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Kyoto University
Eddy Correlation Measurements of Carbon Dioxide Flux over Coastal Sea Surface

By Xiaohu Liu, Haruna Ito, Yasushi Mitsuta, Sigehisa Nakamura, Hiroshi Yoshioka, Taichi Hayashi, Shigeatsu Serizawa and Eiji Ohtaki

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Abstract

The carbon dioxide flux over coastal seawater was measured by the eddy correlation technique at the Shirahama Oceanographic Tower Station of Kyoto University on August 23 and 24, 1994. The mean value of carbon dioxide fluxes measured is 0.10 mgm⁻²s⁻¹ with a standard deviation of 0.09 mgm⁻²s⁻¹. These upward fluxes are within ranges obtained over the Sea of Japan in 1986 and 1987. It is also noted that the present values of upward fluxes are about one tenth of the downward flux of carbon dioxide measured over actively growing paddy fields. Within a particular set of environmental conditions, the feasibility of applying the aerodynamic technique and the bulk technique to measuring the carbon dioxide flux over the ocean is demonstrated.

1. Introduction

It is well known that the carbon dioxide concentration in the atmosphere is increasing. The carbon dioxide concentration in the atmosphere is determined by the balance of the carbon dioxide fluxes between atmosphere and ocean, and between atmosphere and land biota. Particularly, the significance of the oceans as the carbon dioxide sink has been well supported in recent years. However, disagreement arises in flux estimates of carbon dioxide over the oceans. This results in uncertainty of the total global carbon dioxide budget from 20 to 50% of total fossil combustion (e.g., Broecker et al., 1979; Tans et al., 1990). In order to improve our understanding of the ocean’s role in the global budget, representative measurements of carbon dioxide flux are needed.

The eddy correlation technique is the most promising technique to measure fluxes of physical quantities in the atmospheric boundary layer. In recent years, many researchers reported reliable fluxes of carbon dioxide measured by the eddy correlation technique over vegetated fields (e.g., Anderson et al., 1984; Ohtaki, 1984 and 1985). However, only a few studies have been reported on the carbon dioxide fluxes over the ocean. Smith and Jones (1985) measured the carbon dioxide flux at Sable Island during late autumn. Wesely et al. (1982) reported that the carbon dioxide was transported upward when the sea water was gradually warming. Ohtaki et al. (1989) carried out...
preliminary experiments during October in 1986 and 1987 off the coast of the Sea of Japan, and obtained an upward flux of carbon dioxide. We thus felt that the eddy correlation technique should be validated again with other meteorological techniques such as the aerodynamic or bulk technique.

This paper, at first, presents the basic equation of carbon dioxide flux which includes correction terms due to air density fluctuations. Then, based upon a field experiment, we have assessed the correction terms from the sensible heat and the latent heat fluxes. Finally, the carbon dioxide fluxes from the eddy correlation technique are compared with those measured by the aerodynamic technique and the bulk technique, respectively.

2. Basic equation

The total flux of carbon dioxide is presented by

$$F = \bar{w}' \bar{\rho}_c' + \bar{\rho}_c' \bar{w}'$$

where $\bar{\rho}_c$ is the density of carbon dioxide. The overbar denotes a mean over a sampling time and the prime denotes a deviation from the mean. In the recent study, taking into account preliminary cospectral calculations of vertical velocity and carbon dioxide, the carbon dioxide flux is calculated using data of 15 min duration. Webb et al. (1980) proposed the governing constraint that the mean vertical flux of dry air constituent should be zero:

$$\bar{w} \bar{\rho}_a = \bar{\rho}_a \bar{w}' + \bar{\rho}_a \bar{w}' = 0.$$ (2)

Here $\bar{\rho}_a$ is the density of dry air. The right hand side of Eq. (2) gives the mean vertical velocity component as

$$\bar{w} = -\bar{\rho}_a \bar{w}' / \bar{\rho}_a.$$ (3)

