Multiple Methods to Partition Evapotranspiration in a Maize Field

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ABSTRACT

Partitioning evapotranspiration (ET) into soil evaporation $E$ and plant transpiration $T$ is important, but it is still a theoretical and technical challenge. The isotopic technique is considered to be an effective method, but it is difficult to quantify the isotopic composition of transpiration $\delta_T$ and evaporation $\delta_E$ directly and continuously; few previous studies determined $\delta_T$ successfully under a non-steady state (NSS). Here, multiple methods were used to partition ET in a maize field and a new flow-through chamber system was refined to provide direct and continuous measurement of $\delta_T$ and $\delta_E$. An eddy covariance and lysimeter (EC-L)-based method and two isotope-based methods [isotope combined with the Craig-Gordon model (Iso-CG) and isotope using chamber measurement (Iso-M)] were applied to partition ET. Results showed the transpiration fraction $F_T$ in Iso-CG was consistent with EC-L at both diurnal and growing season time scales, but $F_T$ calculated by Iso-M was less than Iso-CG and EC-L. The chamber system method presented here to determine $\delta_T$ under NSS and isotope steady state (ISS) was robust, but there could be some deviation in measuring $\delta_E$. The $F_T$ varied from 52% to 91%, with a mean of 78% during the entire growing season, and it was well described by a function of LAI, with a nonlinear relationship of $F_T = 0.71LAI^{0.14}$. The results demonstrated the feasibility of the isotope-based chamber system to partition ET. This technique and its further development may enable field ET partitioning accurately and continuously and improve understanding of water cycling through the soil–plant–atmosphere continuum.

1. Introduction

Evapotranspiration (ET) plays an important role in the soil–plant–atmosphere continuum, as it provides abundant information about water and heat transfer through the continuum (Valipour 2014, 2015; Valipour and Eslamian 2014). ET partitioning is one of the most significant ecohydrological challenges and has important implications not only for water budget but also for understanding feedback between vegetation dynamics and water as well as biogeochemical cycles (Dirmeyer and Brubaker 2007; Newman et al. 2006; Wang et al. 2015). Various methods and techniques have been developed for ET partitioning (Kool et al. 2014; Sutanto et al. 2014). Conventional methods are to combine hydrometric measurements (e.g., sap flow) to estimate transpiration with other methods (e.g., weighing lysimeter measurements) to measure evaporation (Cavagnaro et al. 2011; Kelliher et al. 1992; Mitchell et al. 2009), or to combine the eddy correlation method to measure ET with other methods to estimate soil evaporation $E$ and plant transpiration $T$ using model simulations based on aerodynamic and biophysiological theories (Wei et al. 2015; Zhao et al. 2015). All these partition methods suffer from poor spatial representation, and the spatial density of the measurement is usually limited by instrumentation. Modeling methods are useful for estimating year-to-year variability in response to climate, but they require refinements to be used for field validations (Yepez et al. 2003). A complementary method is using the stable hydrogen and oxygen isotopes ($\delta^{18}O$ and $\deltaD$) of liquid water and water vapor to partition ET (Evaristo et al. 2015; Good et al. 2014; Sutanto et al. 2014; Wang et al. 2014). Isotope-based ET partition methods can help alleviate the above-mentioned limitations and provide insights to hydrological processes (Gat 1996). Isotope-based ET partition approaches have become common since...
it is relatively easy and robust to measure stable isotopes in water (Sutanto et al. 2014), especially with the newer spectroscopy-based techniques (Wang et al. 2009).

