

\[ \delta^{2}H \] isotopic flux partitioning of evapotranspiration over a grass field following a water pulse and subsequent dry down

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Abstract The partitioning of surface vapor flux \( (F_{ET}) \) into evaporation \( (F_{E}) \) and transpiration \( (F_{T}) \) is theoretically possible because of distinct differences in end-member stable isotope composition. In this study, we combine high-frequency laser spectroscopy with eddy covariance techniques to critically evaluate isotope flux partitioning of \( F_{ET} \) over a grass field during a 15 day experiment. Following the application of a 30 mm water pulse, green grass coverage at the study site increased from 0 to 10% of ground surface area after 6 days and then began to senesce. Using isotope flux partitioning, transpiration increased as a fraction of total vapor flux from 0% to 40% during the green-up phase, after which this ratio decreased while exhibiting hysteresis with respect to green grass coverage. Daily daytime leaf-level gas exchange measurements compare well with daily isotope flux partitioning averages (RMSE = 0.0018 g m\(^{-2}\) s\(^{-1}\)). Overall the average ratio of \( F_{T} \) to \( F_{ET} \) was 29%, where uncertainties in Keeling plot intercepts and transpiration composition resulted in an average of uncertainty of \( \sim 5\% \) in our isotopic partitioning of \( F_{ET} \). Flux-variance similarity partitioning was partially consistent with the isotope-based approach, with divergence occurring after rainfall and when the grass was stressed. Over the average diurnal cycle, local meteorological conditions, particularly net radiation and relative humidity, are shown to control partitioning. At longer time scales, green leaf area and available soil water control \( F_{E}/F_{ET} \). Finally, we demonstrate the feasibility of combining isotope flux partitioning and flux-variance similarity theory to estimate water use efficiency at the landscape scale.

1. Introduction

Knowledge of ecosystem controls on hydrologic cycling is needed to understand both leaf and field-scale biophysical processes [Rodriguez-Iturbe et al., 1999; Caylor et al., 2006; Wang et al., 2010] as well as mesoscale water resource and climate dynamics [Lawrence et al., 2007]. A diverse set of measurement networks such as FluxNet and National Ecological Observatory Network (NEON) are directed at estimating field-scale bulk evapotranspiration flux, \( F_{ET} \), across various ecosystems [Baldocchi et al., 2001; Keller et al., 2008]. However, the partitioning of surface fluxes into constituent components of evaporation \( (F_{E}) \) and transpiration \( (F_{T}) \) remains predominately model driven in practice [Stoy et al., 2006; Aubinet et al., 2012]. Theoretical approaches such as those of Shuttleworth and Wallace [1985] are able to model \( F_{ET} \) and its components \( F_{E} \) and \( F_{T} \), yet they require detailed knowledge of soil and leaf conductances, parameters that are difficult to measure both accurately and continuously during long studies [Stannard, 1993]. The development of methods to accurately partition \( F_{ET} \) thus remains a focus of contemporary hydrologic research.

Measurement of plant water use at the scale of individual leaves or plants is readily accomplished through leaf-level gas exchange [Huxman et al., 2004] and sap flux techniques [Williams et al., 2004; Raz-Yaseef et al., 2012]. Similarly, microlysimeters and high-precision soil moisture monitoring equipment provide measurements of evaporation from bare soils at small scales [Raz-Yaseef et al., 2010; Zhang et al., 2011]. A number of hydrologic studies have been directed at partitioning \( F_{ET} \) utilizing combinations of point measurements of \( F_{E} \) and/or \( F_{T} \) with landscape measurements of \( F_{ET} \) [Williams et al., 2004; Raz-Yaseef et al., 2010, 2012]. Combinations of point and other direct mass loss measurements [Wang et al., 2010] have demonstrated the ability to partition fluxes, however, many experimental artifacts are introduced though these observation
strategies. The exclusion of roots from lysimeters alters soil water dynamics and may not provide a representative evaporate flux, while plant chamber methods influence biophysical process. The problems of scaling individual point measurements to the landscape scale remains a challenge due to heterogeneity in the spatial configuration of plant canopies, diversity in species composition, and differences in biophysical processes within landscapes. Furthermore, the equipment necessary to continuously monitor ecosystems with point-scale measurements presents serious logistical challenges such as uninterrupted sample collection or maintenance of multiple instruments, and often only a small subset of the community can be monitored.

Current research issues require evapotranspiration partitioning methods operating with continuous observations from field-deployed instrumentation. The instruments, in turn, require calibration, and the overall methods require independent validation because standard methods are still being established. Moran et al. [2009] proposed a method to partition $F_{ET}$ based on surface temperature measurements. This semiempirical method requires long time series of temperature and flux measurements to estimate a daily flux partition. Scanlon and Sahu [2008] and Scanlon and Kustas [2010] have proposed utilizing flux-variance similarity theory to partition fluxes. This method has the ability to partition both carbon dioxide and water vapor fluxes continuously based on high-frequency observations typical of eddy covariance systems by making use of correlations between water vapor and carbon dioxide concentrations. Flux-variance similarity partitioning, however, requires the a priori estimation of the ecosystem water use efficiency, a parameter difficult to assess beyond the leaf scale, particularly in heterogeneous environments.

Differences in the stable isotope composition of transpiration, $\delta_T$ [see methods for isotope terminology and units], and evaporation, $\delta_E$, provide the opportunity to partition $F_{ET}$ at the landscape scale. Yakir and Sternberg [2000] theorized that the end-member difference (i.e., $\delta_T - \delta_E$), in combination with the observation of the bulk flux composition, $\delta_{ET}$, can be used for isotope flux partitioning. Studies by Wang and Yakir [2000] and Williams et al. [2004] employed cold traps to sample vapor isotope profiles over wheat and olive canopy to estimate isotope flux partitioning. Yepez et al. [2003, 2005] utilized a combination of cold trapped vapor profiles and chamber methods at a study site in the semiarid southwestern United States to separate $F_T$ and $F_E$. A highly controlled vegetation chamber with all exhaust gasses trapped and analyzed was used by Rothfuss et al. [2010] for isotope flux partitioning. Most recently, Zhang et al. [2011] partitioned $F_{ET}$ over a wheat field and estimated the depth of water uptake in the root zone. All the above studies utilized methods to capture and store vapor, then analyzed the collected liquid through traditional laboratory techniques. This collection and analysis step has limited the temporal resolution of past isotope flux partitioning studies to relatively long sampling intervals.

The development of stable isotope laser spectroscopy allows for continuous monitoring of flux isotopic composition at spatial and temporal scales relevant to landscape-scale processes [Lee et al., 2005, 2006, 2007; Griffis et al., 2010, 2011; Sturm et al., 2012; Good et al., 2012]. Welp et al. [2008] used high-frequency measurements of $\delta_{ET}$ above a canopy to assess leaf water enrichment over a soybean field with the assumption of no evaporation. Isotope flux partitioning at the field scale (e.g., 100s of m$^2$) has been successfully employed by Wang et al. [2010] in the controlled environment of Biosphere 2 with potted plants in different configurations. Haaverd et al. [2011] assimilated high-frequency isotope measurements through a Bayesian framework to estimate the added information isotope flux partitioning provides to a soil-vegetation-atmosphere transfer modeling scheme. In a tall forest canopy where 85% of $F_{ET}$ was derived from transpiration, Haaverd et al. [2011] concluded that isotope observations did not improve partitioning estimates. However, in arid and semiarid regions, evaporation is a substantial component of the hydrologic budget, and isotopic differences between $F_T$ and $F_E$ may provide valuable information about environmental processes.

Thus, further demonstration and application of isotope flux partitioning is required before adoption by the larger flux community.

In this paper, we present the results of a field campaign directed at continuous observation of the isotopic composition of evapotranspiration with the objective of partitioning $F_{ET}$ across a variety of vegetation conditions in African grassland during the dry season. A high-frequency (1 Hz) laser-based isotope analyzer intake tube was colocated with eddy covariance equipment over a homogenous $C_4$ grass field, which was watered with a total of 30 mm applied over 3 days. We made measurements over a 2 week dry-down period, and demonstrate here that isotope flux partitioning can capture shifts in transpiration and evaporation fluxes. We compared our partitioning estimates to scaled leaf-level measurements of transpiration as well as flux-variance similarity partitioning. The hydrologic drivers of evapotranspiration partitioning were
investigated over both the diurnal cycle and the entire 2 week experiment. Finally, we combined isotope flux partitioning with flux-variance similarity theory and used the isotope-based partitioning results to estimate landscape water use efficiency.

2. Methodology

The stable isotopic composition of water is expressed in δ notation, \( \delta = (R/R_{VSMOW} - 1) \), where \( R \) is the ratio of rare to abundant isotopes (i.e., \(^2\)H and \(^1\)H respectively) and \( R_{VSMOW} \) refers to the same ratio in Vienna Standard Mean Ocean Water (VSMOW) [De Laeter et al., 2003]. The δ values are reported in per mil \( [\%] \) notation, which is equivalent to \( 1 \times 10^3 \) [Coplen, 2011]. We applied a 30 mm water pulse in a desiccated perennial grass field (Figure 1) and utilized isotope flux partitioning to understand the mechanisms controlling \( F_T \) and \( F_E \) following grass green-up and subsequent leaf senescence.

