A New Measurement of CO_2 Eddy Flux in the Nearshore Atmospheric Surface Layer

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Fluxes of CO_2 in the atmospheric surface layer have been measured at a shoreline site by the eddy correlation method using a new CO_2 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 pCO_2 between water and air. As in an earlier study, a negative correlation of CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 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 (pCO_2) 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 CO_2 fluxes over a flooded rice paddy from profiles in the atmospheric surface layer. Large water-to-air CO_2 concentration differences (up to 1600 ppm) were generated by biological decay, and CO_2 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 CO_2. It was inferred that during periods of increasing winds, surf zone activity entrained air and CO_2 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 CO_2 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 CO_2, 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 CO_2 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 CO_2 exchange. A first step will be to develop a capability to measure CO_2 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 CO_2 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 CO_2 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 CO_2 and H_2O 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 CO_2 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 CO_2 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 CO_2 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 CO_2 fluctuations over the ocean. Temperature and humidity fluctuations also enter into the CO_2 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 CO_2.

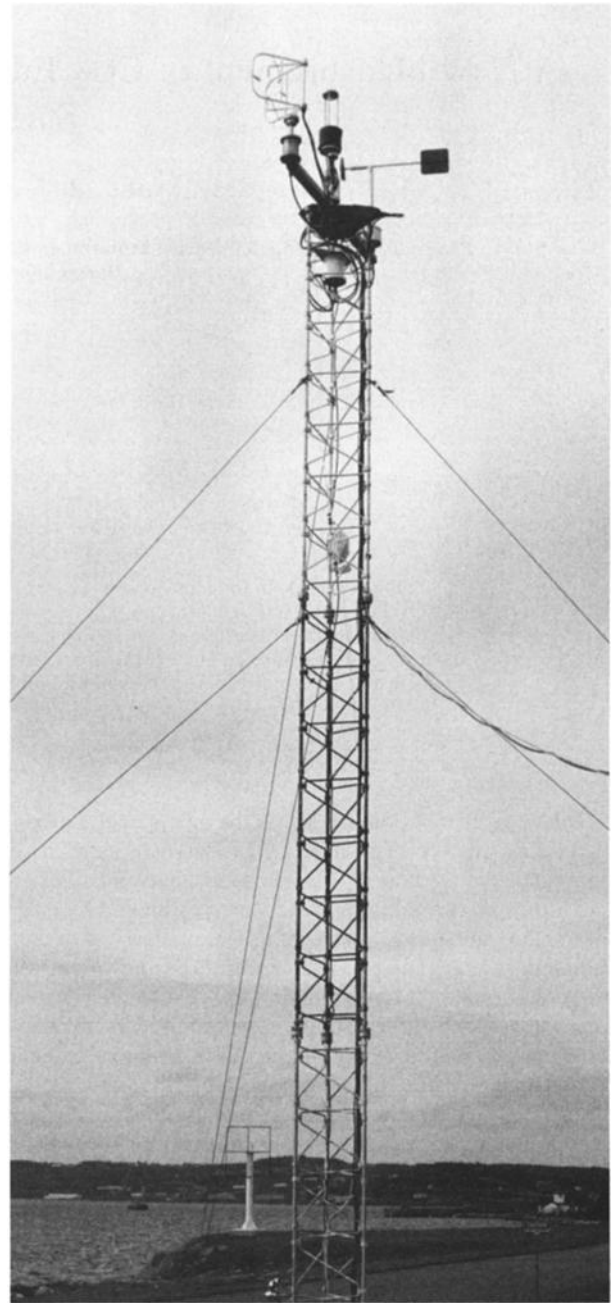Instruments were mounted on a 10-m mast about 20 m downwind from a steep, rocky embankment about 3 m high

Fig. 1. Instrument mast at the Bedford Basin experimental site, showing (from left to right at top of mast) the sonic anemometer, infrared CO_2 and water vapor sensor, and propellor anemometer.

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 pCO_2 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

