A New Measurement of CO₂ Eddy Flux in the Nearshore Atmospheric Surface Layer

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Fluxes of CO₂ in the atmospheric surface layer have been measured at a shoreline site by the eddy correlation method using a new CO₂ sensor with greater sensitivity than the ones used in earlier studies. In this experiment, preliminary to more extensive measurements at an offshore site, 13 upward and downward fluxes were observed to respond to differences in pCO₂ between water and air. As in an earlier study, a negative correlation of CO₂ flux was found with hourly change in wind speed.

INTRODUCTION

The eddy correlation method is the only direct method for measuring the vertical flux of gases such as CO₂ over homogeneous surfaces. Gas exchange between the ocean and atmosphere traditionally has been estimated by measuring or in some way estimating parameters of a simple diffusion model [Danckwerts, 1970; Liss and Slinn, 1983]. An indirect method for estimating CO₂ exchange is based on an analogy with the exchange rate required to explain the deficiency of radon in the upper ocean (relative to equilibrium concentration in sea water) due to its escape to the atmosphere. The inherent averaging time of several days makes it difficult to relate the exchange rate to controlling environmental parameters such as wind speed, sea state, and concentration of CO₂ in surface water, all of which typically vary over shorter intervals. Other isotopic methods have much longer averaging times.

Only a few eddy correlation measurements of fluxes of CO₂ over the ocean have been reported [Jones and Smith, 1977; Wesely et al., 1982; Smith and Jones, 1985; Ohtaki et al., 1989]. These generated controversy and even skepticism [O'Brien, 1986; Broecker et al., 1986; Smith and Jones, 1986; Wesely, 1986]. The flux values have generally been larger than estimates based on radon and other geochemical methods. They have not been accompanied by very precise determinations of partial pressure (pCO₂) in the surface water, which makes comparisons of piston velocities or exchange coefficients difficult. The eddy flux measurements, which are averaged over about 15 to 60 min and can show responses to changes in environmental conditions, have not been continued long enough in sequence (several days) to emulate the averaging inherent in radon profile estimates of gas exchange. Jones and Smith [1977] attributed upward fluxes of 0.02 to 0.04 mg m⁻² s⁻¹ to decreasing solubility due to seasonal warming. Wesely et al. [1982] reported even larger fluxes. Using the same experimental setup, they also reported a few downward fluxes over fresh water at a 9-m tower in Lake Michigan which showed no serious discrepancy with the radon results. Denmead [1989] derived CO₂ fluxes over a flooded rice paddy from profiles in the atmospheric surface layer. Large water-to-air CO₂ concentration differences (up to 1600 ppm) were generated by biological decay, and CO₂ transfer velocities were reported to be comparable to those derived from oceanic radon profiles.

The average of 13 eddy flux measurements reported by Smith and Jones [1985] on November 4, 11, and 14, 1978, is only −0.001 mg m⁻² s⁻¹, not significantly different from zero. In spite of the negligible mean value, these fluxes did show a correlation with the rate of change of wind speed. In storms or surf zones where breaking waves entrain substantial volumes of air in bubbles, seen as whitecaps persisting for tens of seconds, surface waters can be supersaturated [Thorpe, 1982, 1984] with atmospheric constituents including CO₂. It was inferred that during periods of increasing winds, surf zone activity entrained air and CO₂ which were subsequently released during periods of decreasing winds. All of the marine data were taken at masts on shore, and presumably all sites had a surf zone upwind of the sensors. Broecker et al. [1986] argued that the marine CO₂ eddy flux values are transient fluxes within the atmosphere that do not originate at the air-sea interface or that they are experimental artifacts. Wesely [1986] replied that direct comparison of coastal and open-ocean results is not justified because the dominant processes may be quite different. Smith and Jones [1986] pointed out that even though the short-term variation of their fluxes might originate in the surf zone, the small average value is not at all incompatible with the results of isotopic methods [e.g., Deacon, 1981; Roether and Kromer, 1984; Smethie et al., 1985; Wanninkhof et al., 1985, 1987].
Agricultural micrometeorologists have had considerable success in measuring CO₂, water vapor, and other eddy fluxes over crops from both towers and low-flying aircraft and in relating these fluxes to evapotranspiration and plant metabolism [Austin et al., 1987; Chahuneau et al., 1989, Desjardins et al., 1989]. Over actively growing crops the CO₂ flux is typically -1 to -2 mg m⁻² s⁻¹; the difficulty of measuring the flux over the sea arises mainly from its much smaller value. It is also difficult to provide a site away from the influence of a coast or shallow water: a ship is generally unsuitable because of its motion and the flow distortion by its hull, and there are limitations to flying aircraft at low levels over the ocean. The difficulties are compounded by salt spray, which is hostile to optical and electronic devices. In spite of these difficulties, the time is ripe to resolve perceived differences between micrometeorological and isotopic determinations of sea surface CO₂ exchange. A first step will be to develop a capability to measure CO₂ flux and related parameters at coastal sites which require relatively simple logistics. We report in this paper eddy flux measurements obtained using a recently developed, more sensitive CO₂ sensor.

