984; Wilhelms and Gulliver, 1991; Jähne and Monahan, 1995; Donelan et al., 2002; McGillis et al., 2004a; Borges and Wanninkhof, 2007; Garbe et al., 2007).

In 1994, the Coastal Ocean Processes (CoOP) Program supported a study to examine the exchange of CO_2 and other climate- and weather-relevant compounds (CWRC) in the coastal ocean. The study was in recognition of the growing concern for the impact of greenhouse and other gases on climate and of the key role the coastal ocean may play in processing these gases. Therefore, CoOP initiated the Coastal Air-Sea Chemical Exchange (CASCEX) project, which involved field experiments off the US west coast at Monterey, California, and off the east coast in the Mid-Atlantic Bight. The project concentrated on investigations to improve our ability to estimate CWRC fluxes in coastal regions.

In particular, the project provided an opportunity to develop some of the first in situ sensors to estimate the fluxes on shorter temporal and spatial scales using micrometeorological and thermal imagery techniques. Improvement of these techniques was critical to investigating the processes governing gas exchange in the coastal environment where biogeochemical and physical processes act on shorter time scales than in the open ocean. Specifically, although the coastal ocean's role in the uptake of anthropogenic CO_2 is widely debated (Borges, 2005), its importance in processing the carbon from terrestrial sources (e.g., through rivers, runoff, and groundwater) and exporting carbon to the open ocean has been well established (Ducklow and McCallister, 2004).

Additionally, there was a need in the gas-exchange community to either reconcile or explain the significant differences found between the micrometeorological and indirect, but better established, estimates of gas transfer velocities. Prior to the CoOP experiments, determining the rate at which CO_2 was exchanged between the ocean and atmosphere was a very controversial subject. Specifically, indirect methods such as the radiocarbon, radon, and radioisotopic methods give long, time-averaged transfer velocities ranging from 12–24 cm hr^{-1} (Peng et al., 1979; Broecker and Peng, 1982; Jähne, 1985; Broecker et al., 1986). Although a few estimates over the Great Lakes by Donelan and Drennan (1995) were more in line with these estimates, most previous estimates of transfer velocity using direct covariance (eddy correlation) flux estimates were orders of magnitude larger (e.g., Jones and Smith, 1977; Wesely et al., 1982; Smith and Jones, 1985). Although physical processes may have been responsible for some of this discrepancy, Broecker et al. (1986) provided compelling evidence that CO_2 sensors available at the time were simply not sensitive enough to measure the CO_2 signal.

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A FIRST STEP TOWARD COMMUNITY CONSENSUS

The CASCEX experiments represent the first step towards reconciling the indirect but widely applied estimates of gas exchange (e.g., equation 1) with more direct estimates based on micrometeorological approaches and thermal imagery over the coastal ocean. CASCEX initiated and continued the development of sensors, many of which were being used only in laboratory studies, to measure gas exchange at sufficient resolution to investigate these processes. The techniques developed during CASCEX and subsequent programs have allowed us to investigate the behavior of the transfer velocity at low and high wind speeds where oceanic stratification (e.g., McGillis et al., 2004b) and wave breaking (e.g., Woolf, 2005), respectively, strongly influence turbulent exchange. Although basic questions remain about which environmental processes are most important in controlling the exchange, these measurements and techniques have led to a growing consensus in the scientific community about the behavior of the gas transfer velocity. For example, radiocarbon, mass balance, and micrometeorological techniques all suggest that the transfer velocity varies as the square of the wind speed under low to moderate wind conditions (e.g., Wanninkhof, 1992).

In the sections that follow, we provide a retrospective look at the CASCEX project. We begin by describing the field programs and summarizing the major scientific results from the project with appropriate references. We then focus on the sensors and techniques that were developed during the CASCEX project and the role they have played in subsequent and ongoing studies. We describe the sensors developed to measure the fluxes and mean concentrations required to: (1) ascertain the environmental mechanisms controlling gas exchange, (2) quantify the coastal ocean and atmosphere gas characteristics, and (3) improve our parameterization of the transfer velocity required to perform estimates of coastal CWRC budgets and to improve climate models.

THE CASCEX FIELD EXPERIMENTS

Two field experiments were conducted under the CoOP CASCEX project. The first study took place aboard R/V *New Horizon* off Monterey, California, in April and May 1995. This experiment leveraged some of the assets deployed during the Marine Boundary Layers (MBL) experiment supported by the US Office of Naval Research (ONR), which included R/P FLIP, R/V *Wecoma*, and the LongEZ aircraft. The second CASCEX experiment took place on R/V *Oceanus* in the Mid-Atlantic Bight in June and July 1997. The objective of these studies was to understand the effects of atmospheric, oceanic, and interfacial processes on air-sea gas exchange. Jointly, groups from the Woods Hole Oceanographic Institution, the University of Rhode Island, the Scripps Institution of Oceanography, and the University of Heidelberg deployed a new suite of in situ instruments to measure gas transfer velocity; momentum, heat, water vapor, dimethylsulfide (DMS), and CO_2 fluxes; directional wave spectra; surface microlayer chemical enrichment; and near-subsurface turbulence on the short time scales commensurate with natural forcing variability. Measurements were made with ship-based instrumentation and with a newly developed, remotely operated research catamaran known as LADAS (Laser Slope Gauge/Acoustic Doppler Current Profiler/Anemometry Package/Surface Sampler). Figure 1 shows LADAS being deployed from R/V *Oceanus*.