TABLE 1. Eddy Fluxes and Associated Results

	Run												
	4	5.1	5.2	6	8	9	10	11	12	14	15	17.1	18
Date, Nov. 1989	10	10	10	10	10	10	10	10	11	11	11	11	11
Start time, UT	1420	1515	1545	1644	1837	1930	2023	2106	1452	1602	1652	1828	1907
Duration, s	2568	1800	1800	2559	2908	2944	1740	1200	1860	2837	2664	1260	1080
U_{10}, m s^{-1}	8.93	8.20	7.90	7.45	6.52	6.21	3.67	2.85	6.22	6.88	6.33	4.92	6.10
$\Delta U/\Delta t$, m s^{-1} h^{-1}		-0.89	-0.60	-0.42		-0.36	-3.55	-1.27		0.51	-0.68		1.49
T_a, °C	12.55	12.77	12.84	12.51	12.34	12.21	11.42	10.39	7.56	8.08	8.66	8.96	9.37
T_s, °C	10.55	10.55	10.55	10.55	10.55	10.50	10.50	10.35	8.65	8.88	8.98	9.30	9.45
$\langle \rho_v \rangle$, g m^{-3}	11.54	11.14	10.73	9.59	7.92	7.12	7.88	8.56	6.74	6.44	6.13	6.44	6.70
$\langle \rho_c \rangle$, mg m^{-3}	580	586	588	599	610	611	630	645	647	595	594	606	601
ρ_{Cs}, mg m^{-3}	643	643	643	643	643	643	643	643	455	455	455	454	454
$-\langle u_1 u_3 \rangle$, m^2 s^{-2}	0.138	0.143	0.125	0.100	0.118	0.059	0.025	0.008	0.105	0.080	0.014	0.054	0.042
$\langle t u_3 \rangle$, C m s^{-1}	-0.027	-0.027	-0.029	-0.022	-0.015	-0.010	-0.005	-0.002	0.005	0.002	-0.002	-0.004	-0.006
$\langle \rho_v u_3 \rangle$, g m^{-2} s^{-1}	-0.025	-0.015	-0.011	0.006	0.030	0.027	0.017	0.007	0.033	0.039	0.032	0.033	0.021
$\langle \rho_c u_3 \rangle$, mg m^{-2} s^{-1}	0.113	0.099	0.078	0.027	0.020	0.016	0.048	0.022	-0.063	-0.034	-0.011	-0.090	-0.062
F_C, mg m^{-2} s^{-1}	0.047	0.036	0.014	-0.016	0.002	0.007	0.045	0.022	-0.034	-0.011	-0.001	-0.083	-0.064
$10^3 C_{10}$	1.73	2.12	2.00	1.80	2.77	1.54	1.89	0.94	2.71	1.68	0.34	2.03	1.12
$10^3 C_T$	1.50	1.49	1.58	1.47	1.31	0.99	1.55		0.73	0.43			
$10^3 C_E$	1.38	1.14	1.20		2.85	1.80	2.83	2.78	3.12	2.65	2.04	2.65	1.60
$10^3 C_C$	0.084	0.078	0.032		0.009	0.035	0.949		0.028	0.012	0.001	0.106	0.071

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 southwesterly 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 CO$_2$ 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 CO$_2$ analysis because oscillations of approximately 2 min period were observed on the CO$_2$ 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 CO$_2$ 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 water of Bedford Basin. The surface analysis for the period suggests some subsidence and associated drying of this
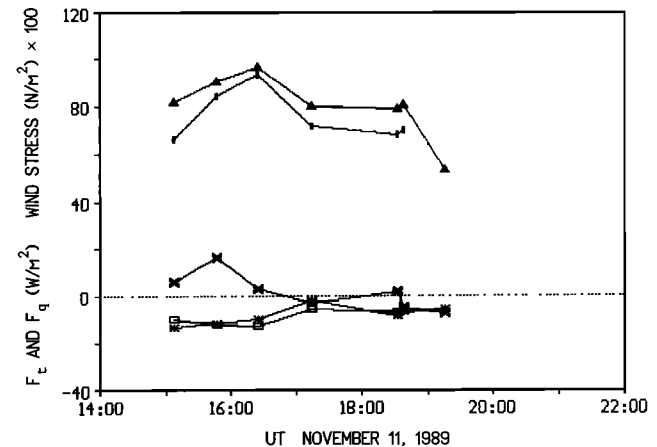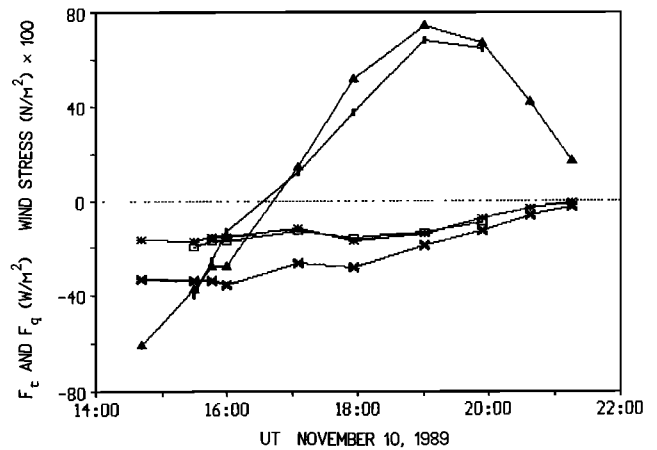