THE BEDFORD BASIN EXPERIMENT

Method

Eddy correlation flux measurements were made at the shore of Bedford Basin (Figure 1) during a 1-week experiment, November 5–11, 1989. The general approach to eddy correlation flux measurement was the same as in the earlier measurements [Jones and Smith, 1977; Smith and Jones, 1985]. The major difference from the earlier work was a more sensitive detector of atmospheric CO₂ fluctuations. Other instrumentation was equivalent to that used earlier.

A sonic anemometer-thermometer (Kaijo Denki Ltd., Tokyo, model DAT 300) and a glass-coated microthermistor were used to sense wind and temperature fluctuations. An infrared sensor [Chahuneau et al., 1989] gives partial density of CO₂ and H₂O from relative absorption at pairs of wavelengths (4.3 and 3.9 μm and 2.6 and 3.9 μm, respectively), over an open path of 0.25 m, with frequency response of 30 Hz. It was designed to measure CO₂ fluxes over agricultural crops [Chahuneau et al., 1989], where fluxes are substantially larger than those expected over the ocean. Its peak-to-peak noise level of ±0.3 mg CO₂ m⁻³ is at least an order of magnitude less than the sensor used by Jones and Smith [1977] and Smith and Jones [1985]. Because the noise is not correlated with vertical wind fluctuations, reasonably accurate estimates of the covariance of vertical wind with CO₂ fluctuations are possible. We can expect to be able to measure fluxes an order of magnitude smaller than those reported previously (-0.04 to 0.02 mg m⁻² s⁻¹), i.e., as small as 0.002 mg m⁻² s⁻¹. Ideally, we would desire still lower noise levels for measuring CO₂ fluxes over the ocean. Temperature and humidity fluctuations also enter into the CO₂ flux calculation [Smith and Jones, 1979; Webb et al., 1980]; the difference between the "raw" and "corrected" fluxes (Table 1) also includes an adjustment for cross talk in the sensor due to overlap of the infrared absorption bands of water vapor and CO₂.

Instruments were mounted on a 10-m mast about 20 m downwind from a steep, rocky embankment about 3 m high at the shoreline. The fetch over water was 2.6 to 3.6 km for winds from 222° to 278°. According to the Gash [1986] model, at a height of 10 m the fetch over water contributes at least 90% of the eddy flux [Schuepp et al., 1990]. The shoreline site was not ideal, and it would be preferable to work at an offshore tower, away from airflow distortion, wave breaking, and inhomogeneities of pCO₂ in nearshore waters. This experiment was designed as a precursor to a more ambitious program at an offshore site.

Results

Suitable onshore winds were present only on November 10 and 11, 1989. On November 10 we have data from 1400 to

Fig. 1. Instrument mast at the Bedford Basin experimental site, showing (from left to right at top of mast) the sonic anemometer, infrared CO₂ and water vapor sensor, and propellor anemometer.
TABLE 1. Eddy Fluxes and Associated Results