2.1. Isotope Flux Partitioning Theory

Isotope flux partitioning is directed at determining the amount of transpiration flux, \( F_T \) \([\text{g m}^{-2} \text{s}^{-1}]\), in the bulk evapotranspiration flux, \( F_{ET} \) \([\text{g m}^{-2} \text{s}^{-1}]\). The ratio of these fluxes, \( f_{T/ET} \), is found via measurement of the composition of water molecules derived from fluxes with distinct isotopic signatures. \( f_{T/ET} \) is calculated as

\[
f_{T/ET} = \frac{F_T}{F_{ET}} = \frac{\delta_{ET}}{\delta_T} - \frac{\delta_E}{\delta_T} \tag{1}
\]

where \( \delta_{ET} [\%] \) is the isotopic composition of the bulk evapotranspiration, \( \delta_E [\%] \) is the isotopic composition of evaporated water, and \( \delta_T [\%] \) is the isotopic composition of transpired water. The linear mixing model in (1) has been utilized in previous studies to partition water vapor fluxes [Yakir and Sternberg, 2000; Williams et al., 2004; Yepez et al., 2005; Wang et al., 2010].

![Figure 1](image_url). Experimental setup during the field campaign, with an eddy covariance system positioned in the center of the wetted area. The intake tube of an off-axis integrated cavity output spectrometer (DLT-100 Los Gatos Research Inc., Mountain View, CA) was colocated with the eddy covariance system at 40 cm above a 5 cm sparse grass canopy. Leaf-level gas exchange measurements were also made with hand-held equipment (Li-6400XT, LI-COR Biosciences, Lincoln, NE, USA) throughout the field campaign. Prevailing winds were predominantly from the North-East.
The isotopic composition of the $F_{ET}$ is determined through the use of a Keeling mixing model [Keeling, 1958; Yakir and Sternberg, 2000; Yepez et al., 2005; Good et al., 2012]. Assuming that background vapor concentration ($q_B$) and composition ($\delta_B$) are constant over short time periods (e.g., 30 min), the instantaneous isotopic composition in the air above a surface, $\delta_A [\%]$ is given by

$$\delta_A = (\delta_B - \delta_{ET}) \frac{q_B}{q_A} + \delta_{ET},$$

(2)

which is a linear mixing between isotopic end-members $\delta_B$ and $\delta_{ET}$. Utilizing equation (2), a regression between $\delta_A$ and the reciprocal of its vapor concentration, $q_A$ [g m$^{-3}$], produces in a line whose $y$ intercept is equal to the surface flux composition $\delta_{ET}$. Further analysis of this linear relationship allows for a simple assessment of the uncertainties of surface flux composition estimates [Pataki et al., 2003; Zobitz et al., 2006; Good et al., 2012].

The value of $\delta_{ET}$ is measured through direct observation with a simple leaf chamber following Wang et al. [2012]. A transparent leaf chamber, placed around leaf samples, captures transpired water that is then drawn into a water vapor isotope analyzer. Assuming background vapor composition and concentrations are constant during a leaf-sampling event (~3 min) allows for the unmixing of ambient water vapor and leaf transpiration compositions [Haverd et al., 2011; Wang et al., 2012]. The value of $\delta_T$ is then calculated as

$$\delta_T = \frac{q_m\delta_M - q_A\delta_A}{q_M - q_A},$$

(3)

where $q_m$ [g m$^{-3}$] and $\delta_M$ [\%] are the water vapor concentration and isotopic composition measured when the chamber is clamped on a leaf [Wang et al., 2012].

The isotopic composition of soil evaporation is estimated using the Craig and Gordon [1965] model in conjunction with measurements of the soil liquid water isotopic composition, $\delta_S [\%]$. The Craig-Gordon (CG) model estimates the combined effect of equilibrium and kinetic fractionation during the phase change of water from liquid to vapor. Atmospheric relative humidity, $h_a$, soil temperature, $T_S$ [°C], as well as the gradient between $\delta_S$ and the vapor in equilibrium with $\delta_S$ in the soil, determine the composition of soil evaporation [Gat, 1996; Honta et al., 2008]. Further adjustments to the CG model are made following Soderberg et al. [2012], accounting for the effect of soil moisture, $\theta_S$ [m$^3$ m$^{-3}$], on soil relative humidity, $h_a$ and soil vapor transport via the kinetic fractionation factor $\epsilon_a$. The value of $\delta_T$ is calculated as

$$\delta_T = \frac{(x_a h_s \delta_S - h_s' \delta_A) - (h_s \delta_s + \epsilon_s)}{(h_s - h_s') + \epsilon_s}.$$

(4)

where the equilibrium vapor-liquid fractionation factor $x_a = (1 - \epsilon_a)$ is calculated as a function of $T_S$ following Majoube [1971]. Note that atmospheric relative humidity is renormalized to the surface temperature, $h_s' = h_s e_A' / e_s'$, with $e_A'$ representing the saturated vapor pressure [kPa] in the atmosphere and $e_s'$ representing the saturated vapor pressure at the soil surface. Because of the extremely dry conditions at the study site, soil vapor saturation is not assumed and instead the relative humidity within the soil is adjusted as function of the soil water potential via the Kelvin equation, $h_s = \exp (M \psi_s / RT_S)$ [Mathieu and Bariac, 1996; Soderberg et al., 2012]. Finally, the kinetic effect is incorporated as

$$\epsilon_a = n (h_s - h_s') \left[ 1 - \left( \frac{D_s}{D} \right) \right],$$

(5)

where the ratio of molecular diffusion coefficients of water vapor in dry air $D/D$ is taken as 0.9757 from Merlivat [1978]. The aerodynamic diffusion parameter, $n$ varies from 1/2 when the soil is saturated ($\theta_S = \theta_{sat}$), to 1 when the is soil dried to residual moisture levels ($\theta_S = \theta_{res}$), as [Mathieu and Bariac, 1996; Soderberg et al., 2012]

$$n = 1 - \frac{1}{2} \left( \frac{\theta_S - \theta_{res}}{\theta_{sat} - \theta_{res}} \right).$$

(6)
2.2. Experimental Setup

The objective of this field experiment was to characterize $f_{T/ET}$ over the green-up and senescence of a typical dry land grass patch in response to a large pulse of soil moisture. The field observations were conducted from 7th to 21st February 2011, in the middle of the dry season (December through March) at the Mpala Research Center in central Kenya (0.3229°N, 36.9028°E). A grass field devoid of green leaf area which had not received rainfall for 49 days, and only 12 mm in the previous 3 months, was selected and is shown in Figure 1. A circular region with a radius of 13 m (area = 530 m²) was then watered for 3 days using water with a $\delta^2$H of 4.25‰ (average precipitation $\delta^2$H for this region is $-7.6$‰ [Soderberg et al., 2013]). For each of these 3 days, a volume of water equivalent to a 10 mm rainfall event was applied by hand with watering cans, resulting in ~16,000 L applied uniformly within the treatment. The field received additional rainfall of 6.7 mm ($\delta^2$H of rain water was 9.44‰) in the predawn period 8 days after the first watering as shown in Figure 2. Watering began on the 8th of February 2011, and throughout this article this date is referred to as day 0, with all other dates expressed relative to the first day of watering. No data were collected on day 9 due to equipment and logistical problems.

The grass patch consisted of sparse cover of a C4 herbaceous layer dominated by species from the Cynodon genus. Two 26 m line transects [Floyd and Anderson, 1987] were surveyed by counting the millimeters of green leaf contacting a tape-measure edge on days 5–13 to quantify green leaf fractional coverage ($P_c$), with no green leaf area observed before or during watering. Leaf area index (LAI) is estimated based on the relationship between plant canopy gap frequencies and LAI, where LAI = $-\ln (1 - P_c) / G(0)$ [Nilson, 1971], with $G(0)$ the projection of unit foliage area on the plane perpendicular to the view direction. Because all green leaf area consisted of new leaf blades spreading on the ground from nodes in grass stolons, the leaf angle distribution is treated as horizontal in this very low sparse canopy, i.e., $G(0) \approx 1$. The time series of the grass green-up and die-off is shown in Figure 2.

A set of two $\approx 10 \times 10 \times 30$ cm soil columns were extracted and used to determine soil texture and root distribution. Of the collected dry root biomass, 87% was found to occur in the upper 20 cm of soil. Each of these 3 days, a volume of water equivalent to a 10 mm rainfall event was applied by hand with watering cans, resulting in ~16,000 L applied uniformly within the treatment. The field received additional rainfall of 6.7 mm ($\delta^2$H of rain water was 9.44‰) in the predawn period 8 days after the first watering as shown in Figure 2. Watering began on the 8th of February 2011, and throughout this article this date is referred to as day 0, with all other dates expressed relative to the first day of watering. No data were collected on day 9 due to equipment and logistical problems.