Several studies have conducted experiments using an isotopic approach to separate ET (Coenders-Gerrits et al. 2014; Dirmeyer and Brubaker 2007; Dubbert et al. 2014; Rothfuss et al. 2010; Schlaepfer et al. 2014; Schlesinger and Jasechko 2014; Wang et al. 2013; Wang et al. 2016; Wen et al. 2016; Williams et al. 2004; Yepez et al. 2003). For the isotopic composition of evapotranspiration $\delta_{ET}$, it is typically measured using a Keeling plot method. Another method is using the flux-gradient technique with measurements from multiple heights above the canopy (Good et al. 2012; Hu et al. 2014; Lee et al. 2007; Wen et al. 2016). For evaporation isotopic composition $\delta_E$, it has most commonly been assessed using the Craig–Gordon model (Craig and Gordon 1965), as the model has been proven to be a robust tool in determining $\delta_E$ (Braud et al. 2009; Haverd et al. 2011; Horita et al. 2008; Mathieu and Bariac 1996; Soderberg et al. 2012; Wang et al. 2010; Wen et al. 2016; Zhang et al. 2011). However, there are many sensitive parameters in this model (e.g., the kinetic fractionation factor and the isotopic composition of liquid water at the soil evaporating front) that can result in a large uncertainty if those parameters could not be determined accurately (Cappa et al. 2003; Dubbert et al. 2013; Majoube 1971; Wei et al. 2015). For the isotopic composition of transpiration $\delta_T$, it is typically measured using stem or xylem water under the assumption that it is equal to that of root uptake, maintaining a condition referred to as isotopic steady state (ISS; Flanagan and Ehleringer 1991; Zhang et al. 2011; Zhao et al. 2016). However, the ISS is typically only met for short time frames during a day (Lee et al. 2007; Peters and Yakir 2010; Welp et al. 2008) with stable vapor pressure deficit and high transpiration rate (Harwood et al. 1998). The non-steady-state (NSS) conditions induced by changes in humidity and leaf energy balance (Farquhar and Cernusak 2005; Lai et al. 2008) often occur at other times. In addition, the stem/xylem-based $\delta_T$ method is destructive in nature, which makes it difficult to implement continuous measurements. Therefore, it is critical to measure $\delta_T$ and $\delta_E$ directly and continuously, especially for measuring the $\delta_T$ at NSS, and there remains a need for a method to make rapid observations of $\delta_T$ in the field at high precision. If the problem could be solved completely, the scale and accuracy of field ET partition would be further improved. Wang et al. (2012) developed a chamber-based method coupled with a spectroscopy technique to continuously monitor $\delta_T$, but this method has not been widely tested in diverse field conditions, especially under NSS conditions.

In this study, multiple methods were used to partition ET in a maize field. The authors refined and verified a method that provided direct and potentially continuous quantification of the $\delta_T$ and $\delta_E$ using a flow-through dynamic chamber system, which was difficult to achieve in the previous studies. Very few previous studies compared the results of different ET partitioning methods [e.g., isotope-based methods vs eddy covariance (EC)-based methods]. In addition, the NSS conditions were often neglected in previous studies. The method in this study allowed us to have direct access to NSS isotopic compositions of transpiration and evaporation, which would reduce the calculation errors and uncertainties of $\delta_T$ and $\delta_E$ determination. The specific objectives of this study were 1) to refine and verify the flow-through chamber control method of determining $\delta_T$ and $\delta_E$ under NSS; 2) to identify the temporal characteristics of isotopic variation in soil, vegetation, and evapotranspiration over a maize field; and 3) to quantify the contribution of plant transpiration to evapotranspiration $F_T$ at the daily to season scale using multiple methods and evaluate their performance.

2. Materials and methods

a. Study site

The methods were tested in a maize field at Shiyanghe Experimental Station of China Agricultural University, located in Wuwei City, Gansu Province, in northwestern China (37°52’N, 102°51’E; altitude 1581 m). The mean annual sunshine duration is over 3000 h, and long-term mean annual temperature is 8°C. The region is scarce in water resources with a mean annual evaporation of 2000 mm (from a free water surface) and mean annual precipitation of 164 mm. The groundwater table is 30–40 m below the surface. The experimental soil texture is loamy and sandy loam, with field capacity of 0.28 cm$^{-3}$.

b. Field experimental design

Maize was planted with row spacing of 40 cm and plant spacing of 30 cm. The plant density was about 66 000 plants per hectare and the total area was about 39 ha. Crops were sowed on 20 April and harvested on 15 September 2015.

An open-path eddy covariance system was installed in the middle of the maize field. The sensor height was adjusted weekly to keep the relative height of 1.0 m
above the maize canopy. Maize is the principal crop cultivated in the surrounding region, and its planting area is large enough to provide adequate fetch length for eddy covariance measurements. The minimum fetch length is 100 m. The soil temperature was measured at 5 cm depth. The vertical fluctuations of wind, temperature, and water vapor density were measured at 0.1-s intervals, and temperature and humidity at 10-min intervals. The 10-min statistics (average, variance, and covariance) were computed (Li et al. 2013).