<table>
<thead>
<tr>
<th>Run</th>
<th>4</th>
<th>5.1</th>
<th>5.2</th>
<th>6</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>14</th>
<th>15</th>
<th>17.1</th>
<th>18</th>
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<tbody>
<tr>
<td>Date, Nov. 1989</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>11</td>
<td>11</td>
<td>11</td>
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</tr>
<tr>
<td>Start time, UT</td>
<td>1420</td>
<td>1515</td>
<td>1545</td>
<td>1644</td>
<td>1837</td>
<td>1930</td>
<td>2023</td>
<td>2106</td>
<td>1452</td>
<td>1652</td>
<td>1602</td>
<td>1828</td>
<td>1907</td>
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<td>Duration, s</td>
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<td>1800</td>
<td>1800</td>
<td>2559</td>
<td>2908</td>
<td>2944</td>
<td>2106</td>
<td>2300</td>
<td>1860</td>
<td>2837</td>
<td>2664</td>
<td>2760</td>
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<tr>
<td>$U_{10}$, m s$^{-1}$</td>
<td>8.93</td>
<td>8.20</td>
<td>7.90</td>
<td>7.45</td>
<td>6.52</td>
<td>6.21</td>
<td>6.70</td>
<td>7.10</td>
<td>6.21</td>
<td>6.88</td>
<td>6.33</td>
<td>6.10</td>
<td>6.10</td>
</tr>
<tr>
<td>$\Delta U/\Delta t$, m s$^{-1}$ h$^{-1}$</td>
<td>-0.89</td>
<td>-0.60</td>
<td>-0.42</td>
<td>-0.36</td>
<td>-0.35</td>
<td>-0.17</td>
<td>-0.51</td>
<td>-0.68</td>
<td>-0.51</td>
<td>-0.86</td>
<td>-0.96</td>
<td>9.37</td>
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<tr>
<td>$(p_{\lambda})$, g m$^{-3}$</td>
<td>11.54</td>
<td>11.14</td>
<td>10.73</td>
<td>9.59</td>
<td>7.92</td>
<td>7.12</td>
<td>7.88</td>
<td>6.56</td>
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<td>599</td>
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<td>612</td>
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<td>616</td>
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<tr>
<td>$(\rho C_{w})$, mg m$^{-2}$ s$^{-2}$</td>
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<td>643</td>
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<tr>
<td>$(-\mathbf{w}).(\rho U_{3})$, C m s$^{-1}$ s$^{-2}$</td>
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<td>-0.027</td>
<td>-0.029</td>
<td>-0.022</td>
<td>-0.025</td>
<td>-0.015</td>
<td>-0.010</td>
<td>-0.005</td>
<td>-0.002</td>
<td>0.005</td>
<td>0.002</td>
<td>-0.002</td>
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<tr>
<td>$(-\mathbf{w}).(\rho U_{3})$, g m$^{-3}$</td>
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<td>-0.015</td>
<td>-0.011</td>
<td>0.006</td>
<td>0.030</td>
<td>0.027</td>
<td>0.017</td>
<td>0.007</td>
<td>0.033</td>
<td>0.039</td>
<td>0.032</td>
<td>0.033</td>
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<tr>
<td>$(p_{\rho C_{w}})$, mg m$^{-2}$ s$^{-1}$</td>
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<td>0.099</td>
<td>0.078</td>
<td>0.027</td>
<td>0.020</td>
<td>0.016</td>
<td>0.048</td>
<td>0.022</td>
<td>-0.063</td>
<td>-0.034</td>
<td>-0.011</td>
<td>-0.090</td>
<td>-0.062</td>
</tr>
<tr>
<td>$F_{C_{w}}$, mg m$^{-2}$ s$^{-1}$</td>
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<td>0.036</td>
<td>0.014</td>
<td>-0.016</td>
<td>0.002</td>
<td>0.007</td>
<td>0.045</td>
<td>0.022</td>
<td>-0.034</td>
<td>-0.011</td>
<td>-0.001</td>
<td>-0.083</td>
<td>-0.064</td>
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<td>$10^{3} C_{10}$</td>
<td>1.73</td>
<td>2.12</td>
<td>2.00</td>
<td>1.80</td>
<td>1.54</td>
<td>1.89</td>
<td>0.94</td>
<td>2.71</td>
<td>1.68</td>
<td>0.34</td>
<td>2.03</td>
<td>1.12</td>
<td></td>
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<tr>
<td>$10^{3} C_{T}$</td>
<td>1.50</td>
<td>1.49</td>
<td>1.38</td>
<td>1.47</td>
<td>1.31</td>
<td>1.35</td>
<td>0.73</td>
<td>0.43</td>
<td>0.73</td>
<td>0.43</td>
<td>0.73</td>
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<tr>
<td>$10^{3} C_{C}$</td>
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<td>1.20</td>
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<td>2.65</td>
<td>2.04</td>
<td>2.65</td>
<td>1.60</td>
<td></td>
</tr>
</tbody>
</table>

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2200 UT, after the passage at about 1300 UT on November 10, of a cold front associated with a weak frontal wave tracking north of the Gulf of St. Lawrence. (Local time is 4 hours behind UT.) The winds ahead of the cold front were 10 - 20 m s$^{-1}$ from the south-southeast. The warm, moist air in this part of the cyclone was presumably above the surface boundary layer generated by the southwestery flow across Bedford Basin, and the boundary layer associated with the land surface upwind of the basin. Observed wind speeds and directions were similar to surface winds reported over a wide area behind the cold front.