Figure 1. Deployment of the LADAS platform from R/V *Oceanus* during the 1997 CASCEX cruise. The instrumented mast on the starboard side of LADAS supports two sonic anemometers and four samplers with Tenex traps for DMS profiles. LADAS was released from its tether and remotely controlled to operate beyond the wake of the ship. *Photo by Sean McKenna*

The ship-based systems included a high-resolution infrared imaging system capable of estimating the air-sea gas exchange, and a direct covariance flux system (DCFS) (Edson et al., 1998). Vertical profiles of DMS were measured from both the ship and LADAS to provide additional estimates of the gas flux using the profile method and a newly developed micro-gas chromatograph (micro-GC) (Dacey et al., 1999; McGillis et al., 2001a). The catamaran carried systems to quantify the surface wave characteristics using a scanning laser slope gauge and a wave-wire array (Hara et al., 1998), and an additional meteorological package to quantify the near-surface atmospheric turbulence. A fluorometry package measured microlayer enrichments of colored dissolved organic matter (CDOM) (Frew et al., 2004). Subsurface instrumentation included an array of acoustic current meters to measure the near-surface current profile and various turbulence statistics.

These field experiments represent the first coincident measurements of atmospheric forcing, surface chemical enrichment, small-scale surface roughness, and gas transfer rates, allowing several aspects of gas exchange mechanisms to be studied. Results from the CoOP ’95 cruise were published by Haußecker (1996) and Jähne and Haußecker (1998); those from the CoOP ’97 cruise were published by Schimpf et al. (2004) and Frew et al. (2004). These investigations relied heavily on the use of thermal imagery to compute the transfer velocity using surface renewal theory (Schimpf et al., 2004). These estimates were in good agreement with previously published wind-speed-dependent parameterizations of transfer velocity.

Frew et al. (2004) compared the transfer velocity estimates with the surface wave measurements from LADAS and found an even stronger correlation with mean square slope of short wind waves. They found that the wind speed-dependent parameterization overpredicted the transfer velocity at low wind speeds in the presence of surface films. However, the reported gas transfer parameterization based on the mean square slope gave a better prediction even in the presence of surface films. This type of parameterization is particularly attractive for use with satellites as remotely sensed estimates of wave slope can be used to estimate the transfer velocity from space to provide global estimates of gas flux (Frew et al., 2007).

These more sophisticated parameterizations of transfer velocity (e.g., based on wave statistics or subsurface turbulence) play a key role in improving our understanding of the processes that control gas exchange. However, wind-speed-dependent parameterizations of the transfer coefficients are likely to remain important components of global climate models (GCMs) as they are reasonably accurate and easy to implement (i.e., they don't require a separate wave model). Therefore, in the sections that follow, we focus our attention on the micrometeorological methods that readily lend themselves to this type of parameterization. We examine those techniques that were successfully developed and deployed during the CoOP experiments. We also briefly describe how these techniques were improved in subsequent programs, and conclude with a summary on the state-of-the-art in wind-speed-dependent parameterizations of gas transfer velocity.

MICROMETEOROLOGICAL SENSORS AND TECHNIQUES

Micrometeorological methods have been used for decades to measure gas exchange over land. For example, direct covariance and profile methods are routinely employed to measure the CO_2 flux over vegetative fields and forest canopies where the signal-to-noise ratio for CO_2 sensors is high. Infrared gas analyzers (IRGA) are commonly used to measure CO_2 concentration by absorbance (Edson, 2001). The direct covariance method correlates the gas concentration with the vertical velocity typically measured using sonic anemometers to provide a direct estimate of the flux:

$$F_G = \overline{w'G'} \qquad (2)$$

where the overbar represents a time average, and w' and G' are the fluctuating components of the vertical velocity and gas of interest, respectively. The profile method assumes that the gradient is directly proportional to the flux:

$$F_G = -K_M \frac{d\overline{G}}{dz} \qquad (3)$$

where z is the height above the surface and K_M is the variable of proportionality known as the eddy diffusivity for mass. The eddy diffusivity is typically determined using parameterizations that rely on Monin-Obukhov similarity theory (e.g., Edson et al., 2004).

Another important consideration in accurately measuring these fluxes concerns the nature of the gas measurement itself. For example, if the gas sensor measures the mixing ratio, r_G (mass of gas per mass of dry air), then the fluctuating component is simply $G' = \rho_a r_G'$, where ρ_a is the mean density of dry air. However, many gas analyzers measure the density of the gas, ρ_G, in mass or moles of gas per volume of moist air. When the density is used to estimate the flux, Webb et al. (1980) showed that the flux must be corrected for the density variations caused by water vapor and temperature.