Six microlysimeter systems (MLS) were used to measure evaporation in the maize field. They were weighed daily (and hourly in isotope sampling days) to calculate water loss gravimetrically using electronic balances. The MLS had a cylinder shape with a diameter of 10 cm and a height of 20 cm, constructed primarily of polyvinyl chloride (PVC). The containers were sealed by filter paper and gauze, which can ensure the water exchange between the soil inside and outside the container. No measurements were conducted during the irrigation or precipitation events.

Sampling of atmospheric water vapor (ambient atmospheric, evaporation, and transpiration water vapor), soil water, and stem water were conducted from 22 May to 16 August 2015 (sampling times are listed in Table 2, which is described in greater detail below). Water vapor was collected using cold-trap multi-channel equipment (AWVCT04, LICA United Technology, China) in dynamic chamber measurements (Fig. 1) at a flow rate of 500–1500 cm³ min⁻¹, which can collect water at 1.0–1.5 mL h⁻¹ from the vapor. The custom-built chambers followed the design of Pape et al. (2009). The method of this system fundamentally follows the basic gas exchange principles developed by Wang et al. (2012). The chambers were made of acrylic glass with volumes of 40 × 60 × 80 and 40 × 60 × 170 cm³, respectively. Several holes in the supporting acrylic glass frame allow the installation of inlet and outlet ducts as well as of sample tubes and mixing fans. The ambient water vapor was sampled at heights of 1, 2, and 4 m. The soil samples were collected (with a bucket auger) at depths of 0–5 and 5–10 cm, and the corresponding maize stems were collected at 5 cm above soil surface. Soil and stem water samples were extracted using the vacuum extraction system (LI-2000, LICA United Technology, China). All the water samples were stored in airtight containers at 4°C. The stable isotopic compositions (δD and δ¹⁸O) of the water samples were measured by a liquid water isotope analyzer (Picarro L2130i, Picarro, United States). The isotope compositions relative to the Standard Mean Ocean Water (SMOW) were calculated as follows:

\[
\delta^{18}O (or \delta D) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000, \tag{1}
\]

where \(R_{\text{sample}}\) and \(R_{\text{standard}}\) are the \(^{18}\text{O}^{16}\text{O}\) (or D/H) molar ratios of the sample and standard water (SMOW) and the analytical precision was <2.0‰ for δD and <0.1‰ for δ¹⁸O.

In this study, two isotope-based methods were used to partition the ET, and one eddy covariance–based method was used to verify this partitioning (Table 1).

**c. Isotopic quantification methods**

1) **MASS BALANCE EQUATIONS TO PARTITION ET**

By measuring the isotopic compositions of ET, E, and \(T\) and applying a simple two-source mixing model, the proportion of soil evaporation flux \(F_E\) and plant
transpiration flux (i.e., \( F_T \)) can be determined as (Ehleringer et al. 1991)

\[
F_E = \frac{E}{ET} = \frac{\delta_{ET} - \delta_T}{\delta_E - \delta_T} \tag{2}
\]

and

\[
F_T = \frac{T}{ET} = \frac{\delta_{ET} - \delta_E}{\delta_T - \delta_E}. \tag{3}
\]

2) KEELING PLOT APPROACH FOR \( \delta_{ET} \)

The Keeling plot approach is usually applied to estimate \( \delta_{ET} \) (Good et al. 2014, 2012; Keeling 1958). The isotope composition of the water vapor present in the background atmosphere \( \delta_{bg} \), within atmospheric water vapor at the measurement height \( \delta_V \), and that coming from ET sources (i.e., \( \delta_{ET} \)) can be linked by a mass balance equation:

\[
\delta_V = Q_{bg}(\delta_{bg} - \delta_{ET})\left(\frac{1}{Q_V}\right) + \delta_{ET}, \tag{4}
\]

where \( Q_V \) and \( Q_{bg} \) are the water vapor concentration at the measurement height and the background atmosphere, respectively. This Keeling-type relationship is linear with a slope of \( Q_{bg}(\delta_{bg} - \delta_{ET}) \) and an intercept \( \delta_{ET} \) that represents the net isotopic contribution from the ET flux. Two assumptions must be satisfied (Wang et al. 2010; Zhang et al. 2011) here: 1) \( Q_{bg}, \delta_{bg}, \) and \( \delta_{ET} \) are constant over the observation period, which means that the slope of \( Q_{bg}(\delta_{bg} - \delta_{ET}) \) should be constant; and 2) temporal variations in \( \delta_V \) are caused by ET only.