During the morning (prior to 1600 UT) the water vapor flux was downward; it increased gradually until midafternoon (1900 UT) then decreased with the drop in wind (Figure 2). Small downward vapor fluxes in similar situations have also been reported by Anderson and Smith [1981]. The CO2 flux (Figure 3) was small and mainly upward (0.01 to 0.04 mg m$^{-2}$ s$^{-1}$). One run (BIO [Bedford Institute of Oceanography] run 7) was deleted from CO2 analysis because oscillations of approximately 2 min period were observed on the CO2 signal. These are thought to be associated with the passage of clouds, possibly causing variations in radiative heating of the sensor case. They were detected during this experiment because fluctuations in CO2 were much smaller than in agricultural experiments.

A new low center, which first appeared at 0600 UT on November 11 just southeast of the measuring site, created unfavorable wind conditions in the morning (local time) on November 11. However, this system tracked rapidly northeastward over the next 12 hours, and associated northeasterly winds did not reach our site. Data were recorded from 1430 to 2000 UT in onshore breezes of 5 to 8 m s$^{-1}$ which were part of a general west-southwesterly flow associated with a large, weak anticyclone centered over the southeastern United States. On November 11 the mesoscale trajectories of air particles were over land for a few hundred kilometers upstream of the west of Bedford Basin. The surface analysis for the period suggests some subsidence and associated drying of this
Fig. 3. CO2 flux. Symbols are as follows: open squares and dotted line, raw flux \( (\text{pC}/\text{m}^3) \); solid squares and solid line, corrected flux \( F_C \).

airflow. Initially there was a small upward sensible heat flux, which fell to near zero in the afternoon. The evaporative rate was steady at 6 to 8 g m\(^{-2}\) s\(^{-1}\). The larger evaporative fluxes seen on November 11, as opposed to November 10, are consistent with the synoptic situations noted above. CO2 fluxes were mainly downward, in the range \(-0.07\) to \(0.01\) mg m\(^{-2}\) s\(^{-1}\) (Figure 3), again following downgradient as expected.

**Data Logging and Analysis**

Time series data from the sonic anemometer, the CO2 and water vapor sensor, and the thermistor were logged simultaneously using systems developed at the Bedford Institute of Oceanography and the Land Resource Research Centre (LRRC). The BIO system recorded time series data over runs usually of 45 min duration, and these were later analyzed off-line. The LRRC system computed fluxes and turbulence statistics over regular intervals of 2, 10, 30, and 60 min, and offered the option of logging the time series data [Chahuneau et al., 1989]. Both analysis systems rotated the wind coordinates to align the x axis with the mean wind; in the BIO system, rotation was applied to each sample in the time series, while the LRRC system first computed fluxes and other statistics in the anemometer axes and then combined these to obtain results in rotated axes. To compare the two systems, we have grouped and averaged the LRRC 10-min data to approximately match the BIO run times; the wind stress and water vapor fluxes (Figure 2) show excellent agreement in spite of slight mismatch in run times and slightly different algorithms. The LRRC flux values tend to be a few per cent smaller because they do not include contributions to the fluxes at periods of 10–45 min.

The influence of flow distortion by the embankment at the shoreline was seen as a mean updraft; the wind tilt for the BIO data runs was 5.9°–9.5°. From previous experience we expect 1°–2° updraft due to flow distortion by the anemometer and its supports. The mean drag coefficient (Table 1),

\[
C_{10} = -\langle u_1 u_3 \rangle / U_{10}^2 = (1.77 \pm 0.75) \times 10^{-3}
\]

was significantly (52%) higher than expected for open sea conditions at the same wind speeds, \(1.17 \times 10^{-3}\) [Smith, 1988]. About half of this difference is due to the short fetch, where the additional wind stress helps to support growth of surface waves; the remainder is taken to be the influence of wind drag on the land and the embankment upwind of the mast. The wind stress is more influenced by distortion than the scalar fluxes because it is formed from covariance with the horizontal wind, which is more influenced than the scalar temperature, humidity and CO2 concentration. The mean heat flux coefficient (Table 1) for nine runs with at least 1° air-sea temperature difference is

\[
C_T = \langle u_2 u_3 \rangle / U_{10} (T_s - T) = (1.3 \pm 0.3) \times 10^{-3}
\]