Subsamples of the extracted soils were analyzed for water potential, $\psi_s$ [MPa], using a potentiometer (WP4-T, Decagon Devices, Pullman WA). A Campbell [1974] type power law $\psi_s = \psi_{sat} / (1 - b \phi)$ was developed for the red sandy loam soils at the study site, with $\psi_{sat} = 3.1 \times 10^{-2}$ MPa and $b = 3.1$ based on 41 aggregated samples ($r^2 = 0.83$). The time series of average volumetric water content in the upper 20 cm of soil is provided in Figure 2.

From 1 day preceding, the first wetting event (day $-1$) through 2 weeks afterward (day 13) an eddy covariance system was
mounted at 40 cm on a tripod in the center of the circular region. The eddy covariance setup consisted of a three-dimensional sonic anemometer (CSAT-3, Campbell Scientific, Logan UT) and an infrared gas analyzer (Li-7500, LiCor Biosciences, Lincoln NB). Water vapor and carbon dioxide concentrations as well as vertical, streamwise, and crosswind component wind speeds were measured at 10 Hz. Net radiation (NR-LITE, Campbell Scientific, Logan UT), relative humidity (HMP45C, Campbell Scientific, Logan UT), and air temperature (HMP45C, Campbell Scientific, Logan UT) were also measured at 1.2 m. Postprocessing of the high-frequency data involved removal of data spikes larger than 4× the standard deviation of the time series. Coordinate rotation was applied such that mean vertical and crosswind velocities are zero. Standard corrections were applied to the 10 Hz open path flux estimates to account for the dynamic response of sensors, 30 min block averaging, lateral sensor separation, vector and scalar path averaging, and digital filtering [Moore, 1986; Lee et al., 2004]. Density corrections (Webb-Pearman-Leuning (WPL)) were applied to the water vapor and carbon dioxide fluxes [Lee et al., 2004]. Average correction factors for the sensible heat flux, latent heat flux, and CO2 flux were 1.58 ± 0.13, 1.19 ± 0.22, and 1.19 ± 0.22, respectively.

2.3. Isotope Measurements

Isotope measurements were conducted utilizing an off-axis integrated cavity output spectroscopy system (ICOS; DLT-100 Los Gatos Research Inc., LGR Mountain View, Calif.). Air was drawn into the ICOS system via Teflon tubing (14 m long, 1/4” outer diameter) with its intake colocated with the CSAT-3 and Li-7500 at a flow rate of ~ 500 mL min⁻¹. Calibration of the ICOS system was performed before, during, and after the 2 week experiment with a liquid water nebulizer (Water Vapor Isotopic Standard Source (WVISS), Los Gatos Research, Inc., manufactured in 2009). All standard waters measured on this instrument within a year of the field campaign have a standard deviation of 2.1‰ for δ²H and 0.78‰ for δ¹⁸O (n = 203; with Los Gatos Research Working Standards 1, 3, and 5). Raw values for analyses of a single working standard (LGR-WSS, δ²H = −9.8‰) performed before and during the experiment (2, 13, 15, and 17 February) had a standard deviation of 1.8‰ (n = 4), comparable to the long-term standard deviation with this standard of 1.9‰ (n = 89). Intensive calibrations were also performed on this instrument (26 August 2011 to 13 September 2011) using three standards covering a range of 188‰ for δ²H. On eight separate days during this period, multiple calibrations were conducted (average n = 8 standards ran per day), with single-day calibration standard deviations ranging from 0.5‰ to 3.3‰, with a mean of 1.9‰ across all δ²H standards. Raw values for each standard had standard deviations of 1.4‰ (n = 16), 1.3‰ (n = 17), and 1.3‰ (n = 18). No trends were observed in the measured values relative to standard composition, and instrument drift is assumed minor and treated as random instrumental noise adding uncertainty in δ₂H values. The effect of this uncertainty on the overall 𝐸𝑇 partitioning is explored in section 3.2.

The dependency of ICOS measurements on water vapor mixing ratios for Los Gatos Research systems has been show to be instrument specific [Sturm and Knohl, 2010; Rambo et al., 2011], and has been previously reported to be negligible for this particular instrument (ICOS2 of Good et al. [2012]). The linear relationship between either δ²H or δ¹⁸O and mixing ratios in this ICOS was determined by Good et al. [2012] to have 𝑟² values of 0.00 and 0.03, respectively. (n = 36 over a range of 20,000 ppmv). However, given the possibility of bias at very low mixing ratios all individual ambient vapor measurements below 5000 ppmv were removed from analysis (less than the 0.6% of all data). The correlation between δ¹⁸O or δ²H and cavity temperature has also been found to be minor, with 𝑟² values of 0.09 and 0.13, respectively (n = 149 over a temperature range of 0.5°C). The optical cell is maintained at a temperature of 49°C and a pressure of 52 hPa; additionally, the case in which the instrument rests is fan cooled. All 30 min blocks during which the optical cell had conditions farther than ±0.5°C away from the operating temperature or ±0.1 hPa away from the operating pressure were removed from the analysis. Details of the ICOS system optical cell and function are presented in Boer et al. [2002].

The ICOS system was utilized to estimate the isotopic composition of the aggregated evapotranspiration flux, δET. The value of δET was found though a Keeling mixing model (equation (2)) for each half-hour flux averaging block (138 half-hour blocks). The ICOS system reports isotopic composition and water vapor concentration measurements at 1 Hz. In each 30 min block, ~1800 pairs of δA and qA data points were used to assess δET. Uncertainty assessments following Good et al. [2012] were performed on each 30 min estimate of δET, where σA ≈ σA/√(N), with σA the standard deviation of differences between individual δA measurements and each Keeling mixing line, C, the coefficient of variability for qA in each 30 min block, and N the number of data points in each 30 min block. If measurement errors in δA are the only source of error in
the Keeling plot then \( \sigma_{\delta_0} \) should approach the previously assessed instrument uncertainty (2.1‰ for this ICOS system). Throughout the course of this experiment, values of \( \sigma_{\delta_0} \) ranged from 1.3‰ to 8.9‰ with an average value of 2.8‰. Any increase in \( \sigma_{\delta_0} \) values beyond that of the measurement uncertainty is attributed to unwanted footprint contributions, source water variability, and any other unknowns. Those periods where \( \delta_{\text{ET}} \) was greater than 10‰ or operational conditions were not met were not removed (94 blocks remain). Periods where \( \delta_{\text{ET}} \) fell below \( \delta_2 \) by more than 2 times the calculated \( \delta_{\text{ET}} \) uncertainty and periods where \( \delta_{\text{ET}} \) fell above \( \delta_1 \) by more than 2 times the calculated \( \delta_{\text{ET}} \) uncertainty were also removed (78 remain). Half-hour periods where \( \delta_{\text{ET}} \) was beyond the end-member value but within acceptable error (2 \( \times \delta_{\text{ET}} \)) were set as fully transpiring or fully evaporating. Estimates of \( \delta_{\text{ET}} \) for each day and associated standard deviations are shown in Figure 3.

Estimates of the isotopic composition of transpired water (\( \delta_1 \)) were obtained by direct measurements with the ICOS system [Wang et al., 2012]. Four times each day between 10:00 AM and 5:00 PM the ICOS system was connected to a custom leaf chamber (part no. 6400-05, LI-COR Biosciences, Lincoln, NE, USA) which was placed around a small clump of green leaves. After the isotopic composition and vapor concentrations stabilized, a 100 s sampling period was used to determine values of \( q_{\text{M}} \) and \( \delta_{\text{M}} \) for equation (3). Ambient values of water vapor concentration (\( q_A \)) and isotopic composition (\( \delta_A \)) were obtained by letting the chamber sit open for 90 s adjacent to the sampling point immediately before clamping the chamber onto a leaf. Measurements during which chamber concentrations did not stabilize were not used, nor were measurements with vapor concentration spikes after the leaf removal, indicating condensation (12.5% of leaf measurements). Small clumps (area \( \leq 4 \text{ cm}^2 \)) of grass were dug up, separated into aboveground and belowground parts, sealed in glass Vacutainer vials, and frozen until distillation. Water within the plant...

