Accurate Measurement of Air-Sea CO₂ Flux with Open-path Eddy-Covariance

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Abstract. Air-sea CO₂ flux is more than an order of magnitude smaller than that over vegetations. Considering the global area of oceans, the accurate measurement of air-sea CO₂ flux is indispensable. Open-path eddy covariance is most hopeful as it directly measures turbulent fluctuations in undisturbed condition. Closed-path eddy covariance is sometimes used including possible attenuation of CO₂ fluctuation. Both of the systems have merits and demerits and we should understand the scientific or technical basis of both systems. In the present paper, we have roughly reviewed the background of eddy covariance CO₂ flux measurement and pointed out important issues in both of the system. For the open-path system, application of the WPL-correction, and window contamination by sea salt aerosol are discussed. For the closed-path system, turbulent signal attenuation and remaining WPL correction due to temperature fluctuation are discussed. Eddy-covariance is considered as very promising as it measures small time scale (less than an hour) variation of air-sea fluxes. There are a lot of discussion for the transfer velocity parameterization for bulk air-sea CO₂ flux estimates. So we should make every effort to solve these important issues on CO₂ eddy covariance measurement.

Key Words: air-sea flux, eddy-covariance, CO₂ flux, open-path, closed-path

1. Introduction

Air-sea energy flux of sensible/latent heat or momentum flux is normally evaluated with bulk aerodynamic formula, and the bulk transfer coefficient is parameterized based on eddy-covariance method. While, air-sea CO₂ flux is traditionally evaluated with bulk method using transfer velocities, which is based on mass balance method not on eddy-covariance. Over land surfaces, surface CO₂ flux is measured with eddy-covariance method as the global standard as used in ‘Fluxnet’.

Eddy-covariance method (ECM) is applied to surface flux measurement with
the development of sonic anemometer-thermometer since 1970’s. ECM does not need physical assumptions and is considered as direct standard method. As compared to sensible heat flux, water vapor flux (latent heat flux) was rather difficult due to requirement of high response optical hygrometer. But it is now available as infra-red H2O gas analyzer including CO2 gas analyzer. Based on these ECM fluxes, bulk transfer coefficients of momentum, sensible/ latent heat are parameterized (Fairall et al. 2003).

The situation of air-sea CO2 flux is quite different from air-sea energy or momentum flux parameterization, as the CO2 gas analyzer had not enough resolution for small CO2 fluctuation over sea surface. As a traditional estimate of air-sea CO2 flux, bulk method is applied using air-sea delta-pCO2. In the bulk method, the transfer velocity is parameterized as a function of mean wind speed, based on mass-balance model using isotope tracers (Liss and Merlivat 1986).

Eddy-covariance gas flux (Fc) is basically calculated from following equation.

\[ F_c = \overline{w'}c' \] (1)

Here, \( w' \) and \( c' \) are turbulent fluctuations of vertical wind speed and gas density, and they are obtained from the Reynolds decomposition as (mean value + fluctuation).

\[ w = \overline{w} + w', \quad c = \overline{c} + c' \] (2)

The first ECM CO2 flux measurement over ocean is reported by Jones and Smith (1977). It was carried out on an offshore tower. They used a sonic anemometer and an open-path infrared CO2 sensor (originally developed by the authors). They have reported that CO2 flux was 0.022−0.035 mg m\(^{-2}\) s\(^{-1}\). Wesely et al. (1982), Smith and Jones (1985) have also reported 0.05−0.3 mg m\(^{-2}\) s\(^{-1}\) and −0.044 ~ +0.023 mg m\(^{-2}\) s\(^{-1}\), respectively, based on their eddy covariance measurements. Refereeing to these micrometeorological measurements, Broecker et al. (1986) and Liss and Merlivat (1986) have noted that those micrometeorological CO2 flux values were 100 times larger than the values using the bulk method, which is based on pCO2 (CO2 partial pressure) difference between air and sea. Those papers claimed the poor accuracy of the ECM, and CO2 flux based on ECM is not reliable. Smith and Jones (1986) and Wesely (1986) have replied that CO2 flux values based on the their ECM based CO2 flux is are reasonable.

Ohtaki et al. (1989) and Smith et al. (1991) have duplicated ECMs with new open-path CO2 sensors and reported still larger CO2 eddy flux (nearly 0.05 mg m\(^{-2}\)
than the traditional values. At the moment, the WPL correction (Webb et al. 1980) was introduced to calculate total CO$_2$ flux. This correction term is almost the same magnitude as the raw eddy-covariance and this WPL correction is considered as essential for the eddy CO$_2$ flux calculation including land surface CO$_2$ flux. Additionally, these previous micrometeorological measurements were carried out at coastal sites.