which is about 30% higher than over the open ocean [Smith, 1988] but is typical for short-fetch situations. For 12 runs with at least 1 g m\(^{-3}\) difference between surface and 10-m water vapor density the mean evaporation coefficient at our shoreline site,

\[
\text{Table 2. Analysis of Surface Water Samples}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
Run & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 12 & 15 & 17 \\
\hline
Date, Nov. 1989 & & & & & & & & & & & & & \\
\hline
\(T_s\), °C & 10.55 & 10.55 & 10.55 & 10.3 & 10.3 & 10.55 & 10.5 & 8.65 & 8.98 & 9.3 \\
\hline
Si, \(\mu\text{mol} / \text{L}\) & 5.06 & 4.77 & 4.64 & 4.33 & 3.30 & 3.63 & 4.41 & 14.94 & 12.81 & 14.10 \\
\hline
PO4, \(\mu\text{mol} / \text{L}\) & 1.01 & 0.97 & 1.07 & 1.00 & 0.92 & 1.00 & 0.81 & 1.30 & 0.98 & 1.12 \\
\hline
NO3, \(\mu\text{mol} / \text{L}\) & 4.91 & 3.90 & 3.19 & 3.69 & 2.80 & 2.98 & 3.24 & 8.26 & 5.85 & 8.32 \\
\hline
Salinity, psu ** & 29.00 & 28.76 & 28.01 & 29.38 & 29.36 & 29.49 & 27.83 & 20.37 & 22.18 & 21.94 \\
\hline
Total carbonate, \(\mu\text{mol} / \text{L}\) & 1.862 & 1.862 & 1.861 & 1.854 & 1.862 & 1.862 & 1.858 & 1.756 & 1.393 & 1.482 \\
\hline
Total alkalinity, \(\mu\text{mol} / \text{L}\) & 1.998 & 1.992 & 2.007 & 2.012 & 2.017 & 2.002 & 1.888 & 1.480 & 1.591 & 1.554 \\
\hline
\(p\text{CO}_2\) & 360 & 372 & 327 & 311 & 321 & 346 & 325 & 230 & 226 & 257 \\
\hline
\end{tabular}
\]

**"Practical salinity units" or parts per thousand salinity.**
\[ C_E = \frac{(\rho_s u_3)/(\rho_s - \rho_w)}{(2.17 \pm 0.72) \times 10^{-3}} \]  

is some 80% higher than expected over the open ocean, i.e., \(1.2 \times 10^{-3}\) [Smith, 1989]. Coefficients for downward vapor flux were smaller than the others.

Surface water samples taken at the shoreline were analyzed for salinity and nutrients. Total alkalinity (\(A_t\)) and total inorganic carbon (\(C_t\)) were determined using a potentiometric titration method (Table 2). Values for the partial pressure of \(CO_2\) in the water (\(pCO_2\)) were calculated from \(A_t\) and \(C_t\). Under laboratory conditions, typical analytical precision is \(\pm 0.15\%\) in \(A_t\) and \(C_t\). Because of the lack of an appropriate standard, the accuracy of \(A_t\) and \(C_t\) may be several times worse than the precision. This can introduce a considerable error in the calculation of \(pCO_2\); if the accuracy is \(0.15\%\), this alone would result in an inaccuracy of approximately \(\pm 13\ \mu\text{atm}\) in \(pCO_2\). Uncertainty of \(0.5\%\) in \(A_t\) and \(C_t\) would increase this estimate to an average of \(\pm 45\ \mu\text{atm}\).

A "bias" in determining \(C_t\) in surface waters results from its calculation from potentiometric titration data using a model that may be incomplete because it does not include an unknown organic protolyte. \(C_t\) values may be overestimated by up to \(20\ \mu\text{mol kg}^{-1}\), although \(5\ \mu\text{mol kg}^{-1}\) is more typical [Bradshaw and Brewer, 1988]. If the unknown organic protolyte is associated with primary productivity, it may have contributed even less during the late fall season of our experiment. We chose to ignore this possible correction.

Values of \(\Delta pCO_2\) lie in the range \(-100\) to \(+60\ \mu\text{atm}\) (sea to air). In a number of cases the direction of \(\Delta pCO_2\) is uncertain. Assuming that variations in \(pCO_2\) during each day are not significant, we will use the average values of \(338 \pm 23\) (standard deviation) and \(238 \pm 17\ \mu\text{atm}\) on November 10 and 11, respectively. A major reduction in \(pCO_2\) of the surface seawater from November 10 to 11 can be accounted for by freshwater runoff. A onshore wind, which is at least an order of magnitude larger than estimates based on radon profiles in the open sea [e.g., Smethie et al., 1985] where different processes may predominate. Liss and Merlivat [1986] proposed an exchange rate based on gas emission in lakes and wind-water tunnels which at \(10\ \text{m s}^{-1}\) wind speed amounts to \(V_p = 5.2 \times 10^{-5}\ \text{m s}^{-1}\), as opposed to \(6.5 \times 10^{-4}\ \text{m s}^{-1}\) from equation (5).