3) THE CRAIG–GORDON MODE FOR \( \delta_E \)

Based on the Craig–Gordon mode (Craig and Gordon 1965), the evaporation vapor isotopic composition (i.e., \( \delta_E \)) is calculated, which accounts for equilibrium and kinetic fractionation during phase change and diffusion of water vapor to the mixed boundary layer near the soil surface:

\[
\delta_E = \delta_L/\alpha - h\delta_V - e^* - (1 - h)e_K/1000, \tag{5}
\]

where \( \delta_L \) is the isotopic composition of liquid water at the soil evaporating front (at 0–5 and 5–10 cm in this study), \( \alpha \) is the temperature-dependent equilibrium fractionation factor from liquid to vapor that was calculated by Eqs. (6) and (7) with soil temperature (Cappa et al. 2003; Majoube 1971), \( e^* = 1000[1 - (1/\alpha)] \), \( \delta_V \) is the isotopic composition of the atmospheric water vapor at the measurement height, and \( h \) is the relative humidity normalized to the temperature of the evaporation front. Variable \( e_K \) is the kinetic fractionation factor defined by Eq. (8) (Cappa et al. 2003; Wei et al. 2015):

\[
\alpha^{(18)O} = \frac{1}{1000}(1.137 \times 10^6/T^2 - 0.4156 \times 10^3/T - 2.0667) + 1, \tag{6}
\]

\[
\alpha(D) = \frac{1}{1000}(24.844 \times 10^6/T^2 - 76.248 \times 10^3/T + 52.612) + 1, \tag{7}
\]

\[
e_K = n(1 - D / D) \times 10^3, \tag{8}
\]

where \( D / D \) is the molecular diffusion coefficients ratio of water vapor in dry air, which is taken as 0.9839 (Cappa et al. 2003), and \( n \) is used to understand the isotopic enrichment of liquid water during evaporation, which is taken as 50.67 (Kim and Lee 2011; Wei et al. 2015).

4) THE UNCERTAINTY OF PARTITION

As \( \delta_{ET} \) was determined by a Keeling plot, \( \delta_E \) was calculated by the Craig–Gordon mode and compared to our dynamic chamber measurements, and \( \delta_T \) was measured by this flow-through chamber system, the contribution of soil evaporation to total evapotranspiration (i.e., \( F_E \)) and plant transpiration to total evapotranspiration (i.e., \( F_T \)) was calculated by Eqs. (2) and (3); here the uncertainty of the partition ( \( d_{F_T} \) and \( d_{F_E} \), respectively) due to the measurement precision and calculation error was calculated, following the method (Phillips and Gregg 2001; Rothfuss et al. 2010).
Fig. 2. Diurnal variations of water vapor isotope compositions. Variable $\delta_{E(CG)}$ is the $\delta_E$ calculated by the Craig-Gordon model, $\delta_{E(M)}$ is the $\delta_E$ measured by our dynamic chamber measurements system, $\delta_T$ is isotope composition of transpiration vapor measured by our chamber system, $\delta_{ET}$ is isotope composition of the ET vapor calculated by the Keeling plot, $\delta_V$ is isotope composition of the atmospheric water vapor at the measurement height, and $\delta_L$ is isotope composition of the soil water (0-10 cm).

\[ d_{F_T} = \sqrt{\sigma_{F_T}^2}, \]
\[ = \sqrt{\frac{1}{\left(\delta_T - \delta_E\right)} \left[\sigma_{\delta_{ET}}^2 + F_T^2\sigma_{\delta_V}^2 + (1 - F_T)^2\sigma_{\delta_E}^2\right]} \quad \text{and} \]
\[ d_{F_E} = \sqrt{\sigma_{F_E}^2}, \]
\[ = \sqrt{\frac{1}{\left(\delta_E - \delta_T\right)} \left[\sigma_{\delta_{ET}}^2 + F_E^2\sigma_{\delta_V}^2 + (1 - F_E)^2\sigma_{\delta_E}^2\right]} \quad \text{(9)}\]

where $\sigma_{\delta_{ET}}$, $\sigma_{\delta_V}$, and $\sigma_{\delta_E}$ represent the standard errors of the mean isotopic composition of ET, $E$, and $T$.

