Improving the CO₂ storage measurements with a single profile system in a tall-dense-canopy temperate forest

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ABSTRACT

The CO₂ storage (F_s) measurement can contribute significantly to the estimation of the net ecosystem exchange of CO₂ (NEE) especially in tall-canopy forest ecosystems. The F_s is often measured with a profile of CO₂ concentration or with an eddy covariance system at the tower top, but few studies investigated potential errors in the F_s measurements. We assessed the errors in F_s relevant to the vertical distribution of sampling levels and window sizes of averaging time of CO₂ mixing ratio and their effects on NEE in a temperate deciduous forest site in Northeast China using the standardized major axis method. The CO₂ storage per unit height typically decreased with the height increasing, suggesting that the below-canopy layer need a higher spatial resolution. CO₂ storage could be underestimated by up to one third based only on the tower-top measurement. The uncertainty (standard deviation) of the F_s decreased with the length of the averaging time window increasing. However, taking time averaging of CO₂ mixing ratio caused significant underestimate of F_s , and consequently led to significant underestimates of CO₂ uptake and release at a 30-min time scale. Our results highlight that appropriately combining spatial resolution and temporal resolution (response time for a whole sampling of all levels) is essential to improving the F_s estimates with the existing CO₂ profile systems in forest ecosystems. Since the systematic bias and random error in F_s estimate with a single profile system are irreconcilable, there is an urgent need to develop a fast response planar-averaging profile or measure the instantaneous vertical-mean concentration to improve the accuracy of F_s measurement.

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1. Introduction

Rapid development of the FLUXNET network (Baldocchi et al., 2001) has greatly improved our understanding of carbon and water fluxes in terrestrial ecosystems in recent years (Papale et al., 2015). The eddy covariance (EC) method provides direct flux measurements of trace gas and energy across the atmosphere–ecosystem interface without disturbing the vegetation and the soil (Aubinet et al., 2012). There are more than 600 active sites globally (Papale et al., 2015), among which dozens have more than a decade of the duration of the time series (Baldocchi, 2014). Generally, the net ecosystem exchange of CO₂ (NEE) can be estimated by summing the vertical eddy flux (F_c), the advection term, and the storage term (F_s) (Aubinet et al., 2005). The F_c can be a close estimation of NEE under ideal conditions (horizontal homogeneity, enough footprint,

flat terrain or after appropriate axis choice, strong turbulent mixing, and steady state conditions) (Aubinet et al., 2012; Baldocchi, 2003). However, the conditions in field are rarely ideal, which leads to frequent underestimation of NEE due to ignoring considerable contributions of the advection and F_s especially in tall-canopy forest ecosystems (Papale et al., 2006; Yang et al., 2007).

Great efforts have been made on improving the accuracy of F_c and advection (Aubinet et al., 2012), but few studies investigated the errors of F_s . The F_s can be significant at short time periods such as half-hours, particularly around sunrise, sunset, or at night (e.g., Dolman et al., 2002; Finnigan, 2006; Yang et al., 2007). Therefore, the F_s should be taken into account because of potential error propagation in the gap-filling processing for annual NEE estimation (Papale et al., 2006). As long as the F_s is properly tackled, potential underestimations of NEE on calm nights can be greatly reduced after the critical friction velocity filtering (Papale et al., 2006; Yang et al., 2007) or by using the data in the early evening period (van Gorsel et al., 2007).

The first objective of this study is to assess the effect of vertical configuration of a CO₂ profile system on F_s estimates. An essential issue of F_s is the uncertainty caused by the spatial and temporal

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Nomenclature

χ_c	Molar mixing ratio of CO ₂ ($\mu\text{mol mol}^{-1}$)
c_c	Molar fraction of CO ₂ ($\mu\text{mol mol}^{-1}$)
c_v	Molar fraction of water vapor (mmol mol^{-1})
ρ_a	Moist air molar density (mol m^{-3})
ρ_c	CO ₂ density (mg m^{-3})
ρ_{dz}	Molar density of dry air at 36 m (mol m^{-3})
$\Delta\chi_c/\Delta t$	Time derivative of CO ₂ mixing ratio
$\Delta\chi_{cz}$	Change of the molar mixing ratio of CO ₂ at the EC height ($\mu\text{mol mol}^{-1}$)
Δt	Time interval between the two samplings (1800 s)
EC	Eddy covariance
F_c	Vertical eddy flux ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
F_s	Storage term ($\mu\text{mol m}^{-2} \text{s}^{-1}$ or $\mu\text{mol m}^{-3} \text{s}^{-1}$)
$F_{s,EC}$	Storage term by the tower-top method ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
$F_{s,p}$	Storage term by the eight-level profile system ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
$F_{s,p36m}$	Storage term by the top level of the profile system ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
H	Height of the EC system (36 m)
IRGA	Infrared gas analyzer
LAI	Leaf area index ($\text{m}^2 \text{m}^{-2}$)
M	Number of time windows for averaging of CO ₂ mixing ratio in a flux averaging period (30 min)
M_c	Molar mass of CO ₂
N	Number of sampling levels of a profile system
NEE	Net ecosystem exchange of CO ₂ ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
OLS	Ordinary least square
P	Length of the window (min)
SD	Standard deviation
SMA	Standardized major axis

variability in CO₂ concentration. The F_s for a single flux tower design is often estimated from a single vertical profile of CO₂ concentration (Finnigan, 2006). A literature review highlighted that there were substantial differences in sampling designs of CO₂ concentration profile systems, e.g., the number and vertical distribution of sampling levels, time needed for a complete profile measurement, and the percentage of the effective measurement time (Table S1). The simplest method for estimating F_s is based on the change in CO₂ density (or molar mixing ratio) measured by the EC system (the tower-top method) if a profile is not available. Some researchers assume that estimates of F_s based on tower-top and profile measurements are interchangeable (Carrara et al., 2003; Hollinger et al., 1994; Knohl et al., 2003), thus the tower-top method is widely used when profile measurements are not available. However, others report that the tower-top method substantially underestimates F_s compared with the profile system (Gu et al., 2012; Iwata et al., 2005; Yang et al., 2007, 1999). Then how many measurement levels are required to accurately quantify the CO₂ mixing ratio profile may depend on canopy complexity and height (Munger et al., 2012). For example, Yang et al. (2007) reported that more sampling levels were needed at the Missouri Ozark flux site in order to achieve the same level of accuracy as at a boreal aspen site (Yang et al., 1999), perhaps because of the difference in their canopy complexity (vertical complex vs. simple) (Yang et al., 2007). But it is not clear whether the difference in topography (e.g., the top of a ridge vs. flat terrain) contributes to it. In this study, we investigated the vertical configuration of an eight-level profile in a temperate forest at the Maoershan flux tower site in Northeast China with vertical complex canopy structure over the toe slope in a small valley. We will examine the relative importance of the complexity in canopy struc-

ture and topography on determination of the number of sampling levels and their vertical distribution.