Fig. 2. Wind stress and fluxes of sensible heat and water vapor measured by two methods. Symbols are as follows: asterisks and open squares, wind stress × 100 from BIO and LRRC analyses, respectively; solid triangles and rectangles, latent heat flux from BIO and LRRC; and crosses, sensible heat flux, BIO analysis.
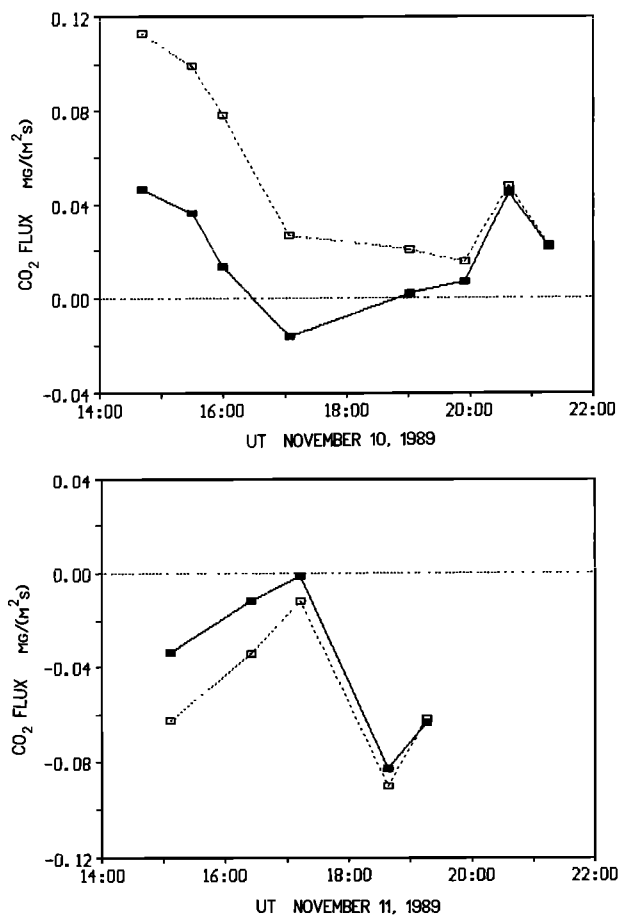
Fig. 3. CO_2 flux. Symbols are as follows: open squares and dotted line, raw flux $\langle \rho_c u_3 \rangle$; solid squares and solid line, corrected flux F_c.

airflow. Initially there was a small upward sensible heat flux, which fell to near zero in the afternoon. The evaporation 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. CO_2 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 CO_2 and water vapor sensor, and the thermistor were logged simul-

taneously 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, 1.17×10^{-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 CO_2 concentration. The mean heat flux coefficient (Table 1) for nine runs with at least 1° air-sea temperature difference is

$$C_T = \langle t u_3 \rangle / U_{10}(T_s - T) = (1.3 \pm 0.3) \times 10^{-3} \quad (1)$$

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,

TABLE 2. Analysis of Surface Water Samples

	Run									
	4	5	6	7	8	9	10	12	15	17
Date, Nov. 1989	10	10	10	10	10	10	10	11	11	11
T_s, °C	10.55	10.55	10.55	10.3	10.3	10.55	10.5	8.65	8.98	9.3
Si, μmol/L	5.06	4.77	4.64	4.33	3.30	3.63	4.41	14.94	12.81	14.10
PO₄, μmol/L	1.01	0.97	1.07	1.00	0.92	1.00	0.81	1.30	0.98	1.12
NO₃, μmol/L	4.91	3.90	3.19	3.69	2.80	2.98	3.24	8.26	5.85	8.32
Salinity, psu*	29.00	28.76	28.01	29.38	29.56	29.49	27.83	20.37	22.18	21.94
Total carbonate, μmol/L	1.862	1.862	1.861	1.854	1.862	1.862	1.858	1.756	1.393	1.482
Total alkalinity, μmol/L	1.998	1.992	2.007	2.012	2.017	2.002	1.888	1.480	1.591	1.554
pCO₂	360	372	327	311	321	346	325	230	226	257

*"Practical salinity units" or parts per thousand salinity.

$$C_E = \langle \rho_v u_3 \rangle / (\rho_s - \overline{\rho_v}) = (2.17 \pm 0.72) \times 10^{-3} \quad (2)$$

is some 80% higher than expected over the open ocean, i.e., 1.2×10^{-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 ± 13 μatm in pCO_2. Uncertainty of 0.5% in A_t and C_t would increase this estimate to an average of ± 45 μatm.