The rate of change of wind speed between sequential pairs of data runs is \(\Delta U/\Delta t\), with \(\Delta t\) the difference in midrun times. The \(CO_2\) flux, averaged over sequential pairs of runs, follows the hourly rate of change in wind speed in a similar way to the Sable Island results of Smith and Jones [1985, equation 5] (dashed line in Figure 5), even though the present site had no visible surf zone. The squared correlation \((r^2 = 0.88)\) of a "neutral" regression

\[ F_C(\text{mg m}^{-2} \text{ s}^{-1}) = -0.012 - 0.042 \Delta U/\Delta t \quad (\text{m s}^{-1} \text{ h}^{-1}) \]

Figure 4. \(CO_2\) flux \(F_C\) versus product of wind speed and sea-air \(CO_2\) difference. The line is equation (3).

Interpretation

A plot of \(F_C\) against the product of wind speed and partial density difference \(\Delta pC = pC_C - pC\) (Figure 4) shows two clusters of points, one from November 10 with upward fluxes and one from November 11 with mainly downward fluxes. It is not clear that we can assign meaning to the variations during each day, unlike the water vapor and sensible heat fluxes which had systematic variations during the daily series. A mean of two regression lines (with each variable in turn taken as the dependent variable (i.e., a "neutral" regression) for 13 runs (Table 1) is

\[ F_C = 0.065 \times 10^{-3} U_{10} \Delta pC + 0.010 \text{ mg m}^{-2} \text{ s}^{-1} \]  

with squared correlation \(r^2 = 0.50\). Because of the aforementioned deficiencies of the site and the statistical uncertainties in fitting to a small quantity of scattered data, this result is of only local significance; it is given to illustrate the potential application of this type of study and not as a general result. With the small intercept neglected, equation (3) corresponds to an exchange coefficient

\[ C_C = F_C/(U_{10} \Delta pC) = 0.065 \times 10^{-3} \]  

Again with the last term neglected, this is equivalent to a piston velocity

\[ V_p = F_C/\Delta pC = 6.5 \times 10^{-3} \quad U_{10} \]  

which is at least an order of magnitude larger than estimates based on radon profiles in the open sea [e.g., Smethie et al., 1985] where different processes may predominate.
Fig. 5. CO₂ flux $F_C$ averaged over sequential pairs of data runs versus hourly rate of change of wind speed; solid line is neutral regression (equation (6)), dashed line is from Smith and Jones [1985].

with only one change in general conditions, we must be cautious about cause-and-effect interpretations. For example, air and water temperatures are positively correlated with each other and with $pCO_2$ of the surface water, presumably owing to changing winds and associated freshwater movement. Conclusions drawn from this data set are tentative until confirmed or altered by results of further experiments.

CONCLUSIONS

A sensor developed for agricultural flux studies was able to resolve CO₂ fluctuations in the marine atmospheric surface layer at a coastal site. Both upward and downward fluxes were observed in response to daily variations in CO₂ in surface seawater, and the fluxes were comparable in size to those reported earlier [Jones and Smith, 1977; Smith and Jones, 1985]. Correlation of $F_C$ with $U_{10}Δp_C$ is an encouraging indicator of the validity of the eddy correlation measurements.

The sensitivity of $pCO_2$ to water temperature (about 4% °C⁻¹) and to salinity argues for making CO₂ flux measurements in waters which are less complicated by freshwater input and mixing of water masses with different temperatures and salinities. Our next experiment is planned at an offshore platform in the North Sea, in collaboration with colleagues from the Royal Netherlands Meteorological Institute. With measurements spanning a 4-week period at a site better exposed to the marine surface layer, we will study variations of sea surface CO₂ flux on hourly and longer scales in response to environmental variations.

Our results demonstrate the problem of using indirect measurements of total carbonate and total alkalinity for calculating the surface $pCO_2$, and hence $ΔpCO_2$. Direct measurement of $pCO_2$ or $ΔpCO_2$ is preferable.

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REFERENCES


Thorpe, S. A., The role of bubbles produced by breaking waves in


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