3. Results

a. Isotopic compositions of different water vapor by modeling and measurements

Temporal dynamics of water vapor isotopic compositions at the daily scale were shown in Fig. 2. There were similar and strong diurnal variations in the atmospheric water vapor isotopic compositions (i.e., $\delta_V$) at the measurement heights of 1, 2, and 4 m (Fig. 2a). There was a slight decrease in $\delta_V$ from early morning to midday, and $\delta_V$ increased from midday to late afternoon. Such patterns are mainly driven by the cycles of solar radiation that result in the variation of water vapor concentrations (Wang et al. 2010). The liquid soil water isotopic composition (i.e., $\delta_L$) in shallow soils showed an inverse pattern. It increased from early morning to midday but decreased from midday to late afternoon (Fig. 2b), mainly because the stronger evaporation at noon enriched the $\delta^{18}O$ in shallow soil but depleted the atmospheric water vapor. At the same time, the changes are likely caused by root water transport from deeper to shallower layers (Lu et al. 2016). Similar diurnal variations of maximum midday patterns in $\delta_{ET}$ (Fig. 2b) were due to greater contributions of transpiration fraction at noon (Wang et al. 2010; Wang et al. 2015). The $\delta^{18}O$ in different water vapor presented laminar distribution. That is, the $\delta^{18}O$ followed the order of $\delta_L > \delta_T > \delta_{ET} > \delta_{E(CG)}$, where $\delta_{E(M)}$ is the isotopic composition of evaporation from chamber measurements and $\delta_{E(CG)}$ is the isotopic composition of evaporation from the Craig-Gordon model, but there were no very clear diurnal variations patterns in the $\delta_T$. There was a slight decrease in $\delta_{E(M)}$ and $\delta_{E(CG)}$ from early morning to midday and a slight increase from midday to late afternoon, which was mostly related to the light isotope contribution of evaporation vapor and water movement from deeper to shallower layer, caused by maize roots.

During the whole growing season, significant differences were found in the average values of isotopic compositions for different water vapors (Fig. 3). The $\delta_{E(CG)}$ was less than chamber-based measurements (i.e., $\delta_{E(M)}$). The distributions ranged from $-30.44\%$ to $-18.78\%$ and $-23.66\%$ to $-16.28\%$ for $\delta_{E(CG)}$ and $\delta_{E(M)}$, respectively. The chamber-based $\delta_T$ showed a small variation in the growing season, with the distributions ranging from $-15.25\%$ to $-9.50\%$. Similar isotopic composition ranges were observed in the ET vapor and atmospheric water vapor, ranging from $-18.48\%$ to $-12.66\%$ and $-21.66\%$ to $-13.70\%$, respectively. The shallow liquid soil water isotopic composition (i.e., $\delta_L$) was generally enriched with heavy isotopes, and the distributions ranged from $0.70\%$ to $-9.52\%$.

b. ET partitioning

Diurnal variations of the ET partitioning patterns (i.e., $F_T$) in Fig. 4 showed that the partitioning results
from the isotope using chamber measurement (Iso-M) method were less than the isotope combined with the Craig–Gordon model (Iso-CG) and eddy covariance and lysimeter (EC-L)-based methods. Transpiration accounted for 73%, 85%, and 86% of ET, respectively, using the three methods at the middle [day of year (DOY) 193–204] of the growing season for maize. In the early morning [0700 local time (LT)], $F_T$ was 87%, 88%, and 88% using the three methods, respectively. With the strengthening of solar radiation, both evaporation and transpiration increased, resulting in a decrease in $F_T$ from early morning to midmorning and then an increase until noon. In the late afternoon, $F_T$ was lower, at 59%, 72%, and 73% using the three methods, respectively.