<table>
<thead>
<tr>
<th>Time after 1st water pulse [Days]</th>
<th>Isotopic composition, ( \delta^2\text{H} ) [%]</th>
</tr>
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<tbody>
<tr>
<td>-1 0 1 2 3 4 5 6 7 8 9 10 11 12 13</td>
<td>Irrigated water ( \delta^2\text{H}=4.25 )</td>
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<tr>
<td></td>
<td>Additional rain water ( \delta^2\text{H}=9.44 )</td>
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<tr>
<th>( \delta_{\text{ET}} ) (Keeling Plot)</th>
<th>( \delta_2 ) (Craig Gordon)</th>
<th>( \delta_3 ) (Chamber Measurements)</th>
<th>( \delta_4 ) (Distillations)</th>
</tr>
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<tbody>
<tr>
<td>( F_{\text{c}} ) Isotope flux partitioning</td>
<td>( F_{\text{a}} ) Isotope flux partitioning</td>
<td>( F_{\text{L}} ) Leaf-level measurements</td>
<td>( F_{\text{f}} ) Flux-variance similarity partitioning</td>
</tr>
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**Figure 3.** Isotopic composition of bulk evapotranspiration flux, \( \delta_{\text{ET}} \) (red squares), evaporation flux, \( \delta_2 \) (blue triangles), transpiration flux, \( \delta_3 \) (inverted green triangles), and soil water composition, \( \delta_4 \) (filled circles), are used to partition evapotranspiration into \( F_{\text{c}} \) and \( F_{\text{a}} \) between 10:00 AM and 5:00 PM. The value of \( \delta_{\text{ET}} \) relative to \( \delta_2 \) and \( \delta_3 \) determines the transpiration and evaporation fluxes (bar graph). Error bars depict the standard deviation for \( \delta_{\text{ET}}, \delta_2, \delta_3, \) and partitioned fluxes. Estimates of \( F_{\text{c}} \) obtained from scaled leaf-level observations (white crosses) and flux-variance similarity partitioning (smaller red circles) are also shown.
material was extracted via vacuum distillation on a glass line following West et al. [2006]. The distilled water was then analyzed using the WVISS and ICOS system. Due to the possibility of contamination of the ICOS measurements from the water obtained through distillation of organic material [West et al., 2010; Schultz et al., 2011], only the direct measurements of $\delta_T$ with the chamber method were utilized. Trends were not observed in the four measurements of $\delta_T$ collected each day and therefore these values were averaged to obtain a daily $\delta_T$ value (average daily standard error of $\delta_T = 5.9^{\circ}/_{\mu}$1), which was applied to all 30 min blocks for that day. Estimates of $\delta_T$ from chamber measurements are shown in Figure 3.

Estimates of the isotopic composition of soil evaporation $\delta_E$ were obtained through the Craig and Gordon [1965] model given in equation (4). A portion of the soils extracted for water content analysis were vacuum distilled in the same manner as the plant material. Organic contamination of extracted soil water is not significant [West et al., 2010], and soil $\delta_E$ values were utilized in equation (4) to estimate $\delta_E$. Values of $\delta_E$ and $\psi_S$ were assumed constant each day and a different $\delta_E$ was calculated for each 30 min block based on changes in atmospheric conditions ($v_{aw}$, $h_a$, $T_a$) and soil temperature (see equations (4)–(6) and Appendix A). Average daily soil liquid isotope composition from samples collected from depths of 1–20 cm and the estimated evaporation composition are shown in Figure 3. On days when soil water isotope composition was not measured, this value was linearly interpolated.

### 2.4. Leaf-Level Observations and Flux-Variance Similarity Theory

Direct measurements of leaf-level gas exchange were taken on days 3–8 and 10–13 using a chamber-based hand-held photosynthesis system (Li-6400XT, LI-COR Biosciences, Lincoln, NE, USA). Estimates of leaf transpiration $F_{\text{leaf}}$ [g m$^{-2}$ s$^{-1}$], leaf net photosynthesis, $F_p$ [g m$^{-2}$ s$^{-1}$], and estimates of the intercellular to atmospheric $\text{CO}_2$ concentration, $c/c_a$, where obtained from measurements of three to five leaves with the Li-6400XT system at approximately hourly intervals between 10 AM and 5 PM local time, resulting in a total of 484 measurements of each variable over the entire period. Transpiration rates per unit leaf area were measured by using of LAI based on the transect surveys to estimate transpiration values per square meter within the watered area.

Following the approach of Netzel et al. [2008], we scaled $F_{\text{leaf}}$ by percent of flux arriving at our eddy covariance system originating from within the watered area ($p_r$, see section 2.5) to determine the transpiration flux equivalent to that estimated with the isotopic approach. In this approach, we assumed $F_{ET}$ beyond the watered area is equal to fluxes measured before irrigation. Thus, $F_T = p_r F_{\text{leaf}}/LAI + (1 - p_r) F_{ET}/F_{ET}/F_{ET}/F_{ET}/F_{ET}/F_{ET}$, with the transpired fraction in the nonirrigated area $F_{ET}/F_{ET}$ set as both 0 and 1 to give approximate bounds. Because most flux originates from within the watered area, the difference between assuming all flux from beyond the irrigated area is due to transpiration versus evaporation is minor at 0.0016 g m$^{-2}$ s$^{-1}$, and we present the average value (i.e., $F_{ET}/F_{ET}$ $= 0.5$).

Flux-variance similarity theory [Scanlon and Sahu, 2008; Scanlon and Kustas, 2010] was also used to obtain another estimate of $F_T$ and $F_{ET}$. This approach has previously been used to partition fluxes over wheat [Scanlon and Sahu, 2008], a C3 crop, and over corn [Scanlon and Kustas, 2010, 2012], which is a C4 crop. Similarity theory is based on the assumption that the transfer efficiencies of stomatal scalars are greater than those of nonstomatal scalars. From this assumption and the work of Katul et al. [1995] and Bink and Meesters [1997], the correlation between evaporated water and transpired water is approximated by the ratio of the transfer efficiencies of the evaporation flux to that of the transpiration flux. A similar assumption is made with respect to photosynthesis, $F_p$, and respiration, $F_R$, giving

$$
\rho_{q_T, q_S} \approx \rho_{w,q_T} / \rho_{w,q_S} \quad \text{and} \quad \rho_{c_T, c_S} \approx \rho_{w,c_T} / \rho_{w,c_S},
$$

where $\rho$ is the correlation coefficient, and subscript $q$ refers to water vapor, $c$ refers to carbon dioxide, and $w$ refers to vertical wind speed. The above assumptions imply that transpiration and photosynthesis are perfectly anticorrelated ($\rho_{q_T, c_S} = -1$), evaporation and respiration are perfectly correlated ($\rho_{q_T, c_S} = 1$), and the correlation between evaporation and transpiration is the negative of the correlation between photosynthesis and respiration ($\rho_{q_T, q_S} = -\rho_{c_T, c_S}$).

Combining these statements leads to a system of equations in which the fluxes ($F_T$, $F_E$, $F_P$, and $F_R$), standard deviations of the scalar concentrations from each source ($\sigma_{q_T}, \sigma_{q_S}, \sigma_{c_T}, \text{ and } \sigma_{c_S}$), and the correlations
between flux-derived scalars ($\rho_q$, $q_0$, and $\rho_{c_h}$) are 10 unknowns. Ten equations ($WUE = F_P/F_T$, and equations (5a), (5b), (8a), (10a), (10b), (11c), (12a), (12b), (18) of Scanlon and Sahu [2008]) are then solved simultaneously to estimate the partitioning of water vapor flux and carbon dioxide flux. A key input to the flux-variance similarity partitioning method is the water use efficiency, $WUE$ [mg CO$_2$ g$^{-1}$ H$_2$O], of the vegetation. Water use efficiency is the ratio of carbon assimilation to water lost to transpiration ($WUE = F_P/F_T$) and is important indicator of biophysical functionality [Bacon, 2004]. $WUE$ is modeled-based gradients between interstomatal and leaf surface concentrations of carbon dioxide and water vapor [Campbell and Norman, 1998]. Leaf surface concentrations are estimated based on stability corrected logarithmic concentration profiles. Following Scanlon and Sahu [2008], interstomatal water vapor is assumed saturated at the measured air temperature and interstomatal carbon dioxide is estimated based on an average ratio of internal to ambient CO$_2$. This value, $c_i/c_A = 0.21$, was obtained directly from the Li-6400 leaf-level measurements and is slightly lower the typical reported values of $0.3–0.4$ [Jones, 1992; Bunce, 2005], though values less then this have been reported under stressed conditions.

2.5. Footprint Considerations and Experimental Artifacts

Our experimental framework is aimed at providing a detailed analysis of the ecohydrologic processes occurring in a natural savanna during different stages of growth. Conducting this experiment at an open field at the Mpala Research Centre ensures realistic conditions found in an actual dry land, but also brings extreme difficulties in work environment. Because of the possibility of equipment damage from wildlife, the eddy covariance system operated during daytime hours only (~10:00 AM to 5:00 PM local time) and was removed from the field at night. The site location is within a very dry region with a mean annual precipitation of ~600 mm, and the irrigation water was trucked in from a nearby river, thus limiting the extent to which we could irrigate the experimental setting. Due to the limited size of the watered region, turbulent eddies carrying dry air from beyond the experiment were also sampled at the eddy covariance tripod location. Furthermore, the irrigation of a small patch within a very arid region may lead to oasis conditions wherein the turbulent regime above the watered area differs from that beyond the irrigated extent. Finally, because of power and other logistical difficulties, air was only sampled at a single height, and only a temporal Keeling plot approach, as opposed to the more reliable multheight flux-gradient technique [Wang and Yakir, 2000; Griffis et al., 2004, 2005; Santos et al., 2012], is available for estimation of source isotopic composition.