The need for this correction can be illustrated by considering an upward buoyancy flux of warm, moist air from the ocean surface. This air is typically replaced by cooler, dryer (denser) air from aloft. Therefore, a small mean vertical velocity must be present to preserve the assumption of zero mean vertical mass flux of dry air (Fuehrer and Friehe, 2002). To see how this vertical velocity affects the gas flux, we consider a perfectly level and accurate anemometer over a horizontally homogeneous surface. In this setting, such an ideal device would be able to measure the appropriate vertical mean and the fluctuations about it. This vertical velocity could then be correlated with the gas density to estimate the flux, i.e., $F_G = \overline{w\rho_G}$.

Even when the ocean is considered horizontally homogeneous, this approach is not practical in the marine surface layer where platform motion and flow distortion make it nearly impossible to measure the true mean vertical velocity from real sensors. Therefore, the direct covariance fluxes are computed by correlating the fluctuations about their respective means and applying a correction for the missing vertical velocity contribution:

$$F_G = \overline{w'\rho_G'} + \overline{w}\,\overline{\rho_G} \qquad (4)$$

where $\overline{w}$ is commonly estimated using the approach of Webb et al. (1980) and includes terms to account for the sensible and latent heat fluxes. The community now refers to this approach as the Webb correction. A recent review of the Webb correction and similar approaches is given in Fuehrer and Friehe (2002).

A correction of this sort is required for all forms of micrometeorological methods, for example, the direct covariance, profile, and bulk methods (see Webb et al., 1980; Fairall et al., 1996). Although this term often represents a negligible correction for water vapor fluxes, it is often a significant correction for CO_2 fluxes. For example, Figure 2 shows the magnitude of the correction over an oceanic CO_2 sink region, where the Webb correction reduces the measured flux in the presence of a positive latent heat flux. The correction can be substantially larger than the flux itself in regions of strong heat fluxes. In fact, the correction can change the sign of the measured versus actual flux over CO_2 source regions with large positive heat fluxes. This observation has led investigators to reduce this correction by physically drying air samples before they reach the

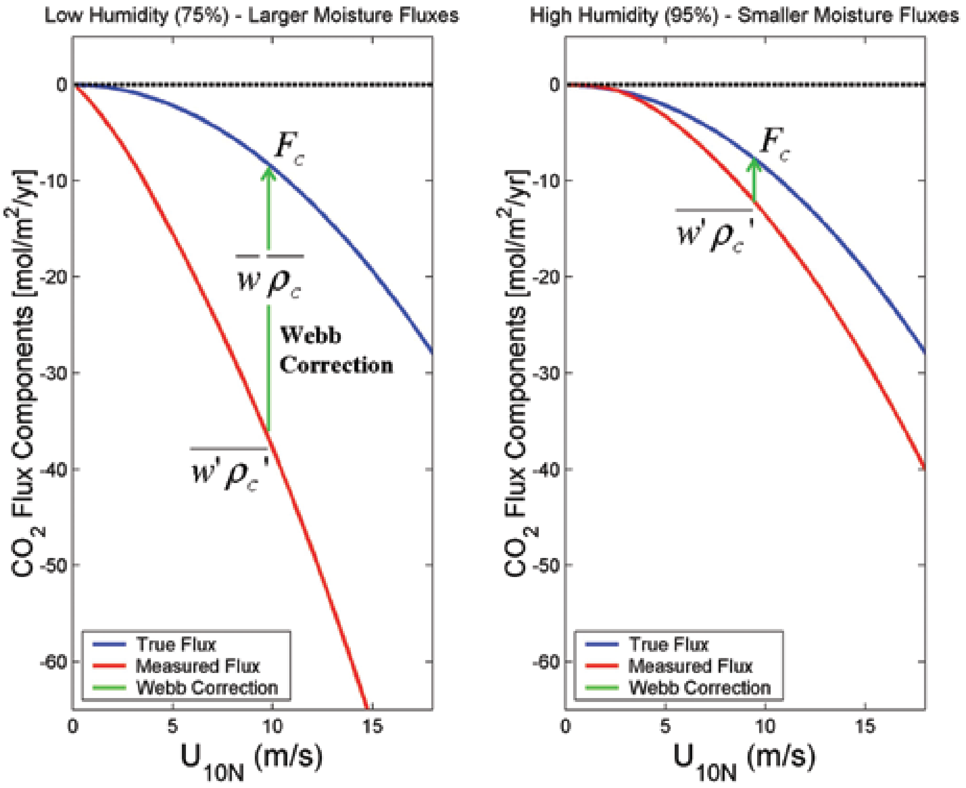

Figure 2. This figure illustrates the need to Webb correct the measured CO_2 fluxes to accurately estimate the true flux. Representative values of the measured and true fluxes are shown in red and blue, respectively, as a function of wind speed. The magnitude of the correction is indicated by the green arrow, that is, the Webb correction is added to the measured flux (red line) to estimate the true flux (blue line). The size of the correction is a function of the magnitude of the heat fluxes, which is illustrated by looking at the moisture (latent heat) flux component of the Webb correction under conditions of low (left panel) and high (right panel) relative humidity. The left panel shows that the correction is two to three times larger than the true flux under low relative humidity conditions and large latent heat fluxes. The right panel shows that the correction is considerably smaller at near neutral conditions, but is not negligible even at a relative humidity of 95%.

detector to remove the moisture. This step allows the sensors to directly measure a concentration that can be more readily converted to the mixing ratio, but at the expense of sensor response. Our approach in the CoOP project and subsequent field programs has been to measure the moisture and temperature fluctuations and "dry" the sample numerically (McGillis et al., 2001b).