In the late 1990’s, two integrated CO$_2$ flux projects were carried out. Called as ASGAMAGE and GasEx-98, both of the traditional bulk method and ECM were applied. ECM results of these projects have been reported by Jacobs et al. (1999) and McGillis et al. (2001) respectively. In the ASGAMAGE project, open-path CO$_2$ sensors were used and the cross-sensitivity analysis between CO$_2$ and H$_2$O has been reported by Koshiek (2000). In the GasEx-98 project, a closed-path CO$_2$ sensor was used; and this was the first on-board eddy CO$_2$ flux experiment over open sea. McGillis et al. (2001) have reported almost consistent CO$_2$ fluxes with the bulk method except for higher wind speed region. However, their measurements are based on the ‘closed-path’ method and ideal ‘open-path’ method is not reported.

2. Open-path/Closed-path CO$_2$ density measurements

The gas analyzer for turbulence measurement was originally developed as “open-path” type as it is directly measure open air volume corresponding to sonic anemometer acoustic path. This is essential for eddy-covariance measurement. Traditional gas analyzer is the “closed-path” type, using intake tube from the open air to gas analyzer. It is applied for mean gas concentration measurement as accurate absolute gas density. Recently, this closed-path system is applied to eddy-covariance measurement over forest with the development of fast response closed-path analyzer. As mentioned in the last section, the closed-path system was also applied to air-sea CO$_2$ flux measurement (GasEx) and evaluated transfer velocity was almost consistent with the previous studies based on mass balance method (McGillis et al. 2001).

Open-path (OP) and closed-path (CP) systems are schematically compared in Figure 1 to show the signal attenuation and time delay by the intake tube of CP. The time delay and amplitude attenuation depend on the intake tube length and pumping speed. These two issues in CP can lead to important loss of eddy flux, as the eddy-covariance method requires simultaneously measured vertical wind speed and CO$_2$ density, and the CO$_2$ density fluctuation should be as large as open air fluctuation. As compared to land surface CO$_2$ flux over vegetation, air-sea CO$_2$ flux is an order of magnitude smaller. Then CP based eddy CO$_2$ flux might include
significant loss of eddy flux, and application of the open-path system is essential for accurate evaluation of CO$_2$ flux.

Present authors have experienced on-board eddy-covariance system including ship motion correction for wind velocity fluctuations (Takahashi et al. 2005) as shown in Figure 2. CO$_2$ flux measurement system was introduced using open-path CO$_2$ analyzer (Licor; LI-7500) and found that evaluated CO$_2$ transfer velocity is an order of magnitude larger than the traditional parameterization even when the WPL correction is introduced (Tsukamoto et al. 2004). So we found that the results from open-path sensor and closed-path sensor are still inconsistent.

Figure 1  Schematic figure of the open-path system (OPGA) and closed-path system (CPGA).

Figure 2  Open-path eddy-covariance measurement system on board (top of the foremast) R/V MIRAI.
2.1 WPL correction due to air density fluctuation

It is well known that WPL correction is essential for eddy-covariance CO2 flux especially in small fluxes as observed over ocean. The WPL correction was introduced by Webb, Pearman and Leuning (Webb et al. 1980) as an important calculation for trace gas fluxes. Recently, a lot of discussions are raised in this issue and it is almost agreed in the eddy flux community that original WPL correction theory is correct and should be applied. However, this is only discussed theoretically and experimental validation was only presented as one article (Ham and Heilman, 2003). The correction is caused by air density fluctuation due to temperature and water vapor turbulent fluctuations. The gas analyzer measures CO2 density ($\rho_c$) in ‘mg/m^3’ and local time changes of air temperature ($T$) and water vapor ($\rho_v$) lead to dry air volume change. Then apparent CO2 density ($\rho_c$) is variable even when CO2 mixing ratio ($\chi_c$) is kept constant. Following equation explains the WPL correction.

\[
F_{c\_total} = \overline{w'}\rho_c + \frac{\overline{\rho_v}}{\rho_d} \overline{w'\rho_v'} + \left(1 + \mu \sigma \right) \frac{\overline{\rho_v}}{T} \overline{w'T'}
\]  

\[
\chi_c = \frac{\rho_c}{\rho_d}
\]