It was clear that the partitioning result in Iso-CG was consistent with EC-L, both in the diurnal variations (Fig. 4) and the whole maize growing season scale (Fig. 5). The $F_T$ varied from 52% to 91%, with a mean of 78% using the Iso-CG method, and from 52% to 93% (with the same period of Iso-CG), with a mean of 78% using the EC-L method. However, the partitioning results of Iso-M were less than Iso-CG and EC-L (Fig. 5), with $F_T$ varying from 21% to 86%, and a mean of 67% at growing season scale. Before DOY 165 and after DOY 215, $F_T$ of Iso-M was much smaller than using the other two methods. We suspect that two factors contribute to this. First, the leaf area index (LAI) was lower during these two periods. Second, the measurement condition was windy during these two periods, which may cause a different turbulent component for the vapor between chamber system and outside. These two factors might result in less shading or stronger warming within the chamber during these two periods, which will cause higher evaporation and higher $\delta_E$ measured by the chamber system. This will result in underestimation of $F_T$. It is suggested that, though our chamber measurement system was applicable in $\delta_T$ measurement, there could be some deviation in measuring $\delta_E$, especially in the early growing season and the late growing season.

4. Discussion

a. Partitioning results by multiple methods

Our results show that evaporation vapor isotopic compositions measured by our chamber system [i.e., $\delta_{E(M)}$] are larger than those measured by the Craig–Gordon model [i.e., $\delta_{E(CG)}$]. The partitioning results (i.e., $F_T$) using the Iso-M method are less than using Iso-CG and EC-L, but results are consistent between methods of Iso-CG and EC-L. These results suggest that our Iso-CG method robustly partitions the ET, but there could be some deviation in the Iso-M method. That is, the $\delta_T$ measured by our dynamic chamber system and $\delta_E$ calculated by the Craig–Gordon model are robust, but there could be some deviation in measuring $\delta_E$ by the dynamic chamber system.

The similar results of larger $\delta_E$ in direct measurement than Craig–Gordon model were also reported by
Braud et al. (2009), who presented a novel controlled experimental setup to measure the isotopic compositions of the bare soil evaporation under NSS conditions. This indicates that whatever the value retained for the kinetic fractionation factor, the calculated evaporation vapor isotopic composition was much lower than the value by direct measurement. It may be because the isotopic composition of evaporation was controlled by the liquid water within very thin soil surface layers, where the dominant liquid water transfer had occurred, or because there was a peak in the isotopic profile (Braud et al. 2009; Haverd et al. 2011). Another possibility is that using averaged values from the upper 0-10 cm of soil for temperature and its isotopic composition $S_{lso}$ also strongly overestimated the amplitude in $\delta E$. This is in agreement with a previous study (Dubbert et al. 2013), suggesting that isotopic composition $\delta^{18}O$ of evaporation is highly sensitive to changes of soil temperature and isotopic composition $\delta^{18}O$ of top soil liquid water. The strongest isotopic enrichment was found at 2-cm soil depth, resulting in the turbulent component for the kinetic fractionation (Dubbert et al. 2013). Besides, the unknown of the resistance between the soil surface and the bulk flow in the chamber may largely influence the results of measuring $\delta E$. That is why the $\delta E(M)$ was larger than the $\delta E(CG)$ in our study.

The transpiration vapor isotopic compositions (i.e., $\delta_T$) measured by our chamber system seem to be a relatively stable parameter (Fig. 3), with the isotopic composition range from $-15.25\%$ to $-9.50\%$. Similar results came from the reports of Wang et al. (2010, 2012), who conducted two direct approaches to determine $\delta_T$: one measures $\delta_T$ within a customized leaf chamber subjected to a 100% di-nitrogen atmosphere, and the other obtains measurements from branches within a standard leaf chamber exposed to ambient air), indicating that the customized chamber method produced a value of $\delta_D = -62.1\%$ ($\delta^{18}O = -9.10\%$), while the other method using a LI-COR leaf chamber produced a value of $\delta_D = -74.1\%$ ($\delta^{18}O = -10.50\%$). Other previous studies (Dubbert et al. 2013; Hu et al. 2014) calculated $\delta_T$ by combining the isotopic composition of leaf water at the evaporating sites with modeling methods and showed that $\delta_T$ was rather negative in the NSS during the morning and increased to values of source water throughout the day. The $\delta_T$ seemed very sensitive and showed a big error in early morning and late afternoon (Hu et al. 2014) mainly because $\delta^{18}O$ in the leaf-water enrichment at the evaporating sites in NSS (Dubbert et al. 2013; Farquhar and Cernusak 2005). Thus, when compared to the modeling and leaf-water-based methods, our direct measurement method by chamber system seemed to be more “steady” in NSS. Besides, in the steady state during the afternoon, the $\delta_T$ measured by our chamber system was consistent with the isotopic compositions of stem water (e.g., $\delta^{18}O = -11.82\%$ at noon of DOY 204). Its applicability is different from the results of $\delta E(M)$ in this study, probably because transpiration vapor produced by maize in the chamber has a relatively large and steady concentration, which is scarcely influenced by ambient air vapor, but not for the $\delta E(M)$ because of insufficient evaporation vapor in the chamber.