OCEANIC APPLICATIONS

Application of these techniques to measure CO_2 flux over the ocean is a challenge due to the low signal levels in the marine atmosphere (i.e., very small r_C fluctuations). The small signal is a direct consequence of CO_2 being in near equilibrium because of its long lifetime in the atmosphere and because it is a waterside-controlled gas (Liss and Slater, 1974; McGillis et al., 2000). The result is very small gradients in the atmospheric surface layer, even in regions of large ΔpCO_2. We have attempted to illustrate the small signals in Figure 3 by plotting a representative profile of CO_2 (e.g., see Figure 6 in McGillis et al., 2004b) in the upper left-hand panel next to a simulation of the resulting CO_2 fluctuations normalized by the mean atmospheric concentration. To resolve the profile requires a precision of 0.1 ppm, which is less than 0.1% of the mean atmospheric concentration. As such, vertical gradients and fluctuations of CO_2 in the marine surface layer are extremely difficult to resolve with sufficient accuracy to estimate the flux using the profile method over the ocean. The small flux also results in a very low signal-to-noise ratio for CO_2, which makes it difficult to resolve the turbulent fluctuations required for the direct covariance method. For example, the standard deviation of the fluctuations shown in Figure 3 is approximately 0.02 ppm for ΔCO_2 of approximately 100 ppm. As pointed out by Broecker et al. (1986), the large transfer velocity values estimated using direct covariance fluxes prior to CoOP were likely due to insufficient signal and too much noise.

Fortunately, this situation began to change leading up to CASCEX with the development of more sensitive IRGAs. CASCEX '97 deployed a prototype dual-wavelength, open-path IRGA (to measure both water vapor and CO_2) developed by the National Oceanic and Atmospheric Administration's (NOAA's) Air Resources Laboratory, Atmospheric Turbulence and Diffusion Division in Oak Ridge, Tennessee. The RMS noise in the CO_2 signal for this device is of order 0.01 ppm, which provides reasonable estimates of the flux for ΔCO_2 greater than approximately 50 ppm, as shown in Figure 3. This instrument was paired with the DCFS (Edson et al., 1998) largely developed as part of the 1995 CASCEX and MBL experiments. CASCEX also deployed a commercially available closed-path sensor (LI-COR 6262) for mean concentrations during the experiment. The closed-path system formed the basis of a fast response CO_2 system that was paired with the DCFS during the GasEx (gas exchange) experiments (McGillis et al., 2001a, b; 2004b).

On the other hand, DMS is somewhat soluble and qualifies as a partially air-side-controlled gas with a readily measurable gradient over the ocean (Hintsa et al., 2004). DMS has a short lifetime in the MBL and usually maintains a large sea-to-air flux. However, DMS has very low absolute concentrations and the main issue leading up to the CoOP experiments was the ability to measure DMS concentrations with sufficient accuracy and precision. Conventional gas chromatographs (GCs) were clearly not fast enough for the direct covariance approach, and the time required to concentrate and process samples hampered our attempts to measure the gradient. However, this issue began to resolve itself in the early nineties with the development of micro-GCs and improved trapping and/or storage techniques. Specifically, the low DMS concentration in the air (e.g., DMS is found in parts per trillion versus parts per million for CO_2) required that it be trapped and extracted before running through a GC. In CoOP ’97, investigators used Tenax TA traps to collect and concentrate the DMS samples before they were run through the micro-GCs. The traps were deployed at multiple heights on LADAS (Figure 4), while the same sampling inlet was moved to different heights to compute the gradient from the bow of R/V *Oceanus* (Dacey et al., 1999).

Technological developments from these studies were refined and implemented in the first open ocean air-sea gas exchange study, the GasEx-1998 program. Figure 5 shows the composite results for transfer velocities based on atmospheric measurements of air-sea gas flux. CASCEX fluxes using the meteorological approaches of the CO_2 direct covariance technique are plotted with the GasEx-1998 CO_2 direct covariance, CO_2 profile, and DMS profile air-sea flux measurements. Also shown for comparison are the waterside-deliberate SF_6-^3He tracer