Given the heightened possibility of experimental artifacts being introduced by our manipulation and the large footprint associated with concentration measurements needed for Keeling plot analysis, a Lagrangian stochastic dispersions model [Wilson and Sawford, 1996; Thomson, 1987] is employed to determine the distribution of locations for water vapor molecules that have left the surface and arrived at our collector. The Lagrangian stochastic dispersion model, fully described in Appendix B, tracks the position and velocity of a large collection of fluid elements through a Markov process and permits footprint modeling in complex environments. Lagrangian stochastic models are the most powerful tool available for investigating atmospheric transport [Wilson and Sawford, 1996] and are particularly suited to complex environments with inhomogeneities where higher-order analytical models are known to fail [Thomson, 1987]. As employed here, the Lagrangian stochastic dispersion model allows for incorporation of differential surface fluxes and turbulence regimes within and beyond the watered area. Simulations were run for each 30 min block separately, given the surface sensible heat flux ($F_H$, [W m$^{-2}$]), latent heat flux ($C_{F_E}$ [W m$^{-2}$]), and friction velocity ($u_*$ [m s$^{-1}$]) within and beyond the irrigated area. Conditions beyond the irrigated area were based on the diurnal cycle observed before the irrigation was applied.

The Lagrangian stochastic dispersion model demonstrates that the large majority of evapotranspired source vapor and fluxes arriving at our collector location originated within the irrigated area (Figure 4). After watering, an average of 76% of the vapor arriving at our collector originated from within the irrigated area, and an average of 81% of the evapotranspiration flux at our collector originated within the watered area. The particle fraction from within the irrigated area is positively correlated with $F_{ET}$ ($\rho = 0.83$) and atmospheric stability $z/L$ ($\rho = 0.50$), and negatively correlated with $F_H$ ($\rho = -0.60$). Wind speed demonstrated little correlation with source origin ($\rho = 0.06$) and wind direction varied little during the experiment (standard deviation of average wind direction was 17°). When the same model is run with uniform conditions, only 40% of vapor and 57% of the flux originated within the irrigated area. Our collector (the LGR ICOS system) measured a mixture of background and irrigated source vapor, with a small percentage of nonirrigated
water also measured. The source composition identified with Keeling plot analysis for each time block therefore includes the minor influence of water vapor of unknown composition from beyond the irrigated area. The additional source water will add variance to the \( \delta_A \) values measured, degrade the \( \delta_v^{-1}/\delta_A \) regression, and add uncertainty to the final intercept \( \delta_{ET} \) estimate. Therefore, careful estimation of uncertainty bounds is required which includes the influence of the interrelated distributions of \( \delta_A \) and \( \delta_{ET} \).

### 3. Results

Estimates of \( f_{ET} \) were obtained from isotope flux partitioning for 10 days and are shown in Figure 3. Before the watering treatment, \( F_{ET} \) was 0.006 g m\(^{-2}\) s\(^{-1}\) (\( \sim 0.5 \) mm d\(^{-1}\)). Subsequent to the watering, \( F_{ET} \) increased rapidly and peaked on the last day of watering at 0.070 g m\(^{-2}\) s\(^{-1}\) (6 mm d\(^{-1}\)). Green leaf area first appeared on day 3, but \( F_T \) continued to dominate the surface flux, with \( f_{ET} \) equal to 16%. Figure 5 depicts the timeline of isotope flux partitioning results from day 3 to day 13. After day 3, \( F_E \) decreased while \( F_T \) increased steadily, with \( f_{ET} \) rising to 40% on day 6. At day 8, when the 6.7 mm event occurred, both \( F_T \) and \( F_E \) peaked, and afterward began to decline.

#### 3.1. Partitioning Intercomparison

Transpiration estimated from isotope flux partitioning compares well with scaled leaf-level measurements, with best agreement obtained from daily average values (Figure 5). Half-hour \( F_T \) results give a root mean square error of 0.0056 g m\(^{-2}\) s\(^{-1}\) between leaf level and isotope flux partitioning methods, with a regression slope of 0.22 and an intercept of 0.006 g m\(^{-2}\) s\(^{-1}\). Analysis of partitioning results averaged to a daily estimate of \( F_T \) (Figure 6) give a root mean square error of 0.0018 g m\(^{-2}\) s\(^{-1}\), with a regression slope of 0.40 and an intercept of 0.004 g m\(^{-2}\) s\(^{-1}\) (\( r^2 = 0.64 \)). These low regression slopes may result from the temporal patterns of \( F_T/ET \), with more evaporation occurring during periods when \( \delta_{ET} \) is more accurately measured.

Flux-variance similarity partitioning results are partially consistent with the isotope flux partitioning results, yet show divergence on days 8, 12, and 13 (Figure 5). On days 0 and 1 (shown in Figure 3), the flux-variance method estimates nonzero transpiration although no green leaf area had yet appeared. On day 8, the flux-variance method estimates a sharp drop in \( f_{ET} \), resulting in a large increase in \( F_E \) and a decrease in \( F_T \). Isotope flux partitioning and leaf-level estimates suggest an increase in both \( F_T \) and \( F_E \) on day 8, with the flux-variance estimate indicating an increase in \( F_T \) but a decrease in \( F_E \). On days 12 and 13, a period when green leaf area began to senesce and soil moisture was limited, the flux-variance similarity partitioning estimated a higher amount of transpiration than isotope flux partitioning.

#### 3.2. Uncertainty in Evapotranspiration Partitioning

Uncertainty in the results of a single isotope two-source mixing model is directly related to the uncertainty in end-member and source estimates (\( \sigma_{\delta_T}, \sigma_{\delta_{ET}}, \) and \( \sigma_{\delta_A} \)) as well as the magnitude of the difference in end-members (\( \delta_T - \delta_A \)) and the final partitioned value of \( f_{ET} \). Assuming source and end-members are...
the morning and again slightly in the late afternoon. Water availability in the root zone showed little
rise throughout the day and peaked in the early evening. Conversely, relative humidity peaked in

3.3. Environmental Controls on Partitioning

Isotope flux partitioning results are used to examine the factors controlling \( F_E \) and \( F_T \) at multiple time
scales. Isotope flux partitioning estimates of \( F_E \) and \( F_T \) are strongly impacted by the average diurnal cycle of
net radiation, air temperature, and relative humidity (Figure 8). Total evapotranspiration was highly corre-
lated with net radiation \( (\rho_{R_n,F_T} = .64) \), with both \( R_n \) and \( F_T \) peaking midday. Average air temperature con-
tinued to rise throughout the day and peaked in the early evening. Conversely, relative humidity peaked in
the morning and again slightly in the late afternoon. Water availability in the root zone showed little

\[
\sigma^2_{F_T} = \frac{\sigma^2_{F_T}}{(\delta_T - \delta_E)^2} + \left(1 - f_{T/ET}\right) \frac{\sigma^2_{\delta_T}}{(\delta_T - \delta_E)^2}
\]

\[
+ \frac{\sigma^2_{\delta_E}}{(\delta_T - \delta_E)^2}
\]

Figure 5. Timeline of average daily transpiration, 10:00 AM and 5:00 PM, (top) flux and (bottom) evaporation flux. Results from isotope flux partitioning (solid blue line) are compared with those of flux-variance similarity partitioning (dashed red line) and scaled leaf-level measurements (crosses). Error bars depict the standard error of the mean of all observations for that day. Days with less than three measurements are marked with open circles.

The value of \( \sigma_{\delta_E} \) is calculated based on the estimated instrument uncertainty propagated though
the Craig-Grodon equation for each half-hour block.

Across all days, the average uncertainty in the bulk evapotranspiration flux isotope composition was 3.1‰.
This uncertainty is smaller than that determined for \( \sigma_{\delta_T} \) (6.0‰) and larger than that of \( \delta_E \) (2.2‰). On average, the partition value, \( f_{T/ET} \), and its uncertainty, \( \sigma_{f_{T/ET}} \), is estimated as 29 ± 5%. As is evident from (8), the results of a partitioning calculation are more sensitive to a particular end-member’s uncertainty (i.e., \( \sigma_{\delta_T} \) or \( \sigma_{\delta_E} \)) as \( f_{T/ET} \) approaches either the fully transpiring or fully evaporating state. Figure 7 depicts the fractional contribu-
tion of uncertainties in bulk flux and end-member composition. At low values of \( f_{T/ET} \), partitioning uncertainty is due mostly to uncertainty in bulk flux composition because \( \delta_E \) is more poorly quantified than \( \delta_T \). As \( f_{T/ET} \) increases, uncertainties in \( \delta_T \) and \( \delta_E \) both degrade the final partitioning estimate accuracy. Because \( \delta_T \) was only measured four times each day, uncertainty in this term is large. Uncertainties in \( \delta_T \) are due to both measurement errors as well as contributions from beyond the watered area, source
water variability, and any other unknown errors. A final average uncertainty of 5% on an average partition
value of 29% represents a relative uncertainty of 17%. Further improvement in the uncertainties of \( \delta_E \) and
\( \delta_T \) is necessary for isotope flux partitioning to separate fluxes of transpiration and evaporation with a high
degree of accuracy.

3.3. Environmental Controls on Partitioning
variation at the subdaily time scale (with the obvious exception of days with watering or rainfall). Throughout the course of the experiment, diurnal variation in $F_{ET}$ was predominantly driven by the total amount of available energy to drive evapotranspiration.

