Novel Keeling plot based methods to estimate the isotopic composition of ambient water vapor

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Highlights:
1. Two new methods were developed to estimate the isotopic composition of ambient vapor.
2. Theoretical derivations were provided for these two methods.
3. Linear regression showed strong agreement between the two methods.
4. The methods provide a possibility to calculate the proportion of evapotranspiration fluxes to total atmospheric vapor using the same instrumental setup for the traditional Keeling plot investigations.
Abstract

Keeling plot approach, a general method to identify the isotopic composition of source atmospheric CO$_2$ and water vapor (i.e., evapotranspiration), has been widely used in terrestrial ecosystems. The isotopic composition of ambient water vapor ($\delta_a$), another important source of atmospheric water vapor, is not able to be estimated to date using the Keeling plot approach.

Here we proposed two new methods to estimate $\delta_a$ using the Keeling plot curves: one using intersection point method and another replying on intermediate value theorem. As actual $\delta_a$ value was difficult to measure directly, we used two indirect approaches to validate our new methods. First, we made an external vapor tracking using Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model to facilitate explaining the variation of $\delta_a$. The trajectory vapor origin results were consistent with the expectations of the $\delta_a$ values estimated by these two methods. Second, regression analysis was used to evaluate the relationship between $\delta_a$ values estimated from these two independent methods and they are in strong agreement. This study provides an analytical framework to estimate $\delta_a$ using existing facilities, and provides important insights into the traditional Keeling plot approach by showing: (a) an evidence that $\delta_a$ was constant in a certain moment among different heights, a key assumption of the Keeling plot approach, (b) a possibility to calculate the proportion of evapotranspiration fluxes to total atmospheric vapor using the same instrumental setup for the traditional Keeling plot investigations, and c) perspectives on estimation of isotope composition of ambient CO$_2$ ($\delta_a^{13}$C).

Key words: HYSPLIT, intersection point, Intermediate Value Theorem, Keeling plot
1. Introduction

Stable isotopes of hydrogen and oxygen ($^1$H$_2$O and H$_2^{18}$O) have been widely used in root water uptake source identification (Corneo et al., 2018; Mahindawansha et al., 2018) and evapotranspiration (ET) partitioning (Brunel et al., 1997) in terrestrial ecosystems based on Craig-Gordon model (Craig and Gordon, 1965), isotope mass balance and mechanism of isotopic fractionation (Majoube, 1971; Merlivat and Jouzel, 1979). After laser spectrometers being utilized to perform continuous high frequency (1 Hz) measurements of the isotopic composition of atmospheric water vapor ($\delta$) and atmospheric water vapor content ($C_v$) (Kerstel and Gianfrani, 2008; Wang et al., 2009), new insights into processes that affect $\delta$, and the number of studies based on continuous ground level isotope measurements was continuously increasing (Wang et al., 2010; Galewsky et al., 2011; Steen-Larsen et al., 2013; Sprenger et al., 2015). Such increase in isotope data abundance allows an isotope-enabled global circulation models (Iso-GCMs) to estimate the variation of vapor isotope parameters at a global scale (Unger et al., 2010).

Keeling plot approach (Keeling, 1958), based on isotope mass balance and two-source assumption, was first used to explain carbon isotope ratios of atmosphere CO$_2$ and to identify the sources that contribute to increases in atmospheric CO$_2$ concentration. It has been further used to estimate isotopic composition of ET ($\delta_{ET}$) in recent two decades (Yakir and Sternberg, 2000). Keeling plot analyses can be applied using $\delta$, and $C_v$ output by laser based analyzer either from different heights (Yepez et al., 2003; Zhang et al., 2011; Good et al., 2012) or at one height with continuous observations (Wei et al., 2015; Keppler et al., 2016). Although the intercept of the curve was commonly used, the slope of the Keeling plot was also used to...
estimate $\delta_{ET}$ by re-arranging the Keeling plot equations (Miller and Tans, 2003; Fiorella et al., 2018). Keeling plot approach was based on bulk water and isotope mass balance using two equations with three unknowns. As a result, the isotopic composition of other potential sources (e.g., water vapor not from ET), as well as isotopic composition of ambient water vapor ($\delta_a$), were not able to be estimated directly using the Keeling plot approach.