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 μmol kg^{-1}, although 5 μmol 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 ΔpCO_2 lie in the range -100 to $+60$ μatm (sea to air). In a number of cases the direction of ΔpCO_2 is uncertain. Assuming that variations in pCO_2 during each day are not significant, we will use the average values of 338 ± 23 (standard deviation) and 238 ± 17 μatm 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 input to Bedford Basin. Rain on November 9 was accompanied by freshwater runoff. A more important source is the Sackville River, which flows into the northern end of the basin. An onshore wind, necessary for making the eddy flux measurements, causes fresh water to pile up in the portion of the basin where our samples are taken. Accumulation of fresh water is evident in a reduction of salinity, accompanied by increases in silicate and phosphate. Assuming that the fresh water has negligible alkalinity and total carbonate, a reduction of salinity from 29 to 22 psu (i.e., by 24%) gives about a 35% reduction in pCO_2, i.e., from about 360 to about 234 μatm, very nearly the change observed from November 10 to 11 (Table 2). We do not have data on biological processes in Bedford Basin, but we do not rule out their possible importance. We are also not sure that water samples collected at the shoreline gave a value of pCO_2 that is representative of the entire upwind footprint area for eddy fluxes.

Interpretation

A plot of F_C against the product of wind speed and partial density difference $\Delta \rho_C = \rho_{Cs} - \rho_C$ (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
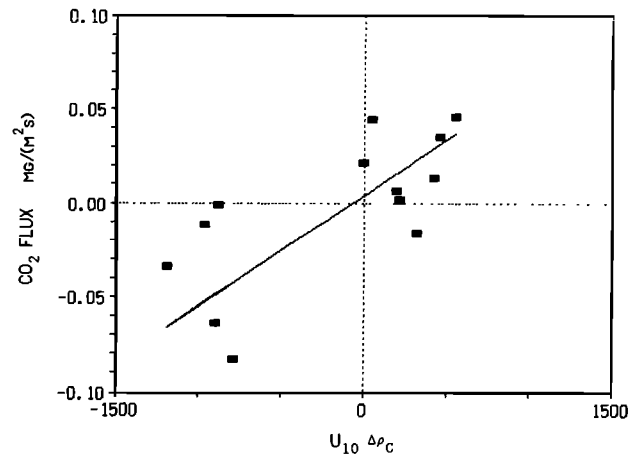
Fig. 4. CO₂ flux F_C versus product of wind speed and sea-air CO₂ difference. The line is equation (3).

variable in turn taken as the dependent variable (i.e., a "neutral" regression) for 13 runs (Table 1) is

$$F_C = 0.065 \times 10^{-3} \ U_{10}\Delta\rho_C + 0.010 \text{ mg m}^{-2} \text{ s}^{-1}) \quad (3)$$

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

$$C_C = F_C/(U_{10}\Delta\rho_C) = 0.065 \times 10^{-3} \quad (4)$$

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

$$V_p = F_C/\Delta\rho_C = 6.5 \times 10^{-5} \ U_{10} \quad (5)$$

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 m s^{-1} wind speed amounts to $V_p = 5.2 \times 10^{-5}$ m s^{-1}, as opposed to 6.5×10^{-4} 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 Δt 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

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

$$(6)$$

(solid line in Figure 5), deleting one point (open square) with a rapid drop in wind between runs 9 and 10, is higher than we found in the expected bulk parameterization (Equation 3). It appears that at the Bedford Basin shoreline site a mechanism associated with changing wind speed again contributed to the hourly variations of CO_2 flux. Having a small data set
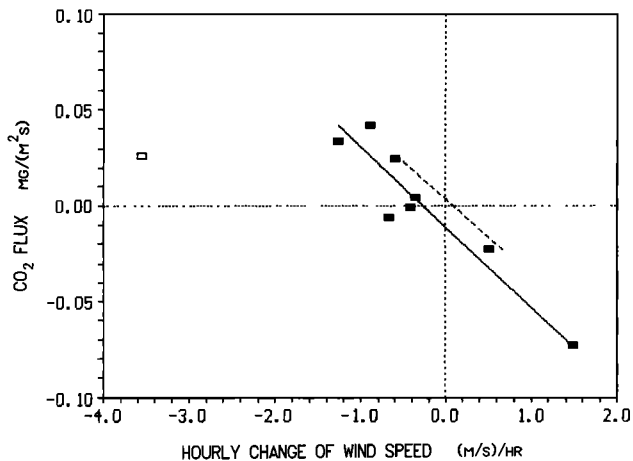
Fig. 5.　CO₂ flux F_C averaged over sequential pairs of data runs versus hourly rate of change of wind speed; solid line is neutral regression (equation (6)), dashed line is from *Smith and Jones* [1985].

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 $U_{10}\Delta\rho_C$ 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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