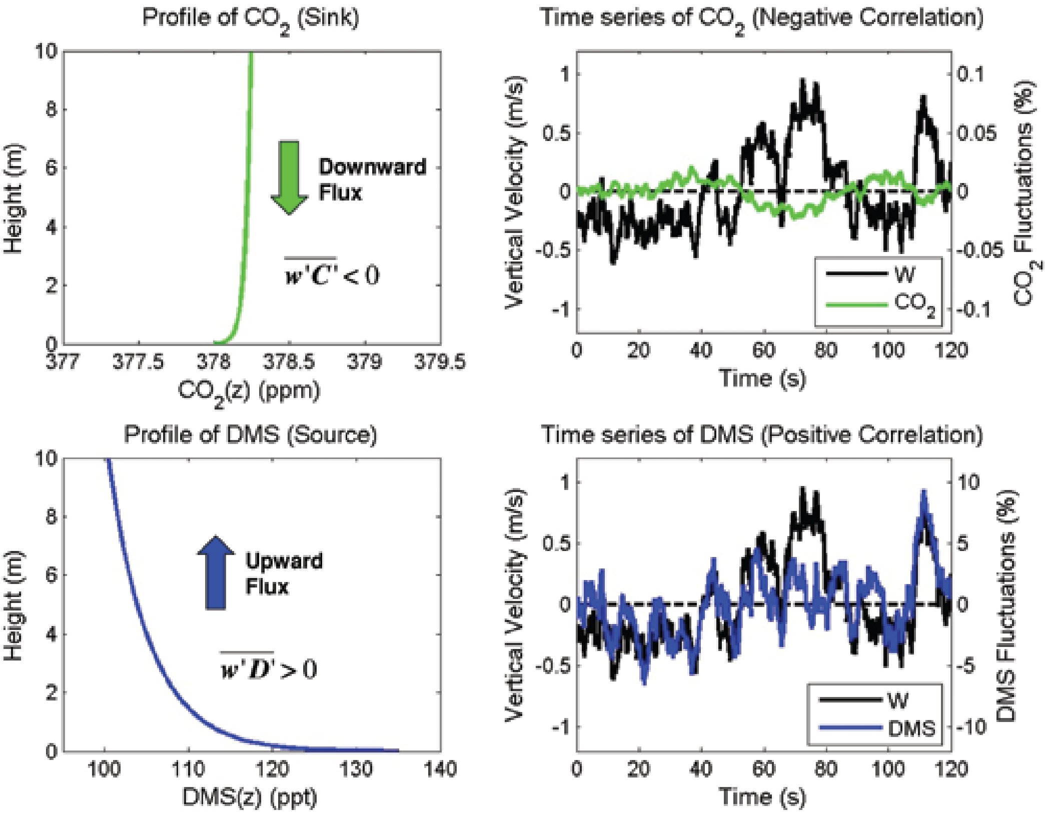

Figure 3. Typical profiles of CO_2 and DMS at right and simulations of the turbulent fluctuations of CO_2, DMS, and vertical velocity based on these profiles at a wind speed of 10 m s^{-1}. The CO_2 profile is representative of a sink region with a bulk air-sea concentration difference of 100 ppm (i.e., the waterside bulk concentration is approximately 278 ppm). The DMS profile is representative of the typical oceanic source of DMS found over the ocean. The CO_2 signal is negatively correlated with the vertical velocity signal while DMS is positively correlated, indicating the expected downward and upward fluxes, respectively. The DMS flux is uniformly positive over the world’s ocean. The downward CO_2 flux shown here is most commonly found at high latitudes, while upward fluxes are expected over the source regions commonly found at lower latitudes. The fluctuations are plotted after normalization by their respective mean concentrations at a height of 10 m. The figure clearly shows how small the CO_2 fluctuations are relative to the mean concentrations, while the DMS fluctuations are orders of magnitude larger compared to their means. On the other hand, the mean concentrations for DMS are orders of magnitude smaller than CO_2 as indicated by the profiles.

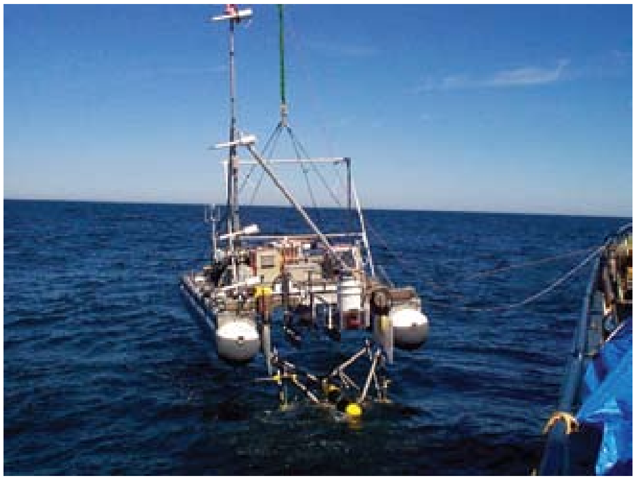

Figure 4. The LADAS platform just before it is lowered into the ocean, showing airside and waterside instrumentation, including, again, the four DMS samplers and two sonic anemometers. The microlayer sampler is visible as two small pontoons cascaded between the larger pontoons. The white canister above and yellow torpedo-shaped device below make up the scanning laser slope gauge. Also visible but less distinct are components of the wave-wire and subsurface-ADV arrays. *Photo by Sean McKenna*