The diurnal cycles of transpiration and evaporation are different than those of total evapotranspiration. Based on the averaged diurnal cycle, $F_{T}$ is the largest flux component and is also highly correlated with net radiation ($\rho_{Rn,T} = 0.57$), however, $F_{T}$ is less correlated with radiation ($\rho_{Rn,T} = 0.30$). For both relative humidity and air temperature, the correlations between total flux and these forcing variables ($\rho_{hr,F} = 0.33$ or $\rho_{Temp,F} = -0.40$) are close to that of the transpired flux ($\rho_{hr,T} = 0.39$ or $\rho_{Temp,T} = -0.44$), while the relationships between these variables and the evaporation flux is weaker ($\rho_{hr,F} = 0.15$ or $\rho_{Temp,F} = -0.19$). Over the average diurnal cycle, isotope flux partitioning indicates that $F_{T}$ peaks in the late morning (11:00 AM–12:30 PM) and again in the late afternoon (3:30 PM–4:30 PM), while showing depressed $F_{T}$ values in the early afternoon (2:00 PM–3:30 PM). The early afternoon period corresponds to both high net radiation and high temperatures. Given the low green leaf area ($LAI \leq 0.1$), photosynthesis is not expected to be radiation limited. Instead, plant regulation of stomatal conductance appears to lower $F_{T}$ during periods of high temperatures and high net radiation as may be expected from leaf physiology models [Jones, 1992].

Over the time scale of multiple days, large shifts of $f_{T/ET}$ are observed despite similar meteorological cycles. Daily average isotope flux partitioning results comparing the transpired fraction to green leaf coverage, the 5 cm soil water potential, and the center of mass of soil water are shown in Figure 9. At multiday time scales, a complex combination of green leaf area and available water controls $f_{T/ET}$. Green
leaf area and \( f_{T/ET} \) are initially very low (Figure 9, left). As the green leaf area increases, so does the portion of \( F_E \) derived from transpiration. After day 8, \( f_{T/ET} \) and green leaf area decline, yet not along the same trajectory as their prior respective increases from day 3–8. This hysteresis with respect to leaf area is strongest on day 12, where a similar amount of green leaf as on day 6 results in a \( f_{T/ET} \) substantially smaller.

The availability of water for transpiration and evaporation is related to the soil water potential and the vertical location of water in the soil column as represented by the center of mass of soil water, \( z_{CM} \) [cm] (Figure 9). As long as water potential at 5 cm is above \(-5\) MPa, \( F_T \) increases as a portion of the total flux up to a maximum \( f_{T/ET} \) of 40% on day 6. \( f_{T/ET} \) remains above 25% from days 6 to 8 while green leaf continues to increase. Once the 5 cm potential falls below \(-5\) MPa, \( f_{T/ET} \) begins to decrease along with green leaf area. These dynamics suggest \(-5\) MPa as a likely wilting point for the grasses within our study area. The 6.7 mm rainfall between days 7 and 8 increased the 5 cm soil water potential, but this increase was insufficient to cause further increases in green leaf area. The center of mass of soil water was near the surface (7.3 cm below ground level) following the 30 mm watering, and reached a maximum depth of around 10.5 cm by day 13. The center of mass shifted from 10 to 6.8 cm on day 8 in response to the rain pulse, but returned to 9.4 cm by day 10. Transpiration is most strongly correlated to green leaf area (.64) while higher evaporation is most closely correlated with water centered at a shallow depth in the soil column (.72).

### 3.4. Combining Isotope Flux Partitioning and Flux-Variance Similarity Theory to Estimate Landscape Water Use Efficiency

WUE is governed by leaf physiochemical functioning and may be an indicator of plant water stress. Plants utilizing the C₄ pathway typically have higher WUE and are able to survive in arid environments more readily than C₃ species [Jones, 1992; Bacon, 2004]. Knowledge of WUE characteristics is important for understanding and potentially improving ecosystem and agricultural productivity, yet WUE is difficult to measure at the field scale because of the confounding effects of evaporation and respiration. To accurately estimate...
vegetation WUE at the landscape scale, nonstomatal fluxes of evaporation and soil respiration need to be removed from the bulk fluxes ($F_{ET}$ and $F_C$). By combining isotope flux partitioning and flux-variance similarity theory, estimates of the carbon dioxide partitioning and landscape WUE are obtained based on knowledge of the evapotranspiration partitioning and the covariance structure of water vapor and carbon dioxide.

Flux-variance similarity partitioning consists of a system of interconnected equations and unknowns as outlined in section 2.4. Scanlon and Sahu [2008] and Scanlon and Kustas [2010] model WUE based on concentration profiles and use it as an input to the flux-variance similarity partitioning method with the objective of partitioning water vapor and carbon dioxide fluxes. Alternatively, WUE may be considered an unknown and instead the isotope flux partitioning $F_T$ estimates may be considered an input. In this case, the water vapor partitioning results may be used in an inversion implementation of flux-variance theory to derive the partitioning of the carbon flux. To obtain the CO$_2$ partitioning, the solution to the set of flux-variance similarity equations proceeds in the same manner as in Scanlon and Sahu [2008], with an initial guess at the WUE as estimated in section 2.4. The resulting partitioned estimates are compared to those obtained from isotope flux partitioning and the WUE is iteratively adjusted until the two methods' estimates of $F_T/ET$ converge.

The same criteria for realistic flux results as the original implementation of Laga-riás et al. [1998] was implemented in the MATLAB programming environment (Math-Works Inc., Natick USA, version R2012a) by minimizing the difference between the flux-variance similarity $F_T/ET$ estimate and that obtained from isotope flux partitioning. We found that when $F_T$ values became very small the results become unstable. This is expected because $F_T$ forms the denominator of WUE such that $WUE \to \infty$ as $F_T \to 0$. The absolute difference between the leaf level and isotope flux partitioning with similarity theory becomes very large below a value of approximately 0.005 g m$^{-2}$ s$^{-1}$. Therefore, all individual 30 min blocks where $F_T \leq 0.005$ g m$^{-2}$ s$^{-1}$ were removed for this method. After filtering $F_T$ values below this threshold, the half-hour RMSE difference between the leaf level and inversion flux-variance similarity WUE estimates was 21.9 mg CO$_2$ g$^{-1}$ H$_2$O.

Leaf-level measurements show a gradual increase in WUE as the experiment continued, likely due to decreasing soil water potential (Figure 10). The modeled values of WUE based on log-profiles of temperature, water vapor, and carbon dioxide are highly variable [Scanlon and Kustas, 2010, equation 11], particularly on day 8 when the WUE = 196 mg CO$_2$ g$^{-1}$ H$_2$O. When the similarity partitioning method is inverted to estimate the WUE and the results are averaged to daily estimates the RMSE was 8.7 mg CO$_2$ g$^{-1}$ H$_2$O when
values below 0.005 g m$^{-2}$ s$^{-2}$ are removed. Thus, based on leaf-level measurements, the combined isotope and flux-variance method provides better estimates of $WUE$ than the straightforward modeling. The isotope flux partitioning and inverse flux-variance calculations produce trends in $WUE$ estimates (solid line Figure 10; slope $= 0.15$, p value $= 0.85$) with values slightly higher than the leaf-level measurements. The trend of increasing $WUE$ that is observed in the leaf-level measurements (dotted line Figure 10: slope $= 0.54$, p value $= 0.06$) is qualitatively matched by the results of the inverse flux-variance implementation but is not statistically significant in either linear regression.

4. Discussion

The results presented here indicate that isotope flux partitioning is able to estimate the transpired fraction of surface vapor flux with an uncertainty of $\sim$5% during periods of diurnal change and daily shifts in green leaf area. Validation of landscape level partitioning methods remains challenging because of the difficulty of accurately assessing $F_T$ over large areas. Our comparison of isotope flux partitioning with direct leaf-level transpiration measurements over a homogeneous area is a rigorous test of partitioning methodology. However, even the scaling of leaf-level gas exchange data potentially encompasses significant errors including small sample size, fine-scale heterogeneity in vegetation structure, soil heterogeneity, variability in plant ecophysiology across the flux footprint, and the relative amount of transpiration arriving at the eddy covariance system. The inherent difficulties in scaling from individual leaf measurements to field-scale estimates indicates the need for landscape-scale methods such as isotope flux partitioning, and at the same time accentuates the difficulty in validating them.

Logistical difficulties limited the transportation and application of water over large areas at the Kenya research station. As a consequence, the areal extent of the watering treatment was restricted to a 13 m radius circle. Sunrise and sunset at the field site was approximately 6:30 AM and 6:30 PM local time, so a small portion daily evapotranspiration likely occurred outside our measurement windows. Furthermore,
evaporation likely continued throughout the night at low rates. Thus, our partitioning estimates only address the daytime hours during which our equipment was running. The eddy covariance system was placed low in order to minimize the amount of turbulent eddies originating from beyond the watered area observed at the sonic anemometer. The grass canopy was extremely short (5 cm) and placement of the eddy covariance system at 40 cm resulted in a instrument height 8 × the canopy height, well beyond the typical 4 × canopy height suggested in literature [Aubinet et al., 2012; Burba and Anderson, 2010]. The low placement of the system results a measurement height 4 × the sonic anemometer path length of 10 cm. This is within the range where Kristensen and Fitzjarraud [1984] found 1-D line averaging did not significantly affect surface fluxes; however, van Dijk [2002] found larger flux attenuation with 3-D sonic anemometers. We have corrected for cospectral attenuation of flux through frequency response corrections [Moore, 1986] and after these corrections find the energy budget at the site is closed to within 12.8% with a RMSE of 74.9 W m⁻² s⁻¹. Furthermore, the total mass of water applied (30 mm per square meter) is consistent with the sum of evapotranspired water based on an average flux of 0.02 g m⁻² s⁻¹ over 14 days (24 mm per square meter).