In this study, we proposed two new methods to estimate $\delta_a$, one based on the intersection of two Keeling plots of two continuous observation moments and another based on intermediate value theorem. Proposition and proof were provided, and the new methods were tested using field observations. As direct observations of $\delta_a$ rarely exist (Griffis et al., 2016), we tested our methods by (a) making an external water vapor tracking investigation according to HYSPLIT model to explain the variation of estimated $\delta_a$, and (b) making a regression analysis using $\delta_a$ estimated by these two independent methods.

2. Materials and Methods

2.1 Theory

The atmospheric vapor concentration in an ecosystem reflects the combination of ambient vapor that is already exist in the atmosphere and the vapor that is added through evaporation (E) and transpiration (T) (Yakir and Sternberg, 2000). Keeling plot approach is based on the combination of a bulk water mass balance equation and an isotope mass balance equation:

$$C_v = C_a + C_{ET},$$

$$C_v\delta_v = C_a\delta_a + C_{ET}\delta_{ET},$$

where $\delta_a$, $\delta_{ET}$ and $\delta_v$ are isotope composition of ambient water vapor, ET, and atmospheric water.
vapor, respectively, and \( C_a, \) \( C_{ET} \) and \( C_v \) are the corresponding concentrations of water vapor.

Note that all quantities here are time dependent, and \( \delta_a \) and \( C_v \) also depend on heights.

Combining Eq. (1) and Eq. (2), we have the following traditional linear Keeling plot relationship between \( \delta_v \) and \( 1/C_v \) with intercept \( \delta_{ET} \) and slope \( C_a(\delta_a - \delta_{ET}) \),

\[
\delta_v = C_a(\delta_a - \delta_{ET})/C_v + \delta_{ET}
\]  

(3)

For a given time, with various measurements of \( \delta_v \) and \( C_v \) collected at different heights, we are able to estimate the intercept \( \delta_{ET} \) and slope \( C_a(\delta_a - \delta_{ET}) \) for this moment from regression analysis (Zhang et al., 2011; Wang et al., 2013). Here we focus on the estimation of \( \delta_a \) using two new methods proposed below.

**Intersection point method.** Note that for two nearby time points \( t_1 \) and \( t_2 \), we could use local constant approximation to estimate \( \delta_a \) within this time interval since it is changing smoothly over time. By assuming local constant for \( C_a \) and \( \delta_a \) within this time interval, we have

\[
\delta_{v_1} = C_a(\delta_a - \delta_{ET_1})/C_{v_1} + \delta_{ET_1}
\]

(4)

\[
\delta_{v_2} = C_a(\delta_a - \delta_{ET_2})/C_{v_2} + \delta_{ET_2}
\]

(5)

where \( \delta_{ET_1}, \delta_{v_1} \) and \( C_{v_1} \) represent the value at \( t \) for \( i=1, 2 \). From (4) and (5), we can solve \( \delta_a \) as:

\[
\delta_a = \frac{C_{v_1}\delta_{ET_2}(\delta_{ET_2}-\delta_{v_2})-C_{v_2}\delta_{ET_1}(\delta_{ET_1}-\delta_{v_1})}{C_{v_1}(\delta_{ET_2}-\delta_{v_2})-C_{v_2}(\delta_{ET_1}-\delta_{v_1})}
\]

(6)

The local constant approximation idea was first described in Yamanaka and Shimizu (2007) as an assumption to quantify the contribution of local ET to total atmospheric vapor.