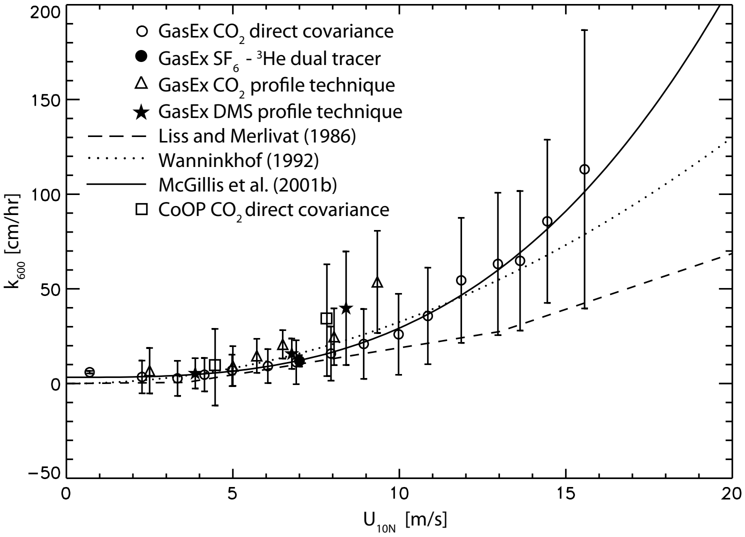

Figure 5. Gas-transfer velocity versus wind-speed measurements from CoOP and GasEx-1998. A cubic wind speed relationship from McGillis et al. (2001b), with a finite zero-wind-speed offset, is fit to this data and shown for comparison. Transfer velocity versus wind speed relationships based on ^{14}C budgets (solid line) and on lake and wind-tunnel experiments (dotted line) are shown for comparison.

results and a range of wind speed-gas exchange parameterizations.

Later experiments simply collected the gas in Tedlar bags, which allowed the investigators to store the DMS without loss for extended periods until it could be concentrated and analyzed in a more controlled laboratory setting (Zemmelink et al., 2002). The success of these experiments led to the development of more sophisticated profiling systems deployed during the Fluxes, Air-sea Interaction, and Remote Sensing (FAIRS) (Hintsa et al., 2004) and GasEx-2001 experiments (Zemmelink et al., 2004). In these subsequent experiments, the use of Tedlar bags to collect DMS samples allowed investigators to implement the relaxed eddy accumulation method. In this method, air is conditionally sampled into two separate bags, one containing the air samples measured in updrafts ($w' > 0$) and the other in downdrafts ($w' < 0$).

Therefore, this method is essentially using the vertical velocity measurements shown in Figure 3 and sampling the air into one bag when the fluctuations are above the $w' = 0$ line and into another bag when they are below the line. After a given time (usually 10–30 minutes), the gas concentrations in the two samples are measured, and their difference is proportional to the flux:

$$F_G = \beta\sigma_W(\overline{G}_{up} - \overline{G}_{down}) \qquad (5)$$

where σ_W is the standard deviation of the vertical velocity, $\overline{G}_{up}$ and $\overline{G}_{down}$ are the concentrations in the updrafts and downdrafts, respectively, and β is a calibration coefficient. This approach was successfully used to estimate fluxes during the FAIRS and GasEx-2001 experiments and showed reasonably good agreement with fluxes determined using the profile method (Zemmelink et al., 2004; Hintsa et al., 2004).

The most recent advance in the measurement of DMS flux over the ocean has involved the implementation of atmospheric pressure ionization mass spectrometry (APIMS). APIMS detectors have developed to the point where they can continuously measure DMS concentration at high flow rates to estimate the flux using the direct covariance method (Bandy et al., 2002; Huebert et al., 2004; Marandino et al., 2007). The successful implementation of the direct covariance technique for DMS opens up a much larger portion of the global ocean to investigation of gas exchange due to its larger signal.

OCEANOGRAPHIC SENSORS AND TECHNIQUES

Waterside measurements provide the concentration difference required to compute the gas transfer velocity when combined with any of the above estimates of the fluxes. In early CoOP experiments, these data were collected with underway pCO_2 (e.g., Wanninkhof and Thoning, 1993) and DMS analyzers (Dacey et al., 1999), plumbed to a ship's seawater line. These systems typically have a response time of a few minutes. On R/P FLIP, where space was limited, newly developed pCO_2 sensors (SAMI-CO_2; DeGrandpre et al., 1995) were mounted on FLIP's hull. Autonomous O_2 sensors (YSI, Inc.) were also deployed with the CO_2 sensors. Although the pCO_2 sensors provide data for Equation 1, O_2 measurements are valuable for discerning the processes that control sea surface pCO_2 variability and, through a mass balance, for comparison to changes in mixed-layer O_2 due to gas exchange (DeGrandpre et al., 1998).

In recent years, several CoOP-funded investigators have applied micrometeorological techniques to the waterside. The development of robust and rapid response sensors for O_2 and three-dimensional currents (e.g., ADVs) has made it possible to perform direct covariance measurements below the ocean surface (Berg et al., 2003; Berg and Huettel, this issue). These micro-oceanographic measurements have focused on O_2 fluxes just above the sediment-water interface where gradients are large. Unfortunately, application of the direct covariance method to determine the flux just beneath the ocean surface remains a challenge. For example, near the ocean surface, both platform motion and wave orbital velocities are typically an order of magnitude larger than the turbulent fluctuation required to estimate the fluxes. Additionally, we do not have fast response sensors for sub- and near-surface concentrations for

MAYBE IT'S NOT JUST ABOUT AIR-WATER GAS EXCHANGE

By Richard A. Jahnke

There is considerable interest in quantifying the air-sea exchange of CO_2 in coastal ecosystems. As repositories of terrestrial organic carbon that cannot be accounted for in sediment deposits, early researchers presumed that coastal waters were regions of significant CO_2 efflux to the atmosphere. However, recent global syntheses of direct estimates of CO_2 air-sea fluxes on continental shelves generally suggest that shelf waters are net sinks for atmospheric CO_2 globally (Cai et al., 2006; Borges et al., 2005), removing roughly 0.3 Pg C a^{-1}, while nearshore and estuarine waters are generally a net source.

