Accurate Measurement of Air-Sea CO_2 Flux with Open-path Eddy-Covariance

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Abstract. Air-sea CO_2 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 CO_2 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 CO_2 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 CO_2 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 discussions for the transfer velocity parameterization for bulk air-sea CO_2 flux estimates. So we should make every effort to solve these important issues on CO_2 eddy covariance measurement.
Key Words: air-sea flux, eddy-covariance, CO_2 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 CO_2 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 CO_2 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 H_2O gas analyzer including CO_2 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 CO_2 flux is quite different from air-sea energy or momentum flux parameterization, as the CO_2 gas analyzer had not enough resolution for small CO_2 fluctuation over sea surface. As a traditional estimate of air-sea CO_2 flux, bulk method is applied using air-sea delta-pCO_2. 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.

$$F_c = \overline{w'c'} \tag{1}$$

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).

$$w = \overline{w} + w', c = \overline{c} + c' \tag{2}$$

The first ECM CO_2 flux measurement over ocean is reported by Jones and Smith (1977). It was carried out on a offshore tower. They used a sonic anemometer and an open-path infrared CO_2 sensor (originally developed by the authors). They have reported that CO_2 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 CO_2 flux values were 100 times larger than the values using the bulk method, which is based on pCO_2 (CO_2 partial pressure) difference between air and sea. Those papers claimed the poor accuracy of the ECM, and CO_2 flux based on ECM is not reliable. Smith and Jones (1986) and Wesely (1986) have replied that CO_2 flux values based on the their ECM based CO_2 flux is are reasonable.

Ohtaki *et al*. (1989) and Smith *et al*. (1991) have duplicated ECMs with new open-path CO_2 sensors and reported still larger CO_2 eddy flux (nearly 0.05 mg m^{-2}

s^{-1}) 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_2O 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

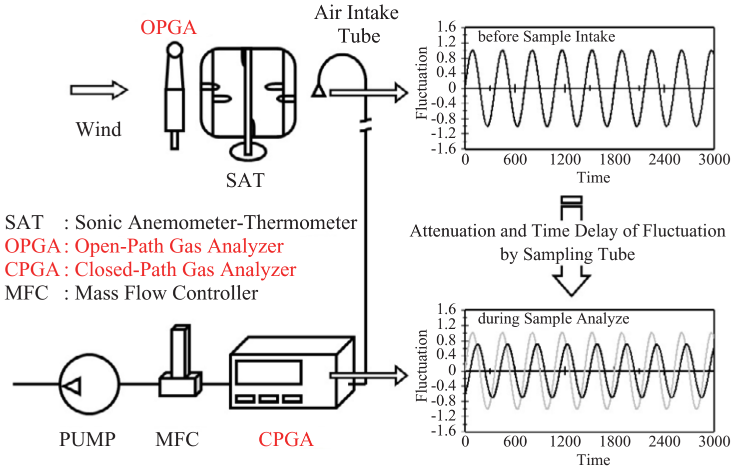

Figure 1 Schematic figure of the open-path system (OPGA) and closed-path system (CPGA).

Figure 2 Open-path eddy-covariance measurement system on board (top of the foremast) R/V MIRAI.

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.

2.1 WPL correction due to air density fluctuation

It is well known that WPL correction is essential for eddy-covariance CO_2 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 CO_2 density (ρ_c) in 'mg/m^3' and local time changes of air temperature (T) and water vapor (ρ_v) lead to dry air volume change. Then apparent CO_2 density (ρ_c) is variable even when CO_2 mixing ratio (χ_c) is kept constant. Following equation explains the WPL correction.

$$F_c\_\mathrm{total} = \overline{w'\rho'_c} + \mu\frac{\overline{\rho_c}}{\overline{\rho_d}}\overline{w'\rho'_v} + (1+\mu\sigma)\frac{\overline{\rho_c}}{\overline{T}}\overline{w'T'} \tag{3}$$

$$\chi_c = \frac{\rho_c}{\rho_d} \tag{4}$$

Here, total CO_2 flux (Fc_total) is expressed as the sum of raw CO_2 flux (1st term), water vapor flux correction term (2nd term) and sensible heat flux correction term (3rd term) in Eq.(3). In this equation, μ is the ratio of molecular weights of dry air and water vapor and σ is the ratio of water vapor density (ρ_v) to dry air density (ρ_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' CO_2 flux. The apparent raw CO_2 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 CO_2 flux over Indian Ocean. As shown in the results, raw CO_2 flux shows apparently negative (downward) flux. When WPL correction is applied, the total flux changes the direction to upward, consistent to air-sea CO_2 fugacity gradient (ΔfCO_2).

Alternative way to evaluate CO_2 flux including the air density correction is to use 'mixing ratio' of CO_2 as noted by Webb *et al*. (1980). Conversion from CO_2 density (ρ_c) to mixing ratio (χ_c) is expressed as Eq (4). The dry air density (ρ_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 CO_2

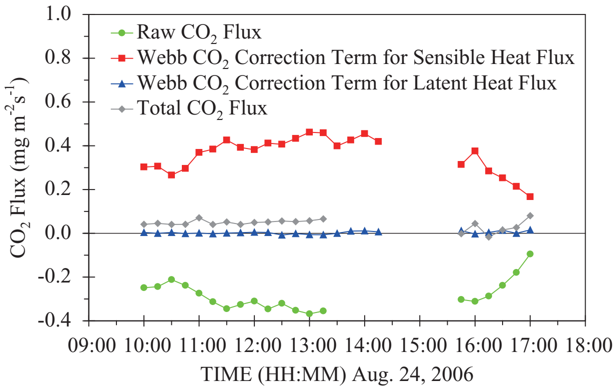

Figure 3 Time series of the raw CO_2 flux, WPL correction terms for the sensible heat flux and latent heat flux and total CO_2 flux over dry asphalt surface (Kondo and Tsukamoto, 2008)