b. The uncertainty of partitioning results and comparison with other studies

The uncertainties of partitioning results (i.e., $d_{Fr}$) calculated by Eq. (9) are listed in Table 2 and are within a smaller range (from 1.4% to 14.1%) at both daily scale and growing season scale, indicating that the transpiration fraction estimated by Iso-CG method is feasible. There seems to be a slight increasing pattern of $d_{Fr}$ in the growing season, reaching 14.1% and 10.9% (Table 2) on DOY 215 and DOY 216, respectively, mainly because sampling at night causes larger measurement errors because of the influence of vapor condensation. Rothfuss et al. (2010) showed a larger uncertainty range of 2%-74%, suggesting that using different values of kinetic fractionation factor in the Craig–Gordon model results in a large range of uncertainties, though uncertainties also come from measurement errors. For example, the uncertainty in isotopic compositions of shallow soil water can significantly affect the accuracy (Rothfuss et al. 2010; Wei et al. 2015). For the leaf-water isotope–based method, the uncertainties mainly come from leaf sampling precision as it has large differences in isotopic composition
Table 2. The sampling time period and the uncertainty of the transpiration fraction (i.e., $F_t$; data from Iso-CG method). The $d_{F_t}$ (0%–100%), the uncertainty of partitioning result calculated by Eq. (9), assessment of the measurement precision and calculation error, is affected by the variability of isotopic signatures and sample size and time. The smaller $d_{F_t}$ indicates the smaller error of the partitioning result. The boldface text indicates the high values of the uncertainty.

<table>
<thead>
<tr>
<th>DOY</th>
<th>Sampling time period (LT)</th>
<th>Min $d_{F_t}$ (%)</th>
<th>Avg $d_{F_t}$ (%)</th>
<th>Max $d_{F_t}$ (%)</th>
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<td>215</td>
<td>0100–2300</td>
<td><strong>4.3</strong></td>
<td><strong>7.2</strong></td>
<td><strong>14.1</strong></td>
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<tr>
<td>216</td>
<td>0100–2300</td>
<td><strong>5.2</strong></td>
<td><strong>6.7</strong></td>
<td><strong>10.9</strong></td>
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<tr>
<td>227</td>
<td>0700–2100</td>
<td>3.3</td>
<td>3.9</td>
<td>5.4</td>
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<td>234</td>
<td>1200–1400</td>
<td>2.6</td>
<td>4.8</td>
<td>6.9</td>
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</table>

In different leaf sites, and there is obvious diurnal variation in leaf isotopic compositions (Flanagan and Ehleringer 1991; Wang et al. 2012; Welp et al. 2008). In this study, the uncertainties may mainly come from the microclimate parameters in the chamber system, such as the humidity and temperature. Furthermore, the shallow soil sampling depth and its temperature need to be taken into particular attention.

The relationship of $F_T$ and LAI was established and compared with other studies. It is clear that $F_T$ could be well described by a function of LAI (Fig. 6). Many previous studies have identified this relationship between $F_T$ and LAI (Wang et al. 2010, 2014; Wei et al. 2015). Our results of the Iso-CG method generally agree with Wang et al. (2014), which in the global-scale nonlinear relationship is $F_T = 0.77LAI^{0.10}$, and it is also close to the result of Wei et al. (2015), with the nonlinear relationship of $F_T = 0.67LAI^{0.25}$. The nonlinear relationship of $F_T = 0.91LAI^{0.07}$ in the agricultural system of Wang et al. (2014) deviates from our results, probably because it is the result of a quantile regression that is more like upper envelopes, while our results use the least squares regression. When LAI $> 2$, the $F_T$ estimated by the Iso-CG method is slightly less than in past studies and was mostly related to weather conditions. The strong solar radiation and long sunshine duration (over 3000 h yr$^{-1}$) in northwestern China could cause high soil evaporation in spite of the LAI being relatively large. However, when compared to other studies, our results of Iso-M tend to have a lower proportion of transpiration under the same LAI conditions, particularly for the point (LAI $\approx 3$, $F_T \approx 0.5$) deviating from the curve of $F_T = 0.52LAI^{0.32}$ (Fig. 6). This data point was collected during a windy day. The underestimation of $F_T$ using the Iso-M method is probably because the chamber system cannot measure $\delta_E$ reliably under strong windy conditions. Based on this, it is suggested that our isotope-based method of Iso-CG is applicable in field observations, but the method of Iso-M needs to be further developed. Nevertheless, LAI could be a useful tool to understand the contribution of transpiration vapor to evapotranspiration, even at the global scale (Wang et al. 2014).