The exclusive focus on air-water exchange, however, overlooks the potential contribution from intertidal plants, such as salt marsh grasses and mangrove trees, which remove CO_2 directly from the atmosphere and release a significant portion directly to coastal waters through losses from roots and by the degradation of leaf litter and other detritus (Figure 1). A significant portion of this carbon will not immediately escape back to the atmosphere. Rather, it may be transported laterally onto the continental shelf and into the open ocean because most organic forms have a low vapor pressure, and in inorganic form, carbon has a long gas equilibration time at the pH of seawater.

Accurate global estimates of the intertidal plant CO_2 pump are not yet achievable, but several lines of evidence suggest that it could be significant. A recent compilation by Bouillon et al. (2008) suggests that above-ground net primary production of mangrove systems is much greater than the estimated emission of CO_2 from the associated surrounding aquatic compartment, implying significant lateral loss of carbon. Wang and Cai (2004) report a similar imbalance for salt marshes. Recently, atmospheric tower eddy correlation CO_2 flux estimates confirm a large imbalance between net plant uptake and local release to the atmosphere from underlying sediments and waters, implying a major lateral loss (Yan et al., 2008). Shelfwide carbon budgets confirm that a significant portion of the exported carbon is not rapidly lost to the atmosphere but is delivered to the open ocean (Thomas et al., 2004). Measured local imbalances extrapolated globally using estimates of global salt marsh and mangrove areas suggest a potential atmosphere-to-coastal water transfer of approximately 0.5 Pg C a^{-1}. This magnitude of transfer is consistent with estimates from global gross production of salt marsh and mangrove systems of 1.44 Pg C a^{-1} (Gattuso et al., 1998) and carbon export estimates from mangrove ecosystems (Robertson et al., 1991).