**Intermediate Value Theorem (IVT) method.** Denote the slope as \( k = C_a(\delta_a - \delta_{ET}) \).

Since \( C_a < C_v = C_a + C_{ET} \), we have \( C_a = \frac{k}{\delta_a - \delta_{ET}} < C_v \). We can rearrange \( \frac{k}{\delta_a - \delta_{ET}} < C_v \) to attain \( \delta_a < \frac{k}{C_v} + \delta_{ET} = \delta_v \) when \( k < 0 \), and \( \delta_a > \frac{k}{C_v} + \delta_{ET} = \delta_v \) when \( k > 0 \).
For the smooth function \( \delta_a(t) \) defined on the interval \([t_1, t_2]\) with the two time points satisfying \( k(t_1) k(t_2) < 0 \), depending on the sign of the slopes \( k(t_1) \) and \( k(t_2) \) and the order of \( \delta_{v_1} = \delta'(t_1) \) and \( \delta_{v_2} = \delta'(t_2) \) at the two time points \( t_1 \) and \( t_2 \), it will correspond to one of the six cases in Fig. 1. For all of the six situations, by the intermediate value theorem, there exists a sub-interval \([t_1', t_2'] \subset [t_1, t_2]\) such that the whole range of \( \{ \delta_a(t) : t \in [t_1', t_2'] \} \) is within \([\min(\delta_{v_1}, \delta_{v_2}), \max(\delta_{v_1}, \delta_{v_2})]\). Thus for the two nearby time points \( t_1 \) and \( t_2 \) with \( k_1 \) and \( k_2 \) having different sign, \( \delta_a \) will be between \( \delta_{v_1} \) and \( \delta_{v_2} \). This is the key observation to estimate the parameter of interest \( \delta_a \) based on Intermediate Value Theorem, which leads to approximation of \( \delta_a \) within the time interval between \( t_1 \) and \( t_2 \) using \( \delta_{v_1} \) and \( \delta_{v_2} \):

\[
\delta_a \approx \frac{\delta_{v_1} + \delta_{v_2}}{2} \quad (7)
\]

Using this method, we are able to compute \( \delta_a \) using data points when the slopes of Keeling plots change sign between two adjacent time points.

2.2 Field observations

2.2.1 Study site

A field measurement was conducted over a maize field (39 ha) from 1st May 2017 to 1st September 2017 at Shiyanghe Experimental Station of China Agricultural University, located in Wuwei of Gansu Province, northwest China (37°85′N, 102°88′E; altitude 1581m). The region belongs to temperate continental climate and is in the oasis within the Shiyang river basin. The annual mean temperature of the study area is about 8.8°C with pan evaporation of 2000 mm, annual precipitation of 164.4 mm, mean sunshine duration of 3000 h, and frost-free period of more than 150 d. The local crops are irrigated using groundwater with electrical conductivity of 0.62 dSm⁻¹. The groundwater table is 30-40 m below the surface. Maize was
sowed on 23 April and harvested on 15 September 2017, with row spacing of 40 cm and plant spacing of 23 cm. The maize growing stage was divided into seedling stage (April 21st–May 20th), jointing stage (May 21st–July 10th), heading period (July 11th–July 31st), pustulation period (August 1st–August 31st) and mature period (September 1st–September 20th).

2.2.2 Instrument setup and measurement design

A 24-meter flux tower, located in the middle of maize field, was used to measure ET flux and isotopic composition of water vapor at different heights. The field is approximately 600 m long and 240 m wide, with a 10% slope decreasing from southwest to northeast. Five gas traps were installed on the flux tower at heights of 4 m, 8 m, 12 m, 16 m and 20 m, respectively. An iron pillar was placed 20 m away from the flux tower. Three gas traps were installed on the iron pillar, one was close to the canopy, and the other two were 2 m and 3 m above the ground. Canopy gas trap was adjusted weekly according to the height of maize.