Because of the limited extent of the watered surface area, our system measured turbulent eddies carrying fluxes originating from beyond the treatment area. However, as shown by Neftel et al. [2008] with EC flux measurements of adjacent but distinct fields, proper consideration of the flux footprint allows for the reconstruction of measured eddy covariance fluxes based on separate flux information from distinct sources. Our footprint calculations show that on average 81% of the observed flux originated from within the watered are while 19% originated from beyond the watered area. While this current configuration is not the ideal setup for measuring fluxes over a grass surface, the configuration we chose represents a compromise between flux observation and experimental limits. Because of the similarity between the bulk mass flux measured and water applied, closure of the energy budget to 13%, and excellent matching of scaled leaf level and isotope flux partitioning transpiration measurements, we have confidence in both our estimates of surface fluxes and the isotope partitioning methodology.

The isotope flux partitioning technique is predicated on separate characterization of δᵣ, δₑ, and δₑ, as well as a distinct difference between δₑ and δₑ. Measurements of the isotopic composition of transpiration were obtained through direct measurement in this study and assumed to be unchanging over the diurnal cycle. Large diurnal shifts are known to occur in plant liquid water isotope values over the course of the day and these shifts in plant water affect the composition of transpired water [Farquhar and Cernusak, 2005; Farquhar et al., 2007]. Our measured δₑ values fall above the extracted soil water compositions, indicating non-steady state conditions during the day. As noted by Dongmann et al. [1974], over longer periods transpired water composition must approach that of water entering the leaf. However, this applies only when leaf water content is not changing, a condition not present in the green-up and dry down of this experiment. Clear trends were not observed in the four measurements of δₑ collected each day, and therefore, a single daily average value of δₑ was used.

The Craig and Gordon [1965] model has been utilized in previous studies to estimate the isotopic composition of evaporated water [Yepez et al., 2003; Williams et al., 2004; Yepez et al., 2005; Wang et al., 2010, 2013]. As noted by Wang et al. [2013], the final value of f₁,ET is most sensitive to changes in δₑ while shifts in α due to temperature are relatively small in comparison. Recently, Soderberg et al. [2012] reviewed methods of characterizing reservoirs and fluxes of stable isotopes of water in the vadose zone and found that adjusting the Craig and Gordon [1965] framework in dry soils can lead to either enhanced or diminished fractionation. For the soils at the study site in Kenya, the consideration of relative humidity less than 100% in the vadose zone and increased vapor diffusion in unsaturated soils results in an enhancement of the kinetic fractionation relative to the classical form of the Craig and Gordon [1965] model (see Appendix A for details). This shift was highly consistent with a standard deviation of 0.43% across all days. With the exception of day –1 when the soil was extremely dry (ψₛ = –125 MPa) all soil water potentials fell between –20 and –0.5 MPa, the range in which δₑ is least sensitive to ψₛ values [see Soderberg et al., 2012, Figure 2]. The n values (equation (14)) determined by Mathieu and Bariac [1996] are based on experiments with drying soils not open water as is typically considered. Calculation of δₑ (average of –66.3%o) with these n values is consistent with our observed δₑ estimates (average of –70.19%o) during low LAI days 0–3 when no transpiration was likely occurring and thus provided further validations for these soil moisture-based n values.
Currently there is no standard method for measuring the isotopic composition of evapotranspiration flux and a variety of techniques have been applied in recent studies. The most reliable method, the flux-gradient technique [Wang and Yakir, 2000; Griffis et al., 2004, 2005; Good et al., 2012; Santos et al., 2012], was not able to be applied in this situation, though its use would likely decrease uncertainty in our $\delta_{ET}$ estimates. However, the Keeling mixing model has been shown to produce reliable results which can approach the flux-gradient technique [Good et al., 2012; Santos et al., 2012] if the quality control filtering is applied to remove periods with large uncertainty. Furthermore, application of Keeling plots over short time intervals (less than 1 h) reduces complications that arise due to the nonstationarity of surface and micrometeorological conditions and also minimizes the impact of possible shifts in background and source isotopic composition [Good et al., 2012].

Throughout the experiment relatively constant midday meteorological conditions and strong surface heating suggest that the planetary boundary layer is expected be high (~ 2.5 km [Culf, 1992]). In that situation, any entrained vapor must mix with a large volume of boundary layer moisture and thus any effects on planetary boundary layer background composition are dampened. Any $\delta_{ET}$ values with uncertainties larger than 10$^\%$ were excluded; however, even with this filtering, days such as −1 still show large variability, likely due to low flux rates. Retained uncertainties in $\delta_{ET}$ were 3.1$^\%$ on average, which is much less than the average $\delta_{ET}$ difference of 94$^\%$. The presence of vapor originating from beyond the watered area will affect the Keeling plot [Griffis et al., 2007], thus our analysis reflects partitioning based on the observed bulk flux composition over the entire footprint and end-members assessed for the plot. However, as demonstrated by the Lagrangian stochastic dispersion model, the concentration (and flux) footprints are strongly weighted toward the watered area; the similarity of these footprints thereby allows an intercomparison of these methodologies.

Flux-variance similarity theory provides estimates of evaporation and transpiration similar to isotope flux partitioning during the majority of the experiment. Prediction of nonzero $F_T$ values in the initial days of the experiment (0–2) likely arise due to numerical instabilities caused by near-zero terms in the denominator of equations. On day 8, the similarity method indicates a suppression of $F_T$, while isotope flux partitioning does not. As noted in Scanlon and Kustas [2012], rainfall may suppress transpiration and increase evaporation as the total $F_{ET}$ flux approaches potential evapotranspiration. These effects are particularly relevant when leaf area index is larger and when substantial amounts of water may be stored in the canopy during and immediately after rainfall [Scanlon and Kustas, 2012]. In our study, leaf area index remained very low (LAI ≪ 1). Potential evapotranspiration was on average 8.7 times greater then that of $F_{ET}$, and three times greater than peak $F_{ET}$ observed on day 8. We neither expect transpiration to be suppressed in this setting, nor do we observe lower $F_T$ from our leaf-level measurements. This drop in flux-variance similarity $F_T$ may be due to a wet canopy altering the relationship between transfer efficiencies, though more research into the flux-variance method is required.

During the final 2 days of the experiment, the isotope partitioning and the flux-variance approach diverge, with isotope flux partitioning and leaf-level results both below the estimates of the similarity partitioning method. The very negative soil water potential and decrease in green leaf area during the later half of the experiment imply stressed conditions under which the assumption that leaf temperature and air temperature are the same may break down. During stressed conditions, as leaves lose the ability to maintain their temperature via evaporation, this would lower $WUE$ values, based on an average $c/v$ ratio, are about 10 mg g$^{-1}$ larger than those obtained from the leaf-level observations, indicating that the flux-variance $F_T$ is too large. Furthermore, when the similarity partitioning method is inverted to estimate $WUE$, the results are similar to hand-held observations with an average absolute difference of 8.7 mg g$^{-1}$ for daily averages (when $F_T$ values below 0.005 g m$^{-2}$ s$^{-2}$ are removed). Finally, the short grass in this study results in very small vertical separation between the transpiring canopy and the evaporating surface. This small spatial separation may diminish differences in transport efficiencies between stomatal and nonstomatal-derived scalars. The possibility of combining flux-variance similarity assumptions and isotopic methods to determine $WUE$, $F_T$, $F_E$, and $F_R$ simultaneously is an exciting avenue for further research.

5. Conclusion

We have, for the first time, tested the landscape-scale partitioning of water vapor fluxes with isotopic methods against the flux-variance similarity theory approach. At the daily time scale, we demonstrate that
isotope flux partitioning is able to partition the total flux of water vapor into its constituent components of transpiration and evaporation, with an estimated average uncertainty of 5% of a total transpired fraction of 29%. Our isotope flux partitioning results compare well with scaled leaf-level results and taken together form a comprehensive demonstration of the isotopic approach to flux partitioning. However, large uncertainties and instrumental requirements suggest that improvement in techniques, such as gradient-based δET estimates, is required to accurately partition fluxes for long periods of time without continuous in-person field observations. Improvements in δET measurements will lead to the most direct improvement in partitioning estimates. Additional research is required into methods for automated measurement of soil water and transpired water composition in order to consistently partition ET over seasonal and annual time scales.

The portion of water vapor leaving the surface via the stomatal pathway was shown to be dependent on both the green leaf area, vegetation status, and the vertical location of moisture within the soil column. Our method was able to identify stomatal control of transpiration during the course of the diurnal cycle as well as a critical soil water potential wilting point. Consideration of plant water stress will be required in model- ing and predicting specific surface vapor fluxes in future settings, particularly for flux-variance similarity theory. Finally, the combined flux-variance similarity with isotope techniques can be used to estimate WUE and carbon dioxide flux partitioning. The ability to assess WUE at landscape scales opens the possibility of investigating leaf physiology and productivity in a wide variety of settings if partitioning estimates can be made reliably.