Our second objective is to quantify the uncertainty (random error) in F_s due to discrete measurements for each level by a single infrared gas analyzer (IRGA). Many researchers use the design of single-IRGA with multiple inlets for CO₂ concentration gradient to remove the systematic errors between IRGAs (Table S1; Munger et al., 2012). The air from each inlet (height level) is sequentially flowed through a manifold and measured with an IRGA (Munger et al., 2012; Xu et al., 1999). The actual measurement from each inlet is thus discrete, and the effective measurement time for each height is much shorter than the averaging period (varying from 8% to 80% for single profile systems, Table S1). Because of the wavelike fluctuation of CO₂ concentration, the instantaneous or small time-window averaged CO₂ concentration may introduce large uncertainty in F_s (Heinesch et al., 2007; Marcolla et al., 2014; van Gorsel et al., 2011). van Gorsel et al. (2011) reported that the uncertainty caused by the wavelike motion of CO₂ concentration and discrete measurement was approximately $0.9 \mu\text{mol m}^{-2} \text{s}^{-1}$ in an open-canopy forest, which was large compared to the F_s of $0.3 \mu\text{mol m}^{-2} \text{s}^{-1}$. Compared to the open-canopy forest, we will quantify the uncertainty of F_s measured with a profile system in our dense-canopy forest.

The third objective is to test whether time averaging of CO₂ concentration underestimates the F_s and consequently NEE. Theoretically, the F_s is the change rate of the instantaneous CO₂ concentration integrated in the control volume (Finnigan, 2006). For a single flux tower, it is the difference between instantaneous CO₂ concentration profiles at the tower measured at the beginning and end of the flux-averaging period, divided by the length of this period (Finnigan, 2006; Xu et al., 1999). The instantaneous CO₂ concentration profile for a single tower can be very noisy due to wind gusts and may not represent the average concentration of the whole control volume. To reduce the random error caused by insufficient spatial sampling, researchers adopt the strategy of replacing the spatial averaging by time-averaging (Finnigan, 2006). However, Finnigan (2006) inferred that the time-averaging procedure can underestimate F_s by at least 50% in most conditions because of filtering high frequency information. Using the single-point high-frequency CO₂ density measurement by the EC system, Yang et al. (2007) qualitatively verified the theoretical inference by Finnigan (2006). In contrast, Ohkubo et al. (2008) augured that the difference in F_s calculated based on a profile system by different sizes of time-averaging window was negligible. Whether the discrepancy is caused by the difference between single-point and profile measurements needs further studies. We will explore how the time averaging of CO₂ concentration influences the F_s and NEE.

In this study, we extended the work conducted by Yang et al. (1999) and Yang et al. (2007), and conducted our study in a temperate broad leaved deciduous forest at the Maoershan Forest Ecosystem Research Station in Northeast China. The fast cycling (one cycle of sequential measurements over the eight levels is completed in 2 min) eight-level profile (AP100, Campbell Scientific Inc., Logan, UT, USA) (Table S1; Wang et al., 2013b) provides us an opportunity to quantify uncertainty due to the discrete measurement and time averaging of CO₂ concentration. The hilly terrain and wind regime are common properties in forest ecosystems. A classic mountain-valley wind system over forest canopy was previously found at the Maoershan site (Wang et al., 2015). The F_s also had a typical diurnal variation in the forest ecosystem, with the negative peak occurring in the early morning and the positive maximum in the early evening (Wang et al., 2013b). Therefore, assessing the effects of sampling strategy and time averaging of the profile system on estimating F_s at the Maoershan site is of importance for assessing the NEE of forest ecosystems in Northeast China, and also has implications for other forest sites. We calculated the

F_s based on CO_2 mixing ratio instead of CO_2 density (Yang et al., 2007, 1999) based on previous studies (Gu et al., 2012; Lee and Massman, 2011; Leuning, 2007; Wang et al., 2013b). The difference in estimated F_s between subprofile and the eight-level profile baseline was assessed by the standardized major axis (SMA) approach (Warton et al., 2006), rather than the ordinary least square (OLS) regression (Björkegren et al., 2015; Yang et al., 2007, 1999) that is inappropriate to assess the difference between two estimates. Our objectives are to: (1) explore the effect of vertical configuration on F_s estimates and test if there is any systematic difference in estimates of F_s between the tower-top method and the profile system, (2) assess the uncertainty of F_s due to discrete sampling, and (3) quantify the impact of the length of averaging time window on F_s .

2. Materials

2.1. Site description

The EC flux tower was established in 2007 at the Maoershan Forest Ecosystem Research Station of Northeast Forestry University, Heilongjiang Province, Northeast China ($45^\circ 24' \text{N}$, $127^\circ 40' \text{E}$, 400 m a.s.l.). The climate is a continental monsoon climate with a windy and dry spring, a warm and humid summer, and a dry and cold winter (Wang et al., 2013a). The mean (1989–2009) annual air temperature is 3.1°C , and the mean January and July air temperatures are -18.5°C and $+22.0^\circ \text{C}$, respectively. The mean annual precipitation is 629 mm, of which $\sim 50\%$ falls between June and August. The mean slope around the tower is $\sim 9^\circ$, and the slope of the valley center is $\sim 1^\circ$ along the valley (Wang et al., 2015).

The forest around the EC flux tower was about 60-year old, with a canopy height of 18–20 m. The dominant tree species include *Ulmus japonica* Sarg., *Fraxinus mandshurica* Rupr., *Betula platyphylla* Suk., *Populus davidiana* Dode, *Juglans mandshurica* Maxim., etc. Based on the inventory of 106 circular plots (with diameters of 20 m) within the fetch ($1500 \text{ m} \times 400 \text{ m}$), the mean basal area and tree biomass density were $24.16 \text{ m}^2 \text{ hm}^{-2}$ and $155.64 \text{ Mg ha}^{-1}$, respectively (Liu et al., 2016). The maximum leaf area (semi-surface leaf area) index (LAI) of the canopy, measured with the litter fall collection method, was about $5.7 \text{ m}^2 \text{ m}^{-2}$ in eight $20 \times 30 \text{ m}$ permanent plots (Wang et al., 2015). A 1–8 m high and well-developed understory is dominated by *Syngia reticulata* var. *mandshurica*, which contributed 27% to the stand LAI (Wang et al., 2015).

2.2. Instrumentation and data collection

An open-path eddy covariance system (LI-7500, Li-Cor Inc, Lincoln, NE, USA; CAST3, Campbell Scientific Inc, USA) was installed at the 36 m height. The $\text{CO}_2/\text{H}_2\text{O}$ concentrations were measured at 0.5, 2.0, 4.0, 8.0, 16.0, 20.0, 28.0, and 36.0 m above the ground surface using the AP100 (Campbell Scientific Inc, USA). The AP100 was designed similar to the system by Xu et al. (1999). The profiling system included the following components: an air sampling system, a calibration and flow control system, a closed-path IRGA (LI-840, Li-Cor Inc, USA), and a datalogger (CR1000, Campbell Scientific Inc, USA).

Each intake had a coarse filter with a rain diverter and a $7 \mu\text{m}$ filter. A precision orifice in each line was used to set the flow rate and the pressure in the system. And a 0.5 W heater was used to prevent condensation. The tubings had an inner diameter of 1/4 inch, and were made of high-density polyethylene bonded to an overlapped aluminum tape with an ethylene copolymer coating. The polyethylene liner reduced the interaction of water vapor with the walls of the tubing.