In situ δv and Cv collected by the eight gas traps were monitored by an isotope and gas concentration analyzer (L2130-i, Picarro Inc., Sunnyvale, CA, USA), which was a wavelength scanned cavity ring down spectrocope (WS-CRDS) instrument. Vapor specifications include a measurement range from 1000 to 50000 ppm, the precision is 0.040‰ to 0.25‰ for δ18O (Zhao et al., 2019). Interfacing with the gas trap and the isotope analyzer, Teflon tube was wrapped by thermal insulation cotton to avoid vapor condensation during transmission. The measurement of δv and Cv on 19th May, 11th June, 20th July, and 12th August were selected to test the theoretical framework because they fit the criteria requirements of the IP method and IVT method: 1) a complete and continuous 24-hour dataset and 2) opposite Keeling plots slope occurrence at least once in a day. These four days corresponded to seedling stage, jointing stage,
heading stage, and pustulation stage, respectively, through the maize growth period.

2.2.3 Calibration of $\delta_v$ and $C_v$

The water vapor from eight inlets were sampled continuously over a 24-hour-period. Since only one analyzer was used to measure the $\delta_v$ and $C_v$, the values of eight sampling inlets were recorded in turn every 225s in a 30 mins cycle. The switch procedure was automatic. As the analyzer makes a measurement every 0.9-1s, approximately 259-264 values for each inlet was recorded within the cycle. For each 225s measurement period, No. 195 to No. 253 data points were used to avoid memory issue and influence of transient pressure variation. The mean value of the selected data points was regarded as the measured $\delta_v$ and $C_v$ in a specific inlet. Measured $C_v$ was used directly as actual $C_v$, while measured $\delta_v$ was calibrated to minimize the influence of isotopic concentration dependence. The $C_v$ in our measurement ranged from 5386 ppm to 30255 ppm. Thus, $C_v$ gradients of 10000 ppm, 20000 ppm and 30000 ppm were selected as calibration concentrations to improve the precision of $\delta_v$.

2.3 Explanations of $\delta_a$ using backward trajectories

To explain the variations of estimated $\delta_a$, air mass backward trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1997; Draxler, 2003; Stein et al., 2015; Kaseke et al., 2018) and meteorological data from the Global Data Assimilation System 0.5 Degree (GDAS0p5) with 0.5°×0.5° spatial resolution and 3-hour time resolution for the selected four days. Five hundred meters height was selected in the modeling. Each backward trajectory was initialized from the station (37°85′N, 102°88′E) at 12:00 pm (local time), and calculated backward for 72 hours. Four trajectories were computed.
3. Results

3.1 Diurnal variations of $\delta_{ET}$, $\delta_v$, $k$ and ambient vapor source in four typical days during the maize growing period

The parameters of the Keeling plot curve in four typical days were shown in Fig. 2. The average $\delta_{ET}$ were $-15.23\%$, $-10.20\%$, $-8.20\%$ and $-10.59\%$, respectively in the four typical days. At daytime (7:00am-7:00pm), average $\delta_{ET}$ were $-11.75\%$, $-8.42\%$, $-5.76\%$ and $-9.00\%$, respectively, while at nighttime (7:00pm-7:00am the next day), average $\delta_{ET}$ were $-18.76\%$, $-11.98\%$, $-10.63\%$ and $-12.18\%$, respectively. The trend of $\delta_v$ values were similar to $\delta_{ET}$, but with a smaller fluctuation than $\delta_{ET}$. About 65% of $k$ values were negative during the four days, and most positive $k$ values occurred at nighttime (82%). The 500 m height water vapor backward trajectories revealed that vapor was from outside the study regions on 19th May and 20th July while vapor was from local ET on 11th June and 12th August (Fig. 3).

3.2 Diurnal variations of $\delta_a$ using two methods during the maize growing period

Data screening was needed on the calculation of $\delta_a$. When $\delta_a$ was not satisfied with the relationship of $\delta_{ET}<\delta_v<\delta_a$ or $\delta_{ET}>\delta_v>\delta_a$, these $\delta_a$ values were in contradiction with Eq. (1) and were not used. As a result, 88 and 26 of $\delta_a$ values were attained based on IP method and IVT method, respectively during the four days (Fig. 2).