In a review of isotope-based studies, Wen et al. (2016) showed that the relative transpiration fraction (i.e., $F_T$) varied from 71% to 96%, with a mean of 87% in the maize growing season. Sutanto et al. (2014) found that the contribution of $T$ to ET was generally more than 70%, and the average $F_T$ reported from Wei et al. (2015) was 80%. In this study, the ET partitioning results of the Iso-CG method are in good agreement with the EC-L method, where $F_T$ varied from 52% to 93% and had a mean of 78% in the maize growing season. In the diurnal variations, $F_T$ varied from 72% to 89% with a mean of 88% (DOY 193–204). In the early morning (0700 LT), $F_T$ was 88%, which is due to low soil temperature resulting in weak evaporation. In the late afternoon, $F_T$ was lower at 72%, possibly because the soil temperature decreased slowly, causing evaporation to decrease slowly, but transpiration rapidly decreased as a result of weak radiation. However, isotope-based methods tend to result in a higher transpiration fraction than other
methods (Jasechko et al. 2013; Sutanto et al. 2014; Wen et al. 2016). Actually, there is no consensus as to which ET partition methods are most accurate, and it is challenging to validate and benchmark the isotope-based methods (Good et al. 2014; Sutanto et al. 2014; Wen et al. 2016). Other ET partition methods, such as the water balance and other model simulation methods, may result in a significant error in the ET partitioning due to the coarse measurements or neglect of the outflow and groundwater recharge in the water balance (Wei et al. 2015). Lysimeter is considered to be a reliable method to measure evaporation and is often combined with the eddy covariance measurements, but it may suffer from poor temporal and spatial representation (Kool et al. 2014; Zhang et al. 2011). Meanwhile, compared to other methods, the isotope-based method has its limitations of scaling up from leaf level to canopy scale. The sources of error in this isotope-based study may come from the variability of isotopic signatures, sample size, sampling time, and weather conditions. Therefore, it is still a great challenge in ET partitioning.

5. Conclusions and perspectives

This paper presented a set of field experiments aimed at providing direct and potentially continuous quantification of the isotopic composition of transpiration $\delta_T$ and evaporation $\delta_E$ to partition the evapotranspiration (ET). This method was targeted toward application in maize fields and based on the isotopic mass balance of water vapor within a flow-through chamber system. It was able to 1) measure the isotopic composition of transpiration and evaporation directly using the chamber system, 2) partition the ET using two isotope-based methods and one eddy covariance–based method, and 3) verify the new method by comparing the partition results with other methods and by establishing relationships between transpiration fraction $F_T$ and the leaf area index (LAI). Results demonstrated the feasibility of our method (Iso-CG) and our chamber system method to determine $\delta_T$ was robust, but there could be some deviation in measuring $\delta_E$. For the partitioning results, the relative transpiration fraction varied from 52% to 91% with an average value of 78% during the maize growing season. The $F_T$ could be well described by a function of LAI, with the nonlinear relationship of $F_T = 0.711 \text{LAI}^{0.14}$. Therefore, LAI could be a useful tool to understand the contribution of transpiration to evapotranspiration in the field.

There are very few direct methods to measure isotopic composition of plant transpiration and soil evaporation. The authors expect that future refinement of methods will allow for accurate and continuous measurement of transpiration and evaporation isotopic composition. For some limitations of determining evaporation isotopic composition, the authors recommend that field experiments pay particular attention to sampling precision at the evaporation front in the surface soil and its temperature.

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