The pressure in the tubing and IRGA was maintained approximately at half of the local atmospheric pressure to further prevent

condensation and reduce the interaction of the water vapor with the walls of the tubing, which reduced the settling time after switching to the new level. Air was drawn continuously from eight heights through tubings of equal length and diameter, each connected to a three-way solenoid valve mounted on a manifold. The flow from each inlet was directed either to the analyzer (only when the level is selected) or the pump, so that the system was constantly flushed and followed the ambient concentration changes when the corresponding level was not selected. The flow from only one intake line went through the analyzer at one time, which was further filtered with a $1 \mu\text{m}$ pore size PTFE filter (Acro50, Pall Corporation, MI, USA). The valves were switched sequentially every 15 s; the first 7 s reading was removed to purge the tubings and the path of IRGA to getting an equilibration; and the reading in the next 8 s was recorded with a datalogger. The 7 s' delay before logging the data was based on the apparatus equilibration time (less than 5 s), which allowed the system to complete one cycle of sequential measurements over the eight height levels within a short interval (a 2-min cycle) and 15 cycles in a flux-averaging period (30 min). The datalogger recorded the CO_2 and H_2O concentrations (molar fraction) at 2-min and 30-min time intervals. The calibration system, controlled by the datalogger, compensated for any deviations in the calibration of the IRGA with the gas sources of known concentrations (zero and span of CO_2). The LI-840 IRGA was automatically calibrated for zero and span of CO_2 once a day at 10:00 a.m., and also manually calibrated once a month to remove potential long-term drifts.

The temperature/relative humidity profile was composed of five HMP45C probes (Vaisala, Helsinki, Finland) with aspirated radiation shield (076B, Met One Instruments Inc., USA) at heights of 2.0, 16.0, 28.0, 36.0 and 48.0 m. Air temperature and relative humidity were measured once every two seconds for all heights and recorded the 30-min averages. The barometric pressure was measured at 28 m above the ground surface.

3. Data processing

The CO_2 molar fraction is constrained in the ranges between $300 \mu\text{mol mol}^{-1}$ and $900 \mu\text{mol mol}^{-1}$ within the canopy (below 20 m above the ground), and between $300 \mu\text{mol mol}^{-1}$ and $600 \mu\text{mol mol}^{-1}$ above the canopy (Jiao et al., 2011). The F_s out of the range (between $-45 \mu\text{mol m}^{-2} \text{ s}^{-1}$ and $45 \mu\text{mol m}^{-2} \text{ s}^{-1}$) was also excluded in further analysis. The CO_2 profile and F_s data during precipitation were included because the closed IRGA was not influenced by precipitation (Wang et al., 2013b), while the LI-7500 data during precipitation were excluded. The data coverage rates were 95% for the profile and 80% for the LI-7500 after the quality control. Data gapfilling was not implemented because we were focusing on the flux density and avoiding other uncertainties caused by gapfilling (Wang et al., 2013b). To explore the effect of canopy density on F_s , we divided the calendar year into two seasons: the leaf-on season (11 May to 5 October) and leaf-off season (the other times) (Wang et al., 2015) based on the canopy phenology (Liu et al., 2015).

3.1. Calculation of CO_2 storage

The dry molar fraction of CO_2 (molar mixing ratio relative to the dry air) was adopted to calculate the F_s (Gu et al., 2012; Kowalski, 2008; Leuning, 2007), because it was conservative to expansion and contraction of the air column below the measurement height (Kowalski and Serrano-Ortiz, 2007; Lee and Massman, 2011). At the Maoershan site, Wang et al. (2013b) found using CO_2 density to calculate the storage could overestimate 8.5%, but the error of using mixing ratio was only 0.1%. For the tower-top measurement, the output of CO_2 concentration of the LI-7500 was gas density,

which was firstly converted to CO₂ molar mixing ratio (χ_c , $\mu\text{mol mol}^{-1}$) as Wang et al. (2013b),

$$\chi_c = \frac{\rho_c \times 10^3}{M_c \rho_a (1 - c_v \times 10^{-3})} \quad (1)$$

where ρ_c is CO₂ density (mg m^{-3}), M_c is molar mass of CO₂ (44.01 g mol^{-1}), ρ_a is moist air molar density (mol m^{-3}), and c_v is molar fraction of water vapor (mmol mol^{-1}). Then the F_s estimated by the tower-top method ($F_{s,EC}$, $\mu\text{mol m}^{-2} \text{ s}^{-1}$) was calculated as,

$$F_{s,EC} = \frac{\Delta \chi_{cz}}{\rho_{dz} \Delta t} h \quad (2)$$

where ρ_{dz} is the molar density of dry air at the 36 m (mol m^{-3}), $\Delta \chi_{cz}$ is the change in the molar mixing ratio of CO₂ at the EC height ($\mu\text{mol mol}^{-1}$), Δt is the time interval between the two samplings (1800s), and h stands for the height of the EC system (36 m). For the profile system, the molar fraction of CO₂ by the LI-840 was also transformed to molar mixing ratio as (Leuning, 2007; Montagnani et al., 2009),

$$\chi_c = \frac{c_c \times 10^{-6}}{1 - c_v \times 10^{-3}} \quad (3)$$

where c_c is molar fraction of CO₂ ($\mu\text{mol mol}^{-1}$), and c_v is molar fraction of water vapor (mmol mol^{-1}). And the F_s estimated by the eight-level profile systems ($F_{s,p}$, $\mu\text{mol m}^{-2} \text{ s}^{-1}$) was calculated as (Gu et al., 2012; Lee and Massman, 2011; Leuning, 2007),

$$F_{s,p} = \overline{\rho_d}(h) \int_0^h \frac{\partial \chi_c}{\partial t} dz = \overline{\rho_d}(h) \sum_i^8 \frac{\Delta \chi_{ci}}{\Delta t} h_i \quad (4)$$

where χ_{ci} represents the molar mixing ratio of CO₂ at each sampling height section ($\mu\text{mol mol}^{-1}$). $\Delta \chi_{ci}/\Delta t$ between two adjacent levels were averaged to get a more representative for the layer. At the bottom level, the measurement right at the ground surface was linearly extrapolated based on the low two layers (0.5 and 2 m). The CO₂ measurements at the levels where air temperature was not measured were obtained by applying linear interpolation to the two adjacent measurements (Yang et al., 2007).

3.2. Effect of vertical configuration of a profile system on CO₂ storage estimates

The data set used in this section covered the whole year of 2009. The SMA line-fitting approach (Warton et al., 2006) was used to test the consistency between F_s estimates by continuous (tower-top measurement by LI-7500, $F_{s,EC}$) and by discrete (36.0 m height of the profile, $F_{s,p36m}$) samplings, and by tower-top ($F_{s,EC}$) and by profile ($F_{s,p}$) measurement. The effect of F_s calculations based on $F_{s,EC}$ and $F_{s,p}$ on NEE was also assessed by the SMA approach. The SMA test is used because it is suitable for consistency test between two methods, while the OLS regression is often used for predictive purposes (Warton et al., 2006). We found that the OLS approach substantially underestimated the slopes of the fitted lines compared with those by the SMA approach (Supplementary material S1, giving an example of time-averaging effect on F_s). Similarly, Wilson et al. (2002) also found that the OLS tended to underestimate the slope for the energy balance, and the underestimation increased with R^2 decreasing.