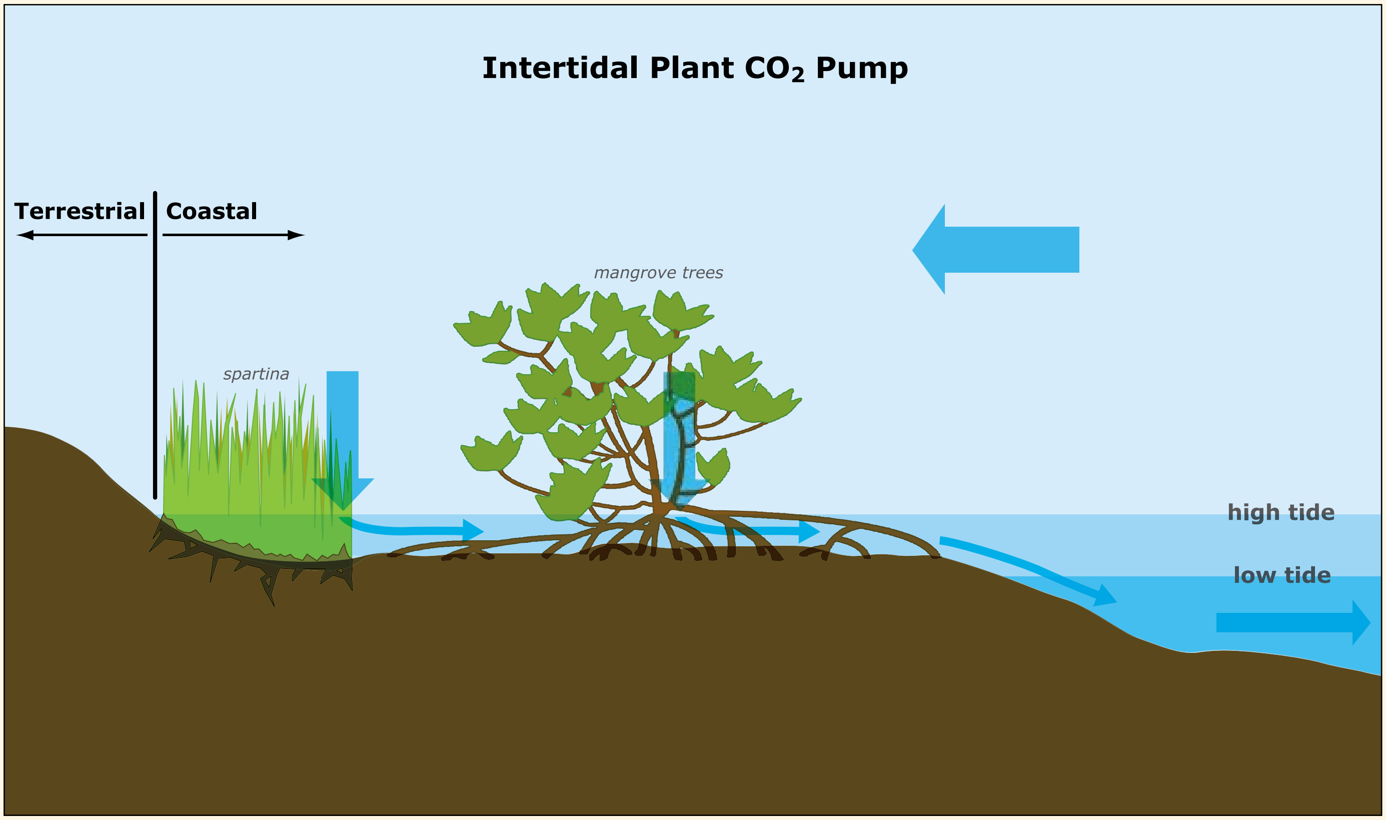

Figure 1. Schematic of the intertidal plant CO_2 pump. Plants such as salt marsh grasses and mangrove trees remove CO_2 directly from the atmosphere. Degradation of plant litter and release through roots directly transfers carbon to the coastal aquatic system independent of air-water gas exchange.

Although great uncertainty in the net flux estimate remains, there are no conflicting observations. Taken at face value, this preliminary estimate of intertidal plant CO_2 transfer is larger than net coastal air-water exchange (sum of estuarine, nearshore, and continental shelf exchange) and of similar magnitude as pre-industrial global ocean evasion (0.6 Pg a^{-1}; Sarmiento and Gruber, 2002). Furthermore, it is important to note that the intertidal plant transfer is a unidirectional "pump" and not an exchange process. It is likely to be relatively insensitive to increasing atmospheric CO_2 concentrations but may be altered through other impacts such as coastal development and sea level rise. It is clear that net air-ocean CO_2 transfer in coastal ecosystems cannot be quantitatively determined solely by assessing air-water exchange but that future studies must adopt a more holistic approach that includes assessing other transfer pathways, such as the intertidal plant pump and groundwater discharge.

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many gases of interest.

Fortunately, the sources of velocity contamination due to platform motion and waves can be significantly reduced by averaging the waterside gas concentration at a given depth over many wave periods. Because both CO_2 and DMS are predominantly under waterside transport control, they often exhibit large gradients just beneath the ocean surface. This condition makes it possible for wave-following moorings and drifters to resolve the near-subsurface gradient, which can then be used with the micro-oceanographic profile method to estimate the flux (McGillis et al., 2004b). Considerably slower sensors can also be used, such that the analytical demands are greatly relaxed for these measurements. These micro-oceanographic approaches have become an important component of the GasEx and other field programs. Their flux estimates provide an excellent complement to micrometeorological measurements for investigating the processes that drive air-sea exchange.

SUMMARY

The CoOP-sponsored CASCEX project produced a number of important scientific findings on many of the processes that control gas exchange, for example, the role of gravity-capillary waves (Hara et al., 1998), surface renewal (Garbe et al., 2004), surfactants (Frew et al., 2004), and atmospheric forcing (Schimpf et al., 2004) on their transfer. The CASCEX project is also notable for the technological advances in gas exchange sensors and techniques that were developed. For example, CASCEX investigators pioneered the use of micro-GCs to measure DMS profiles and estimate DMS flux. This technique was refined and successfully deployed during the 2000 FAIRS experiment to estimate DMS fluxes alongside a relaxed eddy flux system. The CASCEX cruises also marked the initial deployment of a system using the controlled flux technique at sea. This system helped spur the development of other active and passive IR techniques for use during GasEx and FAIRS.

These CASCEX studies also spurred innovations in dissolved gas measurement technology on the ocean side of the air-sea interface. These innovations include the development of in situ pCO_2 sensors, low-power and small-sized gas equilibrators, total gas tension sensors, and rapid, high-sample-throughput systems for shipboard analysis (e.g., for DMS). Not only are these measurements required for calculating gas transfer rates from airside direct flux measurements, but they also have advanced our understanding of the processes that control dissolved gases. Further advances in rapid-response, in situ chemical sensors (e.g., for O_2) are making waterside direct flux measurements possible.

CASCEX provided an important step toward reconciling the indirect but widely accepted estimates of gas exchange with more direct estimates based on micrometeorological approaches and thermal imagery. Micrometeorological techniques have been used subsequently to estimate CO_2 fluxes and transfer velocities over regions of the global ocean where ΔpCO_2 is large. For example, the fluxes from the GasEx campaigns are being used to improve our understanding of how high winds, sea state, and oceanic stratification impact these parameterizations. Significant progress has also been made in our ability to estimate DMS fluxes using micrometeorological techniques, including the direct covariance approach. These and other advances in sensor technology are opening up even larger regions of the global ocean to investigation of gas exchange and its role in climate change.

ACKNOWLEDGEMENTS

Funding for this work was provided by the National Science Foundation (NSF) CoOP program under grants OCE-9410534 and OCE-9711285 while the authors were employed at the Woods Hole Oceanographic Institution. Continued support has been provided by NSF under the GasEx program (OCE-9711218, OCE-9986724, OCE-0647475). The authors would also like to acknowledge the contributions of the other investigators in the CASCEX project, including John Dacey, Tetsu Hara, Horst Haussecker, Bernd Jähne, Sean McKenna, Robert Nelson, Uwe Schimpf, Mete Uz, Suzanne Wetzel, and especially Erik Bock who led the CASCEX efforts.

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