Table 1 Air-sea CO_2 flux evaluated from OP eddy-covariance including WPL correction and bulk flux estimated from mean wind speed and air-sea CO_2 fugacity (fCO_2) difference during MR05-03 over equatorial Indian Ocean (Kondo and Tsukamoto, 2007)

Stations (MR05-03) Indian Ocean	Wind speed (m/s)	ΔfCO_2 (μatm)	Bulk CO_2flux (μg m^{-2}s^{-1})	CO_2 flux by OP eddy-covariance (μg m^{-2}s^{-1})			
				Raw Flux	WPL_sensible heat flux term	WPL_water vapor flux term	Total flux
Station A	3.4	+27.3	+0.51	−51.95	+22.94	+38.62	+9.62
Station B	4.7	+16.6	+0.59	−62.66	+17.05	+46.50	+0.59

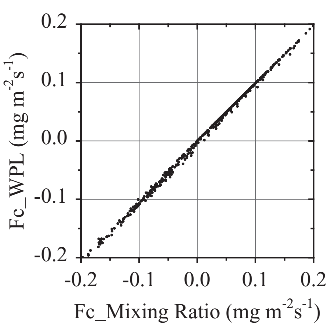

Figure 4 Comparison between the CO_2 flux including the WPL correction (Fc_WPL) and the CO_2 flux directly calculated from CO_2 mixing ratio covarinaces (Fc_Mixing Ratio).

mixing ratio (χ_c) based on measured CO_2 density, air temperature and water vapor density The calculated covariance of $\overline{w'\chi'_c}$ 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

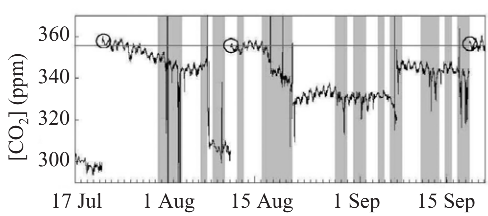

Figure 5 Apparent decrease of CO_2 molar fraction measured by Li-7500 due to optical window contamination (Serrano-Ortizet *et al*. 2007)

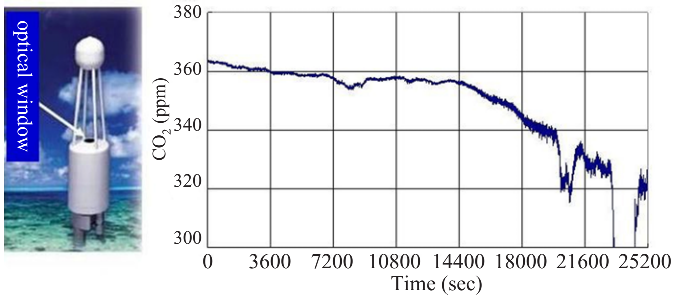

Figure 6 Apparent decrease of CO_2 molar density accompanied by increase of CO_2 fluctuation amplitude due to optical window contamination.

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_2O 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_2O 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_2O 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_2O density. This difference can be due to lower S/N value of CO_2 density in the small CO_2 fluctuation over ocean. H_2O 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

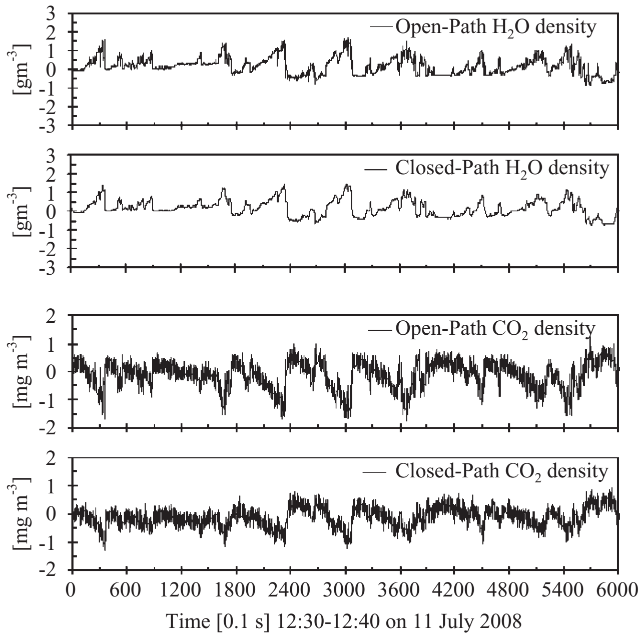

Figure 7 Time series of H_2O and CO_2 gas densities by open-path system and closed-path system.

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 CO_2 flux measurement have adopted more than 10m length tube.

3. Conclusion

Air-sea CO_2 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 CO_2 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 CO_2 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 CO_2 flux is reported as much larger values than the mass balance based parameterization.

Closed-path based CO_2 flux is almost consistent with mass balance model, but signal attenuation effect is not well understood. One of the reasons of the higher CO_2 flux in OP can be due to cross talk effct when the optical window is contaminated by salt aerosols, but this cannot explain the total difference of CO_2 flux.

As a conclusion, air-sea CO_2 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.

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