The NEE was calculated as,

$$NEE = F_c + F_s \quad (5)$$

where F_c and F_s are eddy and storage fluxes of CO₂ ($\mu\text{mol m}^{-2} \text{ s}^{-1}$), respectively. The advection term of NEE is omitted as did all single-tower designs (Aubinet et al., 2012). The F_c data were processed with the flux measurement standard procedures, including despiking, time-lag removing, planar-fit tilt correction, frequency

response correction, WPL correction, and quality control (Aubinet et al., 2012).

To examine the effect of vertical configuration of a profile on F_s , we used the eight-level profile system as a benchmark to test subsets of the full profile system as did Yang et al. (2007). The subset profiles were grouped based on the total number of measurement levels in each profile. Within a group, all subset profiles contained the same number of measurement levels but different combinations of measurement heights. The topmost level (36 m) was always included as the top boundary in all subset profiles except the one-level measurement. Again, the SMA method was used to test the possible biases of the subset profiles based on the slopes and intercepts of the fitted lines (Warton et al., 2006). Because the intercepts of F_s for most combinations against the $F_{s,p}$ were within $[-0.04, 0.04 \mu\text{mol m}^{-2} \text{ s}^{-1}]$ (except the 0.5 m height for one-level of $-0.08 \mu\text{mol m}^{-2} \text{ s}^{-1}$), the slopes could be used to correct the biases of subset profile combinations.

3.3. Uncertainty of CO₂ storage estimates due to discrete sampling

The data set in this section derived from the 2-min averaged CO₂ molar fraction measured by the profile from 10 June 2008 to 31 December 2009 (the data from 2 July to 16 August of 2009 were missing). Based on the fast response profile system of AP100 (2-min for one cycle of all eight-level), we calculated F_s for 15 time windows varying from 2 min to 30 min, which increased with a time step of 2 min. The number of measurements (M) of time windows for averaging of CO₂ mixing ratio in a flux averaging period (30 min) depended on the length of the time window [$M = (30 - P)/2 + 1$, where P is the length of the window (min)], e.g., 15 moving independent 2-min time windows, or 14 moving 4-min windows (allowing partly overlap between moving windows). We noted that calculating the F_s for each flux-averaging period by averaging all independent or moving windows is inappropriate, because performing such averaging is identical to doing averaging CO₂ concentration for all independent windows in the flux averaging period (Supplementary material S2). Therefore, we used the mean CO₂ mixing ratio of the time window in the middle of a flux averaging period.

According to previous studies on uncertainty analysis (Heinesch et al., 2007; Marcolla et al., 2014), the standard deviation (SD) of the estimates for all windows in a given flux period was adopted as a measure of uncertainty of F_s induced from discrete sampling. We performed no interpolation between cycles because any interpolation would introduce additional uncertainties (Björkegren et al., 2015).

3.4. Effect of time-averaging on CO₂ storage estimates

The data set for this section was the same as that in Section 3.3. The recordings of CO₂ concentrations for each cycle of a whole sampling of all levels gave us an opportunity to analyze the effect of time-averaging of CO₂ concentrations on F_s estimates using profile systems. The fast profile data had an advantage in spatial representation than the tower-top measurement of CO₂ density from LI-7500 by Yang et al. (2007). The slopes and intercepts of the SMA fitted lines were used to assess the systematic bias of the magnitude of F_s . We also compared the NEE based on the 2-min-window F_s and the 30-min-window F_s using the SMA method.

Fig. 1. Diurnal variations in vertical contours of seasonal means of CO_2 molar mixing ratio ($\mu\text{mol mol}^{-1}$) during the leaf-on (a) and leaf-off seasons (b).

4. Results and discussion

4.1. Vertical distributions of CO_2 mixing ratio and storage

The seasonal averaged daily courses of CO_2 molar mixing ratio (χ_c) profile (Fig. 1) showed that the CO_2 accumulated at night and

depleted after sunrise. The χ_c was always higher below the canopy than above the canopy, with the greatest gradient of χ_c occurring at night in the leaf-on season. The χ_c rapidly decreased after sunrise. Because the depletion of χ_c was more dramatic near the ground surface due to turbulent mixing, the vertical gradient declined to its minimum around the noon. The χ_c started to increase at the forest floor before sunset, and then extended to the whole canopy till the early evening. The diurnal evolution of χ_c was much less in the leaf-off season than the leaf-on season (Fig. 1b). Such diurnal variation in χ_c was similar to those in boreal (Yang et al., 1999), temperate (Leuning et al., 2008; Ohkubo and Kosugi, 2008; Yang et al., 2007) and tropical (Araújo et al., 2008; Huttyra et al., 2008; Ohkubo et al., 2008; Yao et al., 2012) forests, suggesting that the Maershan flux site shared a common feature with many forest sites.

The magnitude of the time derivative of CO_2 mixing ratio ($\Delta\chi_c/\Delta t$) decreased from the forest floor to the 36 m (the EC system height; Fig. 2a and b). In the leaf-on season, the $\Delta\chi_c/\Delta t$ during the period of nocturnal stable boundary layer (21:30–5:30) was slightly positive (weakly accumulating CO_2); that in the morning transition phase (6:00–8:30) was strongly negative (strongly releasing CO_2); that in the period of daytime convective boundary layer (09:30–16:00) was slightly negative or near neutral; and that in the evening transition phase (16:30–21:00) was strongly positive (strongly accumulating CO_2) but smaller in magnitude than that in the morning transition phase. Although the magnitude decreased by one order, the daily change of the vertical profile was similar in the leaf-off season to that in the leaf-on season. The standard deviation (SD) of $\Delta\chi_c/\Delta t$ also decreased with height increasing (Fig. 2c and d), and its vertical gradient was more dramatic at night and in the morning transition phase. Vertically, both magnitudes of mean and SD of $\Delta\chi_c/\Delta t$ were higher below 8 m, intermediate between 8–20 m, and lower above 20 m. Therefore we separated the whole air column below the EC height into three vertical sections to evaluate the contributions of different layers to the total F_s : below-canopy layer (0–8 m), canopy layer (8–20 m) and above-canopy layer (20–36 m).

Fig. 2. Vertical profiles of the mean and standard deviation (SD) of the time derivative of CO_2 molar mixing ratio ($\Delta\chi_c/\Delta t$) during the leaf-on (a,c) and leaf-off seasons (b,d).

Table 1
Comparison of the mean CO_2 storage flux (F_s) of different vertical sections below the measurement height of eddy covariance for different periods in the leaf-on and leaf-off seasons. The contribution of each vertical section to the total storage is given in the parentheses.