Eq. (1) with substitution for $\bar{w}$ from Eq. (3) gives

$$F = \bar{w}' \bar{\rho}_c' - \bar{\rho}_a \bar{w}' \bar{\rho}_a + \bar{\rho}_a \bar{w}' \bar{\rho}_a' + (1 + \mu \sigma) \bar{\rho}_a \bar{w}' \bar{\rho}_a'.$$ (4)

Here $\mu = m_v / m_w$ is the ratio of molecular weights of dry air to water, and $\sigma = \bar{\rho}_w / \bar{\rho}_a$. $\bar{\rho}_w$ is the density of water vapor and $T$ is the temperature. The first term on the right hand side of Eq. (4') is the raw value of carbon dioxide flux obtained by the eddy correlation technique. The second and third terms on the right hand side are fluxes of carbon dioxide contributed from both latent and sensible heat flux.

By introduction of the mixing length relationships $\bar{\rho}_c' = -l \bar{\rho}_c / \bar{\rho}_c$ and $\bar{\rho}_a' = -l \bar{\rho}_a / \bar{\rho}_a$, where $l$ is the mixing length, Eq. (4) can be rewritten as

$$F = -l \bar{\rho}_c / \bar{\rho}_c + \bar{\rho}_c \bar{w}' l \bar{\rho}_a / \bar{\rho}_a$$

$$= -\bar{\rho}_a K_c l (\bar{\rho}_c / \bar{\rho}_a) / dz.$$ (5)
where \( \frac{\bar{\rho}_c}{\rho_a} \) is the mixing ratio of carbon dioxide. \( K_c = \overline{\omega l} = ku_*z / \phi_c \) is the eddy diffusivity of carbon dioxide. \( k \) is the von Kármán constant and \( u_* \) is the friction velocity. \( \phi_c \) is the nondimensional gradient of carbon dioxide, and represented by \((1-16z/L)^{-1/2}\) under unstable conditions. Here, \( z \) and \( L \) are respectively the measuring height and the Monin-Obukhov stability length. The carbon dioxide fluxes measured by the eddy correlation technique, Eq. (4), can be compared with the values measured by the aerodynamic technique, Eq. (5).

3. Site and instrumentation

The carbon dioxide flux over the ocean was measured at the Shirahama Oceanographic Tower Station of Kyoto University on August 23 and 24, 1994. The Tower Station is located at the mouth of Tanabe bay, Wakayama Prefecture (Fig. 1). As can be seen in the figure, the fetch is sufficient to westerly winds, while it is about 600 m to southerly winds. The tower is made of steel angles with a small instrumentation room from 6.0 m to 8.2 m in height, and a working floor at 4.3 m above the mean sea level (Photo. 1). The eddy correlation sensors such as a three dimensional sonic anemometer-thermometer (Kaijyo Co., DA-600), and a fast response carbon dioxide-humidity sensor (Advanet Co., E009) were mounted on the roof of the instrumentation room 10 m in height. Output signals from eddy correlation sensors were sampled at a rate of 10 Hz, and stored on the portable magnetic storage of a data acquisition system. Fluxes of carbon dioxide and other turbulence statistics were calculated using digital data for 15 min durations. It should be noted that there was an upward component in vertical wind velocity, mainly due to the blocking effects of the instrumentation room on the air flow. The inclination of the stream line ranged from 6 to 11 degrees. In order to remove blocking effects, one dimensional coordinate rotation (i.e. \( w = 0 \)) was applied to the flux calculations.

The carbon dioxide flux was also measured by the aerodynamic technique. The air

![Fig. 1 Location of Shirahama Oceanographic Tower Station.](image-url)
intakes for measurements of concentration difference of carbon dioxide were mounted at 0.9 m and 15.5 m above seawater. The concentration difference of carbon dioxide was measured by a non-dispersive infrared gas analyzer (Shimazu Co., URA-106).