Here, total CO2 flux ($F_{c\_total}$) is expressed as the sum of raw CO2 flux (1st term), water vapor flux correction term (2nd term) and sensible heat flux correction term (3rd term) in Eq.(3). In this equation, $\mu$ is the ratio of molecular weights of dry air and water vapor and $\sigma$ is the ratio of water vapor density ($\rho_v$) to dry air density ($\rho_d$). Present authors have originally tried the experimental validation with their own technique (Kondo and Tsukamoto, 2008). The experiment was carried out over a large parking lot (dry asphalt surface) which is considered as almost ‘zero’ CO2 flux. The apparent raw CO2 flux was negative (downward), but WPL correction terms almost cancel the negative raw flux to nearly zero flux as shown in Figure 3. According to the experimental results, the importance of the WPL correction is experimentally verified.

Table 1 shows the results of WPL correction applied to air-sea CO2 flux over Indian Ocean. As shown in the results, raw CO2 flux shows apparently negative (downward) flux. When WPL correction is applied, the total flux changes the direction to upward, consistent to air-sea CO2 fugacity gradient ($\Delta f_{CO2}$).

Alternative way to evaluate CO2 flux including the air density correction is to use ‘mixing ratio’ of CO2 as noted by Webb et al. (1980). Conversion from CO2 density ($\rho_c$) to mixing ratio ($\chi_c$) is expressed as Eq (4). The dry air density ($\rho_d$) is calculated using the equation of state for the dry air using air temperature and atmospheric pressure. This is also checked experimentally calculating the CO2
Table 1  Air-sea CO₂ flux evaluated from OP eddy-covariance including WPL correction and bulk flux estimated from mean wind speed and air-sea CO₂ fugacity (fCO₂) difference during MR05-03 over equatorial Indian Ocean (Kondo and Tsukamoto, 2007)

<table>
<thead>
<tr>
<th>Stations (MR05-03)</th>
<th>Wind speed (m/s)</th>
<th>ΔfCO₂ (μatm)</th>
<th>Bulk CO₂ flux (μg m⁻²s⁻¹)</th>
<th>CO₂ flux by OP eddy-covariance (μg m⁻²s⁻¹)</th>
<th>Raw Flux</th>
<th>WPL_sensible heat flux term</th>
<th>WPL_water vapor flux term</th>
<th>Total flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Station A</td>
<td>3.4</td>
<td>+27.3</td>
<td>+0.51</td>
<td>-51.95</td>
<td>+22.94</td>
<td>+38.62</td>
<td>+9.62</td>
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</tr>
<tr>
<td>Station B</td>
<td>4.7</td>
<td>+16.6</td>
<td>+0.59</td>
<td>-62.66</td>
<td>+17.05</td>
<td>+46.50</td>
<td>+0.59</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3  Time series of the raw CO₂ flux, WPL correction terms for the sensible heat flux and latent heat flux and total CO₂ flux over dry asphalt surface (Kondo and Tsukamoto, 2008)

Figure 4  Comparison between the CO₂ flux including the WPL correction (Fc_WPL) and the CO₂ flux directly calculated from CO₂ mixing ratio covariances (Fc_Mixing Ratio).
mixing ratio ($\chi_c$) based on measured CO$_2$ density, air temperature and water vapor density. The calculated covariance of $w'\chi'_c$ values were consistent with the WPL corrected CO$_2$ fluxes (Figure 4). Thus the WPL correction including the air density fluctuation or mixing ratio covariance is found to be valid as accurate CO$_2$ flux evaluation.

2.2 Window contamination on open-path gas analyzer

It is also known that the open-path analyzer include an important issue of optical window contamination, as the optical window is exposed to various weather condition. In the raining condition, it is apparently impossible to measure. In the non-precipitation conditions, it is sometimes experienced that absolute value of CO$_2$ decreases (Figure 5) as pointed by Serrano-Ortiz (2007) due to window contamination by aerosols (sea salt) or dusts. They only report the apparent decrease of CO$_2$ density, but present authors have found that the fluctuation amplitude of CO$_2$ is also affected by this contamination effect. As shown in Figure 6, CO$_2$ density gradually decreases accompanying amplitude increase even when the mean CO$_2$ density is kept constant in another independent NDIR. This apparent larger CO$_2$ fluctuation can lead to overestimation of eddy CO$_2$ flux.