Season	Period	F_s ($\mu\text{mol m}^{-2} \text{s}^{-1}$)			
		0–8 m	8–20 m	20–36 m	0–36 m
Leaf-on	Night (21:30–5:30)	0.214 (48.3%)	0.121 (27.3%)	0.109 (24.4%)	0.444 (100%)
	Morning transition (6:00–8:30)	–1.511 (32.2%)	–1.593 (34.0%)	–1.584 (33.8%)	–4.688 (100%)
	Day (9:00–16:00)	–0.128 (31.5%)	–0.115 (28.3%)	–0.164 (41.2%)	–0.407 (100%)
	Evening transition (16:30–21:00)	0.737 (27.8%)	0.920 (34.6%)	1.000 (37.6%)	2.657 (100%)
Leaf-off	Night (20:30–6:30)	0.006 (–108.7%)	–0.003 (61.5%)	–0.008 (147.2%)	–0.005 (100%)
	Morning transition (7:00–9:30)	–0.148 (41.9%)	–0.116 (32.8%)	–0.089 (25.3%)	–0.353 (100%)
	Day (10:00–16:30)	–0.014 (21.3%)	–0.023 (34.5%)	–0.029 (44.2%)	–0.066 (100%)
	Evening transition (17:00–20:00)	0.134 (30.8%)	0.149 (34.4%)	0.151 (34.8%)	0.435 (100%)

The F_s per unit height also varied with vertical sections (Fig. 3) as did the mean $\Delta\chi_c/\Delta t$ (Fig. 2). The F_s per unit height in the below-canopy layer was higher than those above for both leaf-on and leaf-off seasons, particular at dusk and night. In the morning transition phase (6:00–8:30), the peak of below-canopy F_s was slightly lagged those in the upper layers (Fig. 3a). In the evening transition phase (16:30–21:00), the peak of F_s occurred earlier in the below-canopy layer than did those aloft. Volume percentages of the below-canopy, canopy, and above-canopy layers (22%, 33% and 44%, respectively) also influenced the contribution of specific vertical sections to the total F_s . For example, during the night in the leaf-on season, the F_s per unit height increased from below-canopy, canopy, to above-canopy layer, with the corresponding contributions of 48.3%, 27.3%, and 24.4%, respectively (Table 1). Although the magnitude of F_s was much lower in the leaf-off season, the diurnal courses and relative magnitudes of F_s per unit height from the three sections were similar to those in the leaf-on season (Fig. 3b). Note that the data of leaf-off-night were within the typical measurement errors, thus the relative contribution of particular layer varied considerably than those of the other periods. During the night, the direction of the below-canopy F_s sometimes differed from those in the other two layers (Table 1), mainly due to the near neutral values in the dormant season (Wang et al., 2015). These results illustrated that the layer near the ground surface tended to contribute dis-

proportionally higher to its height percentage than did the upper layers.

The magnitude of F_s in this study was well within the range in temperate forests (Aubinet et al., 2005; Gu et al., 2012). The vertical distribution of F_s at the Maoershan site was consistent with that at the Moflux site (Yang et al., 2007), but differed from that at the Southern Old Aspen (SOA) site where more than 85% of the increase in F_s in late night occurred above 9 m (Yang et al., 1999). We speculate that this difference may mainly result from the difference in the complexity of canopy structure, probably not the distance to the ridge as previously considered for advection (Aubinet et al., 2005). The Moflux flux tower is located on the top of a ridge (Yang et al., 2007), while the Maoershan flux tower is on the toe of a valley sidewall. The only common feature for canopy structure and terrain the Moflux and the Maoershan sites is a complex canopy (well-developed understory layer). The SOA site had an open canopy structure (total LAI was $4.1 \text{ m}^2 \text{ m}^{-2}$, with a 2-m-tall shrub layer contributed 40%, and a trunk space height of 9–15 m) and a relative flat terrain (Yang et al., 1999). In the late night, the acceleration of the wind weakened the subcanopy inversion and moderately increased whole-canopy turbulence mixing (Mahrt et al., 2000), accordingly the increase in F_s mainly occurred in the upper layer (Yang et al., 1999). This situation probably does not occur in dense-canopy forest sites where the radiational cooling is often at the canopy top and the subcanopy stratification might become neutral or even unstable at night (Wang et al., 2015). Therefore, the canopy structure probably plays a more important role in the vertical distribution of F_s than did the topography. To optimize the vertical distribution of a profile system for the F_s measurement, it is needed to consider canopy structure and thermal stratification, as well as the topography (Munger et al., 2012; Yang et al., 2007).

4.2. Effects of vertical configuration of a profile on CO_2 storage estimates

Profile designs varied considerably at global forest sites, most of which had 4–12 levels that distributed from ground surface to 70 m height (Table S1). We assessed the bias of subprofiles by the regression slope of subprofiles against the eight-level profile with the SMA approach. At our site, the effectiveness (R^2) of the best configuration increased with the number of sampling levels (N) increasing (Fig. 4a), while the systematic bias on the magnitude of F_s (deviation of the slope from 1) decreased (Fig. 4b). The effectiveness of a configuration was too low to get a precise estimate of F_s if the sample size $N \leq 2$ (Table S2). When the N was four or more, the subprofile with optimal vertical distribution could provide a reasonable estimate of F_s (Fig. 4 and Table S2). Yang et al. (2007) reported that when the N equaled to four or less, any combination could not measure F_s accurately at the complex-canopy Moflux site, but three levels was good enough for the simple-canopy SOA site (Yang et al., 1999). These results confirm that more sampling lev-

Fig. 3. Diurnal variations in mean CO_2 storage flux per unit height (F_s) from the three vertical sections below the measurement height of eddy covariance during the leaf-on (a) and leaf-off seasons (b). 0–8 m: below-canopy layer; 8–20 m: canopy layer; 20–36 m: above-canopy layer.

Fig. 4. The coefficients of determination (R^2) (a) and slope (b) for the regression lines of CO_2 storage flux estimates using various vertical configurations versus estimates from eight sampling heights. Y is the F_s calculated by subprofile, and X is the F_s calculated by the eight-level profile system ($F_{s,p}$). The solid line in (a) is the configuration with the lowest bias (the slope is closest to 1). The solid and dashed lines in (b) are the configurations with the highest and the lowest R^2 , respectively.

els are needed in complex-canopy forests than in simple-canopy forests.

For a given N , the most effective combination (with the highest R^2) had a very low bias in F_s , but the combination with the lowest bias (as indicated by the slope and intercept of the fitted-line between sub-combination and the baseline) was not necessary the most effective combination (Fig. 4, Table S2). So the biases are more important than the R^2 because our concern is to avoid any systematic error (non-unit slope and non-zero intercept). Using the OLS regression is better for prediction purpose than comparison of the difference in estimates between two methods using the SMA test in this study. Therefore we suspect that the criteria of previous studies using the OLS regression (e.g., Björkegren et al., 2015; Yang et al., 2007, 1999) might biased the errors of subprofiles, although the overall trends are similar. Combinations with the lowest biases in the magnitudes of F_s and the highest effectiveness require sampling slightly denser in the subcanopy layer than that above, because of larger $\Delta\chi_c/\Delta t$ in this layer (Fig. 2). For a dense-canopy forest, it was preferred to allocate at least two levels under the canopy and two or more levels over the canopy (Table S2; Yang et al., 2007). To optimize a profile to measure the F_s , one needs to balance the $\Delta\chi_c/\Delta t$ and the layer thickness (Yang et al., 2007).

The diurnal variation in $F_{s,p36m}$ (discrete sampling by the profile) was consistent with the $F_{s,EC}$ (continuous sampling by the EC system), and similar to that of $F_{s,p}$ (Fig. 5). The F_s reached its minimum in the morning, peaked in the early evening and declined rapidly until the late night, inconsistent with those by Aubinet et al. (2005). These results support the alternative method of friction velocity threshold for filtering the nocturnal NEE (Van Gorsel et al., 2009; van Gorsel et al., 2007).