As for the IP method, 46.8% of $\delta_a$ values were acceptable, and 59.1% of acceptable $\delta_a$ values were during the daytime (7:00am-7:00pm). The average $\delta_a$ values were $-12.95\%$, $-12.13\%$, $-14.39\%$ and $-12.77\%$ for the four days, respectively. Smaller values occurred on 19th May ($-12.95\%$) and 20th July ($-14.39\%$) than those on 11th June ($-12.13\%$) and 12th August ($-12.77\%$). The average $\delta_a$ values in all four days were $-13.60\%$ and $-12.04\%$ during the
daytime and the nighttime, respectively.

As for the IVT method, only 13.8% of δ_a values were acceptable, and 34.6% of acceptable δ_a values were during the daytime (7:00am-7:00pm). The average δ_a values were -13.93%, -11.03%, -14.76% and -11.83% for the four days, respectively. Smaller values occurred on 19th May (-13.93%) and 20th July (-14.67%) than those on 11th June (-11.03%) and 12th August (-11.83%). The average δ_a values in all four days were -12.84% and -12.86% during the daytime and the nighttime, respectively.

Fourteen observation periods overlapped for δ_a calculation using both methods, which accounted for 15.9% of δ_a values using IP method (δ_a(IP)) and 53.8% of δ_a values using IVT method (δ_a(IVT)). Linear regression between δ_a(IP) and δ_a(IVT) was significant for these fourteen observation periods with slope close to one (Fig. 4. δ_a(IP) = 0.95δ_a(IVT) - 0.75, R² = 0.98, p<0.01, n=14).

4. Discussion

4.1 The reliability of δ_a estimating methods

The IP method was based on the assumption that the ambient sources were the same between two continuous observation moments. This is a reasonable assumption for short time intervals. For the IVT method, δ_a was derived from δ_v in two continuous moments when their Keeling plot slopes were opposite. The opposite slopes of the Keeling plots were the only requirement. As δ_v was almost constant in two continuously moments, δ_a(IVT) was able to be constrained into a small range. The derivation was supported by the intermediate value theorem. Therefore, both methods of estimating δ_a were theoretically sound.

The δ_a results were also examined by HYSPLIT backward trajectories to identify the
different sources of water vapor, which assesses the reliability of both methods indirectly. Based on the trajectory analysis, water vapor in the study area came from westerlies, northern polar region and local recirculation. Water vapor from southwest monsoon and northwest Pacific were not detected in this study. Based on the isotope variation of meteoric water (Fricke et al., 1999), water vapor from westerlies and northern polar was more $^{18}$O depleted than local recycled moisture through ET. It was also reported that the water vapor from outside the study regions will lower $\delta_v$ values (Ma et al., 2014; Chen et al., 2015). Backward trajectory revealed the local origin of water vapor on 11th June and 12th August. The calculated $\delta_v$ values on 11th June and 12th August based on the IP method and interval intermediate value theorem approach was higher than those in other two days, which was consistent with our expectation. The results indicate that quantifying $\delta_v$ using the IP method and intermediate value theorem approach was reliable. The reliability of two methods were also supported by the close relationship of $\delta_v$ using these two independent methods.

4.2 The application of $\delta_v$ for moisture recycling

When $\delta_v$ was estimated, moisture recycling (e.g., $f_{ET}$, the contribution of ET fluxes to the total water vapor) can be estimated using the following equations with known $\delta_v$, $\delta_{ET}$, $\delta_v$, $C_{ET}$ and $C_v$:

$$C_{ET} = C_v \cdot \frac{\delta_v - \delta_v}{\delta_v - \delta_{ET}}$$

(8)

$$f_{ET} = \frac{C_{ET}}{C_v}$$

(9)