We found that optical window contamination can lead to apparent larger CO$_2$ fluctuations and larger CO$_2$ flux even when the WPL correction is applied. Then we have selected dataset only when the open-path optical window is kept clean. Actually, we clean up the window manually, before the ‘flux run’, when the ship steams up against the wind for the on-board flux measurements. Kondo and Tsukamoto (2007) published the results of open-path CO$_2$ flux measurement when free from the open-path window contamination effect. They also found that open-path ECM result is still larger than the bulk CO$_2$ flux as shown in Table 1.

Considering the apparent larger CO$_2$ fluctuation/flux, Prytherch et al. (2010) described that it is due to cross-talk effect by optical window contamination. They found that usual data processing including the WPL correction lead to apparently larger air-sea CO$_2$ flux and transfer velocity. This seems consistent with our results.

![Figure 5](image-url)

_Figure 5_ Apparent decrease of CO$_2$ molar fraction measured by Li-7500 due to optical window contamination (Serrano-Ortiz et al. 2007)
that apparently larger fluctuation/flux of CO$_2$ when window contamination is observed. In order to correct for this cross-talk effect, Prytherch et al. (2010) proposed the PKT-correction for the open-path gas analyzer. But there is no physical explanation to the cross-talk effect and theoretical basis for the correction algorithm is not well described. They just describe the apparent relations between CO$_2$ mixing ratio and relative humidity. So it is still a big issue how to process the apparent larger flux when optical window is contaminated.

2.3 Attenuation of turbulent fluctuation in closed-path system

We have also tested closed-path (CP) system as compared to open-path (OP) system on R/V MIRAI. Figure 7 shows an example of H$_2$O and CO$_2$ density fluctuations by open-path (LI-7500) and closed-path (LI-7000) systems based on 10Hz sampling data over ocean (Kondo and Tsukamoto, 2009). Significant decrease of high frequency H$_2$O fluctuation was confirmed on the CP time series and spectral analysis even when the tube length was only 3.2m (diameter 1/4 inch, air pumping speed is 12L/min). CO$_2$ density fluctuation shows negatively correlated with H$_2$O density and total amplitude of the CP system decreased about 2/3 of the OP system. High frequency attenuation was not clearly observed as H$_2$O density. This difference can be due to lower S/N value of CO$_2$ density in the small CO$_2$ fluctuation over ocean. H$_2$O density fluctuation has enough S/N value and clear high frequency attenuation was observed in spectral analysis (Kondo and Tsukamoto, 2009). Total decrease of CO$_2$ density amplitude can be explained by attenuated air temperature fluctuation in the sampling tube. As mentioned in section 2.1, WPL correction theory explains the apparent CO$_2$ density variation due to air temperature fluctuation. The contribution of temperature fluctuation term is different between OP and CP systems. Unfortunately, actual air temperature fluctuation is not measured but measures sampling chamber temperature in the closed-path gas analyzer. So, exact WPL correction or mixing
ratio conversion is still in question. In the present results, we have adopted short tube to be minimized signal attenuation. While, previous air-sea closed-path CO₂ flux measurement have adopted more than 10m length tube.

3. Conclusion

Air-sea CO₂ flux evaluation with eddy-covariance method is considered as indispensable tool to understand global carbon budget in small time scale parameterization. However, there is a lot of important issues to be discussed to improve the flux accuracy, because the CO₂ flux over ocean is more than an order of magnitude smaller than land surface vegetation.

Air-sea energy flux parameterization in bulk aerodynamic method is based on eddy-covariance measurement and there is no systematic difference between eddy-covariance energy fluxes and bulk fluxes. While air-sea CO₂ flux parameterization is originally based on isotopic mass balance method in large time scale. This is quite different situation from energy flux parameterization in the background.

As the result of open ocean measurements, open-path based CO₂ flux is reported as much larger values than the mass balance based parameterization.

\[\text{Figure 7} \text{ Time series of } \text{H}_2\text{O} \text{ and CO}_2 \text{ gas densities by open-path system and closed-path system.}\]
Closed-path based CO₂ flux is almost consistent with mass balance model, but signal attenuation effect is not well understood. One of the reasons of the higher CO₂ flux in OP can be due to cross talk effect when the optical window is contaminated by salt aerosols, but this cannot explain the total difference of CO₂ flux.

As a conclusion, air-sea CO₂ flux is very small and we should be very careful to accurate measurement including WPL correction, optical window contamination for the open-path system and signal attenuation for the closed-path system.

References