We further quantified the difference in F_s estimates between the tower-top method and the profile measurement. The SMA test between $F_{s,EC}$ and $F_{s,p36m}$ showed that the slope (0.929) was not significantly ($P > 0.05$) different from unit, and the intercept (-0.059) was neither significantly ($P > 0.05$) different from zero (Fig. 6). However, the $F_{s,EC}$ was systematically lower in magnitude than the $F_{s,p}$, with the greatest difference occurring at the morning transition phase (Fig. 5). The slope (0.654) was significantly ($P < 0.001$) lower than one, but the intercept was not significantly ($P > 0.05$) different from zero (Fig. 6). This indicated that the tower-top measure-

Fig. 5. Diurnal variation in yearly means of CO_2 storage flux (F_s) estimated from the eight-level profile system ($F_{s,p}$), the top-level of profile system ($F_{s,p36m}$), and the EC system ($F_{s,EC}$).

Fig. 6. Comparisons of the CO_2 storage fluxes between different methods. The LI-7500 ($F_{s,EC}$) versus the top-level of profile system ($F_{s,p36m}$) (a) and the $F_{s,EC}$ versus the eight-level profile system ($F_{s,p}$) (b). The yearly mean 30-min values at the same time of each day are used ($N = 48$). The dash lines are the reference lines with unit-slope and zero-intercept.

ment underestimated the F_s by 34.6% compared with the reference 8-level profile system, qualitatively in accordance with previous studies (Iwata et al., 2005; Gu et al., 2012; Björkegren et al., 2015). The number of sampling levels and the vertical distributions varied considerably among sites (Table S1). This partly results in the disagreement on whether the tower-top method can safely replace the profile method. We noticed that previous studies that considered the two methods being interchangeable all lack adequate information, such as the sampling period (for one cycle of the whole profile), the percentage of the effective measurement time (with the purging time subtracted) to the average interval (Table S1), the time scale of the dataset, etc. Such obscurities should be clarified in order to increase the reliability of the interchangeableness of two methods.

In order to assess the effect of the two estimates of F_s on NEE, we compared the tower-top based NEE ($F_c + F_{s,EC}$) and the profile-based NEE ($F_c + F_{s,p}$) in Table 2. The deviations of the slopes from one were within 5%, while the intercepts for the leaf-on daytime ($0.560 \mu\text{mol m}^{-2} \text{s}^{-1}$) and leaf-on nighttime ($-0.864 \mu\text{mol m}^{-2} \text{s}^{-1}$) were highly significantly ($P < 0.001$) different from zero. The large intercepts demonstrated the tower-top method underestimated the daytime CO_2 uptake and the nocturnal CO_2 release because the NEE was negative in daytime and positive

Table 2

Results of the standardized major axis (SMA) line-fitting for the estimates of net ecosystem exchange of CO₂ (NEE) calculated by the tower-top based NEE ($F_c + F_{s,EC}$) and the profile-based NEE ($F_c + F_{s,p}$), respectively. F_c is eddy flux; and $F_{s,EC}$ and $F_{s,p}$ are storage fluxes based on eddy covariance system and eight-level profile system for 30 min time window, correspondingly. The model form is $F_c + F_{s,EC} = a + b(F_c + F_{s,p})$. * and ** indicate significant ($P < 0.05$) and highly significant ($P < 0.01$) differences, respectively, in slope from unit or intercept from zero. All line-fittings are highly significant ($P < 0.001$). Sample size (N), determination coefficient (R^2), and 95% confidence interval (CI) are given.

Time period	N	R^2	Slope	95% CI of slope	Intercept	95% CI of intercept
The whole year	12632	0.750	1.009*	1.000, 1.018	0.020	−0.049, 0.088
Leaf-on daytime	3170	0.789	1.027**	1.010, 1.043	0.560**	0.357, 0.763
Leaf-on nighttime	1598	0.578	1.030	0.998, 1.063	−0.864**	−1.228, −0.502
Leaf-off daytime	3798	0.748	1.009	0.993, 1.025	0.040	−0.021, 0.102
Leaf-off nighttime	4066	0.657	1.047**	1.029, 1.066	−0.013	−0.072, 0.046

Fig. 7. Diurnal variations in standard deviations (SD, used as an uncertainty measure) of CO₂ storage flux (F_s) calculated from the eight-level CO₂ dry molar fraction for the averaging window size varying from 2 min to 28 min.

at night in the leaf-on season. According to Papale et al. (2006), using the tower-top method to estimate F_s lead to an error of $25 \text{ g C m}^{-2} \text{ yr}^{-1}$ on the annual NEE; and the underestimations can be up to the order of $100 \text{ g C m}^{-2} \text{ yr}^{-1}$ on the gross primary productivity and ecosystem respiration. Therefore, it should be cautious to use the tower-top method to measure F_s at least at forest sites. If a profile system is not available in old dataset, one may explore the possibility to retrieve a “storage correction factor” through a regression between the storage measured with the profile system and a series of variables (Papale et al., 2006), models considering the mean diurnal variation (Hutry et al., 2008), or just a simple linear model similar in Fig. 6b. The associated uncertainty may be less important than the systematic bias of underestimation of photosynthesis and respiration.

4.3. Uncertainty of CO₂ storage estimates

The uncertainty of F_s was higher at night than in the day as expected (Fig. 7). Surprisingly, the peak of uncertainty of F_s occurred in late night, rather than in the transition phase of the boundary-layer when the magnitude of F_s peaked. The uncertainty of F_s for the 28-min window in the transition periods during the leaf-on season (around $0.4 \mu\text{mol m}^{-2} \text{ s}^{-1}$) was relatively small ($\sim 10\%$) compared to the magnitude of F_s , but it was large in the nighttime. During the leaf-on season, the relative uncertainty of F_s (the ratio of the SD of F_s to the magnitude of F_s) was 10% in the transition periods, 50% between 8:00–16:00, and about 100% in the nighttime. Additionally, the uncertainty of F_s systematically diminished with the length of the time window (for averaging CO₂ mixing ratio) increasing (Fig. 8), although its diurnal pattern was similar for different time windows (Fig. 7). For the leaf-on season, the uncertainties for the 2-min window in the daytime ($2.47 \mu\text{mol m}^{-2} \text{ s}^{-1}$) and in the nighttime ($4.44 \mu\text{mol m}^{-2} \text{ s}^{-1}$) were 12.4 and 12.7 times of those for the 28-min in the corresponding time. The large

uncertainty of F_s for small window might be unacceptable to NEE calculating.