According to Eq. (8) and Eq. (9), $f_{ET}$ was only related to $\delta_v$, $\delta_v$, and $\delta_{ET}$. These three parameters were obtained for relatively small temporal and spatial scales in this study, making it possible to estimate $f_{ET}$ at a tower scale. The $f_{ET}$ estimate will provide a baseline value for
rainfall recycling ratio calculations. Previous studies quantified the contribution of recycled vapor to annual or monthly precipitation in river basins using two-element mixture model (Kong et al., 2013) and three-element mixture (Peng et al., 2011). At the watershed scale, recycled vapor rate refers to the contributions of moisture from terrestrial ET to annual or monthly precipitation (Trenberth, 1999). It is a key part of local water cycle and the atmospheric water vapor balance (Seneviratne et al., 2006; Aemisegger et al., 2014). In our study, the role of \( f_{ET} \) to regional vapor is similar to the role of recycled vapor rate to annual or monthly precipitation, but \( f_{ET} \) was calculated with fine temporal (e.g., hourly) and spatial (i.e., field scale) scales. At the watershed scale, assumption was made that no isotopic fractionation between transpiration and source water (Flanagan et al., 1991); advected vapor was assumed to be the precipitation vapor of the upwind station (Peng et al., 2011). However, the isotope composition of transpiration is variable in a day especially under non-steady-state conditions (Farquhar and Cernusak, 2005; Lai et al., 2008). In addition, sometimes it is difficult to select an upwind station without precipitation events. In this study, a field site was selected to calculate the proportion of ET fluxes to total atmospheric vapor and \( f_{ET} \) was only related to \( \delta_a, \delta_v, \) and \( \delta_{ET} \) according to Eq. (8) and Eq. (9). This indicates that \( f_{ET} \) calculations is possible for small temporal and spatial scales after estimating \( \delta_a \) using the methods we proposed.

4.3 Implications of \( \delta_a \)

The signature of \( \delta_E \) and \( \delta_T \) was first introduced by a hypothetical graph shown on Fig. 5a (Moreira et al., 1997). Line 1 and line 2 was idealized Keeling plot with pure T and pure E, and Line 3 was the Keeling plot with mixed T and E. The IVT method in this study provided a general explanation of this figure. As T is a major component of ET in the daytime in non-arid
region, the slope is generally negative. When E dominates ET in an ecosystem, such as in the nighttime in non-arid region or in arid region, the slope should be positive. Mathematically, negative slope is due to $\delta_{ET} < \delta_a$ and positive slope is due to $\delta_{ET} > \delta_a$. It also reflected that IVT method could only be used in non-arid ecosystems. Yamanaka and Shimizu (2007) used the assumption that $\delta_a$ of an area of 219.9 km$^2$ was represented by the intersection point of two Keeling plot lines in different sites with synchronous measurements and they used the intersection value as an approximate value of $\delta_a$. This study was conducted in a maize field using 30-min interval measurements, the results indicate that accurate $\delta_{a(IP)}$ could be estimated from the intersection of two Keeling plots regardless the slope being positive or negative, while the $\delta_{a(IVT)}$ should be restricted in the area between two dotted lines as shown in Fig. 5b (i.e., between the minimum value of $\delta_a$ in positive slope and the maximum value of $\delta_a$ in negative slope).

While this study is about water vapor $^{18}$O, the “Keeling plot” was first used by Keeling (1958, 1961) to interpret carbon isotope ratios of mixed CO$_2$ and to identify the sources that contribute to increases in atmospheric CO$_2$ concentrations on a regional basis. Compared with ET in water vapor which is consisted of E and T, net ecosystem CO$_2$ exchange (NEE) is comprised of soil respiration (R) and gross primary productivity (GPP). As $^{13}$CO$_2$ isotopic Keeling plot reveals a positive slope during both daytime and nighttime (Yakir and Wang, 1996; Unger et al., 2010), the IVT method may not be able to estimate ambient $^{13}$CO$_2$ isotopic composition ($\delta_a$) since there are no opposite slopes in a day. In such case, the IP method may be implemented in two continuous moments to estimate $\delta_a$ and may consequently further calculate the contribution of NEE to atmospheric CO$_2$. 
5. Conclusions

In this study, we established two methods to quantify $\delta_a$ using intersection point method and the Intermediate Value Theorem method. The IVT method was used under the condition of opposite slope of Keeling plots in two continuously moments. The results of estimated $\delta_{a(IP)}$ and $\delta_{a(IVT)}$ were consistent with the expectation whether it was local origin or regional origin using external vapor tracking investigation by HYSPLIT model. The linear regression between $\delta_{a(IP)}$ and $\delta_{a(IVT)}$ was highly ($R^2=0.98$, $p < 0.01$) significant.