In order to estimate carbon dioxide flux by the bulk technique, the concentration measurements of carbon dioxide in the surface seawater ($p\text{CO}_2$) and in the atmosphere ($P\text{CO}_2$) were also carried out. Detailed specifications of $p\text{CO}_2$ and $P\text{CO}_2$ instruments have been given by Ohtaki et al. (1993) and Yamashita et al. (1993).

4. Results

Fig. 2 shows the time course variations of the three components in the right hand side of Eq. (4') measured on August 24, 1994. Prevailing winds are west in the morning from 10:30 to 13:00, and shift to south in the afternoon from 13:00 to 15:30. The $\bar{w}\rho$ is negative during westerly winds, and changes to positive during southerly winds. The second and third terms of the right hand side in Eq. (4') ranged from 0.01 to 0.02 ppm m s$^{-1}$. It is noted that the total flux of carbon dioxide ($F$) ranged from about −0.01 to 0.06 ppm m s$^{-1}$ under westerly winds and 0.08 to 0.15 ppm m s$^{-1}$ under southerly winds, denoting the upward transport of carbon dioxide. We know the situation that when the seawater temperature increases, the solubility of carbon dioxide into seawater decreases and the partial pressure of carbon dioxide increases. Thus, we can imagine here that the present upward transport of carbon dioxide is attributable to the seasonal warming of seawater because the experiment was carried out during the summer season in Japan. The mean air temperature at 10 m above the sea surface was about 28 °C. Taking into account the conversion rate of 1 CO$_2$ ppm = 1.78 mg m$^{-3}$, the mean value of upward carbon dioxide flux comes to about 0.10 mg m$^{-2}$s$^{-1}$ with the standard deviation
of 0.09 mg m\(^{-2}\)s\(^{-1}\). This value is within the range of carbon dioxide fluxes obtained over the Sea of Japan during October 1986 and 1987 (Ohtaki et al., 1989). It should be noted that the present values of upward flux are about one tenth of the downward flux of carbon dioxide measured over actively growing paddy fields (Ohtaki and Oikawa, 1991).

The carbon dioxide flux, \(F\) (AD), calculated by the aerodynamic technique using Eq. (5), is shown in Fig. 3. The wind speed (\(U\)) at 10 m, the carbon dioxide difference (\(\Delta C\)) between 0.9 and 15.5 m above the sea surface, and the eddy diffusivity (\(K_{10}\)) are also plotted in the figure. \(\Delta C\) was about 0.28 ± 0.05 ppm during westerly winds and about 0.45 ± 0.05 ppm during southerly winds. The \(K_{10}\) was about 2 m\(^2\)s\(^{-1}\) in the present study. The \(F(AD)\) ranged from 0.03 to 0.06 ppm m s\(^{-1}\) in westerly winds, and from 0.05 to 0.10 ppm m s\(^{-1}\) in southerly winds.

Fig. 4 shows the comparison of carbon dioxide fluxes estimated by the eddy correlation technique, \(CO_2(\text{EC})\), and the aerodynamic technique, \(CO_2(\text{AD})\). The solid line means one to one correspondence. It is apparent from the figure that the \(CO_2(\text{EC})\) values show larger scatters than do those of \(CO_2(\text{AD})\). It should also be noted that the fluxes of \(CO_2(\text{EC})\) are smaller than those of \(CO_2(\text{AD})\) under westerly winds, while the opposite situation occurred under southerly winds. Further measurements are now required under more widely varying wind, temperature, and oceanic conditions in order to obtain more consistent relationship between flux values measured by the eddy correlation technique and the aerodynamic technique. However, we are very much encouraged by the present results which indicate that the meteorological techniques based on the tower system are applicable to the measurement of the carbon dioxide flux over the ocean.

In the present study, we tried to measure the carbon dioxide concentration in the surface sea water (pCO\(_2\)) using a newly developed instrument (e. g., Ohtaki et al., 1994), and to estimate the carbon dioxide flux by the bulk technique. Four examples of pCO\(_2\) values are presented in Table 1 together with values of sea water temperature (\(T_s\)), pH
Fig. 3  Time variation of carbon dioxide flux measured by aerodynamic technique $F$ (AD).