The uncertainties in F_s are rarely assessed in the literature. Heinesch et al. (2007) estimated an upper limit of the uncertainty due to sampling time was about $0.42 \mu\text{mol m}^{-2} \text{ s}^{-1}$ (10% of F_s) for eight measurements in the 30-min window at the Vielsalm site, using one-point measurement at the 1-m height. Their estimate of upper limit of absolute uncertainty was similar to or higher than the uncertainty in this study (Fig. 8). However, the uncertainty of F_s was estimated to be $0.9 \mu\text{mol m}^{-2} \text{ s}^{-1}$ (300%) by the wavelet analysis in an open-canopy forest (van Gorsel et al., 2011). The disparities among these studies may be attributed to three potential factors: (1) Differences in vertical structure of forest canopy cause discrepancy in period of oscillation of χ_c . The gravity waves

Fig. 8. Changes in standard deviations (SD, used as an uncertainty measure) of CO₂ storage flux (F_s) calculated from the eight-level CO₂ dry molar fraction with averaging window size for different periods.

in the open canopy lead to large fluctuation of CO_2 concentration; and the period is about 3 min (van Gorsel et al., 2011). In contrast, the canopy at the Vielsalm site and the Maoershan site are dense and complex. A wavelet analysis indicated that the CO_2 concentration commonly oscillated in 1–2 min at the Maoershan site (Wang, unpublished data). (2) Different sampling protocols are applied. van Gorsel et al. (2011) and the present study used the profile data and with different designs (Table S1), but Heinesch et al. (2007) used the high-frequency data at 1 m level and assumed a similar uncertainty at all levels. (3) Different proxies of uncertainty are adopted. Heinesch et al. (2007) and this study adopted the SD as a measure of uncertainty, while van Gorsel et al. (2011) used the wavelet analysis to quantify the theoretical uncertainty. Nevertheless, the uncertainties caused by the temporal fluctuation should be appreciated compared with the spatial variability in CO_2 concentrations (de Araújo et al., 2010; Montagnani et al., 2009).

4.4. Effects of time averaging of CO_2 mixing ratio on CO_2 storage estimates

As the length of the averaging time window increasing from 2 min to 28 min, the R^2 and the slope of the SMA fitted line were both convergent to one (Fig. 9a and b), and the intercept was approaching to zero (Fig. 9c). Because the range of intercept ($-0.454 \mu\text{mol m}^{-2} \text{s}^{-1}$ – $0.162 \mu\text{mol m}^{-2} \text{s}^{-1}$) was much lower than that of the $F_{s,p}$ ($-3.022 \mu\text{mol m}^{-2} \text{s}^{-1}$ – $2.034 \mu\text{mol m}^{-2} \text{s}^{-1}$, Fig. 5), the slope was the dominant contributor of the error. The trend of the slope indicated that the underestimate in F_s increased as time window of χ_c became longer. The F_s based on the 2-min time window was 1.4 times of that by the 30-min window for all the time, 1.5 times of that during the leaf-on nighttime, and 1.2 times during the leaf-off nighttime. For the same length of window from different periods, the magnitude of the bias ranked in the order of the leaf-on nighttime > the leaf-off nighttime > the leaf-on daytime > the leaf-off daytime (Fig. 9b). These findings indicated that using the 30-min mean χ_c to calculate the F_s could result in a significant negative bias, which were consistent with Finnigan (2006), Yang et al. (2007) and Björkegren et al. (2015). In contrast, Ohkubo et al. (2008) reported that the length of time averaging had no effect on the F_s in a tropical rainforest site. We mathematically assessed the two approaches [(1) calculating F_s based on time-derivative of the 30-min mean χ_c , and (2) averaging all F_s for all short-time windows in 30-min], and obtained identical results (Supplementary material S1). Therefore, using time-averaging of a single profile of CO_2 concentration, instead of spatial averaging of instantaneous CO_2 concentration, leads to a significant underestimate of F_s .

Theoretically, the F_s is the change rate of the instantaneous CO_2 concentration ($\Delta\chi_c/\Delta t$) integrated in the control volume (Finnigan, 2006). The $\Delta\chi_c/\Delta t$ is nonlinear because of the “U” or “V” shape of the mean diurnal variation in CO_2 concentration for a given height (e.g. Jiao et al., 2011). Performing any averaging of CO_2 concentration before calculating the F_s removes some high-frequency components of change (including both noise and real change), which will lead to underestimate the $\Delta\chi_c/\Delta t$ and consequently underestimate the F_s . The extent of underestimation will increase with window size of averaging time increasing (Fig. 9; Björkegren et al., 2015; Yang et al., 2007). This corresponds to the “transient” (short time scale) nature of F_s in non-steady state conditions (Gu et al., 2012).

The underestimation of time averaging of CO_2 mixing ratio for calculating F_s also has implications on the energy storage and energy balance related to the EC method. Leuning et al. (2012) found that for the La Thuile dataset, the slope of the linear regression (forced through the origin) between turbulent heat flux (the sum of sensible and latent heat fluxes) and available energy (the difference between the net radiation and the heat flux through

Fig. 9. Effects of averaging window size on determination coefficient (R^2) (a), slope (b), and intercept (c) of standardized major axis line-fitting between time series of the CO_2 storage calculated from the eight-level averaged CO_2 dry molar fraction and that from the 30 min-averaged CO_2 dry molar fraction.

the soil surface) increased by 0.15 from 0.75 for the half-hourly time-step (when half-hourly averages were used for regression) to 0.90 for the daily time-step (when daily averages were used for the regression); this is an estimate of the energy storage in canopy (biomass and air). However, direct estimate of energy storage in canopy for the half-hour time-step is on average only 7% even for 15 tall-canopy (height > 8m) ecosystems (Wilson et al., 2002). We speculated that the half-hour energy storage in the canopy calculated from the half-hour mean temperature and moisture might be substantially underestimated compared with the real values in forest ecosystems.

We further examined the biases in calculated NEEs by taking time averaging for χ_c for calculating F_s (Table 3). We found that the magnitude of NEE was overall underestimated by more than 5% with the 30-min-window-based F_s . The rate of CO_2 uptake was significantly underestimated during the leaf-on daytime, while the rate of CO_2 release was underestimated during the nighttime. We speculate that the widely observed underestimation of the

Table 3
Results of standardized major axis (SMA) line-fitting for the estimates of net ecosystem exchange of CO₂ (NEE) calculated from the 2 min- and 30 min-window-based CO₂ molar mixing ratio from the eight-level profile system, respectively. The NEE is calculated as the sum of eddy flux (F_c) and change in storage term ($F_{s,p}$). The model form is $F_c + F_{s,p,2min} = a + b(F_c + F_{s,p,30min})$. All line-fittings are highly significant ($P < 0.001$); and all slopes and intercepts are highly significant ($P < 0.001$) different from unit and zero, respectively. Sample size (N), determination coefficient (R^2), and 95% confidence interval (CI) are given.

Time period	N	R^2	Slope	95% CI of slope	Intercept	95% CI of intercept
The whole year	18970	0.855	1.071	1.065, 1.077	0.121	0.079, 0.161
Leaf-on daytime	4875	0.854	1.057	1.046, 1.068	−0.209	−0.339, −0.079
Leaf-on nighttime	2763	0.815	1.051	1.034, 1.068	1.058	0.895, 1.221
Leaf-off daytime	5228	0.798	1.057	1.045, 1.070	−0.103	−0.132, −0.074
Leaf-off nighttime	6104	0.700	1.140	1.125, 1.156	0.094	0.065, 0.123

nocturnal ecosystem respiration (Lavigne et al., 1997; Speckman et al., 2015) may be reduced if a short time-window for averaging χ_c was used for calculating F_s , because of the large positive intercept ($1.058 \mu\text{mol m}^{-2} \text{s}^{-1}$) in the leaf-on season and large slope (1.140) in the leaf-off season (Table 3). However, the long-term NEE might be less affected than the gross primary production and ecosystem respiration after flux partitioning (Papale et al., 2006) due to partial offsets of the underestimations of both CO₂ uptake and release.