This study provided insights into the traditional Keeling plot and provided two methods to estimate $\delta_a$ using the same instrumental setup for the traditional Keeling plot investigations. The results shown an evidence that $\delta_a$ was constant in a certain moment among different heights, a key assumption of Keeling plot approach. The estimated $\delta_a$ will make it possible to calculate the ET contribution to regional vapor at a 30 min interval at field scale. The results indicate that using similar framework, $\delta_{a^{13}C}$ is also solvable by the IP method.

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7. Code and Data availability
8. Author contribution

YY, TD and LW conceptualized the main research questions. YY collected data and performed the data analyses. YY and LW wrote the first draft. HW contributed to additional data analyses. All the authors contributed ideas and edited the manuscript.

9. Competing interests

There authors declare no competing interests.

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Fig. 1 Theoretical diagrams of all possible combinations of the relationships between isotope composition of ambient vapor ($\delta_a$) and observed isotope composition of atmospheric vapor ($\delta_v$) of two continuous moments $t_1$ and $t_2$ ($t_1 < t_2$). $\delta_{a1}$ and $\delta_{a2}$ represent $\delta_a$ value in $t_1$ and $t_2$, respectively. $\delta_{v1}$ and $\delta_{v2}$ represent $\delta_v$ value in $t_1$ and $t_2$, respectively. $t_1'$ and $t_2'$ represent the time of two specific moments between $t_1$ and $t_2$ with $t_1 < t_1' < t_2' < t_2$. For all of the six situations, there exists some sub-intervals $[t_{1}', t_{2}'] \subset [t_{1}, t_{2}]$ such that the whole range of $\{\delta_{a}(t): t \in [t_{1}', t_{2}']\}$ is within $[\min(\delta_{v1}, \delta_{v2}), \max(\delta_{v1}, \delta_{v2})]$. 
Fig. 2 The average values of the isotope composition of evapotranspiration vapor ($\delta_{\text{ET}}$), the isotope composition of atmospheric vapor ($\delta_v$), the estimated isotope composition of ambient vapor using the intersection point method ($\delta_{\text{a(IP)}}$) and the Intermediate Value Theorem method ($\delta_{\text{a(IVT)}}$) in daytime (7:00 am-7:00 pm) and nighttime (7:00 pm-7:00 am), respectively on May 19th, June 11th, July 20th, and August 12th.
Fig. 3 Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) backward Trajectory on 19th May (a), 11th June (b), 20th July (c) and 12th August 2019 (d), respectively, which were initialized at 12:00 pm and were calculated backward for 72 hours.
Fig. 4 Linear regression between the estimated isotope composition of ambient vapor using the intersection point method ($\delta_a$(IP)) and the Intermediate Value Theorem method ($\delta_a$(IVT)) for all the observation periods meeting the criteria of each method.

\[ \delta_a(IIP) = 0.948 \delta_a(IVT) - 0.748 \]

\[ R^2 = 0.978 \]
Fig. 5 Hypothetical graph of the idealized Keeling plot curve of the isotope composition of evaporation vapor ($\delta_E$) curve (line 1), the isotope composition of transpiration vapor ($\delta_T$) curve (line 2) and the isotope composition of evapotranspiration vapor ($\delta_{ET}$) curve (area 3) (a), and hypothetical graph of idealized $\delta_E$, $\delta_T$ lines and the interval of possible the isotope composition of ambient vapor ($\delta_a$) in the Keeling plots (b).