- $U$: wind speed at 10 m height above the seawater
- $\Delta C$: CO$_2$ difference between 0.9 and 15.5 m above the seawater
- $K_{10}$: Eddy diffusivity of carbon dioxide

Fig. 4  Comparison of carbon dioxide fluxes measured by the eddy correlation technique, CO$_2$ flux (EC), and by the aerodynamic technique, CO$_2$ flux (AD).
Table 1  Comparison of measured pCO₂ with pCO₂ calculated from pH and carbonate alkalinity.

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<th>Date</th>
<th>Time</th>
<th>Ts(°C)</th>
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<th>S(%)</th>
<th>pCO₂(ppm) meas.</th>
<th>pCO₂(ppm) cal.</th>
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<td>378.3</td>
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<td>33.7</td>
<td>373.4</td>
<td>378.7</td>
</tr>
</tbody>
</table>

and salinity (S). The average value of measured pCO₂ is 376.0 ppm, which can be checked by the pCO₂ value calculated using equilibrium relationships (Ohtaki et al., 1995),

\[ pCO₂ = CA \times (10^{-pH})^2 / [\alpha(2K'_1 K'_2 + K'_1 10^{-pH})], \]  

where CA is the carbonate alkalinity, approximated by 0.06555 S. \( \alpha \) is the solubility coefficient of carbon dioxide in the seawater (Weiss, 1974). \( K'_1 \) and \( K'_2 \) are the apparent dissociation constants of carbonic acid in seawater (Mehrbach et al., 1973). The pCO₂ values calculated are shown in the last column in Table 1. The average value of calculated pCO₂ is 378.6 ppm, showing good agreement with the average value of pCO₂ measured, indicating the reliability of our measurement.

The carbon dioxide concentration in the atmosphere (PCO₂) was measured from 11:30 to 15:30 on August 24. The mean value of PCO₂ was 354.3 ppm with the standard deviation of 3.9 ppm. This means that the PCO₂ in the atmosphere is smaller by about 20 ppm than the pCO₂ in seawater, representing the upward transport of carbon dioxide. If the bulk coefficient of water vapor (ca. 1.5 x 10⁻³, Tsukamoto et al., 1991) is applicable to carbon dioxide transport, the upward flux of carbon dioxide of 0.12 ppm m s⁻¹ is obtained taking into account relevant parameters obtained in the present study: concentration difference pCO₂ - PCO₂ = 20 ppm and wind speed at 10 m height = 4 m s⁻¹. It is interesting to see that the carbon dioxide flux estimated by the bulk technique is close to the values measured by the eddy correlation technique and the aerodynamic technique mentioned above. This result also supports the useful application of the eddy correlation technique and the aerodynamic technique based on the tower system to the measurement of the carbon dioxide flux over the ocean.

5. Conclusions

The carbon dioxide flux over the ocean was measured by the eddy correlation technique based on the tower system. The mean value of total carbon dioxide fluxes measured was about 0.10 mg m⁻² s⁻¹ with the standard deviation of 0.09 mg m⁻² s⁻¹, showing the upward flux of carbon dioxide. These values are within the range obtained over the Sea of Japan during October 1986 and 1987 (Ohtaki et al., 1989), while present fluxes are about one tenth of the downward flux of carbon dioxide measured over actively growing paddy fields. The upward flux of carbon dioxide is attributed to the seasonal warming
of seawater because the experiment was carried out during the summer season in Japan. It is noted that the carbon dioxide flux measured by the eddy correlation technique agrees with those measured by both the aerodynamic and bulk technique.

The results given above were obtained under moderate meteorological conditions. Further efforts are required under more widely varying meteorological and marine chemical conditions to clearly establish the most representative technique for the measurement of carbon dioxide flux over the ocean.

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References