Performing the time-averaging of χ_c measured by a single profile can reduce the random error in F_s , but may increase the systematic underestimation of its magnitude. So the random error and systematic error in F_s were irreconcilable for a single profile system. The response time of 2 min for the single profile system in present study is one of the fastest systems in the literature (from 60 s to 1800s, Table S1). The systematic bias may be minimized if a single cycle measurement is used to calculate the F_s despite of its potential random error. Adding a buffer volume before IRGA may be a possible way to reduce the random error in χ_c due to the temporal oscillation (Marcolla et al., 2014). However, using a buffer volume is also a low-pass filtering of the CO₂ concentration, which is similar to taking a time averaging. Hence the buffer volume should be carefully balanced between noise-filter and high frequency loss, ideally measuring the spatial averaging instantaneous χ_c . A fast response planar-averaging profile is a possible way to solve this problem. For example, simultaneous sampling from multiple points (“line sampling”) at the same height level can reduce the uncertainty due to spatial (horizontal) variation in χ_c (Marcolla et al., 2014), but this doesn't seem practical in most cases. The novel design of the profile system, e.g., AP200 (Campbell Scientific Inc, USA), uses a buffer volume with a residence time of 2 min and completes a cycle of eight-level sampling within 2 min, which may effectively decrease the stochastic variation due to gust (Campbell Scientific, 2010). Combination of a fast-response line or plane sampling strategy and an appropriate buffer volume to mixing the air may be the direction of new generation of CO₂ profile for F_s measurement. In theory, the F_s measurement doesn't directly require a profile of CO₂ mixing ratio at all. Instead, a profile is used to better represent the spatial mean of CO₂ mixing ratio. Therefore, if F_s is the only concern, it is recommended sampling all levels simultaneously and measuring the mean concentration after mixing in a small buffer volume. Such design can measure the nearly instantaneous CO₂ mixing ratio of the whole profile, but has no information on the vertical gradient of CO₂ mixing ratio. In this case, the vertical configuration of all levels is forced to distribute with equal distance in order to better represent the whole control volume, or at least the vertical direction (c.f. Noormets et al., 2007). And the flow rate must be identical for all levels, which can be controlled with the same length of tubing as the AP100 system.

Theoretically, sampling protocols for F_s measurements should consider the frequency of coherent structure or the integral time scale of scalar concentration. Coherent structure is well-organized ramp-like motion for scalar time series (Gao and Li, 1993). The typical duration of coherent structure above and within forest canopy is between 14–116s by the wavelet analysis (Cava et al., 2004;

Dias Júnior et al., 2013; Gao and Li, 1993; Lu and Fitzjarrald, 1994; Steiner et al., 2011; Thomas and Foken, 2005). However, some studies detected that the duration of coherent structure increased from unstable to stable conditions (Steiner et al., 2011) or varied within a day (Dias Júnior et al., 2013). Other motions such as canopy or gravity waves might significantly contribute to the spectral properties of the scalar time series particularly under stable conditions (Cava et al., 2004; Lee and Barr, 1998; van Gorsel et al., 2011), although they are not as frequent as does the coherent structure. This makes that the frequency of coherent structure can only be used as a rough reference for sampling interval of one cycle of all levels of a profile. According to Finnigan (2006), the integral time scale was an important parameter to determine the bias in F_s . The typical integral time scale of CO₂ density at our site was about 100 s in both leaf-on and leaf-off seasons, thus a 2-min time window might be a reasonable choice to avoid noise in CO₂ concentrations caused by the wave-like motions.

Another sampling problem is the decoupling of canopy/subcanopy layer with the ambient air in clear and calm nights, when the above- and sub-canopy air layers relation can be significantly weakened. Decoupling is commonly characterized with the vertical gradient of the bulk Richardson number (a measure of stability) (Van Gorsel et al., 2009) or with vertical shear of mean wind direction (Alekseychik et al., 2013). The decoupling suppressed the vertical mixing and exchange of mass and energy (Burns et al., 2011; van Gorsel et al., 2011), thus might changed the gradient and time scale of scalar concentration measurements for the F_s calculation. However, the occurrence and depth of decoupling sublayers are highly dependent on the canopy structure and atmospheric stability (Burns et al., 2011; Wang et al., 2015). For forests with sparse understory and clear trunk space, the decoupling sublayer was often constrained within the subcanopy (Heinesch et al., 2007; van Gorsel et al., 2011) and might increase its depth up to the whole canopy at very stable conditions (Alekseychik et al., 2013). For forests with dense canopy, the decoupling regime might be more complex and even extend to the daytime due to the radiative heating/cooling and thermal isolation of the canopy (Froelich and Schmid, 2006; Pypker et al., 2007; Wang et al., 2015). At our site, the above canopy decoupling (wind direction shear between height levels beyond a threshold of 20°) had a probability of 22% in the daytime and 39% in the nighttime, and the below-canopy misalignment occurred with a frequency of more than 70% in both daytime and nocturnal occasions. So it is difficult to design a sampling system according to the variations in depth and timing of decoupling. However, the topography and canopy structure might have general implications for the regime of decoupling (van Gorsel et al., 2011; Wang et al., 2015), which might be helpful for design profile systems for F_s estimates.

5. Conclusions

The CO₂ storage in a tall-canopy forest (F_s) makes significant contributions to NEE estimation in the early morning and nighttime. Vertically, the χ_c and the magnitudes of its time derivative

($\Delta\chi_c/\Delta t$) decreased with the height increasing. So the below-canopy layer contributed disproportionately higher to its height percentage than did the upper layers. The profile configuration should be optimized by balancing the magnitude of $\Delta\chi_c/\Delta t$ and the depth of the layer. Increasing the number of sampling levels in a profiling system generally increased the accuracy in estimating F_s . Four sampling levels or more can be used to measure F_s if they are distributed relatively denser below the dense forest canopy at the Maoershan site. The CO_2 storage based on the tower-top measurement of CO_2 density could be underestimated by up to one third. Additionally, time-averaging of χ_c reduced the random error in F_s , but led to significant underestimation of F_s . The traditional 30-min time window of χ_c resulted in an underestimate of F_s by more than one third, and consequently led to significant underestimates of CO_2 uptake in the daytime and CO_2 release in the nighttime in leaf-on season. To minimize such systematic bias, a cycle of all levels of a fast-response profile system is recommended to calculate the F_s despite of potential random errors. There was a tradeoff between spatial representation and temporal resolution (response time for a whole sampling of all levels) for the existing CO_2 profile systems. Because the random error and the systematic bias in F_s are irreconcilable, it is needed to develop a fast response system to measure the vertical profile of planar mean CO_2 concentration or measure the instantaneous vertical-mean concentration (but not concern the vertical profile itself) to reduce the error of F_s and thus NEE in forest ecosystems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.agrformet.2016.07.020>.

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