Appendix A: Craig-Gordon Equation for Unsaturated Soils

The Craig and Gordon [1965] formulation for the isotopic composition of evaporated water is derived following Gat [1996], but with the relative humidity in the soil column, hS, taken to be less than saturation. This approach is functionally the same as the use of the activity of water by Soderberg et al. [2012] to incorporate soil water status into the Craig-Gordon model. Relative humidity in the soil is a function of the soil water potential following the Kelvin equation, hS = exp (Mψs/RTs) [Mathieu and Bariac, 1996; Soderberg et al., 2012]. The difference between the normalized atmospheric humidity h'w = hAeSRS and hS for both the rare and bulk flux are multiplied by the conductance (1/r, where r is the resistance) to calculate the separate fluxes.

The ratio of the flux of the rare isotopologue FR to the bulk FET evaporation is taken as the ratio of two Fickian diffusion equations dominated by the vapor pressure gradient between the soil, es [kPa], and the atmosphere, eA, as

\[
R_F = \frac{F_R}{F_E} = \frac{e_A e_S - e_A R_A}{(e_S - e_A)}.
\]

Equation (A1) is then written in terms of relative humidity and converted to δ notation as

\[
\delta_F = \frac{(x_s h_S \delta_S - h_A \delta_A) + (x_A h_S - h_A') + (h_S - h_A') r/r}{(h_S - h_A') r/r}.
\]

We define vapor-liquid equilibrium enrichment, \(e_v \equiv (1 - x_s)\), and kinetic enrichment, \(e_k \equiv (h_S - h_A')(r/r - 1)\). Making these substitutions gives us

\[
\delta_F = \frac{(x_s h_S \delta_S - h_A' \delta_A) - (h_S e_v + e_k)}{(h_S - h_A') + e_k}.
\]

Equation (A3) simplifies to the classical Craig and Gordon [1965] formulation when \(h_S = 1\).

The vapor-liquid equilibrium fractionation factor \(x_s\) and enrichment \(e_v\) are calculated as a function of T3 by inverting the empirical liquid-vapor equation of Majoube [1971]. The resistance to water flux for both the rare isotopologue and the bulk flux consists of a diffusive layer, \(r(D)\) and a turbulent layer, \(r(T)\). These
resistances are added in series \( (r = r(D) + r(T); n = r(D) + r(F) ) \) and the turbulent resistance is assumed to be equal for both fluxes (i.e., \( r(F) = r(T)) \). Therefore, \( n_x \) is may be rearranged to

\[
\begin{align*}
\varepsilon_x &= (h_S - h_A) \left[ \frac{r(D)}{r} \right] \left[ \frac{r(D)}{r(T)} - 1 \right].
\end{align*}
\]

Equation (A4)

The diffusive flux in the laminar layer is proportional to the molecular diffusivity coefficient \( r(D) \propto D^{-n} \), where \( n \) is an aerodynamic parameter. The ratio \( r(D)/r \approx 1 \), but may reach lower values in strongly evaporating humid environments [Gat, 1996; Horita et al., 2008]. The kinetic enrichment is then

\[
\begin{align*}
\varepsilon_x &= (h_S - h_A) \left[ \frac{D}{D} \right]^{-n} - 1
\end{align*}
\]

(A5)

Note that dividing equation (A3) by \( h_S \) produces the classical Craig and Gordon [1965] formulation with atmospheric relativity adjusted for soil moisture content as in Soderberg et al. [2012]. The aerodynamic diffusion parameter, \( n \) varies from 1/2 when the soil is saturated \( (\theta_S = \theta_{sat}) \), to 1 when the soil is dried to residual moisture levels \( (\theta_S = \theta_{res}) \), as [Mathieu and Bariac, 1996]

\[
\begin{align*}
n &= 1 - \frac{1}{2} \left( \frac{\theta_S - \theta_{sat}}{\theta_{sat} - \theta_{res}} \right).
\end{align*}
\]

(A6)

**Appendix B: Lagrangian Stochastic Dispersion Model**

The Lagrangian stochastic dispersion model employed here is based on Wilson and Sawford [1996] and Thomson [1987] as outlined in Hsieh et al. [2000]. Within the model, the turbulence regime is expressed as a function of the momentum flux, \( F_M \) and sensible heat flux, \( F_h \) via the friction velocity \( (u_s) \) and Obukhov length \( (L) \). Given the turbulence regime, fluid parcels are advected and dispersed following a memoryless Markov process by tracking the location \((x, z)\) and velocity \((u, w)\) of all individuals separately.

For each simulation, a large number \((M)\) of fluid particles are released from random locations on the model surface. The number of particles released from the watered and unwatered portions is weighted relative to their estimated \( F_M \) flux and area. Latent heat, sensible heat, and momentum flux outside the watered area are based on the diurnal cycle observed before the irrigation. The domain is 1000 m in length and 100 m in height, with the watered area centered 900 m from the upwind edge. A 10 cm square collector region is located 40 cm above the surface in the center of the watered region. The concentration footprint, \( f_c(x, x_m, z_m) \), for a collector located at \( x_m \) and height \( z_m \) from a location on the surface is given by

\[
\begin{align*}
f_c(x|x_m, z_m) = \frac{1}{N_m} \frac{d(n_x)}{dx},
\end{align*}
\]

(B1)

where \( n_x \) is the number of particles that passed though the collector originating from \( x \) and \( N_m \) is the total number of particles released that passed though the collector. Similarly, for the footprint of the measured flux, \( f_i(x|x_m, z_m) \), at the collector is

\[
\begin{align*}
f_i(x|x_m, z_m) = \frac{1}{N_m} \frac{d(n_{+} - n_{-})}{dx}.
\end{align*}
\]

(B2)

Where \( n_{+} \) and \( n_{-} \) are the number of upward and downward moving particles that passed through the collector originating at \( x \). The percent of the measured concentration \( (p_c) \) or flux \( (p_f) \) at the collector from the irrigated area is then calculated by integrating \((B1)\) or \((B2)\) as \( p_c = \int f_c(x)dx \) and \( p_f = \int f_i(x)dx \), where \( A \) is the irrigated area.
The location of a fluid particle evolves from time step \( n \) to time step \( n + 1 \) as a function of horizontal and vertical winds as

\[
x_{n+1} = x_n + u_n \Delta t, \tag{B3}
\]

and

\[
z_{n+1} = z_n + w_n \Delta t. \tag{B4}
\]

Here the horizontal mean wind profile is calculated from Monin-Obukhov similarity theory [Kaimal and Finnigan, 1994] as

\[
u_n = \frac{u^*}{K} \left( \ln \left( \frac{z_n}{z_0} \right) - \psi_m(z_n/L) \right). \tag{B5}
\]

The roughness length is \( z_0 = 0.1h \), where grass height \( h \) is 10 cm, and \( K \) is the von Karman constant (0.4). Under the assumption of a Markov process, the evolution of vertical windspeed is expressed as

\[
w_{n+1} = w_n + a(z_n, w_n, t) \Delta t + b(z_n, w_n, t) \Delta v, \tag{B6}
\]

where \( \Delta v \) is a Gaussian random number with mean zero and variance \( \Delta t \). In (B6), the drift coefficient \( a \) and random acceleration coefficient \( b \) are calculated as

\[
a = -\frac{w}{t_j} + \frac{1}{2} \frac{\partial \sigma^2_w}{\partial z} \left( 1 + \frac{w^2}{\sigma^2_w} \right), \tag{B7}
\]

and

\[
b = \left( \frac{2 \sigma^2_w}{t_j} \right)^{1/2}. \tag{B8}
\]

The discrete time step \( \Delta t \) is set at 0.1 \( t_l \), where the Lagrangian time scale, \( t_l \), is estimated as

\[
t_l = \frac{kz_u}{\phi_h \sigma^2_{w}}. \tag{B9}
\]

The Eulerian vertical velocity variance profile is calculated as

\[
\sigma^2_w = \begin{cases} 1.25 u_* (1 - 3z/L)^{1/3} & \text{for } z/L < 0, \\ 1.25 u_* & \text{for } z/L \geq 0 \end{cases}. \tag{B10}
\]

The stability correction functions for the velocity (\( \psi_m \)) and heat (\( \phi_h \)) profiles are:

\[
\psi_m = \begin{cases} 2 \ln \left( \frac{y+1}{2} \right) + \ln \left( \frac{y^2+1}{2} \right) + 2 \tan^{-1} \left( \frac{1-y}{1+y} \right) & \text{for } z/L < 0, \\ -\beta z/L & \text{for } z/L \geq 0 \end{cases}, \tag{B11}
\]

\[
\phi_h = \begin{cases} 0.32 (0.037 - z/L)^{-1/3} & \text{for } z/L < 0, \\ 1 + 5z/L & \text{for } z/L \geq 0 \end{cases}. \tag{B12}
\]

with \( y = (1 - az/L)^{1/4} \), \( a = 16 \), and \( \beta = 5 \).
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